Zinc Oxide Heterostructures for Electron Confinement

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I, Matthew Sparks, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the work.
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Completing a PhD can be a very isolating undertaking. Many PhD students before me have detailed how a PhD can make them feel cut off as they pursue their individual project. But no matter how strong this feeling may appear at times, it is an illusion. There are always those around you who will lend you an ear or their support, you need only to seek them out. Here I hope to acknowledge the individuals I reached out to throughout this PhD without whom this work would not have been possible. Some of you may not have realised the support you gave me, I thank you all the same.

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Abstract

Two-dimensional electron gases (2DEGs) at the ZnO/ZnMgO interface are promising for spintronics and quantum computing applications due to the combination of low spin-orbit coupling and high electron mobility. This thesis proposes that these 2DEGs could be used to achieve voltage-tuneable Josephson junctions (JJs). To achieve this, the 2DEG needs a high superconducting coherence length, which requires both a high carrier concentration and electron mobility.

This thesis summarises methods to enhance ZnO 2DEG quality using pre-growth processing on ZnO substrates, and testing ZnO/ZnMgO heterostructure fabrication on alternative substrate materials. This is achieved through rapid thermal treatment of commercially available ZnO and by exploring growth on a- and c-plane sapphire.

Rapid thermal annealing of ZnO substrates is shown to greatly improve substrate quality. Devices produced on thermally treated substrates demonstrate 2DEG behaviour with mobilities and carrier concentrations of $4.8 \times 10^4$ cm$^2$/Vs and $5.05 \times 10^{12}$ cm$^{-2}$ respectively. This translates to a long mean free path (1800 nm) and a long clean-limit coherence length (120 nm) at 2K, making the sample well suited for voltage-tuneable Josephson junctions. The high 2DEG mobility is attributed to a reduction in substrate defect density due to the thermal treatment.

Later chapters show how thin MgO buffer layers can be used to achieve Zn-polar ZnO layers on c-plane sapphire. The Zn-polar layers are used to produce ZnMgO/ZnO heterostructures which could provide the basis of 2DEG formation on non-ZnO substrates. Practical means of controlling Zn-polarity on a-plane sapphire could not be found, so an alternative heterostructure is produced which utilises
polarity discontinuity at the ZnO/ZnMgO interface.

Finally a road-map for future research is presented. This includes suggestions for retrofitting working ZnO 2DEG devices to measure proximity superconductivity through the 2DEG. It is explained how this proximity superconductivity can be tuned through electrical gates, and how this component could be used to achieve tuneable superconducting qubits.
Impact Statement

Quantum computing is a fast growing field with wide reaching applications for a variety of sectors, chief among them being encryption and computer modelling. While several methods for achieving quantum computing exist, superconducting architectures are arguably the most promising. One of the major limitations faced in superconducting systems is scalability: qubits are typically limited to interactions with nearest neighbours or have interactions mediated by harmonic buses, which also have limited reach dictated by the devices’ physical architecture.

To facilitate greater inter-connectivity and achieve ad hoc switching, independently tunable qubits are needed. This could be achieved by creating qubits with tuneable Josephson junctions (JJs). One method for well controlled tuneable JJs, with limited cross talk, involves the patterning of electrical gates onto the non-superconducting barrier. These gates would facilitate manipulation of the barrier’s electrical properties. These gates would need to be patterned on the scale of 100nm, which is too large to allow proximity superconductivity across typical insulating barrier materials.

Two dimensional electron gases (2DEGs) have both high mobility, thereby facilitating long coherence lengths, but are also easily tunable via electrical gates. ZnO 2DEGs have been fabricated with exceptionally high mobilities and could serve as these gated barriers. However recent attempts to produce ZnO 2DEGs have been limited by substrate defects, such as lithium.

This work documents methods for treating commercially available ZnO substrates and alternative substrates for ZnO/ZnMgO fabrication. Of these methods, rapid thermal annealing of ZnO substrates is effective in improving substrate
quality. Growth on these substrates is shown to greatly improve the mobility of resulting 2DEGs. These 2DEGs are suitable for realising tunable JJs, and subsequently, tunable qubits. This work therefore has wide reaching implications for the development of scalable superconducting quantum computing architectures. The lessons learned from ZnO 2DEG improvement could also be applied to other technologies relying on high-quality ZnO/ZnMgO growth, such as solar cells and light emitting diodes, to name but a few.
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Chapter 1

Introduction

Over the last century, the human experience has altered dramatically. Nowadays in the developed world, almost everyone has access to devices in their pockets that can be used to gather information, check current events, entertain or connect with others. This revolution is thanks to developments in semiconductor science and the varied applications these materials have. Silicon is the pre-eminent material, making up the billions of transistors that comprise the processors in our computers and phones.

A notable point in the history of semiconductor research is the creation of the first transistor at Bell Laboratories in 1947. This discovery, which is the ancestor for all modern day computation technology, was awarded the Nobel Prize in Physics in 1956. Since then research in the field has only increased with a drive to make semiconductor devices ever more compact and efficient. The rate of improvement is encapsulated in Moore’s law which asserts “the number of transistors on a chip will double every two years while the cost of computers is halved” [1]. Over the past five decades, manufacturers have kept up with this model. The field has seen a tremendous increase in the number of transistors per chip. For example in 1971 a leading Texas instruments microprocessor had 8000 transistors while in 2015 Oracle SPARC M7 chip had 10 billion [2].

In modern times it seems Moore’s law may be coming to an end. Transistors are now being fabricated in the nanoscale regime with top-of-the-line transistors measuring in at 14nm, smaller than most viruses [3]. While there seems to be some
scope to push these devices even smaller, with IBM demonstrating a 5nm transistor in 2017, devices are starting to approach the point where quantum effects become significant. Indeed, it has been predicted that with exceptional effort, manufacturers may be able to reach the 2-3nm limit in the early 2020s, but there is some argument over whether such a sample could even be considered a device, since it would only be 10 atoms wide [3].

At these dimensions, the physics for electrical conduction breaks down as the effects of electron tunneling become significant. Conduction though the device is now ruled by quantum effects. Faced with this dilemma, many researchers state that Moore’s law has reached its limit, thus abandoning ambitions to continually achieve exponential increase in transistor number. Instead research is focused on ‘More than Moore’ (MTM) computing. Rather than attempting to increase transistor number, MTM research involves manipulating the material used in chip production to yield new effects. Such processes include embedding optical sensors and emitters directly into silicon, or creating chipset skyscrapers by layering multiple thin-films of transistors on top of one another. Other methods include altering the paradigm of computing entirely by utilising other physical effects as a means of performing calculations, such as quantum computing.

Quantum computing was arguably first conceived in 1980 when Paul Benioffe described a quantum mechanical model for a Turing machine [4]. Research in this field grew rapidly, as it was shown that a quantum computer has the capacity to perform tasks that would take an inordinate amount of time on a classical computer. Shor’s algorithm for effective prime-factor calculation [5] and Grover’s algorithm for efficient database searching [6] are two well-known examples, but there are many more. This transition to a quantum paradigm seems like a natural progression; after all, classical computing components are now being limited by quantum effects due to their nano-scale size, why not utilise these effects to enhance computation?

At present there are several potential avenues for achieving quantum computing but one area that has shown much promise in recent years is superconducting quantum circuits [7]. The fundamental component of the
superconducting quantum computer is the Josephson qubit. In a simplified picture, the qubit consists of a ring of superconducting material broken by some non-superconducting element. This break is a Josephson junction (JJ), a small separation in a superconducting channel which can permit the coherent quantum tunnelling of electron pairs. The qubit can occupy a ground state or an excited state, analogous to the 0 and 1 used in classical computing.

For a quantum computer to be completely viable, control over these qubits must be absolute. This can be achieved by manipulating the rate at which electrons tunnel across the JJ, which in turn affects the properties of the qubit. More specifically, one must tune the Josephson Energy $E_J$ of the junction to tune the qubit’s transition frequency. $E_J$ is the energy stored in a JJ when a super current flows through it. In modern day tuneable superconducting flux qubits, this is done through the application of a magnetic field [8]. In this design, in the place of a single JJ there is a small loop broken by two JJs, as depicted in figure 1.1. A magnetic field is applied through this loop which alters the $E_J$ of the JJs, thereby tuning the qubit. However magnetic fields are not well localised which can lead to cross-talk between devices. This cross-talk can be overcome through precise calibration but this process can take a great deal of time and effort to set up.

We could circumvent the cross-talk issues if we could tune the qubits without

**Figure 1.1:** Graphical depiction of magnetic field-tuneable flux qubit.
the need for magnetic fields. This could be done using a semiconducting material for the JJ barrier and tuning the semiconductor’s electrical properties via local electrical gates. By tuning the barrier material we can alter $E_J$ and thereby alter the qubit’s transition frequency. An ideal candidate for barrier material would be a semiconductor-based 2D electron gas (2DEG), as these systems have already been used to achieve JJs tuned via electric fields [9]. A schematic of such an electrical gate tuneable 2DEG JJ is depicted in figure 1.2.

For practical fabrication reasons, these hypothetical electric gates would need to have dimensions of the order of 10-100nm. Such devices could feasibly be fabricated using modern day electron-beam lithography (EBL) techniques. These gates would need to sit between the superconducting contacts of our 2DEG, so this effectively gives us a lower-limit for the separation between our contacts. This could be problematic, since if the separation between the superconducting contacts is too great, Cooper pairs will not be able to tunnel from one contact to another and the device would not act as a JJ.

To determine how wide our junction can be without destroying the tunneling behaviour, we need to consider the superconductor proximity effect. In simplified terms, when a superconducting material is in electrical contact with non-superconducting material, the superconductivity will bleed into the non-superconducting material. This is the superconducting proximity effect. The

Figure 1.2: Schematic cross-section of gated superconducting-2DEG-superconducting Josephson junction.
superconductivity can permeate into the non-superconducting material out to a
distance known as the coherence length $\xi$. This coherence length is dependant on a
number of properties of the non-superconducting material, but chief among them is
carrier mobility. To achieve a tuneable JJ which can be fabricated by EBL, we will
need to use a material that has a coherence length on the order of 100nm.

To achieve the concept for a tuneable JJ, we will need a material that is
non-superconducting and has a high mobility at low temperatures. One way to
achieve these requirements is with ZnO-based two dimensional electron gases
(2DEGs). In the remainder of this introduction, we will justify why we are
interested in 2DEGs and why the ZnO-based 2DEGs specifically. We will also
touch on some issues related to ZnO-based 2DEGs and how we have overcome
them in this work. Finally we will codify the properties we need to see in our ZnO
2DEGs to consider them a viable candidate for tuneable JJ applications.

1.1 Why Two Dimensional Electron Gases?

2DEGs have been integral to the study of semiconductors since their discovery at
Bell Laboratories in 1979 [10]. This is due in part to the role they play in the
fabrication of high electron mobility transistors (HEMTs). HEMTs have several
properties that are advantageous to Si based devices, such as a high gain, making
them well suited for amplifier applications, low noise due to low current variation,
and higher switching speeds due to low minority carrier concentration. These
properties are all well suited to 4G/5G amplifiers [11].

2DEGs have also facilitated the observation of novel low-dimensional physics.
The low-dimensionality of these systems demonstrate the fundamental properties
of electron–impurity and electron–electron interactions [12]. 2DEGs have played
a part in improving our understanding of these interactions and have been involved
in two Nobel Prizes; the 1985 awarded to Klaus von Klitzing for “the discovery of
the quantized Hall effect” [13] and the 1995 awarded to Robert B. Laughlin, Horst
L. Stormer and Daniel C. Tsui for their discovery of “a new form of quantum fluid
with fractionally charged excitations” [12].
1.2 Why ZnO?

At present 2DEGs have demonstrated mobilities as high as $3 \times 10^7 \text{cm}^2/\text{Vs}$ [14, 15], far in excess of bulk semiconductor values. In a conventional semiconductor, dopants inject additional carriers to the system. However, dopant ions also act as scattering centres, hampering the carrier mobility. In a 2DEG the carriers are bound to the material interface and are spatially removed from the dopant ions. This means the dopants do not contribute to carrier scattering. This is why 2DEGs demonstrate high electron mobilities. These high mobilities make 2DEGs well suited to our needs, and should result in high coherence lengths in these systems. Additionally, there is a long history of using electrical gates to manipulate 2DEG electrical properties, providing a good foundation for the gates that would be integral in a tuneable JJ device.

This research is specifically interested in intrinsic 2DEG systems, where the 2DEG forms at the point of growth. Since these 2DEGs require no external field to form, they can be tuned via electrical gates, thereby facilitating a tuneable JJ design, as described earlier.

The mechanisms behind intrinsic 2DEG formation are now well understood. Research continues to find novel applications for these systems. Most 2DEG research was, and still is, conducted with AlGaAs/GaAs heterostructures. As this area of research has matured, other material systems have been created with fundamentally different properties, including AlGaN/GaN, LaAlO$_3$/SrTiO$_3$ (LAO/STO) and ZnO/ZnMgO. The distinction between intrinsic and extrinsic 2DEGs, and the various merits of the major intrinsic 2DEG systems, will be explained in more detail later in this thesis. Here in we will give a brief introduction to ZnO and explain why ZnO/ZnMgO 2DEGs are the focus of this research.

1.2 Why ZnO?

ZnO/ZnMgO heterostructures have been shown to be a viable high mobility 2DEG system, reaching mobilities as high as $1 \times 10^6 \text{cm}^2/\text{Vs}$ [16]. ZnO-based structures have also been used to demonstrate fractional quantum Hall states [17]. In addition, ZnO has potential quantum computing and spintronics applications due to its low
spin-orbit coupling, which facilitates long spin coherence times [18]. Finally ZnO’s wide band gap (3.37eV at room temperature [19]) renders ZnO transparent to the visible spectrum and provides the basis for many optoelectronic device applications in the ultra-violet spectrum [20].

ZnO had its debut in the electrical engineering community as a possible substrate for GaN growth. It was later noted that ZnO possesses many interesting electrical properties in its own right [19]. As previously mentioned, ZnO is transparent to light in the visible spectrum, meaning ZnO-based transistors are not adversely affected when exposed to light. As well as the optoelectronic, piezoelectric, spintronic and 2DEG applications previously discussed, ZnO also has a high exciton binding energy at 67meV, three times larger than GaN. As such ZnO has a wealth of possible applications, including field emission sources [21], gas, chemical and biological sensors [22], UV light emitters [23], and UV-spectrum solar cells [24], to name but a few. It is also worth mentioning that Zn and O are both non-toxic and earth-abundant.

ZnO’s electrical, magnetic, and optical properties can be tuned further through alloying, doping, heterostructure growth, and quantum-well formation. All of these processes have already been employed to produce a number of useful devices, such as laser diodes [25] and thin-film field effect transistors for use in transparent electronics [26].

Ternary elements can be added to ZnO to manipulate the band gap. The three main elements used for this are Mg, V and Cd. Mg and V can be used to broaden the band gap, while Cd is used to narrow it [19]. Mg has a similar atomic radius to Zn (For Mg$^{2+}$ the radius is 72pm while for Zn$^{2+}$ it is 74pm) therefore substitutional Mg results in minimal changes to the ZnO crystal morphology, producing minimal strain at the ZnO/ZnMgO interface [27]. Mg is also non-toxic in contrast to alternative III/V semiconductors systems, which typically require rare or toxic dopant materials, resulting in a larger lattice mismatch with the host material.

There have also been many attempts to capitalise on the optoelectrical properties of ZnO through both $n$- and $p$- type doping. ZnO is naturally $n$—type
1.3. A Note on ZnO Substrate Quality

due to the presence of O vacancies ($V_O$) and Zn interstitials ($Zn_i$) [24]. *n*-type doping of ZnO is relatively easy compared to *p*-type doping and can be achieved by substituting group—III elements such as Al, Ga and In for Zn, or by substituting group—VII elements such as Cl and I for O [24]. *n*-type ZnO has been demonstrated with resistances as low as $1.2 \times 10^{-4}\Omega \text{cm}$ using Ga-doping [28]. *p*-type doping of ZnO is difficult in part due to native defects such as $Zn_i$ or $V_O$ compensating the dopants [24]. Known acceptors for ZnO include group—I elements such as Li, Na, K, Cu, Ag, Zn vacancies, and group—V elements such as N, P and As [24]. Experimental examples of *p*-type ZnO include N-doped ZnO by Look at al. [29] and Cu-doped films by Sahal et al. [30].

There are some commercial advantages to using ZnO. ZnO substrates are available as wafers up to 50mm in diameter and can be cleaved along specific orientation or terminations as required. This is particularly significant as the ZnO unit cell is polarized along the crystallographic c-axis. Furthermore ZnO is ionic, meaning both wet and dry etching may be used as part of the device fabrication process without adversely affecting the bulk crystal structure [31].

1.3 A Note on ZnO Substrate Quality

To date, all record breaking ZnO-based devices have been grown on Tokyo Denpa substrates, which are no longer available. This is because the Tokyo Denpa group used a $25M$ platinum crucible for crystal growth. Crucibles are eroded during the hydrothermal growth process. The Tokyo Denpa platinum crucible was exhausted several years ago and the group have been unable to secure funding for a replacement. Tokyo Denpa substrates had a high level of purity not found in alternative substrates on the market. This is believed to be due to Li defects which arise at the point of growth. This thesis seeks to overcome this issue by either finding some treatment which removes Li from the ZnO substrate, or by finding an alternative substrate that is compatible with ZnO and ZnMgO epitaxy.

There is growing evidence that thermally treating ZnO to temperatures in excess of 1000°C can promote Li out-diffusion in substrates and improve overall
substrate quality [32, 33]. This thesis attempts to exploit and develop the thermal treatment of ZnO to achieve high carrier concentration, high mobility 2DEGs. We observe a reduction in room temperature resistance as a function of rapid thermal anneals, which is used as a proxy for substrate defect density. This work culminates in the observation of a high mobility \((4.8 \times 10^4 \text{ cm}^2/\text{Vs})\) and high carrier concentration \((5.05 \times 10^{12} \text{ cm}^{-2})\) 2DEG grown by MBE on a thermally treated substrate.

There have also been efforts to grow ZnO onto alternative substrates. C-plane sapphire is commonly used for ZnO thin film growth despite large lattice mismatch (18\%) due to its high purity and low cost. There are multiple demonstrations of ZnO being grown at temperatures below 900\(^\circ\)C with molecular beam epitaxy (MBE) [34], radio frequency sputtering [35], chemical vapour deposition (CVD) [36] and pulsed laser deposition (PLD) [37]. Additionally MgO buffer layers can be used to control ZnO polarity on c-plane sapphire [38]. A similar effect can be achieved by annealing a-plane sapphire before growth [39]. These alternative substrates are explored in this thesis.

### 1.4 Tuneable Josephson Junction Requirements

Let us now revisit the question of tuneable JJs. We have mentioned that mobility is an important factor in determining coherence length, but how exactly are these parameters related? How do we know if our 2DEG will support a coherence length on the 100nm scale given its carrier mobility? This section explains the fundamental relationships governing coherence length in a proximitised 2DEG. We also define a critical mobility \(\mu_c\), the value at which any further increase in 2DEG mobility does not result in an increase in the coherence length.

In the 2DEG there are two coherence length calculations, one for the ‘clean limit’ (where the electron mean free path \(\ell\), is greater than the coherence length \(\xi\), in the material) and one for the ‘dirty limit’ (where the mean free path is shorter than the coherence length). In a 2D system the electron mean free path is given by \(\ell = \nu_F \tau\), where \(\nu_F\) is the Fermi velocity, \(\tau\) is the elastic scattering time. In 2D,
Figure 1.3: Graphical depiction of the relationship between coherence length and mobility. \( \mu_c \) represents the critical mobility at which \( \ell = \xi_c \) where \( \xi_c \) is the clean coherence length.

\[ \nu_F = \hbar (2\pi n_s)^{1/2} / m^* \] and \( \tau = \mu m^* / e \) where \( n_s \) is the 2DEG carrier concentration, \( \mu \) is carrier mobility, \( e \) is electron charge and \( \hbar \) is the reduced Planck’s constant [40]. Hence the mean free path in a 2DEG can be written as:

\[ \ell = \frac{(2\pi n_s)^{1/2} \hbar \mu}{e} \]  

(1.1)

The coherence length in the clean limit (\( \xi_c \)) is given by:

\[ \xi_c = \frac{\hbar^2 (2\pi n_s)^{1/2}}{2\pi k_B T m^*} \]  

(1.2)

while in the dirty limit the coherence length is given by:

\[ \xi_d = \left( \frac{\hbar^2 \mu n_s}{k_B T m^*} \right)^{1/2} \]  

(1.3)

where \( T \) is the temperature of the 2DEG system and \( k_B \) is the Boltzmann constant and \( m^* \) is the effective electron mass.

Let us now imagine a scenario where \( \mu \) can scale independently of \( n \). With \( n \) at some finite value, the relationship between \( \mu \) and the coherence length \( \xi \) follows the
1.4. Tuneable Josephson Junction Requirements

For low $\mu$, $\ell$ will be small since $\ell$ is proportional to $\mu$. Hence the system is in the dirty limit and the coherence length scales as $\mu^{1/2}$. At some finite mobility $\mu_c$, the mean free path will exceed the clean coherence length $\xi_c$. This must occur as $\ell$ scales with $\mu$ at a faster rate than $\xi_{dl}$. As $\mu$ increases further, the mean free path $\ell$ increases but the coherence length remains constant since the $\xi_c$ relationship is $\mu$-independent. This means there is a 2DEG mobility above which the coherence length does not increase with system mobility. We label this mobility as the ‘critical mobility’ $\mu_c$.

We can determine the critical mobility by equating the mean free path and the clean coherence length:

$$\ell = \xi_c$$ (1.4)

$$\frac{(2\pi n_s)^{1/2} \hbar \mu_c}{e} = \frac{\hbar^2 (2\pi n_s)^{1/2}}{2\pi k_B T m^*}$$ (1.5)

which gives:

$$\mu_c = \frac{e\hbar}{2\pi k_B T m^*}$$ (1.6)

The critical mobility is inversely dependent on the effective mass of charge carriers in the 2DEG but is independent of the carrier concentration and carrier mobility of the system. Previous work in ZnO 2DEGs at the LCN has determined $m^*$ to be in the range 0.17-0.32$m_e$, where $m_e$ is the mass of an electron in a vacuum [41]. Plugging this into equation 1.6 indicates $\mu_c$ has a range of $3 \times 10^3 - 6.3 \times 10^3$cm$^2$/Vs for ZnO 2DEGs at 2K (We use 2K as this is the temperature at which we are experimentally able to determine carrier concentration and mobility at the LCN). This gives us a lower bound for ZnO 2DEG mobility. If we can exceed this critical mobility range, we know that we are in the clean coherence limit and further increase in mobility will not result in an increase in coherence length.

Now let us consider the clean-limit coherence length relationship. From equation 1.2 we note that $\xi_c \propto n^{1/2}$, so carrier concentration affects the upper limit of the coherence length in the 2DEG. From this equation, we can show that to get a coherence length on the order of 100nm at 2K, we need a carrier concentration on the order of $10^{12}$cm$^{-2}$. Falson et al. were able to achieve their impressively high
1.4. Tuneable Josephson Junction Requirements

mobility samples in part by growing interfaces with lower carrier concentrations, typically on the order of $10^{10}$ cm$^{-2}$ [16]. Therefore 2DEGs like those demonstrated by Falson et al. do not meet all of our requirements.

In summary this work aims to produce ZnO 2DEGs that would be suitable for tuneable JJ device applications. To achieve this, we must produce 2DEGs with a mobility in excess of the critical mobility $3.3 - 6.3 \times 10^3 \text{cm}^2/\text{Vs}$ and a carrier concentration in excess of $10^{12}$ cm$^{-2}$. In this thesis, we will demonstrate a 2DEG with carrier concentration of $n = 5.05 \times 10^{12}$ cm$^{-2}$ and $4.8 \times 10^4$ cm$^2$/Vs, thereby fulfilling both criteria.

1.4.1 Structure of this Thesis

In this thesis we use molecular beam epitaxy (MBE) to grow high quality ZnO films and ZnO/ZnMgO heterostructures. We perform structural, optical, and chemical analysis on these structures using a variety of material characterisation techniques. We then pattern these structures into devices and characterise their electrical properties. We use this to extract 2DEG parameters and prove that our devices fulfil our requirements.

Chapters 2-4 provide an introduction to confined electron spaces (chapter 2) before discussing ZnO 2DEGs in detail (chapter 3) and then describing some of the electrical properties that are unique to 2DEGs (chapter 4).

Chapter 5 covers the full experimental methods used to produce the work in this thesis including MBE growth, material characterisation, device fabrication, and electrical characterisation.

Chapter 6 details the experiments conducted on ZnO substrates. It starts by demonstrating how rapid thermal treatment leads to a reduction in room temperature conductivity of ZnO substrates. It then details work aimed at achieving 2DEG formation by growing heterostructures onto treated and untreated samples. The material and electrical structures are extracted. Electrical analysis reveals that a 2DEG has formed and it fulfills both the carrier concentration and mobility criteria we set out to achieve. Further analysis is conducted on this sample to ascertain what the dominant scattering mechanisms are in this structure.
Chapter 7 details ZnMgO/ZnO heterostructure growth on a-plane sapphire. It starts with a study of ZnO film growth directly on a-plane sapphire, aimed at finding optimal growing conditions. It then documents O-polar ZnO/ZnMgO/ZnO multi-layer growth on a-plane sapphire. These structures are then structurally, chemically, and electrically characterised.

Chapter 8 concerns ZnMgO/ZnO structures grown on c-plane sapphire. It begins by detailing how MgO buffer layers can be used to achieve Zn-polar ZnO growth on c-plane sapphire. The next part of the chapter shows how these Zn-polar ZnO layers are used as the basis for a Zn-polar ZnO/ZnMgO heterostructure on c-plane sapphire. As in earlier chapters, these structures are also structurally, chemically, and electrically characterised.

In chapter 9 we summarise the work laid out though out this thesis, and suggest ways this work could be further developed.
Chapter 2

Confined Electron Spaces: History and Development

Confined electron systems refer to a group of conductive materials where carrier motion is confined in one or multiple dimensions. These range from weakly confined systems, such as two-dimensional electron gases (2DEGs), where the carriers (typically electrons) are restrained in one dimension, to heavily restricted zero-dimensional systems, where a combination of material properties and external fields confine carriers to distinct quantum wells. The material properties of such low dimensional structures differ significantly from bulk material. In bulk material carriers are free to move through, and are subject to interactions with, the entirety of the material. In low dimensional systems the electrons are confined to specific regions of the material and become spatially separated from the rest of the bulk, thereby restricting carrier-bulk interactions.

This thesis focuses on the growth of 2DEGs where carriers (electrons in this case) become confined to a two-dimensional plane. These systems can be produced when two semiconductors are brought into contact. The band mismatch between the materials will encourage charge carriers to cross the boundary which results in charge accumulations and the formation of quantum wells. These wells limit the electrons’ interactions with the bulk material and subsequently result in improved mobility. Additionally the 2D density of states facilitates the observation of interesting phenomena, such as quantised transport and higher mobility. To
produce these structures, one must be able to produce high-quality thin films with low defect densities.

This chapter explores several types of 2DEG, working chronologically from the earliest form of 2DEGs to modern day devices. The origin, benefits and drawbacks of each system will be discussed. The concept of polarisation-induced 2DEGs will be introduced with a brief look at AlGaN/GaN systems. ZnO/ZnMgO systems are then explored in greater detail in chapter 3.

### 2.1 Discovery and Development

2DEGs were initially produced as a necessary component for field effect transistors (FETs). By confining conduction to a 2D plane, one can deplete the number of carriers in a given region by applying an external electric field. This provides an easy mechanism whereby one can quickly turn the conduction across the length of a channel on or off.

The first observation of such a device was the Si MOSFET (metal-oxide semiconductor FET). This consists of a 3-dimensional semiconductor (Si in this case) which has been doped with p-type carriers and a metal top gate which is insulated from the Si via a SiO$_2$ layer [42]. When a positive gate voltage is applied, holes in the Si below the insulator get pushed into the bulk, creating a depleted layer near the gate at the Si/SiO$_2$ interface. In addition the positive charge attracts electrons from the bulk to the surface. If the gate voltage is high enough a negative charge-carrier inversion layer forms at the semiconductor/insulator interface, thereby producing a confined electron space. The tunability of these systems is their biggest asset and resulted in devices like these being the building blocks for all modern-day computing equipment. However using extrinsic electric fields for confinement results in poor spatial isolation of charge carriers from the bulk. Additionally the high density of ions in the p-type material act as scattering centres. Subsequently these devices suffer from high scattering and low carrier mobility.
2.2 Intrinsic 2DEGs

Intrinsic 2DEGs are formed by an internal electric field across the interface of two semiconductors. Unlike their extrinsic counterparts, intrinsic 2DEGs often demonstrate higher electron mobility compared to the bulk material. This is due to separation of the carriers from scattering centres in the material bulk. Intrinsic systems didn’t see wide-scale implementation until the 1980s when the rise of MBE [43] and metal organic chemical vapor deposition MOCVD [44] technology made it easier to produce high crystal quality, high purity films. These techniques were only made possible by prior developments in vacuum technologies and the purity of available sources. MBE and MOCVD are now widespread in the semiconductor community as they provide a high level of control over interface abruptness, material surface quality and dopant incorporation.

In intrinsic systems, the 2DEG originates at the point of growth due to the difference in band gaps between the two materials. Electrons move from one material to the other to compensate the difference in Fermi energy. This leads to band bending resulting in an approximately triangular quantum well forming at or

Figure 2.1: Energy band diagram of intrinsic 2DEG showing bending in conduction and valence band. Fermi energy is marked to show the formation of the triangular quantum well.
near the material interface. Such a well is illustrated in figure 2.1. An ideal system sees the electrons transfer from the doped material to a quantum well in the undoped material. In this way the additional carriers from the dopants are incorporated into the conduction channel but these carriers are spatially separated from their source ions which can act as charge scattering centres. Electrons within the well can be treated approximately as particles in a box with quantised energy levels. Hence we see the formation of energy levels in the 2DEG.

At sufficiently low temperatures all states up to the Fermi energy will be filled in the 2DEG. Furthermore if the difference between the lowest energy and highest energy state in the well exceeds $k_BT$, where $k_B$ is the Boltzmann constant and $T$ is temperature, there will be no unoccupied states for electrons to thermally scatter into. This lack of thermal scattering combined with the reduction in impurity scattering is what gives the 2DEG its high mobility.

A significant drawback for these systems is that to produce a larger number of charge carriers a larger quantity of dopant is needed. This results in an increase in scattering due to dopant ions as well as strain at the interface due to lattice mismatch, which in turn leads to interface roughness and associated scattering. This scattering reduces the mobility of the 2DEG system and, in extreme cases, can prevent the formation of the 2DEG altogether.

### 2.2.1 AlGaAs/GaAs Systems

The generic intrinsic 2DEG system outlined above is based on the AlGaAs/GaAs 2DEG. In AlGaAs the Al sits at the Ga sites in the crystal structure and widens the material’s band gap. The bandgap can be modulated by varying the Al content. When the GaAs and AlGaAs are brought into contact the Fermi energy is pinned within the band gap of both materials and the conduction band of the two materials sit at different levels. If the contact at the interface is ideal, electrons from the AlGaAs layer will flow into the GaAs layer [45] resulting in band-bending and the formation of an approximately triangular well like the one shown in figure 2.1. Additional developments have been made to add gate electrodes to this type of 2DEG and thereby precisely control the 2DEG current density [46].
One advantage that these systems have over Si MOSFETs is that the 2DEG arises in a region where there are no charge donors (as shown in figure 2.2). As such the electrons experience no scattering from interactions with donor ions and so can theoretically achieve much higher mobilities. Therefore doping this type of 2DEG is particularly effective as doping of the AlGaAs region close to the interface leads to an increase in carriers in the undoped region. For example when n type dopants are added to the AlGaAs layer dopant electrons accumulate in the triangular shaped potential in the GaAs layer close to the interface. These electrons are spatially separated from the dopants in the AlGaAs layer and so have an increased mobility compared to the free electrons in the AlGaAs layer [47].

2DEG quality is primarily determined by physical properties of the systems, i.e. atomically sharp interfaces with low dislocation density and uniformly strained heteroepitaxial layers. However 2DEG quality can also be influenced by band-gap engineering. Adding small amounts of In to GaAs reduces the GaAs band gap and leads to deeper quantum well at the AlGaAs interface resulting in greater carrier isolation, a lower effective electron mass and improved electron mobility [48, 49, 50]. However In content should be kept below 15% as excess In incorporation leads to increased mismatch at the heterostructure interface. This results in strain of the crystal layers which relaxes at some critical thickness resulting in defects which are detrimental to 2DEG performance [49]. One can increase this critical thickness by reducing the overall In content [51].

GaAs based devices have been the workhorse for 2DEG research for many
2.2. Intrinsic 2DEGs

years and have achieved low temperature mobilities as high as $3 \times 10^7$ cm$^2$/Vs [52]. They have also been used to observe a variety of interesting phenomena including spin qubits and the fractional quantum Hall effect [15, 53, 54].

2.2.2 Polarised (AlGaN/GaN) Systems

AlGaN/GaN systems differ from those discussed so far as the polarity of the growth materials starts to play a substantial role in the formation of the 2DEG. GaN has a wurtzite cell structure. For binary A-B components with a wurtzite structure, the crystal will form with an alternating A-B bilayer structure (defined as the [0001] direction) or an alternating B-A bilayer structure ([0001] direction). The corresponding A and B terminated surfaces are defined as (0001) and (0001) respectively [55]. In this instance the Ga and N are the A and B components respectively.

Due to this alternating structure a spontaneous charge polarisation is produced pointing from Ga to N. In the absence of an external electric field the total polarisation of the GaN film is the sum of the spontaneous polarisation $P_{SP}$ and piezoelectric polarisation $P_{PE}$ caused by tensile strain in the crystal growth direction. AlGaN has greater spontaneous and piezoelectric polarisation [56] and so a polarisation discontinuity arises at the AlGaN/GaN interface.

Figure 2.3: Schematic of crystal structure for wurtzite Ga-polar and N-polar GaN. Figure taken from [55]
2.2. Intrinsic 2DEGs

At a sufficiently abrupt interface, the polarisation can decrease and increase within a single bilayer leading to a fixed charge density given by [55]:

\[ \sigma = P(top) + P(bottom) \]
\[ = \{P_{PE}(top) - P_{PE}(bottom)\} + \{P_{SP}(top) - P_{SP}(bottom)\} \]  

(2.1)

Where \(P_{PE}\) polarisation from the piezoelectric effect due to strain of the polarised layers, and \(P_{PE}\) is polarisation from spontaneous polarisation. If the sheet charge is positive, free-electrons will move to compensate the charge. These electrons arise from the naturally occurring free electron background in GaN and AlGaN [55]. Positive sheet charge can be easily achieved by growing Ga(Al)-polar AlGaN onto Ga-polar GaN with observed mobilities up to 51,700 cm\(^2\)/Vs at 13K [57].

AlGaN is significant for the purposes of this thesis as it is perhaps the closest system to ZnMgO in terms of its formation and physical properties. Both systems rely on polarisation to achieve strong confinement which facilitates the observation of properties not observed in other intrinsic systems. AlGaN systems have been researched longer than ZnO based heterostructures. As a result physical properties observed in AlGaN systems are often indicative of phenomena present in ZnO systems. Several of the underlying theoretical explanations for behaviour observed in ZnO based samples were first derived for AlGaN systems.

As ZnO 2DEGs are the basis of this thesis they warrant a more thorough description. Hence the following chapter focuses solely on ZnO material properties, the types of 2DEGs one can produce on ZnO and how these 2DEGs can be tuned through growth techniques.
Chapter 3

ZnO/ZnMgO Heterostructures

This chapter outlines the properties of ZnO and the types of 2DEG that this material facilitates. Particular attention is paid to the bandgap and polarisation engineering achievable in ZnO ternary compound growth. Such engineering is the mechanism through which 2DEGs are produced and controlled. This chapter will explain why heterostructures grown on Zn-polar ZnO are the preferred structure for mobility enhancement and why these structures are the basis of this thesis.

3.1 ZnO material properties

Much like the AlGaN/GaN systems detailed in the previous chapter, ZnO/ZnMgO 2DEGs form at the point of growth with electron accumulation driven by the polarisation of ZnO [58]. The ZnO unit cell has an hexagonal wurtzite structure with an off-centre Zn atom along the c-axis. As such the ZnO unit cell lacks inversion symmetry, which results in a spontaneous charge polarisation along the c-axis. Figure 3.1 shows the structure of the ZnO unit cell as well as the polarisation direction.

ZnO’s properties can be tuned through the addition of ternary and quarternary elements. Two notable examples of ternary materials include ZnCdO, where the band gap reduces with Cd concentration [59] and ZnMgO, where the band gap broadens with Mg concentration [60]. ZnBeMgO is arguably the most common quarternary compound, where Be is used to counteract some of the lattice strain due to Mg inclusion, while still facilitating band gap broadening [61, 62].
The band gap is not the only thing manipulable in ZnO - the polarisation can also be tuned through ternary and quarternary growth. The spontaneous polarisation in ZnO arises from a lack of inversion symmetry in the unit cell. In ZnMgO the Mg atoms have a smaller atomic radius than Zn and sit at Zn sites. Therefore Mg incorporation leads to a reduced c-parameter compared to ZnO but the charge imbalance is the same. The polarisation in ZnMgO is therefore higher than in ZnO. Hence growing ZnO and ZnMgO in intimate contact results in a polar discontinuity at the interface, shown to be crucial to ZnO/ZnMgO 2DEG formation [58].

The polar discontinuity at the interface results in an uncompensated bound charge. This bound charge produces an electric field driving charge carriers to the interface [63]. The sign of the bound charge, and thereby the carriers attracted to the interface, depends on the orientation of the polarisation.

Additionally Mg incorporation results in a slight increase in the in-plane a-parameter in ZnO, which produces strain at the ZnO/ZnMgO interface. However this increase is small, varying by 0.05x were x is the Mg concentration. Low Mg concentrations (ranging from x = 0.05 - 0.1) can be employed to achieve coherent epitaxial ZnMgO films on ZnO with little strain [64, 65]. Furthermore coherent
growth can be achieved with high Mg concentrations in strained films [66]. These features have inspired much research into ZnO/ZnMgO interfaces for quantum confinement applications.

The polarisation and band gap of Zn$_{1-x}$Mg$_x$O can be controlled by changing the Mg concentration $x$. Isakov has shown the bandgap of Zn$_{1-x}$Mg$_x$O can be given as a function of $x$ [67]:

$$E_{Zn_{1-x}Mg_xO} = (3.38 + 1.55x)\text{eV}$$ (3.1)

Meanwhile Malashevich et al. [68] gives polarisation as a function of $x$:

$$P_{Zn_{1-x}Mg_xO} = (0.0322 + 0.024x)\text{Cm}^{-2}$$ (3.2)

These equations are only valid up until Mg concentrations of 0.2. For concentrations above this point, the band gap and polarisation increase faster than $x$ [63].

The Mg gradient near the ZnO/ZnMgO interface can be controlled by varying the Zn-flux during MBE growth [66]. For low Zn-flux, with a relative beam pressure of $1 \times 10^{-7}$ Torr and below, the Mg gradient is more diffuse. When growing ZnMgO on ZnO, the film becomes lattice matched [69] and Mg incorporation is determined by the amount of excess energy the system has compared to that needed to grow a lattice mismatched unit cell. For high Zn flux, with incident flux in the $1 \times 10^{-7}$ - $1 \times 10^{-6}$ Torr range, equilibrium is not reached, resulting in more abrupt Mg interfaces. Interface abruptness can also be controlled by altering the growth temperature [66]. At higher growth temperatures, Mg re-evaporation is greater. This slows the rate of Mg incorporation and results in a less abrupt film.

The polarisation of the ZnO is intrinsically linked to the orientation of the ZnO unit cell. Therefore it is important to factor in the polarisation of ZnO when fabricating ZnO/ZnMgO heterostructures. Interfaces can be non-polar, meaning the crystal growth direction is perpendicular to the [0001] axis (aka the c-axis). Alternatively if the heterointerface is polar, with growth direction being parallel to the c-axis, then it can be either O- or Zn-polar. These faces are not equivalent,
3.2 Band Gap at Interface

As will be shown later in this chapter. The O- and Zn- polar faces are sometimes referred to as n-type and p-type, respectively. This refers to the types of carriers needed to compensate the polarisation mismatch at the respective interface.

3.2 Band Gap at Interface

At the ZnO/ZnMgO interface, the band profiles are affected by a combination of the band mismatch, polarisation discontinuity, and the free charges which can redistribute to screen electric fields. The resulting band profile can be solved theoretically via the self-consistent 1D Poisson-Schrodinger equation solver [70]. Figure 3.2a shows example profiles for Zn-, O- and non-polar infinitely abrupt ZnO/Zn$_{1-x}$Mg$_x$O interfaces, where x = 0.4 and the temperature is 4K. Figure 3.2b shows the corresponding carrier density distribution for these interfaces. These figures can be found in [71]. The non-polar interface (red line) has the simplest band profile, where there is a band discontinuity at the interface due to differing band gaps in ZnO and Zn$_{0.6}$Mg$_{0.4}$O.

In the Zn-polar interface (blue), the polarisation and bandgap discontinuities...
3.3. Thin Film ZnO/ZnMgO Heterostructures

at the interface are additive. An approximately triangular quantum well forms at the interface. Free charge carriers arise from native shallow donors in ZnMgO, travel to the interface, fall into the well, and become confined. This is shown by the large spike in charge carriers seen in blue (figure 3.2b). The electron confinement at the interface is why this structure is labelled as ‘n-type’. At low temperatures the carriers in the well relax into the lowest energy levels. Figure 3.2b indicates the 2DEG forms close to the interface in the ZnO layer. This observation has been confirmed through depth profiles of carrier concentration [72]. Further analysis indicates electrons in the 2DEG arise from bulk donors in the ZnMgO layer [73]. This is ideal for high mobility, high carrier 2DEG formation, since the electrons are spatially separated from their donor ions, which would otherwise act as scattering centres, limiting mobility.

In the O-polar case (green), the polarisation and bandgap discontinuity at the interface are subtractive. Free carriers are driven away from the interface and are redistributed, as shown in green in figure 3.2b. This process is highly dependent on the density of free electrons, which will vary from sample to sample. Note that figure 3.2a shows a very shallow quantum well at the ZnO/ZnMgO interface in the valence band.

3.3 Thin Film ZnO/ZnMgO Heterostructures

ZnO/ZnMgO heterostructures have been the subject of focused research for some time and are fabricated by a range of techniques including; MBE [16], MOVPE [74], PLD [75] and CVD [76]. Additionally there are a number of substrates that have been utilised for ZnO/ZnMgO growth including; c-plane [77] and a-plane [78] sapphire, ScAlMgO₄ (SCAM) [79] and single crystal ZnO [16].

Crystal quality is highly significant when fabricating heterostructures. Both the growth method and substrate used can significantly impact the resulting 2DEG. Out of the methods stated above MBE provides the best control over the material deposition. MBE also has the highest quality interface fabrication and has been used to produce ZnO heterostructures with electron mobilities of $10^6\text{cm}^2/\text{Vs}$ [16].
Not only are such measurements several orders of magnitude higher than bulk ZnO, they are higher than mobilities seen in 2DEGs grown by other crystal deposition methods, which are typically in the region of $10^2$-$10^3 \text{cm}^2/\text{Vs}$. Moreover, choice of substrate has a large impact on the quality of the resulting 2DEG. Depositing ZnO onto a substrate with poor lattice matching will result in a strained ZnO film. At some critical thickness, this strain will relax resulting in the formation of defects. Such defects act as classical scattering centres, limiting 2DEG mobility. In extreme cases, these defects can prevent the formation of 2DEGs altogether. Furthermore, the substrate used will affect the polarity of ZnO deposited on it. C-sapphire is commonly used for ZnO deposition, despite its large (18.8%) lattice mismatch; it is cheap and easy to source. ZnO grows O-polar (000\(\bar{1}\)) when deposited on c-sapphire but its polarity can be flipped to Zn-polar (0001) through the use of a thin MgO buffer [80]. Growing on a-sapphire also results in O-polar ZnO [81], though there is evidence that annealing a-sapphire in nitrogen plasma can lead to subsequent Zn-polar ZnO growth [82]. On single crystal ZnO substrates, subsequent ZnO/ZnMgO growth has the same orientation as the substrate surface. ZnO substrates are available in O-, Zn- and non-polar faces.

### 3.3.1 Non-Polar Interfaces

Non-polar interfaces have no polarisation mismatch at the interface. Carrier confinement is solely due to the band-gap mismatch. Such a profile is shown in figure 3.2a in red. Non-polar interfaces are employed in situations where band tilting, due to the internal electric fields of polar ZnO/ZnMgO, would interfere with device properties. Non-polar interfaces have been used to demonstrate ZnO quantum wells in both a-plane [83] and m-plane [84, 85] ZnO.

Non-polar systems can be used to fabricate abrupt interfaces with consistent well widths and improved crystallographic quality, when compared to their polar counterparts [83, 84, 85]. However, without the polarisation discontinuity at the interface, the carriers are not as confined as in polar systems [86], so non-polar interfaces typically show far lower mobilities than polar devices. When the polarisation and band gap are additive, the polarisation discontinuity also drives
carriers to the interface, thereby increasing carrier density.

3.3.2 Polar Interfaces

In polar heterostructures, the polar discontinuity at the interface results in a narrow, approximately-triangular well. Electrons fall into these wells forming a 2DEG. While these devices have been demonstrated in O-polar [77] and Zn-polar [87] heterostructures, the O-polar interfaces have far lower mobilities. This is because in O-polar interfaces the polarisation discontinuity also affects Mg distribution at the interface. According to the theoretical 1D self-consistent Poisson-Schrodinger fitting, if an abrupt O-polar interface is formed, it could produce a region of p-type ZnO due to the polarisation mismatch. Instead Mg redistributes across the interface to avoid the formation of p-type regions [86]. This Mg redistribution reduces the abruptness of the interface, reducing confinement and carrier screening, thereby reducing 2DEG mobility. Experimental observations of ZnO heterostructures have shown that the polarisation discontinuity at the interface is integral to strong carrier confinement [58]. The priority of this research is to optimise ZnO 2DEG mobility. O-polar interfaces are therefore not suitable due to their mobility limitations.

In Zn-polar interfaces, the polarisation discontinuity results in quantum confinement that is sufficient to produce 2DEGs at room temperature [88]. Room temperature 2DEG mobility has been shown to increase with Mg concentration [73]. Room temperature mobilities are typically in the range of $10^2 \text{cm}^2/\text{V}\cdot\text{s}$. To achieve higher mobilities, the samples must be cooled to low temperatures of 2K or below. Currently the highest mobility observed in ZnO 2DEGs occurs in low-Mg content heterostructures with values in excess of $10^6 \text{cm}^2/\text{V}\cdot\text{s}$ at 2K [16]. At low temperatures, small Mg concentrations are beneficial since Mg incorporation increases lattice mismatch, resulting in higher interface roughness [88]. Furthermore increasing Mg content pushes the 2DEG closer to the interface, thereby increasing the effect of interface roughness scattering (IRS). At low temperatures the quantum well does not need to be particularly deep, so low Mg concentrations still achieve confinement. For temperatures of 2K and below, Mg concentrations of $x \sim 0.01$ are optimal for high mobility [16]. At lower
concentrations the well is too shallow to sufficiently screen against charged impurity scattering. For concentrations above 0.01, the interface roughness scattering becomes the limiting factor [88].

3.4 Summary

ZnO-based systems can be used to facilitate 2DEG formation using a combination of band gap engineering and polarisation discontinuity at the interface. While 2DEGs can be produced that rely on just the band gap discontinuity (non-polar systems), the polarisation discontinuity greatly increases electron confinement and drives additional carriers to the interface, thereby improving 2DEG mobility and carrier concentration. Both the band gap and polarisation can be linearly tuned via the Mg concentration. Now that the mechanisms for 2DEG formation in ZnO have been discussed, the following chapter briefly describes some of the unique electrical phenomena observed in these 2DEGs, which are referenced frequently throughout the experimental chapters.
This chapter will cover the fundamental electrical properties at play in a 2D electron gas (2DEG) system, making particular reference to the ZnO/ZnMgO system. The following discussion is considered canonical information for this field. Therefore the structure of this chapter will closely follow the general approach laid out in “Transport in Nanostructures” by Ferry and Goodnick [89].

4.1 Charge Confinement in a 2DEG

As explained in the previous chapter, the conduction-band discontinuity at the ZnO/ZnMgO heterostructure results in band-bending and the formation of a potential well. This results in the formation of a 2DEG at the interface. The electrons in this well are confined in the z-direction, defined as the plane normal to the heterostructure interface. This confinement produces discrete energy levels in the ZnO region, much like those formed for an electron in a quantum well.

The Schrödinger equation can be solved within this conduction-band well to determine the energy levels. The curved structure of the conduction band (as depicted in figure 4.1) makes this solution non-trivial. To overcome this issue, it is commonplace to approximate the region at the interface as a triangular potential well. Solving the Schrödinger equation with this assumption gives energy levels
4.2. Electrical properties of an infinite 2DEG

To further understand conduction in the 2DEG we will start with the model for an infinitely sized 2DEG; i.e. a 2D conductive plane which extends infinitely in the x and y direction. In the absence of an electric field the sheet resistance, given

\[ R_{\text{sheet}} = \left( \frac{\hbar^2}{2m^*} \right)^{1/3} \left[ \frac{3\pi F_{\text{eff}}}{2} \left( \ell - \frac{1}{4} \right) \right]^{2/3} \]  

where \( \ell \) is a positive integer denoting the level number for energies above the conduction band edge. \( m^* \) is the effective mass of electrons with momentum normal to the interface and \( F_{\text{eff}} \) is the effective electric field at the interface given by

\[ F_{\text{eff}} = \frac{e}{\varepsilon_{\text{ZnO}}} \left( n_{\text{depl}} + \frac{n_{2\text{DEG}}}{2} \right) \]  

Here \( n_{2\text{DEG}} \) is the density of acceptors \( N_A \) per unit area in the depleted region (of width \( W_{2\text{DEG}} \)) on the ZnO side of the interface \( n_{2\text{DEG}} = N_A W_{2\text{DEG}} \). \( n_{2\text{DEG}} \) is the density of electrons per unit area and \( \varepsilon_{\text{ZnO}} \) is the electrical permittivity of ZnO.

4.2 Electrical properties of an infinite 2DEG

Figure 4.1: Diagram of the realistic conduction band in ZnO/ZnMgO interfaces, and the triangular well assumption.

with quantised energy given by:

\[ E_\ell = \left( \frac{\hbar^2}{2m^*} \right)^{1/3} \left[ \frac{3\pi F_{\text{eff}}}{2} \left( \ell - \frac{1}{4} \right) \right]^{2/3} \]  

(4.1)

where \( \ell \) is a positive integer denoting the level number for energies above the conduction band edge. \( m^* \) is the effective mass of electrons with momentum normal to the interface and \( F_{\text{eff}} \) is the effective electric field at the interface given by

\[ F_{\text{eff}} = \frac{e}{\varepsilon_{\text{ZnO}}} \left( n_{\text{depl}} + \frac{n_{2\text{DEG}}}{2} \right) \]  

(4.2)
as resistance per square, is equivalent to the inverse of sheet conductance, given as \( \sigma_{sh} = n_{sh} e \mu \), where \( n_{sh} \) is the sheet carrier concentration and \( \mu \) is the carrier mobility. It follows that in an electric field of size \( E \), the current per unit width in the 2DEG is given by \( J = \sigma_{sh} E \).

The unique property of the 2DEG electrical system becomes clear when we consider the application of a perpendicular magnetic field (denoted as a field with flux density \( B \) applied in the \( z \)-direction). In this scenario, electrons with finite velocity \( v \) will experience a Lorentz force given by \(-evB\). This force is always perpendicular to the direction of motion, meaning the electrons will describe circular orbits with a radius of \( r \) and an orbital frequency of \( \omega_c \). The central force for circular motion is given by \( m r \omega_c \), known as the cyclotron frequency. By equating this to the Lorentz force, and noting that \( v = \omega_c \), it can be shown that

\[
\omega_c = \frac{eB}{m} \tag{4.3}
\]

where \( m \) is the average mass of the electron over the circular orbit.

Only certain discrete values of the orbital radius, and hence only certain energies of the electrons are permitted. These allowed energies are given by:

\[
E_n = E_\ell + \left(n + \frac{1}{2}\right) \hbar \omega_c \tag{4.4}
\]

The discrete energy levels, denoted by \( n = 0, 1, 2,... \) are known as Landau levels. The spacing of these levels, equal to \( \hbar \omega_c \), can be tuned by varying the applied magnetic field since \( \omega_c \) is proportional to \( B \). The orbital radii for the corresponding Landau level is given by:

\[
r_n = \sqrt{\frac{2\hbar \left(n + \frac{1}{2}\right)}{eB}} \tag{4.5}
\]

The lowest orbital radius, \( r_0 \), is also known as the ‘magnetic length’ \( \ell_m \) and is given by \( \sqrt{\hbar/eB} \).
4.2. Electrical properties of an infinite 2DEG

In zero field, the density of states per unit area is given by [89]:

\[ g(E)_{2D} = \frac{m}{\pi \hbar^2} \]  \hspace{1cm} (4.6)

When a non-zero magnetic field is applied to the 2DEG, all states with energy within \( \pm \hbar \omega_c / 2 \) of each Landau level are condensed into the nearest Landau level. Therefore in a non-zero field the number of states per unit area per Landau level is given by:

\[ g_{LL} = g(E)_{2D} \hbar \omega_c = \frac{eB}{\pi \hbar} \] \hspace{1cm} (4.7)

Each state can hold one electron, meaning that for a given sheet carrier density of \( n_{sh} \), the highest occupied Landau level at \( T=0 \) is given by:

\[ n_{\text{max}} = \text{Int}(n_L - 1) \] \hspace{1cm} (4.8)

where \( \text{Int}(x) \) is the integer component of \( x \). \( n_L \) is the Landau index given by:

\[ n_L = \frac{n_{sh} \hbar}{g_{LL}} = \frac{\pi \hbar n_{sh}}{eB} \] \hspace{1cm} (4.9)

Therefore the Fermi energy can be calculated from equation 4.4 using \( n = n_{\text{max}} \).

Now consider the case of magnetic field increasing from zero. At zero magnetic field, the Fermi level is set by the highest occupied Landau level. As the field increases, so does the Landau level spacing due to the \( \omega_c \) dependence. The number of states in the lower Landau levels increases according to equation 4.7. At some critical field \( B_c \), there will be enough states in the levels below \( n_{\text{max}} \) to accommodate all the electrons in the system, and so \( n_{\text{max}} \) will drop by one. This is accompanied by a drop of \( \hbar \omega_c \) in the Fermi energy. The inverse field at which there is a jump from Landau level \( (k+1) \) to \( k \) is given by

\[ \frac{1}{B} = k \frac{2e}{hn_{sh} \hbar} \] \hspace{1cm} (4.10)

In an electrical transport measurement, at fixed voltage and sheet carrier...
4.3 Conduction Through 2DEG Edge States

As the previous sections show, electrons in an infinite 2DEG in a perpendicular magnetic field are confined to circular orbits. In other words, the net momentum of concentration, this results in a drop in conductivity. Hence at \( B = B_c \) there is a local maximum conductivity with respect to magnetic field.

As the field increases, this process repeats: the Landau level spacing increases, the electrons collapse into lower levels, the Landau level number drops by one, the Fermi energy reduces by \( \hbar \omega_c \). This leads to periodic oscillations in the longitudinal resistivity of the 2DEG as a function of electric fields. These are known as Shubnikov-de Haas (SdH) oscillations. Figure 4.2 shows a visual representation of typical SdH oscillations.

To observe SdH oscillations the Landau level separation must be greater than the thermal energy \( kT \). Defects can also impede SdH observation as they lead to Landau level broadening. Defect broadening is given by:

\[
\Gamma = \hbar \sqrt{\frac{2 \omega}{\pi \tau_f}}
\]  

(4.11)

where \( \tau_f \) is the mean time between scattering events for electrons. Hence, SdH oscillations can only be observed when \( \hbar \omega > \Gamma \).

4.3 Conduction Through 2DEG Edge States

Figure 4.2: Qualitative example of typical SdH oscillations. \( R_0 \) refers to resistance at zero field.
electrons in such a system is zero. However if the 2DEG is confined in one direction, say the x-direction for the purpose of this example, the electrons near the edge of this plane will not be able to complete a full orbit. Instead they will scatter off the edge of the plane, travelling in a semicircular path until they hit the boundary again, when the whole process repeats. In this way, the electrons propagate along the edge of the 2DEG with a non-zero momentum, as illustrated in figure 4.3a. These regions of electrons with non-zero momentum are known as edge states. Electrons in these states are confined to the edges of the 2DEG, acting as a quasi-one dimensional ballistic conductor, as will be shown in this section.

Consider a 2D system restricted in the x-direction, subject to a perpendicular field $B$ resulting in circulating electrons with an orbit of size $r_n$. Orbits with a centre more than distance $r_n$ from either edge of the 2DEG are unaffected, contributing no momentum to the y-direction. Conversely orbits within $r_n$ of a edge will scatter, resulting in a ‘skipping orbit’, as illustrated in figure 4.3a. The states along the top edge of the 2DEG carry current in the opposite direction to the one along the bottom edge. In the absence of an electric field, these top and bottom channels

![Figure 4.3: Plan view of cyclotron and skipping orbits in a 2DEG (a) and the special traversing orbital case (b).](image)
4.3. Conduction Through 2DEG Edge States

exactly cancel, resulting in no net momentum in the y-direction. If a finite electric field is applied parallel to the 2D channel, the propagation direction of one of these states will be energetically favourable resulting in the current being entirely carried by the edge states. In the event where cyclotron orbits are within \( r_n \) of both edges, the result is a ‘traversing orbital’, illustrated in figure 4.3b.

Skipping orbitals have a non-zero momentum \( k_y \) in the y-direction, thereby contributing additional kinetic energy to the Landau levels. To account for this, equation 4.4 is modified to:

\[
E_n = E_l + \left( n + \frac{1}{2} \right) \hbar \omega_c + \frac{\hbar^2 k_y^2}{2M} \tag{4.12}
\]

where \( M \) is the effective mass of the skipping orbits. If it is assumed that the potential \( V \) confining the 2DEG in the x-direction is parabolic, with some natural frequency \( \omega_0 \), then \( M \) can be given as

\[
M = m^* \left( 1 + \frac{\omega_c^2}{\omega_0^2} \right) \tag{4.13}
\]

where \( m^* \) is the 2DEG electron effective mass. In large fields \( \omega_c \) and \( m^* \) are large meaning the y-momentum is small, so the edge states play a negligible role. In low field the opposite is true, \( \omega_c \) is small and \( M \approx m^* \). The density of state becomes equivalent to that of a one-dimensional conductor. The mechanisms at play in a 1D system are explained in more detail in the following section.

Figure 4.4 illustrates the structure of the Landau levels for a sample with width \( W \). The figure is plotted as a function of the position of the cyclotron orbital centre. Centres far from the edge of the 2DEG have a spectrum similar to that of an infinite 2DEG i.e they follow a behaviour laid out in equation 4.4 with levels separated by \( \hbar \omega_c \). Near the edges there is additional kinetic energy, as explained by equation 4.12.

Electrons in the edge states cannot backscatter off defects. When the skipping orbital is interrupted the electron can complete a cyclotron orbital at the point of collision and re-establish the skipping orbit, as shown in figure 4.5. Electron
4.3. Conduction Through 2DEG Edge States

Figure 4.4: Landau levels with energy level $E$ plotted as a function of the distance from the centre of a sample of width $W$. Landau level number is also shown here.

Figure 4.5: Illustration of how circulating currents avoid reflection. At the point of collision the particle simply completes a full cycle and re-establishes the skipping orbital.
momentum in an edge state can only be reversed if the electron scatters to the edge state on the opposite side of the 2DEG. The cyclotron radius denotes how far an electron can ‘stray’ from the edge state. To give an idea of scale, a 5T field will result in a magnetic length of approximately 11nm, hence backscattering is negligible in macroscopic-scale samples.

4.4 Ballistic One-Dimensional Conduction

As stated in the previous section, in magnetic field the conduction through a 2DEG is primarily though the edge states. These edge states act as 1D ballistic conductors. This section will explain the theory behind such systems which will act as a background for the explanation of the quantum Hall effect in the following section.

In a ballistic system, the electron mean-free-path is comparable to the electron spacing. Whereas a diffusive system would see an electron scatter several times as it passes along the channel from source to drain, a ballistic system sees an electron travel through the channel largely unscattered. As a result, electron mobility plays no role in determining the conduction of such a system.

Consider a 1D ballistic channel at zero temperature. For the sake of simplicity assume there is a singular 1D conduction channel throughout the conductor, that is to say that only one electron may traverse the channel at any given energy, at any given time. For the sake of this derivation it is also assumed that the conductor is connected via two reservoirs via ideal (scatter-free) conductors. For a two terminal measurement set up, a voltage $V_{2T}$ is applied across the channel. This raises the potential energy of one reservoir compared to the other, leading to a current flow of electrons with an energy range $E$ to $E + \delta E$ given by

$$\delta I(E) = eu(E)g(E)\Gamma(E)\delta E \quad (4.14)$$

where $u(E)$ is the electron velocity at energy $E$, $g(E)$ is the electron density of state per unit energy per unit length, and $\Gamma(E)$ is the transmission probability (the probability that an electron leaves the reservoir with the higher potential energy and
4.4. Ballistic One-Dimensional Conduction

travels to the lower energy reservoir). The current can be determined via integration:

\[ I = \int_{E_F}^{E_F + eV_{2t}} e u(E) g(E) \Gamma(E) dE \]  \hspace{1cm} (4.15)

The following known relations for \( E \) and \( g(E) \) are substituted in [89]:

\[ E = \frac{m^* u^2}{2} \]  \hspace{1cm} (4.16)

\[ g(E) = \frac{m^*}{\hbar \pi \sqrt{(2m^*E)}} = \frac{1}{\hbar \pi u(E)} \]  \hspace{1cm} (4.17)

where \( m^* \) is the electron effective mass. The transmission probability is approximated to be energy independent such that \( \Gamma(E) = \Gamma \). Thus two-terminal conductance for a 1D conductor is given as:

\[ G_{2t} = \frac{I}{V_{2t}} = \frac{2e^2}{h} \Gamma \]  \hspace{1cm} (4.18)

Hence for high transmission (i.e. when \( \Gamma \approx 1 \)) \( G_{2t} \) is equal to \( 2e^2/h = 77.48 \mu \text{S} \). This is also referred to as the ‘conductance quantum’ and is denoted by \( G_Q \).

Correspondingly the ‘resistance quantum’ is given by \( R_Q = G_Q^{-1} \) and is equal to \( 12.907 \text{k}\Omega \).

Now assume a four-terminal set up. Under these conditions the potential difference \( V_{4t} \) will be across two points along the channel between the source and drain reservoirs. By considering the potential difference across the channel in terms of the current flow, the four-terminal potential difference is derived as [89]

\[ V_{4t} = (1 - \Gamma)V_{2t} \]  \hspace{1cm} (4.19)

meaning the four-terminal conduction is given as

\[ G_{4t} = \frac{I}{V_{4t}} = \frac{2e^2}{h} \frac{\Gamma}{1 - \Gamma} \]  \hspace{1cm} (4.20)

this is known as the ‘Landau formula’ and it gives the conductance of any ballistic
4.5. Quantum Hall Effect in a 2DEG

The integer quantum Hall effect is a phenomenon where the Hall resistance plateaus as a function of the applied electrical and magnetic field. This was first observed by Klitzing et al. [13] who also noted that these plateaus form independent of the geometry of the device; an observation that has been repeated multiple times since. Klitzing et al. made their observations by measuring a transverse voltage across a silicon metal-oxide-semiconductor field-effect transistor at a constant magnetic field (ranging from 1 to 10T) against a sweeping gate voltage. Their results are shown in figure 4.6.

To understand the quantum Hall effect first consider the case where the applied field is such that the Fermi energy lies between two Landau Levels. The number of occupied Landau levels is \( N_L = \text{Int}(n_L) \) where \( n_L \) is given by equation 4.9. In such a system current is only carried by states near the Fermi energy, i.e. \( N_L \) edge states, all of which act as ballistic one-dimensional conductors. Current transport through the 2DEG “bulk” is suppressed as long as the Landau level separation is greater than \( kT \). As explained in section 4.3, as long as the 2DEG channel width is significantly larger than the magnetic length, the back-scattering probability is approximately zero. Hence the transmission is \( \Gamma \approx 1 \), and thus the 4-terminal conductivity shown in equation 4.20 tends to infinity and the longitudinal resistance tends to zero.

To determine the Hall resistance first consider that the potential difference is being measured between two contacts that are arranged along a Hall bar perpendicular to the applied potential difference between source and drain. These perpendicular contacts are labelled \( p1 \) and \( p2 \) and have respective voltages of \( V_{p1} \) and \( V_{p2} \). Now, under the assumption that \( \Gamma = 1 \), consider the two-terminal Landau
4.5. Quantum Hall Effect in a 2DEG

Figure 4.6: Plot from Klitzing et al. [13] showing the Hall effect measured in a metal-oxide-semiconductor field-effect transistor. Figure shows the Hall voltage, $U_H$, and the voltage drop between potential probes, $U_{pp}$, as a function of the gate voltage $V_g$ at $T = 1.5K$. Magnetic field is constant at 18T and the source drain current is $1µA$. Inset shows a top view of the device used with dimensions of length $L = 400µm$, width $W = 50µm$ and probe to probe distance of $L_{pp} = 130µm$. Figure taken from [13]

The formula between $p1$ and the source $S$ (which has voltage $V_S$):

$$I = \frac{2NLe^2}{h} (V_S - V_{p1})$$  \hspace{1cm} (4.21)

thus, the Hall resistance is given by

$$r_H = \frac{V_{p2} - V_{p1}}{I} = \frac{h}{2NLe^2} \frac{V_{p2} - V_{p1}}{V_S - V_{p1}}$$  \hspace{1cm} (4.22)

Since $S$ and $P2$ are connected by an edge state with no back-scattering, $V_S = V_{p2}$. Hence:

$$r_H = \frac{h}{2NLe^2}$$  \hspace{1cm} (4.23)

Thus when the magnetic field is such that the Fermi energy is between Landau
levels, the longitudinal resistance is zero and the Hall resistance is quantised and independent of applied field. When the number of occupied Landau levels $N_L$ changes by one, the Hall conductance (given by $1/r_H$) change by a factor of $2e^2/h$.

Now consider the case where the field is such that the Fermi energy coincides with a Landau level. This facilitates a conduction path across the width of the 2DEG, connecting the forward and backward edge states. This allows electrons to scatter from one edge state to the edge state propagating in the opposite direction. In other words, back-scattering is now facilitated and the longitudinal resistance is now finite. The Hall resistance takes some intermediate value between $h/2N_le^2$ and $h/2(N_L-1)e^2$ depending on the transmission probability of the resistive conduction channel.

Figure 4.6 shows how the longitudinal and Hall resistance vary with field. When the Hall resistance jumps from one plateau to another the filling factor changes and longitudinal resistance become finite. When the Hall resistance plateaus the Landau levels are well separated and the longitudinal resistance is essentially zero except when the Hall resistance is changing.

4.6 Fractional Quantum Hall Effect

While a full analysis of the fractional quantum Hall effect is beyond the scope of this thesis, a brief description is included here as it is one of the more unique phenomena in 2DEG systems and it has been demonstrated in ZnO-based systems. The fractional quantum Hall effect is defined for any fractional filling factor, $\nu$ [12]. In these scenarios $R_{xx}$ vanishes and $R_{xy}$ becomes quantised at fractional filling factors. This arises when the electrons in the 2DEG act as a single object (a quasi-particle) with fractional charge. More accurately, a system demonstrating the fractional quantum Hall effect is modelled as an incompressible quantum liquid and is often described by the Laughlin wave function [90].

When presenting the equations governing the FQHE it is useful to consider the number of electrons per applied flux quantum. The equation for $n_l$ can be rewritten
as:

\[ n_L = \frac{2\pi \hbar N_{2DEG} A}{e A \Phi} \]  
(4.24)

where \( N_{2DEG} \) is the total number of electrons in the 2DEG and \( \Phi \) is the magnetic flux applied perpendicularly to a Hall bar of area \( A \). The above equation can be simplified to

\[ n_L = \frac{N_{2DEG}}{\Phi / \Phi_0} \]  
(4.25)

where \( \Phi_0 \) is the magnetic flux quantum given by \( \Phi_0 = h/e \). Thus the filling factor can be thought of in terms of the number of electrons in the 2DEG per flux quantum. For example, in the \( n_L = 1/3 \) state the quasiparticle consists of three flux quanta per electron.

### 4.7 Summary

Here we have presented several electrical properties unique to 2DEG systems and explained their origins. Some of these properties, namely the SDH oscillations and the Hall effect, will be observed in our 2DEG samples in chapter 6. However before we explore these observations, we must establish how we fabricated and measured our samples. This is detailed in the following chapter.
Chapter 5

Sample Growth and Characterisation

This chapter details the machines used to fabricate samples, specifically molecular beam epitaxy. Material characterisation methods, such as XRD and XPS, are then explained as these techniques are essential to determining MBE crystal growth quality. Next the process of converting samples into devices is outlined, as are the methods used to electrically measure these devices.

5.1 Molecular Beam Epitaxy: System Summary

The samples presented in this work were grown by a process known as molecular beam epitaxy (MBE). The process involves evaporating desired growth materials onto a substrate under ultra-high vacuum (UHV), defined as pressures of $10^{-9}$ Torr or less. The use of UHV and source materials with purities exceeding 5N (99.999%) result in the growth of high purity, epitaxial films. Modern day MBE systems are equipped with multiple material cells, which can be used simultaneously. This facilitates the growth of binary, ternary and even quaternary materials in situ. The system described here is used to fabricate binary (ZnO and MgO) and ternary materials (ZnMgO).

Nitrogen and oxygen are commonly incorporated in MBE growth to fabricate oxide and nitride materials respectively. These gases are weakly-interactive in their natural state and cannot simply be injected into an MBE system to facilitate nitride or oxide growth. A more reactive form of oxygen, ozone (O₃), is used in some systems for oxide production. However it is more common to see MBEs
5.1. Molecular Beam Epitaxy: System Summary

equipped with plasma sources that energetically activate the oxygen or nitrogen and project it at the samples. Plasma systems have the added benefit of directionality, using magnetic fields to direct the activated gas towards the sample. The MBE system used throughout this work is equipped with an oxygen plasma source, later described in more detail.

Figure 5.1 shows a side-on schematic of our MBE system (a) as well as a photo of the system in our lab (b). An ion pump and cryo-pump are used to achieve a growth chamber base pressure of $10^{-10}$ Torr. Note the effusion cells and oxygen plasma source are labelled at the base of figure 5.1a. Coloured cones show artistic representations of how the material is projected from these sources towards the samples. The system is also equipped with a liquid nitrogen filled jacket which acts as both a heat dump for the material cells and as a cold trap for thermally activated growth materials. This cold trap helps to remove excess deposition material that did not adhere to the sample during growth. The substrate is suspended at the incident point of the incoming material beams. Under UHV the mean free path of the incoming material is larger than the dimensions of the chamber, meaning that for incident fluxes of $10^{-4}$ Torr and below, there is no inter-beam mixing before the substrate surface. Inter-beam mixing can lead to grains of the growth material forming in the chamber, which are detrimental to smooth surface growth. To ensure a uniform flux across the substrate and to promote layer-by-layer film growth, the sample is rotated at 20rpm during growth.

The right side of the image shows the load lock, separated from the main chamber via a gate valve and pumped on by a rough pumping system. The rough pumping systems consists of a turbo pump and a scroll pump. The gate valve allows samples to be loaded into the system from atmosphere without disrupting the vacuum in the main chamber. Once a sample is loaded into the load lock, it is rough pumped until it reaches a pressure of $10^{-8}$ Torr. Then the gate valve is opened and the sample is transferred into the main chamber via the transfer arm. The arm is then retracted and the gate valve remains closed while the MBE is used for growth.
Figure 5.1: (a) Side-on schematic of SVTA MBE system used in this study (b) Photograph of the same system with key components labelled.
5.1. Molecular Beam Epitaxy: System Summary

5.1.1 Ultra-High Vacuum Formation

Achieving UHV is a multi-stage process in which several pumps must be operated in a specific order. First the chamber must be rough pumped to a pressure of $10^{-4}$ Torr using a scroll pump. A typical scroll pump consists of two interlocking spirals or ‘scrolls’. In most devices one of these scrolls remains stationary while the other orbits eccentrically within the other’s confines. As the edges of the spirals approach each other at various points, they compress gas towards the centre of the interlocking spirals, where it is removed by the motion of the pump. Fresh air trapped further up the spiral rushes to fill the gap. In this way the pump can be used to either remove fluid from one system or compress fluid into another. The scroll pump is the only pump attached to the MBE which can pump on a chamber at atmospheric pressure. It is therefore the first pump operated when attempting to reach UHV. Unassisted our scroll pump (a Triscroll 300 series) is capable of reaching pressures down to $10^{-4}$ Torr, after which the turbo pump is used to achieve lower vacuum.

The turbo pump consists of several turbine propellers mounted onto a single rotating axle. Each turbine consists of thin metallic blades angled so that they drive gasses down and out of the system when the axis is spinning. Turbo pumps, as the name suggests, typically have high rotation speeds. Our turbo pump, a HiPace 300 series, achieves 1000rpm during standard operation. As stated above, the turbine blades are very thin. This is to reduce angular momentum about the drive shaft at high rpm. However this does mean that blades can be bent or broken if the system is suddenly exposed to high pressure. This is why the scroll is used to achieve an initial low pressure before the turbo is activated. The scroll also back-ends the turbo. Working in tandem, the turbo and scroll can achieve pressures of $10^{-8}$ Torr. During standard operation the turbo and scroll are used to pump down the load lock and are isolated from the main chamber.

Once a pressure of $10^{-8}$ Torr has been reached, the main chamber can be opened to a cryo-pump and ion pump to achieve ultra-high vacuum. Both of these pumps use gas entrapment to achieve low pressures. The cryo-pump uses
compressed He at 14K to cool a cold head cylinder. High boiling-point materials condense when brought into contact with the cylinder, adhering to its surface. Over time the build-up of these materials will impede the efficiency of the cryo-pump, so the pump must be regenerated once a month to maintain optimal performance. Regeneration involves isolating the cryo-pump from the main chamber, turning off the cooling and opening the pump to an external scroll pump. As the cylinder warms, materials on its surface re-evaporate and are removed by the scroll. This process is typically run for a minimum of 12 hours.

The ion pump helps remove low boiling-point materials that are not captured by the cryo-pump. The ion pump consists of a series of positively charged anodes, electrically isolated from a surrounding cathode. The whole system is supported in a magnetic field which drives free electrons to the anodes where they become trapped and circulate, producing a plasma. When a gas molecule encounters this plasma it is ionised. The ion is repelled from the anode towards the cathode where it reacts and binds to the material surface, thereby being removed from the system. The cathodes will be eroded over time, especially in high pressure environments where the rate of material sputtering is increased. For this reason the ion pump should not be used for pressures exceeding $10^{-8}$ Torr and not operated during growth.

Liquid nitrogen is used to cool the chamber walls and remove residual gas which arises during growth by condensing high boiling-point materials to the chamber surface. This process is analogous to how the cryo-pump operates. Over time there will be a build-up of material on the chamber walls, which can re-evaporate during growth. This re-evaporation results in a higher resting vacuum pressure in the MBE and a reduction in film quality. To prevent this the chamber must be baked every few months to remove unwanted residual materials from the system. During a bake the ion pump and cryo-pump are isolated from the main chamber and deactivated. The chamber is opened to the turbo and scroll pump via the load lock. The chamber is then wrapped in an insulating fiberglass jacket and heated to 220 °C. Residual material is evaporated off of the chamber walls and is pumped away by the turbo and scroll over the course of several days.
5.1.2 Knudsen Effusion Cells

Zinc (6N purity) and magnesium (5.5N) are supplied to the system by Knudsen effusion cells. Figure 5.2 shows the basic layout of a typical Knudsen effusion cell. The cells are equipped with two filaments, one surrounding the main body and one at the tip of the crucible at the aperture. The measurable beam flux produced by the cell is controlled by cell body temperature, with higher temperatures producing higher fluxes. The tip filament is set at a temperature 50°C higher than the body, to reduce material deposition around the cell aperture and encourage even distribution of beam flux. Pneumatic shutters are used for speedy switching between element beams in situ.

The flux produced by the cell is measured using a Granville Philips nude Bayard-Alpert ionization gauge. The actual flux produced by the cell at any given temperature depends on a number of factors including the amount of material remaining in the cell, condensation around the aperture, cell temperature, and so on. For this reason calibration of the beam equivalent pressure (BEP) must be conducted every time the vacuum is broken. As a rule, BEP is measured for all heated cells at the start and end of each sample growth.
5.1.3 Plasma Formation

Oxygen (5.5N) is supplied via a radio frequency (RF) plasma. The oxygen plasma facilitates the formation of oxide films and is free from radicals. The plasma is created by a standard capacitively–coupled plasma source (SVTA) at a frequency of 13.56MHz. Plasma power is supplied by a 300W water-cooled copper coil. Within the coil is a pyrolytic boron cylinder, where oxygen is introduced via a leak valve. The leak valve facilitates control over the oxygen flow rate into the main chamber. During growth, the flow rate is maintained between 2-3 sccm (standard cubic centimetre per minute).

The plasma is operated in low brightness mode (low power, high pressure) producing low energy ions which do not mill the sample surface. By contrast low brightness mode produces high energy ions which results in a destructive oxygen beam which is not conducive for crystallographic growth.

The gas injected by the RF plasma is measured by a residual gas analyser quadrupole mass spectrometer. When the plasma has been ignited and stable for 15 minutes, the partial pressure of H$_2$, N$_2$, CO$_2$ and Ar radicals are reduced. H$_2$, H$_2$O and CO radicals are still detectable but are at partial pressures three orders of magnitude lower than the oxygen pressure, rendering their presence negligible. Despite not severely impacting the growth, the H content is high enough to give the plasma a distinctly pinkish glow when observed through the viewing port. H content likely arises from water contamination in the tubes connecting the oxygen cylinder and MBE.

5.1.4 Substrate Heating

When loaded into the chamber, the sample is mounted in a two inch sample holder. This holder is suspended with the growing face pointing down towards the effusion cells. A radiative heater is positioned above the sample holder, facing the back of the sample. The substrate temperature is approximated using a thermocouple situated above the heater at a distance equal to the separation between the sample and the heater. This layout is shown schematically in figure 5.3.

This readout is not a perfect representation of sample surface temperature,
5.1. Molecular Beam Epitaxy: System Summary

Figure 5.3: Schematic showing the sample heating and thermometry layout of the MBE. Figure provided by Dr Kennedy [71]. A thermocouple is located at separations \( d \) from the thermometer. This separation is equal to the separation between the sample and heater. The thermocouple acts as a thermometer giving an approximation of sample temperature which is used as feedback for the PLD (programmable logic device) loops. A pyrometer measures the black body spectrum of the sample and provides the primary measure of the sample temperature. The black box indicates the boundary between vacuum and atmospheric pressure.

Figure 5.4: Photo of sample holder with accompanying side-view schematic showing how the substrate is suspended in the holder during growth. Figure provided my Dr Kennedy [71].

as it does not account for thermal gradient in the substrate. The thermocouple reads the temperature of the sample holder and this is used as a proxy for substrate temperatures during growth. The thermocouple facilitates measurement of temperatures exceeding 400°C and has been shown to observe 2°C fluctuations in temperature during growth.

5.1.5 Sample Holder

The sample holder consists of two molybdenum discs stacked one on top of the other. The top disc has a 10mm × 10mm hole cut into it that the sample sits inside.
There are four 1-2mm clips at the edge of the sample recess, which push the loaded sample back and down so it maintains direct contact with the rear molybdenum plate. This helps to facilitate uniform heating across the entire sample. Figure 5.4 shows a photo of the holder and a diagram illustrating how the sample sits in the holder during growth. There is a small amount of extra heating in the regions underneath the pins that hold the sample in place. This is visible to the naked eye, as the regions immediately around the points, where the pins touch the sample surface, take on a oil-slick rainbow-like sheen. The growth rate decreases with substrate temperature due to increased elemental re-evaporation from the sample surface. Therefore film thickness will reduce around the points where the pins hold the sample, since substrate temperature in the area close to the pins is higher than the surrounding substrate. The oil-slick-like appearance comes from light refracting through the sloped film. These sloped regions are confined to edges of the sample and so do not impact the quality of devices, which are made in the central regions of the ZnO/ZnMgO films.

5.1.6 Growth Dynamics

5.1.6.1 Thin Film Growth Dynamics

The exact mechanisms behind film growth depend on a wide range of parameters, a complete theoretical analysis is beyond the scope of this thesis. However a rough approximation can be achieved using three primary growth parameters; the incoming particle flux $F$, the rate of material adsorption onto the sample surface (the sticking coefficient) $r_a$ and the rate of de-adsorption $r_d$ (the rate at which material did not adhere to the sample and drifts back into the chamber). The derivation presented here follows the steps laid out in [41].

First we calculate the rate at which particles leave the growth surface for a given incident flux $F$ and fixed rate of particle adsorption/de-adsorption:

$$\frac{dn_{\text{free}}}{dt} = -r_a n_{\text{free}} - r_d n_{\text{free}} + F$$

(5.1)

where $n_{\text{free}}$ is the number of particles leaving the growth surface. Dynamic
equilibrium is achieved when the number of atoms on the sample surface is constant i.e.
\[
\frac{dn_{\text{free}}}{dt} = 0 \quad (5.2)
\]
\[
F = r_a n_{\text{free}} + r_d n_{\text{free}} \quad (5.3)
\]
This relationship can be used to determine the growth rate \( R_{\text{growth}} \):
\[
R_{\text{growth}} = \frac{r_a F}{r_a + r_d} = \frac{F}{1 + r_d/r_a} r_a n_{\text{free}} \quad (5.4)
\]
Next the rate of adsorption and de-adsorption must be accounted for. This is given by:
\[
r_{a,d} = v_{a,d} \exp \left( -\frac{\Delta E_{d,a}}{k_B T} \right) \quad (5.5)
\]
where \( E_{a,d} \) is activation energy for a given adsorption/de-adsorption process. \( v_{d,a} \) is the corresponding frequency factor for a given process. Combining all of the above equations gives:
\[
R_{\text{growth}} = \frac{F}{1 + (v_d/v_a) \exp \left( -\frac{\Delta E_d + \Delta E_a}{k_B T} \right)} \quad (5.6)
\]
This relationship can be used to determine the growth rate of the system such as well as the ratio of de-adsorption to adsorption (\( v_d/v_a \)) and the difference in activation energy of both processes.

These growth dynamics can give rise to three types of epitaxial growth: Volmer-Weber (VW), Frank-van der Merwe (FM) and Stranski-Krastanov (SK). VW growth occurs when adatom—adatom interactions are stronger than adatom-substrate ones. As a result the growth material will clump together, producing localised islands. This growth is three dimensional and results in a rough film. In FM growth the adatom-substrate interactions dominate, meaning a complete layer will form across the entire substrate before subsequent layers do. This produces very smooth films with layer-by-layer growth. SK growth describes the intermediate process where 2D films form alongside 3D islands, with the transition of layer-by-layer to island growth occurring at some critical thickness, depending on the physical and chemical properties of the film and substrate. This
transition is the result of strain arising from lattice mismatch between substrate and film.

5.1.6.2 Ternary Compound Growth

ZnMgO is a ternary compound (a material comprised of three different elements). There will be a significant focus on the Mg concentration of such films and the effect this has on the 2DEG formed at the ZnO/ZnMgO interface. Vegards law states that the lattice parameters of a ternary compound are approximately equal to the relative mixtures of the two materials, providing both materials have the same lattice structure. ZnO has a hexagonal wurtzite structure, whereas MgO is cubic rock-salt, therefore this does not apply here. Instead an empirical view of the inclusion of the Mg and its effect on the overall crystal structure must be used. A basis for this study is to look at the ratios between material fluxes incident on the substrate. The material flux is proportional to [41]:

\[ J(P_{BEP}) \propto \frac{P_{BEP}}{\mu} \sqrt{\frac{T}{M}} \quad (5.7) \]

where \( P_{BEP} \) is beam equivalent pressure of Mg, \( T \) is the source temperature, \( M \) is the molecular mass and \( \mu \) is the ionisation coefficient relative to \( N_2 \) given by:

\[ \mu = [(0.4Z/14) + 0.6] \quad (5.8) \]

where \( Z \) is the atomic number.

One of the most accurate means of determining the Mg concentration is to measure the lattice parameters and energy gap of the film. Kozuka et al. have demonstrated how the Mg concentration can be determined within a range of 0.004 to 0.4 concentration using a combination of X-ray diffraction, Rutherford back-scattering spectroscopy, secondary ion spectroscopy and photo-luminescence analysis [91]. This information is illustrated in figure 5.5. From this analysis Kozuka et al. recorded the following:

\[ \Delta c(\AA) = -0.069x_{Mg} \quad (5.9) \]
5.1. Molecular Beam Epitaxy: System Summary

![Figure 5.5](image)

**Figure 5.5:** (a) Log-log and (b) linear plots of the energy difference ($\Delta E$) between localized emission from Mg$_x$Zn$_{1-x}$O films and free exciton emission from ZnO as a function of $x$ at 100 K (empty circles) and 10 K (filled circles). The free exciton energy of ZnO is 3.377 eV at 10 K and 3.368 eV at 100 K. The dashed lines are the fitting for the data below $x=0.015$ at 100 K. The error bars in $x$ indicate the full width at half maximum of the spread of the concentrations observed for a film of constant Mg concentration, while those in the $\Delta E$ are the full width at half maximum of the localized exciton peaks at 100K. Figure and citation from [91].

$$\Delta E(eV) = 2.2x_M$$

(5.10)

where $\Delta c(\text{Å})$ is the change in lattice parameter and $\Delta E(eV)$ is the band gap change, in both cases measured with respect to ZnO. It should be noted that these values were derived for ZnMgO grown on ZnO substrates. For the purposes of this work, it is assumed that the same relation holds for ZnMgO deposited onto ZnO films grown on non-ZnO substrates.

Precise incorporation of Mg into ZnMgO can be controlled through a variety of factors. It is known that lower ZnMgO growth rates lead to higher overall Mg incorporation due to preferential re-evaporation of Zn from the growing surface [88]. The Mg content is therefore highly dependent upon temperature [24], since higher growth temperatures leads to slower growth rates. More specifically, higher growth temperatures enhance Mg incorporation because MgO and Mg have high vapour pressures compared to ZnO and Zn [92]. With that said, high growth temperatures (700°C and above) are often employed when depositing ZnMgO, as
there is evidence that these high temperatures enhance two-dimensional growth [88]. Additionally Coke et al. have demonstrated that using higher Zn fluxes, when depositing ZnMgO, produce more abrupt ZnO/ZnMgO interfaces [66]. For lower Zn fluxes result in a lower deposition rate, this allows the system to reach equilibrium through re-evaporation and surface migration. In such a system, the film becomes lattice latched whereby the Mg content is proportional to the excess energy in the system compared to the energy needed to grow a lattice-mismatched unit cell [66]. This lattice latched process is described in more detail by Del et al. [93]. At high relative Zn fluxes, equilibrium is not reached so the redistribution of Mg throughout ZnO is inhibited. This results in a more abrupt ZnO/ZnMgO interface.

5.2 Sample Characterisation

Following growth, the samples are characterised using a number of techniques. These techniques are used to determine information about the films including crystallographic orientation and polarity, film thickness and surface quality.

5.2.1 Atomic Force Microscopy

Interface smoothness is a key factor in the production of any 2DEG. Atomic force microscopy (AFM) provides an excellent way of recording surface roughness for thin films. In this project we have used non-contact tapping mode AFM to obtain topological surface maps of films. In non-contact mode, the cantilever oscillates at its resonant frequency. When it approaches the surface, the oscillation is damped due to Van Der Waals forces between the tip and the surface. The cantilever is retracted the resonance frequency is restored. The change in cantilever position is recorded and converted into a topological map. The readout is line mean fitted, with the mean being subtracted line by line. Surface roughness is given by the root-mean square of a given area. It is only appropriate to compare roughness of regions of the same size.
5.2. Sample Characterisation

5.2.2 X-ray Diffraction

X-ray diffraction is used to determine lattice properties through analysing reflected X-rays at various angles. The lattice parameters can be used to calculate Mg concentration of ZnMgO layers and crystalline quality. The basic XRD set-up is illustrated in figure 5.6. Measurements are based on Bragg’s law which is given by

\[ 2d\sin\theta = n\lambda \]  (5.11)

where \( n \) is an integer value, \( \lambda \) is the wavelength of the incident X-rays, \( d \) is the inter-plane spacing and \( 2\theta \) is the angle between the incident and reflected X-ray beam, as shown in figure 5.6. To measure the Bragg diffraction angle, a \( 2\theta-\omega \) scan (sometimes referred to as a coupled scan) is conducted where \( \omega \) is defined as the incoming angle of the incident electron beam, as shown in figure 5.6. In this mode the reflected beam intensity is plotted against \( 2\theta \) where \( \omega \) also changes relative to \( 2\theta \), so that \( \omega = 1/2 \times 2\theta + \text{offset} \). In an ideal scenario \( 2\theta = \omega \) but this is rarely the case due to less than optimal parameters in the sample, such as film strain and curvature, and sample holder (sample not lying perfectly flat) leading to an offset.

Constructive interference occurs only when Braggs law is satisfied. Since the X-ray wavelength \( \lambda \) is fixed we will get peaks at specific angles based on the separation of families of planes. The \( 2\theta/\omega \) scan shows a series of peaks which
5.2. Sample Characterisation

relate to different crystal planes. If the measured material is known, these peaks can be assigned to various planes depending on the parameters used in the experiment. Peaks appear at Miller indices \((hkl)\) related by a scale factor, e.g \((002), (004), (006)\). Some peaks are cancelled out by destructive interference from reflected X-rays. These are referred to as ‘forbidden peaks’. In hexagonal geometry the forbidden peaks are found at \(h + 2k = 3n\) for odd values of \(l\).

Omega rocking curves can be taken to determine the full width at half maximum (FWHM) of each peak. This is characteristic of film crystal quality: narrower peaks represent more uniform films, while a greater density of defects and dislocations result in wider ones. There is a small mismatch between ZnMgO and ZnO inducing strain, which can be observed using the rocking curve analysis.

In this work, XRD scans were carried out on a Rigaku Smartlab using a Ge(002) \(\times 4\) bounce analyser with Cu-K alpha \((\lambda = 1.54056\text{Å})\) radiation. This set up provides the greatest precision to intensity range with a resolution of 5 arc-seconds. Bragg Brentano geometry was used for a convergent beam for greater accuracy.

By comparing the location of the ZnMgO and ZnO XRD peaks, the Mg concentration can be calculated [91]. This method works for Mg concentrations ranging from 0.023 to the solubility limit of 0.4. Additionally XRD can give a gauge of ZnO/ZnMgO layer quality through the observation of Pendellösung fringes. Pendellösung fringes arise due to interference between incident and reflected X-rays. The fringes are not observed if the crystal contains defects or compositional inhomogeneities, since these will degrade the phase coherence of the X-rays and prevent interference.

5.2.3 X-ray Photoelectric Spectroscopy

X-ray photoelectric spectroscopy (XPS) uses X-rays of a known energy to excite electrons out of a material. The kinetic energy and quantity of electrons are then recorded to build up a spectrum. This spectrum is used to determine the binding energy of the electrons, which provides information about the quantity and species of materials present. XPS allows a thorough analysis of chemical composition.
XPS is highly surface sensitive (3nm penetration depth) so by coupling controlled sputtering processes with XPS scans, one can generate an atomic composition depth profile of the sample. Measurements are made with a 400µm diameter X-ray beam. Plots show the quantity of electrons detected against their corresponding binding energy.

There are three types of peak that will appear on XPS plots; photoelectric, Auger and satellite peaks. Photoelectric peaks provide a combination of the characteristic binding energy of the chemical component, as defined by its molecular environment and the energy of the incident X-ray beam. The readout of the kinetic energy is relative to the X-ray source energy. Therefore the peak binding energy changes if the source is changed. Each peak is assigned to a specific orbital of an atom and the percentage composition of said atom can be determined using the area under these peaks (after subtracting background).

Auger peaks are dependent on both the chemical environment and energy state of the parent molecule the electron is emitted from; therefore Auger peaks are not dependent on the X-ray source. Hence these peaks do not change if the source is changed relative to the kinetic energy. When an inner-electron is ejected from an atom by high energy X-rays, it leaves behind a vacancy. Outer-electrons can relax into this vacancy by emitting a photon. If this photon interacts with another outer electron it can be sufficiently energetic to eject said outer-electron. This process is depicted in figure 5.7. These electrons are Auger electrons which contribute to the aforementioned Auger peaks.
Satellite peaks are produced when excited electrons collide with additional electrons while being ejected, causing those additional electrons to also be ejected. This results in a peak near a photo-peak but with a lower binding energy (due to some energy being lost in the interaction). The size, shape and presence of the satellite peak can be used to determine information about the molecular environment.

The system used to collect data in this work is a Therm-source K-Alpha fitted with a monochromatic Al-K alpha X-ray source (E = 1486.36 eV). This achieves an ultimate source resolution of 0.5 eV. An electron flood gun is used to repopulate ejected electrons from the sample. Milling is achieved via an argon 3000V plasma. Milling steps typically last for 60s, milling away 5nm of ZnO/ZnMgO in each step. The instrument is operated using Thermo Avantage software, which allows automated execution and data processing with instrumental offsets.

### 5.2.4 Scanning Electron Microscopy

In scanning electron microscopes (SEMs), a high energy electron beam is directed at the sample and rastered across the material surface using electrostatic deflection. When electrons from this beam enter the material they undergo a number of elastic and inelastic scattering events. Each electron scatters in this way until either it’s energy approaches zero or it scatters back out of the material surface as back scattered electrons (BSE’s). BSE’s account for the majority of the energy of surface emitted electrons, with energies ranging from close to zero up to the energy of the primary beam. A typical BSE will have undergone multiple collisions before reemerging, straying far from the point where the primary beam made contact with the sample. Hence BSEs achieve poor spatial resolution. BSEs can be used for composition analysis since the probability of back-scattering is related to the atomic number of the target material. Elements with a higher atomic number have a higher probability of backscattering incident electrons and so appear brighter in BSE imagining.

To achieve high spatial resolution one must use only the secondary electrons (SEs) present at the sample surface. SE’s are produced when the incident beam
in-elastically scatters with bound electrons in the material, thereby scattering them out of the surface. SE’s have a much lower energy and range than their BSE counterparts. As a result, SE’s are only produced near the point where the primary beam collided with the sample, meaning SE yield is dependent on sample morphology. By focusing on the SE’s produced at the sample surface, SEMs allow high imaging resolution of <10nm. SE’s can be differentiated from BSE’s due to their significantly lower energies. This is achieved via a voltage-biased screen near the detector which is tuned to the primary beam energy to ensure that only SEs reach the detector. Throughout this work, we only focus on the high resolution, SE-based SEM imaging.

In this work, a Carl Zeiss 1540 Cross-Beam SEM was used. In insulating samples, excessive exposure to individual areas can result in image deformation. This is because bombardment with the charged beam causes charge buildup. In an insulator, this charge cannot dissipate, instead repelling the incoming beam, distorting the final image. Samples used throughout this work are grown on insulating substrates. Hence a lower acceleration voltage of 0.2 kV was used so that charge would build up more slowly.

5.3 Controlling ZnO Polarity

As discussed in chapter 3, the polarity of ZnO is critical to high-mobility 2DEG formation. To encourage electron migration and confinement at the heterostructure interface, a positive sheet-charge density must be induced. This is achieved by growing ZnMgO onto Zn-polar ZnO [86, 87]. This section presents several of the most common methods used for determining ZnO polarity. The pros and cons of these method are compared and used to justify our decision to employ XPS-valance band analysis as our primary method of polarisation determination. We demonstrate that this method does work by measuring the two faces of our ZnO substrates.

5.3.1 Destructive Wet Etching

The Zn-polar face of ZnO is known to be much more resilient to HCl etching than the O-polar face. This phenomenon can be explained via the dangling bond model
5.3. Controlling ZnO Polarity

Figure 5.8: The Zn-polar (a) and O-polar (b) face of the ZnO substrate after a 30 second 7:2000 HCl:water etch.

[31, 94]. This model states that the Zinc terminated face of ZnO [0001] has a $\delta$ on the sp3 hybridized orbital. This charge causes the electron orbital to retract, thereby reducing susceptibility to wet etching. Resultantly HCl can only etch the Zn-polar layers at defects (such as screw dislocations) where the charge of the polar face is disrupted [31]. When HCl attacks these points, hexagonal pits form, as explained in more detail by Hülpkes et al. [31]. The O-face is etched at a significantly higher rate and appears rough after etching. Following etching, the two orientations can be distinguished when viewed by the naked eye. Figure 5.8 shows optical microscope images of both the Zn- and O-face after etching.

While this is an easy means of determining ZnO polarity, it is destructive and not ideal for this research. It would be preferable to employ a technique which is compatible with ZnMgO growth after the ZnO film orientation has been determined.

5.3.2 XRD Anomalous k-Edge Adsorption

One non-destructive method presented by Tampo et al. [95] involves comparing the normalised X-ray diffraction intensity either side of the Zn-K-edge (which occurs at approximately $2\theta = 28.5^\circ$). These intensities at $2\theta$ less than/greater than the k-edge are referred to as the pre-/ post-Zn-K-edge intensity respectively. Figure (5.9) shows a visual representation of the normalised XRD spectrum for O- and Zn-polar ZnMgO, and where the pre- and post-$n$-K-edge intensities are measured. The wurtzite cell of ZnO is not centro-symmetric. Therefore Fresnel’s law does not
5.3. Controlling ZnO Polarity

Figure 5.9: The normalised diffraction curves produce by the (0002) and (000\text{̅}2) planes of ZnO epilayers on sapphire c-plane. Intensities were normalized at $2\theta = 29.5^\circ$. Circles indicate where the pre- and post-post-Zn-K-edge intensity are measured ($2\theta = 27^\circ$ and 29.5° respectively). Figure adapted from [95]

Figure 5.10: The intensity ratio between $2\theta = 27.0^\circ$ and 29.5° for each polar ZnO layer. The intensity ratio was dependent on the layer thickness and independent of sapphire orientation. The line fits show how this ratio changes in O- and Zn-polar films as a function of film thickness. Figure taken from [95]

hold and so the intensity of the (0001) and (000\text{̅}1) orientations will differ. Tampo et al. were able to demonstrate that the O-face intensity is consistently higher than Zn-face intensity at a range of thicknesses. This data is presented in figure 5.10.

This process is non-destructive but requires previous characterisation of
5.3. Controlling ZnO Polarity

various thicknesses of ZnO. Additionally this method requires the incidents X-ray beam to be continuous, with the X-ray wavelength varying along the $\theta - 2\theta$ scan. Such a measurement is a very bespoke application of X-ray diffraction and would take some calibration to set up. Ultimately the acquisition of this data was considered too time intensive for this research.

5.3.3 XPS Valence Profile

XPS analysis can also be used for non-destructive ZnO polarity determination. Allen et al. demonstrated that the near-surface atomic composition, and valence band electronic structure, differ significantly in the Zn- and O-polar face [96]. More specifically the lowest binding-energy valence-band peak was found to be significantly more intense in the Zn-face compared to the O-face. This phenomenon is demonstrated in figure 5.11.

This technique is simple to conduct, non-destructive, and does not require extensive calibration. As such, it was selected as the practical method for ZnO polarity determination. However before this method can be trusted, it must be tested. When determining polarity with ZnO substrates, the process is trivial since suppliers cut the substrates so that the orientation can be ascertained, with orientation being determined at the point of growth.

By loading a ZnO substrate into an XPS system and measuring the valence profile for the Zn- and O-polar faces, the effectiveness of the XPS polarity determination method can be assessed. Our data is shown in figure 5.12. The valence bands have been normalised by dividing the data set by the amplitude of the higher binding energy (BE) peak. The peak amplitude was determined by Gaussian curve-fit. The 5eV BE peak (referred to hereafter as BE$_1$ peak) clearly has a higher amplitude in the Zn-face as predicted by Allen et al. [96]. Looking at the ratio between the amplitudes of the BE$_1$ peak and the 8eV BE peak (the BE$_2$ peak), we observe that the Zn- and O-polar faces have a BE$_1$/BE$_2$ ratio of 1.2 and 1.0 respectively. Therefore a peak ratio of 1.2 is used as a quantitative indicator of Zn-polarity.

With an established method for ZnO polarity determination, the next stage
5.4. Device Fabrication and Electrical Characterisation

![Figure 5.11](image.png)

**Figure 5.11:** Valence band-XPS spectra from the polar and non-polar faces of ZnO substrate. Zn-polar face (black circles) has a higher intensity for peak I when compared to the O-polar face (white circles). Allen *et al.* also analysed the valence profile of the side of the substrate (grey triangles) but this is not relevant to determining substrate Zn/O-polarity. Bulk ZnO measured using Al K radiation (1486.6 eV). Figure adapted from Allen *et al.* [96]

is to find a means of achieving Zn-polar ZnO on other substrates. This thesis is concerned with the growth of ZnO/ZnMgO heterostructures on a-plane and c-plane sapphire. Chapters 7 and 8 explore methods of achieving Zn-polar ZnO layers on a-plane and c-plane sapphire, respectively. These substrates were chosen since they are cheap, easy to source and have a history of being used for ZnO growth. These alternative substrates may provide a more reliable means of realising ZnO-2DEGs than using ZnO substrates.

### 5.4 Device Fabrication and Electrical Characterisation

This section covers how samples were converted into devices suitable for electrical measurement. The instruments used to measure these devices are also discussed.
Figure 5.12: The normalised valence spectra of the Zn-polar (red) and the O-polar (blue) face of a Pi-Kem ZnO substrate. These substrates come with an epi-polished O and Zn face denoted by substrate geometry, so orientation was known before measuring.

5.4.1 Device Fabrication

After growth samples are cleaned in acetone, 2-propanol and deionised (DI) water and then baked for 20 minutes at 200°C. The purpose of this bake is to dehydrate the sample and act as a thermal cleaning step. The devices are then masked using S1818 photoresist (Fig. 5.13(a)) and Hall bars are patterned using a chrome-on-glass mask and ultra-violet exposure (Fig. 5.13(b)). Exposed resist is removed by submerging in MF26A developer for 60s with mild agitation (Fig. 5.13(c)). This leaves behind resist features in the desired Hall bar shape. Samples are then loaded into the SVS6000 system and milled down to the substrate level using a high power, low pressure argon plasma (Fig. 5.13(d)). The plasma is typically set at 1000V-23A. This results in a ZnO etch rate of approximately 5nm per minute. The resist features protect the ZnO below them, resulting in raised mesa features after sufficient milling. The remaining resist is removed from the sample using acetone and mild agitation (Fig. 5.13(e)).

Once the mesas have been formed, the contacts can be patterned onto the samples. The mesas are essential for contacting the 2DEG by exposing the edges of the channel directly to the contacts. Prior to contact deposition, the samples are
5.4. Device Fabrication and Electrical Characterisation

Figure 5.13: Schematic of mesa etch process. First, sample is coated with S1805 photo-resist and a photo-mask is brought into contact with the sample (a). The sample is then exposed to UV light and bonds in the resist under the clear regions of the mask are broken (b). The exposed resist is then removed (c) and the sample is etched with argon plasma (d). The resist is removed and a raised mesa with 2DEG remains.

Once again solvent cleaned and dehydrated as detailed above, before being coated with LOR10B and S1818 (Fig. 5.14(a)). Contact patterns are then exposed using UV and developed in MF26A for 60s with mild agitation (Fig. 5.14(b)). LOR10B is more susceptible to UV exposure, leading to an undercut when developed, as demonstrated in figure 5.14(c). This helps to ensure a clean lift-off after contact deposition. Samples are then loaded into the SVS6000 system and subjected to a two minute argon mill to clean the sample surface. Contacts are then deposited by sputtering in situ and consist of an 8nm Ti layer (Fig. 5.14(c)) followed by a 50nm Au layer (Fig. 5.14(d)). Ti is used to improve Au adhesion to the ZnO surface and to achieve ohmic contact with the sample. Contacts of this type have been used on ZnO for decades and provide good ohmic contact to the material [97]. The remaining resist is lifted off in 1165 resist remover overnight (Fig. 5.14(e)). Lift-off can be expedited to 30 minutes using 1165 heated to 50°C. Following lift-off, the samples are rinsed in isopropanol alcohol and nitrogen blow-dried before being stored away for future measurements. Acetone should never be used for lift-off of 1165 as it produces cross-links in this particular resist, making it near impossible to remove.
5.4. Device Fabrication and Electrical Characterisation

Figure 5.14: Schematic of device fabrication process. First, sample is coated with LOR10B and S1805 photo-resist and a photo-mask is brought into contact with the sample (a). The sample is then exposed to UV light and bonds in the resist under the clear regions of the mask are broken (b). LOR10B is more susceptible to UV exposure than S1805 so some of the area under the opaque region of the mask is exposed too. When the exposed resist is developed this results in an undercut as shown in (c) which helps ensure contacts are not damaged during lift-off. Ti is then deposited onto the developed sample (c) followed by an Au deposition (d). The resist is removed during lift-off and the Ti/Au contacts remain.

The typical device design consists of a raised mesa measuring 10µm in width with 10×120µm channels running parallel to the main mesa with 50µm spacing. These channels connect to the main electrical contacts via Ti/Au channels and facilitate transmission line measurements along the length of the mesa. Figure 5.15 shows the mask used for mesa and contact formation. Figure 5.16 shows an example of a completed device.

5.4.2 Electrical Measurements

Room temperature 4-point electrical measurements are taken using a Keithley 4200 IV CV semiconductor characterisation system readout. Contact to the sample is made by bringing 4-point probe needles into direct contact with the patterned sample contacts.

For low temperature measurements, the samples are wire-bonded to the appropriate puck before being loaded into the Quantum Design, Physical Property
Figure 5.15: The photo mask used to make the mesa (a) and contacts (b) for our samples.

Figure 5.16: Example of completed mesa device with Ti/Au connectors.
5.4. Device Fabrication and Electrical Characterisation

Measurement System (PPMS). This machine is capable of conducting electrical measurements as low as 2K, under standard operation. This can be driven even lower using the He-probe insert, which bottoms out at 0.35K. Additionally the PPMS can measure across a field range of \( \pm 14T \) while maintaining these low temperatures. These properties make the PPMS ideal for observing several 2DEG-specific electrical properties such as the standard and quantum Hall effects, and Shubnikov-de Haas oscillations.

Throughout this project two of the PPMS’s modes were used to measure the samples; AC transport (ACT) and resistivity. The ACT mode is a 4-point measurement set up, where current is supplied via a AC source. The amplitude and frequency of the AC oscillations can be set by the user. Throughout this thesis ACT measurements are conducted at 0.01 mA and 19 Hz. Voltage is auto-ranged by the software to find best gain. The ACT mode is used for the Hall measurements and most longitudinal measurements throughout this thesis.

High resistance samples cannot be measured in the ACT set up because they cause the measurement system to short across the PPMS internal circuits. This short manifests as a negative resistance on the system readout. For such samples, the resistance is measured in resistivity mode. This too is a 4-point measurement set up, only instead, a DC source is used. Current range is determined by the user. The measurement is then conducted at positive and negative DC drive current across the given range. Resistance is calculated from an IV fit of these two values.

Preliminary low temperature measurements, or measurements that cannot be performed in the PPMS, are taken using a helium-cooled probe station. This has a similar set up to the room temperature measurements, except a continuous flow of evaporating liquid helium is used to cool the sample. In this way one can reach temperatures within a range of 5-300k. A heater is then used to warm to any desired temperature. The cooled probe station is also connected to the Keithley 4200 to conduct electrical measurements.
Chapter 6

ZnMgO on ZnO Substrates

6.1 Experimental Outline

To achieve high mobility 2DEGs, scattering centres must be kept to a minimum. These defects can take many forms including alloy scattering, electron-electron scattering, crystalline defects and atomic impurity scattering. Alloy scattering has little impact on ZnO/ZnMgO heterostructures because the 2DEG forms in the ZnO layer, away from the Mg donors [72, 73]. Electron-induced scattering is related to the electron density, controlled by the Mg concentration [72, 98].

Crystalline defect scattering arises from epitaxial mismatch with the substrate. Single-crystal ZnO substrates are readily available. Two-inch ZnO wafers can be grown using seeded vapour-phase (SVP) [99], hydrothermal [100] and melt methods [101]. Single crystal substrates have been used to demonstrate 2DEGs with low crystalline-defect scattering [16]. Using ZnO substrates simplifies heterostructure fabrication since, in principle, a 2DEG can be formed by growing ZnMgO directly onto the substrate.

It has been shown that for MBE-grown ZnO/ZnMgO interfaces, interface roughness scattering and atomic impurity scattering are the dominant limiters of electron mobility [102]. A certain amount of roughness is inevitable when growing directly onto ZnO substrates. The main cause of roughness is atomic steps arising due to cut misalignment when the crystal is cleaved. These steps can be mitigated through chemical etching and by growing homoepitaxial ZnO layers onto the ZnO
substrate prior to interface fabrication. Overcoming atomic impurities is not trivial. Single-crystal ZnO is susceptible to defects which arise during hydrothermal growth [33]. Lithium is one of the more prominent defects in thermally grown ZnO and has been shown to significantly reduce ZnO conductivity [32, 33, 103] and harm 2DEG formation [104].

High mobility ZnO/ZnMgO 2DEGs, like those demonstrated by Falson et al. [16], have been realised on exceptionally low-impurity ZnO substrates grown in a platinum-lined autoclave [103, 105]. This equipment has since been decommissioned. Presently only ZnO crystals grown in rhenium/iridium-lined autoclaves are available. Experiments at the LCN have attempted to use these lower-quality substrates to realise 2DEGs by depositing ZnMgO directly onto cleaned and HCL etched samples [41, 66]. In this way, Coke et al. were able to achieve 2DEGs with mobilities as high as $10^3 \text{cm}^2/\text{Vs}$ [66]. However these 2DEGs could not be produced reliably because there was a large amount of crystal quality variation between substrate batches, and indeed, within individual batches. Furthermore the mobilities demonstrated by Coke et al. were below the $3.3 \times 10^3 \text{cm}^2/\text{Vs}$ necessary to achieve a system in the clean coherence length limit, as detailed in chapter 1.

This chapter contains methods used to remove defects from rhenium/iridium-lined autoclave-grown ZnO substrates with the intent of increasing 2DEG mobility and achieving a system in the clean coherence length limit. In pursuit of this goal, ZnO substrates were subjected to multiple anneals at 1000°C and the resulting structural quality was assessed using XRD rocking curves and $2\theta/\Omega$ scans. The room temperature resistance of these samples was then measured using a transmission line setup. Room temperature substrate resistance was used as a proxy for defect density. A reduction in substrate resistance was noted after 15 high temperature anneals, which was attributed to a reduction in the defect density of the substrates.

The effects of annealing on 2DEG formation were assessed by depositing ZnMgO films onto annealed and unannealed samples. The structural properties of these films were measured using XRD and XPS. The electrical properties were
assessed using a PPMS for low-temperature and high field measurements. The presence of a 2DEG was demonstrated through observation of Shubnikov de Haas (SdH) oscillations at 2K. This 2DEG shows mobility of $4.8 \times 10^4 \text{cm}^2/\text{Vs}$, well in excess of the critical mobility $\mu_c$ necessary for clean coherence length limit. This 2DEG had a high carrier concentration of $n = 5.05 \times 10^{12} \text{cm}^{-2}$, meaning it has a clean coherence length of 122nm at 2K. Additionally the observation of SdH oscillations showed at least a factor 3 reduction in the scattering rate in the annealed sample, compared with its unannealed counterpart. This has been attributed to a removal of defects in the substrate caused by high-temperature annealing.

Two ZnMgO/ZnO-substrate samples were grown outside the LCN, at the Polish Academy of Science (PAS). These samples were fabricated as part of a collaboration with Kozanecki and his colleagues. While these samples were grown with different apparatus, they are structurally similar to the LCN samples. The structural and electrical properties of these samples were assessed and compared to their home-grown counterparts.

### 6.2 Substrate Preparation: Rapid Thermal Processing

Throughout this chapter, 10 × 10 mm single crystal ZnO grown by Pi-Kem in a rhenium/iridium-lined autoclave were used as substrates. These substrates were also used by Coke et al. [41] who noted a large variation in crystal quality. These variations were substantial enough that the substrates were seen to be of differing shades of yellow when observed with the naked eye. As a result, Coke experienced significant difficulty in reliably reproducing ZnO 2DEGs, which limited the possibility of finding unique applications. These variations are attributed to differing quantities of defects in the substrates, arising at the point of growth.

Lithium impurities are particularly prevalent in hydrothermally grown ZnO. This is problematic since lithium acts as an acceptor in ZnO and reduces substrate conductivity [32, 33, 103]. Li has been shown to be detrimental to 2DEG formation [104]. Experiments indicate that Li is highly mobile [106] with growing evidence that annealing above 1000°C can promote Li migration to the ZnO
surface, eventually resulting in Li out-diffusion and an overall lower defect density [33, 32, 107]. This observation is due to upward band bending present in the surface of n-type ZnO. This bending results in a small electrostatic field which pushes positively charged impurities towards the substrate surface, while pushing negatively charged impurities away from the surface. This process is illustrated in figure 6.1. This force is too small to have any notable affect at room temperature but at higher temperatures, when Li is more mobile, this force is enough to bias Li diffusion towards the substrate surface. This is more pronounced at the negatively charged O-polar face [32]. As explained in chapter 3, ZnMgO should be deposited on the Zn-polar face, so that the polar discontinuity drives charge carriers to the interface. Therefore the preferential O-face migration of Li is beneficial.

![Figure 6.1: Band bending close to the substrate surface. Arrow indicates the force acting on an impurity with positive charge $q$ in a field produced by band bending $E$. The impurity density is represented by green shading between bands with lighter shades indicating a lower impurity concentration. Figure taken with permission from [108].](image)

To investigate the effects of annealing on substrate quality, ZnO substrates were subjected to a series of rapid thermal anneals to 1000°C. The structural properties of the samples were measured using XRD as a function of the number of anneals. We lack the facilities to measure Li concentration directly, however as stated above, Li impurities are known to directly affect substrate conductivity. Coke et al. have already demonstrated a link between low room-temperature substrate resistance and high 2DEG mobility [41]. Therefore room-temperature resistivity can be used as a gauge of ZnO substrate quality. The electrical properties of these substrates were recorded and compared to substrates which have previously shown 2DEG behaviour.
6.2. Substrate Preparation: Rapid Thermal Processing

6.2.1 Experimental Methods

The substrates used in this experiment were the aforementioned hydrothermally grown ZnO by Pi-Kem. Substrates have a Zn-faced (0001) epi-polished surface with a maximum mis-cut angle of 0.5 degrees. The following samples are from the same 10mm x 10mm x 0.5mm chip. This is to avoid variations that could arise from dissimilar growth conditions. This chip was diced into 6 equally sized pieces before further treatment.

The Solaris 150 rapid thermal processor (RTP) was used for high temperature processing throughout this study. The Solaris cannot maintain temperatures of 1000°C for longer than 5s at a time. Therefore the following study observes the effects that heating to 1000°C multiple times has on the resistivity of the ZnO substrates. Hereafter the process of heating the sample to 1000°C, maintaining that temperature for 5s, and then cooling the sample, is referred to as a ‘cycle’. During each anneal the Solaris chamber is filled with 5N purity nitrogen at atmospheric pressure. At the end of each cycle, the sample is cooled to 100°C before the next cycle begins. The Solaris is water cooled and only takes \( \sim 1-2 \) minutes to cool from 1000°C to 100°C.

Prior to annealing, the substrates pieces were etched in a 7:200 HCl:water solution for 30s to remove any residual ZnO dust produced by the mechanical epi-polishing conducted by the grower. The use of HCl is well documented in ZnO substrate preparation and has been shown to result in a substrate surface ideal for epitaxial growth [109]. Samples were then rinsed in deionized (DI) water.

As stated in chapter 3, the Zn-polar face of ZnO is more stable than its O counterpart. As a result the Zn-face is more resistant to wet-etching. This observation is explained via the dangling bond model which states the zinc terminated face [0001] has a \( \delta \) negative charge associated on the sp3 hybridized orbital. This forces the electron orbital to contract, thereby reducing the surface solubility [31].

After annealing, the substrates are subjected to another 30s etch in diluted HCl before being rinsed in DI water. Since Li migrates to the wet-etch-susceptible
6.2. Substrate Preparation: Rapid Thermal Processing

Figure 6.2: Illustration of how Li impurities (yellow circles) are removed from the ZnO substrate (blue rectangles) through the annealing and etch process. Arrow indicated the direction of the Zn-polar face.

O-face following an anneal, this second HCl etch is intended to remove the Li-rich surface layer. In this way the overall Li content of the sample can be significantly reduced. This process is illustrated in figure 6.2.

6.2.2 Structural Analysis

To assess crystallographic quality, X-ray diffraction omega rocking curves were taken for each sample near the (002) peak. Figure 6.3 shows a plot of the full width at half maximum (FWHM) for these samples as a function of the number of cycles. There is no clear correlation between cycle number and FWHM. This fits our expectations for a high quality single crystal substrates. Small errors in equipment can cause an apparent increase in FWHM. This may be why the point for 5 cycles is so removed from the other data points.

2θ/ω scans showed that both (002) and (101) ZnO peaks are present in these samples (figure 6.4a). The (002) peak has a high intensity and is well defined, which is what we would expect for a high quality single crystal substrate. The (101) peaks were visible in all ZnO samples including the 0-cycle sample. The presence of this second crystallographic orientation is dissatisfactory since these substrates should be single crystal c-plane ZnO. The presence of another crystal orientation will impose strain at the ZnO/ZnMgO interface and will impede 2DEG formation. This secondary peak may be due to surface reconstruction arising from the high temperature anneal. This theory does not explain the observation of the (101) peak seen in the 0-cycle sample. The samples were not analysed using XRD before high-temperature anneal/HCl etch, so it is unclear whether this (101) crystallisation is present in the substrates upon delivery or is due to the treatment. The (101) peak
6.2. Substrate Preparation: Rapid Thermal Processing

Figure 6.3: Full width at half maximum of the (002) ZnO peak as a function of number of RTP cycle to 1000°C.

may be from ZnO dust particles on the substrate surface caused by unintentional scratches or from mechanical polishing.

The intensity of the (101) peak was plotted as a function of the number of cycles in figure 6.4b. The unannealed sample shows a low peak intensity of approximately 400 counts while all other samples show an order of magnitude increase. Therefore heat treatment seems to promote the substrate to relax into (101) orientation (likely at the surface) but additional cycles do not promote further relaxation. This suggests heat treatment is detrimental to the crystal uniformity of ZnO substrates.

Figure 6.4: (a) XRD spectrum from the unannealed ZnO substrate sample. (b) ZnO (101) peak intensity as a function of number of RTP cycles to 1000°C.
Next the impact of heat treatment on Li defect removal is assessed. Attempts were made to determine the Li concentration in each ZnO sample using XPS. In all cases, the XPS only showed background at the Li peak location. This does not necessarily mean there is no Li present; the Li1S peak is particularly hard to detect and has no secondary peaks which would otherwise assist in the confirmation of Li percentage. The XPS used for these experiments has an atomic percentage detection limit of $\sim 1\%$ which equates to $\sim 5 \times 10^{19}$ atoms/cm$^3$. Other groups detect Li concentration in ZnO using secondary ion mass spectroscopy (SIMS) [33, 107, 110]. These systems show that initial Li concentration in untreated ZnO samples is the order of $10^{17}$ cm$^{-3}$. This is well below the XPS detection limit; while most SIMS systems have an Li detection limit of $(3 \times 10^{13}$ Li cm$^{-3}$) [33]. SIMS measurements were not utilised as there was no such facility available at the LCN during this research.

### 6.2.3 Electrical Analysis

After thermal processing, the substrates are degreased in acetone and IPA. The samples are then briefly milled with an argon plasma for 2 minutes before being patterned with an array of $300\mu m \times 300\mu m$ Ti/Au contacts. Contact separation is $200\mu m$. An optical image of one such device is shown in figure 6.5. These contacts
Transmission line measurements (TLMs) were used to determine the contact and sheet resistance of our thermally treated samples. A TLM consists of a series of two-point measurements taken along a conduction line with resistance recorded as a function of the contact separation. In this way, one can determine both the resistance per cm $R_{pcm}$ and contact resistance $R_c$ of the sample. The devices used for this experiment do not have a clearly defined conduction path. The device design means the pads that are not being used as the source or drain for the measurement could act as shorts, providing a conduction path through the contact that has a lower resistance than passing through the substrate underneath. This process is illustrated in figure 6.6. Alternatively if the conduction path remains within the substrate between the source and drain contact, the measurement has a typical TLM setup, as shown in figure 6.7.

<table>
<thead>
<tr>
<th>Number of inter-contact separations (n)</th>
<th>Resistance R/n = 2Rc + LRpcm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$2R_c + LR_{pcm}$</td>
</tr>
<tr>
<td>2</td>
<td>$4R_c + 2LR_{pcm}$</td>
</tr>
<tr>
<td>3</td>
<td>$6R_c + 3LR_{pcm}$</td>
</tr>
</tbody>
</table>

**Figure 6.6:** Graphical depiction of the contact-shorted TLM model which assumes the conduction path is shorted by any contact pads between the source and drain contacts. The mock plot shows how these measurements can be used to determine in-line resistance ($R_{pcm}$) and contact resistance ($R_c$).
Figure 6.7: Graphical depiction of the the substrate-dominated model which assumes that conduction path remains inside the substrate between the source and drain contacts. The mock plot shows how these measurements can be used to determine in-line resistance \( R_{pcm} \) and contact resistance \( R_c \).

The case where the conduction is shorted through unconnected contacts (the contact-shorted case) is considered first. In this case, the resistance is recorded as a function of the number of contact pads along the transmission line, including the source and drain contacts. As shown in figure 6.6, the total resistance across \( n \) inter-contact separations is given by:

\[
R_{total} = 2nR_c + nLR_{pcm}
\]  

(6.1)

where \( L \) is the separation between pads (0.02cm), \( R_c \) is the contact resistance and \( R_{pcm} \) is the resistance through the substrate per cm.

Plotting that resistance as a function of the number of contacts gives a straight line with the relationship:

\[
R_{total} = (2R_c + LR_{pcm})n
\]  

(6.2)

Hence the plot should cut through origin and the product of \( R_c \) and \( R_{pcm} \) can be derived from the line fit gradient. Measurements were taken between pairs of samples along the same horizontal line of contacts. The resistance was plotted as a function of the number of inter-contact separations. Figure 6.8 shows an example...
6.2. Substrate Preparation: Rapid Thermal Processing

Figure 6.8: Resistance vs pad number plot for 5 cycle ZnO sample. Note that the intercept is non-zero in contrast to the model laid out in figure 6.6

of such a plot from the 5-cycle sample.

All other plots showed behaviour similar to the 5-cycle sample; none of the sample fits had an intercept that passed through the origin. Intercepts were on the order of 100Ω. This was an order of magnitude higher than the error seen in each fit, which was in the range of 1-10Ω. Therefore it was determined the contact-shorted model does not accurately represent the conduction path in these measurements.

Now consider the case where conduction remains in the substrate between the source and drain, the substrate-dominated case. As shown in figure 6.7, the total resistance between any two contacts can be modelled by:

\[ R_{\text{total}} = 2R_c + LR_{\text{pcm}} \]  \hspace{1cm} (6.3)

where \( R_c \) is the contact resistivity, \( R_{\text{pcm}} \) is the in-plane resistance per cm and \( L \) is the contact-to-contact separation.

By plotting the resistance as a function of contact separation, one can extract the resistivity and contact resistance from the gradient and intercept of this plot respectively, as shown in figure 6.7. Measurements were taken between pairs of samples along the same horizontal line of contacts. The resistance for each pair was
6.2. Substrate Preparation: Rapid Thermal Processing

Figure 6.9: TLM plot for 5 cycle ZnO sample with $R_{pcm}$ and $R_c$ of $7 \pm 1 \, \Omega/cm$ and $0.38 \pm 0.01 \, \Omega \, \text{cm}^2$. For this measurement, the set up was the same as that laid out in 6.7

plotted as a function of contact separation. Figure 6.9 shows an example plot for the 5-cycle sample. In this case, a linear fit is observed which seems to fit the model well. Therefore it can be asserted that the conduction path remains in the substrate between the source and drain.

Now that a model for contact resistance has been determined, the impact of substrate thermal treatment can be assessed. Figure 6.10 shows the contact resistance and resistivity of the ZnO substrates as a function of the number of cycles.

Note that in this experiment $R_{pcm}$ is used as a proxy for sheet resistance. The resistance measurements could not be converted to sheet resistance as this measurement setup will include spreading resistance due to non-uniform flow. Nevertheless $R_{pcm}$ should still give a good indication of substrate resistivity. The contact resistance is given in $\Omega \, \text{cm}^2$.

From figure 6.10 we note that $R_{pcm}$ increases significantly after a single cycle. Since annealing promotes Li surface migration, this increase in resistivity could be attributed to an increase in the defects close to the substrate surface. Subsequent cycles show a continued reduction in resistivity. This may be interpreted as additional cycles promoting Li out-diffusion from the ZnO substrate.
Figure 6.10: ZnO substrate resistivity (a) and contact resistance (b) as a function of the number of 1000°C, 5s cycles. Substrate resistance reduces with successive cycles which may be indicative of Li out-diffusion from the substrate and improves crystallographic quality. These figures also appear in [108]
6.3. ZnO/ZnMgO Interface Fabrication

The connection between contact resistance and high-temperature cycles is less clear. If it is assumed that the 12 cycle result is an outlier, then it could be argued that the contact resistance follows a similar behaviour to the substrate resistivity. An initial increase in resistance is observed following a single cycle but this resistance reduces with successive cycles. This behaviour could also be attributed to Li diffusion to the substrate surface followed by Li out-diffusion as additional cycles are applied. Notably the TLM for the 12 cycle sample is measured across multiple contacts, therefore the outlier high resistance observed in the 12 cycle sample is not due to a single contact, but is indicative of a resistance increase across all contacts.

6.3 ZnO/ZnMgO Interface Fabrication

Experiments were conducted to see if the improved substrate electrical quality due to thermal treatment would translate to improved 2DEG formation. To test this, samples were grown in pairs, one with a substrate that had been exposed to rapid thermal annealing and one that had not (referred to hereafter as ‘treated’ and ‘untreated’ respectively).

6.3.1 Experimental Methods

For this experiment four ZnO substrates were selected from the same batch from our supplier. All samples were degreased in acetone and IPA, then etched in HCl:H₂O 7:200 solution for 30s in order to reduce sample-to-sample variation as much as possible. Two of these substrates were loaded into the Solaris RTP and subjected to fifteen consecutive 1000°C cycles, following the same procedure previously outlined. The substrates were then separated into two pairs, each one consisting of a thermally treated substrate and a non-annealed substrate.

For the first pair, a 40nm ZnMgO layer was deposited at 750°C directly onto the ZnO substrate. The sample with the treated substrate and untreated substrate are referred to as sample A and B respectively. For the second pair, the process was repeated except a 100nm homoepitaxial ZnO buffer layer was grown on the substrates at 500C before ZnMgO deposition. ZnO homoepitaxial layers have
been shown to greatly increase the quality of subsequent ZnMgO growth on ZnO substrates [111, 112]. In this pair, treated and untreated ZnO substrates are referred to as C and D respectively.

For samples A-D the ZnMgO layer has been grown to a thickness of 40nm. This is because Ghosh has modelled the ZnO/ZnMgO interface and shown that carrier concentration in the ZnO/ZnMgO 2DEG increases roughly linearly with ZnMgO thickness until abruptly saturating at approximately 40nm [113]. This model suggests increasing ZnMgO layer thickness above 40nm leads to no improvement in ZnMgO 2DEG quality. Hence 40nm of ZnMgO is used when engineering ZnO/ZnMgO interfaces throughout this study.

When growing the ZnMgO layers for samples A-D, the Zn-flux was maintained as close to $5 \times 10^{-7}$ Torr as possible. This value of flux is used because earlier samples show that higher Zn fluxes lead to more abrupt ZnO/ZnMgO interfaces which lead to higher 2DEG mobilities [41]. However prolonged growth with Zn fluxes of $1 \times 10^{-6}$ Torr and higher have been shown to cause the beam-flux monitor on the LCN MBE to fail. $5 \times 10^{-7}$ Torr Zn-flux is chosen as a practical compromise between abrupt interface fabrication and continual MBE performance. ZnMgO growth was conducted with a Mg/Zn flux ratio as close to 1:20 as possible. Growing above this ratio frequently resulted in observation of a rock-salt MgO peak in XRD analysis, indicating phase separation in the ZnMgO layer [41]. This results in rough ZnO/ZnMgO interfaces which disrupts 2DEG formation, as shown in chapter 3.

To better demonstrate the points outlined above, another pair of LCN-grown samples are used. These samples were also grown on treated (sample E) and untreated (sample F) substrates. However, E and F were grown with a Zn-flux of $1 \times 10^{-7}$ Torr and a Mg/Zn flux ratio of 1/10. The ZnMgO layer for these samples was also larger, being 100nm thick.

While attempts were made to keep both the Zn-flux and the Zn/Mg flux ratio to the values detailed above, some variation is inevitable during growth. Table 6.1 shows the fluxes for sample A-F recorded after growth using the MBE’s beam flux
6.3. ZnO/ZnMgO Interface Fabrication

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Sample Structure</th>
<th>Zn-Flux ($\times 10^{-7}$) Torr</th>
<th>Mg-Flux ($\times 10^{-8}$) Torr</th>
<th>Mg/Zn Flux Ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>ZnO(T)/ZnMgO</td>
<td>5.0 ± 0.1</td>
<td>2.5 ± 0.1</td>
<td>5.0 ± 0.2</td>
</tr>
<tr>
<td>B</td>
<td>ZnO(U)/ZnMgO</td>
<td>4.6 ± 0.1</td>
<td>2.2 ± 0.1</td>
<td>4.8 ± 0.2</td>
</tr>
<tr>
<td>C</td>
<td>ZnO(T)/ZnO Buffer/ZnMgO</td>
<td>4.8 ± 0.1</td>
<td>1.8 ± 0.1</td>
<td>3.8 ± 0.2</td>
</tr>
<tr>
<td>D</td>
<td>ZnO(U)/ZnO Buffer/ZnMgO</td>
<td>4.3 ± 0.1</td>
<td>1.9 ± 0.1</td>
<td>4.4 ± 0.3</td>
</tr>
<tr>
<td>E</td>
<td>ZnO(T)/ZnMgO</td>
<td>1.0 ± 0.1</td>
<td>4.7 ± 0.1</td>
<td>47 ± 5</td>
</tr>
<tr>
<td>F</td>
<td>ZnO(U)/ZnMgO</td>
<td>1.1 ± 0.1</td>
<td>4.8 ± 0.1</td>
<td>44 ± 5</td>
</tr>
<tr>
<td>P1</td>
<td>ZnO(1100°C+ 800°C)/ZnMgO</td>
<td>10.00 ± 0.01</td>
<td>2.36 ± 0.01</td>
<td>2.36 ± 0.01</td>
</tr>
<tr>
<td>P2</td>
<td>ZnO(1100°C)/ZnMgO</td>
<td>10.0 ± 0.01</td>
<td>2.36 ± 0.01</td>
<td>2.36 ± 0.01</td>
</tr>
</tbody>
</table>

Table 6.1: Table of ZnO substrate samples referred to throughout this chapter. (T) and (U) denote treated and untreated substrates, respectively. In samples P1 and P2 the temperatures refer to anneals the substrates were subjected to before growth.

Finally, the PAS-grown samples are also assessed in this chapter. The PAS samples were not subjected to these rapid thermal cycles because A Kozanecki et al. have furnaces capable of heating ZnO to 1000°C for extended periods. The Polish samples will hereafter be refereed to as P1 and P2. Prior to growth, P1 was subjected to a 5 minute 1100°C anneal in oxygen flow. P1 was then transferred to the growth chamber and annealed for a further 30 minutes at 800°C in oxygen flow, as an additional cleaning step. ZnMgO was then deposited onto the samples at 700°C with a Zn-flux of $1 \times 10^{-6}$ Torr and an Mg flux of $2.39 \times 10^{-8}$ Torr to a thickness of ~150nm. P2 was subjected to a 10 minute a 1100°C anneal in oxygen flow prior to growth. ZnMgO was then deposited onto P2 with the same conditions as P1, except this time the ZnMgO layer is only ~100nm thick. Film thickness was as determined by growth rate. The information of samples P1 and P2 can also be found in table 6.1.

The remainder of the chapter will refer to these initial growth parameters shown in table 6.1, assessing how they have impacted upon the structural and electrical properties of the grown samples.
Figure 6.11: XRD plots for samples A-through-F. Peaks are labelled with their corresponding crystal planes. Insert in each plot shows a closeup of the (004) ZnO peak and ZnMgO shoulder peak (except for sample A where no ZnMgO peak is present).
6.3. ZnO/ZnMgO Interface Fabrication

Figure 6.12: Plots of the PL spectra for sample P1 (a) and P2 (c) across a range of temperatures. Measurements conducted by A. Kozanecki and colleagues. Both measurements are conducted with excitation beam of wavelength 302.4nm and power 5mW. ZnO substrate peaks are indicated in both plots. Other peaks are labeled with the energy at the peaks centre and correspond to ZnMgO layers. XRD plots for samples P1 (C) and P2 (D). Peaks are labelled with their corresponding crystal planes. Insert in each plot shows a closeup of the (0004) ZnO peak and ZnMgO shoulder peak.

6.3.2 X-ray diffraction Analysis

Samples A-F were initially analysed using X-ray diffraction. From XRD the presence of ZnMgO can be verified and the Mg content can be determined by comparing the positions of the ZnO peak and ZnMgO shoulder peak. This process was explained in detail in chapter 3. XRD readings for samples A-to-F are displayed in figure 6.11 and the recorded Mg concentration of the ZnMgO layer for each sample is displayed in table 6.2.

Note that the Mg concentration for A and F in table 6.2 is left blank. In sample A no ZnMgO shoulder peak is present, as show in figure 6.11a. In sample F a
Table 6.2: Table of $x$ concentration $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ layer on treated and untreated ZnO substrate samples. Mg content column is empty for sample A and F as no ZnMgO peak was observed in the XRD plot. The 3 Mg contents list for P2 are from the 3 distinct peaks visible in that P2 XRD spectrum, as illustrated in figure 6.13.

ZnMgO peak is present (figure 6.11f) but it is low intensity and very wide making it difficult to fit. It is unclear why this is the case since the MBE was set up correctly for ZnMgO growth. Samples A and B were grown on the same day and under nominally the same conditions so it is unclear why one should show a well defined ZnMgO peak corresponding to an Mg concentration of 9% while the other shows no ZnMgO. Another thing unusual about the XRD plot for sample A is the presence of a very weak peak which is found at an angle corresponding to the MgO (200) peak. This is indicative of phase separation in this sample’s ZnMgO layer which could explain the absence of the ZnMgO peak. The low intensity of this peak indicates a low concentration and poor formation of MgO. Alternatively the low intensity could be because the MgO planes are not aligned to the XRD’s spectrometer.

The XRD reading for F also shows an MgO peak. While still low in intensity, this MgO peak is more pronounced than the one observed in figure 6.11a. Therefore, it is likely that the low intensity and large broadening of the ZnMgO peak in sample F is also a result of unintentional MgO separation in the ZnMgO layer. This isn’t surprising since the Mg/Zn flux ratio for sample F is larger than A so excess Mg
6.3. ZnO/ZnMgO Interface Fabrication

incorporation which could lead to separation is likely.

XRD for samples B though E display the expected ZnO (002) and (004) peaks with well-resolved ZnMgO shoulders. This indicates the presence of crystallographic ZnMgO and good formation of the ZnO/ZnMgO interface. Note that in the plots for samples B-F the forbidden (003) peak is visible with low intensity. These peaks can be attributed to the Renninger effect in which a strong diffracted beam of x-rays acts as a source beam and is diffracted further through the crystal. For such a strong diffraction beam to occur a highly coherent crystal is needed. Therefore the observation of these forbidden peaks indicates the ZnO substrates are of very high crystallographic quality.

Before sending samples to the LCN, Kozanecki conducted photo-luminescence scans of P1 and P2 across a range of temperatures. These are shown in figure 6.12. The readout for P1 shows a low peak corresponding to the ZnO substrate as well as a more pronounced peak, presumably from the ZnMgO layer at the surface of the sample. This is the response one would expect from a coherent ZnMgO layer on ZnO substrate. P2 on the other hand shows two pronounced peaks beside the substrate peak. This would indicate that there are two distinct, coherent ZnMgO layers present on the sample with different concentrations of Mg. Furthermore both of these peaks have a higher energy than the peak observed in P1. This indicated that both of the P2 ZnMgO layers have a higher Mg contain than those seen in P1, as explained by Kozuka et al. [91].

The multiple peaks observed in the the PL response for P2 suggest that P2 contains multiple distinct ZnMgO layers with varying concentrations of Mg. To confirm if this is the case, P1 and P2 were subjected to XRD measurements, as shown in figure 6.12

The spectra for P1 show a forbidden (003) ZnO peak and a single ZnMgO (004) which corresponds to an Mg concentration of 8.89%. Much like in the Pl plots, P2 demonstrates multiple peaks corresponding to multiple coherent ZnMgO layers. This is shown more clearly in figure 6.13. While the PL scans show two peaks for the P2 sample there are three observed in the XRD spectrum. It is possible
6.3. ZnO/ZnMgO Interface Fabrication

Figure 6.13: XRD plot of the (004) peak of P2. Insert shows close up of upper part of ZnO (004) peak so that the lowest angle shoulder peak may be observed more clearly. Peaks have been labelled with their corresponding Mg concentrations, x.

the peak at $72.5902^\circ$ is so close to the ZnO peak that it is lost in the substrate peak in the PL measurement. The two further out peaks at $72.7579^\circ$ and $73.0865^\circ$ likely correspond to the 3.557 eV and 3.64 eV PL peaks respectively. This gives further support to the assertion that P2 contains multiple coherent ZnMgO films with distinct Mg concentrations. The $72.5902^\circ$, $72.7579^\circ$ and $73.0865^\circ$ XRD peaks correspond to Mg concentrations of 0.68%, 5.0%, 13% respectively. This data is displayed in table 6.2.

Next, the Mg concentration determined from the XRD spectrum has been plotted against the Mg/Zn flux ratio, as shown in figure 6.14. The PAS-grown samples are plotted as triangles to distinguish. When plotting P2, the largest determined XRD content (13%) is used. There seems to be a linear relationship between samples B, C and D as illustrated by the dotted line in the insert. One would expect this to be the case; as relative Mg flux increases so too does the Mg content in the resultant film. Sample E seems to loosely follow this trend having both the highest Mg content and relative Mg flux out of the LCN samples plotted.

The fact that P1 and P2 do not seem to obey this trend at all illustrates how
significant variations in the growth system can lead to significant differences in the films produced. This is why when growing with MBE it is important to learn how the system performs based on different inputs. The same recipe repeated on two separate systems will not necessarily return the same result.

### 6.3.3 X-ray Spectroscopy Analysis

XPS depth profiling was used to determine the elemental composition of the samples as a function of distance from the ZnO/ZnMgO interface. The XPS determines elemental percentage by exposing the sample to x-rays and recording the spectrum of electrons excited out of the material. This results in a series of peaks which correspond to specific elemental electron orbitals. The area under these curves can then be calculated and compared to each other to return the relative elemental percentage of the material. An example scan from the untreated ZnO sample is shown in figure 6.15 where peaks corresponding to species-specific orbital energies have been labelled. Unlabelled peaks are Auger peaks the origin of which
6.3. ZnO/ZnMgO Interface Fabrication

was explained in chapter 5.

![XPS spectrum](image)

**Figure 6.15:** XPS spectrum taken after the first etch on the untreated ZnO sample. Colour indicates the atomic species (including associated Auger peaks). Peaks that correspond to a species-specific orbital energy have been labelled. Shirley background is subtracted from this survey and the area under the Mg1s and Zn2p3 peaks are used to determine the relative atomic percentage of Mg and Zn respectively.

As part of the XPS depth profile, the samples are ion-milled at each step before the XPS spectrum is recorded. For each mill the sample is exposed to a 3000eV argon plasma for 40s. Calibration with an unprocessed ZnO substrate shows that these conditions give a milling rate of approximately 5 nm per milling step.

CasaXPS software is used to extract the atomic percentages for each etch level, using the method outlined above. However, if the first scan of a material contains an element, the software will expect that element to be present in subsequent scans. While conducting a depth profile, there may come a point where one or more of the elements present in the surface of the sample is no longer present. Nevertheless CasaXPS will still try to fit to these elements. Since the XPS measurement has some random noise associated with it, this fit will always retain a non-zero value. This value is typically less than 10%. An example plot for the full depth profile for sample F is shown in figure 6.16.

Figure 6.17 and 6.18 show the XPS depth profiles at the ZnO/ZnMgO interface for samples C-F. Coke *et al.* showed that interfaces with a gradient approaching 1%/nm demonstrate the highest mobility 2DEGs [66]. Compared to Coke *et al.*, sample C, E and F have relatively diffuse interfaces while sample D is quite abrupt.
Figure 6.16: XPS spectrum depth profile Mg content for sample F. Dashed line shows point where Mg content is effectively zero. Mg content beyond the dashed line is due to CasaXPS fitting to noise.

Figure 6.17: Comparison of Mg gradient at ZnO/MgZnO for sample C (green) and D (magenta). Least mean square linear fit used to extract Mg gradients are shown in the corresponding colour. Gradients for C and D are 0.28%/nm and 0.83%/nm respectively.
Figure 6.18: Comparison of Mg gradient at ZnO/MgZnO for sample E (red) and F (blue). Colour of x-axis corresponds to sample data of the same colour. Least mean square fit linear used to extract Mg gradient are shown in the corresponding sample colour. Gradients for E and F are are 0.14%/nm and 0.53%/nm respectively.

Note the Mg composition determined by XPS is significantly larger than the readings for XRD. The XPS measurement of samples D, E and F show an Mg content in excess of 40% near the sample surface. This is above the segregation limit of ZnMgO, however MgO peaks were only observed in the XRD analysis of samples F. One possible explanation is the surface layer of this sample is not ZnMgO but instead a poorly crystalline Mg-rich phase. This Mg-rich layer has no coherent orientation and is either amorphous or is comprised of a random assortment of different crystallographic orientations. Such a layer cannot be observed by XRD and so no MgO peak is observed in samples C, D and E. The observation of an MgO peak in F can be attributed to the fact that F shows the highest Mg content of all the samples in both XRD and XPS. The high Mg content has facilitated the formation of a coherent MgO layer in the samples.

The observation of the ZnMgO shoulder peaks in the XRD indicated that a coherent ZnMgO layer is still forming somewhere in the samples C-F in spite of the Mg-rich phase. Most likely this ZnMgO film is near the ZnO layer where the Mg content determined by the XPS dips below the 40% segregation limit.
While the upper layer is not one coherent ZnMgO film, the depth profile measurements can still give an indication of interface abruptness. Using depth profiles in this way Coke et al. demonstrated a link between interface abruptness and 2DEG quality, with more abrupt interfaces demonstrating higher mobilities [66].

It is interesting to note that in both cases the thermally-treated samples (C and E) demonstrate more diffuse interfaces than their untreated counterparts. It is possible that the thermal treatment of ZnO relaxes the surface resulting in a higher surface roughness. This results in a less abrupt interface as incident ZnMgO grows unevenly across the peaks and valleys on the rough substrates.

The depth profile in both plots are across a larger depth than one would expect given the intended thickness of the ZnMgO layers. Argon milling is known to increase surface roughness. Therefore the diffuse interface could be due to relatively rich Mg-crystal peaks amid Mg-poor values left behind by the argon anneal. Another possibility is that the reading for Mg concentration is accurate since Mg is highly mobile in ZnO [66] and easily diffuses into the ZnO substrate, reducing interface abruptness.

Before XPS depth profiles could be taken for the PAS-grown samples, the thickness of the ZnMgO layers needed to be determined. This was achieved by imaging the edge of the sample using SEM. As stated in chapter 5, the samples are cleaved into four before being subjected to destructive processes, such as electrical device fabrication or XPS milling. By observing the sample along the edge, where the break occurred, the individual crystal layers can be distinguished. P1 was imaged since it was grown for the longest time with an estimated thickness of 150nm. A mill long enough to reach the substrate in sample P1 should suffice for P2.

Figure 6.19 shows the SEM image taken for sample P1. This shows that the thickness of the ZnMgO is almost double what was expected. As already stated, Mg appears to be highly mobile in ZnO. LCN-based growth of ZnMgO on ZnO is often accompanied by Mg diffusing into the ZnO layer, greatly reducing interface
6.3. ZnO/ZnMgO Interface Fabrication

Figure 6.19: SEM image of the cleaved edge of P1

Figure 6.20: Comparison of Mg gradient at ZnO/MgZnO for sample P1 (cyan) and P2 (orange). Least mean square linear fits used to extract Mg gradient are shown in the corresponding sample colour. Gradients for P1 and P2 are are 0.094%/nm and 0.077%/nm respectively.

abruptness. It seems this is also the case for PAS-grown samples.

Figure 6.20 shows the Mg content at the ZnMgO/ZnO interface for samples P1 and P2. Much as with the LCN-grown samples, the XPS results show much higher Mg content than what is determined by XRD. This indicates that these samples also suffer from disordered, Mg-rich phase close to the sample surface.
This is curious since the Mg content in both samples is below the separation limit for ZnMgO. To understand this relationship, the maximum Mg content determined by XPS (XPSMg) is plotted as a function to the Mg content determined by XRD (XRDMg) in figure 6.21. The LCN samples are plotted as circles, the PAS samples as triangles. F is not plotted as there was no ZnMgO peak present in the XRD scan for F.

Figure 6.21 shows there is a correlation between the Mg percentage from XPS and the percentage from XRD. This is to be expected since a larger Mg content in the XRD reading should indicate a higher overall Mg content in the sample which is then observed in XPS. While the XPS measurement may not give an accurate reading of the Mg percentage in our samples, they can qualitatively distinguish samples with a higher or lower Mg content. This indicated that XPS depth profiles are not entirely untrustworthy; they can still give a qualitative indication of the Mg distribution and interface abruptness of our systems. P1 and P2 are clearly separated from samples C, D and E in this plot. This can be attributed to the fact that P1 and P2 were grown with different equipment, or because they were grown with Zn fluxes an order of magnitude higher than the LCN samples.

Another interesting feature is that sample P1 does seem to have a thicker ZnMgO layer than P2, notable by the way the P1 response is roughly linear from 0-250nm from the sample surface, while the P2 is roughly linear from 0-100nm. However the diffuse region of Mg seems to terminate at 400nm for the sample surface in P1 and P2.

Both samples show fairly diffuse interfaces with gradients of 0.094%/nm for P1 and 0.077%/nm for P2. This seems to directly contradict the SEM scan in figure 6.19, which shows a clear and sharp distinction between the ZnMgO and ZnO layers. With the LCN-grown samples, it was noted that ZnMgO layers deposited on substrates subjected to anneals at 1000 °C produce more diffuse interfaces. This may explain why P1 and P2 both show diffuse interfaces. Also note that P2 was annealed at 1100°C, twice as long as P1. This extra anneal time is the reason that P2’s interface is more diffuse. If this is assumed to be the case, it would indicate
6.3. ZnO/ZnMgO Interface Fabrication

**Figure 6.21**: Plot of maximum Mg content determined by XPS against the maximum XRD content determined by XRD. All points are labelled with the samples they correspond to. The PAS and LCN samples are plotted with triangles and circles respectively to clearly distinguish the two groups.

**Figure 6.22**: Mg gradient determined by XPS as a function of Zn flux used during ZnMgO layer growth. Samples C, D, E, and F are plotted in green, magenta, red and blue, respectively. Black points are from data taken by Coke [41]

that the 800 °C cleaning anneal used on P1 does not significantly alter the ZnO substrate, only anneals above 1000 °C alter the substrate. Without a larger pool of samples with a larger variation in anneal times and temperatures, it is difficult to draw any systematic conclusions on this theory.
In earlier work at the LCN, Coke et al. showed a correlation between Zn-flux and interface abruptness [41]. To show how these latest samples line up with this data, the values for sample C-P2 have been plotted alongside Coke’s data in figure 6.22. Coke’s data is plotted in black while samples C-P2 are colour-coded as per the corresponding colours used for the XPS plots. Once again P1 and P2 seem to be outliers in this data set, possibly due to the samples being grown under vastly different conditions. Samples C-F seem to agree with Coke’s data.

6.3.4 Electrical Characterisation

Following structural analysis the samples were patterned into device structures for electrical testing. Samples were loaded into the SVS 6000 system and were milled to produce a raised mesa that would facilitate contact to the 2DEG. This involved milling to a depth of 100nm for sample C and D, a mill to a depth of 200nm for sample E and F, and a depth of 500nm for P1 and P2. Finally Ti/Au contacts were patterned onto the samples (50nm Ti sputter deposition followed by 10nm Au). For further details on device design and fabrication, refer to chapter 5.

All samples were loaded into the PPMS systems and resistance across the mesas was measured as a function of temperature from 300-2K. A four-point measurement setup was used with an AC 19Hz 0.01mA current. Samples A, B and E proved too resistive to measure in the PPMS system.

Plots for samples C, D, F, P1 and P2 are shown in figure 6.23. Sample C shows an initial rise in resistance as the temperature falls from 300K to 200K. This is typical of semiconductor freeze-out. As the sample cools, the electrons in the semiconductor lose the thermal energy needed to reach the conduction band. This results in a decrease in charge carriers and an increase in resistance.

As the temperature continues to drop, the resistance reaches a maximum at approximately 160K, before sharply decreasing with temperature. This decrease is attributed to 2DEG formation as charge carriers collapse into the conduction band quantum-well at the ZnO/ZnMgO interface. Below 100°C the resistance starts to plateau, as the majority of carriers are confined at the interface and the 2DEG becomes the dominating conduction path. The plateau is present since resistance
Figure 6.23: Resistance vs temperature measurements for samples C, D, F, P1 and P2 at zero field. Measurements are conducted from 300k to 2k using PPMS with 4-point setup.
is independent of temperature in a 2D system, where electron-electron interactions are the primary scattering mechanism at low temperatures [114].

Sample D seems to initially follow the same behaviour as sample C. There is a rise in resistance on cooling between 300-200K. The resistance then drops and appears to plateau at around 100K. However there is an increase in resistance below 50K. This behaviour suggests that the charge carriers start to become confined in the quantum-well but the channel freezes-out at lower temperatures. This cannot be the case for 2D systems since resistance in a 2DEG is temperature independent, as stated above. Previous 2DEG studies have demonstrated an increase in resistivity attributed to the electron interference effect [115]. This occurs when the mean free path of the electrons ($l_e$) is comparable to the Fermi wavelength $\lambda_F$ [115, 116, 117].

For a 2D system, the ratio between mean free path and Fermi wavelength is given by:

$$\frac{l_e}{\lambda_F} = \frac{h/e^2}{2\pi R_s} \quad (6.4)$$

where $R_s$ is the 2DEG sheet resistance. A ratio of 1 indicates that conduction is dominated by electron interference. At 2K the ratio for sample D is 0.71, so in principle the electron interference should be significant.

Two devices were measurable on sample F. Figures 6.23c and 6.23d are of the left and right mesa respectively. Both mesas show an increase in resistance as temperature decreases. This response is indicative of semiconductor freeze-out. There is little indication of carrier confinement in either of these mesas. There is a sharp drop in the right mesa below 50K, which could be indicative of a 2DEG forming at low temperatures. This possibility will be explored further through magnetoresistance measurements in the following section.

Turning our attention to the PAS-grown samples, P1 and P2, these show an initial increase in resistance that begins to flatten out at 150K. From here, the resistance in both samples is roughly linear until approximately 80K, at which point the resistance starts to increase exponentially as the temperature drops. This behaviour indicates a 2DEG forms below 150K but freezes out below 80K. This behaviour is very similar to sample D, where the increase in resistance at low
temperatures was attributed to the electron interference effect. Therefore P1 and P2 do not have working 2DEGS at 2K.

6.3.5 Magnetoresistance Measurements

While the RvT graphs give some indication of 2DEG formation, there is more that can be learnt by checking the samples response to magnetic field. Once cooled to 2K, the samples were exposed to a magnetic field ranging from 0-14T. The field was applied perpendicular to the ZnO/ZnMgO interface. Figure 6.24 shows the resistance and magnetoresistance as a function of applied magnetic field.

6.3.6 Sample C: Shubnikov de Haas (SdH) Oscillations

First we will focus on the magnetoresistance response of sample C which is shown in figure 6.24a. Sample C shows periodic oscillations in resistance/magnetoresistance as a function of applied magnetic field. These are Shubnikov de Haas (SdH) oscillations. As explained in Chapter 4, this behaviour is only present in 2D confined electron spaces. Thermal treatment of the ZnO substrate followed by ZnO buffer growth was successful in achieving 2DEG formation.

The SdH oscillations present in the magnetoresistance for sample C can be used to determine the mobility and carrier concentrations of the 2DEG. The relationship between carrier concentration and SdH periodicity is given by:

$$\Delta \left( \frac{1}{B} \right) = \frac{2e}{nh}$$

(6.5)

where \(n\) is the carrier concentration, \(B\) is perpendicular magnetic field, \(e\) is electron charge and \(h\) is Planck’s constant. By plotting the inverse of the applied perpendicular magnetic field against the peak number, where the first observed peak, when sweeping from 0T to 14T, is arbitrarily assigned the value 1, the carrier concentration can be determined from the gradient. Such a plot is shown in figure 6.25. Using this method, the carrier concentration of sample C was determined to be 5.05 \times 10^{12} \text{cm}^{-2}.

The carrier concentration can also be determined by measuring the device in the Hall geometry and plotting the Hall voltage \(V_H\) as a function of magnetic field \(B\).
Figure 6.24: RvH measurements for samples C, D, F, P1 and P2. Measurements were conducted using 4-point setup at 2K in PPMS. Magnetic field is applied perpendicular to conduction channel. Inserts are included for mesa 1 and 2 of sample F to highlight behaviour observed at low field.
Figure 6.25: $1/B$ vs peak number for sample C. Magnetic field is taken at the apex of each peak. Least-mean-square linear fit use to determine carrier concentration is shown as dashed line.

Figure 6.26: Hall voltage vs magnetic field for sample C at 2K.
This process was conducted for sample C and the resulting plot is shown in figure 6.26. The oscillatory behaviour at high fields is due to SDH oscillations as some longitudinal conductance is incorporated into the measurement. Nevertheless the strong linear relationship at low field is sufficient to determine carrier concentration. The Hall coefficient is given by

$$R_H = \frac{V_H t}{IB} = -\frac{1}{ne} \quad (6.6)$$

where $t$ is the thickness of the conduction channel, $I$ is the current, $e$ is the electron charge and $n$ is the sheet carrier concentration. Using this method, $n$ was calculated to be $6.47 \times 10^{12}$ cm$^{-2}$, comparable to the result from SDH determination.

Now that carrier concentration is known, mobility can be determined using the following relation:

$$\mu = \frac{1}{R_0 \frac{1}{enW/L}} \quad (6.7)$$

where $R_0$ is the resistance at zero field, $W$ is the width of the channel and $L$ is the channel length. The carrier concentration determined from SdH is used. This gives a mobility of $4.8 \times 10^4$ cm$^2$/Vs. This value is three orders of magnitude higher than low-temperature mobility of ZnO [118]. Furthermore this mobility is one order of magnitude higher than mobilities achieved by Coke et al. [41, 66]. It is known that carrier concentration scales inversely to 2DEG mobility since higher carrier concentration leads to enhanced carrier-carrier scattering. However carrier concentration for sample C is higher then any demonstrated by Coke et al. This indicates that sample C demonstrates improved confinement and/or a cleaner interface than those previously achieved by Coke et al.

Coke et al. showed that samples with lower zero-field room-temperature resistance ($R_{rt}$) had higher 2DEG carrier mobility when cooled. $R_{rt}$ for sample C is two orders of magnitude lower than Coke’s highest mobility sample (83Ω to 1600Ω). However samples C, E and F all show room temperature resistances of a similar order of magnitude to those demonstrated by Coke’s samples. So while $R_{rt}$ is a good indicator of low-temperature mobility in working 2DEG samples, a low
R_{rt} does not necessarily indicate 2DEG formation.

Taking the values for carrier concentration and mobility, and plugging them into the equations for the mean-free-path $\ell$ and the coherence length $\xi$ shown in chapter 1, gives $\ell = 1770\text{nm}$ and $\xi = 122\text{nm}$ at 2K. These values are calculated based on the assumption that $m^* = 0.3m_e$ [16, 65]. This indicates that sample C is well within the clean limit and the coherence length is over 100nm at 2K. Therefore these 2DEGs are well suited for tuneable Josephson junction fabrication. Further increases in mobility are not necessary since the coherence length is mobility-independent in the clean-regime.

### 6.3.7 Sample D: Negative Magnetoresistance

Now we turn our attention to sample C’s unannealed counterpart, sample D. The magnetoresistance response for sample D is shown in figure 6.24b. Sample D shows no SdH oscillations but a negative magnetoresistance is observed across the entire range of applied magnetic field. This result is similar to those shown by Das *et al.* [115]. Das showed positive magnetoconductance (negative magnetoresistance) at a range of temperatures for ZnO 2DEGs achieved on c-plane sapphire.

Das *et al.* explain their observations by considering the effects of weak localisation. As stated earlier, sample D has conduction that appears to be dictated by electron interference at 2K. Weak localisation arises in a disordered system where multiple scattering events cause electrons to become localised in closed paths. Das *et al.* state this dephasing element primarily arises from electron-electron collisions in the ZnO 2DEG. Perpendicular magnetic field destroys time-reversal symmetry [119]. In such a field, electron pairs in closed paths acquire a phase shift given by $\varphi/\varphi_0$, where $\varphi$ is the magnetic flux enclosed in the closed path and $\varphi_0 = \hbar c/2e$ is the flux quantum. Hence in a perpendicular magnetic field, the phase coherence of the electron waves is destroyed and the localisation effect is suppressed. Therefore the presence of weak localisation gives rise to negative magnetoresistance [117, 119].

This indicates that sample D also demonstrates confined electron space behaviour. Unlike sample C, this space is too disordered to demonstrate SdH
oscillations but is confined enough to show negative magnetoresistance due to weak localisation, a fundamentally quantum behaviour. From XPS it is clear that sample D has an abrupt interface, so the cause of this disorder is not from poor confinement. The Mg concentration of D is larger than C and excess Mg can lead to interface roughness, increasing electron scattering and disorder. However XRD shows that the Mg content of D is well below the segregation limit of ZnMgO. Furthermore the Mg content of C and D are comparable, so this theory seems unlikely. D is grown on an untreated ZnO substrate, so it is possible that the disorder arises from Li concentration in the ZnO layer. Li ions in ZnO act as scattering centres [120]. Additionally Li defects are highly mobile in ZnO [33, 120] so overgrowth of ZnO on the ZnO substrate may not fully impede Li propagation towards the ZnO/ZnMgO interface.

6.3.8 Sample P1 and P2: Negative Magnetoresistance

Now consider the responses for samples P1 and P2 plotted in figure 6.24e and 6.24f respectively. P1 and P2 show very similar behaviour to sample D. The magnetoresistance is negative which is indicative of a highly disordered confined electron space, which is too disordered to demonstrate SdH oscillations. In the case of sample D, the disorder was attributed to a lack of thermal treatment and the presence of Li in the sample acting as scattering centres. The same cannot be said for P1 and P2 which have both been thermally treated above 1000°C. In P1 and P2 the disorder likely arises from poor confinement due to the high diffusivity at the interfaces, as demonstrated via XPS earlier during material characterisation.

6.3.9 Sample F: Positive and Negative Magnetoresistance

Finally we consider the behaviour of left and right mesa from sample F plotted in figure 6.24c and 6.24d respectively. The left mesa on sample F shows an initial linear magnetoresistance which saturates at ~ 4T. This behaviour is observed in impurity semiconductors, i.e. where conduction is partially due to electrons excited into the conduction band from impurity donors [121]. There seems to be no conduction through a confined electron space in this mesa. Instead all conduction
6.3. ZnO/ZnMgO Interface Fabrication

is through the substrate.

The right mesa of F shows a very different response. There is an initial increase in resistance which then saturates and decreases at 0.25T. This behaviour can be explained by considering magnetoresistance effects in the Anderson-localised system. Anderson showed in a sufficiently disordered system (such as a semiconductor with impurities or defects) the electron probability function becomes localised [122]. In these instances conduction through the material takes place via a series of quantum tunnelling events between localised regions.

Anderson localisation is comprised of three electronic states; unoccupied (UO), singularly occupied (SO) and doubly occupied (DO) [123]. Each of these states are localised to a specific region of the material defined by the localisation length $\xi_{\ell\ell}$. Kamimura et al. [123] show that in a magnetic field, the spins of the SO states start to align with the field. This limits the amount of tunnelling that can occur between SO state, as the probability of finding two SO states with anti-parallel spins decreases. This leads to a reduction in conductivity and is observed as a positive magnetoresistance [123]. At sufficiently high field, the electrons are spin-polarised and the positive magnetoresistance component saturates. While SO-to-SO scattering is now frozen out, SO electrons can hop into UO states (SO-to-UO scattering). This scattering is mediated by the localisation length, which dictates the range over which a hopping interaction can occur. Kamimura et al. shows that the localisation length is proportional to the applied field, leading to an increase in the number of electrons in the SO state hopping into the UO state. This results in a negative magnetoresistance component which scales with field [123]. Therefore the SO-to-SO and SO-to-UO scattering events combine to produce a magnetoresistance that initially increases and then decreases, as shown in figure 6.27. This behaviour is similar to the low field behavior in the right mesa of sample F, depicted in the insert in figure 6.24d.

The high field data from the right mesa of sample is similar to data presented by Silva et al. who show how application of a magnetic field to an n-doped semiconductor leads to a separation of spin-up/spin-down conduction bands, which
causes negative magnetoresistance [124]. This negative component saturates and gives way to a positive component, following behaviour similar to that of a pure conductive material in a magnetic field. This behaviour is shown in figure 6.28 which resembles the 2-8T region from the right mesa of sample F.

It is also possible that the negative magnetoresistance seen in the right mesa of sample F is the result of weak localisation. If this is the case, it would indicate that weak localisation is the dominant effect dictating conduction up to approximately 4T after which the effect of spin separation becomes more significant. Silva et al. also explain the observation of both negative and positive magnetoresistance. Therefore a combination of Anderson localisation in low-field, and spin separated conduction bands at high field, is the accepted explanation or the behaviour seen in the right mesa. There is no evidence of a 2DEG present in sample F.

The discrepancy between the left and right mesa could be the result of damage sustained to the left mesa. The measurement of the left mesa seems to be consistent with measurements of a semiconductor with impurity donors, which may indicate that the untreated ZnO substrate is actually the sample being measured.

Note the zero field resistance of F in both mesas is an order of magnitude higher than that observed in samples C and D. This may be the result of differences in the Mg/Zn-flux ratios between C/D and F. This is difficult to prove as the Mg
content from the XRD of F is inconclusive. Perhaps the use of homoepitaxial ZnO growth on samples C and D are responsible for improved carrier confinement at the ZnO/ZnMgO interface. This is evident by observation of SdH oscillations in C and weak localisation D. It seems that SdH oscillations are only observed when both RTP and ZnO buffer growth are used on the same sample. Further growths will need to be conducted to confirm if this observation can be reliably repeated.

6.4 Scattering Sources

The SdH oscillations can be used to determine the scattering sources in the 2DEG. In this section, the classical and quantum scattering rates are calculated for the 2DEG in sample C, and are compared to 2DEGs grown by Coke et al. [41]. The classical and quantum scattering rates will be compared to determine which is dominant.
6.4. Scattering Sources

Figure 6.29: RvH plots for sample C at temperatures ranging from 2-10K in 2K increments. SdH oscillations are clearly visible at all temperatures.

### 6.4.1 Classical Scattering Rate

To determine the classical scattering rate, one must first calculate the effective mass. The effective mass is affected by scattering events and correlations between charge carriers. The effective mass therefore acts as an indirect measure of scattering and disorder in the system. The value can be determined from the temperature dependence of the SdH oscillations. Sample C was measured in a 0-14T perpendicular field at temperatures ranging from 2-10K in 2K steps. These scans are shown in figure 6.29. To calculate the effective mass, the natural log of the SdH oscillation amplitude (A), divided by the temperature (T), is plotted as a function of temperature. The effective mass ($m^*$) can be calculated using the equation

$$
\Delta R_{xx}^{osc} \propto A = \frac{A^T}{\sinh A} 4e^{-\pi/\left(\omega_c \tau_{tot}\right)}
$$

(6.8)
Figure 6.30: Plot of \( \ln(A/T) \) as a function of temperature from sample C. Each point represents the location of a peak at the given field. Dotted lines are linear fits at each value of field. Gradient are extracted so that effective mass can be determined.

where \( \Delta R_{xx}^{osc} \) is the amplitude of the oscillation in magnetoresistance with the background removed. \( A^T \) accounts for thermal broadening at temperature \( T \), and is given by \( A^T = 2\pi^2 kT/\hbar \omega_c \), where \( \omega_c \) is the cyclotron frequency given by \( \omega_c = eB/m^* \) and \( \tau_{tot} \) is the total scattering lifetime. This equation can be simplified using the approximation \( \sinh(\chi) \approx \exp(\chi/2) \) and the derivation shown in appendix C of [41]. The equation becomes [125]

\[
\ln\left(\frac{A}{T}\right) = C_2 - \frac{2\pi^2 k_B T m^*}{e\hbar B}
\]  

(6.9)

where \( C_2 \) is a temperature-independent term at a constant field, \( B \). Amplitude is measured from the base of a given local minimum to the tip of the next local maximum (measuring from low to high field). \( B \) in this case refers to the field where the local maximum occurs. The plot for this data is shown in figure 6.30.

The fits in figure 6.30 have a gradient of \( 2\pi^2 k_B T m^* / e\hbar B \). Therefore by plotting the absolute value of the gradient in figure 6.30 as a function of \( 1/B \), one can extract the effective mass from the gradient of this new relationship. This data is shown in
6.4. Scattering Sources

Figure 6.31: Gradients taken from the fits in figure 6.30 plotted as a function of $1/B$. The colours of the point correspond to those used in figure 6.30. Gradient of plot is used to determine effective mass ($m^*$) for sample C.

The fit in figure 6.31 gives the average effective mass as $0.322m_e$, which matches the ranges seen by other groups analysing ZnO 2DEGs [65]. However the effective mass for each individual fit in figure 6.30 can also be plotted as a function of field. This plot is shown in figure 6.32. The fit has a gradient of $2.8 \times 10^{-3}m_eT^{-1}$, far smaller than the error in each measurement. This shows that $m^*$ does not vary significantly with applied magnetic field.

Now that the average effective mass is known, the classical scattering rate can be determined. The classical scattering time $\tau_c$ encapsulates all classical scattering events, including phonon, ion and defect scattering. It can be calculated using the equation

$$\sigma = ne^2 \tau_c / m^*$$  \hspace{1cm} (6.10)

where $\sigma$ is the conductivity, $\mu$ is the mobility and $e$ is electron charge. The conductivity of the 2DEG can be calculated using the expression $\sigma = ne\mu$. Hence
6.4. Scattering Sources

Figure 6.32: Effective masses calculated from fits in figure 6.30 plotted as a function of field with error bars from said fits. Dashed line shows the fitting to this data and has a slope of $2.8 \times 10^{-3} \text{m}_e \text{T}^{-1}$.

the expression of the classical scattering time can be simplified to [126]:

$$\tau_t = \frac{m^* \mu}{e} \quad (6.11)$$

Using the value for mobility extracted from the SdH oscillations at 2K, the classical scattering time is determined as 8.8ps, an order of magnitude higher than values demonstrated by Coke et al. [41].

6.4.2 Quantum Scattering Rate

Now that the effective mass is known, the quantum scattering time can also be determined. The quantum scattering rate is related to Heisenberg’s uncertainty principle, $\Delta E \Delta t \geq (1/2)\hbar$ which leads to quantum mechanical broadening of a single-particle electron state. The quantum scattering rate accounts for the single-particle relaxation time in this quantum mechanical broadened state. In a confined electron space, the quantum scattering time $\tau_q$ can be determined using
the following equation

\[ \ln \left( \frac{\Delta R_{xx}}{4D_T(B)R_0} \right) = C_3 - \frac{\pi m^*}{e \tau_Q B} \]  

(6.12)

where \( C_3 \) is constant at a given temperature \( T \), \( \Delta R_{xx}/R_0 \) is the normalized amplitude of the SdH resistance oscillations, with amplitude being measured between neighbouring maxima and minima as explained in section 1.13.1. \( D_T \) is the thermal damping factor given by

\[ D_T = \frac{2\pi k_B T / \hbar \omega_c}{\sinh(2\pi k_B T / \hbar \omega_c)} \]  

(6.13)

where \( \omega_c \) is the cyclotron frequency, which is related to the effective mass, \( m^* \) by \( \omega_c = eB/m^* \). By plotting the logarithmic part of equation 1.11 against \( 1/B \), one can extract the quantum scattering time, \( \tau_q \), from the gradient fit. This type of plot is known as a “Dingle” plot [127]. Figure 6.33 shows a Dingle plot for sample C at 2K. From the Dingle plot, it is clear that there is a deviation from linearity at lower fields. The linearity of the points at higher field indicates there is only one conduction channel in the sample at 2K. The fit to the points at high field can be used to determine \( \tau_q \). In figure 6.33 it is clear that points at low fields (the points plotted as black triangles) are not following a linear relationship when compared to the rest of the data, so these points are not included in the fit. For points where \( 1/B < 0.14T^{-1} \) the points follow a roughly linear relationship, though it is not clear precisely which points should be used in the fit. To accommodate for this, figure 6.33 shows the two most extreme fits that can be fitted to this data. The lowest gradient fit (indicated by the dot-dashed line) is fitted to the data at the highest field (plotted as cyan squares). The highest gradient fit (the dashed line) is fitted to all the data where \( 1/B > 0.14T^{-1} \) (plotted as cyan squares and red circles). The low and high gradient fits correspond to a \( \tau_q \) of 0.13ps and 0.17ps respectively. This gives an effective range of possible \( \tau_q \) values for sample C. These values are comparable to the times demonstrated by Coke et al. [41].
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6.4.3 Electron-electron scattering time

Scattering events can also occur between electrons, though this form of scattering is notably difficult to extract. The effect of electron-electron scattering can be extracted from the continuous longitudinal resistance underlying SdH oscillations at high field, measured across a range of temperatures. This takes the form of a parabolic negative magnetoresistance in the low field range. This behaviour is attributed to electron-electron interactions and has previously been observed in GaAs/AlGaAs 2DEGs [128]. However this fit can only be seen in devices where the oscillations are suppressed. Sample C shows strong, well defined, oscillations and does not show the low field magnetoresistance indicative of EEI interactions[128]. As a result, this particular form of scattering cannot be quantitatively analysed for sample C.

Figure 6.33: Dingle plot showing fitting used to determine the quantum scattering time $\tau_q$. The low-gradient fit (dot-dashed line) is fitted to the points plotted as cyan squares. The high-gradient fit (dashed line) is fitted to the data plotted as cyan squares and red circles. Data plotted as black triangles is not used in either fit. All data is at 2K.
6.4.4 Determination of Scattering Mechanisms

Comparing the classical and quantum scattering times can provide information regarding the dominant scattering mechanisms at play in the 2DEG. The quantum scattering time $\tau_Q$ gives the mean time a carrier remains in a specific state before scattering into another. Hence when calculating $\tau_Q$ all scattering events are weighted equally. However the classical scattering time $\tau_t$ is a measure of how long a charge carrier remains travelling in a particular direction. As a result, determination of $\tau_t$ contains a factor of $[1 - \cos(\theta)]$ where $\theta$ is the scattering angle [126]. This term means scattering events with a larger scattering angle are more heavily weighted than smaller angle events. Therefore angular weighting of scattering events in the classical regime can lead to $\tau_t$ being quite different from $\tau_Q$.

For short-order scattering (e.g. alloy disorder scattering) the classical and quantum scattering are relatively similar and $\tau_t/\tau_Q \sim 1$. Larger ratios are indicative of long-range scattering mechanisms (e.g. Coulomb field of background charges in quantum field). The largest values for $\tau_t/\tau_Q$ are expected for scattering due to remote Coulomb centres, such as ionized impurities [129]. This form of scattering is highly angle-dependent and is largest for small angles. This results in $\tau_t \geq \tau_Q$ because of the $[1 - \cos(\theta)]$ relationship mentioned above.

For sample C, the $\tau_t/\tau_Q$ ratio is found to be $\sim 68$, an order of magnitude higher than the results shown by Coke et al. [41]. Larger $\tau_t/\tau_Q$ ratios indicate quantum scattering is dominant, which in turn implies a strong confinement at the 2DEG. $\tau_t/\tau_Q$ ratios of the order $10^1$ or higher are considered large and are indicative of long range scattering mechanisms, as explained above.

One of the primary sources of such long-range scattering is alloy disorder scattering caused by alloy impurities in the substrate. Coke demonstrated that alloy scattering was the most prominent mechanism for impeding mobility in their structures. From this observation, Coke asserted that Li defects were the primary mobility-limitation mechanism in their devices. Li impurities and their associated defects act as point defects in the conduction channel and thereby increase scattering.
Sample C shows a large $\tau_t/\tau_Q$ ratio and therefore has conduction dominated by quantum-scattering. Therefore while the thermal treatment of our substrates has lead to a significant increase in mobility, alloy defects still seem to be the main inhibitor of mobility. To achieve mobilities greater than those seen in sample C the substrate quality must be further improved.

Coke also demonstrated the classical scattering time is strongly dependent on the sample room-temperature resistance (with low resistance indicating a small scattering rate). Sample C shows an order of magnitude reduction in room-temperature substrate resistance compared to Coke et al.’s samples ($\sim 0.2k\Omega$ vs $\sim 1.5k\Omega$ respectively). Room-temperature substrate resistance provides a good gauge of substrate quality and, therefore, a crude indication of defect density. Sample C has an order of magnitude higher $\tau_t/\tau_Q$ ratio and an order of magnitude higher mobility than Coke et al.’s samples. This correlation further supports the assertion that alloy scattering is the dominant scattering mechanism in sample C.

### 6.5 Summary and Outlook

This chapter found that with the correct preparation (rapid thermal processing and ZnO buffer growth), high carrier-concentration and high-mobility 2DEGs can be achieved on commercially available ZnO substrates. Of the eight samples shown in this section, only five could be measured electrically, and of these only one demonstrated 2DEG behaviour. With that said, this sample has demonstrated a mobility of $4.8 \times 10^4 \text{ cm}^2/\text{Vs}$. This is significantly higher than the mobilities of ZnO 2DEGs previously grown at the LCN using the MBE system (which reached a maximum of $3.1 \times 10^3 \text{ cm}^2/\text{Vs}$).

One of the reasons for this improvement may be the addition of high-temperature heat-treatment to the ZnO substrates. It was shown that successive anneal cycles of temperatures exceeding 1000°C result in a reduction in substrate resistance, with 15 successive cycles showing the most improvement. This drop in resistance is attributed to the removal of impurities in the ZnO substrate, most notably Li, which is known to be present in hydrothermally grown ZnO. Other groups with the
6.5. Summary and Outlook

capabilities to directly measure Li concentration have shown how annealing ZnO at 1000°C and above can promote Li out-diffusion [32, 33, 107].

Analysis of scattering mechanisms in this 2DEG indicated that the mobility of the system is dominated by long-range quantum scattering. Based on observations made by Coke et al., the most likely culprit is Li defects in the substrate. With that said, sample C demonstrates a $\tau_t/\tau_Q$, an order of magnitude higher than those demonstrated by Coke et al., which is accompanied by a higher order of magnitude mobility. Therefore while thermal treatment has lead to a reduction in scattering, likely due to defect removal, further annealing is required to achieve higher mobilities.

Should this work continue, more time should be allocated to heat treatment of ZnO substrates. More sample pairs like C and D (similar growth on a treated and untreated substrate) should be attempted under a range of different growth parameters (ZnO homoepitaxial growth prior to ZnMgO deposition, varying Mg content in ZnMgO layer, varying growth temperature of ZnMgO, and so on). Whether thermal treatment of ZnO substrates leads to reproducible 2DEG formation across substrates from the same batch is yet to be determined. Furthermore heat treatment should be attempted across multiple ZnO substrate batches to assess whether batch-to-batch variation in substrate quantity is still too significant for reliable 2DEG formation, as was observed by Coke et al. [41].

Furthermore the literature shows that annealing ZnO at high temperatures leads to increased surface roughness [130]. We have focused on analysing the bulk structural qualities of processed ZnO, so the effects of cycles on surface roughness were not assessed. Throughout this thesis, we have stated that surface roughness at the interface has a drastic effect on 2DEG formation. It is therefore vital that the relationship between the number of cycles and surface roughness is understood. Future work should use atomic force microscopy to analyse ZnO substrate surface roughness as a function of the number of cycles. HCl etch can reduce roughness of the Zn-face of ZnO and so could be used to reduce surface roughness introduced by high temperature annealing. Future work should be conducted to find the optimum
HCl concentration and etch duration for achieving smooth a ZnO surface after annealing.

The following questions remain unanswered: Can additional thermal treatment lead to a further improvement of 2DEG mobility? Are there additional reductions to substrate resistance for 20 cycles and beyond? At the time of writing, the LCN does not allow annealing of ZnO in any of its furnaces capable of sustaining 1000°C for prolonged periods. Should there come a time when such a facility becomes available, thermal treatment of ZnO substrates should be attempted for longer exposures on the scale of 10-30 minutes. The affects that these anneals have on substrate quality and 2DEG formation should be assessed.

Compared to earlier work, the LCN-grown samples demonstrate interface abruptness similar to those grown by Coke et al. There does seem to be a link between thermally treated ZnO and lower interface abruptness. This may indicate that higher Zn-fluxes are needed to compensate and further improve 2DEG quality. As previously mentioned, the MBE’s beam flux monitor can short and stop giving reading if fluxes on the order of $1 \times 10^{-6}$ Torr are used repeatedly. This makes it impossible to measure Zn and Mg fluxes before and after growth, thereby making it difficult to tune growth conditions. However this still gives some room for flux increase from those shown in this chapter. Zn-fluxes of $6 - 8 \times 10^{-7}$ Torr with a relative Mg flux of 5% are recommended for future tests. Should these conditions consistently show improved abruptness, especially on treated substrates, they should be carried forward.

This chapter has also studied the effect that homoepitaxial growth of ZnO has on 2DEG quality. It seems this is conducive to improved confinement, with C, D, P1 and P2 demonstrating quantum electrical properties. SdH oscillations are not observed in D, P1 and P2 but plateau observed in the resistance as a function of temperatures imply the formation of a confined electron space, which freezes out at lower temperatures. This freeze-out is attributed to disorder present in the confined electron space. The negative parabolic magnetoresistance present in these samples would indicate electron-electron scattering is the primary inhibitor of
2DEG formation. However this data set is small, lacking a systematic comparison with a pair of processed and unprocessed samples with ZnMgO grown directly onto the substrate under comparable conditions.

The ZnO 2DEG present in sample C has the highest mobility achieved so far at the LCN. This $4.8 \times 10^4$ cm$^2$/Vs is an order of magnitude higher than the $3.3 \times 10^3$ cm$^2$/Vs critical mobility needed to realise gated proximity effect 2DEGs, as shown in chapter 1. Further increases in mobility are not necessary for achieving tuneable JJ devices, as this sample is in the clean limit. Hence the coherence length in the 2DEG would be mobility-independent. Furthermore the mobility and carrier concentration demonstrated in this sample are comparable, or greater than, values reported in InAs-based devices currently being used to demonstrate 2DEG-based, tunable JJ devices [131]. In short, if the recipe for this 2DEG can be reliably repeated, this system is well-suited to realising tuneable 2DEG-based JJs. Future experiments should be conducted to assess whether a combination of thermal treatment and ZnO buffer growth can reliably produce 2DEG samples with mobilities comparable to those demonstrated here.

While the PAS samples have not shown conclusive evidence of a 2DEG formation, the observation of a confined electron space is promising. PAS’s easy access to high temperature ZnO substrate treatment could be a great asset for the future. The issue of interface abruptness will need to be tackled. This should be achievable by growing at lower temperatures and higher Zn-fluxes. The ZnMgO layers should be grown for shorter periods as only 40nm of ZnMgO are essential for optimum carrier confinement, as explained in chapter 6.
Chapter 7

ZnO/ZnMgO on a-Plane Sapphire

As stated in earlier chapters, commercially available ZnO substrates host a range of defects which are detrimental to 2DEG formation. However ZnO substrates are not essential to 2DEG formation; there are a variety of substrates that have been used for MBE ZnO growth in the past. Instead of relying on ZnO substrate quality we could deposit the entire ZnO/ZnMgO interface onto alternative substrates via MBE.

Sapphire substrates were chosen for this research. These substrates have a long history of being used for ZnO deposition and are also cheap and easy to source. Sapphire substrates are typically available in a-, c- and r-plane orientation. This thesis focuses on a- and c- orientation, as in both cases ZnO grows c-axially when deposited directly onto the substrate. As explained in chapter 3, this is essential for ZnO 2DEG formation as this is the axis along which the polarity discontinuity is orientated.

The polarisation must be Zn-polar to achieve electron confinement at the interface. When grown directly on a-plane sapphire, ZnO grows O-polar. We start by exploring some methods for achieving Zn-polar ZnO growth on a-plane sapphire which have been demonstrated in the literature. While we do not observe Zn-polar growth from these attempts, we do learn a lot about optimal growth conditions for ZnO films on a-sapphire. Using these conditions, we propose an alternative ‘inverted’ ZnO/ZnMgO structure, which could facilitate 2DEG formation. We are successful in growing these ‘inverted structures’ on a-plane sapphire substrate and believe future developments may allow 2DEG measurements to be performed.
7.1 ZnO Polarity on a-plane Sapphire

Meng et al. have shown pre-growth vacuum annealing of a-plane sapphire in nitrogen plasma can lead to Zn-polarity in subsequent ZnO layers [82]. Meng et al. also demonstrated that subjecting substrates to an oxygen plasma anneal, followed by nitrogen plasma, leads to an O-polar ZnO layer [82]. The MBE setup at the LCN lacks the means to achieve nitrogen anneals in situ, so this method of polarity control is beyond this research.

Another potential method of ZnO-polarity control on a-sapphire is by controlling the oxygen concentration during growth. There is evidence that low Zn fluxes lead to O-polar films [132] while high Zn flux leads to Zn polar films [133]. It is unclear where the boundary between ‘low’ and ‘high’ lies in this context. Ding et al. [133] showed that an oxygen flow rate of 1sccm and power of 300W in a radio frequency plasma source is sufficient to produce Zn-polar ZnO in MBE growth [133]. To test this independently, seven ZnO films were grown on a-plane sapphire. The first four samples were grown with constant plasma power set at 300W with an oxygen flow rate ranging from 1sccm to 4sccm. The other three samples were grown with constant oxygen flow rate set at 2sccm and power varied from 250W to 500W. 2sccm was chosen as the constant flow rate as this was the minimum flow rate at which the plasma source can maintain a plasma of 500W. The 300W 2sccm sample is used in both the data sets. Each growth lasted for one hour producing a ≈100nm film.

The Valence bands for each film were normalised according to the height of the BE$_2$ peak. Figure 7.1 shows example normalised valence plots taken from the films grown with O-plasma at 300W, 1sccm (cyan) and 250W, 2sccm (purple). The BE$_1$/BE$_2$ amplitude ratios was calculated from the valence band data of each film. These ratios are shown as a function of plasma power and flow rate in figure 7.2. As discussed in chapter 5, the Zn- and O- faces of ZnO should have a BE$_1$/BE$_2$ peak amplitude ratio of 1.2 and 1.0 respectively. Aside from the 250W 2sccm sample, all BE$_1$/BE$_2$ ratios were close to 1.0, indicating these samples are O-polar. The peak ratio for the 250W 2sccm sample is ∼ 1.1 so it is likely not Zn-polar. Perhaps this
7.1. ZnO Polarity on a-plane Sapphire

![Plot of valence bands from the ZnO film with the highest and lowest BE\textsubscript{1}/BE\textsubscript{2} ratios. The high ratio valence band is taken from the film grown with a plasma at 250W, 2sccm, and is plotted in purple. The low ratio valence band is taken from the film grown with a plasma at 300W, 1sccm, and is plotted in cyan.]

Figure 7.1: Plot of valence bands from the ZnO film with the highest and lowest BE\textsubscript{1}/BE\textsubscript{2} ratios. The high ratio valence band is taken from the film grown with a plasma at 250W, 2sccm, and is plotted in purple. The low ratio valence band is taken from the film grown with a plasma at 300W, 1sccm, and is plotted in cyan.

sample is strained by the low level of active oxygen during growth, which has led to deviation in the BE\textsubscript{1}/BE\textsubscript{2} ratio.

While it seems the LCN MBE setup cannot achieve Zn-polar ZnO on a-plane sapphire, it should be noted that Zn-polar films are not essential for 2DEG formation. 2DEGs have been demonstrated in O-polar ZnO/ZnMgO interfaces [134, 135]. These O-polar interfaces tend to have a lower mobility than their Zn-polar counterparts since the confinement is not driven by a polar discontinuity. Instead the quantum well arises entirely due to a band-gap discontinuity, as explained in chapter 3. As a result, the carriers are not as well screened from scattering centres and so conduction is reduced. Nevertheless reliable formation of O-polar ZnO 2DEGs is still of significance to this research as they could still be used to produce tuneable Josephson junction devices.

The proposed a-sapphire-based device structure consists of an O-polar ZnO on top of O-polar ZnMgO (as depicted in figure 7.3). This sample design has
7.1. ZnO Polarity on a-plane Sapphire

Figure 7.2: Plot of the BE$_1$/BE$_2$ ratios for ZnO films grown on a-plane sapphire. Ratio is represented by the point colour and is plotted as a function of oxygen flow rate and power of the plasma used to produce these films. BE$_1$/BE$_2$ peak amplitudes were calculated by Gaussian curve-fitting to peak. All peak ratios are below 1.2 so all films are determined to be O-polar.

Figure 7.3: Schematic of the cross-section of a ZnO/ZnMgO 2DEG structure on a-plane sapphire.
been used by Yano et al. who achieved 2DEGs with mobilities up to 980cm$^2$/Vs on a-plane sapphire [58]. These mobilities are relatively low compared to ZnO substrate growths from the literature but higher mobilities may be achieved through optimisation of ZnO buffer and ZnMgO growth.

Prior to fabricating these structures, it is important that the growth of ZnO on a-plane sapphire is optimised. The aforementioned seven samples give a good range of oxygen growth parameters. The effect these parameters have on ZnO quality will now be discussed.

### 7.2 Crystal Growth Optimisation

One simple means of assessing crystallographic quality is to observe the full width at half maxima (FWHM) of the XRD peaks. Narrower peaks represent less variation in crystallographic parameters, indicating a higher crystal quality. XRD scans were taken for each ZnO film: an example plot is shown in figure 7.4. The FWHM of the ZnO (002) peak is then extracted from each scan and plotted as a function of plasma power and flow rate, shown in figure 7.5. There is no clear correlation between plasma power and FWHM. There does seem to be a correlation with O$_2$...
flow rate indicated by the curve fit in the figure. For optimal crystal parameters, ZnO should be grown with stoichiometric condition i.e. when Zn and O flux are approximately equal [136]. Under O-rich condition, the crystalline quality of ZnO is reduced [136, 137]. This is demonstrated in the broadening of FWHM as O\textsubscript{2} flow rate is increased.

It seems that growing at 300W 1sccm provides the narrowest FWHM, while growing at 400W 2sccm provides the broadest. The 250W 2sccm film also has a relatively high FWHM at 0.86 degrees. The wide FWHM and inconclusive peak ratio of the 250W sample may be indicative of a heavily strained O-polar ZnO film.

The ZnO rocking curves for growths with plasma power of 300-400W are comprised of two overlapping peaks, as shown in figure 7.6. This could be a sign that there are two ZnO layers, one strained and one relaxed. The full implications of this second peak are not completely understood, but it is possible that at some finite thickness a strained ZnO layer relaxes into a distinct layer. This would give rise to two overlapping rocking curves when observed via XRD.
Figure 7.6: Rocking curve of the ZnO (002) peak from the 400W 2sccm sample. The rocking curve shows two overlapping peaks (one wide, one narrow) which may correspond to a strained and relaxed ZnO layer respectively.

Finally AFM images were taken of each sample to assess how the growth conditions affected the ZnO film surface roughness. Figure 7.7 shows two example AFM plots taken from the 300W 3sccm sample and the 250W 2sccm sample. Measurements like these were conducted across all samples. We took five 5µm × 5µm scans in different places near the centre of the sample. We then calculated the average and standard deviation of the root mean square (Rms) roughness across the five scans performed on each sample. Figure 7.8 shows this data plotted as a function of plasma power and O₂ flow.

A plasma of 300W and 3sccm produces the smoothest film with a roughness of 1.0 ± 0.2nm. This highly smooth film is an ideal recipe for ZnO buffer growth. 250W and 2sccm gives the highest roughness at 12 ± 2nm. The roughness of the 250W films seems like an outlier compared to the other films, yet repeated measurements of this sample have returned similar values. This roughness contradicts the FWHM data where the 250W and 2sccm sample showed the narrowest rocking curve. Roughness can be the result of relaxation of strained lattices, yet relaxation can also cause a broadening of the omega rocking curve [138].
Figure 7.7: AFM images of a 5µm × 5 µm region from the smoothest ZnO film grown with oxygen plasma at 300W and 3sccm (a) and the roughest film grown with oxygen plasma at 250W and 2sccm (b). Films have a root mean square roughness of 1.0±0.2nm and 12±2nm respectively. Periodic diagonal lines visible in (a) may be the result of substrate mis-cut leading to steps in subsequent ZnO growth.
Figure 7.8: Average root mean square roughness of the ZnO films grown on a-plane sapphire as a function of changing O$_2$ flow rate (red) and changing plasma power (blue). The error bars show the standard deviation in root mean square roughness.
This data indicates that growing with O-plasma settings of 300W and 3sccm lead to smooth ZnO film growth, ideal for buffer growth of ZnMgO interfaces. These conditions are used for ZnO and ZnMgO growth on the samples discussed in the latter part of this chapter.

### 7.2.1 ZnO/ZnMgO Interface Fabrication

Now that the optimal growth conditions for the ZnO layers has been determined, the O-polar ZnO/ZnMgO interface can be fabricated. a-plane sapphire substrates were degreased in acetone and IPA before being loaded into the MBE. The substrates were heated to 200°C in the loadlock for thermal cleaning. The samples were then loaded into the MBE main chamber and a 100nm ZnO buffer layer was deposited onto the a-plane sapphire at 500°C with O\textsubscript{2} plasma at 300W, 3sccm. Four samples were grown with differing growth conditions. Sample G has a 40nm ZnMgO layer deposited at 700°C. Sample H has a similar 40nm ZnMgO layer deposited but at 500°C. This is to assess how lower growth temperature affects ZnMgO crystallographic quality and MgO content.

Sample I is annealed at 750°C for 10 minutes and then a 40nm ZnMgO layer is deposited at 500°C. Anneals are prevalent in other cases of ZnO/ZnMgO heterostructures grown on sapphire, as they are linked to an improvement of overall ZnO/ZnMgO surface quality [78]. Finally on sample J the ZnMgO is deposited on to the ZnO layer at 500°C followed by a 40nm ZnO capping layer also deposited at 500°C.

All ZnMgO layers are grown to a thickness of 40nm since evidence suggests that the carrier concentration in the ZnMgO/ZnO interface saturates when the ZnMgO layer reaches this thickness [113]. Much as in chapter 6, the Zn-flux is maintained as close to $5 \times 10^{-7}$ Torr as possible, since this facilitates higher ZnO/ZnMgO interface abruptness while avoiding damage to the MBE’s Beam flux monitor. During ZnMgO deposition, Mg/Zn flux ratio is maintained at approximately 1:20. Table 7.1 lists sample G-J and their respective growth parameters.
Table 7.1: Table of a-plane substrate samples referred to throughout this chapter.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Sample Structure</th>
<th>ZnMgO Growth Temp (°C)</th>
<th>Zn-Flux (× 10⁻⁷ Torr)</th>
<th>Mg-Flux (× 10⁻⁷ Torr)</th>
<th>Mg/Zn Flux Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>Al₂O₃/ZnO/ZnMgO</td>
<td>700</td>
<td>5.2</td>
<td>0.23</td>
<td>0.046</td>
</tr>
<tr>
<td>H</td>
<td>Al₂O₃/ZnO/ZnMgO</td>
<td>500</td>
<td>5.1</td>
<td>0.24</td>
<td>0.047</td>
</tr>
<tr>
<td>I</td>
<td>Al₂O₃/ZnO/(anneal)/ZnMgO</td>
<td>500</td>
<td>5.0</td>
<td>0.24</td>
<td>0.048</td>
</tr>
<tr>
<td>J</td>
<td>Al₂O₃/ZnO/ZnMgO/ZnO cap</td>
<td>500</td>
<td>5.1</td>
<td>0.24</td>
<td>0.047</td>
</tr>
</tbody>
</table>

Figure 7.9: XRD scans of ZnO/ZnMgO layers deposited on a-plane sapphire. Peaks have been labelled with their corresponding crystallographic plane. Inserts show scans across the ZnO (004) peak. Insert scans were taken at slower speed compared to full scan so that peak intensity is higher and features of the (004) peaks are more pronounced.

7.3 Material Characterisation

The XRD spectrum of the samples was taken to verify the presence of ZnO and ZnMgO on the sapphire substrate. Note that in the 30-80° scan the ZnMgO peaks have a relatively low intensity, especially when compared to the XRD analysis from the ZnO substrate samples shown in chapter 6. To compensate, slower scans have
been taken across $2\theta/\omega$ of 72-74°, so that the ZnO (004) peaks may be seen more clearly. These slower scans are shown in the inserts of figure 7.9. In all scans only the a-plane sapphire, ZnO peaks and ZnMgO peaks are present. Unlike the growth on the ZnO substrates, there are no MgO peaks present in these scans. This suggests there is no segregation in the ZnMgO layer.

Sample I shows a lower intensity ZnO (004) peak than G and H. This may indicate that the high temperature anneal applied to sample I has adversely affected the growth of the ZnMgO layer. This observation requires more rigorous analysis before it can be confirmed.

As stated in chapter 5, the Mg content of the ZnMgO layer can be determined by comparing the location of the ZnO (004) and ZnMgO (004) peaks. The centre of each peak was determined using a double Gaussian fit. An example fit is shown in figure 7.10. The Mg content for samples G-J is shown in table 7.2.

XRD fits of the ZnO/ZnMgO shoulder show that Mg content is fairly consistent across samples G-J. The shift in growth temperature on the ZnMgO layer from 700°C to 500°C doesn’t seem to have impacted Mg incorporation.

**Figure 7.10:** Double Gaussian fit (red) to sample H XRD scan (blue). The difference in the centre of the peaks was calculated as 0.5 degrees, giving a c-parameter shift of -0.86pm and an inferred Mg content of 0.1.
### Table 7.2: Table of x concentration Mg$_x$Zn$_{1-x}$O layer grown on ZnO buffers on a-plane sapphire substrates.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Mg Percentage Determined by XRD</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>0.10</td>
</tr>
<tr>
<td>H</td>
<td>0.13</td>
</tr>
<tr>
<td>I</td>
<td>0.11</td>
</tr>
<tr>
<td>J</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Next the samples were XPS depth-profiled to assess how well the ZnO/ZnMgO interfaces have formed during sample growth. The depth profile for sample G is shown in figure 7.11.

There is clearly a large discrepancy in Mg concentration when comparing the XPS and XRD data for sample G. The XPS data seems to indicate there is roughly 4 times as much Mg as Zn in the ZnMgO layer. This is well above the segregation limit of ZnMgO yet MgO peaks are not observed in the XRD analysis of this sample. This can be explained if it is assumed that the surface film of this sample is not ZnMgO but is instead a poorly crystalline Mg rich phase. This Mg rich layer
has no coherent orientation and is either amorphous or is comprised of a random assortment of different orientations. Such a layer cannot be observed by XRD and so no MgO peak is observed in any of the a-plane sapphire XRD scans.

The observation of the ZnMgO shoulder peaks in the XRD indicated that a coherent ZnMgO layer is still forming somewhere in the sample in-spite of the Mg-rich phase. Most likely this ZnMgO film is near the ZnO layer where the Mg content determined by the XPS dips below the 40% segregation limit.

Figure 7.11 indicates a high level of intermixing at the ZnO/substrate interface and also at the ZnMgO/ZnO interface. Incorporation of Al into the ZnO layer reduces the layer’s crystallographic quality which negatively affects formation of a 2DEG at the ZnO/ZnMgO interface. Indeed, even if the ZnMgO layer in this sample has formed far from the surface, the XPS reading indicates that this interface will be highly contaminated with aluminium inclusion. It is highly unlikely that a 2DEG will form in such a sample. Furthermore since the Mg content is so high at the sample surface it is unlikely that growing a ZnO capping layer on top of this structure will result in a clean ZnO/ZnMgO interface. This does not bode well for the prospects of achieving 2DEG formation on a-plane sapphire.

To achieve 2DEG formation, the Al incorporation must be overcome. This can be done by growing the ZnO buffer significantly thicker. A layer of 200-300nm thick should ensure that no Al makes its way to the ZnO surface. Alternatively it may be better to grow the buffer as two distinct layers. A new sample design may involve growing an initial 500°C 100nm ZnO film on to the substrate and then pause growth, adjust flux and temperature as desired, then deposit the ZnO which will make up the ZnO/ZnMgO interface. ZnMgO should then be deposited using significantly lower Mg/Zn flux ratios, and for much shorter periods so that the Mg-rich phase cannot be allowed to form.

7.4 Electrical Characterisation

The samples were patterned with devices using the methods laid out in chapter 5 and were loaded into the PPMS for electrical measurement. Figure 7.12 shows the
7.4. Electrical Characterisation

Figure 7.12: Resistance vs temperature measurements for samples G, H, I and J at zero field. Measurements are conducted from 300k to 2k using PPMS with 4-point setup.

resistance of each sample as a function of temperature at zero magnetic field.

Sample G-I show near identical behaviour. This exponential increase in resistance at lower temperatures is indicative of semiconductor freeze-out whereby electrons in the material lose the thermal energy they need to remain in the conduction band and drop into the valence band. As a result the charge carriers in the material diminish and the resistivity increases. No 2DEG has formed in these samples: this is likely due to high levels of Al integration in to the ZnO layer introducing excessive disruption at the ZnO/ZnMgO interface. We surmise that figure 7.12 a-c effectively show the resistance of the upper ZnMgO or ZnO semiconductor layer as a function of temperature.

If the effect observed in samples G-I is due to semiconductor freeze out, then we may be able to model the resistance using a simplified thermal activation
relationship of the form:

\[ R \propto e^{E_g/kT} \]  \hspace{1cm} (7.1)

where \( e \) is the natural exponential, \( E_g \) is the semiconductor bandgap, \( k \) is the Boltzmann constant and \( T \) is temperature. Therefore if we plot \( \log(R) \) as a function of \( 1/T \) we should see a linear relationship with a gradient of \( E_g/k \). This is referred to as an ‘Arrhenius’ plot. Arrhenius plots were produced for sample G-I but did not show linear relationships. This indicated that a simple thermal activated carriers model doesn’t hold. This does not rule out the semiconductor freeze out model, since the Arrhenius plot is a very simplified picture and does not take into account defect energy levels between the conduction and valence band, nor does it account for electrons moving between defect levels during a cool down.

Sample J shows an altogether different response with a resistance that gradually decreases with temperature before plateauing at approximately 2\( \Omega \). This reduction is not what one would expect from 2DEG formation were there should be an initial rise in resistance on cooling which then decreases at \( \approx 150K \) and plateaus as shown in chapter 6. Attempts were made to measure the magnetoresistance of these samples at 2K but the samples proved too resistive. We summarise that no 2DEGs have formed in these inverted interfaces at this stage.

7.5 Summary and Outlook

Experiments with the LCN MBE setup were unable to produce Zn-polar growth on a-plane sapphire and the link between Zn-polarity and applied O-pressure is still inconclusive. Growing with O-plasma settings of 300W and 3sccm has been shown to produce smooth ZnO film growth ideal for ZnO and ZnMgO interfaces.

However Zn-polar ZnO films are not the only means of producing ZnO 2DEGS. O-polar interfaces (O-polar ZnMgO deposited on an O-polar ZnO buffer) were investigated. These structures all showed semiconductor freeze-out when cooled to low temperatures. From XPS analysis it is clear that Al interdiffusion into ZnO growth plays a role in this observation. To better assess the possibility of producing O-polar 2DEGs one must deposit an initial 100nm buffer layer which
will be disrupted by Al interdiffusion, then deposit a second ‘clean’ ZnO layer on top. This second layer will be the one that comes into contact with the subsequent ZnMgO layer. This should provide an improved interface due to the lack of Al in the second ZnO layer which should improve the likelihood of observing 2DEG formation in such structures.

The combined XPS and XRD measurements indicate that an Mg-rich, poorly crystalline phase is forming where the ZnMgO layer is expected to be. Furthermore a ZnMgO layer is still detectable in XRD analysis and it is assumed that this if forming close to the ZnMgO/ZnO buffer layer interface. To achieve O-polar interfaces between the ZnMgO and ZnO capping layer, this Mg rich phase must be prevented. This may be avoided by growing with lower Mg/Zn flux ratios and by depositing ZnMgO for shorter periods. This is purely conjecture at this stage and understanding how and when the Mg rich phase forms should be the subject of thorough future study.

Inverted ZnO/ZnMgO structures were tested as a means of realising ZnO 2DEG formation on a-plane sapphire by growing a ZnO capping layer on top of O-polar ZnMgO. The RvT of this sample shows a gradual decrease in resistance as a function of temperature. However this RvT does not follow what one would expect in a typical 2DEG formation response. It is highly unlikely that any 2DEG would be observed due to the Mg-rich phase.

Further experiments are required before the effectiveness of this device structure can be fully assessed. Additional inverted ZnO/ZnMgO structures should be grown. These new structures should be structurally assessed via XRD and depth profiles should be taken from sample surface down to the substrate. Finally the resistance of the samples should be measured at low temperatures in the PPMS until conclusive measurements are obtained.
Chapter 8

ZnO/ZnMgO on c-Plane Sapphire

As stated in the previous chapter, sapphire is commonly used for ZnO growth and may provide a suitable substrate alternative. Sapphire has a hexagonal corundum crystal structure and is normally described using a hexagonal axis. c-plane sapphire is commonly used to grow c-plane ZnO, despite a significant lattice mismatch of 18.4%. This is because c-plane sapphire is cheap, easy to source and ensures growth along the c-axis. Using this feature, ZnO/ZnMgO 2DEGs have already been achieved using pulsed laser deposition (PLD) and metal-organic vapour deposition (MOVVD) on c-plane sapphire [139, 140].

However the large mismatch between ZnO and c-sapphire impede the fabrication of high quality ZnO films [24]. Therefore to achieve high quality ZnO/ZnMgO interfaces on c-plane sapphire, ZnO growth will need to be optimised to overcome this lattice mismatch. Other groups have demonstrated that a combination of MgO and low temperature ZnO buffer layers can improve ZnO growth on c-plane sapphire [38, 112, 141, 142]. Some have also employed these techniques to demonstrate 2DEG formation with these structures on sapphire substrates[143].

ZnO films directly deposited onto c-plane sapphire consistently grow O-polar [80]. As discussed in the previous chapter, while Zn-polar ZnO/ZnMgO interfaces are not essential for achieving 2DEGs formation at the ZnO/ZnMgO interface, the 2DEG quality is greatly reduced at O-polar interfaces. For the best chance of achieving high mobility and high carrier concentration 2DEGs at the ZnO/ZnMgO
interface, the films should be Zn-polar [72, 73, 144].

This chapter demonstrates how MgO buffer layers can be used to reliably achieve Zn-polar ZnO layers on c-plane sapphire. These MgO layers are then used as the basis of a multilevel crystal structures consisting of MgO buffers, low temperature ZnO buffers, high temperature ZnO film and ZnMgO buffer layer. XRD and XPS analysis are used to show these distinct layers. Electrical analysis shows no sign of 2DEG formation int these structures at present. This is attributed to a large amount of inter-diffusion between heterostructure layers caused by high growth temperatures and low relative Zn-beam-fluxes. We believe the sample design laid out here is nevertheless a strong basis and should yield 2DEGs with further optimisation.

8.1 Substrate Preparation

Prior to growth, the substrates are degreased in acetone, isopropanol and DI water. Samples are then cleaned in a 3:1 sulphuric acid: hydrogen peroxide solution before being loaded into the MBE and subjected to a thermal treatment of 700°C for 30 minutes to improve surface roughness. The substrate is then exposed to a 2sccm, 300W Oxygen plasma, at 500°C for 10 minutes to ensure oxygen termination of the sapphire substrate. This full procedure is well established for improving thin film growth on sapphire with similar processes employed elsewhere [133, 145].

8.2 ZnO Polarity on c-plane Sapphire

There is evidence that controlled growth of MgO layers onto c-sapphire can lead to Zn-polar ZnO. Kato et al. showed an MgO buffer of 3nm or more is needed to achieve this result [80]. When growing MgO directly onto c-plane sapphire, the MgO layer is wurtzite up to a thickness of 1nm. Growth beyond this thickness leads to the layer relaxing into rock-salt islands which dominate from 3nm onwards. This change in atomic structure causes the polarity inversion in subsequent ZnO layers. This process is illustrated in figure 8.1. MgO buffers have previously been employed to achieve Zn-polar ZnO/ZnMgO heterostructures on c-plane sapphire using MBE [73, 140, 142, 146]. The highest mobility 2DEG was demonstrated by
8.2. ZnO Polarity on c-plane Sapphire

Figure 8.1: Schematic of atomic arrangement of ZnO on c-plane sapphire with (a) a 1–nm–thick MgO buffer layer, and with (b) an MgO buffer layer thicker than 3nm. Figure taken from [80].

Tampo et al. showing a mobility of 2750cm²/Vs at 4k [73]. It is hoped through a better understanding of MgO and ZnO growth dynamics on sapphire, mobilities can be further improved.

Figure 8.2: Figure showing the normalised valence spectra of ZnO growth on sapphire with an MgO buffer (blue) and without buffer (red).
To test if MgO buffers did result in Zn-polar ZnO growth, two c-plane sapphire substrates were taken from the same batch. A 10nm MgO buffer layer was deposited onto one substrate using a Mg flux of $\sim 1.5 \times 10^{-7}$ Torr. O-flux was supplied by a radio frequency plasma at 300W and 2sccm. Low temperature ZnO layers were then deposited in-situ onto both samples at 400°C for 1 hour with Zn flux at $\sim 1.5 \times 10^{-7}$ Torr.

The polarity of the ZnO layers is then determined using the XPS valence method described in chapter 5. The valence band spectra for each of these samples are shown in figure 8.2. The valence for the sample with buffer is plotted in blue, the sample with no buffer is shown in red. The plots have been normalised to the amplitude of the $BE_2$ peak. The difference in the $BE_1$ amplitude between the buffer and no buffer sample is clear and in agreement with the data presented by Allen et al. [96]. Furthermore the $BE_1/BE_2$ peak ratio of the buffer and no buffer films were found to be 1.2 and 1.0 respectively. A $BE_1/BE_2$ ratio of 1.2 in the sample with the buffer is indicative of Zn-polarity. Therefore fabrication of a Zn-polar ZnO film onto c-plane sapphire is achieved through the use of MgO buffers.

### 8.2.1 MgO Buffer Growth

To gain a better understanding of MgO growth rate in the LCN MBE system, three MgO films were deposited for 10 minutes with an incident Mg flux of $\sim 1.5 \times 10^{-7}$ Torr and O flux provided by a 2sccm 300W radio frequency plasma. These were grown at 500°C, 600°C and 700°C to assess how Mg deposition changed with temperature.

Figure 8.3 shows the XRD $\theta/2\theta$ scan for the MgO film grown at 600°C. Note the appearance of periodic thickness fringes on either side off the MgO (111) peak. These fringes can be used to determine the thickness of MgO films. Figure 8.4 shows how the peak oscillations and film thickness vary as a function of stage temperature. The extracted dependency of film thickness on substrate temperature is roughly linear.

All these test films are well over the 3nm necessary for ZnO inversion.
8.2. ZnO Polarity on c-plane Sapphire

**Figure 8.3:** Plot of full $2\theta/\omega$ XRD scans for MgO film grown on c-plane sapphire at 600C. Mg (111) peak is visible on the left of the figure with distinctive thickness fringes. Sapphire (006) peaks is visible on the right.

**Figure 8.4:** Plot of $2\theta/\omega$ XRD scans near the MgO (111) peak at various stage temperatures. Insert shows the film thickness as determined by Laue oscillation period as a function of stage temperature. The cross colour in the insert corresponds to the line colour in the main plot.
8.2.2 ZnO/ZnMgO Interface Fabrication

With the growth of MgO now understood, the Zn-polar ZnO/ZnMgO interfaces can be fabricated. Firstly a 20 minute MgO buffer was grown onto c-plane sapphire to the specification outlined in the previous section. This is followed by a low temperature ZnO buffer layer grown for 1 hour at 300°C with a $5 \times 10^{-7}$ Torr beam flux. The low temperature ZnO buffer is used to compensate the mismatch between sapphire and ZnO. Thin ZnO films deposited on sapphire will be strained due to the lattice mismatch. At some critical thickness, the ZnO film will relax resulting in the formation of defects; these are detrimental to 2DEG formation. To circumvent this problem, ZnO is deposited as a bi-layer composed of a low and high temperature layer.

The low temperature layer is deposited to a thickness of approximately 100nm, so that it will relax and result in defect formation. The temperature is then raised and a high quality high temperature ZnO layer is deposited on top. Since there is minimal mismatch between the low and high temperature ZnO layers, there should not be a significant formation of defects in the high temperature layer resulting from crystallographic relaxation. The high temperature layer is therefore ideal for ZnO/ZnMgO interface fabrication. This procedure is commonly used by other groups growing ZnO on c-plane sapphire [80, 141, 142, 147].

The high temperature ZnO layer is deposited at 750°C with a $5 \times 10^{-7}$ Torr beam flux for 1 hour. High growth temperature is used as it leads to lower strain and lower defect concentration in the thin film. Finally a high temperature ZnMgO layer is deposited onto the high temperature ZnO layer. The ZnMgO is grown at high temperatures because Tsukuzaki et al. demonstrated that this leads to high quality ZnMgO films on ZnO substrates, ideal for 2DEG formation. We assume that the same should apply to ZnO films grown on other substrates. The oxygen plasma is kept at 2sccm and 300W throughout all growth stages. The samples were grown with a relative Mg/Zn flux ratio of 1/20. Figure 8.5 shows a layout of this sample structure.
8.3 Material Characterisation

An XRD scan from a typical c-sapphire-based sample is shown in figure 8.6. One would expect to see an MgO peak from the buffer layer at \( \sim 42.92\,\theta/\omega \) but no such peak is visible in any c-sapphire-based sample. This may be due to inter-diffusion at the ZnO/MgO/Al\(_2\)O\(_3\) boundary which would result in a diffuse MgO layer, which is not coherent enough to produce an XRD peak. Well defined ZnMgO (002) peaks, like those shown in figure 8.6, were common in c-sapphire-based samples but were never accompanied by a corresponding (004) ZnMgO peak. This may indicate that the ZnMgO (002) peak is not from the ZnMgO layer, but rather from inter-diffusion...
at the ZnO/MgO buffer layer boundary. Since there were no (004) ZnMgO shoulder peaks present, the Mg content for heterostructures grown on thin films could not be determined.

XPS depth profile were taken down to the substrate surface. Figure 8.7 shows a depth profile for the typical c-sapphire-based sample. This typical sample shows a low Mg concentration in the ZnMgO layer, which has a thickness of approximately 120nm. The MgO buffer is also clearly visible at the 300nm mark and was observed to be roughly 50nm thick, far in excess of the 3nm necessary to invert ZnO polarity. These thicknesses were typical across c-sapphire-based samples. This is problematic since the 50nm MgO layers may be detrimental to the overall sample quality. Cho et al. [147] show MgO films with a thickness of 5nm or more have rough surfaces due to strain relaxation arising from a 5% lattice mismatch between MgO and sapphire. This roughness could inhibit the quality of ZnO layers grown on top and could disrupt 2DEG formation. Efforts should be made to reduce the MgO buffer thickness to a 3-5 nm range.
In future work, MgO films should be grown for significantly shorter periods, ranging from 30 seconds to 5 minutes. The quality of these films should be assessed by AFM (measurements of surface roughness) and XRD (rocking curves measuring crystal quality and 2θ/ω scans measuring film thickness).

From the depth profile, it is evident that there is a large amount of inter-diffusion between the MgO, ZnO and sapphire layer. XPS of all c-sapphire-based samples showed diffuse ZnO/ZnMgO interfaces with low Mg gradients. As an example, XPS for the typical sample shown above, has an Mg gradient of 0.29 %/nm, far below the 1%/nm optimum interface demonstrated by Coke et al. [41]. This diffusivity can be explained by the low ZnO fluxes used and high growth temperature. Future growths on c-plane sapphire will use ZnO fluxes in the $5 \times 10^{-7} - 1 \times 10^{-6}$ Torr range and will test ZnMgO growth temperatures ranging from 500-600°C.

These inter-diffusion regions should be explored further. XPS operation parameters will be optimised to allow depth profile of full sample structure down to the substrate. The extent of Mg inter-diffusion should be explored in more detail by varying ZnO buffer growth temperatures. These structures should be grown with higher Zn-fluxes and the effect this has on interface abruptness should be assessed using XPS.

8.4 Electrical Characterisation

At the time of writing, there has been no success in measuring c-sapphire based samples electrically. Room temperature resistance measurements for these samples return values on the order of 1-10 MΩ. Furthermore these resistances do not reduce with sample temperature. The PPMS consistently shorted out when c-plane sapphire sample temperatures dropped below 200K. The material analysis for these samples indicates there is significant interdiffusion between crystal layers. Therefore the poor electrical quality of these devices is likely indicating heterostructures are not correctly forming; all that is being measured is a highly disordered, diffuse ZnMgAlO alloy. Before pursuing further research with
8.5 Summary and Outlook

Structural analysis has revealed the growth of these samples still requires a great deal of optimisation. These samples have proved too resistive to measure due to a large amount of diffusion both at the sapphire/MgO buffer/low-T ZnO boundary and at the high-T ZnO/ZnMgO boundary. Additionally MgO buffer layers are being grown far thicker than is necessary to invert ZnO polarity. Over-deposition of MgO could be producing highly rough MgO surfaces, which introduces disorder into subsequent ZnO buffer growth. Future work should look at growing MgO buffers for shorter periods ranging from 30 second - 5 minutes, at temperatures ranging from 500-700°C. These buffers should be characterised with a combination of AFM and XRD to determine growth rate, crystallographic quality, critical thickness and film surface roughness. ZnO should then be grown onto these buffers and the orientation of these layers will be determined using the XPS valence method to ensure that thinner MgO buffers still result in Zn-polar ZnO layers. AFM and XRD characterisation should also be conducted on these ZnO layers to see what effect MgO surface roughness has on the quality of subsequent ZnO growths.

As previously explained, low temperature ZnO buffers have been used in these samples as there is evidence that this results in high quality ZnO films on c-plane sapphire. That said, no efforts have been made to determine the optimal parameters for this in our system. In future work, low temperature buffer layers should be grown on optimised MgO buffers on c-plane sapphire at varying temperatures (350-500°C) and varying incident flux ($10^{-7}$ - $10^{-6}$) Torr. These layers should be characterised using AFM and XRD to find the optimum growth parameters for smooth ZnO layers. Additionally the impact high temperature (800°C) anneals have on low temperature ZnO buffer layers should be assessed. It is possible that anneals could be beneficial to subsequent high temperature ZnO growth.

Zn-polar ZnO/ZnMgO interfaces on c-plane sapphire have been demonstrated using MgO interfaces. Presently these interfaces are too diffuse to lead to
2DEG formation. By growing ZnMgO layers at lower temperatures to reduce Mg inter-diffusion and using higher Zn fluxes, these diffusivity issues could be overcome. Suggested ranges include temperatures (500-600°C), Zn fluxes (10^{-7} - 10^{-6}) Torr and incident Mg flux of 0.5 \times 10^{-8} - 10^{-7} Torr. The quality of these ZnMgO layers should be assessed using XRD and AFM and the interface abruptness should be assessed using XPS depth profiles.

Once the growth of Mg buffers is better understood in our system, and abrupt ZnMgO interfaces have been demonstrated via XPS and XRD analysis, the samples should be electrically measured. If there is a 2DEG present, the room temperature resistance should be lower than the Mega-Ohm resistances observed in present samples. If this is the case, the samples should be measurable at low temperatures in the PPMS and should demonstrate SDH oscillations when subjected to strong perpendicular fields. Out of the methods presented in this thesis, c-sapphire-based systems will require the most work to optimise. Heat-treated ZnO remains the most likely system to produce reliable 2DEGs which could be used as the basis for proximity superconductivity experiments.
Chapter 9

Conclusions and Future Work

In this thesis we present work focusing on MBE grown ZnO/ZnMgO heterostructure with the intention of producing high mobility, high carrier concentration 2D electron gasses. These 2DEGs are of interest as they would be well-suited for voltage-tuneable superconducting proximity-effect devices. Three substrates were used as the basis for these devices; ZnO, a-plane and c-plane sapphire. This chapter summarises the outcomes for each of these substrates.

9.1 Conclusions

A 2DEG with a carrier mobility of $4.8 \times 10^4 \text{ cm}^2/\text{Vs}$ and carrier concentration of $5.05 \times 10^{12} \text{ cm}^{-2}$ was demonstrated at 2K on thermally treated ZnO substrates. These values are higher than any achieved previously at the LCN. Furthermore these values are above the thresholds needed to realise clean-limit electron coherence lengths ($\xi$) of over 120 nm and an electron mean free path ($\ell$) of 1770nm at 2K, as shown in chapter 6. Realistically Josephson junctions made with these 2DEGs would be operated at temperatures an order of magnitude lower, on the order of $\sim 20\text{mK}$. Assuming that the 2DEG carrier concentration and mobility are temperature independent at low temperatures, this means we should have a clean coherence length an order of magnitude higher, on the order of $\sim 1\mu\text{m}$. This means we could feasibly pattern electrical gates onto these 2DEGs between superconducting contacts while maintaining a superconducting proximity effect through the 2DEG. The gates can then be used to tune 2DEG conduction and thereby tune the proximity
effect. Hence these 2DEGs are well suited for tuneable superconducting proximity effect device applications. Of course, this assumes perfectly transparent interfaces between the 2DEG and the superconducting contact. In reality some resistance at the interface will reduce the effective coherence length. However since our coherence lengths are an order of magnitude higher than we need to facilitate gate fabrication at 20mK, we are confident that we would be able to fabricate tuneable, proximitised 2DEGs in these systems.

The high mobility observed in the ZnO substrate sample is attributed to a combination of rapid thermal treatment and ZnO buffer growth prior to ZnMgO deposition. In chapter 6 we demonstrate how rapid thermal treatment leads to a reduction in ZnO substrate room-temperature resistance, which is treated as a proxy for ZnO 2DEG density. We posit that this reduction of room-temperature resistance is indicative of Li out-diffusion, which is know to be highly mobile in ZnO above 1000°C [32, 33, 107].

Using Shubnikov-de Hass (SdH) oscillations at varying temperatures we extract the time between various scattering events and use these to show that the conduction in the 2DEG is dominated by long-range scattering sources, such as alloy scattering. Therefore while rapid thermal annealing has lead to improved substrate quality and 2DEG mobility through Li out-diffusion, this work indicates there is still room for improvement.

ZnO/ZnMgO heterostructure grown on ZnO substrates that had not been thermally treated did not show 2DEG behaviour. However these samples did still show confined electron behaviour, evident from the negative magnetoresistance observed at low temperature and high field. These effects indicate that the 2DEG does not form in heterostructures without rapid thermal treatment due to a combination of localisation effects induced by electron-electron scattering.

We have also demonstrated promising growth on a- and c-plane sapphire. On a-plane sapphire we have shown that 2DEGs could also be achieved using O-polar ZnO growth using an inverted heterostructure. We establish a recipe that produces high-quality O-polar ZnO films on a-plane sapphire with narrow rocking curves.
and low surface roughness. The full inverted heterostructure is then successfully fabricated on a-plane sapphire. These heterostructures currently have however not demonstrated 2DEG behaviour. This has been attributed to the diffusivity present at the ZnO/ZnMgO interface. However the heterostructures demonstrated here are a strong base to build on for future work and these inverted structures may promise a reliable means of producing ZnO 2DEGs.

On c-plane sapphire we have demonstrated how ZnO polarity can be controlled via MgO buffer layers. We have used these buffers to reliably achieve Zn-polar ZnO/ZnMgO heterostructures on c-sapphire. Like their a-plane counterparts, c-plane sapphire-based interfaces have not yet demonstrated 2DEG behaviour. This has also been attributed to a lack of abruptness at the ZnO/ZnMgO interface. That said, these Zn-polar interfaces are promising, and should facilitate 2DEG formation once the ZnO/ZnMgO interface fabrication is perfected.

9.2 Future Work

The following sections detail future work that should be conducted on these systems. Suggestions on how to overcome the pitfalls encountered within this research are provided.

9.2.1 Optimising ZnO Thermal Treatment

Before further progress can be made with the ZnO-substrate-based growth, the reproducibility of the thermal treatment process must be assessed. The immediate step would be to create several pairs of ZnO substrates, one which has been thermally treated and one which has not, much like the samples shown in chapter 6. Growth should then be conducted on these substrates while keeping the growth methods consistent across each treated and untreated pair. Some suggestions include directly depositing ZnMgO onto the substrate and using 100nm ZnO buffer layers prior to ZnMgO deposition. The growth parameters presented in chapter 6 can be used as a starting point. If electrical measurements of these samples consistently demonstrate 2DEG formation on treated samples, then the experimental focus can be shifted towards superconductivity proximity effect-based
measurements.

There is room for improvement in the thermal treatment processing too. The number of successive rapid thermal anneals could be increased beyond 15 to check for further significant improvement in ZnO substrate quality and subsequent 2DEG formation. During this thesis, there were no facilities available for prolonged ZnO annealing. If such a facility were to become accessible, then the effects of prolonged high temperature anneals on ZnO should be explored. Ideally this would involve heating ZnO substrates to 1000°C for 10-30 minutes. If these anneals are seen to reduce substrate resistance, similar to the effects seen with rapid thermal annealing, these thermally treated substrates should also be used for heterostructure growth and tested for 2DEG formation.

A correlation was observed between thermally treated substrates and less abrupt ZnO/ZnMgO interfaces. Earlier chapters covered how interface abruptness is tied to 2DEG quality, with more abrupt interfaces leading to greater electron confinement and higher mobility. Therefore future growths on ZnO interfaces should employ higher relative Zn-fluxes to produce sharper ZnO/ZnMgO interfaces. Limitations with the MBE’s beam flux monitor means Zn-fluxes should not regularly exceed $1 \times 10^{-6}$ Torr for prolonged periods. Therefore it is recommended that Zn-fluxes of $6 - 8 \times 10^{-7}$ Torr are used as a starting point. If these parameters are shown to consistently improve ZnO/ZnMgO interface abruptness, they should be used throughout future growths.

### 9.2.2 Growth on Sapphire/ZnO

Chapter 7 shows that growth of ZnO directly onto a-plane sapphire leads to smooth ZnO layers, ideal for subsequent ZnMgO growth. However these samples failed to show 2DEG behaviour and instead showed a response typical of semiconductor freeze-out. One possible reason for this is Al interdiffusion between the ZnO layer and the sapphire substrates, as is evidenced from the diffusion region in the XPS depth profiles of these samples. This issue could be overcome by growing a low-temperature 100nm ZnO layer prior to subsequent ZnO growth. This should minimise the effect the Al interdiffusion has on the ZnMgO layer. Additionally
there were issues with the ZnO/ZnMgO interfaces of these samples having low abruptness. Much as with the ZnO substrate case, this could be counteracted by using higher Zn-fluxes in future experiments.

Chapter 8 shows that ZnO polarity can be controlled on c-plane sapphire using MgO buffer layers. This should facilitate the fabrication of Zn-polar ZnO/ZnMgO interfaces on c-plane sapphire, ideal for 2DEG formation. However there is no evidence of 2DEG formation in such structures, with all devices proving too resistive to measure. This could be due to overgrowth of MgO buffers which produce highly rough surfaces at thicknesses of 5nm or more. MgO buffer layers should be grown to thicknesses of 3-5nm, and checked to determine if these buffers achieve Zn-polarity in subsequent ZnO growth. Additionally as with the other substrates, the ZnO/ZnMgO interfaces in these structures were highly diffuse. To combat this, higher Zn-fluxes should be employed in future growth.

9.2.3 Superconducting Contact to ZnO-Based 2DEGs

Now that a reliable method of 2DEG production has been ascertained, efforts should be made to observe the proximity effect in the 2DEGs. In the introduction it was shown how one can calculate the critical mobility necessary for gateable Josephson junction devices. To achieve a coherence length of 100nm, one needs a carrier concentration of the order $10^{12}\text{cm}^{-2}$ and a mobility of the order of $10^3\text{cm}^2/\text{Vs}$. Future work should determine if these metrics can be ascertained reliably. If this is observed, the next step should be to make superconducting contact to these 2DEGs, so as to measure the superconducting proximity effect.

The first question is how can we make good contact to the 2DEGs to measure this effect? Presently the most promising method is Al sputtering. Al is known to from an ohmic contact to ZnO providing there is an in-situ argon mill prior to Al deposition [148, 149]. Therefore when depositing Al a system should be chosen which facilitates in-situ argon milling prior to deposition. The two likely candidates for Al deposition are sputtering and evaporation. Sputtering Al would lead to films that evenly covers the substrate and edges of the resist. These types of films are tricky to lift-off. This is particularly problematic for these JJ samples which will
likely involve small-nanoscale structures susceptible to lift-off damage. Ideally Al would be deposited via evaporation which typically results in smoother Al films.

Prior to starting full-scale JJ device development, tests should be conducted to see if the Al deposition is suitable for this projects needs. Can the sputtered Al be lifted-off successfully and is it superconducting at low temperatures? What is the Al surface quality like?

Once devices can be fabricated, there are several ways to observe the proximity effect. For one, the proximity effect is proportional to the temperature, with coherence length increasing as temperatures decrease. Therefore there should be some critical temperature during a sample cool-down, where the coherence length will span a given superconducting contact separation and a proximity-effect-enabled supercurrent will be observed across the channel. So a good first experiment would be to measure the conduction across a junction of a given length as temperatures decrease and see if a supercurrent is observed at some finite temperature. Devices should also be fabricated with several pairs of superconducting contacts at increasing separations. At fixed mobility, carrier concentration, and temperature, proximity effect in the 2DEG will have some coherence length $\xi_c$, as explained in the introduction. One would expect there to be a supercurrent through superconducting contact pairs with a separation less than $\xi_c$, while wider contacts should show no such current.

With this established, efforts should be made to moderate the proximity effect though the junction via electrical gates. Should these experiments prove successful, these 2DEG-JJs should be incorporated into superconducting qubit architectures and test if such a device is indeed tunable by influencing the 2DEG proximity effect. A complete description on how to construct such a device is beyond the scope of this thesis.

### 9.2.4 Additional Quantum Applications

Why are we particularly interested in ZnO 2DEGs? One reason is due to another interesting ZnO property: piezoelectricity. This would allow information to be encoded into ZnO through surface acoustic wave (SAW) phonons. There have
already been examples of how phonons can be used for quantum computation in a manner similar to photons, and how the slower propagation speeds of phonons enable new dynamic schemes for processing quantum information [150]. By fabricating 2DEGs on ZnO, one could achieve a scalable gatemon-based quantum computer architecture (similar to that shown in [151]) in conjunction with a microwave SAWs on the piezoelectric ZnO substrate. Such a device would be highly versatile, capable of operating in two quantum regimes simultaneously and could facilitate novel quantum algorithms on its unique architecture.
Appendix A

Publication from this work

The following publication was published using data presented in chapter 6. The reference for this publication is; Matthew J. Sparks, Oscar W. Kennedy, and Paul A. Warburton. RapidThermal Annealing for Surface Optimisation of ZnO Substrates for MBE-Grown Oxide Two-Dimensional Electron Gases. Crystals, 10(9):776,2020.
Rapid Thermal Annealing for Surface Optimisation of ZnO Substrates for MBE-Grown Oxide Two-Dimensional Electron Gases

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Abstract: Two-dimensional electron gases (2DEGs) at the ZnO/ZnMgO interface are promising for applications in spintronics and quantum computing due to the combination of low spin-orbit coupling and high electron mobility. Growing high mobility 2DEGs requires high quality substrates with low impurity densities. In this work we demonstrate a ZnO substrate sample treatment combining high temperature rapid thermal annealing and chemical etching to improve the surface quality for the subsequent growth of 2DEGs. This process enables the growth of a 2DEG with low-temperature mobility of $4.8 \times 10^4$ cm$^2$V$^{-1}$s$^{-1}$. An unannealed control sample shows a scattering rate at least three times greater than the annealed sample.

Keywords: ZnO; heterostructure; 2DEG; molecular beam epitaxy; semiconductor II-VI material

1. Introduction

Two-dimensional electron gases (2DEGs) form at the ZnO/ZnMgO interface due to a combination of polarisation and band-gap discontinuities at the interface [1]. These 2DEGs combine exceptional electron mobilities and consequent long diffusion lengths [2] in a low spin-orbit-coupling material [3]. This allows, in principle, electrons to be transported long distances whilst maintaining spin coherence [4]. Furthermore, fractional quantum Hall states in these 2DEGs realise non-abelian statistics [5,6] and could be used to build topological quantum computers [7]. These properties mean that this material system has significant promise for spintronics and quantum-computation applications.

High mobility 2DEGs require a low density of scattering centres. These can be formed by crystalline defects [8], ionized donors [9], alloy scattering [8], electron–electron scattering [10] or atomic impurities [11]. Minimizing the crystalline defect density requires the use of an epitaxially matched substrate, with the best results found using single-crystal ZnO [2]. Alloy scattering is small in these systems as the polar interface results in electrons being confined within ZnO [12,13]. There is a trade-off to be made between electron density and electron-induced scattering which is determined by the Mg concentration of ZnMgO layers [13,14]. In MBE-grown ZnO/ZnMgO 2DEGs, interface roughness scattering and impurity scattering have been shown to be the dominant factors for electron mobility [8]. It is known, for instance, that lithium acts as an acceptor in ZnO and can significantly reduce ZnO conductivity [15–17] and harm 2DEG formation [11]. Atomic impurities are known to be present in ZnO substrates and are incorporated during hydrothermal growth [16]. Whilst exceptionally low impurity ZnO crystals have been grown using a platinum-lined autoclave [17,18], since the decommissioning of this equipment, only ZnO substrates grown in rhenium/iridium-lined autoclaves are available.
Surface band-bending in n-type ZnO means the bands bend upwards at the ZnO surface. This creates an electric field exerting a small electrostatic force toward (away from) the surface on positively (negatively) charged impurities. At room temperature this force is insufficient to cause impurities to move in the sample, however at elevated temperatures impurities can diffuse in ZnO over several microns [15,16]. The small electric field from band-bending will bias the diffusion of positively charged impurities towards the surface of ZnO. This effect is more pronounced at the negatively charged O-polar face [15]. A combination of thermal annealing and etching can therefore induce positively charged impurities to diffuse to the surface before being etched away as shown schematically in Figure 1a–c.

\[ qE + \text{(d) (e)} \]

(a) (b) (c)

Figure 1. (a) shows the band bending close to the substrate surface. Arrow shows force acting on the impurities with positive charge \( q \) in field produced by band bending \( E \). Uniform impurity distribution is represented by uniform green shaded region between bands. (b) show impurities congregating at the substrate surface at high temperatures, resulting in a depleted impurity density deeper into the substrate. (c) shows the system after impurities have been removed, either through surface evaporation or HCl etching. The depleted impurity region is now close to the substrate surface. (d) shows the measurement setup for the thermally treated substrates as well as a graphical representation of how \( R_L \) was measured. (e) shows the ZnO substrate surface resistance per unit length as a function of the number of anneal cycles to a temperature of 1000 °C for 5 s.

In this work we investigate the combination of substrate annealing and hydrochloric acid etching of hydrothermally grown single crystal ZnO substrates as a preparatory step before 2DEG growth. The annealing stage is designed to cause positively charged impurities to diffuse to the surface, combined with the electric field from surface-band-bending in the intrinsically n-type ZnO [15]. We show that the room temperature crystal surface resistance decreases under this treatment. Additionally we use MBE to grow two ZnO/ZnMgO heterostructure bilayers which are identical apart from the fact that one sample has undergone the anneal/etch procedure but the other has not been annealed. We observe that a 2DEG forms in the heat-treated sample but not in the unannealed sample, confirming that the rapid thermal treatment has enhanced 2DEG formation.

2. Materials & Methods

A single 10 × 10 × 0.5 mm Zn-face (001) epipolished ZnO crystal sourced from SurfaceNet GmbH (Rheine, Germany) was cut into five equally sized pieces. Each piece was degreased in acetone, isopropyl alcohol and deionised water. Four of the pieces were then annealed by a series
of rapid thermal anneals in a Solaris 100 rapid thermal processor system. Each anneal cycle saw the sample raised to 1000 °C in nitrogen at atmospheric pressure for 5 s, before being cooled to 100 °C. After annealing, the samples were etched in 7:200 HCl:water solution for 30 s and then rinsed in deionized water.

These samples were then contacted using a linear array of 300 × 300 µm Ti/Au ohmic contacts with a pitch of 500 µm. These were fabricated onto the Zn-polar face by a lift-off process. Metallisation was performed by Direct Current magnetron sputtering in an SVS 6000 deposition system (Speciality Vacuum Systems LTD, Berkshire, UK). Prior to deposition the surface was cleaned using an in-situ argon ion mill. A device schematic is shown in Figure 1d.

The ZnO/ZnMgO heterostructures were grown on a pair of ZnO substrates, one of which had been subjected to fifteen rapid thermal anneals, followed by a dilute HCl etch. The other sample was not annealed but was etched in HCl. The final HCl processing stage has been shown to result in smooth surfaces terminated in atomic steps, ideal for epitaxial growth [5,19]. Hereafter these samples are referred to as the ‘treated’ and ‘untreated’ sample, respectively. Heterostructures were grown in an SVTA oxygen plasma assisted MBE system. An initial 100 nm ZnO buffer layer was deposited onto the Zn-polar face of the substrate at 500 °C, followed by a 40 nm ZnMgO layer deposited at 750 °C. Buffer layers were employed because ZnO homoepitaxial layers have been shown to greatly increase the quality of subsequent ZnMgO growth on ZnO substrates [20,21]. Table 1 shows the Zn and Mg fluxes used during growth. Oxygen plasma was maintained at an RF power of 300 W and flow rate of 3 SCCM (chamber pressure of 10^{-5} Torr) throughout the growth of all layers.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Zn-Flux (×10^{-7} Torr)</th>
<th>Mg-Flux (×10^{-8} Torr)</th>
<th>Mg/Zn Flux Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated</td>
<td>4.8</td>
<td>1.8</td>
<td>0.038</td>
</tr>
<tr>
<td>Untreated</td>
<td>4.3</td>
<td>1.9</td>
<td>0.044</td>
</tr>
</tbody>
</table>

Hall bars consisting of a mesa measuring 10 µm in width were produced by milling the samples to a depth of 200 nm with an argon plasma in the SVS 6000 system. These were contacted by Ti/Au leads deposited using the same process as detailed above. Electrical characterisation of the samples was conducted with a Quantum Design physical property measurement system (PPMS) across a temperature range of 2 K to 300 K in a perpendicular magnetic field up to 14 T. Measurements were conducted in a 4-point measurement setup with a quasi-static current bias.

3. Results

3.1. Substrate Thermal Processing

By plotting the resistance as a function of contact separation, the substrate surface resistance per unit length $R_L$ can be extracted, as shown in Figure 1d. This measurement is contact resistance independent. $R_L$ is used as a proxy for sheet resistance. Despite non-uniform current flow in this geometry preventing the sheet resistance being extracted, $R_L$ still gives a good indication of substrate resistivity. We plot $R_L$ as a function of the number of annealing cycles in Figure 1e. The resistance initially increases before gradually decreasing and reaching a level lower than that of the untreated substrate. The reduction in resistance after many annealing cycles is promising as it suggests these substrates will result in higher 2DEG mobilities [22], but the non-monotonic behaviour warrants explanation.

In n-type ZnO, the initial rise in resistance suggests an increase in acceptor density close to the substrate surface. The drop in resistance with further cycles suggests that these acceptors are removed from the conduction channel. We consider the effects of lithium impurities which have been established as an electrically limiting defect in ZnO [23]. Experiments have shown that heating ZnO with uniformly distributed Li impurities causes the Li to migrate towards the substrate surface.
where it congregates [15] and can then diffuse out of the crystal. Our data suggests that Li density at
the surface actually increases as the short anneal cycles are insufficient to allow Li to fully diffuse at the
surface. Subsequent anneals allow Li to diffuse to the substrate surface where it may diffuse out of the
crystal or be etched away in the HCl etching stage. The diffusivity of Li in ZnO at 1000 °C from [24]
allows us to estimate that Li will diffuse between 6 and 36 µm per 5 s anneal. This is consistent with
surface depletion regions in single-crystal bulk ZnO being a few micrometers [25]. A single ramp
should be sufficient for Li ions to diffuse to the Zn-polar substrate surface, leading to an increase in
surface resistance. The Zn-polar face is more resistant to HCl etching than the O-polar face [26], so the
primary mechanism for Li removal from this face is surface evaporation due to further annealing [16].
This explains the initial rise then fall of $R_L$ as seen in Figure 1d. Li concentration dynamics could be
better established by measuring elemental secondary ion mass spectroscopy (SIMS) both before and
after annealing.

3.2. 2DEG Growth and Characterisation

Having established a procedure to improve substrate quality by promoting lithium out-diffusion
we verify it by using treated substrates for 2DEG growth. Figure 2a,b shows the x-ray diffraction (XRD)
pattern for the ZnO/ZnMgO heterostructures grown by MBE on treated and untreated substrates. The
presence of ZnMgO is confirmed by the shoulders near the ZnO (002) and (004) peaks. Additionally
the Mg concentration of the ZnMgO layer can be determined by comparing the location of the ZnO
(004) and shoulder peak by using the method outlined in [27]. The Mg content for the treated and
untreated sample are 6.1 % and 7.4 % respectively.

![Figure 2](image-url)

**Figure 2.** X-ray diffraction plots for ZnO/ZnMgO heterostructures grown on treated (a) and untreated
(b) substrates. Insert in XRD plots shows a magnification of the (004) ZnO peak and ZnMgO shoulder
peak with a logarithmic intensity scale.

Figure 3a shows the longitudinal resistance of these samples as a function of temperature as they
were cooled from 300 K to 2 K. Both samples show an initial rise in resistance as the temperature
falls from 300 K to 200 K, which is typical of semiconductor carrier freeze-out. The resistance reaches
a maximum at approximately 160 K before starting to fall. This decrease is attributed to 2DEG
formation, as charge carriers are confined to the conduction band quantum-well at the ZnO/ZnMgO
interface. Below 100 K the resistance in both samples falls slowly as the 2DEG becomes the dominating
conduction path. The resistance of the untreated sample is higher at these temperatures implying more
electron scattering in this sample. Below 50 K the behaviour of the samples diverges: the resistance
of the treated sample continues to fall but the untreated sample resistance starts to increase with
falling temperature.

Figure 3b shows the 2 K longitudinal resistance of the two samples as a function of magnetic field
applied normally to the substrate surface. The treated sample (green) shows clear Shubnikov de Haas
(SdH) oscillations at fields above 5 T, while no such oscillations are observed in the untreated sample
(magenta). The SdH oscillations were used to determine the mobility and carrier concentrations of
the 2DEG following [22]. The insert in Figure 3d shows the fit used to determine these properties.
The extracted sheet carrier concentration of the treated sample is $5.1 \times 10^{12} \text{ cm}^{-2}$ and mobility is $4.8 \times 10^4 \text{ cm}^2/\text{Vs}$ at 2 K. This value is three orders of magnitude higher than the low-temperature mobility of ZnO [28].

The untreated sample shows no SdH oscillations but does show a negative magnetoresistance across the entire range of applied magnetic field. This behaviour is similar to that shown by Das et al. [29] for ZnO 2DEGs on c-plane sapphire substrates and is attributed to weak localisation. This suggests that carriers are at least partially confined in the untreated sample; however, unlike the treated sample, defect scattering prevents the observation of SdH oscillations.

The lack of SdH oscillations in the untreated sample indicates there is either no 2DEG present, or the scattering rate in the 2DEG is too high to observe SdH oscillations. For high contrast SdH oscillations, the separation of the Landau levels $\hbar \omega_c$ must exceed the thermal energy $kT$. Defects (including ionised impurities) broaden the Landau levels. The magnitude of this broadening is given by:

$$\Gamma = h \sqrt{\frac{2 \omega_c}{\pi \tau_f}}$$

where $\tau_f$ is the mean time between electron scattering events [30]. Inserting the relation for cyclotron frequency $\omega_c = eB/m^*$ (where $m^*$ is the effective mass of the electrons in the 2DEG) gives an upper bound on the scattering rate:

$$\tau_f^{-1} < \frac{\pi eB}{2m^*}$$

We take $m^* = 0.3m_e$, which is typical of values seen in the literature [2,31]. No SdH oscillations are observed in the unannealed sample up to a field of 14T. From Equation (2) we extract a lower bound for $\tau_f^{-1}$ of $1.3 \times 10^{13} \text{ s}^{-1}$ for the unannealed sample. In the treated sample, SdH oscillations are visible at fields of 5T suggesting a upper bound for $\tau_f^{-1}$ in this sample of $4.6 \times 10^{12} \text{ s}^{-1}$. Sample treatment has led to at least a factor three decrease in the scattering rate, indicating a reduction in the defect density. This reduction in scattering rate could be attributed to a decrease in interface roughness caused by rapid thermal annealing. Atomic steps are highly desirable for epi-growth, and represent the smoothest surface possible for a given miscut (which will not be changed by annealing). It has been shown that etching in dilute HCl gives atomic step profiles in ZnO surfaces [5,19] and as this is the final
processing step across both substrates, the surfaces should be similar between the control and annealed sample. We therefore think that surface roughness is unlikely to discriminate between samples.

4. Conclusions

In summary, we have demonstrated how to exploit rapid thermal annealing to improve the surface quality of ZnO substrates. We observe a non-monotonic response in the substrate surface resistance as a function of the number of applied anneal cycles at 1000 °C. We propose a model of defect surface-migration and out-diffusion of impurities with successive anneal cycles. We use this substrate treatment to successfully demonstrate SdH oscillations indicative of a high-mobility 2DEG and show that the untreated control sample shows no SdH oscillations. The lack of SdH oscillations in the unannealed sample is attributed to a higher defect density in the sample. Rapid thermal annealing combined with surface etching has led to at least a factor three reduction of the scattering rate in our samples.

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Abbreviations

The following abbreviations are used in this manuscript:

- MBE Molecular beam epitaxy
- PPMS Physical property measurement system
- SdH Shubnikov–de Haas
- SIMS Secondary ion mass spectrometer
- XRD X-ray diffraction

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