Ultraviolet Light Emission from Tunnelling Metal-Insulator-Semiconductor Devices

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Declaration of originality

I declare that the work contained in this thesis is my own work and any resources used from other authors have been referenced in the text and figure captions.

Chen-Sheng Lin

London, September 2017

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Abstract

High efficient light emitting diodes (LEDs) have been successfully applied to the visible lighting market for many years. However, the development of ultraviolet (UV) LEDs is still hindered, where the efficiency of UV-LEDs is significantly lower than that of visible LEDs. The challenges come from the difficulty of obtaining efficient \( p \)-type doped Al\(_x\)Ga\(_{1-x}\)N (especially for the high-aluminium-content materials), light absorption by the \( p \)-type layer, and the complexity of device structures. These problems have motivated the investigation for the feasibility of non \( p \)-doped UV emitters.

This thesis presents a study of UV emissions from simple metal-insulator-semiconductor (MIS) tunnel light emitting diodes, with simple structures and without \( p \)-doped layers. Firstly, epitaxial thin film were deposited and characterized layer by layer, where \( n \)-type Al\(_x\)Ga\(_{1-x}\)N film was used as the active layer and AlN film was used as the insulator layer followed by a semi-transparent metal thin layer for current spreading. Device with different thicknesses of AlN were compared, and its thickness of 10 nm resulted in optimized diode behaviour and maximum UV emissions. More importantly, a region of clear negative differential resistance was observed in the I-V characteristic, indicating free holes in the valence band of \( n \)-type active layer are most likely generated by resonant tunnelling. A decrease in emitted intensity at high injection currents was observed, which is attributed to a reduction in the density of conduction band electrons via Fowler-Nordheim tunnelling occurring in parallel. A defect band in the AlN barrier layer is suggested as the origin of the quantum states via which the resonant tunnelling occurs. Finally, from the measurements of electroluminescence on both the \( n \)-GaN based and the \( n \)-
Al$_x$Ga$_{1-x}$N (x = 0.14) based MIS diodes, near band-edge UV emissions of 365 nm and 335 nm were achieved respectively.

Through the study of MIS light emitting diodes and their achievement of UV light emissions, this research provides a potential solution to solve the problems of current low-efficiency $p$-$n$ junction based UVLEDs.

Keywords:

Ultraviolet LEDs; Tunnelling diodes; Metal-Insulator-Semiconductor diodes; Electroluminescence; AlN/Al$_x$Ga$_{1-x}$N heterojunction
Publications and presentations

The following is a list of publications and presentations during the course of the PhD project.

Publications


Presentations

Oral presentations at International Conference on Nitride Semiconductors (ICNS-12, Strasbourg, France, 2017), and International Workshop on Nitride semiconductors (IWN, Florida, USA, 2016).

Poster presentations at the UK Nitride Consortium (UKNC, United Kingdom, 2015), and International Conference on Nitride Semiconductors (ICNS-11, Beijing, China, 2015)
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<th>Definition</th>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>AC</td>
<td>Alternating current</td>
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<tr>
<td>CV</td>
<td>Capacitance voltage</td>
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<tr>
<td>CVD</td>
<td>Chemical vapour deposition</td>
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<tr>
<td>DC</td>
<td>Direct current</td>
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<td>DFT</td>
<td>Density functional theory</td>
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<td>EL</td>
<td>Electroluminescence</td>
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<td>EQE</td>
<td>External quantum efficiency</td>
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<td>FWHM</td>
<td>Full width at half maximum</td>
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<td>HEMT</td>
<td>High electron mobility transistor</td>
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<td>HVPE</td>
<td>Hydride vapour phase epitaxy</td>
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<td>IC</td>
<td>Integrated Circuit</td>
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<td>IQE</td>
<td>Internal quantum efficiency</td>
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<tr>
<td>IR</td>
<td>Infrared</td>
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<td>IV</td>
<td>Current voltage</td>
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<td>LED</td>
<td>Light emitting diode</td>
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<td>LEE</td>
<td>Light extraction efficiency</td>
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<tr>
<td>LCD</td>
<td>Liquid crystal display</td>
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<td>MBE</td>
<td>Molecular beam epitaxy</td>
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<td>MIS</td>
<td>Metal-insulator-semiconductor</td>
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<tr>
<td>MOCVD</td>
<td>Metal-organic chemical vapour deposition</td>
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<td>MOVPE</td>
<td>Metal-organic vapour phase epitaxy</td>
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<tr>
<td>MQW</td>
<td>Multiple quantum well</td>
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<tr>
<td>NBE</td>
<td>Near-band-edge</td>
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<td>NDR</td>
<td>Negative differential resistance</td>
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<td>NIR</td>
<td>Near-infrared</td>
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<tr>
<td>PL</td>
<td>Photoluminescence</td>
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<td>PLD</td>
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<td>Physical vapour deposition</td>
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<td>QCSE</td>
<td>Quantum-Confined Stark Effect</td>
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<td>RF</td>
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<td>RIE</td>
<td>Reactive ion etching</td>
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<td>RMS</td>
<td>Root-mean-square</td>
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<td>Rapid thermal annealing</td>
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<td>SCLC</td>
<td>Space-charged-limited current</td>
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<td>STM</td>
<td>Scanning tunnelling microscopy</td>
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<td>TCO</td>
<td>Transparent contact oxide</td>
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<td>TDD</td>
<td>Threading dislocation density</td>
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<td>TEM</td>
<td>Transmission electron microscopy</td>
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Chapter 1

Introduction

1.1 Motivation

Group III-nitride semiconductors AlN, GaN and InN are widely used in optoelectronic applications, including laser diodes and light emitting diodes (LEDs) [1]–[6]. Ultraviolet (UV) light emitters based on Al$_{x}$Ga$_{1-x}$N alloys are currently of considerable interest for applications in water disinfection, solar-blind communications, biohazard detection and polymer curing [7], [8]. UV-LEDs offer considerable advantages compared to conventional mercury UV lamps. These include significantly longer lifetimes, lower heat consumption, small and robust form-factors, non-toxic material compositions and the potential for enhanced light output efficiency [9]. However, typical external quantum efficiencies (EQEs) of conventional UV LEDs in the germicidal range of 265–280 nm are around 2%, which is extremely low compared to LEDs emitting in the blue light region [10], [11]. This is due mainly to the difficulty of obtaining efficient $p$-type doping in Al$_{x}$Ga$_{1-x}$N, light absorption by the $p$-type layer, and the high defect densities in complex device structures [10]–[15]. In contrast, metal-insulator-semiconductor (MIS) tunnel diodes have simple structures and do not contain $p$-type material, and therefore are of interest as alternative sources for low-cost UV light emitters.

UV light emission from MIS diodes have been reported previously [16]–[20]. For example, Au/SiO$_2$/ZnO MIS-LEDs have been reported, however the resulting electroluminescence intensity was low and the emission peak was very broad. A relatively thick (~100 nm) insulating layer was also required to obtain diode behaviour [16], [17]. Moreover, MIS-LEDs based on oxide films have been shown to exhibit
crystal quality significantly poorer than that of epitaxially grown nitride semiconductors.

III-nitride materials can be grown with low defect densities, which in principle may enable higher emission intensities. Nitride-based MIS UV LEDs can also serve as a benchmark to establish the performance of MIS UV LEDs relative to conventional UV LEDs. Additionally, theoretical considerations have shown that resonant tunnelling in MIS structures could enhance light emission intensities [21], [22]. As such, the scope for combining the property of light emission and resonant tunnelling within the same device opens the possibility of integrating the electro-optical conversation in digital integrated circuits (ICs) [23]. The study reported here aims to develop an efficient resonant tunnelling light emitting diode, and investigate the efficiencies and operating mechanisms from this resonant tunnelling MIS LEDs.
1.2 Overview of Solid–State Lighting

Lighting accounts for around 20% of global building electricity consumption (Sources: International Energy Agency (IEA) - world energy statistics and balances 2015) [24]. The conversion of electricity to light is inefficient in many traditional lighting applications, including incandescent bulbs and fluorescent bulbs. However, these still comprised 70% (by volume) of the global-sales of lighting devices in 2015 (Sources: IHS Markit). This being so, solid-state lighting technologies offer significant promise for increased lighting efficiency and reduced energy usage.

Solid-state lighting (SSL) is a technology that uses direct band gap semiconductors to directly convert electricity into light, with high efficiency, long lifetime and low heat generation. Three main compound material groups are used in SSL: group IV-IV (Ex: SiC), group II-VI (Ex: ZnSe) and group III-V (Ex: GaN). In particular, group III-Nitride materials attract significant attention due to enhanced material and electrical properties for light generation compared to other materials. Band gap energies and lattice constants for various semiconductors are indicated in Figure 1.1.

Light-emitting diodes (LEDs) were discovered in 1961 when Holonyak and Bevacqua showed that gallium arsenide (GaAs) emitted infrared light when electricity was applied [25]. In 1969, the first large-area GaN was epitaxially grown by Maruska and Tietjen on a sapphire using halide vapour phase epitaxy [26]. This led to fabrication of the first GaN-based LEDs by Maruska in 1972. However, the optical and electrical results were irreproducible due to the inferior quality of epitaxial layers [27].

Advances in modern crystal growth techniques (e.g. molecular beam epitaxy (MBE) and metal-organic chemical vapour deposition (MOCVD) have facilitated the development of LEDs. In order to reduce defects Yoshida et. al. (1983) introduced the idea of growing a buffer layer (AlN film) employing MBE between the hetero interfaces [28]. Moreover, Amano et. al. improved the AlN film quality using MOCVD [29]. In this process the AlN film was grown at 500 °C and GaN grown at 1050 °C. This resulted in smooth interfaces and epitaxial structure.
A major breakthrough occurred (1993) with the invention of efficient blue-emitting LEDs based on $p$-GaN/$n$-InGaN/$n$-GaN double-heterostructures (or so-called quantum well) by Nakamura [30]. These blue LEDs could be coated with a yellow phosphor to produce white light. Subsequently, PN junction based GaN structures with quantum wells have become the standard basis structure for visible light emitters and are widely applied in the commercial lighting market.

Similarly solid-state ultraviolet light emission was also studied with wider band gap materials (i.e. AlGaN) based on a PN junction AlGaN structure with quantum wells [31]. However, due to the character of $p$-doped AlGaN, the UV LEDs have not been fully developed or applied commercially. In this thesis, the idea of developing solid-state UV emitters has been studied. This is covered in the following sections and chapters.
1.3 Properties of Group III-Nitrides

1.3.1 Crystallography

Group III-Nitride semiconductors, i.e. AlN, GaN, InN, and their alloys are employed in several applications including optoelectronic, high power and high frequency devices. Moreover, they are either crystallised in zinc blende (cubic) or wurtzite (hexagonal) structures (Figure 1.2). The wurtzite structure is easier to grow and is more stable under ambient conditions for most III-Nitride materials. The stacking sequence of wurtzite is ABABAB… in the [0001] direction, where one layer represents group III atoms (Al, Ga, or In) and the other layer presents nitrogen atoms.

The wurtzite unit cell is described by three lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $c$. The vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ are equal in length with an angle of 120° between them. The vector $c$ is perpendicular to the plane formed by $\mathbf{a}_1$ and $\mathbf{a}_2$. Lattice parameters of common binary nitride compounds, AlN, GaN and InN, are listed in Table 1.1.

![Figure 1.2](image)

**Figure 1.2** (a) Cubic zinc blende (b) hexagonal wurtzite lattice [32].
Table 1.1 Lattice parameters of AlN, GaN and InN [33].

<table>
<thead>
<tr>
<th>III-Nitride</th>
<th>a (nm)</th>
<th>c (nm)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>0.31106 ± 0.00003</td>
<td>0.49795 ± 0.00002</td>
<td>1.6008 ± 0.00002</td>
</tr>
<tr>
<td>GaN</td>
<td>0.31896 ± 0.00003</td>
<td>0.51855 ± 0.00002</td>
<td>1.6258 ± 0.00002</td>
</tr>
<tr>
<td>InN</td>
<td>0.35378 ± 0.00001</td>
<td>0.57033 ± 0.00001</td>
<td>1.6121 ± 0.00001</td>
</tr>
</tbody>
</table>

1.3.2 Bandstructure and Band Gap Energy

Most group III-V compounds and their alloys have direct band gaps, i.e. the top of the valence band and the bottom of the conduction band occur at the same crystal momentum (k-vector), where Figure 1.3 shows the band structure of wurtzite GaN [34]. This implies that the recombination processes in direct band gap materials is much more efficient compared to indirect band gap materials. Therefore, direct band gap materials such as GaAs, GaN, and InN are widely employed in optical devices. For example, InGaN/GaN quantum well LEDs have been used commercially in the visible lighting [35]–[37]. Additionally, when it comes to the band structure of AlGaN the fundamental valence band crossover issue should be noted, where the crystal field split-off hole band is on the top of the valence band. This leads to dominant transverse-magnetic polarised emission, which is undesirable for the deep UV light emitter as the light propagation parallel to the quantum well plane is difficult for light extraction [38].

![Figure 1.3 Calculated band structure for wurtzite GaN. The bottom of the conduction band is right above the top of the valence band in the k-space at k=Γ [34].](image)
A range of band gap energies can be obtained through varying alloying ratios of group III-V ternary compounds. This allows for the emitting of specific wavelengths of infrared, visible, and ultra-violet light. For example, a band gap energy of 3.42 eV to 6.0 eV may be obtained on varying the aluminium composition ratio $x$ of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ [39], [40]. Figure 1.4 shows the relation between Al composition and the band gap of its ternary compounds. Equation 1.1 shows the empirical equation of $\text{Al}_x\text{Ga}_{1-x}\text{N}$, which can be used to calculate the band gap.

$$E_g(x) = xE_g(\text{AlN}) + (1 - x)E_g(\text{GaN}) - bx(1 - x) \quad (1.1)$$

where $E_g(\text{GaN}) = 3.42$, $E_g(\text{AlN}) = 6.0$, $x$ is the AlN molar fraction, and $b$ is the bowing parameter. The number of bowing parameters has been previously discussed and reported by Biefeld et al.[42]. Based on this a value of 0.62 eV was used for AlGaN in this thesis. It should be noted that $\text{Al}_x\text{In}_{1-x}\text{N}$ does not fit the bowing model, where the explanation can be found in previous reports [43]. For a brief summary,
optical properties and band gap energies of common group III-V compounds are presented in Table 1.2.

**Table 1.2** Band gap energies of group III-V compound materials [2], [41].

<table>
<thead>
<tr>
<th>III-V compounds</th>
<th>Direct / indirect band gap</th>
<th>Band gap energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>Direct</td>
<td>1.42</td>
</tr>
<tr>
<td>GaP</td>
<td>Indirect</td>
<td>2.26</td>
</tr>
<tr>
<td>GaN</td>
<td>Direct</td>
<td>3.42</td>
</tr>
<tr>
<td>InN</td>
<td>Direct</td>
<td>0.67</td>
</tr>
<tr>
<td>AlN</td>
<td>Direct</td>
<td>6.0</td>
</tr>
</tbody>
</table>

1.3.3 Polarisation

Ga and N exhibit different electronegativities (a measure of the tendency of an atom to attract a bonding pair of electrons), so every Ga-N bond is partly ionic and therefore has a certain dipole moment. For a completely symmetric arrangement of the bonds these dipole moments cancel each other on a macroscopic scale. However, in the wurtzite structure, there is an intrinsic asymmetry of bonding in the equilibrium wurtzite crystal structure along the c-axis (Figure 1.2 b shows the asymmetry structure), so the cancellation is incomplete and the net dipole moment along the c-axis results in a spontaneous polarization [44]. Therefore, the polarity [0001] and [000-1] directions are not equivalent, and the (0001) and (000-1) surfaces exhibit different chemical and physical properties. For instance, chemically etched Ga-polar films have a flat and pitted surface while the N-polar surface is rougher with isolated columns or islands [45]. An illustration of the Ga- and N-polarity in GaN wurtzite GaN is shown in Figure 1.5.

Piezoelectric polarisation is a further characteristic which arises in strained and lattice-mismatched wurtzite films. This polarisation has been often calculated to be larger...
than the spontaneous polarisation. Piezoelectric polarisation has been shown to influence carrier distributions, electronic fields, and a wide range of optical and electronic properties in nitride-based materials and devices [46].

Figure 1.5 Illustration of Ga-polar (left) and N-polar (right) wurtzite GaN [2].

1.3.4 Substrate

The choice of substrate plays a key role in thin film growth. The degree of mismatch between the substrate and thin film determines the number of defects present in the film. Moreover, the defects are believed to act as non-radiative recombination centres and affects device performance. In principle, the best substrate for a film growth should have the same lattice constant as the film. For example the best substrate for the growth of GaN film is GaN [47]. However, high-quality bulk single crystal GaN substrates are not cost-effective and alternative substrates are required. The most employed substrates are sapphire (Al$_2$O$_3$), silicon carbide (6H-SiC) and silicon (Si). Due to the application in UV emitters, an aluminium nitride (AlN) substrate has also attracted attention [48].
Sapphire is the most employed substrate in the LEDs market, accounting for 96.3% of LEDs produced in 2015 (according to IHS Markit Ltd [49]). The lattice mismatch between GaN and sapphire is around 16.3%, which is relatively high and results in a high dislocation density ranging from $10^9$ to $10^{11}$ cm$^{-2}$. However, due to its high cost-effectiveness, chemical and thermal stability at high temperature, and transparent to most wavelengths of lights, sapphire still dominates the light emitting industry. Moreover, application of a buffer layer which acts as the nucleation layer, the mismatch between sapphire and a thin film can be reduced [28], [29].

Silicon carbide and GaN have comparable lattice constants (3.5% mismatch), which enables growth of high exipitaxial GaN films with low defect density. However, the cost of silicon carbide is significantly higher than sapphire, making it difficult for widespread application. Moreover, silicon carbide is not applicable for UV LED use as it absorbs light at wavelengths below 427 nm. However, silicon carbide has gained significant attention for application in power electronics due to its properties of high breakdown voltage, high thermal conductivity, low resistance relative to silicon device, and increased reliability in high-temperature operation [50], [51].

Silicon substrate has recently attracted attention in the LEDs industry for its cheap and high-quality wafers in large scale. Also, the processes for silicon are very mature and a lot of equipment has been well developed for the use of silicon processing. Therefore, the integration of III-Nitride device and silicon substrate can be the most cost-effective [52]. However, a large lattice mismatch and big differences in thermal expansion coefficients leads to a high defect density group III-nitride film. For example, wafer cracking and bowing may occur. Moreover, further concerns arise for UV and visible light absorption due to the small band gap of silicon. Nevertheless, silicon is still a promising alternative substrate for the LEDs industry [53].

### 1.3.5 Growth Techniques

Several growth techniques for epitaxial III-Nitride materials have been studied. Hydride vapour phase epitaxy (HVPE) [54], [55], metal organic chemical vapour
deposition (MOCVD) [56], [57] and molecular beam epitaxy (MBE) [58], [59] are the most widely applied methods used for GaN epitaxial growth. HVPE is one of the earliest techniques used for GaN growth and has the advantage of high growth rate. This enables production of bulk GaN layers at relatively low cost. MOCVD has been employed as the main technique, within industry, for the growth of GaN and its alloy (AlGaN and InGaN). It is used to produce high-quality group III-Nitride films for LEDs and laser diodes. MBE can be used to produce very high-quality layers with precise control in thickness, doping and composition. However, low deposition rates are a significant drawback [60].

In recent times sputtering techniques have been gaining attention for use in AlN growth. This technique offers high growth rate at relatively low temperatures making it a cost-effective process [60]–[62].

1.3.6 General Problems with Group III-Nitride Optoelectronics

1.3.6.1 Quantum-Confined Stark Effect (QCSE)

Conventional InGaN/GaN quantum wells are grown in the $c$-direction. The significant strain originated from the large lattice mismatch between the InGaN layer and the GaN layer possesses piezoelectric polarization, while the intrinsic wurtzite crystal structure induces spontaneous polarization. The total polarization fields within the multiple quantum wells (MQWs) result in the spatial separation of electron and hole wave functions and thus in restricting the radiative recombination efficiency. The phenomenon is well known as quantum-confined Stark effect (QCSE) [2], [63]. Additionally, the quantum-confined Stark effect results in the peak emission wavelength decreasing (blue shifting) with increasing drive current due to carrier induced field screening. These problems are especially enhanced for highly strained structures (strong piezoelectric polarization) with high indium contents, making highly efficient longer wavelength LEDs, e.g. green and yellow LEDs, difficult to achieve on $c$-plane GaN [64].
The QCSE can generally be reduced with alternative growth directions such as non-polar or semi-polar planes [64]–[66], where an illustration is shown in Figure 1.6. Currently, many reports have demonstrated that QCSE within the multiple quantum wells can be suppressed by the growth of light emitting diodes on the nano-sized patterned c-plane sapphire substrates (PCSSs), where the strain between films can be reduced significantly and therefore the QCSE was reduced [67], [68].

![Comparison of band gap between polar and non-polar materials](image)

**Figure 1.6** Comparison of band gap between polar and non-polar materials [65].

### 1.3.6.2 Efficiency Droop

Efficiency droop in LEDs is a flaw that results in an efficiency drop. This is one of the most significant challenges for high-power LEDs. The decrease in quantum efficiency occurs when LEDs are subjected to larger drive currents (Figure 1.7). Several explanations have been proposed for the physical origin of efficiency droop. These include dislocations, carrier delocalisation, Auger recombination, poor hole-injection, and electron leakage from the active region [69].
The droop curve (efficiency vs. current density) can be described by equation 1.2 for the model of recombination rate. And the efficiency of radiative recombination can be described by equation 1.3 [70].

\[
R = An + Bn^2 + Cn^3
\]  

(1.2)

\[
\eta = \frac{Bn^2}{An + Bn^2 + Cn^2}
\]  

(1.3)

Where A, B, and C coefficients represent defect-related non-radiative recombination, radiative recombination, and Auger recombination respectively. Besides, \( n \), \( R \), \( \eta \) represent carrier density, recombination rate, and efficiency respectively.

In 2013, researchers at UC Santa Barbara (UCSB) and École Polytechnique confirmed that excitation of the Auger process is responsible for the LED efficiency droop [71]. However, the overall mechanism driving this is still under discussion [72].

![Efficiency versus injected current density](image)

**Figure 1.7** Efficiency versus injected current density – Droop behaviour [73].
1.3.6.3 Current Crowding

Current crowding also results in lower LED efficiency. Current flow crowding is illustrated in Figure 1.8 (a). In the schematic, the \( p \)-type material is usually located on the mesa area and the \( n \)-type contact is located on an \( n \)-type semiconductor active layer. Consequently, injected current crowds at the near lateral edge of the mesa area. A strip-contact structure (Figure 1.8 (b)) has been designed to overcome this problem by incorporating uniform current injection. In this design, current can flow into several slots of the \( n \)-type contacts, resulting in better current distribution.

![Figure 1.8](image)

Figure 1.8 (a) Schematic GaN/InGaN LED structure with lateral current path [74]. (b) Strip-contact structure for uniform current injection [41].

1.3.6.4 Light Absorption

Conventional LEDs require a \( p \)-doped layer and a current spreading layer. In the current LEDs market, \( p \)-GaN (around 3.4 eV) and indium tin oxide (around 3.75 eV) are widely used for the \( p \)-doped layer and current spreading layer respectively [75]. The choice of material for the two layers is important as light may be absorbed if the band gap is smaller than the emitting photon energy. This condition is generally satisfied with the transmission of visible light in the range from 400 nm to 700 nm. However, for UV light emission, the thick \( p \)-GaN layer and the current spreading layer absorb most of the UV light, leading to reduced light extraction efficiency [41], [76].
1.4 Ultraviolet Light Emitting Diodes (UV-LEDs)

The current development of LEDs in visible light is now quite mature and has been applied in several fields including, LCD backlight screens, traffic lights, flashlights and vehicular lighting. However, research in ultra-violet (UV) LEDs, with a wavelength range of 200 nm to 400 nm, is currently active and is attracting significant attention due to several advantages over traditional UV lamps. These include (1) mercury-free composition, (2) higher energy efficiency, (3) more constant light intensity, (4) easier to control the temperature and heat, and (5) longer life-time [12]. Consequently, it is expected that UV-LEDs will be widely employed in future. Moreover, UV LEDs exhibit better colour rendering compared to current white LEDs on the market. It has also been suggested that better white light may be produced by exciting phosphors of three RGB colours, which are UV-red, green, and blue [77].

The UV region in the electromagnetic spectrum is usually categorised into three sub-regions: UV-A (400 nm - 315 nm), UV-B (315 nm - 280 nm), and UV-C (280 nm - 100 nm). Figure 1.9 indicates the UV spectrum and potential applications at different emitting wavelengths. These include environmental protection, lighting, water purification, medical sterilisation and industrial fabrication processes [78].

Even though UV-LEDs have significant application and potential, to date they have not achieved substantial commercial success. This is attributed to their low efficiency and high cost for commercialisation. To describe the light output efficiencies of LEDs, normally external quantum efficiencies (EQEs) are used, the definition of which is expressed by equation 1.4 [41].

\[
\eta_{ext} = \frac{\text{number of photons emitted into free space per second}}{\text{number of electrons injected into LED per second}} = \frac{P}{\hbar \nu} \frac{I}{e}
\]  \hspace{1cm} (1.4)

where \( P \) is the optical power emitted from the LED device, \( I \) is the injection current.

Apart from that, power efficiencies (wall-plug efficiencies) are also often used to describe the light output efficiencies of LEDs, which are defined as equation 1.5 [41].
\[ \eta_{power} = \frac{P}{IV} \]  

Where \( IV \) is the electrical power provided to the LED.

Current UV light output efficiencies, external quantum efficiencies (EQEs), for various wavelengths reported by different leading groups in the world are shown in Figure 1.10 (Data updated in 2015). As indicated, the EQEs of most UVB and UVC emitters are low, which are still in single digit percentage range, and this is further enhanced at shorter emitting wavelengths. It should be noted that in Figure 1.10 the EQE values at 300 - 320 nm seem to be slightly lower than the ones at 280 nm, which were due to the limited tested samples (scant number of commercial sources for UVB and UVC LEDs) [79].

Because of the low efficiencies of current UV LEDs, further improvement and development is needed for bigger commercialisation. This thesis aims to proof a concept of different LED structures (introduced in section 1.6), which may potentially solve the current problems of UV LEDs.

Figure 1.9 Applications of UV light Sources [78].
**Figure 1.10** Reported external quantum efficiencies for PN junction based quantum well LEDs emitting in the UV spectral range [79].
1.5 Conventional PN junction based UV-LEDs

1.5.1 Overview

In conventional LEDs, containing a PN junction based structure, the $p$-region is dominated by positive electric charges (holes) and the $n$-region is dominated by the negative electric charges (electrons). Moreover, the junction between the $p$- and $n$-regions serves as a barrier. This barrier behaves similarly to a band gap and determines the amount of voltage that is required to pass current through the junction barrier. A schematic diagram and band structure of a PN junction LED is presented in Figure 1.11.

Multi-Quantum-Well (MQW) structures (Figure 1.12) have been introduced in order to obtain greater External Quantum Efficiency (EQE) efficiency, due to the increase of blocking carriers and so the enhancement of radiative recombination in the wells [35], [41]. These generally undergo several doping processes in development. The general structure of these devices, from bottom to top, consists of a buffer layer, a $n$-type conductive layer, an electron confinement layer, a multiple quantum wells-based active region, a hole confinement layer, a $p$-type contact layer, and electrodes.

![Figure 1.11 Band structure and working principle of basic PN junction LEDs [80].](image-url)
1.5.2 Problems with Conventional UV LEDs

PN junction based AlGaN MQW LEDs are predominantly used to generate UV light. However, while PN junction based AlGaN MQW UV LEDs with emission wavelength shorter than 360 nm have been achieved [81], the internal quantum efficiency (IQE) shows a dramatic decrease with increasing Al content.

Several key challenges for the PN junction-based AlGaN MQW UV LEDs exist. These are; (i) the metal electrode contact absorbs emitted light [82], (ii) it is very difficult to p-dope AlGaN due to the high dopant ionisation energies. Consequently, the use of p-GaN is favoured. However, p-GaN has a smaller band gap than the active region. This means that it absorbs light emitted from the quantum wells and causes low light extraction efficiency [83]. Furthermore, (iii) good quality AlN and AlGaN are essential to produce high quality deep UV LEDs. In particular, AlGaN with high Al content is necessary to achieve the required band gap. This poses a problem, as high-Al-content AlGaN is significantly more difficult to grow than GaN. This is due to the lower surface mobility of Al adatoms (absorbed atoms that lie on a crystal surface),
compared to Ga adatoms at the growth temperature. As a result the Al adatoms are not able to diffuse to create a smooth layer-by-layer growth front.

Several approaches have been proposed to control the high-Al content issue. A trimethylaluminum (TMA) pre-dose step has been previously introduced prior to the thin film growth to create an Al-polar growth surface. This resulted in a much smoother growing surface and lower threading dislocation density [84]. An alternative approach is the use of increased growth temperatures, approximately 1500˚C. This resulted in a lower dislocation density of about $10^6$ cm$^{-2}$ for the growth of the AlN layer [85]. In regards to lattice-matched structures, growing of bulk AlN as a buffer layer on nano-patterned sapphire substrates has been reported to obtain 10.4% EQE [86]. However, the excessive cost of this method limits its commercial use. Therefore, the development of UV LEDs is still in its early stage. As such the development of new materials, new growth methods, and the re-design of layer structures are feasible research directions for future work in this field.
1.6 Metal-Insulator-Semiconductor (MIS) UV-LEDs

Instead of focusing on the development of conventional UV LEDs by making them even more complicated, in this thesis a new potential structure for UV LEDs is studied, called ‘Metal-Insulator-Semiconductor (MIS) ultraviolet light emitting diodes’. MIS-based UV LEDs have several advantages over conventional PN junction-based UV LEDs. These include no $p$-doping requirement, a very simple structure and highly cost-effective processes. Moreover, the operation of light emitting relies on tunnelling processes, which are explained below, and experimental data proving the effect is presented in Chapters 5 and 6.

A schematic of a basic Metal-Insulator-Semiconductor (MIS) structure is presented in Figure 1.13. In this schematic $d$ is the thickness of an insulator, which is key to controlling tunnelling current, and $V$ is the applied voltage used to generate a field across the device.

![Figure 1.13 Metal-Insulator-Semiconductor (MIS) diode.](image)

1.6.1 Physics of MIS tunnelling device

1.6.1.1 Band structure of the MIS device

The working modes and band structure of an $n$-type doped MIS device can be explained using Figure 1.14. This includes an accumulation mode in picture (a), flat band mode in picture (b), depletion mode in picture (c), and inversion mode in picture (d).
Figure 1.14 Energy band diagram for ideal MIS diode under different bias condition: (a) accumulation mode, (b) flat band mode, (c) depletion mode, and (d) inversion mode. Where $\phi_m$ is the metal work function, $\phi_B$ is the Schottky barrier, $\chi_i$ is the electron affinity of the insulator, $\chi$ is the electron affinity of the semiconductor, $E_c$ is the minimum conduction band energy, $E_v$ is the maximum valence band energy, $E_i$ is the intrinsic Fermi level, $E_{fs}$ is the Fermi level of semiconductor, $\phi_n$ is the potential between $E_c$ and $E_{fs}$, $\phi_{Bn}$ is the potential between $E_{fs}$ and $E_i$, and $E_g$ is the band gap energy.

In the accumulation mode, a positive voltage is applied at the contact, and the conduction band $E_c$ bends down towards the Fermi level $E_f$. This bending yields an accumulation of the majority carriers (electrons) near the interface. In the flat band mode, energy band diagram is flat (the applied bias has no necessity to be zero), where all bands remain flat and the semiconductor and its majority and minority carriers are in thermal equilibrium [87]. In the depletion mode, the contact is under a small negative voltage, and the majority carriers are repelled from the interface, such that the bands bend upwards. As the intrinsic energy $E_i$ gets closer to $E_{fs}$, in the inversion mode, the negative voltage on the metal contact is increased further. This results in the band bending further upwards. Moreover, when $E_i$ crosses $E_{fs}$, the minority carriers (holes) exceed the majority carriers at the interface.

In this work, experimental procedures have been carried out to help understand the working modes of MIS devices for efficient UV light emission. Information gained from the band structure, suggested that controlling carrier confinement at the interface
and current tunnelling through the insulator are of high importance, particularly for efficient radiative recombination which is followed by efficient light emission.

### 1.6.1.2 MIS tunnelling mechanism

In order to control current tunnelling in the MIS devices, an understanding of conduction mechanisms within dielectric films is required. Conduction mechanisms may be classified into two main categories. These are electrode-limited conduction mechanisms and bulk-limited conduction mechanisms.

Electrode-limited conduction mechanisms depend on the electrical properties of the electrode-dielectric contact. Bulk-limited conduction mechanisms depend not only on the electrical properties of the dielectric film but also on the dielectric properties. An expansion of conduction mechanisms groupings is presented in Figure 1.15. Electrode-limited conduction mechanisms include Schottky or thermionic emission, Fowler-Nordheim tunnelling and direct tunnelling. Regarding bulk-limited conduction mechanisms, Poole-Frenkel emission, hopping conduction, space-charge-limited conduction, and defect-assisted tunnelling are included. Most content of this section refers to an open-access review article by Chiu [88], and it also combines with additional information for explaining the tunnelling mechanisms of the MIS UV-LEDs used in the thesis.

![Figure 1.15](image.png)

**Figure 1.15** Classification of conduction mechanism in dielectric films.
Generally, dielectric MIS devices that exhibit high band gaps, high-energy barriers with electrodes and low trap densities are electrode-limited rather than bulk limited. Moreover, bulk-limited conduction mechanisms begin to present a tunnelling process when the insulator becomes progressively defective. All the mechanisms mentioned in Figure 1.15 are explained as follows.

- **Schottky or Thermionic emission:**

Schottky emission is a conduction process whereby electrons attain sufficient energy, via thermal activation, to overcome the energy barrier at the metal-dielectric interface [89]. A schematic band diagram of Schottky emission in MIS structure is presented in Figure 1.16. Schottky emission conduction is regularly observed in dielectric films, particularly at the high temperatures.

![Figure 1.16 Schematic energy band diagram for Schottky emission in MIS structure (modified from [88]), where the blue arrow shows the carriers tunnel over the energy barrier between the metal and the insulator.](image)

The expression for Schottky emission is:

$$J = A^*T^2 \exp \left[ -\frac{q(\phi_B - \frac{qE}{4\pi\varepsilon\varepsilon_0})}{kT} \right]$$

(1.6)
\[ A^* = \frac{4\pi q^2 m^*}{h^3} \] (1.7)

\( J \) is the current density, \( A^* \) is the effective Richardson constant [90], \( m^* \) is the effective electron mass in dielectric, \( T \) is the absolute temperature, \( q \) is the electronic charge, \( \Phi_B \) is the Schottky barrier height, \( E \) is the electric field across the dielectric, \( k \) is the Boltzmann’s constant, \( h \) is the Planck’s constant, \( \varepsilon_0 \) is the permittivity in vacuum, and \( \varepsilon_r \) is the optical dielectric constant.

- **Fowler-Nordheim (F-N) tunnelling:**

F-N tunnelling is the conduction process whereby electrons tunnel through a triangular potential barrier into the conduction band of a dielectric. This process normally occurs when a high electric field is applied. A schematic band diagram of F-N tunnelling in MIS structure is shown in Figure 1.17.

The expression of the F-N tunnelling current is taken from reference [91]:

\[ J = \frac{q^3 E^2}{8\pi h q \Phi_B} \exp \left[ -\frac{8\pi(2qm_T^* \Phi_B)^{1/2}}{3hE} \Phi_B^{3/2} \right] \] (1.8)

where \( m_T^* \) is the tunneling effective mass in the dielectric; the remaining notations are identical to those defined for Schottky emission.

Unlike the thermionic emission where the tunnelling carriers are assisted by thermal energy, F-N tunnelling can be performed without the assistance of thermal energy but by the high electric field across the dielectric layer [92].
Figure 1.17 Schematic energy band diagram of Fowler-Nordheim tunneling in MIS structure (Modified from [88]), where the blue arrow shows the carriers tunnel through the triangle barrier when the device is under high electric field.

- **Direct tunnelling:**

Direct tunnelling, unlike F-N tunnelling, occurs when a device is under the influence of a weaker electric field. The thickness (generally very thin) of the insulator layer is critical for this phenomenon to occur. Moreover, electrons tunnel directly through the barrier, rather than through a triangular barrier. A schematic band diagram for direct tunnelling in MIS structure is presented in Figure 1.18 [88].

The current associated with direct tunnelling through a insulator or semiconductor barrier may be written as,

\[
J = \frac{2q}{(2\pi)^3h} \int_0^\infty \left( f_1 - f_2 \right) \{ \iint P \, dk_y \, dk_z \} \, dE
\]

(1.9)

where \( P \) is the tunnelling probability, \( E \) is the total electron energy, \( h \) is the reduced Planck constant, \( k_y \) and \( k_z \) are the wave vectors in the plane of the barrier (perpendicular to the tunneling direction), and \( f_1 \) and \( f_2 \) are the probabilities of
occupation states either side of the barrier as given by the Fermi–Dirac distribution functions.

Direct tunnelling is gaining significantly when the dielectric layer gets thinner (for SiO\(_2\) it is normally less than about 3.5 nm), whereas Fowler-Nordheim tunnelling dominates when the thickness of tunnelling barrier is thicker (for SiO\(_2\) it is normally around 4-5 nm and above) [88], [93].

![Figure 1.18 Schematic energy band diagram of direct tunnelling in MIS structure (modified from [88]), the blue arrow shows the carriers tunnel directly through the energy barrier.](image)

- **Poole-Frenkel (P-F) Emission:**

  P-F emission occurs when thermally excited electrons emit from traps into the conduction band of a dielectric. This is similar to Schottky emission and is sometimes referred to as internal Schottky emission.

  Applying an electric field across a dielectric film, during P-F emission, may reduce the Coulombic potential energy of trapped electrons [94]. Moreover, this may result in
trapped electrons with a high probability of being thermally excited. As such, the trapped electrons will then be thermally excited out of the traps and into the conduction band of the dielectric. A schematic energy band diagram of P-F emission is shown in Figure 1.19 [88].

The expression for current density due to P-F emission is

$$J = q\mu N_C E \exp \left[ \frac{-q(\Phi_T - \frac{qE}{\pi \varepsilon_r \varepsilon_0})}{kT} \right]$$

(1.10)

where $\mu$ is the electronic drift mobility, $N_C$ is the density of states in the conduction band, $q\Phi_T$ is the trap energy level. The remaining notations have been defined above.

Figure 1.19 Schematic energy band diagram of Poole-Frenkel emission in MIS structure (modified from [88]), where the blue arrows show carriers are emitted from traps into the conduction band of the dielectric layer.
Hopping conduction:

Hopping conduction arises from the tunnelling effect of trapped electrons “hopping” from one trapped site to another in dielectric films [95]. In P-F emission, trapped carriers are able to overcome the trap barrier through a thermionic mechanism. However, in hopping conduction the energy of trapped electrons is lower than the potential barrier between two traps. As such, carriers are transmitted by a tunnel mechanism. A schematic energy band diagram of Hopping conduction is presented in Figure 1.20 [88].

![Figure 1.20](image)

**Figure 1.20** Schematic energy band diagram of hopping conduction in MIS structure (modified from [88]), where the blue arrows show the carriers hop from one trapped site to another.

The expression for hopping conduction is

\[
J = qanv \exp \left[ \frac{qaE}{kT} - \frac{E_a}{kT} \right]
\]

where \(a\) is the mean hopping distance, \(n\) is the electron concentration in the conduction band of dielectric, \(v\) is the frequency of thermal vibration of electrons at trap sites, and
$E_a$ is the activation energy. This is the energy level from trapped states to the bottom of conduction band. All other terms have been defined previously.

- **Space-Charge-Limited (SCL) Conduction:**

The space-charge-limited current in semiconductors or insulating materials, which is parallel to the direction of applied electric field, arises as a result of charged particles (electrons) with specific drift velocity [96]. Moreover, the electric field accelerates these particles. The particles exhibit a proportionality factor, mobility $\mu$, between the magnitudes of the drift-velocity $v$ and the electric field $E$.

$$ v = \mu \ E \quad (1.12) $$

The expression for SCL current can be expressed as

$$ J = \frac{9}{8} \mu \varepsilon \frac{v^2}{d^3} \quad (1.13) $$

where $d$ is the thickness of a thin film and $\varepsilon$ is the static dielectric constant.

In the space-charge limited conduction, the current is dominated by charged carriers injected from the contacts and the current is only dependent on the mobility of carriers, hence, the mobility can be estimated [97]. When traps are present, the traps are filled by strong injection and the space charges appear. Thus a space charge layer in the dielectric builds up and the current is controlled by the space charge limited conduction [88].
• **Defect state assisted tunnelling:**

In the tunnelling mechanisms of Metal-insulator-semiconductor structure, defect-assisted tunnelling (or trap-assisted tunnelling) is an important governing factor, especially when the defect density is high [98], [99]. Unlike direct or Fowler-Nordheim tunnelling, which are one-step tunnelling processes, defects in the dielectric layer give rise to tunnelling processes based on two or more steps [100]. When the defect density is high, the multiple defect states may arise from a defect band, from which the carriers can resonant tunnel through the defect band states when applying a certain bias. In the resonant tunnelling process, the behaviour of negative differential resistance (NDR) can also be seen [101], [102]. In the thesis, clear resonant tunnelling behaviour was measured, which can firmly support the mechanism of defect state assisted tunnelling [103], which are reported and discussed in chapter 5.

### 1.6.2 Review of MIS Light Emitting Diodes

Light emission from nitride-based MIS diodes was first reported by Lagerstedt *et al.* [104]. It was claimed that a blue and UV light emission could be observed when using NaI and Al$_2$O$_3$ as insulators for the MIS device (with insulator thickness from 50 Å to 100 Å). The device structure and luminescence spectrum are presented in Figure 1.21. Broad and weak light emission spectra were observed as a result of a unreliable growth technique and un-optimised device structures (such as insulator material properties and its thicknesses; contact and interface properties, ohmic or Schottky).

Nitride-based MIS LEDs have not been investigated since the development of group III-Nitride PN junction based LEDs in eighties and nighties. However, recent interest in the luminescence property of ZnO (also difficult to be p-doped) has given rise to renewed interest in oxide based MIS-LEDs devices [16–20]. For example, Au/SiO$_2$/ZnO MIS-LEDs (Figure 1.22) have been reported by Chen *et al.* [17]. However, these MIS-LEDs exhibited low electroluminescence intensity, a broad emission peak, a high threshold voltage, and a relatively thick (~100 nm) insulating layer was required in order to obtain diode behaviour. In the article, the hole generation
in the ZnO was proposed by two points of views without supporting data. (1) under the sufficient forward bias, an amount of the electrons in the valence band of ZnO is drawn into the electron traps in the band gap of SiO\textsubscript{2}, therefore an equivalent amount of holes is generated in the valence band of ZnO; (2) electron-hole pairs are generated in the SiO\textsubscript{2} layer through the impact ionization created by the high electric field (Although the lifetime of the electron-hole pairs and the hole’s mobility in the SiO\textsubscript{2} layer are considerably small), after which the holes generated in the region nearby the interface of SiO\textsubscript{2} and ZnO may be swept into the valence band of ZnO by the forward bias [17].

![Figure 1.21](image)

**Figure 1.21** (a) Schematic structure of the early MIS light emitter proposed by Lagerstedt *et. al.* (b) Electroluminescence (EL) from an Au-Al\textsubscript{2}O\textsubscript{3}-GaN device and the photoluminescence (PL) from the same GaN substrate [104].
MIS-LEDs based on Au/MgO/MgZnO have also been reported. These also exhibited poor emission properties. Interestingly, two contradictory mechanisms for light emission were presented. These are shown in Figure 1.23. Zhu et. al. [105] proposed that the MIS tunnel current resulted from impact ionisation by generating injection holes inside the insulator layer when under a forward bias, which was similar to the article published by Chen et. al. [17]. Subsequently Ni et. al. proposed that the UV light emission of MIS-LEDs was generated under a reverse bias instead of under a forward bias [106]. In Ni’s suggestion, when the MIS device was under high reverse bias, both the conduction and valence bands of the MgO layer were bent significantly, which means large amount of electrons can tunnel easily and directly into the conduction band of the MgO layer through the F-N tunnelling process [92]. The electrons were then accelerated greatly because of the high electric field across the thin MgO. Once the accelerated electrons enter into the MgZnO active layer, the electrons in the valence band of the MgZnO may be excited into its conduction band by obtaining energy from the accelerated tunnelling electrons, which can create holes in the valence band of MgZnO. Then the electrons in the conduction band of MgZnO
may recombine radiatively with the holes in the valence band to give UV emission [106].

Figure 1.23 Band diagram schematics of MIS UV LEDs based on the device structure of Au/MgO/MgₓZn₁₋ₓO/n-ZnO. These report contradictory tunnelling mechanisms: (a) forward bias [105], and (b) reverse bias [106].

However, all of these reported MIS-LEDs have been based on oxide films with a crystal quality significantly poorer than that of epitaxially grown nitride semiconductors. Moreover, the oxide-based MIS-LEDs did not indicate data to support the current tunnelling mechanism for recombination, resulting in contradictory mechanisms [17], [106]. Therefore, nitride-based MIS LEDs have been studied in this thesis. A series of material and electrical characterisation have been performed to propose an affirmative tunnelling mechanism. The nitride-based MIS-LEDs can also serve as a benchmark to establish the performance of MIS-LEDs relative to conventional LEDs.

Part of the PhD research has been published in the IEEE Photonics Journal [103], and the information from the paper is also included in the thesis. The cover figure of the published paper can give a brief idea of what was the structure of the studied MIS-LEDs and what was the electron tunnelling mechanism (shown in Figure 1.24).
Figure 1.24 UV emission from resonant tunnelling Metal-insulator-semiconductor light emitting diodes, where no $p$-doping material is required in the device. (a) a schematic structure of the nitride-based MIS LEDs, and (b) a band diagram of the MIS LEDs showing the electron tunnelling mechanism and the electron-hole recombination.

1.6.3 Key factors of MIS UV LEDs

1.6.3.1 Insulator thickness

The thickness of the insulator is one of the most important factors for controlling the tunnelling effect in MIS-based devices. The use of the correct insulator thickness (Figure 1.25) allows for trapping of electrons at the insulator/semiconductor interface. Moreover, holes can drift or be injected into a semiconductor area. This combination enables electroluminescence by recombination of electrons and holes. However, if the insulator is too thin, electrons cannot be trapped at the interface. Instead they tunnel through the insulator layer and do not allow for light generation via hole and electron recombination.
1.6.3.2 The band alignment between layers

The confinement of carriers and the control of tunnelling current are very important for radiative recombination. As such the structure of band alignment needs to be optimised. This can be achieved through the choice of materials, growing techniques, doping concentration, and thermal processes. In this thesis, the band gap of materials has been investigated using UV-Vis optical measurements and doping concentrations were obtained using Hall measurements.

1.6.3.3 Ohmic contact

Efficient injection of electrons and holes plays a key role in electroluminescence. In a MIS device an $n$-type layer semiconductor is employed for electron injection. Therefore, the electrode metal contact with the semiconductor should form an ohmic contact. This will allow for lower resistivity, making the flow of electrons from the semiconductor into the metal easier. The key is application of a metal with a small resistive barrier, which calls for a metal with a work function equal to or smaller than that of the $n$-type semiconductor (Figure 1.26), where $\varphi_m < \varphi_s$. When a positive voltage is applied to the metal, there is no barrier to electrons flowing from semiconductor into the metal. If a positive voltage is applied to the semiconductor, the
effective barrier height for electrons flowing from the metal into the semiconductor will be around $\phi_{Bn}$, which is very small for a heavily doped semiconductor [78]. However, in most of practical cases ohmic contact is difficult to form without additional treatment. To solve this, normally annealing process has to be applied to form a very thin barrier at the interface between the metal and the semiconductor, where the electrons can easily tunnel through the thin barrier by field emission. Detailed information about the mechanisms and annealing conditions were discussed [107], [108]

**Figure 1.26** Band structure of ohmic contact interface between metal and $n$-type semiconductor: (a) before contact, and (b) after contact. (modified from [87])

1.6.3.4 Transparent layer for current spreading

The top metal layer serves as a conductive current-spreading layer as well as a pathway for light extraction in a $n$-type MIS device. This layer is required to be optically transparent to the wavelength of light generated by the light emitting diodes and also conductive for good current spreading. In this research, a very thin 10 nm metal was used for the MIS device. This was used to demonstrate the viability of MIS UV LED. Subsequently, annealed metal layers were also evaluated to achieve transparent contact by forming transparent metal-oxide. The gold transmittance spectra (Figure 1.27) [109] and the transmission of Ni/Au annealing in a range of temperatures [110] (Figure 1.28) are presented below.
Figure 1.27 Calculated transmittance spectra of thin gold films with various nominal thicknesses [109].

Figure 1.28 Transmission spectra of Ni/Au electrodes before and after annealing in O₂ [110].
1.7 Summary

The research in this thesis focuses on the development of solid-state devices for UV light emission. A potential non $p$-doped metal-insulator-semiconductor (MIS) UV light emitting device was studied rather than reviewing the conventional PN junction based UV LEDs. In order to achieve efficient light emission using MIS-based devices, several aspects have been explored. These include material properties, current injection, current tunnelling, carrier confinement, insulator properties and thickness, band alignment, light extraction.

Chapter 2 provides an overview of the characterisation techniques employed in this research, i.e. for the study of material, optical and electrical properties. Chapter 3 explains the device fabrication technique and processes. The material characterisation results for related materials prepared by different growth technique are presented in Chapter 4. The electrical measurement results to support the tunnelling mechanism behind the MIS UV emitter are presented in Chapter 5 and the optical results from the MIS device, UV light emission are presented in Chapter 6. Chapter 7 provides an overview of the conclusions drawn from the research and a plan of future work is suggested.


1.8 References


[98] F. Campabadal and V. Milian, “Trap-Assisted Tunneling in MIS and Schottky


Chapter 2

Characterisation techniques

2.1 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a high-resolution technique invented by Binning, Quate and Gerber in 1986 [1]. This technique is based upon scanning tunnelling microscopy (STM), as developed, by Binning et. al. in 1982 [1], [2]. AFM has become one of the most important tools for imaging, measuring and manipulating matter at the nanoscale, in particular on surface roughness and morphology. This is due to its high vertical resolution, and adaptation to both conductive and non-conductive materials.

The typical structure of an AFM instrument (Figure 2.1) includes a small tip attached to a sensitive cantilever, an optical system on top of the tip, and a data processing system. As the tip is brought closer to a sample, the force between the tip and the sample leads to a deflection of the cantilever. This generates a variation in the vertical and lateral position of the tip. Furthermore, a laser is directed onto the tip and the reflection of the laser is directed to a photodetector. In order to maintain the set force, an electronic feedback controller is used to change the height of the piezo stage by adjusting the voltage applied to the piezo stage [3].

An AFM has three different operating modes. These include contact mode, non-contact mode, and tapping mode. In contact mode, the tip and sample remain in close contact during scanning. This is operated in the repulsive regime of the intermolecular force (Figure 2.2) and large lateral forces are exerted on both the tip and the sample surface as the tip is pulled over a specimen. One major drawback of the contact mode is the tip abrasion, especially when scanning solid-state materials.
In non-contact mode, the tip does not make contact with the sample surface, but rather reacts to the attractive van der Waals forces between the tip and the sample (Figure 2.2). However, attractive forces between the tip and the sample are much weaker than the forces exerted by the contact mode. Thus, low resolution is achieved as oscillations of the tip are difficult to observe by the photodetector.

**Figure 2.1** Schematic diagram of a typical AFM.

**Figure 2.2** Force-distance curve for AFM.
In tapping mode advantages from both contact and non-contact modes can be included, making this mode the most used for solid-state thin films. The cantilever is driven to oscillate near its resonance frequency, which is controlled by a piezoelectric element mounted in the cantilever holder. The amplitude of oscillation typically ranges from 20 nm to 100 nm. As the tip interacts with a sample surface dampening occurs, resulting in a change of the oscillation. The tip oscillation is measured by the photodetector, and a feedback signal is used to adjust the voltage applied to the piezo stage in order to adjust the height of the stage to maintain a set force [3].

In this thesis, all AFM images were generated using the tapping mode on a Bruker Innova AFM. A NCHV tip with a resonant frequency of 320 kHz and a force constant of 42 N/m was used. All measurements were performed at ambient conditions and all images were scanned at 1 Hz with 512 lines and processed using WSxM 4.0 Beta 7.0 with parabola flattening [4].
2.2 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a powerful and non-destructive technique for crystallographic analysis for thin-films, powders and bulk materials. In this work, it was employed to characterise the epitaxial property of thin films. Starting with an incident X-ray into a thin film, X-ray waves can be scattered by each atom and interfere with each other. This interference can be either constructive (overlapping waves add together to produce stronger peaks) or destructive (waves are subtracted from each other) and leads to diffraction patterns on a detector (Figure 2.3).

Bragg’s Law can describe the interactions between X-rays and a crystal. The law states that constructive interference is at its strongest when the path length difference between two X-rays diffracted at a family of crystallographic planes is a multiple of the X-ray wavelength $\lambda$,

$$n\lambda = 2d_{hkl} \sin \theta$$

(2.1)

where $n$ is the order of diffraction, $\lambda$ is the wavelength of an incident wave, $d_{hkl}$ is the lattice spacing of the respective crystallographic plane with Miller indices, and $\theta$ is the angle between the incident X-ray and the scattering planes (Figure 2.4).

**Figure 2.3** Schematics of (a) constructive interference and (b) destructive interference of X-ray incident beam diffracted from parallel planes (Modified from [5]).
A simple illustration of an X-ray diffractometer is presented in Figure 2.5. To generate X-rays, a beam of high-energy accelerated electrons is used to irradiate a metal target. The resultant X-rays are emitted with different wavelengths, depending on the orbital transitions. A filter is applied to obtain monochromatically incident X-rays, for example $K_{\alpha}$ line ($CuK_{\alpha} = 1.5406 \text{ Å}$). Following diffraction by a crystal, scattered X-rays pass through a collimator (located at the front of the detector) to filter out any non-parallel diffracted beams, which could result in a broadening of the diffraction peak. This approach results in an increased resolution in an XRD spectrum.
By changing the setting of measurements, different diffraction geometries can be performed, including symmetric, asymmetric, skew symmetric, and in-plane scattering diffractions (Figure 2.6) [7].

![Possible diffraction geometries](image)

**Figure 2.6** Possible diffraction geometries [7].

A symmetric diffraction is used to determine the interplanar lattice parameters (parallel to the sample surface). Asymmetric and skew symmetric diffractions are used to determine the interplanar lattice parameters of a set of planes which are not parallel to the sample surface. With regard to the in-plane scattering diffraction, planes perpendicular to the sample surface can be measured by setting a very small incidence angle. For further detailed discussion, it can be obtained from the review article “X-ray diffraction of III-nitrides” by M. Moram and M. Vickers [7].

In this work, two types of symmetric (out-of-plane) scans have been applied to the III-nitride semiconductor, ω-scans and ω-2θ scans. ω-scans measure the crystal quality of films by scanning a fixed diffraction spot on a rotating specimen, where the rotation direction is shown in Figure 2.5. A broaden peak indicates a poorly crystallised film, and is normally related to dislocations [7]. ω-2θ scans are coupled scans performed for the determination of lattice parameters, where Bragg’s law is applied to calculate the diffraction angles.

All XRD diffractograms presented in this thesis have been obtained using a PANalytical MRD with a CuKα source. The instrument was operated in high resolution mode, where its angular precision was around 0.0001 degrees.
2.3 Ultraviolet-Visible Spectroscopy

Ultraviolet and visible spectroscopy (UV-Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectral region. This is a non-destructive characterisation technique used to investigate the electro-optical properties of semiconductors. The light source used for measurements ranges from 190 nm to 1200 nm. This is equal to a photo-energy range from 6.53 eV to 1.55 eV, as calculated using Planck’s energy–frequency relation (Equation 2.2),

\[ E = \frac{hc}{\lambda} \]  

where \( E \) is the photon energy normally stated in eV (1 eV = 1.602 × 10\(^{-19}\) J), \( h \) is Planck’s constant (6.626×10\(^{-34}\) Js), \( c \) is the speed of light (3×10\(^{8}\) m/s) and \( \lambda \) is the wavelength of the light.

Figure 2.7 Schematic diagram of an UV/Vis spectrophotometer.

The basic of a UV/Vis spectrophotometer is illustrated in Figure 2.6. Deuterium and tungsten lamps are typical light sources used to generate UV and Visible light. The operation of a UV/Vis spectrophotometer is fairly straightforward. A beam of light from the UV/Visible light source is input into a monochromator, after which a selective wavelength of light is generated and passed through a sample. An electronic
detector is used to measure the intensity of the transmitted beam ($I$), while the intensity of the reference beam ($I_0$) is measured when the sample is removed. The detected signals are then amplified and processed using a computer. The computer is used to transfer the signals into digital data, which is observed as transmittance ($T$).

Transmittance ($T$) can be expressed by the relation shown in Equation 2.3, whereas absorbance (Abs) is obtained using Equation 2.4.

$$ T = \frac{I}{I_0} \quad (2.3) $$

$$ Abs = \log \frac{1}{T} \quad (2.4) $$

Moreover, the absorption coefficient ($\alpha$, eV cm$^{-1}$; Equation 2.5) can be obtained by taking into account the thickness ($d$) of a thin film. The band gap of materials can be calculated using the relationship between absorption coefficient and band gap (Equation 2.6), where $n = \frac{1}{2}$ for a direct optical transition and $n = 2$ for indirect optical transitions [8]–[10].

$$ \alpha = \frac{1}{d} \log \frac{I_0}{I} \quad (2.5) $$

$$ \alpha h v = A(h v - E_g)^n \quad (2.6) $$

In Equation 2.6, $\alpha$, $h$, $v$, $A$, and $E_g$ are the absorption coefficient, Planck’s constant, the light frequency, a constant and the band gap, respectively. Thus the band gap can be obtained as an intercept on the plot of $(\alpha h v)^n$ against $h v$.

In this thesis, an Agilent Technologies Cary 5000 Uv-Vis-NIR spectrophotometer was used for the UV-Vis transmission measurements. These measurements have been carried out at room temperature and the scanning photon wavelength varied from 190 nm to 800 nm. A baseline correction was performed by setting the transmittance of the bare sapphire substrate, which is the same as the substrates of grown samples, to be 100% using a black plate to block the beam for getting a zero correction [10].
2.4 Hall Effect Measurement

A Hall Effect measurement allows for detailed investigation of charge transport properties in semiconductors. A schematic of the Hall Effect measurement is shown in Figure 2.7. In this approach a current is applied along the x-direction to a thin-film semiconductor with length $L_x$, width $L_y$ and thickness $d$. Simultaneously, a magnetic field $B_z$ is applied perpendicular to the flow of carriers, which have velocity $v_x$.

According to Lorentz force carriers will be deflected under the magnetic force as expressed in Equation 2.7. A build up in electrostatic force and a Hall voltage $V_H$ can be measured using Equation 2.8, because of carrier deflection in the y-direction.

$$F = e \left[ E + (v \times B) \right]$$  \hspace{1cm} (2.7)

$$E_y = -\frac{V_H}{L_y}$$ \hspace{1cm} (2.8)

Under equilibrium conditions the electrostatic force will be in balance with the Lorentz force. This can be expressed as Equation 2.9.

$$e \frac{V_H}{L_y} = e v_x B_z$$ \hspace{1cm} (2.9)

Figure 2.8 Schematic illustration of the Hall effect in a thin-film semiconductor, which is under a magnetic field $B_z$ perpendicular to the electric current $I_x$. 
In addition, the current density in the x-direction is represented in Equation 2.10.

\[
\frac{I_X}{L_yd} = nev_x
\]

Combining Equations 2.9 and 2.10 resulting in Equation 2.11 can derive the free carrier concentration, n per unit volume.

\[
n = \frac{I_XB_Z}{eV_Hd}
\]

The Hall mobility \(\mu_H\) can also be obtained from Equation 2.12 by using the measured electrical conductivity \(\sigma\) and the above carrier concentration,

\[
\sigma = ne\mu_H = \frac{\mu_H}{R_H}
\]

where \(R_H=1/ne\) and it is called the Hall coefficient.

Using Equation 2.12 it is observed that electrical conductivity is proportional to the product of mobility and carrier concentration. For example, the same conductivity could come from a small number of electrons with high mobility, or a large number of electrons with low mobility. In general, high concentration can be achieved through the introduction of more dopants, which provide free carriers. However, it is difficult to increase mobility as this depends on a detailed scattering mechanism of carriers [11]. In III-Nitride semiconductors, the electron mobility of AlGaN is generally much lower than the one of GaN. This mainly results from the alloy scattering, which is caused by perturbation of crystal potential due to the random positioning of substituting atom species in a relevant sublattice [12]. In semiconductors, almost always higher mobility leads to better device performance [13].

In this thesis, an 8400 Series Hall Effect Measurement System provided by Lake Shore Cryotronics was used to carry out the experiments, where the van der Pauw geometry was used as the testing structure [14]. Exceptionally low mobility can be obtained for
this setup by using an alternating current (AC) field. As the Hall voltage is proportional to the magnetic field, when an AC field is applied, the Hall voltage signal will also show up as an AC signal. Therefore, undesired DC voltage signals, thermoelectric voltages and misalignment voltages can be easily separated from the AC Hall voltage signal [14]. In order to get high spatial resolution data, a symmetric probe geometry has also been considered [15]. In this work, symmetric square samples with small contacts at the corners have been applied to measure the Hall Effect experiments.


2.5 Photoluminescence Measurement

Photoluminescence is a widely used characterisation technique for investigating semiconductors by optical excitation. This technique requires that the energy of the excitation source is greater than the band gap of the measured samples, in order that the energy can be absorbed by the samples. An electron that has been excited above the conduction band of a material will eventually fall and recombine with the hole (excited below the valance band), after losing some energy through the release of a phonon to the lowest available non-radiative energy level [16].

A schematic of the PL experiment setup is shown in Figure 2.8. A pulsing laser with a fixed wavelength is directed onto the sample via an optical system. When the laser beam is incident on the sample, photoluminescence occurs and light is emitted at wavelengths dependent on the material properties of the sample. The emitted light is then directed into a spectrometer. This spectrometer consists a diffraction grating, which is used to diffract different wavelengths towards an array of photo-detectors that are used to measure the intensity of each wavelength [17].

![Figure 2.9 Schematic diagram of PL experiment set-up.](image)
The energy of the emitted light is related to the difference in energy levels between the excited and equilibrium states. Moreover, the intensity of the emitted light is related to the excitation energy and the related radiative recombination process. Typical energy transitions resulting in photoluminescence and indicating the recombination processes in semiconductor materials are presented in Figure 2.9. When a sample is excited by a laser optical source (with energy $h\nu > E_g$), electron-hole pairs are generated as electrons are excited to the conduction band. These then recombine and emit light by one of several mechanisms (Figure 2.9). In Figure 2.9 (a) is a band-to-band recombination that generates the photoluminescence representing the band gap of the semiconductor, (b) and (c) show the impurity-related traps, trapped electrons and trapped holes, serving as inter-band donors and acceptors for recombination with holes in valence band and electrons in conduction band. In those recombination processes, the emitted photoluminescence wavelengths are shorter than the material’s band gap energy. Finally (d) shows a donor-to-acceptor (D-A) recombination process, where an electron on a neutral donor level recombines with a hole on a neutral acceptor level. Normally, the D-A recombination process is non-radiative [18].

Figure 2.10 Schematic diagram of energy transitions in a semiconductor: (a) band to band (b) donor level to valence band (c) conduction band to acceptor level, and (d) between donor and acceptor level.
A photoluminescence spectrum provides significant material information including the band gap, composition of semiconductor alloys, lattice crystallinity, lattice stress, impurity concentration, and surface behaviour [17]. Moreover, energy levels (dependant on the PL peak positions) of the measured materials are revealed and the impurities (defects) can also be investigated. In addition, the crystalline quality of measured samples can also be characterised using PL peak line width and splitting. Peak broadening and splitting can be used to explain unintentional variations in the confinement energy, which are normally attributed to the crystalline disorder and interface roughness.

In this thesis, an Andor shamrock 303i spectrometer was employed with a wavelength accuracy in the region of 0.04 nm and wavelength repeatability of 4 pm. A pulsed Nd:YAG laser operating at 266 nm was applied as an optical excitation source [19].
2.6 Electroluminescence Measurement

Electroluminescence is the direct conversion of electrical energy into electromagnetic radiation. In this process a material emits light in response to the passage of an electric current or a strong electric field [20].

![Figure 2.11 Schematic diagram of EL experiment set-up.](image)

The setup of basic EL measurement is shown in Figure 2.10. In this setup a voltage power supply is used to apply electric voltage or current to a sample. The electroluminescent light coming from the sample is collected by an optical system. This includes a lens, a collimator, a photomultiplier tube, and the spectrometer. An integrating sphere is routinely applied to collect uniform light. This is because light scattered by the interior of the integrating sphere is evenly distributed over all angles.

The electroluminescence measurements are widely performed in the light emitting diode (LED) industry, from which the emitting wavelength of LEDs and the intensity
of emitting lights can be investigated. In this thesis, the development of UV electroluminescence is the main topic. As such the EL measurement was used extensively to characterise the developed devices. This was carried out using a Keithley 2602A voltage source and Andor shamrock 303i spectrometer.
2.7 Resistivity Measurement

2.7.1 Four-Point Probe Technique

The sheet resistivity of current spreading layers, which are found on the top of light emitters, is an important parameter for obtaining efficient light emission. Therefore, best practice aims to minimise the contact contribution to the measured resistance value.

A four-point probe is a simple apparatus used for measuring sheet resistivity. This is carried out by passing a current through two outer probes and measuring the voltage through the inner probes. The basic setup of the four-point probe measurement is shown in Figure 2.11. A current source is used to supply current through the two outer probes and a voltameter measures the voltage across the two inner two probes, in order to determine the sample resistivity. The space between probes, $S$ ($S \approx 1\text{mm}$) is generally uniform. Equation 2.13 expresses the resistivity ($\rho$) of measured bulk materials [21].

$$\rho = 2\pi s \left(\frac{V}{I}\right)$$

(2.13)

For very thin films, $t < S/2$, the sheet resistivity can be described as in Equation 2.14.

$$\rho_s = \frac{\pi t}{ln2} \left(\frac{V}{I}\right) = 4.532t \left(\frac{V}{I}\right)$$

(2.14)
Figure 2.12 Schematic diagram of a four point probe.

In the thesis, a Jandel 4 Point Probe was employed as a multi-height probe and was connected to a Keithley 2420 source meter.

### 2.7.2 Transmission Line Measurement (TLM)

A metal/semiconductor ohmic contact is of great importance for efficient current injection in light emitters. An ideal ohmic contact should not decrease device performance. Moreover, it should able to supply the required current without a voltage drop across the metal/semiconductor interface.

The basic structure of TLM, from an overview and a cross section, is shown in Figure 2.12. The basis of a standard TLM array is a series of identical contacts deposited on top of a semiconductor with unequal spacing. All contacts are fabricated simultaneously and can therefore be expected to be identical.

The measured total resistance (Equation 2.15) can be obtained when a voltage (V) is applied across two contacts,
\[ R_T = 2R_m + 2R_C + R_{semi} \]  \hspace{1cm} (2.15)

where \( R_T \) is the total measured resistance, \( R_m \) is the metal resistance, \( R_C \) is the contact resistance associated with the metal/semiconductor interface, and \( R_{semi} \) is the semiconductor resistance with contact space \( L \).

The metal resistance of the contact is generally much smaller than the contact resistance of the metal/semiconductor interface, \( R_C \gg R_m \). Therefore, the effect of metal resistance to the total resistance can be neglected. The semiconductor resistance can be expressed as in Equation 2.16, where \( R_S \) is the sheet resistance of semiconductor.

\[ R_{semi} = R_S \frac{L}{W} \]  \hspace{1cm} (2.16)

The total resistance is indicated in equation 2.17.

\[ R_T = 2R_C + R_{semi} = \frac{R_S}{W} L + 2R_C \]  \hspace{1cm} (2.17)

**Figure 2.13** Schematic diagram of a four Transmission Line Measurement: (a) from top view (b) from cross section (modified from [22]).

If the resistance of several two different-space contacts are measured, the measured resistances of each contact can be plotted as in Figure 2.13 [22].
The slope of a line, linearly fit to the measured data, can be described as $R_S/W$. This fit indicates the region in which the sheet resistance of semiconductor can be obtained. Moreover, the y-axis intercept can be used to derive the contact resistance $R_c$, which is $1/2$ the intercept [22]–[24].

\[ \text{Slope} = \frac{R_S}{W} \]

**Figure 2.14** Illustration of a linear fit to TLM data measured, where the contact resistance can be obtained (modified from [22]).

The method of transmission line measurement can also be used to calculate the specific contact resistivity, where an effective length (called transfer length) underneath the contact needs to be concerned [25]. This is because of the current crowding effect at the edge of contacts [26]. Apart from that, the fringe field effect between contacts should also be concerned for the specific contact resistivity [27].
2.8 References


Chapter 3

Device fabrication techniques

3.1 Metal-organic chemical vapour deposition (MOCVD) growth technique

Metal-organic chemical vapour deposition (MOCVD) is a chemical vapour deposition technique that employs metal-organic compounds as precursors. These metal-organic precursors may include trimethylgallium (TMG), trimethylaluminium (TMA) or trimethlyindium (TMI), which are sources of Ga, Al and In. MOCVD performs at close to ambient pressures and produces a relatively high growth rate (~ 1 μm/h). Moreover, it is recognised as one of the most frequently applied methods for the large-scale production of nitride-based thin films, which find application in optoelectronics and electronic devices [1].

The basic idea of chemical vapour deposition (CVD) techniques is the transport of constituent elements from the gas phase to the vapour–solid interface in the form of volatile molecules [2]. The general principles of CVD (Figure 3.1) involve the following steps: (i) Transport of precursors to the growth zone, (ii) gas-phase chemical reactions in the hot zone to form reactive intermediates or by-products, (iii) transport of the precursors and the reactants to the substrate, (iv) adsorption of reactants on the substrate, (v) surface diffusion, nucleation and reactions leading to the growth, and (vi) the desorption and pumping of by-products away from the substrate [3], [4].

The basic chemical reaction for MOCVD of group-III nitrides using a standard source compound, e.g. trimethyl metal precursors, can be described by the overall reaction (Equation 3.1).
MOCVD systems normally operate at pressures ranging from a few millibars to atmospheric pressure. At these pressure conditions molecules interact according to the principles of fluid dynamics. Therefore, in order to control a homogeneous growth a MOCVD reactor is designed to maintain a laminar gas flow. This means that the gas-phase fluid flows in parallel layers, with no disruption between layers [5]. Moreover, turbulent gas flows are excluded resulting in a smooth distribution of reactant on the substrate.

The growth rate in thermal MOCVD can be categorised into three limited modes. This is done according to differences in growth temperature. Figure 3.2 shows the relationship between growth rate and temperature. At low growth temperatures, the growth rate decreases exponentially with the reciprocal of the process temperature (1/T). Moreover, the growth rate is limited by the reaction rate, which is sensitive to the process conditions and it is therefore difficult to control a steady growth rate batch-to-batch.
In the medium growth temperature range the growth rate is nearly independent of temperature. In addition, the growth rate is limited by the transport of the reactants. This is defined as diffusion-limited growth. Moreover, adjusting the precursor concentrations and the thickness of the boundary layer can control a steady growth rate. At very high growth temperature, the growth rate decreases due to enhanced desorption and parasitic deposition at the reactor walls. Normally, the growth temperature in the diffusion-limited-growth regime (Medium-T region in Figure 3.2) is applied to the practical growth.

**Figure 3.2** Growth rate of (001)-oriented GaAs as a function of reciprocal temperature. Brown and gray circles represent measured and simulation data respectively [2], [5].

In-situ monitoring of MOCVD film deposition is generally carried out using a reflectometer. This is done to record and explain the growth process. The reflectivity from a sample surface can be used to determine whether a film is fully coalesced and the period of signal oscillation can be used to obtain the growth rate [6].
The reflectance of growing films is temperature-dependent index (a typical trace is indicated in Figure 3.3), from which various physical properties and changes of film morphology can be studied [6], [7]. A smooth surface is obtained following the initial growth and thickening of the nucleation layer, resulting in increased reflectance intensity. The nucleation layer is annealed, following temperature ramping, resulting in a roughening of the film surface and a drop in the reflectance intensities. This shows the lateral growth and coalescence processes facilitated by the high temperature, which can lead to a smooth film [6]. Oscillations arise as the epitaxial film becomes thicker. This is caused by interference between the beams reflected from the film-substrate interface and the film surface. The film thickness can be calculated by the period of oscillation, D, which is given by D= $\frac{\lambda}{2n}$. Where n is the refractive index of the film and $\lambda$ is the incident wavelength [8].

![Figure 3.3](image)

**Figure 3.3** A typical plot of the reflectance versus time during the growth of a GaN film on sapphire (0001) substrate [9].

All MOCVD-grown films in this thesis were obtained from the National Centre for III-V Technologies at the University of Cambridge, using a Thomas Swan 6 x 2” close-
coupled showerhead reactor (Figure 3.4). TMA, TMG, and NH$_3$ were employed as precursors and hydrogen as carrier gas.

**Figure 3.4** Schematic illustration of a close-coupled showerhead reactor. (Courtesy of M.Kappers)
3.2 Radio frequency magnetron sputtering technique

Sputtering is one of the most important physical vapour deposition (PVD) techniques used to deposit thin films on substrates. The technique is based on the bombardment of energetic particles at a target. The source of energetic particles is generated either by direct current (DC) or radio frequency (RF) power supplies and presented as plasma. In a DC sputtering system, high negative voltages are applied to the cathode (the target) and positively charged ions are attracted from the plasma towards the target. The ions gain energy in an electric field and bombard the target with sufficient energy to initiate sputtering. However, in order to obtain a high deposition rate a high sputtering power is required. This leads to a high voltage operation, which is undesirable and may damage to the thin film as a result of high-energy electrons and secondary ion bombardment.

RF sputtering systems were introduced as an improvement on DC sputtering systems. In RF systems oscillating electrons efficiently ionise the gas, resulting in higher deposition rates. Moreover, RF sputtering can be used to deposit dielectrics. This is not possible using DC sputtering because of charge build up on the target. RF sputtering normally works at very high frequency, i.e. 13.56 MHz. This means that (heavy) ions can no longer follow the switching, and electrons can neutralise positive charging on each electrode during each half cycle.

Magnets can be used to increase the percentage of electrons that take part in ionisation (maximising sputtering efficiency) by confining electron movement [10]. Magnetrons are placed behind a target and a strong magnetic field is applied at right angles. This helps confine electrons near the target surface and causes them to move in a spiral motion until they collide with an Ar atom. Moreover, any heating effect on a wafer substrate can be reduced as the dense plasma is confined near the target and ion loss to the wafers is reduced. A schematic structure of an RF magnetron sputtering system is presented in Figure 3.5.
Figure 3.5 Schematic diagram of RF magnetron sputtering and an illustration of magnetrons employed in a RF sputtering system (modified from [11]).

Sputtering techniques are also used to deposit compounds when a reactive gas (normally oxygen or nitrogen) is applied. This is referred to as reactive sputtering. For the deposition of AlN, high purity nitrogen gas is typically introduced into the plasma (formed by inert (argon) gas). Nitrogen is activated by the plasma, in the reaction processes, and chemically reacts with the surface of the sputtering target. This target is subsequently sputtered away. Control of the relative amounts of the inert and reactive gases and the RF source, can result in high quality AlN thin films [12].

In this research, the reactive sputtering process was carried out using a radio frequency magnetron sputtering system, within a combo sputtering/thermal evaporation system (Mantis Deposition Ltd [13], [14]) with a high vacuum chamber, up to $10^{-9}$ mbar.
3.3 Electron-Beam thermal evaporation deposition

Thermal evaporation is further physical vapour deposition (PVD) technique. The principle of thermal evaporation is fairly straightforward. A source material is generally heated in a vacuum chamber until its surface atoms have sufficient energy to exit the surface. Electron beams (e-beam) are normally used as a heating source in thermal evaporation. In this approach, a target anode is bombarded with an electron beam originating from a charged tungsten filament. Moreover, a high-vacuum chamber is required to achieve efficient e-beam thermal evaporation, whereby the mean free path of evaporated particles is longer than the distance between the evaporation source and the substrate [15]. Per definition, the mean free path is the average distance which an atom or molecule can travel in a vacuum chamber before it collides with another particle.

A schematic diagram of e-beam thermal evaporation is presented in Figure 3.6. In this process a heated filament is used to generate electrons. Moreover, by using a magnetic field the electrons can be deflected and accelerated towards/focused on a small area of the target material requiring evaporation. Thermal energy is generated after an e-beam strikes the target surface. Moreover, the target is melted only after the thermal energy reaches a high threshold. In this setup the target material (pellets) is placed in a crucible, which is selected based on its compatibility with the desired temperature and the evaporated material [16].

Vapour pressure is a key physical property that needs to be taken into account in order to achieve an efficient thermal evaporation rate. Vapour pressure is the pressure at which the vapour phase is in equilibrium with the solid or the liquid phase, at a given temperature. Below this pressure, surface evaporation is faster than condensation [17].

E-beam thermal evaporation is most suitable for deposition of metallic thin films. However, compounds and alloys do not deposit well as they generally exhibit vastly different melting points and vapour pressures.
In summary, thermal evaporation and sputtering are both PVD techniques. Thermal evaporation has several advantages and disadvantages when compared to sputtering. The deposition of thermal evaporation is highly directional. This is good for defining a mask area but poor for step coverage. The deposition rate of thermal evaporation is generally higher than for sputtering and the level of impurity in thermal evaporation is lower, due to high vacuum conditions. However, the deposition material for the thermal evaporation is limited, normally compounds and alloys can not be deposited by thermal evaporation.

In this research, the e-beam thermal evaporation process was carried out using a combo sputtering/thermal evaporation system (Mantis Deposition Ltd [13], [14]) with a high vacuum chamber, up to $10^{-9}$ mbar. Moreover, high voltage (2 kV) was applied to generate high-energy electron beams.

**Figure 3.6** Schematic diagram of e-beam thermal evaporation.
3.4 Patterning

Photolithography is an optical method for transferring a geometric pattern from a photo mask onto a sample. The steps in photolithography are: photosensitive film (Photoresist PR) application, alignment of mask and sample, exposure of photoresist, and the development of patterns.

There are several types of photolithography techniques. In this thesis, the contact-mode photolithography technique was applied to achieve patterning for device fabrication. A brief schematic structure of the photolithography, where a 400 nm UV light was used as an UV light source is shown in Figure 3.7. An experienced process control is required to obtain desired patterns, including sample cleaning, uniform PR coating, proper soft baking, UV exposure according to the PR, time-controlled development, and appropriate hard baking. A series of masks are required to define patterns in different layers, from which alignment keys can be applied in order to align patterns from different layers [18].

Figure 3.7 Schematic illustration of the photolithography.
In this thesis, a Karl Suss MJB3 Mask Aligner (including 400 nm UV light source) was employed to perform the exposure process. A Clariant AZ5214E was used as the photoresist [19], and Merck AZ 400k chemical was applied as a developer [20].

### 3.5 Dry etching

Previously no reliable wet-etch process has been proposed for III-nitride materials, due to high chemical inertness. Therefore, in this work a dry etching technique is applied to etch the III-nitride materials, from which a directionally anisotropic profile can be obtained. In the general reactive ion etching (RIE) is widely used as a dry etching technique. In the RIE process, plasma is initiated in a chamber when an injected gas is ionised by an applied RF electromagnetic field. The ions are accelerated towards and react chemically with the materials on the surface of the sample, forming gaseous by-products that are removed by pumping.

In the RIE process, the choice of etchants is very important in achieving a high etching rate. For example, a mixture of Cl\textsubscript{2}/SF\textsubscript{6} gases is normally applied to etch GaN [21]. However, some materials cannot be etched (or have a very low etching rate) either by wet etching or RIE etching. This is because no suitable chemical and gas etchants exist. For these cases only physical etching, known as ion milling or ion beam etching (IBE) can be used. Physical etching can etch all materials including metals, semiconductors, and compounds with several different etching rates. IBE is most widely applied to etch metals which are difficult to etch using chemical reactions [22].

In this work a mesa structure for the MIS LED is required. This required that both the metal and thin insulator layers have to be etched. IBE has been applied to achieve a single-step etching, forming a precise mesa. This was done as an alternative to employing two masks with etching steps for each of metal and insulator layers. A schematic structure of the IBE technique used in this work is shown in Figure 3.8. In this method ions are first generated in a discharge chamber where atoms of a gas (argon) are ionised by the bombardment of energetic electrons (emitted from the cathode filament and collected by the anode). A magnetic field is then used to contain...
the electrons and increase the probability of ionisation. The bombardment between electrons and gas atoms forms a conductive gas or plasma. A negatively biased grid is then applied to accelerate ions passing through a screen grid to form high energetic ion beams. A neutraliser filament (placed after the accelerator grid) is used to introduce electrons for balancing the positively charged ions. The beam current and voltage are independently controlled to obtain the desired ion energy and beam current density. This is also used to control the etching rate. A vacuum of $10^{-7}$ Torr is normally needed to produce a stable ion beam plasma as well as minimise contamination of particles to the substrate during the etching process. A pressure of $10^{-3}$ Torr is the typical vacuum pressure when the gas is flowing to produce the ion beams. The sample substrate is typically mounted or pasted onto a rotating working stage assembly. A uniform etch profile can then be achieved by controlling the angle of incidence of the ion beams [22].

![Diagram of ion beam etching](image)

**Figure 3.8** Schematic illustration of ion beam etching, a purely physical etching.

In this thesis, an Oxford Applied Research IM 150 was used as the IBE equipment. The ion beam energy was controlled and maintained around 30 mA in order to obtain a stable etching rate and a homogeneous profile. Moreover, a time mode was used to control the etching depth.
3.6 Rapid thermal annealing

Rapid thermal annealing (RTA) refers to a semiconductor manufacturing process used to heat wafers to high temperatures (normally 300 °C to 1200 °C) over a short timescale. RTA is widely applied for the purpose of dopant activation and ohmic electrode contacts. In order to efficiently inject current into LEDs an ohmic contact between the electrode and the n-type current spreading layer is important in this work. As a wide band gap material is typically used as the n-type current injection layer for the UV LEDs, n-GaN or n-AlGaN, a Schottky barrier forms when the metal electrode is deposited. Therefore, a shock RTA process is required to make an ohmic contact. At a particular finite temperature, electrons in the metal can be thermally excited to overcome the potential barrier and diffuse into a semiconductor conduction band, thus forming an ohmic interface. A schematic diagram of a typical RTA system is shown in Figure 3.9. In this system, two rows of parallel heating lamps are located in the chamber, and a pyrometer is used to detect the changing temperature of the wafer.

![Diagram of a typical RTA system](image)

**Figure 3.9** Schematic diagram of a typical rapid thermal annealing system.

In this setup the chamber is encompassed by cooled water, in a wall, to ensure the cooling process. More importantly, in order to prevent surface oxidation during the
thermal treatment an injection of nitrogen ($N_2$) is required. In addition, $O_2$ is used for forming transparent contact oxide (TCO).

In this thesis, a SSI Inc. Solaris 150 Rapid Thermal Processing System was used to carry out the RTA process. A range of RTA temperatures and timescales has been tested and reported in the result chapters [23].
3.7 Fabrication procedure for the MIS UVLEDs

A series of semiconductor processes were investigated and applied to the optimised fabrication processes in order to make functional MIS UVLED devices during this PhD project. The optimised processes can be integrated as two process flows (Figure 3.10 for \(n\)-GaN based device, and Figure 3.11 for \(n\)-AlGaN based device). It is clearly evident from the process flows that the fabrication procedure of the MIS UV LEDs is significantly simpler than conventional UV LEDs. This suggests a cost-effective means to fabricate the UV light emitting device.

![Device fabrication process flow for \(n\)-GaN based MIS UV LEDs.](image)

Figure 3.10 Device fabrication process flow for \(n\)-GaN based MIS UV LEDs.
Figure 3.11 Device fabrication process flow for n-AlGaN based MIS UV LEDs.

A brief explanation of the fabrication processes is as follows. First, n-GaN or n-AlGaN epitaxial films were grown on 2-inch sapphire wafers using the MOCVD equipment at the National Centre for III-V Technology at Cambridge University. These wafers were then diced to exactly $1cm^2$ chips, from which some of the chips were used for material
characterisation and some applied in device fabrication. For the \textit{n}-GaN based samples in Figure 3.10, following proper sample cleaning, MOCVD or RF magnetron sputtering was used to deposit a thin AlN insulator layer onto the \textit{n}-GaN film. In order to spread the injection current evenly, a conductive and semi-transparent metal layer was deposited onto the AlN film by a thermal evaporation process. RTA treatment was applied for certain composition of metal for the enhancement of UV light transmission through the thin metal layer on the top. After the RTA process, samples were ready to be etched and form the mesa structure. Mask and photolithography processes (PR coating / Exposure / Development) were then applied to define the mesa etching areas. A physical bombardment-based ion milling dry etching process was used to form the mesa structure for light emitting. This dry etching process was used to etch away both the metal and AlN insulator layers, thus forming the mesa structure with only one etching process. Following proper PR stripping and sample cleaning, the samples were ready to define the position of the contact electrodes. A second mask with proper photolithography (PR coating / Exposure / Development) was applied again and followed by thermal evaporation for thick metal electrodes. After proper PR stripping, the MIS UV LED devices were ready for running electrical and optical tests.

For \textit{n}-AlGaN based samples, due to the high resistivity of AlGaN a very high temperature thermal annealing treatment (around 900 °C) was required to make an ohmic contact between the \textit{n}-AlGaN and the bottom electrode. However, the high temperature thermal annealing process significantly degraded the thin metal film, which means the thin metal layer can only be deposited after the high temperature annealing process. Therefore, the fabrication process was designed as the Figure 3.11, where four masks were applied for the purpose of making mesa structure, bottom electrodes, top thin metal films, and top electrodes respectively. Detailed description and schematic figures were shown in the Figure 3.11.

Figure 3.12 shows the layout of the patterns on masks when the masks were aligned. Different size of MIS-LEDs and MIS-FETs (field effect transistors) were integrated into the same masks. And the monitoring devices, TLM and CV-test patterns, were also applied to the same masks for the measurement of contact resistance and capacitance, which can help optimise the fabrication processes. Therefore, within one sample, many device properties can be obtained.
In the work, detailed electrical and optical results and a comparison between different processing conditions are discussed in the following chapters: Chapter 4 for material characterisations, Chapter 5 for device-level electrical characterisations, Chapter 6 for UV light optical characterisation (Electroluminescence), and Chapter 7 presents the final conclusions.

**Figure 3.12** Pattern layout on 1 cm x 1 cm samples. It presents the alignment of 4 mask layers and the integration of different functional devices into one chip.
3.8 References


Chapter 4

Material characterisation results

Material characterisation of each layer in a metal-insulator-semiconductor (MIS) device has significant importance, with each layer playing a specific role in the integration of a functional UV light-emitting device. First, the material property of group III-Nitride semiconductor materials, $n$-GaN or $n$-AlGaN, needs to be epitaxially crystalline and conductive with a particular doping concentration. In addition, the composition of the semiconductor compound, $n$-Al$_x$Ga$_{1-x}$N, can be controlled and characterised to obtain certain wavelengths of light. Second, the insulator layer needs to exhibit a wide band gap – in order to block electrons for recombination with holes. The insulator layer is expected to have a dielectric property capable of allowing current to tunnel through with certain film thickness, and most importantly, functioning under high electric fields without breaking down. Finally, the top metal layer serves not only as a current spreading layer but also as a layer that light passes through. Therefore, the metal layer needs to be very conductive, with an optimised optical transmission, which is achieved by trying different materials or applying additional processes in order to obtain high light extraction.

In this chapter the results of material characterisation of each layer (semiconductor layer, insulator layer, and the thin-metal layer) has been discussed in separate sections. The final section of this chapter is a conclusion and integration section, which helps to evaluate the MIS structure from a device viewpoint.
4.1 Semiconductor layer in an MIS device

The semiconductor layer in an MIS device serves the function of an electron-hole recombination active region, particularly where direct band gap materials have been applied. In this work $n$-type GaN and AlGaN have been employed as active semiconductor layers and have been prepared using metal-organic chemical vapour deposition (MOCVD). The material characterisation results for $n$-GaN and $n$-AlGaN layers are reported in section 4.1.1 and section 4.1.2.

4.1.1 $n$-type GaN

A 2 $\mu$m silicon-doped $n$-GaN layer grown by MOCVD at 1020 °C on a 2.5 $\mu$m unintentionally doped GaN buffer layer grown under 540 °C and using $c$-oriented sapphire as substrate was used as the semiconducting layer (the thickness was measured from calibrated tools by the supplier, University of Cambridge). The dislocation density of this layer was shown to be as low as $1\times10^8$ cm$^{-2}$. Detailed information of the growth process and its related dislocations have been described previously in an article reported by the sample provider [1].

The carrier concentration of the $n$-GaN semiconductor layer was obtained by the Hall measurement (detailed measurement and analysis methods have been described in section 2.4). The Hall measurement data is presented in Table 4.1, where the carrier concentration of the $n$-GaN is $6.32\times10^{18}$ cm$^{-3}$ with electron mobility of 209 cm$^2$/V·s.

Table 4.1 Hall measurement results for $n$-GaN.

<table>
<thead>
<tr>
<th>Hall Measurement results</th>
<th>Mean value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mu$H</td>
<td>2.09E2</td>
</tr>
<tr>
<td>Carrier type</td>
<td>N</td>
</tr>
<tr>
<td>$n$</td>
<td>6.32E18</td>
</tr>
<tr>
<td>nsheet</td>
<td>1.26E15</td>
</tr>
<tr>
<td>RH</td>
<td>9.88E-1</td>
</tr>
<tr>
<td>RHsheet</td>
<td>4.94E3</td>
</tr>
<tr>
<td>$\rho$</td>
<td>4.72E-3</td>
</tr>
<tr>
<td>psheet</td>
<td>2.36E1</td>
</tr>
<tr>
<td>VH</td>
<td>-1.5809E-2</td>
</tr>
</tbody>
</table>
The surface morphology of the film has been characterised by AFM (Figure 4.1). A root mean square (RMS) roughness of 0.376 nm was obtained. X-ray diffraction (XRD) has been used to determine the crystal structure and evaluate the crystal quality. The XRD diffractogram of the GaN layer grown on sapphire is presented in Figure 4.2.
Lattice parameters can be determined from the omega-2θ scan (Figure 4.2 (a)), where crystal GaN (0002) was shown. Moreover, the omega scan (rocking curve – Figure 4.2(b)) was used as a measure of single crystal quality. A single crystal GaN layer was achieved with full width half maximum (FWHM) of 0.085°. This value was obtained from the omega scan on the central die of a provided 2-inch wafer, where the edge dies might have slightly different values.

Ultraviolet-visible (UV-vis) spectrophotometry has been used to study the optical properties of the GaN layer (Figure 4.3). The measurement was performed from 800 nm to 200 nm. In the long wavelength region, 800 nm to 380 nm, the sample was shown to exhibit high transparency to the incident light with a very high transmission percentage (low absorbance). Moreover, fringes were seen in this region. These fringes can be used to obtain information regarding layer thickness, refractive indices and extinction coefficients [2], [3]. The transmittance curve becomes a straight line, when the energy of the incident light approaches the band gap of the material, leading to zero transmission (100% absorption). An absorbed energy can be obtained from the spectra and the band gap for the GaN can be derived (i.e. \(1240 / 365 = 3.4\) eV).

Figure 4.3 Transmittance curve for the GaN film, with a blue straight line intercepted with the x-axis at a wavelength of approximately 365 nm.
Figure 4.4 Photoluminescence (PL) spectra for the $n$-GaN layer.

Photoluminescence (PL) has also been used to characterise the GaN layer by optical excitation. PL follows the principle; if the energy of the excitation source is greater than the band gap of the measured sample, then the energy is absorbed. This results in excitement of electrons above the conduction band. These electrons then fall and recombine with the holes. The PL spectra (Figure 4.4) shows a clear peak at 365.4 nm with a FWHM value of 12.9 nm. Thus the band gap of the GaN film can be derived. This value is found to be 3.4 eV, which is identical to the band gap obtained by UV-Vis.
4.1.2 $n$-type AlGaN

To investigate high-energy light emission (deep ultra-violet light), wide band gap materials have to be applied. In this work, Al was introduced to produce ternary compound, Al$_x$Ga$_{1-x}$N, whose band gap energies range from 3.4 eV to 6.2 eV, depending on the Al composition.

In this work, UV emission wavelengths of 335 nm (3.7 eV) and 285 nm (4.35 eV) were established as goals by the simple metal-insulator-semiconductor (MIS) structure. The composition of Al can be calculated for a certain band gap of Al$_x$Ga$_{1-x}$N, using empirical data reported by Schubert [4], which is discussed and presented in the previous section in Figure 1.4. The composition $x$ of Al was obtained as 0.14 for 335 nm and 0.42 for 285 nm.

- $n$-Al$_{0.14}$Ga$_{0.86}$N

The $n$-Al$_{0.14}$Ga$_{0.86}$N sample has been prepared using the MOCVD equipment at the University of Bath (However, only limited samples were supplied and so no additional sample was available to perform the hall measurement). The structure of the sample is 1 µm silicon-doped Al$_{0.14}$Ga$_{0.86}$N grown on an AlN buffer layer using sapphire as the substrate. Several material characterisation techniques were used to check the material properties. The XRD measurement data is presented in Figure 4.5, where the lattice parameters can be calculated from the omega-2θ scan in Figure 4.5 (a) and an omega scan (Figure 4.5 (b)) has been used as a measure of single crystal quality. From the omega-20 scan the composition and orientation of the materials were characterised, where AlGaN (0002) and AlN (0002) were obtained on the $c$-oriental sapphire substrate. A full width half maximum (FWHM) value of 0.21° was also obtained for the crystal AlGaN layer using the omega scan (rocking curve). From the sample supplier, the carrier concentration of the silicon-doped Al$_{0.14}$Ga$_{0.86}$N was expected to be around $6 \times 10^{18}$ cm$^{-3}$.
Figure 4.6 shows the surface morphology of the sample, with an RMS roughness around 9.1 nm. This sample was rougher than other samples. But due to the limitation of obtaining samples and the aim of proving concepts, the sample was still applied for further studies by fabricating it to a device. Figure 4.7 shows the photoluminescence property of the film. A clear peak can be seen at a wavelength of 334.7 nm with the FWHM of 18.9 nm. From the PL peak at the wavelength of 334.7 nm, the direct band gap of the compound can be calculated \( E_g = \frac{1240}{\lambda} \) [5]. The band gap value of around 3.7 eV was derived, and therefore the aluminium composition of 14% can be calculated from equation 1.1 on page 7 \( (b = 0.62 \text{ eV}) \). Figure 4.8 shows the light absorption of the film at the wavelength of around 335 nm (measured by UV-Vis), which also supports the band gap of the material and its aluminium composition.

**Figure 4.5** XRD diffractogram of the Al_{0.14}Ga_{0.86}N semiconductor layer grown on the AlN buffer layer on sapphire substrate. (a) omega-20 scan, and (b) Rocking curve for the peak of AlGaN (0002).

**Figure 4.6** AFM image \((5 \times 5 \mu m^2)\) of the \(n\)-Al_{0.14}Ga_{0.86}N layer.
Figure 4.7 Photoluminescence (PL) spectra for the $n$-$\text{Al}_{0.14}\text{Ga}_{0.86}\text{N}$ layer.

Figure 4.8 Transmittance curve for the $\text{Al}_{0.14}\text{Ga}_{0.86}\text{N}$ film, with a blue dash straight line fitted at the curve dropping area.
A wide band gap sample, \(n\text{-Al}_{0.42}\text{Ga}_{0.58}\text{N}\), has been obtained from National Centre for III-V Technologies at the University of Cambridge. It was grown using MOCVD equipment with high epitaxial quality. The thickness of the silicon-doped \(\text{Al}_{0.42}\text{Ga}_{0.58}\text{N}\) was 300 nm. Moreover, it was grown on top of 800 nm-thick AlN buffer layer with a sapphire substrate. Several material characterisation techniques have been applied to investigate the material properties of this film.

The carrier concentration has been obtained by Hall measurement. The data is presented in Table 4.2. The carrier concentration of the \(n\text{-Al}_{0.42}\text{Ga}_{0.58}\text{N}\) sample is shown to be \(6.59 \times 10^{18} \text{ cm}^{-3}\) with electron mobility of 65.3 \(\text{ cm}^2/\text{V} \cdot \text{s}\). The doping concentration and electron mobility is high [6], which gives the film higher conductivity and better current injection for MIS UVLEDs.

<table>
<thead>
<tr>
<th></th>
<th>Mean value</th>
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<tbody>
<tr>
<td>(\mu_H)</td>
<td>Hall mobility (\text{[cm}^2/\text{V} \cdot \text{s]})</td>
</tr>
<tr>
<td>Carrier type</td>
<td>(\text{N})</td>
</tr>
<tr>
<td>(n)</td>
<td>Carrier concentration (\text{[1/cm}^3)</td>
</tr>
<tr>
<td>(n_{\text{sheet}})</td>
<td>Sheet carrier concentration</td>
</tr>
<tr>
<td>(R_H)</td>
<td>Hall coefficient (\text{[cm}^3/\text{C]})</td>
</tr>
<tr>
<td>(R_{\text{Hsheet}})</td>
<td>Sheet Hall coefficient (\text{[cm}^2/\text{C]})</td>
</tr>
<tr>
<td>(\rho)</td>
<td>Resistivity (\Omega \cdot \text{cm})</td>
</tr>
<tr>
<td>(\rho_{\text{sheet}})</td>
<td>Sheet resistivity (\Omega/\text{cm})</td>
</tr>
<tr>
<td>(V_H)</td>
<td>Hall voltage (\text{[V]})</td>
</tr>
</tbody>
</table>

AFM has also been used to check the surface morphology of the film. A representative AFM image is shown in Figure 4.9. It reveals that the surface of the film is fairly flat with a RMS roughness of 2.38 nm. XRD has been used to determine the crystal structure and evaluate the crystalline quality (Figure 4.10). The lattice parameters can
be determined from the omega-2θ scan (Figure 4.10 (a)) and an omega scan (Figure 4.10 (b)) was used as a measure of the single crystal quality. From the omega-2θ scan, sharp AlGaN (0002) peak was obtained, which showed the epitaxial quality of the material and its film orientation along the $c$-axis on the sapphire substrate. The AlN (0002) peak shows the crystal buffer layer between the AlGaN layer and the substrate. From the omega scan data, a single crystal AlGaN layer was obtained with the full width half maximum (FWHM) value of 0.23°. The measurement of light absorption by UV-vis was also performed to confirm the band gap and the aluminium composition of the material. Figure 4.11 shows the data that the light absorption was at the wavelength of around 285 nm, and the band gap of the material was derived as 4.35 eV. The aluminium composition of the AlGaN can also be obtained from Figure 1.4, which was about 42 %.

Figure 4.9 AFM image (5 × 5 μm$^2$) of the $n$-Al$_{0.42}$Ga$_{0.58}$N layer.
Figure 4.10 XRD diffractogram of the Al$_{0.42}$Ga$_{0.58}$N semiconductor layer grown on AlN buffer layer on sapphire substrate. (a) omega-2θ scan, and (b) rocking curve for the peak of AlGaN (0002).

Figure 4.11 Transmittance curve for the Al$_{0.42}$Ga$_{0.58}$N film, with a blue dash straight line fitted at the curve dropping area.
4.2 Insulator layer in the MIS device

The insulator layer of an MIS device plays a key role in current tunnelling. The insulator material needs to be a resistive wide band gap material. In addition, it is important to have crystalline structure for the prevention of current leakage. In this work, the insulator has to be grown on the GaN or AlGaN. Aluminium Nitride (AlN, 6.2 eV) was chosen to be the insulator. This is based on its wide band gap and low lattice mismatch with GaN and AlGaN. In order to compare the properties of AlN grown by different growth techniques, radio frequency (RF) magnetron sputtering and MOCVD grown AlN films have been compared.

4.2.1 RF magnetron sputtered AlN

AlN deposited by sputtering has several advantages. These include simplicity, better parameter control, cheapness, and relatively low deposition temperature [7]. In this work, the reactive sputtering process has been carried out using a radio frequency magnetron sputtering system (Mantis Deposition Ltd) in the thin film laboratory in Imperial College London with a high vacuum chamber, up to $10^{-9}$ mbar. A 99.999% pure aluminium target disc, 3 inch in diameter, has been used as the sputtering target. 99.999% ultra-high purity nitrogen was used as the gas source.

AlN sputtering deposition was first tested and adapted using previously referenced conditions [7]–[9], i.e. nitrogen gas ratio of 40%, RF power of 200 W, and deposition pressure of $4 \times 10^{-3}$ mbar as fixed conditions. The substrate temperature was set at 800°C, 600°C, 400°C, and room temperature (RT) respectively for comparison. XRD results of the sputtered AlN films (under different substrate temperature) grown on GaN on the sapphire substrate are presented in Figure 4.12.
It can be seen in Figure 4.12 that the sputtered AlN film grown at a substrate temperature of 600 °C provides the best c-axis orientation crystal structure. In addition, the film grown under room temperature has no crystalline structure, and the film grown at 400 °C adopts a minimal crystalline structure. AlN films grown at 800 °C displayed (10-11) orientation co-existing with c-axis orientation. The surface morphology of each of the AlN films has been measured and compared (Figure 4.13). The sample grown at a substrate temperature of 600 °C reveals the smoothest surface (compared to other growth temperature) with a RMS roughness of 0.27 nm. This indicates that high substrate temperatures improve the mobility and diffusion of deposited adatoms on the surface of the substrate. However, when the temperature is too high the deposition orientation is affected by the enhanced desorption rate [10].

Several different N\textsubscript{2} gas concentrations have been applied to investigate the effect of the sputtering gas composition. An RF power of 200W, deposition pressure of $4 \times 10^{-3}$ mbar and substrate temperature of 600 °C were maintained. The results of XRD omega scans for AlN films deposited at N\textsubscript{2} compositions of 16%, 23%, 30%, 40%, and 50%, where the FWHM values of (0002) AlN peaks are $1.48^\circ$, $1.21^\circ$, $0.53^\circ$, $0.43^\circ$, and $1.11^\circ$.
respectively, are presented in Figure 4.14 (a) (the thicknesses of these films might be slightly different, which resulted in little difference of intensities). It reveals that the crystalline quality of the sputtered AlN films improved when the N\textsubscript{2} concentrations increased from 16% to 40%, but then worsened from 40% to 50%. This identifies the optimised condition between N\textsubscript{2} composition and the effect of argon bombardment. Thus, the higher the N\textsubscript{2} composition the lower the argon bombardment [11]. A plot of FWHM vs nitrogen flows is shown in Figure 4.14 (b), which shows the relation between the nitrogen flows and FWHM of the AlN films.

**Figure 4.13** AFM images (5 × 5 μm\textsuperscript{2}) of the sputtered AlN films grown by the substrate temperature of (a) RT (RMS = 0.85 nm), (b) 400 °C (RMS = 0.34 nm), (c) 600 °C (RMS = 0.27 nm), and (d) 800 °C (RMS = 0.43 nm).

**Figure 4.14** (a) XRD diffractogram of omega scans for the sputtered AlN films grown under 600 °C at different Nitrogen compositions, and (b) the plot of FWHM vs nitrogen flows.
4.2.2 MOCVD grown AlN

Aluminium nitride grown using MOCVD has been investigated extensively[12], [13]. In this work, an MOCVD grown AlN insulator has been deposited on GaN for comparison with RF sputtering-grown AlN films. These MOCVD grown AlN films were deposited continuously on the GaN in same growth runs, while those sputtering-grown AlN films were deposited separately from the deposition of GaN since the GaN films were all prepared by the MOCVD technique. Theses MOCVD grown AlN films used in this thesis have been processed at the National Centre for III-V Technologies at University of Cambridge using a Thomas Swan 6 x 2” close-coupled showerhead reactor and a substrate temperature of 1030 °C.

XRD has been used to determine the crystal structure of MOCVD grown AlN and evaluate its crystal quality. The XRD diffractogram of the AlN layer grown on n-GaN with sapphire substrate is presented in Figure 4.15. The omega-2θ scan is shown in Figure 4.15(a) and an omega scan used as a measure of single crystal quality is shown in Figure 4.15(b). A full wavelength half maximum (FWHM) value of 0.29° was obtained from the omega scan data. The surface morphology of the film has been characterised by AFM (Figure 4.16). An RMS roughness of 0.72 nm has been obtained and clear crystalline grain boundary observed.

In the literature, it was often reported that gross cracks were found when MOCVD-grown AlN or AlGaN film was deposited on the GaN layer, which resulted from the large lattice mismatch between AlN (or AlGaN) and GaN. The cracks normally started to form when a critical thickness is exceeded [14]. In this thesis, there was no evidence of gross cracks over all the samples (AlN thickness ranging from 3 nm to 20 nm). This means the critical thickness for the gross crack was not exceeded.
Figure 4.15 XRD diffractogram of the AlN insulator film grown on n-GaN layer on sapphire substrate. (a) omega-2θ scan, and (b) rocking curve for the peak of AlN(0002).

Figure 4.16 AFM image (5 × 5 μm$^2$) of the MOCVD-grown AlN layer.
4.3 Semi-transparent metal layer in the MIS device

The thin semi-transparent metal layer on top of a device performs the function of current spreading to the mesa of the MIS device. In addition, it is along the path of the emitting lights. Therefore, conductivity and optical transmission are key properties for this layer.

Gold is routinely used in order to spread the current as it is a good conductor and is resistant to oxidation [15]. In this work, a 5 nm gold film (deposited by the thermal evaporation) has been used as a current spreading layer. However, the poor adhesion of gold to III-Nitride requires an adhesion layer of either Cr, Ni, or Ti [15]–[18]. In this work, a 5nm film of each of the three adhesion materials has been evaluated. These films have been prepared by sputtering. Furthermore, a thermal treated Ni/Au film has also been prepared for comparison. This is to examine the reported increased transparency of the Ni/Au film after a 500 °C thermal treatment [19], [20].

The optical transmission of the adhesion/gold metal films is presented in Figure 4.17. Both the Cr/Au and Ni/Au (RT) films exhibit low transmission properties at 365 nm (Below: 45%). In addition, both Ti/Au and Ni/Au (500 °C) films have a similar transmission percentage (~ 62%) at 365 nm. Most of the films lose transparency at wavelengths below 300 nm. This effect is most prominent for Ti/Au and least for Cr/Au. Although there was no metal balling up issue in those annealing samples, it is worth noting that the issue of metal balling up is normally a concern for the thin metal annealing at high temperatures, which may degrade the metal property and end up with island structures [21], [22].

The resistivity of each of the thin metal films has been measured and the results provided in Table 4.3. All the metal layers are shown to have low resistivity (from $2.12 \times 10^{-7}$ to $5.31 \times 10^{-7} \, \Omega \cdot \text{m}$). This means that the injection current can be spread to the device efficiently. Ni/Au (RT) is shown to exhibit the lowest resistivity, whereas Cr/Au film shows the highest.

Examination of the transmission and resistivity properties of the thin metal films reveals that Ti/Au is a good candidate for use as a semi-transparent metal layer, in
particular for current spreading with its high optical transmission (63% transparency at 365 nm and 2.57 \times 10^{-7} \ \Omega \cdot \text{m} resistivity). In addition, Ti/Au can be easily deposited without the need for a high temperature annealing process. However, in the deep UV region, data reveals that Cr/Au is the best candidate for current spreading compared to other metal composition (45% transparency at 280 nm).

Additionally, a discussion on the effect of continuous growth between the sputtered AlN layer and the thermal-evaporated semi-transparent metal layer in the sputtering/thermal evaporation system was reported in our previous published literature [23].

![Figure 4.17 Transmittance curves for 10 nm semi-transparent metal films.](image-url)
Table 4.3 Resistivity for the semi-transparent metal layers. 5 nm adhesion metal and 5 nm gold.

<table>
<thead>
<tr>
<th>Composition (5nm/5nm)</th>
<th>Resistivity (Ω·m) at 20°C</th>
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<tbody>
<tr>
<td>Cr/Au</td>
<td>5.31 x 10^{-7}</td>
</tr>
<tr>
<td>Ti/Au</td>
<td>2.57 x 10^{-7}</td>
</tr>
<tr>
<td>Ni/Au (RT)</td>
<td>1.94 x 10^{-7}</td>
</tr>
<tr>
<td>Ni/Au (500°C)</td>
<td>2.12 x 10^{-7}</td>
</tr>
</tbody>
</table>
4.4 Conclusion and MIS device structure overview

In this chapter, several material characterisation techniques have been used to analyse the material properties of each layer in a MIS device. The techniques include X-ray diffraction, AFM scanning, UV-Vis optical transmission, Hall measurement, and photoluminescence.

Results indicate that $n$-type semiconductor layers in the MIS device, including $n$-GaN and $n$-AlGaN, have epitaxial crystal structure and a smooth surface. This not only provides a good structure for the growth of a AlN layer on top, but also revealed strong direct band gap properties allowing efficient luminescence. The MOCVD grown AlN insulator layer has been shown to exhibit a higher crystalline structure, however sputtering grown AlN is more cost-effective. The optimised condition for sputtered AlN, in this work, is 40% $N_2$ of $N_2 + Ar$ gas mixture at 600 °C substrate temperature. Several metal combinations have been investigated for use as semi-transparent current spreading layers. The Ti/Au metal composition shows optimal properties including high optical transmission and high conductivity without treatment at high temperatures.

Based on material characterisation, a functional and efficient MIS UV emitter is most likely to be achieved by using optimised materials. Electrical and optical device testing data are presented in Chapter 5 and Chapter 6.


4.5 References


Chapter 5

Electrical analysis results

5.1 Current - voltage characterisation

Current voltage (IV) measurements were used to investigate the current tunnelling behaviour in the MIS devices. The structure of the device was shown in a schematic figure (Figure 5.1). In order to obtain different wavelengths of UV light, both $n$-GaN and $n$-AlGaN were applied as the semiconductor layer in the MIS device. Regarding the $n$-GaN based MIS device, the material characterisation results of $n$-GaN have been reported in section 4.1.1, where a 2 μm $n$-type silicon-doped GaN (carrier concentration: $6.3 \times 10^{18}$ cm$^{-3}$) was grown by MOCVD on a 2.5 μm unintentionally-doped GaN buffer layer with a low dislocation density of $1 \times 10^8$ cm$^{-2}$, grown on a (0001)-oriented sapphire substrate. Regarding the $n$-AlGaN based MIS device, the material characterisation results of $n$-Al$_{0.14}$Ga$_{0.86}$N and $n$-Al$_{0.42}$Ga$_{0.58}$N have been shown in section 4.1.2, where $n$-AlGaN were grown by MOCVD on AlN buffer layer on a $c$-oriented sapphire substrate. The insulator AlN was grown by both the RF sputtering and MOCVD with several thicknesses to study the tunnelling mechanisms under different conditions (section 4.2).

![Figure 5.1](image.png)  
Figure 5.1 Schematic illustration of a nitride-based MIS UV LED structure.
5.1.1 Ohmic contact electrode

In order to obtain efficient current injection into the $n$-type MIS LEDs, an ohmic contact electrode to the $n$-type active layer, $n$-GaN or $n$-AlGaN, is required. Moreover, an ohmic contact can provide better thermal stability, less heat generation, when applying electrical current. Figure 5.2 (a) shows a schematic illustration of the $n$-GaN based MIS UV LED structure, where Cr/Au was used as the contact electrodes for the injection of current to the active layer. According to reference reported earlier [1], non-alloyed Cr/Au metal exhibited a low contact resistance with $n$-GaN because the work function of chromium is close to the vacuum electron affinity of $n$-GaN [2], [3]. Figure 5.2 (b) shows the ohmic IV result for the non-alloyed (as-deposited) Cr/Au electrode to Cr/Au electrode, where the electrode size was 0.19 mm$^2$. For the discussion of alloyed and non-alloyed Cr/Au metal contacts to $n$-GaN, it was reported by Ming-Lun Lee et al [1], where the transmission line method (TLM) measurements were applied to compare the specific contact resistivity between samples with different thermal treatments.

![Figure 5.2](image)

**Figure 5.2** (a) Schematic illustration of a $n$-GaN-based MIS UV LED structure, and (b) the IV curve of an ohmic contact between the Cr/Au electrode and $n$-GaN.
Regarding the $n$-AlGaN based MIS device, the resistivity of $n$-AlGaN is much higher than that of $n$-GaN. Therefore, thermal treatment was normally applied after the deposition of the contact electrode. Figure 5.3 (a) shows a schematic illustration of the $n$-$\text{Al}_{0.14}\text{Ga}_{0.86}$N based MIS UV LED structure, where Ti/Al/Ni/Au was used as the contact electrodes. Typically, the Rapid Thermal Annealing (RTA) with annealed temperature of above 850 °C is used for making an ohmic contact for AlGaN-based materials [4]. The common concept of the mechanism of ohmic contact formation in the structure is: Ti and Al react with nitrogen from the AlGaN during high temperature annealing, with phases of Ti-N and Al-N at the interface. Nitrogen vacancies will then form at the interface, acting as donors and therefore increasing the net carrier concentration in the AlGaN layer and promoting the tunnelling of electrons through the AlGaN barrier[5], [6]. Finally, gold is used to prevent oxidation of the Ti/Al bilayers and the Ni layer acts as a barrier between the Au and the Al to prevent the formation of a highly resistive alloy [7], [8].

Figure 5.3 (b) shows the IV curve results (before and after RTA) of the Ti/Al/Ni/Au (20 / 100 / 30 / 100 nm) contact electrodes to the $n$-$\text{Al}_{0.14}\text{Ga}_{0.86}$N layer. The thermal treatment was 850 °C for 30 s in a N$_2$ ambient in a RTA furnace (SOLARIS 150). It is clear that the IV curve became linear from a resistive Schottky IV curve. Figure 5.4 (b) shows the comparison of IV curves, before and after RTA, for the contact electrodes Ti/Al/Ni/Au (20 / 100 / 30 / 100 nm) deposited on $n$-$\text{Al}_{0.42}\text{Ga}_{0.58}$ layer. The thermal treatment was 900 °C for 30 s in a N$_2$ ambient. It also shows ohmic behaviour after the annealing, however, due to the high resistivity of high-aluminium content of AlGaN, the injection current to $n$-$\text{Al}_{0.42}\text{Ga}_{0.58}$N layer was about 10 times lower than the one to $n$-$\text{Al}_{0.14}\text{Ga}_{0.86}$N layer.
Figure 5.3 (a) Schematic illustration of a $n$-Al$_{0.14}$Ga$_{0.86}$N-based MIS UV LED structure, and (b) the IV curves of contacts between the electrode and $n$-Al$_{0.14}$Ga$_{0.86}$N (Black line: before annealing; red line: after annealing)

Figure 5.4 (a) Schematic illustration of a $n$-Al$_{0.42}$Ga$_{0.58}$N-based MIS UV LED structure, and (b) the IV curves of contacts between the electrode and $n$-Al$_{0.42}$Ga$_{0.58}$N (Black line: before annealing; red line: after annealing)

5.1.2 Thickness optimisation for MIS tunnelling

The thickness of the insulator layer in the MIS device plays a key role for the current tunnelling and the efficient emission of UV light from the MIS device. If the thickness of the insulator is too thin the injection electrons cannot be blocked efficiently at the interface between the insulator and semiconductor, on the other hand, if the thickness
of the insulator is too thick, no tunnelling currents can be obtained, and thus no
generation of holes for recombination with the blocked electrons [9], [10]. Therefore,
AlN insulator with various thicknesses (3nm, 5nm, 10nm and 20nm) was deposited for
n-GaN-based MIS devices in order to find out the optimised insulator thickness.
Additionally, in order to compare the tunnelling behaviour under different AlN growth
techniques, both RF sputtering-grown and MOCVD-grown AlN films were applied in
experiments.

The IV measurement results of the MIS devices with RF sputtering-grown-AlN
insulator of different thicknesses were shown in Figure 5.5. Nearly ohmic behaviour
was observed for the MIS device with a 3 nm thick AlN layer (Figure 5.5a), indicating
that carriers could readily tunnel through the AlN layer. A 2 nm increase in the AlN
layer thickness, to a total of 5 nm, was sufficient for clear diode-like behaviour to
occur (Figure 5.5b). However, there was significant current leakage under reverse bias,
implying that the AlN was still too thin to form barrier suitable for efficient light
emission. In contrast, ideal diode behaviour with negligible reverse bias current
leakage was observed for the MIS LED with a 10 nm AlN layer (Figure 5.5c). The
behaviour of negative differential resistance (NDR) was also found in this condition,
which will be discussed in following sections. Further increase in the AlN layer
thickness to 20 nm resulted in high diode resistance under forward bias, indicating that
the layer has lower forward current flow which will affect the yield of high light
emission intensity (Figure 5.5d). This differs significantly from previous reports on
oxide-based MIS diodes, where, for example, 50 nm HfO$_2$ was found to be the
optimum insulator thickness for ZnO-based MIS diodes [9], [11]. Figure 5.6 shows the
current densities of those sputtering grown AlN insulators of MIS LEDs, where the
leakage current densities of 3 nm and 5 nm thick insulator devices were very large but
the leakage current densities became stable for the MIS LEDs with a 10 nm and 20 nm
AlN layer (around 1×10$^{-8}$ - 1×10$^{-7}$ A/cm$^2$ at zero voltage).

For the MOCVD-grown-AlN based MIS devices with different insulator thicknesses of
3 nm / 5 nm / 10 nm / 20 nm, the IV measurement results are shown as in Figure 5.7.
Due to higher crystalline quality of the MOCVD-grown AlN (characterised data was
shown in chapter 4), the MIS devices have low leakage current densities and show
clear diode behaviour even with very thin AlN insulator thicknesses, 3 nm and 5 nm.
Figure 5.8 shows the current density of those MOCVD-grown-AlN based MIS devices, it shows that all the device have similar leakage current density, which can be as low as close to $1 \times 10^{-8}$ A/cm$^2$.

Comparing the MIS devices of different AlN growth techniques, the MOCVD-grown AlN insulator shows stronger current blocking ability than the sputtering-grown AlN insulator. But when the thickness of sputtered AlN film was bigger than 10 nm, it shows similar leakage current density as the one of MOCVD-grown AlN when the applied voltage was zero. This suggests that AlN film is a thickness-dependent structure, where a crystal structure transformation (change in phase or crystallinity) may occur when the film is over a critical thickness [12], [13]. For the stress of forward bias, under the same insulator thickness the forward current of MOCVD-AlN devices was smaller than the one of devices with sputtering-grown AlN insulator. Interestingly, both sputtering and MOCVD grown AlN with 10 nm thick, the MIS IV curves show clear resonant tunnelling behaviour, which might correlate to the efficiency of light emission [14]–[16].

Figure 5.5 Current-voltage characteristics of MIS LEDs with sputtering-grown AlN insulator thicknesses of (a) 3 nm, (b) 5 nm, (c) 10 nm and (d) 20 nm.
Figure 5.6 Current densities of MIS LEDs with sputtering-grown AlN insulator thicknesses of (a) 3 nm, (b) 5 nm, (c) 10 nm and (d) 20 nm.

Figure 5.7 Current-voltage characteristics of MIS LEDs with MOCVD-grown AlN insulator thicknesses of (a) 3 nm, (b) 5 nm, (c) 10 nm and (d) 20 nm.
Figure 5.8 Current densities of MIS LEDs with MOCVD-grown AlN insulator thicknesses of (a) 3 nm, (b) 5 nm, (c) 10 nm and (d) 20 nm.
5.1.3 IV results and the comparison between devices

Based on the process optimisation of the contact electrode and the thickness optimisation of the AlN insulator, MIS UV LEDs (different semiconductor active layer) were made by the optimised process, where 10 nm thick AlN was used as the insulator for all the devices and additional thermal treatment was applied to make ohmic contact electrode for \( n \)-AlGaN-based MIS UV LEDs.

Figure 5.9 shows the IV curves of those optimised MIS UV LEDs with different semiconductor active layer for different wavelengths of UV light emission, where Figure 5.9 (a) shows the \( n \)-GaN-based MIS UV LEDs, Figure 5.9 (b) shows the \( n \)-Al\(_{0.14}\)Ga\(_{0.86}\)N-based MIS UV LEDs, and Figure 5.9 (c) shows the \( n \)-Al\(_{0.42}\)Ga\(_{0.58}\)N-based MIS UV LEDs. From the IV results, all the IV behaviours show similar trend, which means the tunnelling mechanism of those devices was similar. The clear distinct difference is the intensity of tunnelling current, where the \( n \)-GaN-based device had the highest tunnelling current (100 mA at 5V) and the \( n \)-Al\(_{0.42}\)Ga\(_{0.58}\)N-based device had the least tunnelling current (5 mA at 5V). The other interesting point is that the \( n \)-GaN-based device shows rougher curve on the forward bias (some negative differential resistance points were found). This is because the lattice mismatch between the AlN/GaN layers is bigger than the lattice mismatch between the AlN/AlGaN layers, so the dislocation density is higher in the AlN films of the \( n \)-GaN-based device, which may form defect bands provided for the resonant tunnelling. The speculation was based on the initial study. Further investigation is required to confirm the idea.

\[
\begin{align*}
\text{(a)} & & \text{(b)} & & \text{(c)}
\end{align*}
\]

**Figure 5.9** Current-voltage characteristics of MIS UV LEDs with different semiconductor active layer (a) \( n \)-GaN, (b) \( n \)-Al\(_{0.14}\)Ga\(_{0.86}\)N, and (c) \( n \)-Al\(_{0.42}\)Ga\(_{0.58}\)N
In our published paper, the effect of manufacturing process was also taken into
discussion. The continuous growth of AlN/metal layers (grown in the same run without
breaking the vacuum) was compared with the one of non-continuous growth (the AlN
and metal layers were grown separately). Due to the prevention of possible
contamination and/or oxidation of the AlN surface, the device with the continuous
growth of AlN and metal layers has better performance on current conduction and light
emission. Detailed information can be obtained from the article [17].
5.2 Temperature dependent current voltage characterisation

Temperature-dependent current voltage measurements (TDIV) were performed on the $n$-GaN-based MIS LED with a 10 nm AlN insulator layer, to reveal more about the conduction mechanism of the MIS diode. The TDIV data are given in Figure 5.10, showing three zones[18]. In the low-bias linear ($I \propto V$) zone (I) region, conduction is dominated by temperature-dependent hopping within the AlN layer [19], where the explanation of the mechanism was discussed in the early section 1.6.1.2. In the exponential ($I \propto \exp(V)^{1/2}$) zone (II) region, conduction is dominated by temperature-dependent Schottky or thermionic emission [20], [21], in which thermally excited electrons in the metal layer are able to overcome the energy barrier of the metal-dielectric interface. The linear plot of $\ln(I)$ vs. $V^{1/2}$ was shown in Figure 5.11(a), which fits well with the expression of schottky presented in the early section of 1.6.1.2. In the high-bias zone (III) region, the dispersion between the curves of different temperatures decreased significantly, which shows temperature-independent behaviour in this region. space charge limited conduction (SCLC) occurs, in which $I \propto (V - V_0)^2$, where $V_0$ is a fitting parameter. A linear plot of $\ln(I)$ vs. $\ln(V)$ is shown in Figure 5.11(b). In this region impact ionization processes dominate, in which holes are generated in the AlN insulator layer under high electric field, and are driven into the $n$-GaN active layer, where recombination occurs, resulting in UV light emission [22].

![Figure 5.10 A temperature-dependent log-log plot of current-voltage (I-V) characteristics of the MIS LED.](image-url)
Figure 5.11 (a) Plot $\ln(I)$ vs. $V^{1/2}$ of I-V data measured at zone II bias voltage at 120K. (b) Plot $\ln(I)$ vs. $\ln(V)$ of I-V data measured at zone III bias voltage at 120K, where the slope $\sim 2.3$ of this linear plot implies that $I$ is proportional to $V^2$. 
5.3 Capacitance-voltage measurement

Capacitance-voltage measurement provides a wealth of information about device and material characterisation, which is widely used to determine semiconductor parameters for MIS-based structure, such as capacitance, insulator thickness, doping concentrations, trap states, and so on. Moreover, the dielectric properties of the insulator materials can be obtained through the C-V measurement [23], [24]. In this research, the C-V characterisation of the MIS devices was measured by frequency dependent capacitance method. In order to reduce the current crowding effect, a circular bottom electrode was used to surround a circular mesa with conductive metal on top of AlN insulator [25], seen as Figure 5.12. From this geometrical structure, the current can inject into the MIS structure evenly, which gives the capacitance-voltage (C-V) measurement accurately.

![Figure 5.12](image)

**Figure 5.12** Schematic structure of C-V measurement for MIS device, using a circular electrode surrounding by mesa to spread or inject current evenly.

Electrical characterization of AlN/GaN interfaces was carried out by capacitance-voltage-frequencies (C-V-f) measurements, and the results of C-V-f performed at the frequency range of 100k/1M/5M Hz at room temperature were shown in Figure 5.13. Figure 5.13 (a) shows the results of C-V-f from the MIS device made by sputtering
grown AlN on $n$-GaN (sample a), while the Figure 5.13 (b) shows the results of $C-V-f$ from the MIS device made by MOCVD grown AlN on $n$-GaN (sample b).

The frequency-dependent C-V characteristics shown in Figure 5.13 presented clear deep-depletion behaviour at room temperature from both samples, which is typical behaviour for wide-band-gap semiconductor MIS structure such as SiO$_2$/SiC and AlN/SiC [26], because the generation rate of the minority carriers (holes) is low at room temperature at the depletion mode. This suggests that the UV emission of the MIS device performed at the accumulation mode.

The dispersion between frequencies suggests that sample a (high dispersion) has higher concentration of interface traps than sample b (low dispersion). Also the values of capacitance give different peaks in different frequency and had a tendency to disappear at high frequency 5M. Such behaviour suggested that there were various kinds of interface states with different lifetimes and they can follow well with lower frequencies than high ones [27]. A clear capacitance drop was found with 1M frequency measurement in sample a, which suggested that there was resonant tunnelling behaviour at the drop area [28].

From the capacitance data, the dielectric constant of the insulator layer, AlN can be calculated from the equation, $C = \frac{k\varepsilon_0 A}{t}$, where $A$ is the area of the capacitor, $k$ is the relative dielectric constant of the insulator, $\varepsilon_0$ is the permittivity of free space, and $t$ is the thickness of the insulator layer. Based on the calculation (under 1M Hz frequency), the dielectric constant is 8.0 to sample a and 8.2 to sample b, which is comparable to the references [28], [29].

From Figure 5.14, the substrate doping concentration can also be calculated by the slope of the $1/C^2$ – V plot [26], where both of the samples doping concentration ($n$-doped GaN) were determined to be around $6 \times 10^{18}$ cm$^{-3}$, close to the data obtained from Hall measurement in Chapter 4.
Figure 5.13 Multi-frequency C-V measurements from the MIS devices, metal/AlN/n-GaN, made by (a) sputtering grown AlN, and (b) MOCVD grown AlN.
Figure 5.14 $1/C^2$ characteristics as a function of bias voltage, measured at 1M Hz frequency for both sample a and sample b.
5.4 Resonant tunnelling behaviour in the MIS device

From the IV-curves in section 5.1, a clear negative differential resistance (NDR) was observed, which means the resonant tunnelling processes occurred. Therefore, apart from the tunnelling mechanisms discussed in section 5.2, another tunnelling mechanism called ‘defects assisted tunnelling’ is suggested to explain the NDR behaviour. An I-V plot of a MIS device, metal/AlN/n-GaN with 10-nm-thick AlN, is used to show the clear NDR behaviour, which is shown in Figure 5.15. One Dimensional Poisson, Drift-Diffusion, and Schrodinger Solver (1D-DDCC) developed by Optoelectronic Device Simulation Lab at NTU was used to obtain band diagrams, using literature values and setting the reference zero level to the Fermi energy of the n-GaN. Detailed information and the structure of the solver can be referenced to the open source [30]. Using the 1D-DDCC solver with the input of quantitative data, band diagrams and tunnelling mechanisms under different forward bias conditions are shown in Figure 5.16, where a defect band was expected to occur in the AlN insulating layer and a broad defect-related band from 3.1 eV - 3.75 eV was observed in the PL spectra, which is shown as an inset in Figure 5.16.

Figure 5.15 is associated with Figure 5.16, where the points a, b, and c in Figure 5.15 correspond to the figures (a), (b), and (c) in Figure 5.16 respectively. In Figure 5.16, the grey areas were used to represent the defect band within the band gap of AlN, and the red arrows were used to indicate the flow of electrons. When the MIS device was placed under low forward bias, electrons were able to undergo thermally-assisted tunnelling through the defect band, but initially with a low probability of tunnelling, as shown in Figure 5.16(a) and as seen above point a in Figure 5.15, resulting in a low density of holes tunnelling through from the valence band of the n-GaN. With an increase in applied bias, the increased band bending results in the defect-band state in the AlN and the Fermi level in the metal coinciding in energy with the valence band in the n-GaN (or nearly so), as shown in Figure 5.16(b) and point b in Figure 5.15, to provide a tunnelling pathway through the barrier layer. At a higher applied bias, the defect band starts to go out of the resonance with valence band, causing a drop in flux of valence band holes undergoing resonant tunnelling, just beyond point b in Figure
5.15. At even higher applied biases, electrons in the $n$-GaN conduction band are able to undergo Fowler-Nordheim tunnelling more readily as shown in Figure 5.16(c) and point c in Figure 5.15, resulting in a loss in electron confinement at the interface between the $n$-GaN and the AlN.

The suggested resonant tunnelling mechanisms agree well with the NDR behaviour, supporting with IV and PL data. The resonant tunnelling behaviour may correlate with the enhanced light emission intensity, where chapter 6 will discuss the electroluminescence properties of those MIS LED devices.

![Figure 5.15](image)

**Figure 5.15** Current-voltage characteristics of MIS device with 10 nm-thick AlN insulator, which contained metal and AlN films which were sputtered in succession without breaking vacuum. The labels a – c refer to different regions of diode behaviour.
Figure 5.16 Energy band diagrams, including schematic tunnelling mechanisms, under different forward-bias conditions: (a) at low forward bias, (b) medium-high forward bias and (c) high forward bias. $E_F$ refers to the Fermi energy of the Au metal contact layer, $E_c$ corresponds to the conduction band and $E_v$ to the valence band. Diagrams (a) – (c) correspond to the regions a – c in Figure 5.15. A PL spectrum of AlN is used to prove the defect band in the film (inset).
5.5 Conclusion

In this chapter, electrical characterisations including current-voltage measurement, temperature-dependent current voltage measurement, and capacitance-voltage-frequency measurement were used to characterise and analyse the electrical performance of the MIS devices.

In order to inject current efficiently to the MIS device, an ohmic contact between the electrode and semiconductor is of importance. The $n$-GaN material was found to perform ohmic contact with the metal of Cr/Au at room temperature without any thermal annealing. Regarding $n$-$\text{Al}_x\text{Ga}_{1-x}$N based material, due to its wider band gap and higher resistivity, Ti/Al/Ni/Au multi-layers were used as the contact electrode and rapid thermal annealing process was required to form the ohmic interface. The data showed that the higher the Al content the higher the annealing temperatures, where 850 °C 30 s RTA was used for $n$-$\text{Al}_{0.14}\text{Ga}_{0.86}$N material and 900 °C 30 s was used for $n$-$\text{Al}_{0.42}\text{Ga}_{0.58}$N material.

Thickness of the AlN insulator layer in MIS device plays a key role for the tunnelling processes. From the experimental results, 10 nm AlN thickness was suggested to be the optimised thickness for the MIS device with the leakage current at zero voltage, which was as low as $1 \times 10^{-8}$ A/cm$^2$. Temperature-dependent current voltage measurement was also used to characterise the tunnelling mechanisms, which suggested that three tunnelling steps were involved, which were hopping, thermionic emission, and space charge limited conduction.

Capacitance-voltage measurement was used to characterise the dielectric properties of the AlN insulator and the traps in the interface. Based on the calculation of the capacitance, the AlN dielectric contact was determined to be around 8, which is comparable to most of references. Deep depletion was found, which suggested that the light emission (electron-hole recombination) performed at the accumulation mode with forward bias. It also suggested that sputtered-AlN-based MIS device has higher traps than the ones coming from MOCVD-grown-AlN-based MIS device.
A defect band in the AlN barrier layer was suggested as origin of the quantum states via which the resonant tunnelling occurs. A series of energy band diagrams were used to support the mechanisms of defect-band assisted resonant tunnelling. A further device characterisation by electroluminescence will be reported in the following chapter, Chapter 6.
5.6 References


Chapter 6

Ultra-violet light emission results

6.1 Electroluminescence from GaN-based MIS device

Electroluminescence measurement (EL) was used to characterise the UV light emission by applying voltages to the MIS device and measuring emission through an UV spectrometer, which is one of the most important measurements to check the functionality of LEDs. In this research, firstly GaN-based MIS devices (TiAu/AlN/n-GaN) were fabricated through the processes described in section 3.7 of Chapter 3. MIS devices made by both sputtering-grown and MOCVD-grown AlN were analysed. Figure 6.1 shows the EL results from the MIS devices with different insulator (AlN) thicknesses, where 3 nm/ 5 nm/ 10 nm/ 20 nm were compared and grown by both RF sputtering (Figure 6.1 a) and MOCVD (Figure 6.1 b) techniques. The devices with different AlN growth techniques had similar performance in terms of the thicknesses of AlN insulator. It clearly shows no emission was observed from the MIS device with a 3 nm AlN layer, consistent with its linear I-V behaviour shown in Chapter 5. In contrast, significant emission was produced from the MIS LEDs with 5 nm and 10 nm AlN layers, with near band edge emission peaks occurring at around 365 nm. Under a forward injection current of 80 mA, much weaker emission was obtained from the MIS LED with a 20 nm AlN layer. In the absence of any p-type material in the MIS structure, the most likely explanation for the supply of holes needed for EL to occur is direct tunnelling of valence band electrons in the n-GaN through AlN barrier to the Au/Cr contact. The reduced emission from the structure with a 20 nm AlN layer provides evidence of this. Moreover, the emission peaks were red-shifted and broadened with increasing injection current. A similar observation has been attributed to local band bending effects at the interface [1]. Therefore, the MIS device with 10 nm thick AlN, either by sputtering growth or MOCVD growth, was the optimal
structure for the most efficient emission. To determine the optimal AlN growth technique for the MIS LEDs, it requires further investigation to control the uncertainties, for example, the sputtered AlN was a non-continuous process after the MOCVD-grown GaN, whereas the MOCVD-AlN was grown continuously on GaN.

**Figure 6.1** EL measurement from the $n$-GaN-based MIS device, metal/AlN/$n$-GaN, fabricated by (a) RF sputtering grown AlN, and (b) MOCVD grown AlN
The MIS devices with 10 nm thick AlN insulator were taken into further investigation by treating with a range of current injections to see the change of light emissions. The EL spectra as a function of injection current for those devices are given in Figure 6.2, where Figure 6.2 (a) shows the data from the device with sputtering grown AlN and Figure 6.2 (b) shows the data from the device with MOCVD grown AlN.

The EL spectra indicate that both of the MIS devices emitted near-band-edge (NBE) UV light (occurred at around 364 nm), which is the same as the PL peak of n-GaN reported in chapter 4. This suggested that the electron-hole recombination of EL was occurring in the semiconductor layer of the MIS devices. The maximum EL emission peak for the sputtered-AlN-based MIS device occurred at a current injection of 80 mA (3.25 V) with a FWHM of 11 ± 1 nm, whereas the EL peak for the MOCVD-AlN-based MIS device occurred at the one of 40 mA (3.1 V) with a FWHM of 12 ± 1 nm. However, emission drop was observed on all devices when applying higher current injection, which means the MIS device are suitable for working within a specific driving voltage. The cause of the behaviour has been discussed a lot in many articles [2], [3], where many speculations were proposed, including dislocations, carrier delocalisation, Auger recombination, poor hole-injection, and electron leakage from the active region. And in conventional LEDs it was widely accepted that the Auger recombination was suggested to be the main cause [4], although the comment is still under discussion. Regarding the efficiency drop of our MIS device, it is possible to exclude Joule heating as a significant influence on device performance: the devices were processed and measured on-wafer, the wafer was clamped to a thermal sink during measurements (both help considerably with local thermal conduction), while a local surface thermocouple probe indicated no temperature changes at the device. Also, the forward resistance (assessed from the I-V curves in Chapter 5) is significantly lower than any commercial LED for which data is available. Similarly, no differences were observed between the I-V curves obtained initially at the start of measurements, and those obtained later after the device had been running at high currents for some time, which further indicates minimal contribution from Joule heating. We attribute this performance stability, in part, to the absence of a resistive p-contact and p-type layer, which should minimise contact resistance and improve current spreading [5]–[7].
An interesting behaviour observed is that a second EL peak (around 375 nm) was formed when applying higher current injection, especially for the MIS device with MOCVD grown AlN. This red-shifted emission peaks were attributed to local band bending effects at the interface [1], because of which this device has potential to be used as emission wavelength tuned device.

**Figure 6.2** EL spectra for MIS LEDs with 10 nm AlN, which was deposited by (a) RF sputtering, and (b) MOCVD.
The results suggested that near-band-edge light emission from the simple GaN-based MIS devices were achieved (the optimal thickness of AlN was 10 nm), regardless of whether the AlN layer was grown by sputtering or MOCVD techniques. From the similar peak emission intensity, there is no clear conclusion of which growth technique of AlN was the best for the MIS LEDs. To confirm this, a further investigation is required, which can also be part of the key future works.
6.2 Electroluminescence from AlGaN-based MIS device

Due to the difficulties of $p$-doping process for AlGaN, the availability of short-wavelength UV light emission is very hard to achieve from $p$-$n$ junction based LED [8]–[12]. Therefore, a non $p$-doped AlGaN-based MIS device was introduced, where the fabrication processes for the devices were described in chapter 3. In order to demonstrate the capability of AlGaN-based UV emission from this simple MIS structure, metal/AlN/$n$-AlGaN, the device was also characterised by electroluminescence measurements for shorter UV light emission. The EL spectrum is shown in Figure 6.3, where a 335 nm emission was achieved with FWHM of around 18 ± 1 nm, basing on the $n$-type Al$_{0.14}$Ga$_{0.86}$N. This 335 nm EL peak is very close to the PL peak from the material of $n$-Al$_{0.14}$Ga$_{0.86}$N, which suggested a NBE emission was obtained. The EL peak in Figure 6.3 shows better FWHM than the one reported from Wang et al [13], where a 340 nm UV light emission with FWHM of 30 nm was achieved from the $p$-$n$ junction based device using Al$_{0.12}$Ga$_{0.88}$N as active material. This suggests that the MIS-based UV emitter can potentially have good quantum confinement for a narrow EL emission peak. Furthermore, this provides an easier approach to achieve deeper UV light emission by the increase of aluminium content in the semiconductor layer of the MIS structure.

![Figure 6.3 EL measurement from the $n$-AlGaN-based MIS device, metal/AlN/$n$-AlGaN.](image-url)
Regarding the emission from the deep UV LED sample, \( n\text{-Al}_{0.42}\text{Ga}_{0.58}\text{N} \)-based MIS device, was not achieved yet. Due to high resistivity of the high-Al content AlGaN, lower current was injected into the device under the same voltage (20 times lower than the current of \( n\text{-GaN} \) sample from Figure 5.9), and therefore little electrons were provided for recombination. The possible solutions will be the increase of conductivity for the high Al-content AlGaN layer by higher doping concentration, or the change of device layer structure to confine more electrons for recombination. Another potential approach to improve the resistance is to make the AlGaN layer thicker (These approaches will be part of the future work).
6.3 Making the MIS UVLED as a product

Finally, the MIS UV emitter was fabricated as a practical LED product through packaging processes. Regarding the packaging processes, the wafer was firstly mounted on a dicing tape which has a sticky backing that holds the wafer on a metal frame. (The dicing tape is normally UV curable tape, which makes the diced chips easier pick-up after reducing adhesion by UV irradiation.) Then the taped wafer was cut by a dicing saw machine, DISCO DAD 3230, to separate the LED device, followed by UV irradiation. The diced LED devices were then picked and placed onto silver TO-Cans, where two pins are isolated. Gold wire-bonding process was then applied to bond the gold wires from the positive and negative electrode pads to the two pins respectively. Therefore, with the TO-Can packaging structure, current can be injected from two pins into the MIS device, from which the electrodes on the LED device can be free of physical crack caused from probing. Figure 6.4 shows the top-view of a processed wafer and the packaging processes for making it as a practical LED product (the images are as shown at the bottom in Figure)

From the demonstration of LED products, it shows the over-all study of the PhD project, including thin-film growth, material characterisation, device fabrication, electrical characterisation, opto-electrical characterisation, and packaging. This complete study makes the PhD research very close to the market in industry. Especially, through process optimisation, the fabrication processes of making MIS UV LEDs products were much simpler than the one of making conventional p-n junction UV LEDs.

The light output efficiency of the MIS UV LED products was expected to be lower than the efficiency of current commercial p-n junction based UV LEDs, although there was no comparison of quantitative data. Nevertheless, the MIS UV LED device still has significant advantages from its simple structure and cost-effective fabrication processes. Through the PhD study, the concept of MIS UV LEDs was proved. With more future works (suggested in Chapter 7), the MIS UV LEDs are believed to be very competitive in the future.
Figure 6.4 Packaging processes, from wafer to chip. A functional LED device was bonded to a TO-Can with encapsulation, which is demonstrated at the bottom by the pictures.
6.4 Conclusion

By the measurement of electroluminescence, a strong near-band-edge emission of 365 nm was obtained from a simple Au/AlN/\textit{n-GaN} resonant tunnelling MIS LED. Different insulator thicknesses were applied into the MIS device for comparison. The optimised thickness of the AlN insulating layer was found to be 10 nm, regardless of whether the AlN layer was grown by sputtering or MOCVD techniques. More importantly, a region of NDR in the I-V characteristic was observed, indicating free holes in the \textit{n-GaN} valence band are most likely generated by resonant tunnelling. The observed decrease in emitted intensity at high injection currents is attributed to a reduction in the density of conduction band electrons in the \textit{n-GaN} via Fowler-Nordheim tunnelling (electrons tunnelled through a triangle potential barrier of AlN insulator caused by high electric field), which was proved by simulated band diagrams. A defect band in the AlN barrier layer was suggested as origin of the quantum states via which the resonant tunnelling occurs.

Furthermore, by introducing aluminium into the semiconductor layer of MIS device (replaced \textit{n-GaN} by \textit{n-AlGaN}), deeper UV wavelength can be obtained because of the larger band-gap active material. In this research, a 335 nm emission was achieved by the \textit{n-AlGaN} based MIS structure with 14\% Aluminium content. This suggested that the UV emission wavelength is tuneable by the adjustment of Aluminium composition in the \textit{n-AlGaN} layer, which means deep UV emission is achievable with the simple MIS structure. Figure 6.5 shows the transition of UV emission, from 365 nm to 335 nm. Deeper UV emission, UVC region, shall potentially be obtained by using 45\%-50\% aluminium content as the \textit{n-AlGaN} active layer under the simple MIS structure.

This proof-of-principle work establishes that UV light can be emitted efficiently from simple nitride-based MIS structure, without the use of \textit{p}-doped material. Future work will be focused on AlGaN-based MIS LEDs for efficient emission in the deep UV for germicidal applications, including the use of electron or hole confinement structures to increase the spatial overlap between electron and hole wavefunctions and hence improve device efficiency.
Figure 6.5 Normalised electroluminescence spectra from the MIS devices, including both the $n$-GaN and $n$-AlGaN based materials. Potentially, if the aluminium content, $x$, goes higher, the UV emission peak can be shifted to even deeper UV range, based on the simple MIS structure.
6.5 References


Chapter 7

Conclusions and future work

7.1 Conclusion

Strong room-temperature ultraviolet (UV) electroluminescence at both 365 nm and 335 nm has been demonstrated from simple Au/AlN/n-GaN and Au/AlN/n-AlGaN metal-insulator-semiconductor (MIS) light emitting diodes (LEDs), which do not contain p-doped material and can be working under low threshold voltage. Current-voltage (IV) and electroluminescence (EL) data indicate that an AlN insulating layer thickness of 10 nm results in optimised diode behaviour and maximum UV emission: at lower thicknesses carriers tunnel easily through the barrier, whereas at greater thicknesses the forward resistivity is excessively high. Additionally, the MIS device showed clear resonant tunnelling characteristics, where a defect-assisted mechanism was introduced to explain the resonance behaviour.

In order to make the MIS device functionalised, materials were optimised layer by layer and nano-fabrication processes were also adjusted. The active semiconductor layer in MIS device was prepared by the MOCVD technique using sapphire as substrates. The epitaxial $n$-GaN film (with doping concentration of $6.3 \times 10^{18}$ cm$^{-3}$) was deposited on an $i$-GaN layer, whereas the epitaxial $n$-AlGaN film (with doping concentration of $6.0 \times 10^{18}$ cm$^{-3}$) was deposited on an AlN buffer layer. Followed by the semiconductor layer, AlN was deposited as an insulator layer to confine electrons. Both sputtering and MOCVD were used to grow the AlN films with optimised deposition conditions, where the MOCVD-grown AlN film was deposited under the temperature of 1030 °C and the RF magnetron sputtered AlN film was grown under 600 °C. The thickness of the insulator layer plays a key role for current tunnelling of the MIS device, and after electrical characterisation an optimised AlN thickness of 10
nm was determined. A very thin semi-transparent metal film was deposited on the mesa for the purpose of current spreading, where a 10 nm Ti/Au layer was applied with high conductivity and low light absorption. To inject currents into the MIS device ohmic probing contacts were needed, where a non-annealed Cr/Au layer was used to be the contact electrode for $n$-GaN and a combination of Ti/Al/Ni/Au multi-layers with 850 °C RTA annealing were used as an ohmic electrode to $n$-AlGaN.

Material characterisation techniques were used to investigate the properties of materials in the MIS device, where both the $n$-GaN and $n$-AlGaN films showed epitaxial structures and smooth surfaces. Clear PL peaks were obtained at 365 nm and 335 nm for the $n$-GaN and $n$-AlGaN films respectively. Both RF sputtering grown AlN and MOCVD grown AlN were compared, and they all showed epitaxial growth once the deposition processes were optimised. Through the design of photo masks, process monitoring devices can be placed into the same wafer, for example the TLM measurement devices and the CV measurement devices were used to obtain the electrode contact resistance and the dielectric constant of AlN film respectively (the overview of wafer patterns were shown in Figure 6.4), where a specific contact resistance ($\rho_c$) of approximately $1.9 \times 10^{-5} \Omega \text{ cm}^2$ and a dielectric constant of around 8.0 for the AlN insulator were obtained.

To understand the tunnelling mechanism of the MIS device, through I-V characterisation of the MIS devices, a region of negative differential resistance (NDR) characteristic of resonant tunnelling behaviour occurs in the I-V curve, which is stable over time and reproducible over repeated measurements. A defect-band assisted resonant tunnelling was introduced to support the behaviour. When the MIS device was placed under low forward bias, electrons were able to undergo thermally-assisted tunnelling through the defect band, but initially with a low probability of tunnelling, resulting in a low density of holes in the valence band of the $n$-GaN. With an increase in applied bias, the increased band bending results in the defect-band state in the AlN and the Fermi level in the metal coinciding in energy with the valence band in the $n$-GaN (or nearly so) to provide a tunnelling pathway for valence band electrons through the barrier layer. This was how the NDR behaviour occurred. At a higher applied bias,
the defect band starts to go out of the resonance with valence band, causing a drop in the creation of valence band and holes via valence band electrons undergoing resonant tunnelling to the metal. At higher applied biases, electrons in the $n$-GaN conduction band are able to undergo direct Fowler-Nordheim tunnelling more readily, resulting in a loss in electron confinement at the interface between the semiconductor layer and the insulator layer.

Therefore, with the control of LED driving voltages, the MIS UV emitter can emit efficient UV light under relatively low threshold voltage. A near-band-edge (NBE) electroluminescent (EL) emission at 365 nm was obtained for the $n$-GaN based MIS device, whereas the $n$-Al$_{0.14}$Ga$_{0.86}$N based MIS device showed its NBE electroluminescent emission at around 335 nm. The research results suggested that the NBE UV emissions can be achieved by the simple non $p$-doped MIS UV LEDs and most importantly the deeper UV emission wavelength can also be achieved and tuned by adding extra aluminium content into the active layer (semiconductor layer) of the MIS device. These research samples were packaged onto a LED TO-Can for the use of prototype demonstration. We believed that through further process optimisations with suitable package techniques the MIS UV LEDs have great potential to become commercially competitive products in the market.
7.2 Future work

In order to enhance the UV light emission intensity in the MIS device, hole blocking layers need to be inserted close to the interface between the active layer and the insulator layer [1], [2]. When the n-type MIS UV LEDs were under forward bias, the electrons can easily be blocked by the AlN insulator layer, whereas the holes can not be confined effectively. Therefore, with the insertion of hole blocking layers, more holes can be confined for the recombination with confined electrons. Through the references, the hole confinement layer can be achieved by the application of band gap engineering [3].

To reduce the light absorption of current spreading layer, several materials were studied and reported [4]–[6]. Among those references, graphene has drawn the most attention due to its high conductivity and low absorption (in both the visible wavelengths and the UV wavelengths) [7], where Figure 7.1 shows transmission spectra in comparison to indium tin oxide (ITO) and fluorine doped tin oxide (FTO) [8]. Therefore, for a future study, graphene could be used to replace the current semi-transparent thin metal of the MIS UV LEDs to reduce the light absorption in 365 nm, 335 nm, or even shorter wavelengths.

![Figure 7.1 Transmittance UV–vis spectra of graphene (black line), ITO (grey dashed line) and FTO (grey solid line).](image)
Without the replacement of current spreading materials, light extraction can still be improved by using the metal as a current spreading layer, where the metal needs to be thick and highly reflective, such as aluminium [9]. With this application, the upward light can be redirected to the backward direction and can be combined with the original backward emission light to higher light extraction through the substrate (A schematic figure is shown in Figure 7.2). Patterned substrates can also be applied in this backside emission device to enhance the light extraction even further [10]. With the application of thick metal, the current can be spread to the LED mesa easily and efficiently, which is another benefit from this application.

Figure 7.2 Using highly reflective metal to direct the emission light to its backside, where the substrate is patterned.
7.3 References


Appendix A

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