ENERGETICALLY DEPOSITED ZNO-BASED TERNARY OXIDES: CHARACTERISATION AND DEVICE APPLICATIONS

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

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Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

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Edwin L H Mayes

22/10/2015
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Personal

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List of Collaborators

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Author Publications


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Abstract

This thesis describes the deposition, characterisation and device applications of ZnO and Zn$_{1-x}$Mg$_x$O films. Energetic deposition methods have been employed since they show promise for producing high performance metal oxide based transparent conducting films. Particular aims of this study were to establish: (1) whether energetic deposition methods could offer tangible benefits over other deposition methods currently employed to prepare ZnO based device layers and (2) whether the control over microstructure afforded in energetic deposition could be combined with compositional control for effective bandgap tuning.

Two energetic deposition methods were used to produce ZnO and Zn$_{1-x}$Mg$_x$O thin films for optoelectronic applications: filtered cathodic vacuum arc (FCVA) and high power impulse magnetron sputtering (HiPIMS). Both these methods provide a high proportion of ionised species in their depositing flux and are capable of coating large areas. Using energetic deposition methods give access to a much greater range of microstructures when compared to non-energetic deposition methods. Energetic deposition is able to take advantage of a process known as dynamic annealing, whereby the kinetic and potential energy of the depositing flux causes local heating of the growing film. This heating will simulate the effects of an increased growth temperature without the need to hold the entire substrate at this temperature. This allows substrates not compatible with high temperatures, such as flexible polymers, to be coated.

In the first phase of this project, FCVA was used to grow thin films of Zn$_{1-x}$Mg$_x$O from a composite ZnMg cathode. Compositional variations were observed and attributed to cathode poisoning effects. However, these variations proved useful in elucidating the relationships between composition, microstructure and properties. In order to probe the microstructure at the level of atomic bonding, x-ray absorption spectroscopy was employed. These measurements revealed the presence of O vacancies and established that the miscibility limit for single phase wurtzite Zn$_{1-x}$Mg$_x$O films was $x=0.37$, consistent with other growth methods.

Device measurements followed in the second phase of the project. FCVA deposition was again used but this time with strategies employed to minimise cathode poisoning and compositional variations. The as prepared Zn$_{1-x}$Mg$_x$O films demonstrated excellent structural properties, moderate n-type carrier concentrations and mobilities comparable with the best previously published. A particular aim of this phase was to demonstrate the applicability of the films to UV sensing. Visible blind UVB detectors were fabricated using graphitic carbon contacts. These demonstrated UV to visible rejection ratios exceeding three orders of magnitude.

HiPIMS was used to grow ZnO films in the third phase of the project. Whilst this growth method had been used by other researchers to produce ZnO, this study lacked detailed microstructural, optical and electrical characterisation. These films displayed carrier mobilities comparable or better than those achieved using conventional magnetron sputtering and moderate n-type carrier concentrations suitable for devices. Schottky
diodes produced on this material, grown at the moderate temperature of 200 °C, exhibited ideality factors less than 2 and rectification ratios up to three orders of magnitude.

Finally, HiPIMS and DC magnetron sputtering were used simultaneously to co-deposit Zn$_{1-x}$Mg$_x$O with a Mg fraction that varied laterally across a 4 inch sapphire wafer. This experiment enabled the determination of the bandgap, microstructure and electronic properties as a function of Mg fraction in a single film. The as deposited film was highly resistive so annealing in the presence of hydrogen was performed to improve the carrier transport properties. Post annealing, carrier concentrations of $\sim 10^{17}$ cm$^{-3}$ and hall mobilities of up to 4.5 cm$^2$ V$^{-1}$ s$^{-1}$ were measured. The material was used to fabricate a notch filtered UVB detector which provided UV to visible rejection ratios of three orders of magnitude.
Chapter 1. Introduction and literature review

1.1 Introduction

This thesis examines the growth of bandgap tuned of ZnO by the addition of Mg to form an alloy, Zn$_{1-x}$Mg$_x$O, using energetic deposition methods. The addition of Mg will alter the bandgap whilst retaining the same crystal structure and other favourable properties of ZnO. Here, the use of large area energetic deposition methods will be explored. These methods offer potential advantages over other commonly used methods for producing high quality ZnO and Zn$_{1-x}$Mg$_x$O thin films. ZnO and related materials may be potential replacements for some material used in semiconductor devices or compliment commonly used materials such as silicon in order to maintain the pace of improvement consumers are accustomed to.

In order to understand why development of new semiconductor materials is important we have to first understand the history of the development of semiconductor materials and devices. Thermionic emission (an electron transport process that is fundamental to semiconductor device function) was first discovered by Frederick Guthrie in 1873 and reported on in his paper “On a relation between heat and static electricity”. Other researchers also made a contribution to understanding this effect but it was not extensively explored until its rediscovery by Thomas Edison in 1880 [1]. Edison found that an electrode placed inside an evacuated bulb near the filament would register no flow of current when a negative bias was applied, but would register a flow when a positive bias was applied. It was not yet understood that electron emission was responsible for the current flow, as electrons would not be discovered until 1897 by J. J. Thomson [2]. Edison produced and patented a device for voltage regulation that exploited what was then called the Edison Effect. Despite the discovery and development of a device by Edison he had little understanding of the science behind the effect. John Ambrose Fleming, after seeing a presentation of an “Edison Effect bulb”, discovered that the Edison Effect could be used to detect radio waves which led to the first two-element vacuum tube. Vacuum tubes opened up possibilities for a range of new devices including radio, amplification, recording and reproduction of sound, telephone networks, digital computers and process control in the first production line type industrial processes. The fragility and poor reliability of vacuum tubes spurred the development of the solid state transistor, which was of particular interest for military applications where hardness and reliability were critical. Julius Edgar Lilienfeld in 1925 patented the first design for a solid state transistor in Canada [3]. Lilienfeld filed additional patents in the USA in 1926 [4] and 1928 [4] but no research papers were produced from the design and no prototype was developed, so the idea disappeared into obscurity. William Shockley along with John Bardeen and Walter Brattain, working at Bell Labs in 1947, demonstrated the first prototype (see Figure 1) of what would later be called the transistor [5].
Shockley had suggested that a patent for the invention be filed with himself named as the inventor, however, lawyers for Bell Labs had discovered the original patents from Lilenfeld and advised against the patent. Instead Shockley, Bardeen and Brattain were named as the inventors of the point contact transistor in 1947 [6] and recognised with the awarding of the Nobel prize for this invention in 1956.

The first transistor devices made use of point contacts to Ge [5]. Following the development of a growth method for producing chemically pure single crystal Ge crystals by Gordon Kidd Teal, significant increases in device performance were achieved [7]. Ge, despite some favourable properties, was not ultimately suited to many of the applications required and was replaced by Si. Ge does have greater mobility than Si improving its high frequency response. However, its small bandgap (0.67 eV for Ge compared to 1.12 eV for Si) leads to a greater leakage current in Ge based devices when compared to Si. This problem is further exacerbated as temperature increases in a process known as thermal runaway. At about 75 °C, pure Ge based devices cease to work entirely. This precludes Ge transistors from many applications. However, some Ge based devices remain in use today primarily for the audio industry where subjective assessment of performance remains [8].

Early innovation in Si based transistors came from two sources. The first was at Bell Telephone Laboratories where the development of the Si based transistor was driven by the need for very low leakage transistors in telephony applications. The second was at Texas Instruments where there was the quest for a transistor that operated reliably in a range of environmental conditions to replace the fragile vacuum tubes in military devices. These imperatives led both Bell Labs and Texas Instruments to independently invent Si based transistors in 1954 within a month of each other. But the rapid commercialisation of the invention by Texas Instruments gave them the edge over the more cautious Bell Labs [9]. The Si transistor market developed rapidly in the 1950s and 1960s. Of the several factors at play in the development of the Si transistor, two were critical: the availability of high purity semiconductor grade Si supplied by DuPont which enabled the production of high
purity single crystal Si, and; a new doping technique, termed diffusion, that replaced the inferior ‘rate-growing’
technique and gave producers greater control of the dopant concentration [10].

Si has consequently become the dominant semiconductor material for several reasons. Compared to Ge, Si enabled more reliable devices that could withstand a much greater range of environmental conditions. This drove demand for high purity single crystal Si and eventually the mature production process for growing high purity Si with relatively low waste we have today. The abundance of Si as feedstock for high purity wafers also made Si cheaper than the Ge alternative. The properties of Si have proven useful for all of the key devices needed for modern microelectronics. Si is able to withstand high temperatures [11] without suffering damage or rendering a device inoperable, which also means that Si can operate in much higher power devices than Ge. Si has a stable native oxide, useful in the fabrication of metal-oxide-semiconductor field effect transistors (MOSFETs). This oxide can be grown from the Si at elevated temperatures and controlled in thickness via annealing time and atmosphere. The forward voltage potential in Si is 0.7 V compared to Ge’s 0.3 V, meaning that a Si device can tolerate significantly more current before thermal runaway. The reverse breakdown voltage of Si can be as high as ~100 V, compared to ~70 V in Ge, allowing Si to rectify higher power signals. With its dominant position and established manufacturing processes, Si will continue as the primary material for microelectronics for some time.

The majority of performance gains to date have come from continued miniaturisation of features. The process moved from 10 µm in the early days of integrated microelectronics, to the current feature size of 22 nm with 14 nm processes slated to make an appearance in 2015 [12]. With feature sizes approaching atomic scales, the rate of improvement will slow. Performance limits of Si based microelectronics will be dictated by the minimum feature size and the gate oxide thickness in MOSFETs (an important fundamental building block in most microelectronic devices). Parasitic resistance and parasitic capacitance, previously considered negligible, will begin to dominate as processes move below 20 nm. Parasitic resistance results from the reduction in scale, leading to significantly smaller source and drain contacts with increased resistance. As processes become smaller than 20 nm, this resistance will play an ever increasing role in the limits of the circuit as a whole. Power density requirements will also increase along with the need to dissipate additional heat. New device geometries, gate materials and related software changes will take a significant amount of time to be implemented into consumer level technology. This is because these processes will affect development at several levels including materials, device design, circuit design, computer architecture and software.

In order to continue the pace of microelectronic innovation, new materials are required that can overcome the problems posed by shrinking features in Si based devices. Viable candidate need to have a wide bandgap as this will determine the degree of reverse leakage. In the same way Si won out over Ge, in part due to its larger bandgap, new materials that are proposed as a Si replacement will also ideally have a wider bandgap than Si. Components based on a wide bandgap material can be smaller than a Si equivalent due to lower leakage, so more devices can be fabricated per unit area when compared to Si. Higher voltages are possible in devices based on a wide bandgap material allowing them to operate faster. A wide bandgap also opens up additional applications such as transparent displays, some of which have already been demonstrated in prototype products [13]. Radiation hardness, the ability of a semiconductor to resist errors caused by radiation, is
important for applications in satellites and other extra-terrestrial applications and areas of nuclear reactors that are exposed to significant amounts of radiation.

New materials that have some of these properties could form parts of advanced microelectronics alongside Si which could help maintain the pace of performance improvement. A material that may compliment Si to extend its useful life and enable the continued gains in performance seen to date is ZnO. ZnO and related materials will never replace silicon for several reasons, but ZnO and related materials can fill several roles in electronic devices such as some solar applications, UV sensing and gas sensing. Degeneratively doped ZnO is a viable replacement for amorphous Si that is often used as a transparent conducting oxide [14].

1.2 Characteristics & requirements for a functional semiconductor

The semiconducting properties of a material originate from its atomic structure. Metals, most of which are highly conductive, have a large number of free electrons available to participate in conduction. In an insulator, all electrons are tightly bound to the atomic nuclei so that a very large force applied via a potential or through heating is required to enable conduction. A semiconductor has a comparatively small number of free electrons at room temperature. This means conduction can occur under an applied potential but with a relatively (to a metal) high resistance.

Si has four valence electrons, each of which is shared with a neighbouring Si atom in a very stable bond; this means there are very few free electrons available for conduction. To make Si conductive it is necessary to dope the Si with atoms of an element with a different number of valence electrons. Dopant atoms will either have one less (such as boron) or one more (such as phosphorus) valence electrons than Si, leaving either free holes (boron) or free electrons (phosphorus). It is these free electrons/holes that allow doped Si to conduct. If a sufficiently large number of impurity atoms are added to Si it will become degeneratively doped and behave more like a metal (conductor). At very low temperatures (approaching absolute zero), a semiconductor will behave as an insulator because electrons have insufficient energy to escape bonds and be able to participate in conduction.

Semiconductors can be categorised by their bandgap characteristics as either direct or indirect. The maximum valence band and minimum conduction band positions are defined by a crystal momentum or k-vector in the Brillouin zone [11]. A direct bandgap has the valence maximum and the conduction band minimum having the same k-vector so a transition can occur between the valence and the conduction band with no momentum change. An indirect bandgap material will have different k-vectors for the valence band maximum and the conduction band minimum. This means that a transition between the valence band maximum and the conduction band minimum requires a change in momentum; this change is usually in the form of a phonon (lattice vibration). This effect means that light emission/absorption in direct bandgap materials is more efficient than materials with an indirect bandgap.

The properties of a semiconductor can be varied through the application of light, heat, applied electric potential, chemical environment or through doping. This thesis will focus on the use of semiconductor materials for light sensing, specifically UV light. The sensitivity of a semiconductor material to light is
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dependent on the optical bandgap. In order for charge carriers to be excited to the conduction band by incident light, a minimum photon energy equal to or greater than the optical bandgap is required. In this way, it is possible to have a semiconductor material that is sensitive to light with a maximum wavelength (or minimum energy). Such a sensor could be considered visible blind, with the appropriate bandgap, as visible light would not have sufficient energy to excite carriers into the conduction band. This property enables sensors to be produced that are sensitive to specific ranges of photon energies.

In order for a semiconductor to be viable for commercial device applications it must fulfill some basic requirements. Doping (the alteration of charge carrier density) must be achievable and stable without significantly altering the other properties of the material. In addition, it must be capable of supporting fundamental device operation. Figure 2 shows band diagrams and schematics of the key devices required to build logic circuits for microelectronics. The symbols $E_c$, $E_v$, $E_i$ and $E_F$ represent the conduction band energy, Fermi energy, valence band energy and the intrinsic Fermi level, respectively. The symbol $q\phi_i$ refers to the built-in potential related to the difference in work function between the p and n type semiconductors and $e\phi_{bi}$ refers to the barrier height. A material must be capable of supporting some or all of these devices for it to be viable for electronic applications.

![Band diagrams and schematics of the key devices required to build logic circuits for microelectronics.](image)

The devices are (a) a PN junction, (b) a metal-semiconductor Schottky junction, (c) an ohmic junction and (d) a metal oxide semiconductor junction. Note the devices schematic included in part (b) (rectifying junction) is structurally identical to the ohmic junction in part (c) the different outcomes are the result of differing contact materials and surface preparation.

1.3 Introducing ZnO

ZnO is a semiconducting metal oxide with properties that make it suitable for several emerging optoelectronic applications. Occurring naturally as the mineral zincite, it is non-toxic to humans and has existing large scale
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applications including topical ointments for treatments of a number of skin ailments, glazing of ceramics and as an additive in paints, rubbers, and even food. One of the first recorded uses of ZnO was as a skin ointment by Indian physicians [15].

ZnO appears white when in powder form but when in single crystal or polycrystalline solid form is transparent with a slight yellow tinge. The most stable phase is the hexagonal (wurtzite) phase. It has a direct bandgap of 3.3 eV at 300 K and a large piezoelectric tensor. ZnO is natively n-type doped. Due to the prevalence of n-type conductivity, this doping has long been attributed to native defects [16]. However, an increasing body of evidence suggests that native n-type conductivity in ZnO results from unintentional hydrogen doping [17].

The semiconductor properties that make ZnO desirable are its wide direct bandgap, high exciton binding energy of 60 meV [18] (more than double the thermal ionisation energy at room temperature of 26 meV), making stable room temperature emission and detection possible. ZnO also has good radiation hardness making it suitable for extra-terrestrial applications.

ZnO has a hexagonal wurtzite structure (shown in Figure 3) with lattice constants of \(a = 3.25 \text{ Å} \) and \(c = 5.2 \text{ Å}\). The wurtzite crystal structure occurs in many binary compounds, such as \(\text{ZnS}, \text{CdS} \) and \(\text{GaN}\). The space group of wurtzite ZnO is \(\text{C}_{6v}^{4}.\text{P}_{63}mc\) with each atom being tetrahedrally (four fold) coordinated. Thin films of ZnO typically have a strong preferred orientation with the c-axis perpendicular to the substrate.

![Figure 3: Several unit cells of the wurtzite structure of ZnO, O= red (darker grey) and Zn= grey (lighter grey).](image)

ZnO has a good thermal stability and will only decompose at \(1975 \degree \text{C}\) [19]. Consequently, high temperature device processing (including annealing) is possible. ZnO is insoluble in water making wet chemical etching as part of photolithographic fabrication possible. It should be noted that despite being insoluble in water even mildly acidic water will etch the ZnO surface. The high refractive index of ZnO (~2 at 550 nm) [20] in its bulk single crystal form makes it a good candidate for some lasing and waveguide applications.

The piezoelectric tensor for ZnO is one of the highest among tetrahedrally bonded semiconductors [21]. The piezoelectric tensor for the wurtzite phase of ZnO has three distinct components and one for the zinc blend
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phase. This property makes ZnO a potentially useful material for micro-power generation by embedding fibres in clothing.

Despite application as an electronic material in the 1900s [22], where it was used in a cats whisker diode, ZnO has yet to see commercial application as an optoelectronic material. Due to its highly non-ohmic resistance, the primary electronic application of ZnO is in varistors. This device sometimes known as a voltage dependant resistor, has a high resistance at low voltage with a much decreased (nonlinear) resistance at high voltage. A varistor is used for control or compensation of excessive current. The nonlinear resistance seen in polycrystalline ZnO is a result of oxygen accumulation at the grain boundaries causing potential barriers which will break down at sufficiently high voltages. The primary limitations on widespread use of ZnO are the lack of reliable p-type doping and the availability of economically viable device grade capable thin film growth methods. Recently ZnO based components have begun to appear in commercial products. One such application is an amorphous compound semiconductor based on ZnO, indium gallium zinc oxide (IGZO), which has been used in thin film transistor (TFT) based displays [13].

1.4 Growth of ZnO single crystal and thin films

Emerging and future applications of ZnO will require high quality single crystals in both thin film and bulk form. There has been substantial progress in the improvement of the quality of ZnO in both film and bulk [23]. Large single crystals (~5 cm) are available [23] and ZnO thin films have been produced using homoepitaxy and heteroepitaxy [24]. There has been some difficulty with the preparation of ZnO substrates for homoepitaxy, at first thought to be simple, however difficulties arise due to the behaviour of single crystal ZnO under vacuum [23].

1.4.1 Bulk single crystal growth of ZnO

There are three main methods for production of bulk ZnO single crystal; gas/vapour transport, melt-growth, and hydrothermal growth.

In the gas/vapour transport method, high purity ZnO powder is heated to high temperatures (~1600 K) to produce Zn vapour which is condensed in an oxygen rich environment to form a crystal that can be several millimetres in diameter and several centimetres long [25-28]. A variation of this method is the seeded vapour transport method, whereby a single crystal seed is used to precipitate single crystal growth. In a similar manner, high purity ZnO powder is heated at one end of a horizontal reaction chamber. The vapour produced is transported using a carrier gas (often H₂) then allowed to coalesce at the other end of the tube, held at a lower temperature. Cutting-edge seed chemical vapour transport methods can produce crystals that are 5 cm in diameter and 1 cm thick. Carrier concentrations of ~10¹⁶ cm⁻³ and room temperature mobilities of 205 cm² V⁻¹ s⁻¹ have been reported [29]. Growth rates for this method are typically relatively slow and in the range of 1 mm per day [29].

The hydrothermal method employs an autoclave (a vessel able to withstand high temperature and large pressure differences). ZnO is dissolved in a solution then heated at one end of a chamber with a temperature gradient to the other end of the chamber. There, a seed crystal is placed so that the solution will condense
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resulting in crystal growth. The hydrothermal method is able to produce very high quality ZnO crystals up to 2 cm in diameter that are suitable for use in homoeptaxial thin film growth. The hydrothermal method is characterised by slow growth; typically lower than 1 mm day$^{-1}$. Hydrothermal growth suffers from the inclusion of impurities such as Li and K [30] with lower concentrations of Al and Fe. However, carrier concentrations as low as $\sim 8 \times 10^{13}$ cm$^{-3}$ have been reported.

Melt grown bulk ZnO has been produced in a process patented by Cermet Inc. [31]. Here the source material is heated using RF energy in a cold crucible with a controlled atmosphere and a seed crystal is then introduced from which the crystal is grown. This method can produce crystals with lower impurity concentrations as the melt is isolated from the crucible by a cooled layer of ZnO. The method is much faster than either the hydrothermal method or the vapour transport methods and is able to produce crystals 1 cm in diameter and several centimetres long with rates of 1-5 mm h$^{-1}$. Melt grown crystals tend to have a lower concentration of extended defects when compared to other bulk growth methods. The material available from Cermet Inc. has n-type conductivity with carrier concentration of $\sim 10^{17}$ cm$^{-3}$ and mobilities of $\sim 130$ cm$^2$ V$^{-1}$ s$^{-1}$ [31, 32]. Melt grown crystal and c-axis oriented and can be easily cut for use as substrates for homoeptaxial growth.

All of the current production methods for bulk crystals result in n-type conductivity. Most of these methods produce ZnO with a green band emission in their photo luminescence, suspected to be associated with Zn vacancies [33].

1.4.2 Thin-film growth methods

Using ZnO single crystal substrates has the advantages of reducing both the concentration of extended defects and incorporation of impurities, and also avoiding thermal mismatch. The majority of ZnO thin film reports in the literature however show a preference for non-native substrates including Si, glass, quartz and sapphire [34, 35] with some reports using GaAs, CaF$_2$ and GaN [35-37]. These preferences mainly reflect the comparatively high cost of ZnO substrates. In addition, isolating the optical and electronic properties of ZnO thin films requires an insulating substrate with a bandgap larger than that of ZnO. Whilst cost has inhibited the uptake of ZnO thin films, the preparation of bulk ZnO for homoeptaxial growth also has difficulties [38, 39].

Most of the current applications of ZnO thin films such as varistors, transparent electrodes and piezoelectric devices make use of polycrystalline films. These films are grown primarily using glass substrates using techniques such as sol-gel synthesis, oxidation of Zn metal films, electro chemical deposition and pyrolysis. These techniques offer large coverage area but typically result in poor crystalline quality and low film density reflected in low carrier mobility.

Emerging optoelectronic applications require significantly higher quality films with a low defect density and low concentrations of impurities. Films of a high quality require more control over the deposition process including the temperature and the partial pressure in growth chambers. Techniques capable of achieving high quality ZnO thin films are molecular beam epitaxy (MBE), chemical vapour deposition (CVD), metal organic chemical vapour deposition (MOCVD), atomic layer deposition (ALD) and pulsed laser deposition (PLD). These techniques, however, either require high processing temperatures, provide low coverage area, or incur high
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Magnetron sputtering offers much higher coverage area and relatively low cost but the films produced from this technique are often lower density with associated rough surface [40].

An insulating transparent substrate is required for ZnO and Zn$_{1-x}$Mg$_x$O thin films grown for device fabrication, and to enable more thorough characterisation. This type of substrate is chosen to electrically isolate the material and, to perform optical characterisation and for device testing. Sapphire (Al$_2$O$_3$) fulfils these requirements. In addition the lattice mismatch between sapphire and a c-axis oriented ZnO film is only 18 % [41]. This will give several benefits including; lower stress in the films, a smaller amorphous buffer layer, and a templating effect which can assist in the nucleation of crystals in the thin film. The mismatch for MgO/Al$_2$O$_3$ is about 8.3 % [42].

1.4.2.1 Thin film growth of ZnO using CVD methods

Molecular beam epitaxy (MBE) is a thin film growth technique known to produce very high purity thin films. Process chambers typically operate in the ultra-high vacuum (UHV) range $\sim 10^{-8}$ Pa. MBE has a lower deposition rate than many other competing techniques with rates lower than 10 nm/min in most situations [18]. Source materials are heated until they sublime or evaporate. The vapour will then condense onto the substrate. As the process typically takes place at low pressure, the mean free path of the gaseous elements is long and consequently, these elements will not react with each other until they reach the substrate. In reactive depositions, an ionised reactive gas source enables low gas flow rate and hence, low process pressure. MBE has been used to produced ZnO [43] and Zn$_{1-x}$Mg$_x$O [44]. The carrier concentrations of ZnO films produced via MBE range from $10^{16}$ to $10^{18}$ cm$^{-3}$ with mobilities from 90-260 cm$^2$ V$^{-1}$ s$^{-1}$ [45-47]. A schematic of a typical MBE system is shown in Figure 4.

![Figure 4: Schematic of a molecular beam epitaxy growth chamber, taken from [14]](image-url)
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Metal organic chemical vapour deposition (MOCVD) is a CVD technique known to produce very high quality thin films. As it is a chemical vapour based technique typical process pressures are in the range of 10⁻760 Torr significantly higher than those employed for most physical vapour deposition (PVD) techniques. In this process high purity precursor gases are injected into a reactor chamber at precisely controlled doses. The substrate sits on a temperature controlled stage. The organic precursor gasses are heated in the absence of oxygen causing them to break down via pyrolysis. The atoms bond to the substrate forming an epitaxial layer. Zn₁₋ₓMgₓO polycrystalline thin films have been prepared using MOCVD [48]. Carrier concentrations of ZnO films produced by MOCVD vary from 10¹⁵ cm⁻³ to 10²⁰ cm⁻³. The chosen substrate also affects the concentration of defects. The lattice mismatch between film and substrate can result in an increased concentration of extended defects and intrinsic point defects. Diffusion of substrates constituents into the film can result in impurities.

1.4.2.2 Thin film growth of ZnO and Zn₁₋ₓMgₓO using PVD methods

ZnO has been grown using popular non-energetic or low-energy (low proportion of ionised species) PVD methods such as evaporation or sputtering. A report on ZnO deposited by e-beam evaporation showed disordered films, indicated from XRD, by the presence of broad reflections from (0002)/(0004) planes and presences of reflections from other orientations. The films consisted of small randomly oriented crystallites as confirmed by HRTEM and electron diffraction. The optical bandgap of the as deposited films was smaller than the commonly reported value of 3.3 eV. The bandgap for room temperature deposited films was 1.51 eV, and improved significantly with increased substrate temperature (100 °C) to 3.08 eV. At 400 °C substrate temperature, the optical bandgap was 3.26 eV. Air annealing was performed on the room temperature (RT) deposited films which showed similar improvements with an optical bandgap of 3.26 eV achieved after 1 hour of annealing at 800 °C [49].

As-deposited, thermally evaporated ZnO films are typically very oxygen deficient and they require post deposition annealing to achieved balanced stoichiometry [50]. XRD indicates films do not have strong preferred orientation and exhibit broad peaks indicative of a nano-crystalline disordered material. During energetic deposition, collision with the energetic depositing ions will cause the reactive gas to be ionised aiding in the formation of stoichiometric oxides, even without the aid of an ionised gas source.

Sputtered ZnO has a generally higher quality than evaporated ZnO. A report on nominally un-doped ZnO by Xing et al. [51] presents films grown at 240 °C on quartz using RF magnetron sputtering with a ceramic ZnO target in a Ar ambient. These films were subsequently annealed at temperatures ranging from 240 °C to 650 °C. XRD indicated a preferred (0002) orientation of the microstructure. The as deposited films were oxygen deficient and only after annealing at 650 °C did the films approach balanced stoichiometry. Electrical characterisation indicated that the as deposited films were insulating. After annealing at 430 °C, the films became conductive enabling Hall Effect measurements. Carrier concentrations in the annealed material ranged from 3 × 10¹⁶ cm⁻³ to 2 × 10¹⁹ cm⁻³ with mobilities of up to 6.7 cm² V⁻¹ s⁻¹. The high carrier concentration seen in these films indicates a high concentration of electrically active defects; this property would make these films less well suited to many electronic applications such as UV sensing and field effect transistors. Depositing fluxes
with greater proportions of ionisation, elevated energy and associated dynamic annealing [52] have been shown to improve structural order leading to better performing films with lower defect densities [53].

Pulsed laser deposition is often considered to be an energetic method. However, the degree of ionisation in the depositing flux is significantly lower when compared to either FCVA or high power impulse magnetron sputtering (HiPIMS). PLD has proven to be one of the best techniques for producing high quality ZnO [54] and Zn$_{1-x}$Mg$_x$O films [55]. XRD analyses of PLD ZnO films reveal FWHMs of the {0002} reflection as small as 0.07°, indicating large grains and high crystalline order. Reported mobilities of up to 140 cm$^2$ V$^{-1}$ s$^{-1}$ are consistent with minimal scattering (either due to grain boundaries or point defects). Carrier concentrations ranging from $7 \times 10^{15}$ cm$^{-3}$ to $5 \times 10^{17}$ cm$^{-3}$ show that PLD can produce films with a low concentration of electrically active defects [54]. Whilst PLD grown ZnO is of sufficient quality for devices, it has yet to be used in industrial applications due to its limited area capability (typically less then $\sim$5 cm$^2$). The high substrate temperatures ($\sim$700 °C) typically required in PLD to produce the best quality ZnO and Zn$_{1-x}$Mg$_x$O also limit the choice of substrate material [54].

In ion beam assisted deposition (IBAD), a non-energetic deposition method such as evaporation or conventional sputtering, is assisted with a beam of ionised gas such as Xe [56]. IBAD has been used to produce high quality mechanical coatings at moderate growth temperatures [57] and can provide more uniform grain orientation and larger grains in ZnO when compared to non-energetic methods [58]. ZnO grown using IBAD has been demonstrated [58, 59] to respond to UV radiation. One such device was based on a photoconductor structure using Al ohmic contacts. A mercury lamp (without a monochromator) was used to test the photoresponse. The response was characterised by a slow rise time (20 min) with a similar time taken to return to dark current levels. This slow response is indicative of a high density of charge traps. Degenerately (Ga) doped ZnO films supporting mobilities of up to 20 cm$^2$ V$^{-1}$ s$^{-1}$ have been produced using Ar$^+$ ion beam assisted sputtering at room temperature [60]. Using an assisting ionised gas and an applied substrate bias often leads to incorporation of the assisting ions [61]. Whilst these impurity defects are often electrically inactive, they can contribute to increased scattering. This problem is not encountered in inherently energetic deposition methods such as FCVA or HiPIMS, making these techniques better suited to producing electronic materials with a lower concentration of defects.

1.4.2.2.1 Thin film growth using HiPIMS and FCVA deposition

Energetic deposition methods are a subset of PVD methods in which the depositing flux is partly or fully ionised. By applying a substrate bias, the operator can control the landing energy of the ions giving greater control of the film microstructure.

Figure 5 shows how energetic deposition can be used to achieve a greater range of microstructures [62]. The figure has three axis thickness ($t^*$), normalised energy ($E^*$) and generalised temperature ($T^*$). By varying these parameters, it is possible to access a variety of microstructures and consequently films properties. The normalized energy and generalised temperature axis are synthetic values based on several parameters that are directly controlled by the operator. The normalised energy axis considered the pressure, and the displacement and heat effects caused by the kinetic energy of bombarding particles. The generalised temperature axis
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considers the sample temperature and the heating effects caused by potential energy energetic particles. An energetic flux can cause an effect termed “dynamic annealing” [52] whereby the energetic ions in the depositing flux have increased mobility allowing them to fill voids resulting in denser films. This enables access to microstructures normally only accessible using elevated substrate temperatures. And is therefore beneficial in situations where higher substrate temperatures are precluded such as when photoresist is present on the substrate.

![Figure 5: The structure zone schematic, this diagram shows how with an energetic ion flux and a heatable/biasable substrate gives access to a range of film microstructure are possible. Taken from a paper by Andre Anders [62].](image)

Evaporation and conventional sputtering would only be able to access a section of the structure zone diagram (limited E*). The inability to change the land energy of the depositing flux means that non-energetic methods are restricted to a band parallel to the generalised temperature axis. Films will typically be less dense and will require higher temperature to achieve the same level of crystallinity.

This project is concerned with assessing two energetic deposition methods, FCVA and HiPIMS for their viability in producing Zn$_{1-x}$Mg$_x$O thin films for optoelectronic applications. The following two subsections will examine the state of the literature in the area of producing metal oxides in general and more specifically ZnO and Zn$_{1-x}$Mg$_x$O thin films.

These energetic methods provide access to more microstructural forms at lower substrate temperatures [62]. Degenerately Al-doped ZnO layers have been grown by FCVA deposition for applications such as transparent conducting coatings [63] and more recently, FCVA grown ZnO has been used in metal semiconductor field-effect transistors exhibiting high channel mobility and excellent long term stability [64]. This project reports on Zn$_{1-x}$Mg$_x$O thin films grown using energetic deposition methods and examines the properties and device
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potential. Moderate growth temperatures (≤ 200 °C) were employed to assess potential compatibility with temperature-sensitive substrates, such as flexible plastics.

Zn$_{1-x}$Mg$_x$O is a ternary oxide based on ZnO. In order to produce Zn$_{1-x}$Mg$_x$O films using a given system a first step is to produce ZnO in order to establish growth parameters that are optimal with this simpler material system. Given the similarity between the materials, the growth parameters used for ZnO will provide a good starting point for production of Zn$_{1-x}$Mg$_x$O. In both cases, HiPIMS and FCVA, this process was followed. ZnO films have been produced using FCVA by several authors [65, 66] on a variety of substrates. ZnO films grown using FCVA have proven to be suitable for several device applications with electronic properties superior to films produced via sputtering [67].

1.4.2.2 Filtered cathodic vacuum arc

FCVA has recently been employed to deposit metal oxides for electronic device applications. An article by Field et al. [68] looked at the effect of biasing the substrate on the microstructure of HfO$_2$ films produced using FCVA. FCVA has been used by Anders et al. to produce degenerately doped ZnO: Al for smart window applications [63]. Recently Elzwawi et al. have demonstrated that FCVA grown ZnO can achieve mobilities of up to ~70 cm$^2$ V$^{-1}$ s$^{-1}$ after post deposition annealing [67].

The earliest reported FCVA grown ZnO thin films were produced and characterised by Xu et al. in 2001 [65, 69, 70]. The authors deposited ZnO onto non-native (100) n-type Si and observed preferred orientation in the 0002 direction at lower growth temperatures and in the 10 1 3 at growth temperatures exceeding 230 °C. In the initial report [69], XRD of ZnO films grown on Si revealed a FWHM of 0.6° and a grain diameter (measured using AFM) of ~200 nm. In a subsequent report [70] using similar growth conditions a peak carrier mobility of 8 cm$^2$ V$^{-1}$ s$^{-1}$ was measured in films deposited at 440 °C. Carrier concentrations varied between 10$^{18}$ cm$^{-3}$ and 10$^{22}$ cm$^{-3}$ depending on the growth temperature. The films grown at lower temperature (120 °C) had the highest carrier concentration at ~3 × 10$^{22}$ cm$^{-3}$. The authors attributed this to oxygen deficiency in the films. The carrier concentration reduced to ~3 × 10$^{18}$ cm$^{-3}$ with increased growth temperature (320 °C). This research group also reported that ZnO deposited from an FCVA at room temperature exhibited high transparency (~90% over the visible region). In two follow-up reports [71, 72], the same research group incorporated FCVA grown ZnO in optical waveguides and LEDs (the latter achieved using a p-GaN layer).

An extensive examination of ZnO films grown on quartz substrates using FCVA was conducted by Wang et al. [73]. A series of ZnO films was deposited at room temperature with a systematically varied oxygen process pressure. Structural, optical and electronic properties of the films were studied. In XRD, the FWHM of the (0002) reflection varied from 0.8° (at 2 × 10$^{-5}$ Torr O pressure) to 0.2° (at 8 × 10$^{-4}$ Torr O$_2$ pressure). Transmission spectroscopy revealed that films deposited at lower oxygen pressure (less than 2 × 10$^{-4}$ Torr) exhibited poor transmission with a shallow absorption edge. The authors attributed this to oxygen deficiency. Hall Effect measurements revealed that carrier mobility increased with increasing oxygen pressure, from ~2 cm$^2$ V$^{-1}$ s$^{-1}$ (at 2 × 10$^{-4}$ Torr O$_2$ pressure) up to ~15 cm$^2$ V$^{-1}$ s$^{-1}$ (at 8 × 10$^{-4}$ Torr O$_2$ pressure) before dropping to 10 cm$^2$ V$^{-1}$ s$^{-1}$ at 10 × 10$^{-4}$ Torr O$_2$ pressure. The carrier concentration decreased as a function of increasing
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Oxygen pressure varying from $1 \times 10^{20}$ cm$^{-3}$ to $9 \times 10^{18}$ cm$^{-3}$. The authors concluded that the primary factor affecting the film quality in the low temperature depositions was the oxygen partial pressure. The optimal O$_2$ partial pressure for room temperature deposition was determined to be $8 \times 10^{-4}$ Torr.

FCVA has also been used for the growth of Al doped ZnO (ZnO:Al), a transparent conducting oxide. ZnO: Al is a potential alternative to indium tin oxide (ITO) with a significant cost advantage being one driving factor. Anders et al. [63] have reported on ZnO: Al layers grown using a pulsed FCVA system. The authors used a 1 ms pulse length with a duty cycle of 3-4 Hz and an arc current of 780 A, significantly higher than the ~60 A often used when growing ZnO in a DC FCVA system. Due to the large number of process variables, the authors focused on growth temperature, rapid thermal annealing time, film thickness and Al content. The authors concluded that resistivity of the films decreased with increased growth temperature (no improvement was seen with growth temperatures greater than 250 °C) and with film thickness. This was attributed to an increase in mobility at higher substrate temperatures. Thicker films had higher mobility and carrier concentration. Rapid thermal annealing yielded significant improvements in carrier mobility for short annealing times (10 s), improvements in mobility were lost at longer annealing (in an N$_2$ ambient) times and annealing times greater than 60 s returned carrier mobility to as deposited levels. Carrier concentration was mostly unaffected by annealing. Increased Al content led to an increase in carrier concentration, but the authors noted that the Al content did not necessarily reflect the amount of Al forming electrically active impurity defects. The highest mobility achieved was 40 cm$^2$ V$^{-1}$ s$^{-1}$ and the lowest resistivity $2 \times 10^{-4}$ Ω.cm. This work suggests that little advantage is gained in depositing ZnO at substrate temperatures greater than 250 °C.

For applications requiring thicker films, growth rate is of critical importance. “Smart windows” (intelligently tinting) often require thick transparent conducting oxide coatings, with very large area coverage. With this requirement in mind, Mendelsberg et al. [74] reported on ZnO: Al films deposited with high growth rates (>250 nm min$^{-1}$). The authors highlight the cathode to substrate distance as an important factor in determining growth rate and film quality. For growth of optical or electronic coatings, a magnetic filter in an FCVA is necessary for minimisation of macro particle incorporation. This requirement necessitates longer cathode to substrate distance. With this increased path length depositing ions lose more kinetic and potential energy, an effect further exacerbated during reactive depositions at higher growth pressures. Employing a substrate bias can compensate for this but can also lead to self-sputtering of the film and a greater concentration of defects. In order to reduce this effect without compromising film quality and to increase the growth rate, the authors made a more compact FCVA system, reducing the cathode to substrate distance by a factor of 2. The authors were able to produce films with a mobility of 30 cm$^2$ V$^{-1}$ s$^{-1}$ using room temperature growth and mobilities as high as 60 cm$^2$ V$^{-1}$ s$^{-1}$ with elevated growth temperatures. Applied bias significantly above the self-bias that is caused by the ionised plasma stream has been found to offer little benefit in ZnO film microstructure for TCO application.

Reports on Zn$_{1-x}$Mg$_x$O grown by FCVA are fewer. Goh et al. [75] reported on LEDs fabricated using FCVA deposited n-Zn$_{1-x}$Mg$_x$O and p-GaN. Whilst a device was presented, material characterisation was limited. Yang et al. [76] report on lasing action from Zn$_{1-x}$Mg$_x$O thin films deposited with varying Mg fraction x. Here, the authors present data on the structural characterisation and optically stimulated light emission but no electrical
characterisation. Tsang et al. [77] report on heterostructure based ZnO/Zn$_{1-x}$Mg$_x$O films for use as waveguides. Films were grown in a two source FCVA system (one Zn source one Zn+Mg source). These articles all describe growth of Zn$_{1-x}$Mg$_x$O using FCVA, however none provide electrical characteristics of the Zn$_{1-x}$Mg$_x$O layers. This leaves unanswered questions; can the electrical characteristics be tuned in FCVA deposition and does energetic deposition benefit carrier transport in Zn$_{1-x}$Mg$_x$O?

1.4.2.2.3 High power impulse magnetron sputtering

HiPIMS is an emerging energetic sputtering technique in which a high power density (up to several kW cm$^{-2}$) is applied to the target in short pulses (40-200 µs) with a long duty cycle (~100-200 Hz). HiPIMS provides a much greater degree of ionisation when compared to direct current magnetron sputtering (DCMS) or radio frequency magnetron sputtering (RFMS). Whilst the average power density is similar to DCMS, the peak power is much higher due to the very high voltage pulses. This results in films with higher densities than those deposited by DCMS with the same average power density. HiPIMS has so far been employed primarily in the tribological coating industry but has demonstrated potential for growth of optical and electronic coatings [78, 79].

There are two methods of producing oxides using magnetron sputtering deposition. It is possible to use a ceramic target with the stoichiometry of the desired film. Alternatively a metal target can be used in a reactive environment. Should the metal target be used, a compound layer on the target surface may form depending on the reactive gas partial pressure. When using a ceramic target or a metal target in the compound forming regime high energy O$^-$ ions can cause film damage. In order to avoid these negative oxygen ions a metal target operating in the non-poisoned mode is required. When using magnetron sputtering to grow ZnO using a Zn metal target and an oxygen ambient, the target surface will oxidise. The oxide will have greater electrical resistance compared to the metal target, increasing the probability of arcing and variable deposition rates. When the reactive gas flow rate is varied during a deposition, a hysteresis effect becomes apparent. The oxide layer forms at a given partial pressure but is removed only at a lower partial pressure than that at which it was originally formed. These effects can be eliminated when operating in HiPIMS mode by moderating pulse length.

Kubart et al. [80] studied the deposition of TiO$_2$ using HiPIMS. Of particular interest to the author was developing a method for growth of stoichiometric oxides using HiPIMS without the need for a feedback loop. The author suggests that the oxidation of the target maybe related to the rarefaction of reactive gasses around the target. When a pulse is initiated the plasma flux will cause rarefaction of the reactive gas in the vicinity of the target. If the off time (time between pulses) is greater than the refill time, a compound layer will form. Armed with this knowledge, partial pressures and pulse frequency could be optimised to avoid transition between the compound and metal regimes. Pulse length was found to be a key factor in determine if the target in a reactive deposition would operate in the metal or compound regime [81]. Shorter pulse led to the target operating in compound monde and longer pulses enabled metallic operation.

Audronis et al. [82] examines reactive deposition using HiPIMS with several target/gas combinations. A key finding was that the oxidation/nitriding of the target depends on the history of use. Also the target cleaning times (unreactive ablation of the target) is significantly greater when compared to DCMS, this is due to energetic ions being implanted forming a thicker compound layer. This is an important consideration for
commercial use as manufacturers will want to maximise the yield from the target so cannot use a new and unablated target for each deposition, or devote significant machine time to removal of the oxide/nitride layer. In order to control the deposition rate and stoichiometry of films deposited using reactive HiPIMS careful selection of pulse length is required.

As HiPIMS is a relatively new energetic deposition method there are limited reports describing its use for ZnO synthesis. Konstantinidis et al. [79] compared the structural and optical properties of ZnO deposited on glass by HiPIMS and DC bipolar pulsed magnetron sputtering (DCBPMS). HiPIMS provided a lower deposition rate but a higher film density and lower surface roughness when compared to the DCBPMS. Both films showed greater than 80% transmission across the visible range with nearly identical transmission spectra. No electrical characterisation was presented in this article.

HiPIMS has also been used to produce Al doped ZnO [83] using a an Al electrode placed in the plasma plume which is then sputtered by energetic ions ejected from the sputter head. The Al content was controlled by applying a variable DC bias to the Al electrode, a larger bias led to a greater Al content. HiPIMS ZnO: Al has also been prepared using a more conventional alloyed Zn/Al target [84].

1.4.2.2.4 Comparison between HiPIMS and conventional magnetron sputtering

Magnetron sputtering uses a conventional sputter head and fixed magnet to confine the ionised sputtering gasses close to the target in order to facilitate a greater number of collisions. Neutral particles will not be confined by the fixed magnets and instead will be ejected then allowed to condense on the substrate forming a film.

The degree of ionisation in magnetron sputtering is low [85]. As such, in order to increase the landing energy of the depositing flux, a very large bias’, in the order of several kV, must be applied in order to alter the film properties appreciably [86]. The ionisation of the sputtered material (originating from the target) is usually less than 1 % [87] with the remainder of ionised species made up of the Ar⁺. This can lead to Ar being incorporated into the film. This is particularly the case when applying a substrate bias of several kV. This can lead to lattice defects [88] which will affect the electrical performance of films.

HiPIMS manages to increase the degree of ionisation in the flux by applying power in short pulses with a long duty cycle. This ensures that the average power density remains similar to conventional magnetron sputtering but the peak power and hence degree of ionisation increases. This process is further explained by Figure 6 which shows a diagrammatic representation of conventional magnetron sputtering (Figure 6 (a)) and HiPIMS (Figure 6 (b)).
HiPIMS is well suited for producing conformal coatings to rough substrates. A low applied bias or even floating potential can aid in producing a more conformal coating when compared to DCMS [89]. The ionised flux of HiPIMS combined with a biased substrate will tend to cause growth normal to the surface with minimal dependency on the orientation relative to the depositing flux vector. HiPIMS produces denser films than DCMS or RFMS. The kinetic and potential energy of the ionised particles ensures adatoms have sufficient mobility to fill voids in the growing film. HiPIMS can be implemented in a conventional sputtering system by only changing the power supply to one that can support short pulses at a high power.

The properties and features of HiPIMS make it a suitable candidate for growth of stoichiometric oxides on a range of substrates without the need for high substrate temperatures. The energetic plasma will serve to ionise the ambient reactive gas aiding in the formation of stoichiometric films. The energetic flux will assist in forming oriented crystalline phases and aid in the growth of conformal coatings on 3D substrates. The energetic flux will minimise the effects of substrate on the microstructure of films so that similar microstructures and electronic properties can be achieved on a range of substrates. Energetic ions will assist with enhanced film adhesion improving coating durability’s. These properties of HiPIMS set this method apart from conventional magnetron sputtering as a method that shows promise for use in advanced electronic and optical device manufacture.

1.4.2.2.5 Conclusions on the different coating options

Table I summarises the advantages and disadvantages of the growth methods used to prepare ZnO and related materials. The techniques able to produce the best quality ZnO films are also often the most costly both in terms of time, capital and ongoing running costs. This suggests there may be a niche where some quality can be sacrificed in order to produce films in a low cost commercially scalable way without the need for significant investment as part of setup costs.
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Table I: A summary of the advantages and disadvantages of the thin film growth methods discussed here and in the introduction chapter.

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBE</td>
<td>High purity, less contamination related defects, Excellent crystallinity (approaches single crystal)</td>
<td>High cost</td>
</tr>
<tr>
<td>MOCVD</td>
<td>High quality crystalline growth</td>
<td>High process temperature (700-1100 °C)</td>
</tr>
<tr>
<td>FCVA</td>
<td>Larger area deposition, Energetic plasma, Low cost, High density films</td>
<td>Can only use a conducting source material, Cathode (source) poisoning, Relatively untested in the area of thin film growth for electronic materials, Macroparticles will not be completely removed</td>
</tr>
<tr>
<td>PLD</td>
<td>Possible to use insulating ceramic targets, Good transfer of stoichiometry from target to film.</td>
<td>Very small deposition area (1-3 cm²), Large area capability, Poisoning effects</td>
</tr>
<tr>
<td>HIPIMS</td>
<td>Extensive control over depositing flux, High density films, Easy to implement in conventional sputtering systems, No marcoparticles</td>
<td>Difficult to produce stoichiometric oxides with high deposition rate</td>
</tr>
<tr>
<td>ALD</td>
<td>Self-limiting process maintains stoichiometry, excellent thickness control</td>
<td>Very Low growth rates (nm h⁻¹)</td>
</tr>
</tbody>
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1.5 Conduction in ZnO

Intentional hydrogen incorporation has been achieved using a range of methods including high temperature annealing [90], remote plasma immersion [91], and ion implantation [92]. Due to the native n-type character of ZnO, p-type doping requires the addition of compensating acceptors before effective doping can occur. Although there have been some successes [24, 93, 94] the long term stability of p-type doping is yet to be demonstrated.

1.5.1 Intentional and unintentional doping

ZnO in both the bulk and thin film form exhibits n-type conductivity natively. Some applications can make use of the high level of n-type conductivity. Many optoelectronic devices however require precise control of doping and the ability to make p-type material. In order to gain control over the carrier concentration it is necessary to reduce the concentration of native defects and incorporation of impurities.

One crucial step in controlling conductivity is to understand the origin of n-type conductivity in ZnO. Unintentional impurities are a problem in ZnO, and are often very difficult, if not impossible, to remove. Impurities originate from source material or precursor gasses. They can also diffuse out of substrates or from process chamber walls. Even in a UHV chamber such as those used in MBE growth, residual gasses are present,
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mostly hydrogen. Modern techniques for quantifying impurities at very low concentrations, such as secondary ion mass spectrometry (SIMS), have opened up new possibilities for understanding impurities in ZnO [95].

Accurately determining the stoichiometry of films is challenging. Techniques that observe the surface will inevitably be dogged by the presence of chemisorbed surface species, while methods that use etching to gain information about the bulk will suffer from the introduction of unintended defects/changes to the measured volume. Even if stoichiometry can be precisely measured the balance may be made up by precipitates, clusters or extended defects such as grain boundaries.

Point defects have often been identified based on changes in conductivity as a function of oxygen partial pressure in the process chamber. This method however, is flawed. A change in oxygen partial pressure produces multiple effects. The absence of oxygen may result in the formation of additional oxygen vacancies. But for example, the presence of oxygen vacancies can result in increased occupation of hydrogen in oxygen vacancy (\(V_O\)) sites (\(H_O\)). The long held belief that oxygen vacancies are related to n-type conductivity was largely drawn from the aforementioned changes in conditions with oxygen pressure however this method does not unambiguously identify oxygen vacancies as the source of conductivity.

The ability to produce p-type conductivity is of great importance to many devices. There have been reports describing p-type material [24, 96-102] but reliability and reproducibility are still problematic. There has been some controversy in the interpretation of results [103] and as yet no p-n junctions have been produced using ZnO.

To employ semiconductor materials as an active device layer in electronics applications, high quality rectifying and ohmic electrodes must be achievable. Whilst the ability to form PN junctions is desirable, and has so far eluded ZnO, this does not mean that ZnO cannot be used to make devices that are technologically important.

1.5.2 Native point defects in ZnO

Intrinsic defects or native defects are crystal defects that involve only the constituent elements [104], as opposed to impurity defects. Intrinsic defects include vacancies, the absence of an atom at a regular lattice position where one is expected and interstitials, the addition of an atom occupying the space between regular lattice atoms. Antisites occur where an atom occupies a regular lattice position it is not expected to, for example in ZnO if Zn occupies an O lattice position or O occupies a Zn lattice position. Intrinsic defects can play a major role in the optical and electronic properties of a semiconductor. Understanding the nature of native defects is therefore important for growing device quality material that will perform reliably and reproducibly. This is particularly the case for ZnO where point defects play a significant role in the character of conductivity. Intrinsic defects for the most part will be more easily formed if they compensate for the prevailing conductivity, *i.e.* donor defects are more easily formed in p-type material and acceptor defects are more easily formed in n-type material. Native defects have often been identified as the cause of the native n-type conductivity observed in ZnO. Specifically, oxygen vacancies were historically considered to be the cause of n-type conductivity [34-45]. This conclusion was based on experiments where the oxygen partial pressure was altered and changes in conductivity were observed that appear to correlate with oxygen deficiency. The nature of native defects has been investigated with the aid of density functional theory calculations in order to accurately
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determine the probability of their occurrence and their role in transport properties. DFT calculations performed by Janotti and Van der Walle determined the formation energy for native point defects in O-rich and Zn-rich regimes. Figure 7, taken from [23], shows the formation energy of ZnO native point defects.

![Figure 7: Formation energies of native point defects as a function of Fermi-level position in ZnO for (a) Zn-rich and (b) O-rich conditions.](image)

Zero on the Fermi level scale corresponds to the valence-band maximum. Only segments corresponding to the lowest energy charge states are shown. The slope of the segments indicates the charge state. Kinks in the curves indicate transitions between different charge states. (this figure has been taken from Janotti and Van de Walle [23])

1.5.2.1 Defect concentrations and formation energies
When considering the role native defects play in the conductivity of ZnO, it is necessary to define their formation energy. The formation energy, denoted $E_f$, affects the concentration of defect sites according to Equation (1) [105], where $c$ is the concentration, $N_{sites}$ is the number of sites; $k_B$ is the Boltzmann’s constant and $T$ is temperature. This equation assumes equilibrium conditions.

$$c = N_{sites} \exp \left( \frac{-E_f}{k_B T} \right)$$

(1)

The formation energy $E_f$ is a free energy, however, the formation volume and formation entropy are not explicitly included. The formation entropy is factored into the derivation [105]. The formation volume is the change in volume when a defect is present; in the dilute regime at low pressure it will be negligible and as such is not included.

The formation energy of native defects can be ascertained using density functional theory (DFT). The formation energy of a given point defect will depend on the growth or annealing conditions. An example would be the formation of an oxygen vacancy which will depend on the relative abundance of the Zn and O atoms. If the defect is charged the formation energy will also depend on the Fermi level, the energy of the electron reservoir.

1.5.2.2 Defect transition levels
Many defects are electrically active and introduce levels in the bandgap. These defects will transition between different charge states [106, 107]. Defect transition levels will determine if a defect will be considered deep or
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shallow. If a defect can be ionised at room temperature, it is considered shallow. If it is unlikely to be ionised at room temperature it is considered deep.

1.5.2.3 Migration barriers and diffusion activation energies

Adding to our knowledge of formation energies and the electronic properties of defects is an understanding of how point defects migrate within the wurtzite structure. Knowledge of migration gives an understanding of how defects form during growth/annealing and how defects diffuse as well as how impurities will be incorporated, a process that is most often governed by point defects. Defect migration is often studied by introducing defects via processes like electron irradiation or ion implantation. The electronic or magnetic responses of these defects are monitored as a function of annealing temperature. When the electronic or magnetic signatures change, it is an indication that the defects have become mobile. Using this information it is possible to determine the activation energy. Given the time consuming nature of such experiments, transition state theory \[108\] is often used to ascertain these values. For either of these techniques it is assumed that changes are the result only of defect migration and not any other process such as the formation of complexes.

1.5.2.4 Oxygen vacancies

Oxygen vacancies in ZnO are the most discussed native defect in ZnO. Oxygen vacancies have often been suggested as the origin of n-type conductivity of ZnO. The $V_0$ defect has the lowest formation energy of any native defect in ZnO (3.72 eV in a neutral charge state) \[23\] and acts as a donor in ZnO. DFT has shown that $V_0$ is too deep to be the origin of n-type conductivity in ZnO \[109-111\]. However, $V_0$ remains an important defect. In n-type ZnO, when the Fermi level is near the conduction band minimum (CBM), $V_0$ will assume a neutral charge state; however in p-type material when the Fermi level is at the valence band maximum (VBM) it will assume a $+2$ charge state, as such it could be the source of compensation in p-type ZnO. In order to avoid formation of this defect when attempting to make p-type material, it is necessary to ensure growth conditions are O-rich.

1.5.2.5 Zn vacancies

The Zn vacancy defect ($V_{Zn}$) forms most readily in O-rich conditions. $V_{Zn}$ results in four O dangling bonds that combine into a doubly occupied symmetric $a_1$ state located deep in the valence band, and three almost degenerate states in the band gap, close to the VBM. These three states are partially occupied by a total of four electrons and, therefore, can accept up to two additional electrons, explaining the acceptor behaviour of $V_{Zn}$ in ZnO. The formation of energy $V_{Zn}$ increases substantially as you move towards the VBM making formation of the defect unlikely in p-type material. This means that the defect will not play a role in conduction in p-type ZnO despite acting as an acceptor.

1.5.2.6 Zn interstitials

Zn interstitials can occupy an octahedral site or a tetrahedral site. The tetrahedral site has one Zn and one O atom as its nearest neighbour at a distance of 0.833 times the length of the non-defective Zn-O bond length. At the octahedral site, a Zn interstitial ($Zn_i$) will have three oxygen and three Zn atoms as nearest neighbours at a distance of 1.07 times the normal bond length. The difference in available space in the lattice structure makes
the octahedral site the more stable of the two sites. The tetrahedral site has an energy 0.9 eV higher than the octahedral and will relax into the octahedral site spontaneously [110, 111]. Zn will induce a state with two electrons above the CBM. These electrons will be transferred to conduction band states which stabilize the \(\text{Zn}^{2+}\) charge state. So the \(\text{Zn}^{\text{i}}\) defect will always donate electrons and act as a shallow donor. As seen in Figure 7, the formation energy of the \(\text{Zn}^{\text{i}}\) defect is high when the Fermi level is near the CBM, this is the case in n-type material, this remains the case in the more favourable Zn-rich condition. The high formation energy of \(\text{Zn}^{\text{i}}\) means that it is unlikely to be responsible for n-type conductivity as it will only occur in very low concentrations. As the Fermi level moves towards the VBM, as is the case for p-type material, the formation energy reduces substantially, so the \(\text{Zn}^{\text{i}}\) could act as a compensating donor in p-type material.

1.5.2.7 Zn antisites, oxygen interstitials and oxygen antisites

The remaining ZnO point defects, Zn antisites (\(\text{Zn}^{\text{O}}\)), oxygen antisites (\(\text{O}^{\text{Zn}}\)) and oxygen interstitials (\(\text{O}^{\text{i}}\)) all have high formation energies and therefore do not occur in concentrations high enough to affect conductivity in ZnO.

1.5.2.8 Summary of defects and their role in ZnO

In summary, oxygen vacancies are deep donors so despite their low formation energy, they are unlikely to be responsible for observed n-type conductivity. However, \(V_{\text{o}}\) may inhibit p-type conductivity. Zn vacancies are deep acceptors with a low formation in n-type conditions and will therefore compensate n-type conductivity. Oxygen interstitials can either be deep acceptors or be electrically inactive depending on the configuration; they have a high formation energy and will not occur in significant concentrations. Zn interstitials are shallow donors but given their high formation energy in n-type conditions, are unlikely to play a significant role in observed n-type conductivity. Oxygen antisites are deep acceptors with the greatest formation energy among the native point defects in ZnO and therefore will not have a significant effect in either n- or p-type conductivity. The Zn antisite has a large formation energy and will act as a shallow donor.

The migration barriers for ZnO native point defects are low which explains the rapid recovery of ZnO after ion implantation even at low annealing temperatures. All point defects are mobile during the most commonly used growth conditions.

1.5.3 Donor impurities

Experiments and calculations performed to date suggest that ZnO native defects are very unlikely to be the origin of the inherent n-type conductivity in ZnO. The next section discusses impurities as a source of n-type conductivity. Some of the common impurities and their character are shown in Table II.
## Table II: Summary of impurity defects in ZnO

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Character</th>
<th>Energy level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Donor [112]</td>
<td></td>
</tr>
<tr>
<td>Ga</td>
<td>Donor [113]</td>
<td>shallow</td>
</tr>
<tr>
<td>In</td>
<td>Donor [114]</td>
<td>shallow</td>
</tr>
<tr>
<td>B</td>
<td>Donor</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>Donor [112]</td>
<td>shallow</td>
</tr>
<tr>
<td>H</td>
<td>Donor [115]</td>
<td>shallow</td>
</tr>
<tr>
<td>Li</td>
<td>Donor (Li) [116] or Acceptor(Li$_2$) [117]</td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>Acceptor [118]</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>Acceptor</td>
<td>Deep [119]</td>
</tr>
<tr>
<td>As</td>
<td>acceptor</td>
<td>Deep [120]</td>
</tr>
<tr>
<td>P</td>
<td>acceptor</td>
<td>Deep [120]</td>
</tr>
<tr>
<td>Sb</td>
<td>acceptor</td>
<td>Shallow [121]</td>
</tr>
<tr>
<td>Ag</td>
<td>acceptor</td>
<td>Deep [119]</td>
</tr>
<tr>
<td>Au</td>
<td>acceptor</td>
<td>Deep [119]</td>
</tr>
</tbody>
</table>

### 1.5.3.1 Boron, aluminium, gallium and indium

Group 13 elements, B, Al, Ga, and In act as donor impurities in ZnO. These elements substitute for Zn in the wurtzite lattice where they act as shallow donors. Ga doping has been demonstrated in ZnO [113] with crystal quality maintained at high concentrations. Al dopant concentrations of up to $8 \times 10^{20}$ cm$^{-3}$ have been achieved in CVD grown ZnO [113]. In has also been demonstrated as a donor in ZnO [122]. Using MOCVD growth, n-type conductivity using boron has been achieved [123]. However, despite acting as n-type carriers, these elements cannot explain the inherent n-type conductivity seen in nearly all bulk and thin film ZnO. They are certainly not present in all methods and are never present in sufficiently large quantities without intentional addition.

### 1.5.3.2 Fluorine

Fluorine acts as a shallow donor when substituting with oxygen at a regular lattice position. This defect has an ionisation energy of 80 meV [124] and a low formation energy. This ensures it is incorporated into the ZnO lattice easily. Intentional F doping of ZnO has been achieved with n-type carrier concentrations of $5 \times 10^{20}$ cm$^{-3}$ [112].

### 1.5.3.3 Hydrogen

Hydrogen has emerged as one of the most important impurity dopants in ZnO. In most semiconductors, hydrogen is an amphoteric impurity, meaning in a p-type material it will act as a donor and in an n-type material it will act as an acceptor, counteracting the prevailing impurity [125-127]. This is not the case in ZnO,
where H occurs in the positive charge state and always acts as a donor. Recent work has shown that interstitial hydrogen can occupy two possible sites in the ZnO lattice and act as a shallow donor [17, 128]. The bond centre site (BC) or the antibonding site (AB\textsubscript{0}), both have comparable formation energies. The incorporation of hydrogen results in significant lattice relaxations. Hydrogen impurities can also be incorporated on the site of an oxygen vacancy. In this case, hydrogen is equally bonded to the four nearest neighbour Zn atoms [128]. This defect, substitutional hydrogen (H\textsubscript{0}), occurs exclusively in the positive charge state H\textsuperscript{+}. Both the substitutional and interstitial forms of hydrogen incorporation have low formation energies [128]. So they can occur in high concentrations. Whilst not the only candidate for the source of n-type conductivity, its pervasive nature means hydrogen is probably the primary source of shallow donors in ZnO. Many growth techniques provide a supply of hydrogen during growth either intentionally, such as in CVD or unintentionally, such as in MBE. In addition, hydrogen can be introduced via wet chemical etching as part of a photolithography step or during annealing in forming gas (a H\textsubscript{2}(5%)N\textsubscript{2}(95%) processing gas).

Experiment has shown that hydrogen can be incorporated into ZnO via annealing [129], implantation [130, 131], or remote plasma exposure [132-134] and is stable up to ~500 °C. This is consistent with the very mobile interstitial hydrogen but with by the much more stable substitutional hydrogen. The often observed effect of varying O partial pressure resulting in changes in conductivity, most often attributed to V\textsubscript{O} can be more adequately explained by the presence of H\textsubscript{0}. Lavrov et al. [134] identified two shallow H donors in single crystal ZnO after introducing hydrogen by DC plasma immersion and annealing. Bond-centered hydrogen tended to be unstable during annealing at moderate temperatures (~190 °C). However, in oxygen-poor ambient this hydrogen became bound within the oxygen vacancies left by the out-diffusing oxygen and in this location, the substitutional hydrogen (H\textsubscript{0}) proved more stable. Thus, in oxygen poor depositions H\textsubscript{0} is more likely leading to higher n-type carrier concentrations.

1.5.4 Acceptor impurities

Acceptor impurities in ZnO have received considerable interest in the hunt for stable and reproducible p-type conductivity. Nitrogen is considered the most promising of the p-type doping candidates. The similar atomic size of nitrogen when compared to oxygen means that a N\textsubscript{0} defect will produce minimal lattice strain. There are numerous reports of p-type conductivity using nitrogen doping [24, 116, 135, 136] Other candidates for p-type impurity dopants are Li, Na, K, Cu, P, As, and Sb.

1.5.4.1 Co-doping

Co-doping is a method of used to overcome prevalent native conductivity by doping with both acceptors and donors. In the case of ZnO, where n-type conductivity is the prevalent, addition of donors during growth will result in reduced formation energy for acceptor impurities. The introduction of donors will shift the Fermi level away from the VMB toward the middle of the E\textsubscript{g}. This will result in lower formation energies for acceptors which will give greater acceptor solubility. In addition the shift in the Fermi level will cause increased formation energies for donor point defects such as oxygen vacancies. The problem with such a strategy is that donor impurities will still be present after growth. To avoid this problem donor defects that are weakly bound and will
diffuse readily can be used. A donor impurity with these properties could be removed using a post growth annealing step at a moderate temperature.

This method has been employed experimentally to achieve p-type conductivity. Using N as an acceptor impurity whilst co-doping with Ga, the report gave a hole concentration of $4 \times 10^{19} \text{ cm}^{-3}$ [137], however there has been difficulty in reproducing this result and other authors have been critical of the result [138]. In this project p-type doping of ZnO or $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ was not attempted and it is not discussed further in this thesis.

1.6 Surface chemistry

The surface chemistry of semiconductors is of vital importance to device fabrication. Surfaces will become interfaces when an electrode is deposited onto a semiconductor surface. The nature of the surface chemistry will affect the performance of ohmic and rectifying contacts. There has been difficulty in forming rectifying contacts to ZnO. Au, which theory suggest, would form a Schottky contact to ZnO due to its high work function and inert nature (Au will not oxidise and draw oxygen from the ZnO surface), instead forms an ohmic contact on an as-grown ZnO surfaces [139]. It has been shown that the reason for this behaviour is the presence of surface states (oxygen vacancies and chemisorbed OH- groups) that result in a charge accumulation layer at the surface. Using an in-situ O/He plasma treatment prior to contact formation can remove the OH- will result in a rectifying Au contact [139]. A diagram of OH- attached is shown in Figure 8.

![Figure 8: Models of the ZnO surface for (a) a bulk terminated face and (b) an OH- terminated face. Taken from [140]](image)

<table>
<thead>
<tr>
<th>(a) Bulk-Terminated</th>
<th>(b) (1 x 1) OH Covered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn-polar face</td>
<td>(1 x 1) H Covered</td>
</tr>
<tr>
<td>$\frac{1}{2} e$</td>
<td>$\text{Zn}$</td>
</tr>
<tr>
<td>$\frac{1}{2} e$</td>
<td>$\text{O}$</td>
</tr>
<tr>
<td>$\frac{3}{2} e$</td>
<td>$\text{H}$</td>
</tr>
<tr>
<td>$\frac{3}{2} e$</td>
<td></td>
</tr>
</tbody>
</table>

There has been little difficulty in achieving reliable ohmic contacts to ZnO. The most common material used for ohmic contacts is Au with a Ti adhesion layer [141] but Al ohmics have also been shown to be effective [142]. There was initial difficulty in forming good rectifying (Schottky) contacts due to the prevalence of adverse surfaces states, such as chemisorbed hydroxyls [143] and oxygen vacancies near the surface [143]. Hydroxyl attachment is due to the polar surface of ZnO. These surface states lead to a charge accumulation layer resulting in band bending at the surface [144]. These surface states inhibit the formation of low leakage
rectifying (Schottky) junctions. Some authors have made use of an oxygen plasma treatment, which removes attached OH\(^-\) groups without damaging the surface prior to contact formation [143]. By using a pure oxygen plasma as opposed to an Ar\(^+\) plasma (commonly used for surface cleaning) surface damage is minimised. Surface damage can lead to inhomogeneity when forming a rectifying contact, which can result in increased leakage in a rectifying junction [145]. Recently however, Allen et al. showed that very high quality rectifying junctions (with an ideality approaching unity) are achieved with partially oxidised noble metal contacts [146].

The use of an active oxygen ambient during contact formation has been shown to both passivate oxygen vacancies (a common native defect) and remove chemisorbed surfaces hydroxyls.

Due to the polar nature of the wurtzite ZnO and Zn\(_{1-x}\)Mg\(_x\)O surface, significant hydroxyl attachment occurs on the surface of thin films. This results in a charge accumulation layer at the surface and downward band bending, making formation of rectifying junctions difficult. In order to overcome this limitation, these surface contaminants must be removed prior to junction formation. This process is typically performed \textit{in-situ} prior to laying down rectifying contacts [147]. Alternatively, it has been achieved by reactively depositing noble metal anodes in the presence of oxygen [146, 148].

\(V_o\) act as a deep donor \(\sim 0.7-1.0\) eV below the conduction band [109, 149] and has been shown to pin the Fermi close to the \(V_o\) defect level. Oxygen vacancies at the surface are therefore significant in determining the quality of Schottky junctions [149].

Both the attachment of OH\(^-\) to the surface and the presence of near surface \(V_o\) will reduce the Schottky barrier height, resulting in increased leakage current and lower ideality. Methods of surface treatment are required in order to passivate oxygen vacancies and remove chemisorbed molecules before contact formation. Methods that can be performed \textit{in-situ} are required as exposure to atmospheric water vapour quickly leads to reattachment of chemisorbed OH\(^-\).

\textbf{1.7 Applications}

Currently, the single largest use of ZnO is as an additive for natural rubbers where it is an anti-fungal agent and aids in the vulcanisation process. ZnO has been used as a white pigment in paints as a replacement for Pb. Whilst ZnO suffers from cracking with age it is not toxic to humans, unlike Pb. The common sun block known as "zinc" and popularised by cricketers is based on ZnO powder and exploits its deep UV absorption properties.

The primary electrical application for ZnO thus far is as varistors. Over the last 10 years new optoelectronic applications for ZnO have emerged. Degenerately Al doped ZnO has been employed in "smart" or electrochromatic (electronically tinted) windows [150]. In a 2012 press release, Sharp presented a display which employs an amorphous InGaZnO based high resolution high pixel density (140 ppi) panel. This is one of the first examples of ZnO-based materials being used in high volume consumer electronics.

Emerging applications currently discussed in the literature include ZnO and Zn\(_{1-x}\)Mg\(_x\)O based field effect transistors, photo-detectors and emitters. The applications explored in this thesis are confined to Schottky junctions and visible blind UVA & UVB photo-detectors.
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1.7.1 Properties and device applications

ZnO has a range of desirable properties that have long been considered useful for optoelectronic applications. The most outstanding property of ZnO is its wide bandgap which enables optoelectronic devices in the blue and UV regions. The desire for material suitable for devices that operate in the UV region has driven significant research in developing both thin film [24, 151, 152] and bulk [29, 153, 154] ZnO.

ZnO has a large exciton binding energy (60 meV [155, 156]) enabling efficient excitonic emission at room temperature and above. When ZnO is compared to a similar compound semiconductor, such as GaN which has an exciton binding energy of 25 meV, it easy to see why there is such a significant interest in investigating ZnO.

Piezoelectric materials will deform under an applied potential, or, generate a potential when deformed. ZnO has large piezoelectric constants; this property originates from the low symmetry of the wurtzite structure and the large electromechanical coupling in ZnO. The piezoelectric properties of ZnO have been demonstrated using a range of techniques including molecular beam epitaxy, sputtering and chemical vapour deposition [157-164].

The surface conductivity of ZnO is very sensitive to chemisorbed species. This sensitivity can be exploited, to enable gas sensing. And ZnO chemical sensors have for example, been used to assess food freshness. This is possible due to the high sensitivity to trimethylamine [165].

The high thermal conductivity of ZnO is perhaps its most exploited property. ZnO has been used in rubber to aid in the vulcanisation process and to increase the thermal conductivity of car tyres. This high conductivity is also useful when using ZnO as a substrate as it can aid in the removal of heat from devices.

The availability of single crystal ZnO is of interest for thin film growth. Single crystals enable homoepitaxial growth of ZnO and heteroepitaxial growth of materials with similar structure such as GaN, where the use of a well matched substrate reduces the number of extended defects limit the performance of devices.

ZnO can be etched using several different solutions [166-168] making it well suited to the photolithographic techniques employed in semiconductor device manufacturing. This can be performed at low temperatures, adding flexibility to the fabrication process. The radiation hardness of ZnO makes it well suited to devices that inhabit extreme environments, such as high altitude and satellite applications as well as terrestrial based applications that encounter radiation, such as nuclear power plants [18].

In addition to the properties described above, the bandgap of ZnO can be altered through the addition of Cd or Mg. The addition of Cd reduces the bandgap, giving access to bandgaps in the blue-green region of the visible spectrum. Through the addition of Mg, it is also possible to increase the bandgap up to 4.0 eV whilst maintaining the wurtzite structure, thus giving access to the UVA and UVB regions. This adds further to the potential applications of ZnO in emitter and detector type devices. ZnO has been considered for use in flexible thin film transistors. When compared to amorphous Si and organic semiconductors, ZnO has a high electron mobility [169-171], giving it a potential edge in applications such as flexible transparent displays. Its flexibility in amorphous and/or polycrystalline form has been demonstrated [172].
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1.7.2 UV sensing using ZnO and Zn_{1-x}Mg_{x}O

An important application for ZnO, and in particular Zn_{1-x}Mg_{x}O application explored in this work, is visible blind photodetectors. The visible blind capabilities of the Zn_{1-x}Mg_{x}O based devices are achieved via bandgap tuning to create a sufficiently wide bandgap such that low energy visible light will not be able to excite carriers into the conduction band.

The internal photoelectric effect is the basis for modern photodetectors \[173\]. A photon incident on a semiconductor material excites a carrier from the valence band into the conduction band. The additional carriers available for conduction decrease the semiconductor resistance, causing an increase in the current flowing through the device.

Quantum efficiency is the probability that an incident photon will result in the generation of an electron hole pair that will contribute to the photocurrent. Quantum efficiency is sometimes referred to as spectral response due to its wavelength dependence. Equation (2) defines quantum efficiency.

\[
\eta \equiv \frac{\text{Number of photogenerated carriers}}{\text{Number of incident photons}}
\]

There are several designs for UV photodetectors that are compatible with ZnO and Zn_{1-x}Mg_{x}O. These include; photoconductors, MSM photodetectors, Schottky photo diodes and p-n junctions (in this case an alternate p-type is used such as p-GaN \[75\]). This work will focus on the MSM structure or back-to-back Schottky junction structure.

Some of the common device structures will be presented below. A photoconductor type detector consists of two ohmic electrodes connected to a piece of semiconductor material. A schematic representation of this device structure is shown in Figure 9 (a). This type of detector will function as a resistor in which the current will drop under UV exposure \[173\]. Incident light of sufficient energy will generate electron-hole pairs resulting in a greater availability of charge carriers which will reduce the resistance of the semiconductor material. The signal is measured by looking at the voltage drop across a high resistance placed in series with the semiconductor material. The advantage of a photocurrent detector is its high internal gain leading to a greater photo response negating the need for amplification. The internal gain however is nonlinear with respect to photon flux, and as such this must be considered in order to make quantifiable measurements. Other issues associated with a photocurrent detector are poor UV:Visible rejection ratio and issues with persistent photoconductivity \[174\].
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Figure 9: Schematics of some common photodetector types, (a) a photocurrent detector, (b) a PN junction photodiode, (c) an MSM photodetector and (d) a Schottky photodiode detector.

A p-n photodiode (Figure 9(b)) uses p- and n-type semiconductor material to form a p-n junction. In operation a bias is applied across this junction. Incident light will generate additional electron hole pairs which will result in an increase in current that is proportional to the incident light. The advantage of a p-n junction type detector is its sensitivity at low temperatures.

A metal-semiconductor-metal junction (Figure 9(c)) consists of a semiconductor substrate supporting with two metal (or semimetal, such as graphitic carbon) Schottky contacts. When a bias is applied across the two Schottky contacts the current is proportional to the incident photon flux. The advantages of this device structure are high speed performance and the ease of integration [175].

Materials suitable for ZnO are generally suitable for use with Zn$_{1-x}$Mg$_x$O due to the very similar electron structure and surface states [176]. Schottky contacts that have been shown to be particularly effective include sub-stoichiometric noble metal oxides [146]. Recently, graphitic carbon ZnO Schottky diodes have exhibited good ideality factors. The graphite was applied in the form a dag or paint consisting of graphite flakes suspended in a solvent such as ethanol or isopropyl alcohol [177].

There are limitations on the sensitivity of a Schottky (MSM) photodetector namely, the device area, operation temperature, and persistent photoconductivity. The device area will set a limit on the number of photons captured. The temperature if sufficiently high, will cause the device to deviate from a thermionic emission mode, resulting a spurious in current response. Persistent photoconductivity, primarily a problem in
polycrystalline and high defect density films, results from the filing of charge traps which will cause an increase in current that will persist after illumination has ceased [178].

Suitable materials to form Schottky anodes to ZnO and Zn$_{1-x}$Mg$_x$O are still being investigated. Materials such as silver [148], platinum [179] and iridium [180] have shown promise particularly when they are reactively deposited. The use of an active oxygen ambient may assist in the removal of OH$^-$ groups from the surface in addition to passivating oxygen vacancies near the surface, enhancing the barrier height.

A possible candidate for forming Schottky contacts to ZnO is carbon. Graphitic carbon can exhibit metal like behaviour and has been proven to form rectifying junction to SiC, Si and other common semiconductors. Schottky contact formations have been demonstrated using HOPV (highly orientated pyrolytic carbon) Graphite has been shown to form rectifying junctions in common semiconductors such as GaAs [181], SiC [181, 182], GaN [181, 183]. Graphite has also been used to form Schottky junctions to commercial ZnO single crystal on the Zn and O polar faces [184] and the stability of the Schottky diode was examined over a range of temperature up to 420 K, Yatskiv et al. [184] shows that thermionic emission remains the dominant mechanism even at 420 K.

1.8 Bandgap tuning

Bandgap tuning is vital for the fabrication of heterostructures, include a succession of similar material layers with dissimilar bandgaps are arranged in layers to promote carrier confinement. Heterostructures are employed in devices such as LEDs, high electron mobility transistors (HEMTs) and quantum well lasers.

1.8.1 Bandgap engineering with Zn$_{1-x}$Mg$_x$O and Zn$_{1-x}$Cd$_x$O alloys

By alloying ZnO with MgO it is possible to increase the bandgap. Alloying ZnO with CdO will reduce the bandgap. A bandgap range of 2.3 eV to 4.0 eV can be achieved whilst retaining the wurtzite structure of ZnO. This thesis focuses on the incorporation of Mg to increase the bandgap of ZnO.

ZnO, with a hexagonal wurtzite structure, has a band-gap of ~3.3 eV, while MgO with the cubic rock-salt structure has a band-gap of ~7.7 eV [18, 185]. A broad range of band-gaps in the UV range of the electromagnetic spectrum can thus be achieved by forming Zn$_{1-x}$Mg$_x$O [18, 186, 187] and since Zn$_{1-x}$Mg$_x$O has stable excitons, high efficiency light emission is possible at room temperature. Wurtzite Zn$_{1-x}$Mg$_x$O is attractive from a device engineering perspective since it can form efficient heterojunctions with ZnO [188]. As the ionic radius of Mg$^{2+}$ is similar to that of Zn$^{2+}$ [186], replacing Zn with Mg causes only a slight distortion in the lattice constant. Therefore, lattice matching between ZnO and Zn$_{1-x}$Mg$_x$O is close, even with Mg fractions up to x = 0.34 [186]. Conflict between the wurtzite structure of ZnO and the cubic structure of MgO however, imposes a miscibility limit in Zn$_{1-x}$Mg$_x$O thin films, reported to be between x = 0.25 and x = 0.44 depending on the deposition technology employed [189-192]. Techniques capable of producing Zn$_{1-x}$Mg$_x$O with high Mg fractions and good electronic/optical properties include pulsed laser deposition [193], molecular beam epitaxy [194] and atomic layer deposition [195]. Unfortunately, these techniques either provide limited deposition area
Chapter 1. Introduction and literature review

or require high substrate temperatures for high quality film growth. Table provides a comparison between basic material properties of ZnO and Zn$_{1-x}$Mg$_x$O.

<table>
<thead>
<tr>
<th>Property</th>
<th>ZnO</th>
<th>Zn$_{1-x}$Mg$_x$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical Bandgap</td>
<td>3.3 eV</td>
<td>3.3 – 5 eV (x=0 to x=0.5)</td>
</tr>
<tr>
<td>Excitons binding energy</td>
<td>60 meV</td>
<td>60 meV</td>
</tr>
<tr>
<td>Carrier mobility</td>
<td>Up to 200 cm$^2$V$^{-1}$s$^{-1}$</td>
<td>Up to 15 cm$^2$V$^{-1}$s$^{-1}$ (homogeneous layer) Or 10$^4$ cm$^2$V$^{-1}$s$^{-1}$ Zn$_{1-x}$Mg$_x$O/ZnO heterolayer</td>
</tr>
<tr>
<td>Decomposition temp.</td>
<td>1975 °C</td>
<td>1975 °C</td>
</tr>
<tr>
<td>Lattice constant c</td>
<td>5.2 angstrom</td>
<td>Varies depending on composition</td>
</tr>
<tr>
<td>Lattice constant a</td>
<td>3.25 angstrom</td>
<td>Varies depending on composition</td>
</tr>
<tr>
<td>Preferred ambient conditions phase</td>
<td>wurzite</td>
<td>For Mg fract. 0&gt;x&gt;0.34 wurzite For Mg fract. 0.34&gt;x&gt;0.44 mixed cubic wurzite For Mg fract. 0.44&gt;x&gt;1 cubic</td>
</tr>
<tr>
<td>Breakdown voltage</td>
<td>5 x 10$^6$ V cm$^{-1}$</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The mobility of carriers is a strong indicator of film quality and is therefore a good benchmark for comparing synthesis methods. Carrier mobilities achieved using various synthesis methods in Zn$_{1-x}$Mg$_x$O are summarised in Table IV.
### Table IV: reported carrier mobilities in single homogeneous layer and (bottom) heterolayered Zn$_{1-x}$Mg$_x$O.

<table>
<thead>
<tr>
<th>Title</th>
<th>Author</th>
<th>Mobility (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>Mag frac. x</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fabrication and vacuum annealing of transparent conductive Ga-doped Zn$<em>{0.9}$Mg$</em>{0.1}$O thin films prepared by pulsed laser deposition technique</td>
<td>Zhiqiang Chen et al. [196]</td>
<td>7.18</td>
<td>0.1 (Ge doped)</td>
</tr>
<tr>
<td>Growth characteristics of single-crystalline Zn$_{1-x}$Mg$_x$O layers by ultrasonic spray assisted mist CVD technique</td>
<td>Hiroyuki Nishinaka et al. [197]</td>
<td>14-18</td>
<td>0.07-0.25 (ZnO buffer layer)</td>
</tr>
<tr>
<td>Effects of Mg content and B doping on structural, electrical and optical properties of Zn$_{1-x}$Mg$_x$O thin films prepared by MOCVD</td>
<td>C. Li et al. [48]</td>
<td>3.5</td>
<td>0.11 (B doped)</td>
</tr>
<tr>
<td>Effect of rapid thermal annealing on Mg$<em>x$Zn$</em>{1-x}$O films prepared by radio-frequency magnetron sputtering</td>
<td>Kuang-Po Hsueh et al. [198]</td>
<td>5.04</td>
<td>0.2</td>
</tr>
<tr>
<td>Optical and electrical properties of gallium-doped Mg$<em>x$Zn$</em>{1-x}$O</td>
<td>Wei Wei et al. [199]</td>
<td>35</td>
<td>0.05 (Ga doped)</td>
</tr>
<tr>
<td>Photo-Impassive Thin-Film Transistor with Mg$<em>x$Zn$</em>{1-x}$O Channel</td>
<td>Akira Ohtomo et al. [200]</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Enhanced Electron Mobility Due to Dopant-Defect Pairing in Conductive Zn$_{1-x}$Mg$_x$O</td>
<td>Yi Ke et al. [201]</td>
<td>11.9</td>
<td>0.3 (Ge doped)</td>
</tr>
<tr>
<td>High Electron Mobility Exceeding 10$^4$ cm$^2$ V$^{-1}$ s$^{-1}$ in Mg$<em>x$Zn$</em>{1-x}$O/ZnO Single Heterostructures Grown by Molecular Beam Epitaxy</td>
<td>Atsushi Tsukazaki et al. [202]</td>
<td>$10^7$</td>
<td>0.05</td>
</tr>
</tbody>
</table>

#### 1.8.2 Synthesis and characterization of Zn$_{1-x}$Mg$_x$O and Zn$_{1-x}$Cd$_x$O alloys

Zn$_{1-x}$Mg$_x$O thin films have been produced using a variety of methods on a range of substrates. Pulsed laser deposition, molecular beam epitaxy and atomic layer deposition have produced thin films with desirable electronic/optical properties [193-195].

Typically, Zn$_{1-x}$Mg$_x$O will retain the wurtzite structure of ZnO up to an Mg fraction of $x \sim 0.34$ [186] although single phase material has been achieved with an Mg fraction $x = 0.37$ using plasma assisted MBE and a sapphire (0001) substrate [203]. The bandgap and exciton binding energy of Zn$_{1-x}$Mg$_x$O increase with increasing Mg fraction [204]. Bandgaps of up to $\sim 3.87$eV are attainable whilst maintaining a single phase material [186].

Mg fractions greater than $x = 0.33$ normally result in a mixed phase, with the competing MgO cubic phase forming. At concentrations greater than $x = 0.44$, the cubic phase dominates. Figure 10 shows the relationship
between Mg fraction, optical bandgap and phase in Zn$_{1-x}$Mg$_x$O. Exact determination of the solubility limit is difficult using XRD as the reflection from the often much smaller and less abundant cubic phase crystals are overshadowed by the dominant wurtzite phase [205]. In order to overcome this, a direct observation technique like cross sectional transmission electron microscopy is required. Soft x-ray XAS can also be used to assess phase composition by examine the Mg K absorption edge [205].

Figure 10: The relationship between Mg fraction and bandgap, reproduced from Ohtomo et al.

The introduction of Mg tends to result in a decrease in the electron mobility. Whilst mobility for polycrystalline ZnO thin films can exceed 100 cm$^2$ V$^{-1}$ s$^{-1}$, the highest mobility reported in a homogeneous layer of Zn$_{1-x}$Mg$_x$O is only 17 cm$^2$ V$^{-1}$ s$^{-1}$ [206]. In comparison, similar films of pure ZnO support a carrier mobility of ~70 cm$^2$ V$^{-1}$ s$^{-1}$ [67].

Like Mg, Cd can be introduced into ZnO and result in a decrease in the optical bandgap. Bandgaps reported of phase pure Zn$_{1-x}$Cd$_x$O range from 3.3 eV (ZnO native) to 2.9 eV [207].

1.9 Post deposition processing

Post deposition processing can take the form of annealing, plasma exposure, or chemical treatment. One of the most common post deposition processing methods employed to modify ZnO is annealing. It is a convenient and effective method for alleviating intrinsic stress [208], removing native defects [209], balancing stoichiometry (for O deficient films) [50], and for the intentional introduction of dopants [210].

Elzwawi et al. [64] annealed ZnO films (grown at 200 °C on sapphire substrates from an FCVA) in O$_2$ at 650 °C, 800 °C and 950 °C. In the films annealed at 650 °C and 800 °C, the grain size increased (as determined from the FWHM of {0002} reflections in XRD and by surface measurements using AFM) with increasing annealing temperature. A corresponding increase in mobility was also observed and attributed to reductions in grain
boundary scattering and defects responsible for charge trapping. The films annealed at 650 °C and 800 °C proved suitable for Schottky diodes and MESFETs, with excellent ideality factors and high channel mobilities observed, respectively. Annealing at 950 °C resulted in a discontinuous surface morphology and a highly resistive film.

1.10 Electrical contacts and devices

Ohmic and rectifying contacts are essential for a material to function as an active layer in electronic devices. The earliest demonstration of ZnO in a device application employing rectifying metal contacts was reported by Fabricius et al. in 1986 [211]. The authors sputtered ZnO (onto glass substrates) from a hot pressed ZnO target. Mn was used as the ohmic contact and Au as the rectifying contact. The diode exhibited rectification but with poor ideality factors (ranging from 2.7 to 3.5). The spectral response, measured from 300 nm to 800 nm exhibited as much as two orders of magnitude increased response to UV light when compared to visible light.

In 2000, Liu et al. [212] deposited Al ohmic contacts on MOCVD grown N doped ZnO to produce an metal-semiconductor-metal (MSM) structured UV photodetector. The authors reported three orders of magnitude increased response in the UV region (350 nm) when compared to the visible (500 nm).

Liang et al. [213], (in 2001) reported Schottky MSM UV photodetectors on MOCVD grown ZnO. Ag rectifying contacts were used to produce a device with an ideality factor of 1.5. A photoresponsivity of 1.5 A/W was observed under a reverse bias of 5 V. As much as three orders of magnitude increased response illumination with $\lambda = 360$ nm when compared to visible (400 nm).

Using single crystal ZnO substrates with Au, Pt and Ir contacts, Brillson et al. (in 2007) [214] determined that near surface defects play a significant role in contact performance. Based on photoluminescence measurements, the as received crystals were categorised as ‘high-defect’ or ‘low-defect’. Pt, Au, and Ir contacts were formed on the as-received material on material exposed to a remote oxygen plasma. In all cases, the plasma treated devices performed better than the as-received devices. The difference in performance was more significant in the low defect samples than in the high defect samples, suggesting that bulk defects in the high defect sample dominated performance and, in high quality (low defect) material, the limiting factor was the presence of surface defects and adsorbents.

A significant finding in the development of Schottky contacts to ZnO was made by Allen et al. [148], who determined that partial oxidation of silver rectifying contacts ($AgO_x$) improved performance. This was attributed to the passivation of oxygen vacancies near the surface and removal of chemisorbed OH$^-$ groups attached to the polar surface. Since discovering the benefits of using partially oxidised metal contacts, several other materials have been investigated. Of these IrO$\x$, offers the greatest stability [67] as unlike Ag, Ir appears not to diffuse across the junction.

Recently, there has been interest in employing graphitic carbon as a rectifying contact material to ZnO and to other semiconductors. Tongay et al. [181] have used several formation methods, including mechanically pressing highly oriented pyrolytic carbon (HOPG) onto the semiconductor surface and direct application of a
colloidal solution of HOPG suspended in 2-butoxyethyl acetate. Contacts formed to n-type Si, GaAs and 4H-SiC exhibited zero bias Schottky barrier heights of 0.4, 0.6 and 1.15 eV respectively.

Graphitic carbon Schottky contacts to bulk single crystal ZnO have been demonstrated by Yatskiv et al. [177]. These contacts were applied directly to the Zn and O faces from a colloidal suspension of graphite. On the O polar face, diode ideality approached unity but on the Zn face, the ideality factor was 2.53. Schottky barrier heights were 0.89 and 0.60 eV respectively. These variations were attributed to the difference in surface defects between the two polar surfaces. PL measurements indicated that the O face was higher quality with a sharper near band edge emission and a less pronounced “orange band” emission, indicative of shallow defect transitions.

Graphitic carbon contacts have several advantages over alternative contact materials. Graphite is relatively impervious to chemical changes such as oxidation [179] which can lead to degradation of contact performance over time. Graphite has a high work function of 4.81 eV, leading to large barrier heights and low leakage in Schottky diodes. It also has excellent thermal stability [215], making it suitable for power devices or high temperature environments.

1.11 Research Rationale

There is a need for low cost transparent electronic materials for a range of applications. ZnO and related materials such as Zn$_{1-x}$Mg$_x$O and degenerately doped ZnO:Al have the necessary properties and can be produced from low cost feed stocks. However, methods for producing the high quality thin films required for most optoelectronic applications typically incur high cost and/or low throughput. Many electronic devices, such as field-effect devices also require ZnO in thin film form [46, 195, 216]. This thesis reports the deposition of ZnO and Zn$_{1-x}$Mg$_x$O using low cost methods with high throughput/large capability.

In many parts of the world, skin damage caused by exposure to solar radiation is a leading cause of disease [217]. Public health initiatives to increase awareness and inform people how they can minimise UV exposure through avoidance, sunscreen and suitable clothing have been effective at reducing incidence of skin damage [218]. However, emerging evidence suggests that a proportion of the population are receiving insufficient sun exposure which is contributing to vitamin D deficiency which ash been linked with diseases including rickets [219] and some forms of cancer [220]. Because of the high degree of variability in incident UV light and the needs of particular individuals for more or less sun exposure, a wearable device that would provide an individual with real-time exposure data would allow them to balance UV protection and vitamin D production. Existing monitoring devices employ costly AlGaN based UV sensors. A bandgap tuned Zn$_{1-x}$Mg$_x$O based sensor could provide a solution for a fraction of the cost and enable deployment to a much greater proportion of the population.

The portion of the electromagnetic spectrum most responsible for skin damage is the UVB (280-310 nm) [221]. Higher energy light is more damaging but very little intensity at these higher energies reaches the Earth’s surface due to absorption by the Earth’s atmosphere. Lower energy light is far more abundant but does not
cause significant skin damage. A sensor that is sensitive to light in the UVB region is therefore most effective at monitoring harmful sunlight exposure.

In its pure form, ZnO is sensitive to light of about 370 nm which falls in the less damaging UVA region. The bandgap must be altered (widened) so that the sensor will not be excited by the lower energy visible and UVA radiation. Alloying with Mg enables this bandgap widening and UVB sensing capability.

This thesis examines the use of energetic PVD methods for growth of device quality ZnO and Zn$_{1-x}$Mg$_x$O thin films. Energetic, in the context of PVD methods, typically refers to methods where a significant proportion of the depositing flux is ionised. An ionised flux coupled with substrate bias provides control over the landing energy of the depositing flux. The landing energy of the ions will affect the microstructure of the film formed [62]. In this way, energetic deposition methods such as FCVA and HiPIMS can give greater control over microstructure when compared to chemical vapour deposition methods or non-energetic PVD techniques.

Central to this are dynamic annealing effects [52], caused by the kinetic and potential energy of the energetic flux leading to greater mobility of adatoms. Typically these provide more crystalline order for a given substrate temperature when compared to non-energetic methods such as sputtering. This effect enables high quality growth on substrates that are incompatible with higher temperatures, such as flexible polymers.

1.12 Research questions

This thesis aims to answer the following questions:

- Are energetic depositing methods viable for growth of Zn$_{1-x}$Mg$_x$O for optoelectronic applications?
- Which FCVA depositing parameters provide the most suitable film properties?
- Can FCVA be used to produce Zn$_{1-x}$Mg$_x$O thin films suitable for electronic devices?
- Is graphitic carbon a suitable Schottky contact material for Zn$_{1-x}$Mg$_x$O? Can it be deposited and patterned using a method compatible with standard lithographic methods?
- Is HiPIMS a viable method for growth of ZnO films for device applications?
- Is HiPIMS a suitable method for growth of Zn$_{1-x}$Mg$_x$O films for device applications?
- Can the carrier concentration in Zn$_{1-x}$Mg$_x$O films be controlled?

Major outcomes of the investigation are:

- Device quality films have been achieved using energetic deposition methods.
- A UV detector device based on FCVA deposited Zn$_{1-x}$Mg$_x$O has been fabricated.
- Graphitic carbon deposited using a photolithographic method has produced rectifying contacts to Zn$_{1-x}$Mg$_x$O.
- HiPIMS has proven capable of producing device quality thin films of ZnO and Zn$_{1-x}$Mg$_x$O.
Chapter 1. Introduction and literature review

1.13 Thesis Outline

This thesis describes the energetic deposition of ZnO and $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films and presents prototype devices. Chapter Two describes the experimental methods used as part of this thesis. Chapters 3 to 6 present four related papers recently published by the author. Finally, Chapter 7 discusses the results from the published papers and their significance to the research field.

Chapter 3 investigates the growth of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films using FCVA and includes structural and compositional characterisation. Chapter 4 investigates $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films grown from a FCVA and includes optical and electronic characterisation. Visible blind UVB photo detector devices were fabricated with rectifying graphitic C contacts. Current-voltage and UV sensing characteristics of these devices are reported.

Chapter 5 examines the HiPIMS ZnO thin films. This chapter presents microstructural and optical characterisation as well as a Schottky diode device based on the material.

Chapter 6 expands on the previous chapter with work on the growth and characterisation of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films produced using HiPIMS. A prototype notch filter based on a MSM structured photodetector and employing graphitic anodes is presented as part of this work.
Chapter 2. Methods and techniques

This chapter describes all methods employed to produce the results in this thesis. It includes the deposition methods used and the structural, compositional, optical and electronic characterisation methods used.

2.1 Thin film deposition methods

This section describes the deposition methods used employed to produce Zn$_{1-x}$Mg$_x$O thin films. A significant feature the two methods (HiPIMS and FCVA) used for Zn$_{1-x}$Mg$_x$O film growth is the energetic nature of their depositing flux.

2.1.1 Non-energetic growth methods

Non-energetic growth methods have little or no ionised species in their depositing flux. A neutral depositing flux cannot have its landing energy controlled via substrate bias. These growth methods have been used to produce metal oxide films including ZnO, but typically produce low density films with high defect densities. Low energy deposition was used in this project to produce electrical contacts for electrical characterisation and device applications.

Evaporative deposition is a PVD technique that relies on heating the source material until it vaporises. This vapour is then allowed to condense on the substrate. The source material is placed in a tungsten boat through which a current is passed, causing it to melt then evaporate. The vapour phase condenses on all surfaces within line of sight of the boat. Evaporation is a low energy deposition method; this property is useful when forming electrodes to semiconductor thin films as it reduces the possibility of surface damage occurring due to energetic bombardment. Surface damage can lead to lateral inhomogeneity known to adversely affect the ideality of Schottky contacts [222].

Graphitic carbon has been demonstrated to form Schottky contacts to several semiconductors [181, 184]. Graphitic carbon has a high work function (4.81 eV [223]) and offers large Schottky barrier heights. In addition carbon has good thermal and chemical stability. These properties suggest that carbon could be a good material for high performance Schottky contacts. When depositing non-metal high melting point materials a different approach is required. In order to produce a graphitic carbon film, a high current (40+ A) is passed through a carbon filament until the filament burns out resulting in the release of a low energy carbon flux. This method was used for graphite-Zn$_{1-x}$Mg$_x$O Schottky based devices presented in this thesis.

The evaporative system (a Dynavac coating system) employed in this thesis has been equipped with a high voltage low current DC power supply (Glassman 1 KV low current power supply). This power supply can be used to produce a glow-discharge oxygen plasma by applying a potential to a pole in an oxygen atmosphere. There are numerous reports [224, 225] showing that the use of an oxygen plasma will remove hydroxyl groups attached to the surface and passivate oxygen vacancies near the surface dramatically improving the
performance of rectifying contacts made to the treated surface. This plasma cleaning method was used to remove surface contaminate from the ZnO or Zn$_{1-x}$Mg$_x$O surface prior to the deposition of rectifying contacts.

2.1.2 Energetic Deposition Methods

2.1.2.1 Filtered Cathodic Vacuum Arc Deposition

FCVA is a high energy deposition technique that uses a high current (~30-150 A) arc discharge to initiate an almost completely ionised plasma from a cathode (or target). Un-filtered cathodic arcs have been used for several decades to produce mechanical coatings where macroparticles (caused by the explosive cathode spot) do not inhibit the coating performance. An electromagnetic filter, placed between the source and deposition chambers, can be inserted to minimise macroparticles and neutral atoms, resulting in films that condenses from an ionized plasma, promoting high density, lower defects and strong adhesion [226]. As the depositing flux produced in an FCVA is largely ionised, it is possible to alter the landing energy of the flux at the substrate by applying a bias to the sample stage/substrate. Process gasses can be bled into the vacuum chamber for reactive depositions of nitrides and oxides [227]. This project used a Nanofilm FCVA system, with an arc current of 42 A and magnetic filter currents of 10 A for both the sections of the double bend filter. A 1 A current was used for the anode confinement coil. A 68 mm diameter cathode was used as the metal source. Figure 11 shows a cross sectional diagram of the FCVA system depicting the source chamber that holds the water cooled cathode (source material), the double bend magnetic filter employed for the removal of macro particles and unionised species and the main vacuum chamber where the bias-able/heat-able substrate resides.

![Figure 11: Diagram of an FCVA system used to deposit ZnO and Zn$_{1-x}$Mg$_x$O thin films.](image)

This FCVA system uses a PID, temperature controlled, sample stage. Samples were assumed to be at the same temperature as the sample stage, this has been confirmed using a surface mounted thermocouple. Test using the surface mounted thermocouple has shown local heating due to the energetic plasma can be as much as 10 °C.
Chapter 2. Methods and techniques

The FCVA system employed in this project is able to effectively coat a 3 inch wafer with minimal thickness variation. By employing scanning coils and/or multiple cathodes it would be possible to coat areas that are 10’s of centimetres in diameter, and, by virtue of the ionised flux complex topologies can be coated whilst maintaining a conformal coating.

2.1.2.2 High Power Impulse Magnetron Sputtering

HiPIMS is an emerging energetic sputtering technique in which a high power density (up to several kW cm\(^{-2}\)) is applied to the target in short pulses (40-200 µs) with a long duty cycle (~100-200 Hz). HiPIMS provides a much greater degree of ionisation when compared to direct current magnetron sputtering (DCMS) or radio frequency magnetron sputtering (RFMS). Whilst the average power density is similar to DCMS, the peak power is much higher due to the very high voltage pulses. This results in films with higher densities than those deposited by DCMS with the same average power density. HiPIMS has so far been employed primarily in the tribological coating industry but has demonstrated potential for growth of optical and electronic coatings [78, 79].

Plasma discharge from a HiPIMS system can be broken down into several steps. After the application of the pulse, electrical breakdown will occur, this will resulting chamber gasses being ionised (Ar or a reactive gas such as O or N). The gas plasma will initiate a metal plasma from the target. The system will eventually reach a steady state where the metal plasma will dominate the gas plasma.

The HiPIMS system used in this project is an AJA Inc. system equipped with up to four targets that can be operated in HiPIMS or DCMS modes. Standard 3” diameter ¼ ” thick sputter targets. The HiPIMS power supply was a GBS Elektronik GmbH RUP7 pulse power supply. The DCMS super supply was an Advanced Energy MDX500.

The deposition rate can be calibrated using an in-chamber quartz thickness monitor. Each target can be tilted independently and the sample stage is height adjustable. These controls allow for deposition angle, substrate to target distance and the projected flux profile to be tuned to the desired values.

The multi target setup in this system allows for co-deposition of different materials simultaneously. Part of this thesis examines the co-deposition of Zn and Mg in a reactive environment to produce Zn\(_{1-x}\)Mg\(_x\)O with a continuously varying range of Mg fractions. The technique could prove useful for studying ternary oxides or nitrides.
2.2 Post deposition treatments

Post deposition treatments of films can assist in altering and improving film properties. Treatments include; annealing in different gaseous environments or in vacuum, plasma treatments, and surface chemical treatments.

Annealing can serve a range of purposes. Annealing can be used to remove defects from a film by giving constituent atoms sufficient energy to rearrange and reform grains or, growing grains reducing the grain boundary density. Annealing can also be used to alter the carrier concentration of a material to better suit a particular application. It has been shown [228] that annealing polycrystalline ZnO in hydrogen will cause hydrogen to diffuse into a film where it can act as a stable shallow donor, increasing carrier concentration and mobility. Conversely, an oxygen present environment during annealing tends to cause a reduction in carrier concentration [229], the effect is suspected to be due to a reduction in the density of V_o defects (where hydrogen is known to bind).

Oxygen plasma treatments can be used to improve the surface properties of ZnO and Zn_{1-x}Mg_xO [143]. Oxygen vacancies at the surface can lead to an electron accumulation layer, resulting in a much higher carrier concentration at the surface [149]. In addition, contaminant oxygen species such as OH⁻ and CO⁻ can exacerbate this effect [140]. Oxygen plasmas can passivate oxygen vacancies near the surface and remove surface attached hydroxyl groups [147]. Oxygen plasma treatment is less likely to result in damage to the film than Ar plasma treatment because of the smaller atomic weight of oxygen ions. This is important in devices as lateral inhomogeneity in rectifying Schottky contacts can result from surface damage [230].
Chapter 2. Methods and techniques

As part of the device fabrication process used in this thesis an oxygen plasma was applied prior to rectifying contact formation. Treatment parameters are as follows: a pressure of 0.1 Torr was established in the vacuum chamber using pure O₂ supplied to the gas inlet valve. A high voltage (low current) power supply was connected to a pole on which the sample being processed is mounted. A 400 V applied bias with the specified atmosphere and pressure results in a glow discharge being ignited. The plasma plume will serve to clean the Zn₁₋ₓMgₓO surface prior to the formation of a rectifying contact.

2.3 Structural Characterisation Techniques

2.3.1 X-ray Diffraction (XRD)

X-ray diffractograms give information about the crystallographic phases present, preferred orientation of crystals and the average size of crystallites in a bulk or thin film sample. XRD directs a characteristic X-ray (Cu kα) beam at the specimen at a range of angles. These x-rays are reflected and when the Bragg condition is satisfied, a peak in reflected intensity will occur. Bragg’s Law (Equation (3))

\[ n\lambda = 2d \sin \theta \]  

(3)

In this project, XRD was performed using a Bruker D4 Endeavour X-ray powder diffractometer. The x-ray radiation produced by this instrument has a wavelength 1.54 Å, derived from a Cu (kα) characteristic x-ray. X-ray intensity is recorded over a range of 2θ = 20°-70°. Samples were mounted on a glass slide to avoid contaminating reflections from the mounting apparatus. An X-ray powder diffraction system has an interaction volume that is typically much deeper than the thickness of the film samples. This interaction volume will therefore extend into the substrate. An XRD system in which x-rays strike the sample at a glancing angle will minimise this effect, as the projected thickness of the film at a glancing angle will be much larger. Glancing incidence was not available to this project, however the presence of peaks from the single crystal substrates (a-plane Al₂O₃ or (100) Si) were useful in determining and correcting shifts associated with sample tilt.

Using the full width half maximum (FWHM) intensity of an XRD peak, it is possible to estimate the average crystallite size using Scherrer’s equation. In Scherrer’s equation (Equation (4)) [231], \( K \) is a dimensionless shape factor usually around 0.9 (this shape factor is suited to roughly spherical crystallites), \( \lambda \) is the wavelength of radiation used, \( B \) is the full width half maximum (FWHM) in radians \( \theta \) is the peak position.

\[ L = \frac{K\lambda}{B \cos \theta} \]  

(4)
Chapter 2. Methods and techniques

2.3.2 Microscopy

Transmission electron microscopy, scanning electron microscopy, atomic force microscopy and optical microscopy were used in this project. These methods are now described.

2.3.2.1 Transmission Electron Microscopy (TEM)

TEM directs a high energy (60-300 kV) beam of electrons at a sample, and then uses the transmitted beam to form an image of that sample. High energy electrons provide higher spatial resolution than light due to their smaller wavelength according to Rayleigh’s criterion [232]. TEM imaging is the most common use of a TEM. The electron beam is passed through a sample, the image magnified and then projected onto a phosphor screen or CCD camera. This method can produce atomic resolution images.

A sample must be prepared for use in a TEM. Samples must be vacuum compatible and electron-transparent in the region of interest. Here, cross-sectional TEM sample preparation involved first slicing the sample into thin strips. These were then ‘sandwiched’ together film-face to film-face, with additional layers of Si on the outer sides. A two part epoxy resin was used to glue this ‘sandwich’ together before it was thinned, initially using mechanical polishing. Final thinning to electron transparency was accomplished using a Gatan precision ion polishing system (PIPS). TEM was used to image the film microstructure whilst electron diffraction was used to determine the degree of crystallinity and which crystal phases were present in the cross sectional thin film samples.

Electron energy loss spectroscopy (EELS) measures the energy lost by high energy electrons after they have passed through the sample. Electrons will be either elastically scattered, meaning they lose no energy or inelastically scattered resulting in a loss of energy. There are several modes of inelastic scattering, phonon excitation, Plasmon excitations, inter- and intra- band transitions and core ionisation events. Core ionisation events will result in an energy loss characteristic of the element and orbital excited. Using the integrated area under the core ionisation peaks and the cross section of interaction, the composition of the sample can be determined. By examining the fine structure of a core ionisation peak, information about the phase and defects can be ascertained.

When a sample is exposed to illumination from a parallel beam of high energy (small wavelength) electrons, the electrons will pass through easily. Due to the small wavelength of electrons, the wavelength of a 200 keV electron is $2.5 \times 10^{-12}$ m, and the relatively large spacing between atoms, the regular crystal structure of a material will act as a diffraction grating. Depending on the sample, a diffraction pattern can vary significantly in appearance. When an electron beam is diffracted from a single crystal material a regular array of spots is produced. The spacing of these spots is determined by the d-spacing planes forming the spots. It is therefore possible to identify phases present in the sample from its diffraction pattern [233].

In some TEMs, it is possible to use a mode where the primary beam is focused to a point on the sample then rastered across the sample. This mode is called scanning transmission electron microscopy (STEM). The transmitted intensity is measured at each point then, using this intensity, an image is formed. Different types of detector configurations can be used to give differing information. A sensor that looks at the primary beam will
produce an image similar to a bright field TEM image. An annulus type detector can be used to collect intensity at higher scattering angles. This image will be somewhat like a dark field image but rather than collecting intensity from a single spot, intensity is collected from a ring. When using an annulus type detector materials that scatter more readily will appear brighter.

Spectrum imaging is a technique that combines a scanning transmission electron microscope with a range of spectroscopic techniques, namely energy dispersive x-ray spectroscopy (EDS) and EELS. By collecting a spectrum at each point along the raster path, the variation in properties observable by these techniques can be mapped out at a very high spatial resolution. Resultant data is referred to as a spectrum image, as each pixel in the image holds spectroscopic information which can be further analysed.

2.3.2.2 Scanning Electron Microscopy (SEM)
A scanning electron microscope (SEM) produces a focused electron beam which is electromagnetically rastered across the sample. When the electron beam strikes the sample, it generates different signals, which can be used to form an image. Differing contrast mechanisms reveal differing aspects of a sample. The primary method of imaging in an SEM is secondary electrons. Secondary electrons are given off when the high energy (3-30kV) beam strikes the sample. A secondary electron typically has a much lower energy than the primary beam (20-50 eV) [234].

Backscattered electrons are, as the name suggests, electrons from the primary beam that have been backscattered 180°. The signal intensity is dependent on the atomic weight of the material from which the electrons are backscattered since the probability of backscattering occurring is dependent on the 4th power of the materials atomic weight. This material based contrast makes the backscatter image mode useful for observing phase separation. A back scatter detector can also be configured to produce an image that gives contrast based on the topology of the surface, useful for seeing micro scale defects such as cracking. The other commonly used signal in SEM is characteristic x-rays (this will be discussed in 2.4.3). In this project a FEI NovaNano SEM 200 was used for images with an attached Oxford X-max® EDS detector.

2.3.2.3 Atomic force microscopy (AFM)
Atomic force microscopy is used to examine the surface morphology of samples. A piezoelectric crystal rasters a probe attached to a cantilever across a sample. As the probe is rastered across the sample, the deflection of the cantilever is measured using a laser reflected from the cantilever. In this way a height map of the sample is constructed. Using this method, several properties of the film’s surface can be measured including surface root mean squared (RMS) roughness representing the average variability in the height of the sample over the analysed area. From the plan view projection, average grain diameter can be estimated. The presence of macro scale defects can be observed, such as macroparticles or pits in the film. These macro scale defects can be the result of the deposition (film growth) process or due to a post deposition treatment such as a plasma cleaning process or a wet chemical treatment process.

In this project non-contact tapping mode was used for all images. A Veeco D3100 AFM was used for all AFM images. The average tip radius was less than 10 nm achieving a resolution of 5 nm point to point.
2.4 Chemical analysis Techniques

2.4.1 X-ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS) is an absorption technique. A beam of photons is directed at the sample with a photon energy that is varied over a range covering the majority of an absorption edge. An absorption edge is produced by the transition of electrons in a particular orbital, for example the excitation of 1s electrons is referred to as the K edge, and similarly the 2s and 2p electrons excitations are called L edges. The signal collected is referred to as x-ray absorption near edge structure (XANES). This signal provides very similar information to EELS in that it is a map of the unoccupied density of states (DOS). XAS is most often done at a synchrotron. XANES typically offers significantly finer energy resolution compared to EELS, at the expense of spatial resolution. The x-ray energy used for collection of XAS data presented in this thesis is performed on a system capable of 0.1 eV energy resolution but the analysis spot is ~400 μm, conversely the energy resolution of the EELS system used here is ~1.2 eV with a spatial resolution of 2 Å. EELS systems capable of similar energy resolution to XAS require a beam monochromator which significantly reduces their signal intensity. The higher energy resolution of XANES makes it better suited to comparisons with theoretical calculations.

This thesis presents XANES spectra that were collected at the soft x-ray beamline at the Australian Synchrotron. A soft x-ray can be defined as an x-ray with energy between ~100 eV and 10 keV [235]. Soft x-rays are well suited to studying thin films due to their relatively shallow penetration depth [236].

2.4.2 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy employs an x-ray source (typically a characteristic x-ray of Al or Mg) directed at a sample in an ultra-high vacuum (UHV) environment. When the x-ray beam strikes the sample photoelectrons are given off. The kinetic energy of these electrons is characteristic of the element, the energy of the excitation x-ray, and the local bonding arrangement of the material being analysed. With knowledge of the incident x-ray beam, it is possible to calculate the binding energy of the element from which the electron was emitted. Equation (5) describes the relationship between the binding energy and the x-ray photon energy, $E_{\text{binding}}$ is the binding energy of an element, $E_{\text{photon}}$ is the energy of the incident x-ray, $E_{\text{kinetic}}$ the kinetic energy of the photoelectron and $\phi$ is the work function which is dependent on the instrument and the material being analysed.

$$E_{\text{binding}} = E_{\text{photon}} - E_{\text{kinetic}} - \phi$$  \hspace{1cm} (5)

XPS can detect elemental concentrations as low as 1%. By integrating the area under XPS peaks, it is possible to determine the relative compositions of elements present. Gaussian peaks fitted to the resultant XPS spectra are used to determine their binding energy, which varies depending on the local bonding arrangement. In this way, it is possible to identify the chemical species present in the sample. If an element is forming multiple species, then it can be possible to deconvolve the contribution from each to quantify the relative amount of each species present.
Chapter 2. Methods and techniques

The XPS presented in this thesis was performed using a Thermo Scientific K alpha instrument. This instrument is equipped with an Al Kα x-ray source (equipped with a monochromator) with an energy resolution of 0.1 eV, a Ar⁺/e⁻ flood gun and an Ar⁺ etching gun capable of energies of 200-3000 eV.

2.4.3 Energy Dispersive X-ray Spectroscopy

Energy dispersive x-ray spectroscopy is an analysis method compatible with both the TEM and SEM and indeed any vacuum system with a high energy electron beam. When a high energy electron strikes matter, an x-ray is emitted that is characteristic of the element and orbital from which it originated. By counting these x-rays and plotting them as a function of their energy, an EDS spectrum is produced. Spectra can be used to quantify those elements present. In a scanning mode, as with SEM and STEM, EDS can be used to create an elemental map of a sample.

2.5 Optical Characterisation Techniques

2.5.1 Ultraviolet/Visible Spectroscopy

Ultraviolet/Visible spectroscopy is used to determine the optical transmittance at a range of wavelengths from the near infrared into the UV. A source or set of sources produces light that is passed through a monochromators to produce. The sample is placed between the monochromated source and detector and (after calibration to take into account variation in source intensity as a function of wavelength) the transmission as a function of wavelength, is determined. Using a given transmission spectra, it is possible to determine the optical bandgap of a material. There are two methods employed in this thesis to calculate optical bandgap from a transmission spectrum. The first is the Tauc method, requiring the absorption coefficient α and a plot of $(\alpha h\nu)^n$ where $n = 2$, $\frac{1}{2}$, depending on whether the bandgap is direct or indirect. Once transmission data has been processed into a Tauc plot the linear region of the curve is extrapolated to the x axis (the photon energy or wavelength axis) to give a precise numerical value for the band gap of the material. The second method uses the derivative of the transmission spectrum, the gradient will be steepest at the absorption edge which will produce a peak in the derivative the position of the peak (on the energy/wavelength axis) is the optical bandgap [237].

2.6 Electrical Characterisation Techniques

2.6.1 Van der Pauw, Hall Effect characterisation

The Van der Pauw method is used to measure the resistivity and the Hall coefficient of a thin film sample. Certain conditions must be satisfied in order for the Van der Pauw method to be viable. Films must be homogeneous and isotropic and have a uniform thickness. The corner contact must be at the edge of the sample (not inset) and the area of each contact must be two orders of magnitude smaller than the square sample area. This method is able to provide some of the electrical properties of the sample being tested. Notably, the resistivity, majority carrier type, majority carrier concentration and the mobility of the majority carrier can all be measured using the Van der Pauw method. In this project, samples were prepared for measurements by depositing ohmic corner contacts onto square samples using a stencil. The contact material of choice was Al due to its ease of deposition and performance as an ohmic contact to ZnO.
Chapter 2. Methods and techniques

The Hall Effect was discovered by Edwin Hall in 1879 [238]. He observed that when a current is applied to a material then placed in a magnetic field perpendicular to the applied current an electric field will be generated that is perpendicular to both.

![Diagram of a sample prepared for measurement using the van der Pauw method.](image)

An Ecopia HMS 3000 system with fixed 0.55 T and 0.91 T magnetic fields was used for Hall measurements presented in this thesis.

2.6.2 Current-Voltage characteristics

Current voltage (I-V) measurements provide a way to determine key parameters of a device. I-V measurements are carried out with a source measurement unit and a probe station. Needle probes are applied to electrical contact pads on the sample. Once electrical contact is established, the source measurement unit applies a bias. Whilst this bias swept over a desired range is applied, the current flow is measured. For example, I-V characteristics from Schottky devices can reveal the ideality, barrier height, rectification ratio and breakdown voltage.

From the I-V curve, several parameters of the devices can be determined. Initially for a Schottky diode the forward rectification ratio can be determined at a given bias by comparing the current under forward bias and the current in reverse bias at the same bias magnitude.

The ideality factor is obtained from the linear region of the forward bias I-V using Equation (6) where $I$ is the current through the diode, $V$ is the voltage across the diode, $I_0$ is the saturation current, $q$ is the elementary charge, $k$ is Boltzmann’s constant, $T$ is the temperature of the system and $n$ is the ideality factor. Ideality factor is a measure of how closely a diode follows the diode equation. Second order effects will always be present causing a diode to deviate from the ideal case, the ideality factor provides a way of measuring this deviation.

\[
I = I_0 \left( \exp\left( \frac{qV}{nkT} \right) - 1 \right)
\] (6)
Chapter 2. Methods and techniques

The ideality factor can also be obtained from a diode $I$-$V$ using Equation (7) assuming a simple model consisting of thermionic emission theory only. This theory is only valid for diodes with an ideality factor of less than ~2; beyond this point thermionic emission ceases to be the dominant process

$$I_{sat} = A A^* T^2 \exp \left[ \frac{-F_{B,s}}{(kT)} \right]$$

Equipment used for this analysis are a Keithley 2400 high voltage low noise source measurement unit, capable of accurately measuring currents as low as 1 pA. This accuracy is required when testing UV Schottky detectors with very small dark currents.

### 2.7 Device fabrication

The primary method of device fabrication employed in this project was photolithography. The process of photolithography involves first mounting a clean substrate, in this case thin film coated sapphire, into a spin coater for the application of photo-resist. The vacuum chuck on a spin coater secures a sample in place, then rotates the sample at between several hundred and a few thousand revolutions per minute. Whilst spinning, resist is pipetted onto the sample where it forms a thin uniform coating. The sample is baked on a hotplate at ~100 °C for ~30 seconds after which it is ready for patterning. A mask aligner, consisting of a UV source, a vacuum chuck for each the sample and a mask, enables alignment of the substrate to the mask features to within ~1 µm. Once aligned, the sample is exposed through the mask to the UV light source. This exposure results in a chemical change in the photoresist, which causes it to become soluble in a developer solution. Once the sample has been developed and rinsed in de-ionised water to remove residual developer, the sample is ready for the formation of contacts. Depending on the desired function of a contact, different materials will be chosen.

Figure 14 shows the process of device fabrication using photolithography. For most devices, it is necessary to perform multiple processes i.e. spin-coat → exposure→ develop→ deposited→ lift off in order to create ohmic and rectifying contacts.

![Figure 14: A typical device fabrication process sequence using photolithography.](image-url)
Chapter 2. Methods and techniques

Optical sensor devices based on ZnO

In this project, flash evaporated partially graphitic anodes were employed as Schottky contacts. This provided photolithographic patterning capability and precisely defined device dimensions. These devices were fabricated as on FCVA and HiPIMS/DCMS grown material with a ‘back-to-back’ or metal-semiconductor-metal Schottky diode configuration. Graphitic carbon was chosen as the “metal” contact due to its high work function, low cost and chemical inertness. The high work function leads to a greater barrier height ($\Phi_B$) [181] than can be achieved with low cost metal contacts. As well as excellent chemical stability [239], graphite also has excellent thermal stability, making it well suited to high temperature applications. By comparison, metal Schottky contacts can degrade under exposure to high temperature. Inter-diffusion with the semiconductor material has been observed and this irreversibly damages rectifying junctions [177].

2.7.1 Spectral Response Measurements

Once a light sensitive device has been fabricated, it must be tested to determine its efficiency and the relative response to different wavelengths of light. This is particularly pertinent when the device is required to respond to UV illumination but not to longer visible wavelengths of light (e.g. visible-blind UV detector). To do this a set of light sources is needed and a source measurement unit. Typically a current-voltage measurement (I-V) is performed first under no illumination or “dark” conditions for a material that may have some sensitivity to visible light a truly dark environment is needed. This dark current is used as a baseline. The sample will then be exposed a specific wavelength of light this will excite more charge carriers increase the current measured when performing an I-V. This process is repeated for several wavelengths. The ratio of dark current to UV exposed current at a given bias along with parameters of the light source and device dimensions can be used to determine the external quantum efficiency of a given device. The quantum efficiency is the number of photo current electrons per incident number of photons. In some cases it is possible to generate more than one photo current electron per incident photon due to internal gain mechanisms.
Chapter 3. Structural characterisation of energetically deposited Zn$_{1-x}$Mg$_x$O films
Structural characterisation of energetically deposited Zn$_{1-x}$Mg$_x$O films

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Zn$_{1-x}$Mg$_x$O thin films have been energetically deposited from a filtered cathodic vacuum arc at moderate temperatures and microstructurally characterised. Partial oxidation (‘poisoning’) of the Zn$_{0.8}$Mg$_{0.2}$ cathode caused layering and phase separation in the films. However, periods of non-reactive ablation steps incorporated into the deposition process minimised the effects of cathode poisoning and enabled dense, phase-pure, wurtzite Zn$_{1-x}$Mg$_x$O to be grown at room temperature and 200 °C. Elevated substrate temperature resulted in enlarged grains and increased surface roughness. Increased substrate bias caused reduced crystalline order. X-ray absorption spectra from the homogeneous Zn$_{1-x}$Mg$_x$O films, revealing local atomic bonding, were similar to spectra from single crystal ZnO but with features indicative of defects related to oxygen deficiency.

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1. Introduction

Zn$_{1-x}$Mg$_x$O is a wide band gap II–VI semiconductor alloy with potential applications including ultraviolet (UV) light sources and detectors. The similar ionic radii of Mg$^{2+}$ and Zn$^{2+}$ mean that the wurtzite structure of ZnO can be preserved in Zn$_{1-x}$Mg$_x$O with Mg fractions up to $x \approx 0.35$ [1]. In this compositional range, ultraviolet band-gaps up to $\sim 4.0$ eV have been achieved [2], with stable excitons enabling high efficiency light emission/detection at room temperature [3]. In Zn$_{1-x}$Mg$_x$O–ZnO superlattices, electron mobilities up to 180,000 cm$^2$ V$^{-1}$ s$^{-1}$ have been achieved at 0.06 K [4] and lasing has been demonstrated [5].

Thin films of Zn$_{1-x}$Mg$_x$O are typically grown by pulsed laser deposition [6], molecular beam epitaxy [7], metal-organic chemical vapour deposition [8], or atomic layer deposition [9]. These techniques normally require substrate temperatures exceeding those suitable for technologically important substrate materials such as flexible plastics. Using the filtered cathodic vacuum arc (FCVA) technique, high quality ZnO-based films have been energetically deposited over large areas at moderate temperatures [10–12]. The energetic depositing flux and associated dynamic annealing occurring in FCVA deposition result in a greater range of accessible microstructures at low growth temperatures when compared with conventional physical vapour deposition [13]. We recently reported Zn$_{1-x}$Mg$_x$O films grown from a FCVA at temperatures $\leq 200$ °C on a-plane sapphire with moderate n-type doping, high carrier mobility and high transparency. These films were incorporated into Schottky diode detectors exhibiting high sensitivity to UVB [12].

Here, we report microstructural measurements performed on FCVA grown Zn$_{1-x}$Mg$_x$O films. Electron microscopy, X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS) have been used to reveal the microstructure, local atomic bonding and compositional variations within the films. These measurements are used to elucidate the ablation and growth processes occurring during deposition.

2. Experimental procedure

All films were deposited onto silicon (100) substrates using a Nanofilm FCVA system equipped with a double bend filter, rotating cathode assembly and biased sample heater/holder. A more detailed discussion of this apparatus is included in Abaffy et al. [14]. A 68 mm diameter, 99.9% purity, Zn$_{0.8}$Mg$_{0.2}$ cathode was ablated with an arc current of 40 A in O$_2$ and Ar partial pressures of 1.38 and 0.07 mTorr, respectively.

The RMS roughness and average grain size in the films were calculated from four 1 $\times$ 1 µm$^2$ atomic force microscope (AFM) scans taken using a Dimension 3100 operating in tapping mode. X-ray diffraction (XRD) measurements were collected on a Bruker D4 diffractometer, equipped with a Cu source. XPS was performed using a Thermo Scientific K-Alpha system equipped with Al k$\alpha$ x-ray source. A flood gun was active during all measurements to minimise sample charging. In-situ sputtering enabled composition
versus depth profiles to be collected. Schofield sensitivity factors required in quantifying the film composition were obtained using a hot-pressed, 99.9% purity Zn$_{0.6}$Mg$_{0.4}$O standard.

Cross-sectional transmission electron microscope (XTEM) specimens were prepared using mechanical polishing and ion beam thinning then imaged in a JEOL 2100F equipped with a Tridiem Gatan Imaging Filter. Bright field/dark field pairs and EELS elemental depth profiles were collected in addition to images and diffraction patterns. XAS and variable energy XPS were performed at the Australian synchrotron using the soft x-ray beam line [15].

3. Results and discussion

Fig. 1(a) shows an XPS depth profile from a Zn$_{1-x}$Mg$_x$O film with clearly visible compositional variations. This thick (~350 nm) film was grown to clearly show the effects of cathode poisoning. An XTEM bright field image and a selected area diffraction pattern from the same area of film are shown in Fig. 2(a) and (b). The bright field image shows columnar microstructure and some evidence of layering. This layered film produced a diffraction pattern that could be indexed to both the wurtzite and cubic phases of Zn$_{1-x}$Mg$_x$O (Fig. 2(b)). The dark field image from the {100} cubic reflection shown in Fig. 2(c) reveals that layers of the cubic phase (~20 nm in thickness) exist parallel to the growth surface. An EELS scan (Fig. 2(d)) along the line indicated in Fig. 2(a) shows a compositional variation through the depth of the film, consistent with its XPS depth profile (Fig. 1(a)). Comparing the dark field image and EELS line scan, the cubic phase appears in the Mg rich layers. This relationship between phase and composition is expected since the miscibility limit of Mg in the ZnO wurtzite phase is $x \approx 0.35$ [1], beyond which a mixed wurtzite/cubic phase forms. Note that the Mg rich layers appear significantly thinner in the EELS line scan than in the XPS depth profile (Fig. 1(a)). This is due to the effects of intermixing and/or preferential sputtering which causes increased roughening of the sputtered area from which the XPS is taken as the depth profile continues.

The layering and phase separation in the films was attributed to cathode poisoning effects, often observed in reactive cathodic arc depositions. Electron micrographs (not shown) revealed that the Zn$_{0.6}$Mg$_{0.4}$O cathode surface consisted of distinct Zn and Mg regions approximately 0.8 mm$^2$ in area i.e. larger than the arc spot [16]. Mg has lower electro-negativity than Zn and therefore oxidises more rapidly to form MgO with significantly higher electrical resistance than either Zn or ZnO. This preferential oxidation of the Mg regions on the cathode surface causes preferential ablation of the Zn regions. During deposition, eventually, with the Zn regions depleted, the arc must ablate oxidised Mg rich regions. These combined effects provide an explanation for the layering in the films observed by XPS and TEM. Furthermore, unstable cathode voltages observed during deposition of layered films (tending to increase erratically from $\sim 20$ V to $\sim 30$ V), also suggested oxidation of the cathode surface.

Zn$_{1-x}$Mg$_x$O films with minimal compositional variation were formed provided the cathode voltage was maintained at or below $\sim 20$ V. The surface oxide on the cathode was removed by passing the deposition (when the cathode voltage exceeded $\sim 20$ V) and inserting a non-reactive ablation period of 300 s. During this period, the magnetic filter coil current was turned down to prevent deposition onto the substrate. After the non-reactive ablation procedure, the cathode voltage was $\sim 15$ V, consistent with removal of surface oxide from the cathode. Fig. 1(b) shows a typical non-layered film deposited from a cathode that has been non-reactively ablated to remove the oxidised top layer. Note that this film is sufficiently thick (~50 nm) for application as a UVB detector but considerably thinner than the film shown in Fig. 2(a) which was deliberately grown for an extended period to highlight the effects of cathode poisoning.

Table 1 summarises deposition and microstructural data (AFM, XRD, XPS) from Zn$_{1-x}$Mg$_x$O films deposited at room temperature and 200 °C with $-50$ and $-100$ V substrate bias. The deposition rate decreases with elevated temperature. This may be due to re-evaporation from the heated substrate during deposition and/or increased self-sputtering, possible during energetic deposition at elevated temperatures. The Mg fractions are all similar but consistently lower than $x=0.20$, the fraction corresponding to the cathode composition. This suggests preferential ablation of the Zn from the cathode and/or preferential evaporation of Mg from the growing film. Elevated temperature causes an increase in the grain size, seen in the AFM images (Fig. 4) and using Scherrer’s analysis [17] on the XRD (0002) full-width at half-maximum (FWHM). The enlarged grains in the films deposited at 200 °C contribute to higher surface roughness.

Fig. 3 shows XRD diffractograms from the Zn$_{1-x}$Mg$_x$O thin films deposited onto Si substrates with the indicated conditions. The (0002) peak is produced by both high temperature films and by the room temperature film deposited with lower substrate bias ($-50$ V). The film deposited at room temperature with $-100$ V substrate bias exhibits a disordered microstructure, suggesting damage caused by the additional energy in the depositing flux. Moderately elevated temperature produced a significant change in the microstructure of the films (as shown in the AFM images of...
Fig. 4) but increased substrate bias broadens the (0002) peak, again suggesting that additional energy in the depositing flux reduces the crystalline order in the films. The shift from 34.4° (the bulk ZnO value) to lower angles is caused by stress which is partially relieved in the film grown at 200°C [18].

AFM micrographs from the Zn$_{1-x}$Mg$_x$O thin films are shown in Fig. 4. In the films deposited at elevated temperature, the increased average grain size is clearly seen. Any effects on the grain size or surface roughness caused by varying the applied substrate bias were not measurable by AFM.

Hydroxyl groups present on ZnO surfaces are known to cause band-bending and sub-surface electron accumulation [19]. The valence band profile in the RT FCVA Zn$_{1-x}$Mg$_x$O film was determined using variable-energy valence-band XPS and is shown in Fig. 5. Given an average incident photon energy of ~300 eV, the energy difference between the valence band edge (VBE) and the Fermi energy (FE) [20] was ~0.5 eV greater than ~3.4 eV optical bandgap expected based on the film composition [1]. Increased average photon energy (resulting in a greater probe depth) yielded lower FE–VBE differences until, with incident photon energies of...
~1500 eV, the energy gap approached ~3.4 eV. These measurements showed that surface band-bending occurred in the Zn$_{1-x}$Mg$_x$O films. As in ZnO, this band-bending was attributed to surface contaminants including hydroxyl groups [21].

FCVA grown Zn$_{1-x}$Mg$_x$O films typically exhibit high n-type carrier concentration [12] with Fermi energy levels located less than 0.1 eV from the conduction band minimum [22]. From Fig. 5, we can therefore infer that the bands are bent downwards at the surface by 0.5 $\pm$ 0.1 eV. This band bending corresponds well with measurements from the m-plane of hydrothermally grown ZnO [22]. Since the surface of our films is granular, it more closely resembles the m-plane face than either the Zn-polar or O-polar faces.

XANES Zn L$_3$-edges from the Zn$_{1-x}$Mg$_x$O films and from a single crystal ZnO substrate are shown in Fig. 6. The near edge structure arises from electron transitions from Zn 2p states to unoccupied Zn 4s states [23,24]. Peak A$_1$ (1016 eV) can be ascribed to the Zn 4s derived state. The remaining features (A$_2$, A$_3$ and A$_4$) can be ascribed to the Zn 4d states [25]. Other authors have reported that the unoccupied Zn 4s states are relatively insensitive to Mg doping [26,27]. The Zn L$_3$-edge from the single crystal ZnO is consistent with previously reported EELS and XAS from ZnO [28]. The peak A$_3$ at ~1025 eV is reduced in intensity and other features are generally broadened in the Zn L$_3$-edges from the FCVA deposited Zn$_{1-x}$Mg$_x$O. This suggests the presence of a significant number of defects in the films.

In the O K-edge XANES (Fig. 7), the spectral features between 531 and 539 eV (B$_1$, B$_2$) can be attributed mainly to O 2p hybridisation, with highly dispersive Zn 4s states forming the bottom of the conduction band. The peak B$_2$ at ~538 eV is due to transitions to
non-dispersive O 2p states and 2px + y states. The region between 539 and 550 eV (B2 and B3) can be assigned to O 2p hybridised with Zn 4p states. Spectral features above 550 eV are due to the O 2p–Zn 4d hybridised states [28].

The O K-edge XANES spectra of Zn1–xMgO films are similar to those of the single crystal ZnO. However, the features in the spectra from the Zn1–xMgO films are less distinct than those from the single crystal ZnO. This could be the result of defects, a reduction in the number of unoccupied O 2p-derived states, or an increase in the number of electrons in O ions after Mg doping is expected since Mg has a significantly smaller electronegativity. More electrons are therefore transferred from Mg to the O 2p states, and the ionic character of the Zn1–xMgO alloys is increased [30,31].

Appreciable broadening of the spectral features in the O K-edges from the Zn1–xMgO films is most noticeable in the peak A2 at 538 eV. Krishnamurthy et al. report similar broadening in O K edge features of Co doped ZnO [26]. They state that calculations show that an oxygen vacancy alters the 1s binding energies of the oxygen atoms in that shell and subsequent shells surrounding the vacancy. In XAS, the 1s–2p dipole excitation of transitions originating from oxygen atoms in the shells surrounding a vacancy can result in a shifting of the XAS onset to lower absorption energies. This lowering and distribution of 1s binding energies also give rise to an effective broadening of all the conduction-band features observed in XAS. Annealing has indicated that defects related to oxygen deficiency are significant in ZnO films deposited by FCVA under similar conditions [11], so their presence within these Zn1–xMgO films is expected and would lead to broadened spectral features.

In Fig. 8, the Mg K-edge from the Zn1–xMgO film grown at 200 °C with floating potential is shown. This spectrum, with three main peaks (labelled C1, C3, C4), is similar to spectra previously produced from wurtzite Zn1–xMgO nanorods [30]. The three peaks are associated primarily with the Mg 3p–O 2p hybridised states. In this Mg K edge, there is no evidence for the presence of cubic Zn1–xMgO. All homogeneous Zn1–xMgO films (with x~0.12) had similar Mg K edges (not shown). For comparison, XANES spectra from films with higher Mg fractions (x~0.37 and x~0.66) prepared in the FCVA system under similar conditions, are also shown in Fig. 8. The additional peak (C2 at ~1310 eV) observed in the film with Mg fraction ~0.66 occurs in Mg K-edge XANES from pure cubic MgO [32] and cubic Zn1–xMgO [33]. Therefore, the Mg K edge XANES from the thin films with Mg fractions <0.37 were produced solely by the wurtzite phase of Zn1–xMgO.

4. Conclusion

Energetically deposited Zn1–xMgO thin films have been microstructurally characterised. The Zn0.8Mg0.2 cathode proved to be prone to oxidation (poisoning), causing both layering and phase separation in the deposited films. Non-reactive ablation steps assisted in minimising cathode poisoning and enabled dense, phase pure, wurtzite Zn1–xMgO to be grown at RT and 200 °C. Elevated substrate temperature resulted in enlarged grains and increased surface roughness whilst increased substrate bias caused reduced crystalline order. XANES from homogeneous FCVA deposited Zn1–xMgO revealed local atomic bonding similar to that in low doped single crystal ZnO but also features consistent with oxygen deficiency.

Acknowledgements

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References

Chapter 4. Ultraviolet detection from graphitic-C/Zn$_{1-x}$Mg$_x$O Schottky devices fabricated at moderate temperatures
Ultraviolet detection from graphitic-C/Zn$_{1-x}$Mg$_x$O Schottky devices fabricated at moderate temperatures

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Ultraviolet (UV) Schottky detector devices were fabricated on polycrystalline wurtzite Zn$_{1-x}$Mg$_x$O films energetically deposited onto a-plane sapphire at room-temperature (RT) and 200°C. The unintentionally doped, transparent, n-Zn$_{1-x}$Mg$_x$O films exhibit low surface roughness (<5% of film thickness), moderate carrier concentration, and Hall mobility up to 15 cm$^2$ V$^{-1}$ s$^{-1}$. The direct bandgaps of the RT and 200°C films (x = 0.24 and x = 0.20) were 3.57 eV and 3.40 eV. Schottky diodes with graphitic anodes formed on these films exhibited barrier heights up to 0.88 eV and ideality factors as low as 1.97. Spectral response measurements demonstrated UV/visible photo-current ratios up to ~10$^4$. [© 2013 AIP Publishing LLC. (http://dx.doi.org/10.1063/1.4826576)]

ZnO with hexagonal wurtzite structure has a bandgap of ~3.3 eV, while MgO with the cubic rock-salt structure has a bandgap of ~7.7 eV. The ionic radius of Mg$^{2+}$ is similar to that of Zn$^{2+}$, so Mg can readily be introduced to form wurtzite Zn$_{1-x}$Mg$_x$O, enabling a broad range of bandgaps in the ultraviolet (UV) to be achieved. High efficiency light emission and detection is possible at room temperature since wurtzite Zn$_{1-x}$Mg$_x$O has stable excitons. This has led to considerable interest in Zn$_{1-x}$Mg$_x$O as a cost-effective, high performance material for UVB (wavelength, $\lambda$ ~ 280 nm–315 nm) sources and detectors.

Growth techniques including pulsed laser deposition (PLD), molecular beam epitaxy, metal-organic chemical vapour deposition (MOCVD), and atomic layer deposition have produced thin films of Zn$_{1-x}$Mg$_x$O with excellent electronic/optical properties. However, these techniques typically require high substrate temperatures for device grade films and/or offer low throughput. The filtered cathodic vacuum arc (FCVA) technique offers low system and operating costs combined with industrial scalability. Also, due to the energetic depositing flux and associated dynamic annealing, FCVA provides access to more microstructural forms at lower substrate temperatures. Degenerately Al-doped ZnO layers have been grown by FCVA deposition for applications such as transparent conducting coatings, and more recently, FCVA grown ZnO has been used in metal semiconductor field effect transistors exhibiting high channel mobility and excellent long term stability. Lasing action has been demonstrated in Zn$_{1-x}$Mg$_x$O films grown by FCVA and patterned to form nano-needles. In this Letter, we report on graphite anode Schottky UVB detectors formed on FCVA grown Zn$_{1-x}$Mg$_x$O films. Moderate growth temperatures ($\lesssim$200°C) were employed to assess potential compatibility with temperature-sensitive substrates, such as flexible plastics.

In FCVA deposition, a low-voltage, high-current arc ablates a conducting cathode. An electromagnetic filter placed between the source and deposition chambers removes unwanted macroparticles and neutral atoms resulting in films that condense from an ionized plasma, promoting high density and strong adhesion. The films in this work were grown in a Nanofilm FCVA with a rotating 99.9% purity Zn$_{0.8}$Mg$_{0.2}$ cathode (diameter 68 mm) ablated using an arc current of 45 A. The filtered plasma was guided into the deposition chamber where the Zn$_{1-x}$Mg$_x$O films were reactively grown in an atmosphere of 1.38 mTorr oxygen and 0.07 mTorr argon. The argon was inlet to the source chamber to reduce oxide growth on the cathode surface. The Zn$_{1-x}$Mg$_x$O films were deposited at a rate of 1–1.5 nm/min on double-sided polished a-plane sapphire substrates at a floating potential. Films were grown at room-temperature (RT) and 200°C.

Fig. 1(a) shows atomic force microscope (AFM) images (measured using a Dimension 3100 AFM in tapping mode), and Fig. 1(b) shows x-ray diffractograms of the [0002] peak (collected using a Bruker D4 diffractometer equipped with a Cu Kz source) from both films. The differing height scales were selected to best show the surface morphology. The films were void of macroparticles, and their root-mean-squared (RMS) surface roughness was <5% of their thickness. Average grain size and roughness increased with the deposition temperature. In the diffractograms (Fig. 1(b)), the [0002] peaks normalised to the [0002] peak at ~34° and substrate peaks are labelled z.

![Image](image_url)

**FIG. 1.** (a) $1 \times 1 \mu$m$^2$ AFM images and (b) X-ray diffractograms from the Zn$_{1-x}$Mg$_x$O films deposited at 200°C and RT. The diffractograms have been normalised to the [0002] peak at ~34° and substrate peaks are labelled z.
peak of the RT film is centered \(\sim 0.1^\circ\) lower than the bulk value for ZnO (34.4°), suggesting the presence of biaxial stress, frequently observed in energetically deposited films.\(^{18}\) The film deposited at 200°C produced an \{0002\} centered at 34.4°, indicating that stress was relieved at the higher temperature. This peak is also narrower, consistent with the larger grains seen in the AFM images. Diffraction peaks attributable to the cubic phases of MgO or Zn\(_{1-x}\)Mg\(_x\)O were not observed from either film.

The average stoichiometry of each film (shown in Table I) was determined from XPS depth profiles collected using a K-Alpha XPS system equipped with an Al K\(\alpha\) source. A hot-pressed 99.9% purity Zn\(_{0.8}\)Mg\(_{0.2}\)O standard was used to generate the Schofield sensitivity factors required in quantifying the film composition. The measured Mg fractions were close to that of the cathode but suggest that Mg may evaporate and/or sputter preferentially during energetic deposition at 200°C.

Figure 2 shows the UV-visible transmission spectra (collected using a Cary 50 spectrometer) and (inset) a Tauc plot calculated from these spectra. Transmission through both films is >75% in the visible region with the thicker RT film exhibiting the lower transmission. In the Tauc plot,\(^{19}\) the extended linear regions show that the Zn\(_{1-x}\)Mg\(_x\)O films have direct optical bandgaps (shown in Table II). These are consistent with previously observed optical bandgaps of thickness \(\sim 20\) nm and diameter 400 nm on the as-prepared RT and 200°C grown Zn\(_{1-x}\)Mg\(_x\)O films. The graphitic microstructure of the evaporated carbon films was confirmed using Raman spectroscopy (not shown).\(^{24}\) Electrical measurements on the graphitic carbon (using van der Pauw contacts) revealed an average resistivity of 0.95 \(\Omega\) cm. The anodes were capped with thermally evaporated Ag or NiCr \((\sim 100\) nm thickness) to increase robustness for device probing. Their lithographically defined dimensions enabled accurate determination of diode parameters from the current-voltage measurements.

The Schottky barrier heights (\(\Phi_b\)) and ideality factors (\(n\)) of typical C-Zn\(_{1-x}\)Mg\(_x\)O Schottky diodes, calculated using standard thermionic emission theory,\(^{25}\) are shown in Table II. The ideality factors of the diodes on the 200°C deposited film were higher than those on the RT film. This difference is attributed to the higher carrier concentration and surface roughness of the 200°C film, leading to an increased probability of tunneling through the potential barrier and lateral inhomogeneity at the device interface.\(^{26}\) The typical Schottky barrier height measured from the RT film is comparable with those previously measured from metallic Schottky anodes to Zn\(_{1-x}\)Mg\(_x\)O.\(^{4}\) The lower barrier in the film deposited at 200°C is similarly attributed to its higher surface roughness. Very similar diode characteristics were obtained from colloidal graphite anodes painted onto both films (with dimensions determined from electron microscope imaging).

Hydroxyl groups present on ZnO surfaces are known to cause band-bending and sub-surface electron accumulation, thereby limiting the performance of ZnO Schottky diodes.\(^{27}\)

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Dep. rate (nm/min)</th>
<th>Thick. (nm)</th>
<th>RMS rough. (nm)</th>
<th>Grain diam. (nm)</th>
<th>Pos. (°)</th>
<th>FWHM (°)</th>
<th>Mg frac.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>1.4</td>
<td>88</td>
<td>0.29</td>
<td>25</td>
<td>34.3</td>
<td>0.68</td>
<td>0.24</td>
</tr>
<tr>
<td>200°C</td>
<td>1.1</td>
<td>60</td>
<td>2.5</td>
<td>37</td>
<td>34.4</td>
<td>0.42</td>
<td>0.17</td>
</tr>
</tbody>
</table>

**TABLE I.** The deposition conditions and microstructural properties of Zn\(_{1-x}\)Mg\(_x\)O films deposited by FCVA onto a-plane sapphire substrates.
The valence band profile in the RT FCVA Zn$_{1-x}$Mg$_x$O film was determined using variable-energy valence-band XPS (collected using the Australian Synchrotron) and is shown in Fig. 3(a). Given an average incident photon energy of $\sim$300 eV, the energy difference between the valence band edge (VBE) and the Fermi energy (FE) was $\sim$0.4 eV greater than the optical bandgap. Increased average photon energy (corresponding to probing deeper into the film) yielded lower FE-VBE differences until, with incident photon energies of $\sim$1500 eV, the energy gap became approximately equal to the optical bandgap. These measurements of depth-dependent FE-VBE energy prove that band-bending occurred in the film. Fig. 3(b) shows XPS O1s spectra taken before and after ex-situ oxygen plasma treatments of the RT film (using a 35 W DC glow discharge with 20 mTorr oxygen pressure for 20 min). The prominent peak attributed to chemisorbed oxygen species (OH$^-$ and CO$_2^-$) indicates significant surface hydroxyl attachment and the fraction of chemisorbed oxygen species dropped by 30% after the plasma process, indicating their partial removal. We therefore believe that the rectification ratios and ideality factors of these diodes were limited by surface contaminants including hydroxyl groups.

Figure 4 shows the dark and UV illuminated ($\lambda_c = 285$ nm and 365 nm) current-voltage characteristics of back-to-back C-Zn$_{1-x}$Mg$_x$O anodes (of diameter 400 $\mu$m and separation 200 $\mu$m) on the RT (Fig. 4(a)) and 200°C (Fig. 4(b)) deposited films. On a purpose-made probe station, these devices were reverse side illuminated (through the sapphire substrates) using light emitting diodes (LEDs) of differing centre wavelengths ($\lambda_c$) and all with full-width-at-half-maxima of $<$20 nm. The irradiance of the LEDs was measured using a calibrated optical measurement system and the current through each of the LEDs was adjusted to provide identical optical power per unit area (3.6 mW/cm$^2$) at the device, irrespective of wavelength. As shown in Fig. 4, the devices on the film deposited at 200°C exhibit an increase in current (at 0.5 V) of three orders of magnitude upon exposure to UVB ($\lambda_c = 285$ nm). The photo-current during UVA ($\lambda_c = 365$ nm) exposure is 20 times smaller. The device on the RT film only exhibits 2 orders increased current during exposure to UVB. This reduced response to UVB can be attributed to the wider bandgap, increased barrier height, and larger series resistance in the RT film.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Opt. bandgap (eV)</th>
<th>$\mu_{Hall}$ (cm$^2$/V.s)</th>
<th>$n$ ($\times 10^{18}$ cm$^{-3}$)</th>
<th>Sheet res. ($\Omega/\square$)</th>
<th>$\Phi_h$ (eV)</th>
<th>$\eta$</th>
<th>Series res. ($\Omega$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>3.57</td>
<td>15</td>
<td>1.1</td>
<td>69 k</td>
<td>0.87</td>
<td>1.95</td>
<td>60 k</td>
</tr>
<tr>
<td>200°C</td>
<td>3.44</td>
<td>5.0</td>
<td>8.1</td>
<td>28 k</td>
<td>0.70</td>
<td>2.7</td>
<td>28 k</td>
</tr>
</tbody>
</table>

TABLE II. Optical/electrical characteristics of the FCVA deposited Zn$_{1-x}$Mg$_x$O films and typical device parameters from C-Zn$_{1-x}$Mg$_x$O Schottky devices formed on these films.

FIG. 3. (a) The energy gap between the upper valence band edge and the Fermi energy as a function of incident photon energy and (b) O1s XPS spectra collected from Zn$_{1-x}$Mg$_x$O films before and after an O plasma treatment.

FIG. 4. Dark and UV illuminated current-voltage characteristics of C-Zn$_{1-x}$Mg$_x$O Schottky junctions formed on FCVA Zn$_{1-x}$Mg$_x$O films deposited at (a) RT and (b) 200°C. The insets on each plot shows quantum efficiencies evaluated at 500 mV bias and a device schematic.
The external quantum efficiencies, $\eta_{\text{EQE}}$ (defined as the number of photo-electrons generated per second divided by the number of photons incident per second) of the devices were calculated from photo-current measurements performed during UV/visible illumination (provided by the LEDs) with fixed optical power density $P_{\text{opt}}$ of 3.6 mW cm$^{-2}$ and with an applied bias of 0.5 V. The device area $A$ was assumed to be equal to the entire region of the film illuminated by the LEDs (0.2 cm$^2$). The number of incident photons $N_p$ was then calculated from $N_p = P_{\text{opt}}A/(hc/\lambda_c)$. Under these conditions, the device on the film deposited at 200 °C demonstrated an $\eta_{\text{EQE}}$ of 8% when exposed to UVB (shown in Fig. 4(b) inset) and UV/visible rejection ratio of $\sim 10^4$. The variation of $\eta_{\text{EQE}}$ with $\lambda_c$ from the RT film (Fig. 4(a)) reflects its lower current during UVB exposure and a higher dark current when compared with the device on the 200 °C deposited film.

This work shows that polycrystalline wurtzite Zn$_{1-x}$Mg$_x$O films deposited from a FCVA at moderate temperatures are of sufficient quality (as prepared) for electronic devices. Thermally evaporated graphitic carbon is shown to form rectifying Schottky contacts to Zn$_{1-x}$Mg$_x$O and using standard optical lithography, devices with accurately defined dimensions were produced. Schottky barrier heights up to 0.87 eV and ideality factors as low as 1.97 are reported from these devices. Spectral response measurements revealed visible-blind UVB detection capability.

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Chapter 5. Characterisation and device applications of ZnO films deposited by high power impulse magnetron sputtering (HiPIMS)
Characterization and device applications of ZnO films deposited by high power impulse magnetron sputtering (HiPIMS)

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Abstract
ZnO films have been reactively deposited on sapphire substrates at 300 °C using a high power impulse magnetron sputtering deposition system and characterized structurally, optically and electronically. The unintentionally doped n-type ZnO films exhibit high transparency, moderate carrier concentration (∼5 × 10^{18} \text{ cm}^{-3}) and a Hall mobility of 8.0 \text{ cm}^{2} \text{ V}^{-1} \text{ s}^{-1}, making them suitable for electronic device applications. Pt/ZnO Schottky diodes formed on the HiPIMS deposited ZnO exhibited rectification ratios up to 10^4 at ±2 V and sensitivity to UV light.

1. Introduction
High quality ZnO films required for devices are typically deposited using techniques such as molecular beam epitaxy [1], metal organic chemical vapour deposition [2] and pulsed laser deposition (PLD) [3]. These techniques are relatively expensive to implement and offer limited throughput when compared with sputtering. The high power impulse magnetron sputtering (HiPIMS) deposition method provides similar large-area/low-cost benefits to conventional magnetron sputtering but superior control over the structural and electronic characteristics of the deposited films [4] due to its energetic, macroparticle-free plasma. HiPIMS typically has a lower deposition rate than direct current (dc) or radio-frequency (RF) magnetron sputtering because much of the energy goes into the generation of high ionization charge states. In reactive operation, the pulsed duty cycle in HiPIMS can be optimized to promote oxygen/nitrogen incorporation and ensure stoichiometric oxides/nitrides [5]. HiPIMS is now a well-established production method for mechanical coatings [6, 7] and has been used to produce transparent conducting Al doped ZnO films [8]. More recently, superconducting Nb layers have been deposited using HiPIMS [9]. However, despite the numerous benefits afforded, reports on production of electronic device layers using HiPIMS are few. Konstantinidis et al [10] reported structural and optical properties of ZnO films deposited on glass but did not report the electronic properties. The ability of HiPIMS to produce metal oxide films with high carrier mobility is under debate. High energy oxygen ions created in reactive HiPIMS are a particular concern and it has been reported that they can strongly influence the micro-structure of some metal oxides [11, 12].

Principle aims of this work were to measure the electronic properties of HiPIMS grown ZnO and determine whether it could be incorporated into functional electronic devices. We describe the structural, optical and electrical characteristics of ZnO films deposited from a HiPIMS deposition system. We also describe the electrical properties and ultraviolet sensitivity of Pt anode Schottky devices fabricated on HiPIMS ZnO. These devices are key components in ZnO electronics with applications in transparent field-effect transistors [13], transparent logic devices [14], ultraviolet photodetectors [15] and gas sensors [16].

2. Experimental
ZnO films were deposited onto c- and α-plane sapphire substrates at 300 °C in an AJA Inc. HiPIMS system equipped with a 99.999% purity 3 inch diameter Zn target. The base pressure prior to deposition was 1 × 10^{-6} Torr and the process gas pressure (with Ar and O\text{2} inlet flow rates of 30 and 15 sccm)
HiPIMS voltage and current waveforms used for the ZnO thin film depositions. was 3.0 mTorr. The HiPIMS pulse parameters (provided by a GBS Electronik GmbH RUP7 power supply) were; pulse length 50 µs, duty cycle 0.5%, voltage 650 V (producing a current 30–35 A). The HiPIMS voltage (black) and current waveforms (dark grey) are shown in figure 1, together with the trigger pulse from the signal generator (light grey). The RUP7 is designed to deliver a current and maintain the pre-set output voltage, and thus has an output inductance. This output inductance and small output capacitance causes the ringing at the start of the voltage pulse, which persists whilst there is no load prior to plasma ignition. The onset of current at 20 µs is associated with plasma ignition. This delay in current onset is typical for HiPIMS systems and is well described by Anders [17]. Subsequent to plasma ignition, the target current increases almost linearly until the end of the voltage pulse. This is typical of HiPIMS operation of a sputtering source as compared with the saturation of current observed in conventional dc sputtering [18]. The deposition rate (∼1 nm min⁻¹) was selected after growth with higher duty cycles (i.e. higher Zn deposition rate) produced sub-stoichiometric ZnO (leading to inappropriately high n-type carrier concentration). In industrial applications, this limitation could be alleviated by delivering oxygen in an activated form through a secondary, inductively coupled plasma generation coil. In this study, this approach was not pursued since only thin (∼30 nm) ZnO films were required for device layers. This thickness was also appropriate for comparison with the (30 nm thick) HiPIMS ZnO films reported by Konstantinidis et al [10].

Following deposition, the surfaces of the films were mapped in tapping mode using a Dimension 3100 atomic force microscope (AFM) and imaged using a scanning electron microscope. A Bruker D4 x-ray diffraction (XRD) system was employed to characterize the crystallinity of the film. A Cary 50 UV–Vis spectrometer was used to obtain the optical transmission over the wavelength range 200–800 nm, enabling the determination of the optical band-gap from a Tauc plot [19]. Raman spectra were obtained using a Renishaw InVia system operating with an excitation wavelength of 514 nm and a grating of 2400 lines/mm.

After microstructural and optical characterization, photolithographically defined Ti/Au (10 nm/100 nm in thickness) Van der Pauw corner contacts were thermally evaporated onto ZnO films supported on diced 10 × 10 mm² c-plane sapphire substrates. Room-temperature Hall effect measurements were performed using these samples in an Ecopia HMS 3000 system with fixed 0.55 and 0.91 T magnetic fields. After the Hall measurements, Pt anodes were deposited using a Gatan 682 precision etching/coating system and defined using photolithographic lift-off. Additional thermally evaporated Ti/Au Ohmic contacts were defined by photolithography and located 10 µm from the Pt anodes. The areas of the anodes ranged from 0.0035 to 0.028 mm². Finally, room-temperature current–voltage characteristics were measured in air using a probe station and Keithley 2410 source-meter interfaced with a personal computer.

3. Results and discussion

Figure 2 shows an AFM image and x-ray diffractogram taken from the HiPIMS grown ZnO film on c-plane sapphire. The regular grain size in the film and its macro-particle free surface are clear in the AFM image of figure 2(a). Electron microscopy revealed the same macro-particle free surface extending over the substrate area (not shown here). This indicates that the operating conditions employed resulted in pure HiPIMS operation without arcing that can result in the generation and inclusion of macro-particles. The x-ray diffractogram in figure 2(b) shows that the ZnO thin film is c-axis oriented. The position of the (0 0 0 2) peak is as expected for bulk ZnO and indicates that little stress exists in the film following deposition.

The microstructural and electrical properties measured from the HiPIMS ZnO films on a-plane and c-plane sapphire substrates are shown in table 1. As observed in ZnO films deposited by PLD [20], the film characteristics do not vary significantly with the orientation of the underlying sapphire.
Table 1. Structural and electrical properties of as-deposited ZnO films grown by HiPIMS and FCVA [21].

<table>
<thead>
<tr>
<th>Growth method</th>
<th>Sapphire substrate orient.</th>
<th>Thick. (nm)</th>
<th>Rough. RMS (nm)</th>
<th>Aver. Grain size (nm²)</th>
<th>(0 0 0 2) centre (°)</th>
<th>FWHM (°)</th>
<th>Hall Mobility (cm² V⁻¹ s⁻¹)</th>
<th>n-type carrier conc. (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HiPIMS</td>
<td>α-plane</td>
<td>30</td>
<td>0.9</td>
<td>1200</td>
<td>34.5</td>
<td>0.70</td>
<td>7.0</td>
<td>4.1 × 10¹⁸</td>
</tr>
<tr>
<td>HiPIMS</td>
<td>c-plane</td>
<td>28</td>
<td>0.8</td>
<td>1300</td>
<td>34.5</td>
<td>0.65</td>
<td>8.0</td>
<td>4.5 × 10¹⁸</td>
</tr>
<tr>
<td>FCVA</td>
<td>α-plane</td>
<td>55</td>
<td>3.0</td>
<td>2000</td>
<td>34.8</td>
<td>0.3</td>
<td>2.0</td>
<td>5.0 × 10¹⁸</td>
</tr>
</tbody>
</table>

Figure 3. (a) Transmission and (b) Tauc plot obtained from a HiPIMS ZnO film grown on α-plane sapphire and 28 nm in thickness.

Table 1 also includes structural and electrical measurements from a ZnO film deposited by filtered cathodic vacuum arc (FCVA) with similar process pressure, substrate temperature and deposition rate [21]. The FCVA grown ZnO film is significantly rougher than the HiPIMS grown film (5.5% versus 3.0% of the ZnO film thickness, respectively). Typically, sputtered ZnO films also exhibit larger RMS roughness. The grain size in the HiPIMS ZnO film is smaller than in the FCVA deposited film and significantly smaller than obtained in PLD grown ZnO films [3]. Konstantinidis et al [10] observed similarly small grain sizes in their HiPIMS deposited ZnO films. They reasoned that ion irradiation and condensation induced the formation of more nucleation clusters while the growth of thick columns with voids was prevented due to resputtering and redeposition [10]. The full-width at half-maximum (FWHM) obtained from the XRD measurements is consistent with the small grain size measured by AFM and considerably larger than the sub-0.1° FWHMs frequently achieved from PLD grown ZnO films [3]. The measured Hall mobility is also lower than the Hall mobility typically obtained in PLD grown ZnO films where values ∼>50 cm² V⁻¹ s⁻¹ have been achieved but exceeds the mobility obtained in the FCVA grown ZnO film, despite the larger grain size in this film. Importantly, the mobility is comparable to that typically achieved in ZnO films grown by conventional magnetron sputtering [22] and the n-type carrier concentration is moderate.

Optical transmission measurements over the 200–800 nm wavelength range are shown in figure 3(a). Transmission in the visible region of the spectrum is approximately 93% for the 30 nm thick ZnO film (on α-plane sapphire) after background correction. This transmission plot is indicative of a high quality ZnO film and similar to previous transmission plots from HiPIMS deposited ZnO [10]. A Tauc plot calculated from the transmission response is shown in figure 3(b) and the optical band-gap obtained from the plot is ∼3.25 eV. The room-temperature band-gap for bulk ZnO is typically reported to be 3.3 eV [23]. The cause of frequently observed narrower band-gaps has been attributed to a valence band-donor transition at ∼3.15 eV [23].

The Raman spectrum obtained from the as-deposited HiPIMS ZnO film with thickness 30 nm and supported on α-plane sapphire is shown in figure 4. It is characteristic of the hexagonal wurtzite phase with principal phonon lines occurring at 380 cm⁻¹ (A1, TO), 395 cm⁻¹ (Quasi-A1, E1, TO), 413 cm⁻¹ (E1, TO), 437.5 cm⁻¹ (E2), 579 cm⁻¹ (A1, LO), 585 cm⁻¹ (Quasi-A1, E1, LO) and 591 cm⁻¹ (E1, LO). Phonon lines occurring at 379, 417, 429 and 644 cm⁻¹ are produced by the underlying α-plane sapphire substrate. It is significant that the feature at ∼580 cm⁻¹ in this spectrum is sharp. Although reported assignments for the bands between 540 and 584 cm⁻¹ in the spectrum of ZnO vary, numerous studies have shown that this spectral region is strongly influenced by the presence of oxygen vacancies and/or interstitial Zn [24]. A strong coupling of free carriers with the E1 (LO) mode causes broadening of the linewidth, frequency down-shift, and asymmetric lineshape [25]. Raman spectra with broad features between 500 and 600 cm⁻¹ have been obtained from ZnO films RF magnetron sputtered at 275 °C and attributed to electric field induced Raman scattering.
caused by band bending at grain boundaries [26]. Since both increased oxygen process pressure and post-deposition annealing reduced the intensity of the feature between 500 and 600 cm$^{-1}$, this band bending could again be linked to the presence of oxygen vacancies and/or interstitial Zn. The Raman measurements shown here therefore indicate that oxygen is efficiently incorporated into the HiPIMS deposited ZnO film, possibly due to the low duty cycle of the HiPIMS process. The Raman measurements do not show any significant defect signatures that can be attributed to the presence of negative oxygen ions in the HiPIMS plasma.

Figure 5 shows the current–voltage characteristic of a Pt diode (area = 0.004 mm$^2$) fabricated on the as-deposited HiPIMS ZnO film supported on $c$-plane sapphire with thickness 28 nm. The rectification ratio at ±2 V exceeds four orders of magnitude at room temperature and in dark conditions. As shown in figure 5, this diode exhibited sensitivity to UV illumination. An increase in current of more than three orders of magnitude occurred upon exposure to a UV light source with an applied potential between −1 and −2 V. Measured 2.0 cm from the diode/calibrated detector, the light source produced an approximately Gaussian irradiance with a peak of 5.5 μW cm$^{-2}$ nm$^{-1}$ at 360 nm, a FWHM of 36 nm and an integrated intensity of 0.21 mW cm$^{-2}$. The diodes were oven baked in air at 180 °C for 1 h and their room-temperature current–voltage characteristics (dark and UV exposed) were unchanged.

The ideality factor ($\eta$) and effective Schottky barrier height ($\Phi_{e\text{ff}}$) extracted from the diode $I(V)$ characteristic in figure 5 using standard thermionic theory [27] are shown in table 2 alongside similar parameters from three surrounding devices. The ideality factors and barrier heights tend to improve with reduced device area. This suggests that the performance of the diodes is limited by defects located at the Pt/ZnO junctions and the number of defects increases with area. The smaller devices with lower ideality factors and lower reverse currents provide higher UV:dark current ratios.

The difficulties experienced in fabricating near-ideal Schottky diodes on ZnO arise due to surface effects including hydroxyl attachment, increased oxygen vacancies and electron accumulation [28]. Numerous surface treatments including hydrogen peroxide immersion [29], oxygen plasma immersion [30, 31], additional interfacial layers [32] and oxygen annealing [21] have been used to improve the performance of Schottky diodes formed on ZnO and could yield improvements on the properties of devices formed on HiPIMS grown ZnO. For example, Pt anodes could be deposited directly onto an oxygen plasma treated ZnO surface in a multi-target HiPIMS system. However, as shown, Schottky devices with functional performance can be formed on ZnO films deposited at moderate temperature by HiPIMS without high temperature annealing, plasma treatment or chemical treatment.

### 4. Conclusion

ZnO films, reactively deposited on sapphire substrates at 300 °C using a HiPIMS deposition system, have been characterized structurally, optically and electronically. The unintentionally doped n-type ZnO films exhibit high transparency, moderate carrier concentration and reasonable Hall mobility, making them suitable for transparent electronic devices. Raman measurements suggest that oxygen is efficiently incorporated into the ZnO film. Pt anode Schottky diodes formed on the films exhibited up to 1.8 × 10$^4$ current rectification at ±2 V and sensitivity to UV light. The work suggests that in addition to mechanical coatings, HiPIMS may be suitable for production of semiconducting metal oxide films for electronics.

### Acknowledgments

The authors would like to thank Phil Wilksch for assistance with UV exposure calibration, Jennifer Hartley from the Industrial Research Institute at Swinburne University of Technology for assistance with the Raman spectroscopy and the RMIT University Microscopy and Microanalysis Facility. The authors also gratefully acknowledge the Australian Research Council for financial support.

### References


Chapter 6. $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films grown using HiPIMS
1. Introduction

Zn$_{1-x}$Mg$_x$O is an optically transparent semiconductor that can exhibit a broad range of band-gaps in the ultraviolet [1–3] from ~3.3 eV (ZnO) to ~7.7 eV (MgO) [3, 4]. Since the ionic radius of Mg$^{2+}$ (0.57 Å) is similar to that of Zn$^{2+}$ (0.60 Å), the lattice constant of ZnO changes little when Zn is replaced with Mg [2]. However, the different structures of ZnO (wurtzite) and MgO (cubic) impose a miscibility limit on wurtzite Zn$_{1-x}$Mg$_x$O (ranging from $x = 0.25$ to $x = 0.44$ depending on deposition method) above which a mixed cubic/wurtzite structure forms [5–8]. In wurtzite Zn$_{1-x}$Mg$_x$O, efficient light emission and absorption are possible at room temperature due to stable excitons, enabling its application in ultraviolet sources and detectors [3]. Other applications include Zn$_{1-x}$Mg$_x$O/ZnO hetero-junctions in which very high carrier mobilities have been demonstrated [9].

Pulsed laser deposition, molecular beam epitaxy and atomic layer deposition have produced thin films of Zn$_{1-x}$Mg$_x$O with desirable electronic/optical properties [7, 8, 10]. These methods do have some disadvantages; either suffering limited deposition rates, limited area capabilities or high substrate temperature requirements. The high power impulse magnetron sputtering (HiPIMS) deposition method provides similar large-area/low-cost benefits to conventional magnetron sputtering but affords superior control over the structural and electronic characteristics of the deposited films [11] due to its energetic plasma. In reactive operation, the pulsed duty cycle in HiPIMS can be optimized to promote oxygen/nitrogen incorporation, enabling deposition of stoichiometric oxides/nitrides [12, 13]. As much of the energy in HiPIMS goes into the generation of high ionization charge states, deposition rates quoted are typically lower than those provided by direct current (dc) or radio-frequency (RF) magnetron sputtering.
However, the deposition rates achievable are adequate for the thin active layers required in many optical/electronic devices. Whilst HiPIMS is an established production method for mechanical coatings [14, 15], its ability to produce metal oxide films with low defect density and high carrier mobility is under debate. High energy oxygen ions created in reactive HiPIMS are a particular concern as they have been shown to strongly influence the micro-structure of some metal oxides [16, 17]. Despite this, high quality transparent conducting Al-doped ZnO films [18] and moderately doped ZnO films [19] have been energetically deposited by HiPIMS. More recently, ZnO and Zn$_{1-x}$Mg$_x$O films (with Mg fraction $x \sim 0.2$) deposited from the energetic plasma of a filtered cathodic vacuum arc (FCVA) have demonstrated optical and electronic properties suitable for device applications [20]. Due in part to the low surface roughness provided by energetic deposition, enhanced hemocompatibility has also been reported from FCVA deposited ZnO [21]. These reports motivate further investigation into energetic deposition of ZnO-based materials.

Here, we report the structural, optical and electronic properties of bandgap tuned Zn$_{1-x}$Mg$_x$O films energetically deposited at moderate temperatures. A reactive co-deposition technique (DCMS Mg, HiPIMS Zn) enabled these properties to be studied as a function of Mg content in a single film.

2. Methods

A Zn$_{1-x}$Mg$_x$O thin film was grown on an a-plane sapphire (100 nm diameter) wafer using a combination of DCMS (Mg) and HiPIMS (Zn) in an Ar/O$_2$ atmosphere with gas pressures of 1.5 and 4.5 mTorr, respectively (total gas pressure 6.0 mTorr). The plasma guns (diameter 3 cm, target purity Zn 99.998% and Mg 99.95%) were arranged on opposite sides of the chamber (both 250 mm from substrate) and (with the aid of a quartz film thickness monitor) tilted relative to the substrate to provide the desired compositional range during deposition (see figure 1). The substrate temperature was 200°C and the HiPIMS pulse width, frequency and peak voltage were respectively, 60 µs, 200 Hz and 600 V (provided by a GBS Elektronik GmbH RUP7 high power pulse generator) producing a time-averaged power of 90 W. The DCMS gun was operated at 124 W average power (provided by an Advanced Energy MDX500). Following deposition, the Zn$_{1-x}$Mg$_x$O coated sapphire was diced into 10 × 10 cm$^2$ samples for further structural, chemical, optical and electrical analysis.

Atomic force micrographs were obtained using a Digital Instruments Dimension 3100 operating in tapping mode with tips of maximum radius 10 nm. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific K-alpha (with Al k$\alpha$ source, spot size 400 µm dia.). X-ray diffraction (XRD) measurements were collected using a Bruker D4 Endeavour in the Bragg-Brentano configuration and equipped with a Cu source (voltage 40 kV, current 35 mA) and a collection area of 6 mm diameter. Scherrer’s analysis [22] was used to estimate the average crystallite size from the diffractograms. Cross-sectional transmission electron microscope (XTEM) specimens were prepared using mechanical polishing and ion beam thinning then imaged in a JEOL 2100F equipped with a field emission gun (FEG) operating at 200 kV. Optical properties were measured (over the spectral range 200–800 nm) using a Varian Cary 50 or an Agilent Cary 5000 UV-Visible spectrometer with apertures of 8 mm$^2$ and 1 mm$^2$, respectively. All measurements were performed at the centre of the 10 mm$^2$ diced samples unless otherwise stated.

Room temperature electrical measurements were performed using an Ecopia HMS 3000 system with a fixed 0.55 T magnetic field. Al Van der Pauw corner contacts (each of area 0.78 mm$^2$) were thermally evaporated through a stencil.
onto the surface of each 10 × 10 mm² thin film sample. Graphitic Schottky anodes (diameter 200 µm) used for device- and photo-detection- measurements were flash evaporated (using a Dynavac thermal evaporator with base pressure of 1 × 10⁻⁶ Torr) from a carbon fibre onto a sample with lithographically patterned photoresist. Ag was evaporated onto the graphite anodes (before the photoresist was dissolved) to aid device probing. UV response measurements were performed using a purpose made probe station equipped with reverse side UV/visible illumination (provided by LEDs with different centre wavelengths [20]).

### Table 1.

Table 1. Compositional, optical and structural properties of the 10 × 10 mm² thin film samples taken from the co-deposited Zn₁₋ₓMgₓO film. Note that films exhibiting two optical bandgaps were phase separated.

<table>
<thead>
<tr>
<th>Mg Fract. (x)</th>
<th>Opt. E_g (eV)</th>
<th>C lattice const. (Å)</th>
<th>Crystallite size (nm)</th>
<th>{0002} FWHM (°)</th>
<th>{0002} peak position (°)</th>
<th>RMS roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.07</td>
<td>3.45</td>
<td>5.27</td>
<td>11</td>
<td>0.87</td>
<td>34.01</td>
<td>1.96</td>
</tr>
<tr>
<td>0.16</td>
<td>3.56</td>
<td>5.26</td>
<td>11</td>
<td>0.91</td>
<td>34.07</td>
<td>2.27</td>
</tr>
<tr>
<td>0.23</td>
<td>3.70</td>
<td>5.24</td>
<td>10</td>
<td>0.97</td>
<td>34.15</td>
<td>1.92</td>
</tr>
<tr>
<td>0.27</td>
<td>3.87</td>
<td>5.22</td>
<td>10</td>
<td>0.98</td>
<td>34.31</td>
<td>0.87</td>
</tr>
<tr>
<td>0.38</td>
<td>3.90/4.91</td>
<td>5.2</td>
<td>10</td>
<td>0.95</td>
<td>34.43</td>
<td>1.74</td>
</tr>
<tr>
<td>0.51</td>
<td>4.05/5.31</td>
<td>5.18</td>
<td>8</td>
<td>1.15</td>
<td>34.62</td>
<td>1.22</td>
</tr>
</tbody>
</table>

3. Results and discussion

The HiPIMS voltage (solid line) and current waveforms (dotted) are shown in figure 2 alongside the trigger pulse (dashed line). The RUP7 power supply delivers a current whilst maintaining the pre-set output voltage so exhibits an output inductance. This output inductance together with a small output capacitance causes the ringing at the start of the voltage pulse, which persists (while there is no load) prior to plasma ignition. After plasma ignition, the target current increases almost linearly until the end of the voltage pulse.
This is caused by the return of a proportion of the ionized sputtered flux to the target, sputtering yet more material. This is typical of HiPIMS operation [23].

Table 1 summarises the structure, composition and optical properties of the co-deposited \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) film. The \( x \) fraction used in the sample labels was measured using XPS. As expected, the highest \( x \) was measured at the wafer location nearest the DCMS Mg gun during deposition. As the distance from the Mg gun increased, \( x \) decreased monotonically.

Figures 3(a)–(c) show AFM images from selected \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) films. The surface morphology appears independent of \( x \) and is similar to that often observed in physical vapour deposited (PVD) \( \text{ZnO} \) films, consisting of well-defined grains with average diameter of \( \sim 35 \) nm. The RMS roughness of all samples was less than 5% of the film thickness (table 1), and no macro-particles were observed. Film thickness ranged from 80 nm to 290 nm depending on the location the sample was taken from on the sapphire wafer.

Figure 3(d) shows \{0 0 0 2\} XRD reflections from the wurtzite phase in \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) samples with differing \( x \) content. With an increase in \( x \), the intensity of the \{0 0 0 2\} reflection decreases. This trend is attributed to decreasing structural order as more Mg is incorporated within the wurtzite phase. Figure 4 shows the \{0 0 2\} peak positions and full-width-at-half-maxima (FWHM) as a function of \( x \) in all films. The \{0 0 2\} peak position shifts monotonically to higher angles as \( x \) increases. This corresponds to a reduction in the \( c \)-axis lattice constant (table 1), caused in part by the smaller ionic radii of \( \text{Mg}^{2+} \) relative to \( \text{Zn}^{2+} \). Compressive stress in the film produces an additional shift that is discussed in more detail later. The FWHM of the \{0 0 2\} peak tends to increase with increasing \( x \), consistent with reduced crystalline order. The \( \sim 10 \) nm average diameter of the crystallites, calculated using Scherrer’s analysis, was found to decrease slightly with increasing \( x \) (see table 1).

Figure 5(a) shows Tauc plots calculated from the UV-visible transmission through the \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) samples with indicated compositions and (b) the optical bandgap across the \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) film as a function of \( x \). Phase separated samples exhibit two bandgaps. The inset shows optical transmission in 1 mm steps across the thin film sample where phase separation occurs, the horizontal arrow indicates increasing Mg content. Note the gradual appearance of a second absorption edge as Mg fraction increases.

Figure 5(b) shows Tauc plots calculated from the UV-visible transmission spectra [24], of \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) samples with \( x \) indicated in the legend. The expected progression to wider bandgaps with increasing \( x \) is illustrated more clearly in figure 5(b). The miscibility limit of Mg in the co-deposited wurtzite \( \text{Zn}_{1-x}\text{Mg}_x\text{O} \) occurred at \( x = 0.32 \pm 0.1 \), as shown in figure 5(b). Samples with \( x > 0.33 \) contained wurtzite and cubic phases, each with distinct band-gaps. In order ascertain the number of bandgaps and therefore phases present, the inflection method [25] rather than the Tauc method was employed.

In figure 6, the microstructure of a section of the co-deposited film with composition \( \text{Zn}_{0.92}\text{Mg}_{0.07}\text{O} \) is shown in TEM micrographs and an accompanying diffraction pattern. Figure 6(a) shows the entire film \( \sim 200 \) nm in thickness with...
the sapphire substrate located at the bottom of the image. Figure 6(c) shows the film/substrate interface region at higher magnification. In this image, the growth appears epitaxial with the <0001> direction normal to the substrate. A very thin (<1 nm) mixed interface is evident but otherwise, film growth on the a-plane sapphire is highly ordered. The lattice constants of ZnO and a-plane sapphire are well matched and high quality film growth on this substrate has been reported using various PVD methods (see for example [26, 27]). A selected area diffraction pattern from the film is shown in figure 6(d) with the major reflections indexed to the wurtzite phase. The preferred orientation seen in the high resolution image is also clearly evident in the diffraction pattern, with the most intense spots (corresponding to the {0002} reflections) aligned normal to the substrate. The streaks, which appear to stem from the intense spots in the clockwise direction, are caused by a gradual change in growth direction. This was confirmed using dark-field imaging with the objective aperture located sequentially along the streaks (not shown). In figure 6(b), the dark-field image taken from the most intense part of the {0002} reflection is shown. This image confirms that the c-axis oriented growth has taken place from the substrate up to a thickness of ~90 nm.

All as-deposited samples of the co-deposited Zn$_{1-x}$Mg$_x$O film exhibited sufficiently high electrical resistance (>100 MΩ) to prevent reliable Hall measurements and implementation within devices. Hydrogen has been shown to behave as a shallow donor in both bulk [28, 29] and polycrystalline ZnO [30] so selected Zn$_{1-x}$Mg$_x$O samples were annealed in an atmosphere containing hydrogen (H$_2$(5%)/N$_2$(95%)) at 550 °C for one-hour with the aim of reducing their resistivity. This process yielded a decrease in resistivity of up to five orders of magnitude (see table 2). By contrast, a sample annealed in air at 550 °C for 1 h exhibited >100 MΩ resistance before and after annealing. The average grain diameter in the air- and hydrogen-annealed Zn$_{1-x}$Mg$_x$O samples (measured from AFM images) increased from ~35 nm to ~45 nm after annealing and stress in the wurtzite samples was relieved by 4–6 GPa (see table 2). Due to this stress, the XRD {0002} peaks (figure 7) produced from the as-deposited samples were asymmetric. In the annealed samples, the {0002} peak shifted to a higher angle and became symmetrical.

Lavrov et al identified two shallow H donors in single crystal ZnO after introducing hydrogen by dc plasma immersion and annealing [31]. Bond-centered hydrogen tended to be unstable during annealing at moderate temperatures (~190 °C). However, in oxygen-poor ambients this hydrogen became bound within the oxygen vacancies left by the out-diffusing oxygen and in this location, the hydrogen (H$_0$) proved more stable. In order to investigate the hydrogen bonding within the Zn$_{1-x}$Mg$_x$O film, a hydrogen-annealed sample was subjected to a second vacuum annealing process (300 °C, 7 × 10$^{-6}$ Torr for 1 h as in [30]). This showed that (unstable) shallow doping by bond-centered or interstitial hydrogen was a minor effect as the resistivity of all samples decreased slightly after the vacuum annealing (attributed to improved Van der Pauw Ohmic contacts).

In granular ZnO films, potential barriers at grain boundaries (GBs) cause increased scattering and decreased carrier mobility (see for example [32]). Chemisorbed oxygen is known to cause carrier depletion in ZnO, leading to increased surface potential barriers [33]. Annealing in hydrogen can remove chemisorbed oxygen from GBs, decreasing the height of potential barriers and increasing carrier mobility. Re-oxidation of the GBs after annealing is largely prevented by the film densification that occurs during annealing [32]. GB potential energy barriers have also been attributed to charge trapping at GB defects [34] that although not well characterised in ZnO, have been correlated with oxygen vacancies and/or film morphology [35, 36]. To summarize, based on the reduced electrical resistivity measured after annealing we can propose that this process caused shallow doping by H$_0$ and/or a decrease in the average GB potential barrier height.

Turning to optical characteristics, samples exhibiting single optical band-gaps prior to annealing exhibited single band-gaps afterwards, indicating a lack of phase transformation. Significantly, the optical bandgaps ($E_g$) changed only slightly following annealing (table 2). In ZnO films deposited at similarly moderate temperatures, a blue shifted $E_g$ has been attributed to a significant amorphous component [37]. The absence of this shift here is consistent with the high quality growth shown in figure 6 and suggests that the higher average energy in the HiPIMS flux may have promoted crystallisation.
Importantly, Srikant et al. reported that due to confinement effects in ZnO films with 30–80 nm diameter grains (as observed here), $E_g$ was sensitive to small changes in GB barrier heights [38]. Therefore, as only very small shifts in $E_g$ were observed after the hydrogen annealing process, we conclude that shallow doping by Ho was more significant than GB modification in reducing the Zn$_{1-x}$Mg$_x$O sample resistivity.

We also note that the moderate carrier concentrations (table 2) achieved after annealing are insufficient to cause significant Burstein–Moss shifts [39].

Figure 7. (a) XRD diffractograms from a Zn$_{0.84}$Mg$_{0.16}$O sample as-deposited and after annealing at 550°C for 1 h in flowing 95% N$_2$, 5% H$_2$ and 1.0μm$^2$ AFM images taken (b) before and (c) after annealing. Not the differing height scales in AFM micrographs.

Figure 8(a) shows a schematic of a UV detector consisting of dual graphite-Zn$_{0.89}$Mg$_{0.11}$O Schottky diodes (connected in series and biased at 500 mV) formed on the hydrogen-annealed sample. The response to UV and visible light with and without filtering is shown in figure 8(b). The nominal bandwidth of the device (~20 nm) is dictated by the difference between the optical band-gaps of the device layer and filter layer. The current response ($I$) to UV light centered at 351 nm is approximately three orders of magnitude above that produced by visible light (470 nm) in the filtered and non-filtered exposures. An order of magnitude reduction in the UVB response of the detector is present when the absorbing Zn$_{0.77}$Mg$_{0.23}$O filter layer is present. Valence-band XPS measurements performed on this film (not shown) revealed significant downward band-bending, indicating the presence of a surface contaminant layer [40]. Due to the well-known effects of surface contaminants on the electrical properties of ZnO-based materials [40], in-situ surface preparation prior to anode deposition is expected to yield improved Schottky contacts to these films. Nevertheless, a functioning UV detector and simple UVB filter layer have been demonstrated. The optimisation of diodes and photodetectors formed on co-deposited Zn$_{1-x}$Mg$_x$O with a range of compositions will be the subject of further work.

Table 2. Electrical, structural and optical properties of selected Zn$_{1-x}$Mg$_x$O samples as deposited and after annealing in (5% H$_2$: 95% N$_2$) at 550°C for 1 h.

<table>
<thead>
<tr>
<th>Mg frac. (%)</th>
<th>${0002}$ 2θ as-dep. (°)</th>
<th>${0002}$ 2θ ann. (°)</th>
<th>FWHM-σ as-dep. (GPa)</th>
<th>FWHM-σ ann. (GPa)</th>
<th>$E_g$ as-dep. (eV)</th>
<th>$E_g$ ann. (eV)</th>
<th>$\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$n$ (cm$^{-3}$)</th>
<th>$\rho$ ann. (Ω·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.38</td>
<td>34.43</td>
<td>34.71</td>
<td>0.951</td>
<td>0.682</td>
<td>−4.2</td>
<td>−0.7</td>
<td>3.90/4.91</td>
<td>3.85/4.92</td>
<td>1.6</td>
</tr>
<tr>
<td>0.27</td>
<td>34.31</td>
<td>34.67</td>
<td>0.982</td>
<td>0.613</td>
<td>−4.5</td>
<td>0.1</td>
<td>3.86</td>
<td>3.82</td>
<td>1.1</td>
</tr>
<tr>
<td>0.21</td>
<td>34.21</td>
<td>34.65</td>
<td>0.951</td>
<td>0.552</td>
<td>−5.2</td>
<td>0.5</td>
<td>3.76</td>
<td>3.76</td>
<td>1.6</td>
</tr>
<tr>
<td>0.14</td>
<td>34.09</td>
<td>34.83</td>
<td>0.931</td>
<td>0.483</td>
<td>−5.9</td>
<td>0.4</td>
<td>3.58</td>
<td>3.58</td>
<td>1.9</td>
</tr>
<tr>
<td>0.11</td>
<td>34.05</td>
<td>34.55</td>
<td>0.904</td>
<td>0.406</td>
<td>−6.1</td>
<td>0.3</td>
<td>3.49</td>
<td>3.50</td>
<td>4.5</td>
</tr>
</tbody>
</table>
4. Conclusions

A Zn$_{1-x}$Mg$_x$O film with composition depending on substrate location was co-sputtered onto a-plane sapphire at 200°C using a combination of DCMS and HiPIMS. Across the compositional range, the Zn$_{1-x}$Mg$_x$O film exhibited low surface roughness and high transparency. The optical bandgap varied monotonically with Mg fraction up to the miscibility limit of $x \approx 0.32$, beyond which a mixed cubic/wurtzite structure formed. Post-deposition annealing in the presence of hydrogen enabled the initially high electrical resistivity to be reduced by up to five orders of magnitude. This was achieved without detectable phase transformation and proved stable. Further annealing in vacuum suggested that shallow hydrogen donors were responsible for the reduced resistivity. A prototype filtered UV detector fabricated using the co-deposited film in the active and filter layers demonstrated sensitivity to UV in a 330–355 nm pass-band and approximately three orders of magnitude UV-to-visible rejection.

Acknowledgments

The authors would like to thank the RMIT microscopy and microanalysis facility, M Allen at The University of Canterbury for assisting with sample annealing, Agilent Technologies Australia for assistance with UV/visible measurements and the Australian Research Council (ARC) for financial support.

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Chapter 7. Discussion, Conclusions and Further Work

This chapter has been divided into sub-sections, the first four of which relate to each of the four papers comprising the results chapters. Important outcomes are drawn together in the subsequent sections and are discussed in the context of previously published work. Finally, conclusions are drawn and avenues for further are suggested.

7.1 Structural characterisation of energetically deposited $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films deposited using FCVA

In Chapter 3, the investigation of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films prepared by FCVA was presented. Films were grown on high conductivity Si wafers using an FCVA deposition system at room temperature and elevated temperature (200 °C) with a low and moderate applied bias (-50 V and -100 V respectively). Variations in film composition occurred despite the fixed cathode composition. These variations were found to result from cathode oxidation (poisoning). The Zn and Mg oxidised at different rates and their oxides exhibited different electrical resistance. These differences led to differing ablation rates for each material and in turn, to variable film composition. A method to minimise the effects of cathode poisoning was found, whereby the cathode was ablated intermittently in a non-reactive environment. XRD analysis showed that films deposited at the higher temperature were more ordered with more intense, sharper peaks. XAS revealed atomic bonding that was similar to ZnO but with features associated with oxygen deficiency. As discussed in section 1.4.2.2.1, little benefit was found in growing films at substrate temperatures greater than 250 °C. For this reason maximum substrate temperatures during growth were limited to 200 °C. Other authors have found a temperature dependant change in growth mode (see section 1.4.2.2.2). They found that when growing $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ on Si substrates using FCVA deposition, films were not predominantly oriented with the c-axis perpendicular to the substrate this was not the case here. All films showed a preferred c-axis orientation regardless of growth temperature.

Variable energy XPS revealed that band bending occurred near the surface (measured using a low photon energy ~200 eV) and reduced deeper into the bulk (using a ~1400 eV photon energy) as previously observed in single crystal and polycrystalline ZnO [139]. This, in conjunction with XPS O1s, showed that surface contaminates (mostly OH$^-$), were present and caused downward band bending at the surface of the films.

XAS was used to examine the local bonding within the film. The O-K edge exhibited similar features to the O-K edge collected from a ZnO single crystal standard. Features were, however, less defined. This was attributed to several factors including the introduction of Mg which changes the ionic character of the material and the presence of native defects such as oxygen vacancies. Analysis of the Mg-K edge from a series of films with differing composition showed that only samples with an Mg fraction greater than the miscibility limit ($x = 0.34$)
produced features consistent with a cubic phase. XAS was found to be able to identify the phase composition of Zn$_{1-x}$Mg$_x$O [205] when not possible using XRD (due to often much less intense reflections from the cubic phase being overshadowed by the more intense peaks wurtzite from the phase).

Cross-sectional TEM was used to examine the phase composition in a film deposited by FCVA from a poisoned cathode. The cathode poisoning resulted in a dynamically changing depositing flux and layering within the film. Brightfield/darkfield imaging showing the phase distribution/composition at high spatial resolutions was compared with an EELS compositional line scans. This revealed the existence of the cubic phase only in sample areas where the Mg fraction exceeded the miscibility limit. This method complimented XAS, in which the cubic phase was identified from local bonding arrangements.

Zn$_{1-x}$Mg$_x$O films grown using MBE on Si substrates [194] the authors find a solubility limit as large as $x = 0.45$ with a growth temperature of 350 °C. From XRD the FWHM of the 0002 reflection of a typical film (x=0.29) was ~1.35 ° this is significantly wider than 0.39 ° indicating that the FCVA grown films have larger grains on average. However, these films were grown at different temperature with the former grown at 400 °C and the latter at 200 °C, this improved grain size could be the result of dynamic annealing due to the energetic flux used in FCVA.

Park et al. [240] reports on Zn$_{1-x}$Mg$_x$O thin films grown using MOCVD. For a typical film (x= 0.49, growth temperature of 500 °C) the FWHM of the 0002 reflection is 0.19 °. This is considerably narrow than reflection produced by FCVA grown films indicating MOCVD is capable of larger grains although this is achieved using considerably high growth temperatures.

### 7.2 Ultraviolet detection from graphitic-C/Zn$_{1-x}$Mg$_x$O Schottky devices fabricated at moderate temperatures

Further work on Zn$_{1-x}$Mg$_x$O thin films produced using FCVA was presented in Chapter 4. In this chapter, electrical characterisation and a functional prototype device for sensing of UV light were presented. Films were deposited in the FCVA at room temperature and 200 °C with no applied substrate bias. AFM and XRD showed that larger grains formed at elevated growth temperature. This was accompanied by a reduction in stress and increased RMS roughness. UV-visible transmission spectroscopy showed a steeper absorption edge in the 200 °C deposited films when compared to the room temperature films. Tauc analysis revealed a bandgap of 3.57 eV and 3.44 eV for the RT and 200 °C, films respectively. Hall characterisation, using the Van der Pauw configuration, revealed carrier mobilities of up to 15 cm$^2$ V$^{-1}$ s$^{-1}$ and n-type carrier concentrations of ~5 x 10$^{18}$ cm$^{-3}$. This result compares favourably with nominally un-doped Zn$_{1-x}$Mg$_x$O produced using other PVD methods (see section 1.4.2).

An MSM structured photo detector was fabricated, using graphitic carbon anodes. Spectral response measurements showed as much as four orders of magnitude increased response when illuminated by UVB radiation when compared to the response from visible light. Surface analysis using XPS again indicated that the surface had a high concentration of chemisorbed OH$^-$ known to cause band bending and impair device
Chapter 7. Discussion, Conclusions and Further Work

performance (see section 1.6). This suggested that devices could be improved by an in-situ treatment of the surface to remove this contaminant prior to contact formation. A remote oxygen plasma treatment can be effective at removing chemosorbed OH [224]. Reported methods[176, 177, 181] for carbon Schottky contact formation (painting printing and mechanical application) are performed in atmosphere precluding a surface treating using O plasma. The method used here is compatible with prior O plasma treatment.

Takagi et al. [207] fabricated a photodetector based on a MBE grown Zn$_{1-x}$Mg$_x$O thin film with composition $x = 0.50$ and a responsivity of 0.37 A W$^{-1}$ with an applied bias of 5 V and three order of magnitude increased response when comparing dark current to illuminated current. Ju et al. [241] presents a device based on a Zn$_{1-x}$Mg$_x$O film grown using MOCVD with a composition $x = 0.52$. The device has a responsivity of 0.5 mA W$^{-1}$ at a bias of 5 V. The responsivity of the devices presented in this chapter were as high as 11 mA W$^{-1}$ at an applied bias of 0.5 V this indicating these devices are comparable to similar devices fabricated. In addition the much lower applied bias used for these devices is favourable as it will result in lower device power consumption.

Although several publications describe Zn$_{1-x}$Mg$_x$O grown using FCVA, until now minimal electrical characterisation had been performed. This Chapter fills this void in the literature. This chapter presents a UV sensing device with detailed characterisation including current voltage measurements, Schottky devices parameters and spectral response measurements. The performance is sufficient for the target application: personal UVB dosimetry.

Graphitic contacts to ZnO have been demonstrated prior (described in section 7.6.2) however, the method used to form contacts used in this chapter has the significant advantage of being compatible with industry standard photolithography. Importantly, these contacts provide excellent thermal and chemical stability coupled with low cost and flexibility.

7.3 Characterization and device applications of ZnO films deposited by high power impulse magnetron sputtering (HiPIMS)

Chapter 5 describes HiPIMS ZnO deposited at moderate temperatures. Microstructural characterisation using AFM and XRD showed uniform grains (with no evidence of macro particles) oriented with the c-axis normal to the substrate. Hall mobilities were 7-8 cm$^2$ V$^{-1}$ s$^{-1}$, and therefore comparable to as-deposited ZnO films grown using the FCVA under similar conditions [242]. Optical characterisation using UV-visible transmission showed over 90% transmission from 450 to 800 nm with a sharp absorption edge occurring at around 380 nm. Tauc analysis revealed a bandgap of 3.25 eV. These films were also used as the active layer in a Pt/ZnO diode. This device provided a rectification ratio of four orders of magnitude at ±2 V bias.

As outlined in section 1.4.2.2.3, previous work on ZnO grown using HiPIMS has been limited in scope with minimal structural and optical characterisation and no electronic characterisation. This chapter provides previously unreported characterisation of HiPIMS deposited ZnO. Chapter 5 also established that the HiPIMS deposition method is suitable for production of ZnO thin films for device applications. Stoichiometric ZnO were reactively deposited from a Zn target with as-deposited carrier mobilities of ~7.5 cm$^2$ V$^{-1}$ s$^{-1}$ and carrier
concentrations of $\sim 5 \times 10^{18}$ cm$^{-3}$ making the films suitable for active layers in electronic devices and Schottky diodes.

7.4 Co-deposition of band-gap tuned Zn$_{1-x}$Mg$_x$O using high impulse power- and dc-magnetron sputtering

Chapter 6 reported on the production of Zn$_{1-x}$Mg$_x$O films grown using a co-deposition process with two plasma guns; one Zn and the other Mg. The Zn target was operated in HiPIMS mode and the Mg target in DCMS mode. Despite only the Zn gun being operated in HiPIMS mode, films still benefited from the dynamic annealing effects inherent in energetic deposition processes, energetic ions will impart their energy in a cascade of collision effecting the entire film microstructure [52]. The films were characterised optically, structurally, chemically and electronically.

Cross sectional TEM imaging and diffraction showed that the co-deposited films grew epitaxial with the c-axis perpendicular to the substrate for the first 90 nm of growth. The remainder of the film showed a gradual shift in the crystal orientation. This was attributed to significant stress in the as-deposited film, confirmed with XRD measurements in which diffractograms showed a shift in the (0002) reflection that was consistent with increased in-plane stress. This result suggests that epitaxial growth can be realised using this method. In the co-deposition film, non-uniform stress measured could have resulted from the asymmetry of the energetic flux and/or the compositional gradient (since the ionic radii of Zn and Mg differ). XRD measurements showed that films with lower Mg fractions (higher proportion of energetic flux) exhibited the highest stress, suggesting that the asymmetry in the flux was the dominant effect [210].

The as deposited films were highly resistive. As outlined in section 1.4.2.2.5, hydrogen has been reported to be a stable n-type carrier in ZnO. For example, annealing in the presence of hydrogen has been shown to increase the room temperature carrier concentration in ZnO [115]. Annealing was used in this project to increase the conductivity of Zn$_{1-x}$Mg$_x$O films grown using the HiPIMS/DCMS co-deposition method. Annealing ZnO in hydrogen at sufficiently high temperatures ($\sim 550^\circ$C) has been reported by numerous authors [17, 115] and results in incorporation of hydrogen into the crystal lattice in a stable, electrically active (n-type) site. Here, hydrogen was incorporated into the films via annealing in forming gas (95% N$_2$: 5% H$_2$) for 1 hour at 550$^\circ$C. The highly resistive (as-deposited) films became significantly less resistive after annealing with moderate carrier concentrations ($\sim 5 \times 10^{17}$ cm$^{-3}$) and mobilities up to 5 cm$^2$ V$^{-1}$ s$^{-1}$. The use of a simple hydrogen annealing procedure to introduce stable shallow donors into Zn$_{1-x}$Mg$_x$O thin films represents a potentially valuable development for the field.

Electrical characterisation was performed and devices were fabricated on the hydrogen annealed films. Using the same method described in Chapter 4, carbon contacts were employed in an MSM structured photodetector device. Devices with C-Zn$_{1-x}$Mg$_x$O-C configuration showed as much as 3.5 orders of magnitude greater response in the UVB when compared to the visible.
Chapter 7. Discussion, Conclusions and Further Work

The use of HiPIMS for growing Zn$_{1-x}$Mg$_x$O films was previously unexplored. In Chapter 6, it was shown that using a co-deposition process, it is possible to produce high quality Zn$_{1-x}$Mg$_x$O films with a range of compositions, all exhibiting excellent transparency. With some post deposition processing, electrical properties were demonstrated that surpass those of films produced using conventional sputtering. Notably, these films exhibited lower carrier concentrations than similar films deposited with similar average energy using FCVA or at a lower energy using magnetron sputtering, making them well suited to applications including UV sensing.

7.5 Overall summary of materials properties and deposition conditions

The primary aim of this project was to explore the use of low cost energetic deposition methods to produce Zn$_{1-x}$Mg$_x$O thin films for optoelectronic applications. The energetic deposition methods used (FCVA and HiPIMS) have proved suitable for growth of Zn$_{1-x}$Mg$_x$O thin films with sufficient quality for device applications. In Chapter 4, a UV sensitive device employing an MSM structure based on FCVA deposited Zn$_{1-x}$Mg$_x$O thin films was described. Similarly, HiPIMS Zn$_{1-x}$Mg$_x$O thin films were subsequently incorporated in UV photodetectors.

Table V compares ZnO and Zn$_{1-x}$Mg$_x$O films produced using both FCVA and HiPIMS deposition methods. The larger FWHM of the (0002) XRD peak in the Zn$_{1-x}$Mg$_x$O films when compared to ZnO supports this assertion and is indicative of reduced crystalline order. In both deposition methods, those Zn$_{1-x}$Mg$_x$O films with the smallest Mg fraction exhibit the highest mobility, this trend held for $x = 0$ (ZnO). FCVA deposited films provided the highest mobility for both ZnO and Zn$_{1-x}$Mg$_x$O films. This is attributed to the larger average grain size and consequently reduced inter grain scattering in the FCVA films when compared with the HiPIMS films (~40 nm compared with ~30 nm).

FCVA is an established deposition method for mechanical coatings with several publications reporting on its use for electronic applications, particularly in the area of transparent conducting oxides. HiPIMS is a relatively new deposition method with its main application being mechanical coatings and has only recently been studied for growth of thin films for electronic applications [79, 243]. Further optimisation of the numerous growth parameters in HiPIMS could lead to improvements in microstructural control and optical/electronic properties.

The carrier concentration is roughly an order of magnitude lower in the HiPIMS deposited Zn$_{1-x}$Mg$_x$O films when compared to all FCVA films and the ZnO film deposited using HiPIMS. The as deposited Zn$_{1-x}$Mg$_x$O films produced using HiPIMS were all highly resistive. The reasons for this are likely to be low carrier concentration/mobility and a larger density of potential barriers at grain boundaries due to smaller grains in these films. Annealing in forming gas at 550 °C for 1 hour led to films with sufficient conduction to enable electronic characterisation. The mechanism for improved electrical performance cannot exclusively be explained by grain enlargement as both vacuum and air annealing using the same temperature and time parameters produced films that remained resistive. Instead the improvements are attributed to a combination of grain enlargement (reduced potential barrier density), reduced potential barrier height through reduction of grain boundaries, the reduction in oxygen accumulation at grain boundaries and the introduction of hydrogen occupying V$_0$ sites (H$_0$), as described by Lavrov [115]and Janotti [128]. The lower carrier concentration in the HiPIMS deposited Zn$_{1-x}$Mg$_x$O films makes them better suited to visible blind UV detection applications, providing lower dark current and therefore making the detector more sensitive.
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The properties of the films prepared in this thesis compare well with those reported on by other authors. The variety of growth processes, compositions and non-native dopants mean that it is difficult to directly compare results with others in the literature. Despite this, it can be shown that the electronic and optical properties compare well with a variety of other methods used to produce single layer Zn$_{1-x}$Mg$_x$O. Nishinaka et al. [197] achieved a mobility of up to 18 cm$^2$ V$^{-1}$ s$^{-1}$ using ultrasonic spray assisted mist CVD. Initially a ZnO buffer layer was grown using sputtering then the CVD grown Zn$_{1-x}$Mg$_x$O layer with an Mg fraction of $x = 0.07$. The authors note that the mobility of the ZnO buffer layer affects the mobility of the Zn$_{1-x}$Mg$_x$O layer. Wei et al. [199] used PLD to grow Ga doped Zn$_{1-x}$Mg$_x$O layers grown using PLD to achieve a mobility of 20 cm$^2$ V$^{-1}$ s$^{-1}$ with an Mg fraction of $x = 0.2$. Ke et al. [244] used PLD employing Ga doped ceramic targets with resultant films having an Mg fraction of 0.29 and a mobility of 11 cm$^2$ V$^{-1}$ s$^{-1}$. Hsueh et al. [198] used radio frequency magnetron sputtering to grow Zn$_{1-x}$Mg$_x$O thin films. The as deposited films had an Mg fraction of 0.2 and were too resistive for electrical characterisation. After annealing at 800 °C for 60s in nitrogen ambient, a mobility of 5 cm$^2$ V$^{-1}$ s$^{-1}$ was achieved with a carrier concentration of $\sim 4 \times 10^{18}$ cm$^{-3}$. Most reports demonstrate similar electrical properties to the films shown here. However, FCVA & HiPIMS offer significantly larger substrate area capability then PLD.

Table V: Comparison of the properties of ZnO and Zn$_{1-x}$Mg$_x$O films produced by FCVA and HiPIMS deposition methods. Data has been collected from Partridge et al. [78], Elzwawi et al. [64], and Mayes et al. [206, 210].

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Growth method</th>
<th>Mg frac. ($x$)</th>
<th>$E_g$ (eV)</th>
<th>Post dep. treatment</th>
<th>$\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$n$ (cm$^3$)</th>
<th>$\rho$ (\textOmega\ cm)</th>
<th>Grain dia. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200. °C</td>
<td>FCVA</td>
<td>0.00</td>
<td>3.3</td>
<td>Anld. At 1 h 800 °C in O$_2$</td>
<td>18</td>
<td>5 x 10$^{18}$</td>
<td>0.83</td>
<td>75</td>
</tr>
<tr>
<td>RT</td>
<td>FCVA</td>
<td>0.17</td>
<td>3.57</td>
<td>As dep.</td>
<td>15</td>
<td>1.1 x 10$^{18}$</td>
<td>69K</td>
<td>25</td>
</tr>
<tr>
<td>200. °C</td>
<td>FCVA</td>
<td>0.24</td>
<td>3.44</td>
<td>As dep.</td>
<td>5.0</td>
<td>8.1 x 10$^{18}$</td>
<td>28K</td>
<td>37</td>
</tr>
<tr>
<td>200. °C</td>
<td>HiPIMS</td>
<td>0.00</td>
<td>3.25</td>
<td>As dep.</td>
<td>7.5</td>
<td>4.3 x 10$^{18}$</td>
<td>N/A</td>
<td>35</td>
</tr>
<tr>
<td>200. °C</td>
<td>HiPIMS</td>
<td>0.38</td>
<td>3.90/4.91</td>
<td>Anld. At 1 h 550 °C in H$_2$(5%)N$_2$(95%)</td>
<td>1.6</td>
<td>9.6 x 10$^{17}$</td>
<td>3.8</td>
<td>39</td>
</tr>
<tr>
<td>200. °C</td>
<td>HiPIMS</td>
<td>0.27</td>
<td>3.86</td>
<td>As dep.</td>
<td>1.1</td>
<td>6.9 x 10$^{17}$</td>
<td>8.7</td>
<td>39</td>
</tr>
<tr>
<td>200. °C</td>
<td>HiPIMS</td>
<td>0.21</td>
<td>3.76</td>
<td>Anld. At 1 h 550 °C in H$_2$(5%)N$_2$(95%)</td>
<td>1.6</td>
<td>7.1 x 10$^{17}$</td>
<td>5.5</td>
<td>38</td>
</tr>
<tr>
<td>200. °C</td>
<td>HiPIMS</td>
<td>0.14</td>
<td>3.58</td>
<td>As dep.</td>
<td>1.9</td>
<td>2.2 x 10$^{17}$</td>
<td>18</td>
<td>38</td>
</tr>
<tr>
<td>200. °C</td>
<td>HiPIMS</td>
<td>0.11</td>
<td>3.49</td>
<td>Anld. At 1 h 800 °C in O$_2$</td>
<td>4.5</td>
<td>8.8 x 10$^{17}$</td>
<td>1.6</td>
<td>37</td>
</tr>
</tbody>
</table>

7.6 Key areas of novelty

7.6.1 Bandgap tuning of ZnO with Mg alloying

The bandgap of ZnO is widened by alloying ZnO with Mg to form Zn$_{1-x}$Mg$_x$O. In this work, two methods for bandgap tuned Zn$_{1-x}$Mg$_x$O were employed. A single composite (Zn$_{0.8}$Mg$_{0.2}$) source was ablated in the FCVA system and two separate sources (Zn and Mg) were sputtered in a HiPIMS system. Method one, suitable for FCVA systems with a single cathode, should produce films with a fixed Zn$_{1-x}$Mg$_x$O ratio for a given target/cathode. However, cathode poisoning, where the Zn and Mg oxidise at different rates to produce a
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Surface with oxides of differing conductivity, can cause variable composition in the deposited films. Method two, suitable for systems with at least two plasma sources, enables the composition to be controlled by adjusting the plasma gun parameters. The negative effects of target poisoning can be minimised as each target (Zn and Mg) can be operated in a steady state regime of low surface oxidation.

During growth of Zn$_{1-x}$Mg$_x$O using FCVA, the effects of target poisoning were apparent and caused a variation in the composition as a function of depth (Chapter 3). This problem was reduced by periodically ablating the target without deposition in a non-reactive environment (Ar only). The optical bandgap of the resulting films was altered from 3.3 eV (ZnO) to values ranging from 3.44 eV to 3.57 eV for Zn$_{1-x}$Mg$_x$O films. Given the fixed composition in the cathode, this variation in optical bandgap was unexpected but again, found to be caused by a measured change in film composition, attributed to cathode poisoning and time varying preferential ablation.

Growth of Zn$_{1-x}$Mg$_x$O films by HiPIMS/DCMS (with HiPIMS Zn gun and DCMS Mg gun) with plasma sources placed on opposite sides of the growth chamber, formed films with variable composition as a function of position (along the axis between the two plasma sources). Their optical bandgaps varied monotonically as a function of composition from 3.45 eV (x = 0.07) up to 4.05 eV (x = 0.51) in wurtzite films. Mg compositions beyond the solubility limit caused the cubic phase to form. The cubic phase of Zn$_{1-x}$Mg$_x$O typically produced larger bandgaps (e.g. 4.43 eV (x = 0.34) to 5.38 eV (x = 0.51)) for a given composition when compared to the wurtzite phase. The sample with the lowest Mg fraction also showed the highest mobility however there was no significant variation in mobility in all other samples.

7.6.2 Electrical contacts and devices

Graphitic carbon contacts have received increased interest in the literature recently and have been demonstrated on Si [181], SiC [181], InP [245], GaN [245], GaAs [181] and ZnO [177, 184]. These contacts have either been painted [177] or printed [245] from colloidal suspensions of graphite flakes. In some cases, highly oriented pyrolytic graphite was mechanically pressed onto the ZnO surface [181]. However, both the mechanical pressing of HOPG flakes and the direct application (painting) methods used to date result in highly variable contact area and are not compatible with industry standard photolithography. The minimum area possible using the printing, painting or mechanical pressing methods results in a contact area that is too large for many devices. In Chapter 4 and 6, a method was developed that uses conventional device fabrication processes and flash evaporation, to form rectifying graphitic C contacts with precisely defined location and dimensions. The flash evaporation method enables treatments such as O plasma exposure to remove chemisorbed OH from the surface [224]. Flexible carbon contacts have potential applications in flexible displays based on ZnO based semiconductors such as indium gallium zinc oxide (IGZO).

7.7 Implications for the wider research field

The Zn$_{1-x}$Mg$_x$O films grown in this project have structural and electronic properties which are similar to, or better than those produced by other commonly used methods. FCVA offers good scalability in terms of deposition area. The maximum temperature used to deposit Zn$_{1-x}$Mg$_x$O films in the FCVA was 200 °C. Other methods such as PLD and MOCVD require higher substrate temperatures [246, 247]. The low temperature
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employed here is compatible with flexible polymer substrates which are expected to find numerous applications in the emerging field of flexible electronics. The increased crystallinity seen in energetically deposited films presented here can, in part, be attributed to the dynamic annealing caused by the energetic flux. As described by Anders [62], the potential and kinetic energy of the depositing flux can cause local annealing. This effect means growth can be performed at lower temperatures whilst maintaining comparable crystallinity to that achieved by lower energy PVD with higher temperatures.

HiPIMS is an emerging technique, with very few reports on its use for growth of optical and electronic thin films. The research presented here provides evidence of the use of HiPIMS for production of optoelectronic coatings and their use in devices.

The role of hydrogen in ZnO has been explored by several authors. The proposal that hydrogen occupies the oxygen vacancy site and in this position is the dominant source of n-type conductivity in ZnO is gaining traction. Annealing, remote plasmas and ion implantation have been used to increase the carrier concentration of ZnO. The use of annealing for the same purpose in Zn$_{1-x}$Mg$_x$O has thus far not been reported. These results represent an advancement for the field and will be of interest to researchers investigating the transport properties of ZnO based materials.

Photolithographically defined carbonaceous Schottky contacts will be of interest to the wider field of semiconductor device research. As stated, carbon has been employed as a high quality, stable rectifying contact to a range of semiconductors by several authors due to its chemical stability and potential as a flexible contact material. However, the methods employed to date are not compatible with photolithography, preventing applications in standard microelectronic fabrication sequences.

7.8 Conclusion

In conclusion, energetically deposited ZnO and Zn$_{1-x}$Mg$_x$O thin films have been structurally, electronically and optically characterised before being incorporated into electronic devices. HiPIMS and FCVA both proved capable of producing these thin films with sufficient quality for use as functioning Schottky diode UV detectors.

Characterisation performed on films grown by FCVA showed that film composition varied during growth as a result of cathode poisoning. Periodic non-reactive ablation was found to minimise this effect. Structural characterisation showed that films grown using elevated temperature (200 °C) and a moderate applied bias (-100 V) were more ordered with a stronger c-axis preferred orientation than films grown at lower temperature and with lower applied bias (-50 V). Films grown at 200 °C exhibited sharper and more intense (0002) XRD peaks when compared to RT grown films. Optical characterisation showed that the optical bandgap was altered from 3.3 eV (the bandgap of native ZnO) to ~3.5 eV. Electrical characteristics compared favourably with similar material grown by other methods. Graphitic carbon contacts were deposited using the flash evaporation method onto photolithographically patterned Zn$_{1-x}$Mg$_x$O. The contacts exhibited rectifying characteristics and were used as the basis for a MSM structured device. From these findings, evaporated graphitic carbon appears to be a suitable material for forming robust rectifying contacts to Zn$_{1-x}$Mg$_x$O.
HiPIMS ZnO films were c-axis oriented with a \{0002\} peak FWHM of 0.7°. As deposited films provided carrier mobilities of \(\sim 7 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}\). Pt Schottky diodes were fabricated on HiPIMS ZnO and exhibited idealities as low as 1.6 and up to four orders of magnitude rectification. These results suggested that HiPIMS could be used to produce device quality ZnO based materials. Zn\(_{1-x}\)Mg\(_x\)O films were grown using a co-deposition process employing HiPIMS and DC magnetron sputtering. As observed by other investigators using differing growth methods, higher Mg content in the co-deposited Zn\(_{1-x}\)Mg\(_x\)O films led to reduced crystalline order. Films exhibited high transparency and bandgaps up to 4.8 eV. Samples of the film in which the Mg content exceeded the solubility limit of Mg in wurtzite ZnO also contained the cubic phase, revealed using TEM and optical transmission measurements.

Recent theoretical and experimental publications have suggested that hydrogen is a possible source of native n-type conductivity in ZnO (and Zn\(_{1-x}\)Mg\(_x\)O). Calculations have shown that the O vacancies, long thought to be responsible for n-type conductivity are donors but are too deep in energy for ionisation to occur at room temperature. Several authors have demonstrated an increase in carrier concentration in ZnO after exposure to hydrogen either through annealing or remote plasma exposure. Post deposition annealing for 1 hour at 550 °C in a hydrogen ambient significantly increased the electrical conductivity of the (initially highly resistive) HiPIMS/DCMS co-deposited Zn\(_{1-x}\)Mg\(_x\)O films. Carrier mobilities of up to 7 cm\(^2\) V\(^{-1}\) s\(^{-1}\) and carrier concentrations of \(10^{17} \text{ cm}^{-3}\) were extracted from room temperature Hall measurements performed on annealed film samples.

The stability of these electrical characteristics after further annealing was consistent with expected behaviour of hydrogen occupying oxygen vacancies. A notch filtered UV photodetector employing graphitic carbon anodes was produced on annealed material and exhibited 3.5 orders of magnitude greater response to UVB than to visible light.

### 7.9 Further work

#### 7.9.1 Reducing variability in thin films

The stability of FCVA Zn\(_{1-x}\)Mg\(_x\)O growth could be increased by using separate Zn and Mg cathodes or by introducing an alternative Mg source e.g. magnetron sputtering. The independent control offered would enable access to the full range of compositions. This setup combined with a higher purity (and better mixed) cathode would minimise variability in film composition caused by cathode poisoning [248].

#### 7.9.2 Alternative substrates

The substrate material used can have a significant on the microstructure and hence electrical properties of films grown on them. Using homoepitaxial substrates could result in films with a much lower concentration of extended defects. Exploring the use of a native ZnO single crystal substrate could also result in significant improvements in film properties.

The relatively low temperature (200 °C) used in both HiPIMS and FCVA Zn\(_{1-x}\)Mg\(_x\)O growth is compatible with many flexible polymer substrates offering new device options such as flexible transparent displays. Growth and characterisation of films grown on flexible polymer substrates would be of significant interest to both
researchers in the field and commercial product manufacturers. Energetic deposition also offers the ability to initially implant (using high deposition energy) to improve adhesion to the substrate.

### 7.9.3 Improving understanding of grain boundary effects

Grain boundaries play a significant role in determining the electrical characteristics of polycrystalline ZnO and Zn$_{1-x}$Mg$_x$O thin films [249, 250]. Characterisation methods able to assess and quantify the composition, structure and defects at the grain boundaries are available. Kelvin probe microscopy has been used to map the surface potential across ZnO grains and grain boundaries. This showed increased potential existed at the grain boundaries. The authors concluded that the density of defects at the grain boundaries significantly affected carrier mobility [67]. Scanning transmission electron microscopy (STEM) with its very high spatial region could be well suited to investigating the character of grain boundaries but this work has yet to be reported in polycrystalline ZnO based materials. When combined with spectroscopic techniques such as energy dispersive x-ray spectroscopy and electron energy loss spectroscopy and diffraction techniques such as nano-beam electron diffraction, STEM could be a powerful method for examining and improving growth and processing of ZnO and Zn$_{1-x}$Mg$_x$O films and indeed other ZnO based oxides such as ZnSe$_{0.1}$ and Zn$_{1-x}$Cd$_x$O.

### 7.9.4 Impurity dopants for energetically deposited ZnO-based materials

As part of further work in this area, alternative donors (other than hydrogen) could be explored. Al has been demonstrated as a suitable donor for ZnO [63]. ZnO: Al has been reported by several authors and has demonstrated applications in smart windows [251]. Both FCVA [63] and HiPIMS [84] deposition methods have produced high quality Al doped ZnO. Other materials such as Ga [252] and Ge [253] have been used to increase the carrier concentration of ZnO to produce a degenerately doped transparent conducting oxide. An examination of how these dopants could be incorporated into ZnO or Zn$_{1-x}$Mg$_x$O could yield better control over carrier concentrations in energetically deposited thin films.

### 7.9.5 Investigating surface and interface chemistry

Surface chemistry plays an important role in the performance of a rectifying contact. When an electrical contact is formed to a semiconductor, the surface of the semiconductor becomes an interface. The nature of the surface chemistry will affect the character of the contact. In ZnO and wurtzite Zn$_{1-x}$Mg$_x$O the surface is rapidly contaminated with OH$^-$ once the material is exposed to atmosphere. Increased understanding of the surface chemistry will aid in developing methods that can improve the performance of junctions.

### 7.9.6 Oxygen plasma treatment prior to formation of carbonaceous contacts

The benefits of oxygen plasma treatments prior to forming rectifying contacts to ZnO have been explored extensively and could yield significant improvements in the performance of devices formed on HiPIMS and FCVA ZnO based materials in particular, plasma treatment prior to growth of carbonaceous based contacts could provide high quality rectifying contacts. Comparison the highest performing Schottky contact materials for ZnO, such as partially oxidised noble metals [146], would be useful in assessing the viability of carbonaceous contacts.
7.9.7 Removing defects that cause persistent photoconductivity

Persistent photoconductivity in ZnO and $\text{Zn}_1-x\text{Mg}_x\text{O}$ can lead to erroneous readings of UV intensity. In a UV exposed device, some defects can act as charge traps that fill due to the photocurrent generated. After exposure is ceased or reduced in intensity, detrapping produces a measurable current above the dark current (or reduced intensity current) for some time. This effect reduces the utility of a device, as short term rapid changes in exposure are not registered. Minimising the responsible defects would produce a more responsive device. An investigation into the origins and possible remedies for persistent photoconductivity is vital for development of UV photodetectors based on ZnO and $\text{Zn}_1-x\text{Mg}_x\text{O}$. A simple measure such as appropriate encapsulation may prove sufficient for many applications.
References


References


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