

High efficiency ultrasound-powered micro-LEDs for optogenetic applications

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List of Symbols

R_{sh}	Sheet resistance
ρ_c	Specific Contact Resistivity
L_s	Current Spreading Length
R_{pp}	Point-to-Point Resistance
λ	Wavelength
η	Ideality factor
r_o	Outer diameter of c-TLM
r_i	Inner diameter of c-TLM
P_{out}	Output Optical Power
P_{in}	Internal Optical Power
h	Planck's Constant
ν	Frequency
E_c	Conduction band
E_v	Valance band
I	Current
V	Voltage
eV	Electron Volt
n	Carrier Concentration
V_{peak}	Bandgap energy corresponding to peak wavelength
V_{junc}	Junction Voltage
V_{appl}	Applied Voltage
T_c	Carrier Temperature
ϕ_B	Work Function
τ_o	Channel opening rate
τ_c	Channel closing rate
k	Boltzmann's constant

List of Acronyms

AA	After Annealing
ACF	Anisotropic Conducting Film
ARC	Anti-Reflection Coating
BA	Before Annealing
BOE	Buffered Oxide
CRT	Cathode Ray Tube
CSF	Cerebrospinal Fluid
ChR	Channelrhodopsin
CSS	Common Sapphire Substrate
CMOS	Complementary Metal Oxide Semiconductor
DI	Deionized Water
DBR	Distributed Bragg Reflector
DH	Double Heterostructure
DSP	Double Side Polished
DDS	Drug Delivery System
EL	Electroluminescence
ESD	Electro-Static Discharge
ELISA	Enzyme-Linked Immunosorbent Assay
EQE	External Quantum Efficiency
EE	Extraction Efficiency
FWHM	Full Width Half Maximum
HVPE	Hydride Vapour Phase Epitaxy
ICP	Inductive Coupled Plasma
IQE	Internal Quantum Efficiency
LED	Light Emitting Diode
LIV	Light-Current-Voltage
LPE	Liquid Phase Epitaxy
LEEBI	Low Energy Electron Beam Irradiation
MC	Merocyanine

MOCVD	Metal Organic Chemical Vapour Deposition
MIS	Metal-Insulator Semiconductor
μ LED	micro-Light Emitting Diode
MBE	Molecular Beam Epitaxy
MQW	Multiple Quantum Well
NFC	Near Field Communication
NIR	Near Infrared
NA	Numerical Aperture
ODR	Omni-Directional Reflector
OCT	Optical Coherence Tomography
PD	Parkinson's Disease
PSS	Patterned Sapphire Substrate
PL	Photoluminescence
PZT	Piezo Electric Transducer
PECVD	Plasma Enhanced Chemical Vapour Deposition
PDMS	polydimethylsiloxane
PCE	Power Conversion Efficiency
QCSE	Quantum Confined Stark Effect
QW	Quantum Well
RF	Radio Frequency
RTA	Rapid Thermal Annealing
RGB	Red Green Blue
RI	Refractive Index
SRH	Shockley-Reed-Hall
SQW	Single Quantum Well
SP	Spiropyran
THF	Tetrahydrofuran
TMAH	Tetramethylammonium hydroxide
TIR	Total Internal Reflection
TP	Transfer Print
TLM	Transmission Line Measurement
UV	Ultraviolet
VPE	Vapour Phase Epitaxy
VLC	Visible Light Communication
WPE	Wall-Plug Efficiency

List of Publications

Conference talks

1. **T.Mondal**, J.Browne, "The smallest ($0.33mm^3$) ultrasound-powered fully-implantable μ LED for activating light sensitive channelrhodopsin" in UK Nitrides Consortium, 2022.

Conference posters

1. **T. Mondal**, K. Laursen, S. Hosseini, A. Rashidi, F. Moradi, and B. Corbett. "Realization of high efficiency ultrasound-powered micro-LEDs for optogenetics." in Integrated Photonics Platforms: Fundamental Research, Manufacturing and Applications, vol. 11364, pp. 113641I. International Society for Optics and Photonics, 2020.
2. **T. Mondal**, K. Laursen, A. Rashidi, S. Hosseini, J. Brown, Z. Li, Z. Shaban, F. Moradi, and B. Corbett, "Integration of ultrasound-powered implantable neural DUSTs for optogenetics and its path to miniaturization", presented at the Photonics Ireland, Dublin, Ireland, 14th-16th June 2021.

Co-authored in peer-reviewed journal articles

1. K. Laursen, A. Rashidi, S. Hosseini, **T. Mondal**, B. Corbett and F. Moradi, "*Ultrasonically Powered Compact Implantable Dust for Optogenetics*", in IEEE Transactions on Biomedical Circuits and Systems, vol. 14, no. 3, pp. 583-594, June 2020.
2. S. Hosseini, K. Laursen, A. Rashidi, **T. Mondal**, B. Corbett and F. Moradi, "*S-MRUT: Secteded-Multiring Ultrasonic Transducer for Selective Powering of Brain Implants*", in IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control, vol. 68, no. 1, pp. 191–200, 2020.
3. A. Rashidi, M. Zamani, **T. Mondal**, S. Hosseini, K. Laursen, B. Corbett and F. Moradi. "Ultrasonically Powered and Controlled Microsystem for Dual-Wavelength Optogenetics

with a Multi-Load Regulation Scheme”, in IEEE Solid-State Circuits Letters, vol. 6, pp. 33-36, 2023.

4. Z. Shaban, Z. Li, B. Roycroft, M. Saei, **T. Mondal**, and B. Corbett, *”Transfer Printing of Roughened GaN-Based Light-Emitting Diodes into Reflective Trenches for Visible Light Communication”*, in Advanced Photonics Research, p.2100312, March 2022.
5. K. Laursen, M. Zamani, Y. Rezaeiyan, S. Hosseini, **T. Mondal**, B. Corbett, A. M. Ouagazzal, M. Amalric and F. Moradi. *”An Ultrasonically-Powered System for 1.06mm³ Implantable Optogenetics and Drug Delivery Dust”*, in IEEE Transactions on Circuits and Systems II: Express Briefs, June 2023.

First author publications

1. **T. Mondal**, k. Laursen, F. Kloosterman, M. Alm, S. Hosseini, Z. Shaban, Z. Li, F. Moradi, and B. Corbett. *”Implant compatible on-demand drug delivery system integrated with ultrasound-powered μ LED with a volume of 0.33 mm³”*, **writing in progress**.

Declaration

I, Tanmay Mondal hereby declare that, unless otherwise stated, this work is my own, and that it has not been submitted for another degree, either at University College Cork or elsewhere.


Tanmay Mondal

Abstract

Gallium nitride (*GaN*) light emitting diodes (LEDs) play the most important role in visible light applications, and more than 87% LEDs are used in indoor/outdoor lighting, automotive lighting, etc. Recent advancements in neuroscience and technology opened a new opportunity for LEDs to be used for optogenetic applications. Optogenetics is an emerging field that combines genetic engineering and light for precise control or monitoring of biological functions of cells, neurons, or organs, and μ LEDs (size $\leq 100 \mu m$) are considered the best candidate as a light source for in-vivo optogenetic applications.

This work focuses on realizing a wireless ultrasound (US) powered implant-compatible device (also called neural DUSTs) enabling in-vivo electrophysiology, optogenetics, and ultra-localized drug delivery in freely moving animals. The device requires a minimum of three components: a PZT (Lead Zirconate Titanate piezoelectric material) cube to harvest the US energy, a rectifier chip for AC-DC conversion, and a μ LED to deliver the optical power. The μ LED should be capable of delivering a minimum of $5 mW/mm^2$ optical power at $\sim 1 mA$ for activating light-sensitive proteins (Channelrhodopsin-2) while the temperature rise is $< 1 ^\circ C$, have an operating voltage below $3.3 V$ (limit of rectifier chip) and custom-made to match physical layout with rectifier. This requires the need for a highly efficient μ LED. It is fortuitous that the optimum wavelength of the cation-selective membrane channel Channelrhodopsin-2 is around $470 nm$ where *GaN* material has the highest efficiency. Indium Gallium Nitride (*InGaN*) quantum well-based efficient blue ($\lambda_{peak} = 483 nm$) and UV ($\lambda_{peak} = 371 nm$) μ LEDs grown on patterned sapphire substrate (PSS) were specifically designed and fabricated with a low turn-on voltage of $2.3 V$ (blue) and $3.1 V$ (UV) which was lower than the corresponding band-gap voltage. A high wall-plug efficiency of 40.7% and 25.4% was measured from the $100 \mu m$ mesa blue and UV μ LEDs, respectively. Investigation with *Ag*-based p-contact showed a further 20% improvement in extraction efficiency. A localized drug delivery system (DDS) based on photochromic spiropyran (SP) was characterized and developed, which activates upon exposure with $370 nm$ UV. The activation of DDS by ultrasound-powered, and the drug release by electrically powered UV μ LED were successfully demonstrated. A new dual-colour μ LEDs (combinations of red, blue, and UV) on a single chip was designed and fabricated targeting dual-colour optogenetic applications. The characterization results presented here highlight challenges, issues resolved, and further improvement scope. Finally, two US-powered implant-compatible DUSTs were developed by integrating a PZT, rectifier chip, and μ LED with a total volume of $2.85 mm^3$ (basic-DUST) and $0.33 mm^3$ (compact-DUST) respectively and demonstrated. To the best of our knowledge, the compact-DUST demo is the smallest implant-compatible US-powered DUST with integrated μ LED.

Future work should be done to achieve more efficient μ LEDs, integrate DUSTs with dual colour μ LEDs and develop a wafer-scale integration process.

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Chapter 1

Introduction

In recent years, thanks to the efforts of many research groups, light-emitting diode (LED) technology has made remarkable progress. LEDs are semiconductor devices that use the recombination of carriers (electrons and holes) to generate light, unlike traditional incandescent lamps, which use heat to generate light. Therefore, LEDs offer higher electrical-to-optical power conversion efficiency compared to incandescent light sources, and they can be made physically smaller than other light sources, making them suitable for applications such as display or medical/surgical systems. As LEDs are solid-state light sources, they offer significantly longer lifetimes, generate less heat and are more robust than conventional ones. The emission wavelength/colour of the LEDs can be varied by changing or modifying different material compositions. For example, the wavelength emitting from an indium gallium nitride (*InGaN*)/gallium nitride (*GaN*) LED can be varied from ultraviolet (UV) to green by increasing the indium (*In*) doping level. *GaN*-based LEDs have demonstrated outstanding potential due to their higher efficiency, higher modulation speed, robustness during atmospheric changes or cold conditions, longer operating lifetime, linear characteristics under continuous mode (CW), and excellent pulse width modulation. The major applications of LEDs were initially limited to visible sources for indoor lighting, automotive lighting, traffic signals, mobile flash, etc. However, *GaN* LEDs are now being researched for applications in many other fields, such as visible light communication (VLC) [1–6], sensors [7–11], optical switches [12, 13], indoor plant-lighting or horticulture [14–16], display technology [17–20], optical coherence tomography (OCT) systems [21–23], etc.

One of the emerging and highly specialized potential applications of LEDs is optogenetics, where light targets and precisely controls defined events in complex biological systems such as freely

moving animals. This thesis aims to demonstrate the design, fabrication and characterization of highly efficient *GaN*-based blue, UV and dual-wavelength μ LEDs and integration of the μ LEDs with complementary metal–oxide–semiconductor (CMOS) rectifier and lead zirconate titanate piezoelectric (PZT) harvester to enable ultrasound powering for the application of wireless optogenetic applications. As the experimental results at Aarhus showed that the CMOS chip could deliver at most about 2.2 *mW* of electrical power (Maximum voltage the CMOS chip can tolerate is 3.3 *V*) to the μ LED, the efficiency of the μ LEDs plays one of the most critical roles in achieving higher optical power density for neural stimulation.

In this introductory chapter, a brief history of the development of *GaN*-based LEDs is discussed with a focus on the blue and near UV part of the spectrum. The fundamental operating principle of LEDs is presented here and also, and a discussion on the efficiency of the LEDs, especially on micro-LEDs (μ LED), is presented. This includes a discussion on fundamental problems for achieving high efficiency with *GaN* LEDs and solutions that have been developed over the years.

1.1 Brief history of GaN LEDs

The fundamental operation of a LED is the generation of light due to the passing through of current or the presence of a strong electrical field which is called electroluminescence (EL). EL was first discovered by Henry Joseph Round in Marconi labs, and he published his report named "A Note on Carborundum" in 1907, stating his observation of yellow EL from a piece of silicon carbide (*SiC*) material [24]. His work led to the foundation of the discovery of LEDs that we are familiar with today. These early devices were Schottky diodes rather than p-n junction diodes with larger turn-on voltages ranging from 10 *V* to 110 *V* under strong forward bias conditions. Nearly 20 years after Round's work, a Russian experimentalist named Oleg Vladimirovich Lossev published his first paper on seeing green light from a *SiC* metal-semiconductor rectifier under reverse bias and photographed the first EL, which was published in 1924 in *Wireless World and Radio Review* [25]. In the late 1960s, *SiC* crystals were grown in a more controlled process and doped with different impurities, made possible to fabricate the first p-n junction devices, which led to blue LEDs [26]. During this time, the efficiency (electrical-to-optical) of *SiC*-based devices was reported to be as low as 0.005% and had no remarkable improvement due to its indirect bandgap [27]. The best efficiency obtained from a

SiC LED emitting at 470 nm was reported in 1993 to be 0.03% [28].

In the early stage of semiconductor technology, III-V material was proposed by H. Welker in 1953 instead of naturally available well-researched II-VI material [29]. III-V materials are not naturally available; instead, they are grown in a controlled process, the technology of which is quite mature at this point. Vapour phase epitaxy (VPE) or liquid phase epitaxy (LPE) technology based bulk grown gallium arsenide (*GaAs*) p-n junction lasers were reported in 1962 by groups in RCA, MIT, GE and IBM [30, 31]. Around 1968-1971 researchers were also able to produce green LEDs by doping isoelectric nitrogen (N) with gallium phosphide (GaP) with an efficiency of about 0.6% [32, 33].

In the late 1960s, James Tietjen and Maruska, who were working for RCA, a leading cathode ray tube (CRT) television manufacturer, wanted to develop flat-screen television. They realized that to create red-green-blue (RGB) pixels, one needs to have LEDs available in these colours. Red LEDs using *GaAsP* and green LEDs using *GaP-N* technology were already established. The only colour needed was blue LED to have full colour, and gallium nitride (*GaN*) is a suitable candidate for that.

GaN is an III-V semiconductor material with a wide bandgap of about 3.4 eV and is able to generate UV-blue wavelengths by direct bandgap emission. Research by R. Juza and H. Hahn in the early 1940s for the preparation of *GaN* powder by reaction of liquid gallium metal with ammonia at high temperature prepared the groundwork for growing single-crystalline *GaN* films. The sapphire substrate was chosen as it is not reactive with ammonia and has higher robustness to grow *GaN*. Initially-grown *GaN* films were a failure as they were poly-crystalline as were grown at lower temperatures (600 °C) to prevent the decomposition of *GaN*. The first single-crystalline *GaN* film was grown on sapphire in 1969 by Tietjen and Maruska using hydride vapour phase epitaxy (HVPE) at 800 °C [34]. It was found that the grown *GaN* is naturally n-type without doping. Researchers took a significant interest in developing blue LEDs, but the main challenge was achieving p-doped *GaN* to form p-n junction diodes. Zinc (*Zn*) was the initial choice to create p-Type *GaN*, but heavy *Zn*-concentration *GaN* films were insulating instead of p-type [35]. Research on undoped, magnesium (*Mg*) and other impurities such as other cadmium (*Cd*), and beryllium (*Be*) were investigated at this point [36–40]. These early Mg-doped p-type *GaN* were semi-insulating, which is an improvement over the *Zn*-doped *GaN*. These early researches resulted in the first metal-insulator-semiconductor (MIS) diode,

which had a peak emission wavelength of 475 nm, and the first current-injected light emitting device had an output power of the order of 1 μW to 5 μW [41].

In 1983, the aluminium nitride (AlN) buffer layer was first grown on a sapphire substrate using molecular beam epitaxy (MBE) by Yoshida et al. [42] and GaN films with low-temperature AlN buffer layer was grown using metal-organic chemical vapour deposition (MOCVD) by Amano et al. [43]. A residual carrier concentration to the order of 10^{17} cm^{-3} was achieved by Amano et al. Instead of a AlN buffer layer, a low-temperature GaN buffer layer to grow high-quality GaN on sapphire was investigated by Nakamura et al. [44] and in 1992, he achieved a high electron mobility of the order of $900 \text{ cm}^2/V.s$ at room temperature on low temperature grown buffer layer [45].

Due to a lack of proper p-type GaN , the research on GaN -based blue LEDs was temporarily ceased till 1989. The first and basic p-type doped GaN was achieved by Akasaki et al. in 1989 and demonstrated p-type conductivity in GaN [46]. Mg dopants were used to achieve p-type conductivity and the activation of Mg was achieved by post-growth annealing using low energy electron beam irradiation (LEEBI) treatment by Amano et al. [47]. A hole concentration of $2 \times 10^{16} \text{ cm}^{-3}$ and mobility of $8 \text{ cm}^2 V^{-1} s^{-1}$ was achieved in this case. Though at this time, the reason behind achieving p-type GaN using LEEBI treatment was not clear to them. Using post-thermal annealing in an NH_3 free ambient gas environment, Nakamura et al. also achieved p-type GaN in 1992 [48]. A hole concentration and mobility of $3 \times 10^{17} \text{ cm}^{-3}$ and $10 \text{ cm}^2 V^{-1} s^{-1}$ were measured respectively in this case.

Finally, in May 1992, the hole compensation mechanism by hydrogen passivation was clarified by Nakamura et al. A model to form hydrogen acceptor complexes in p-type GaN was proposed by them where atomic hydrogen was produced using NH_3 dissociation during growth [49]. The process of passivating Mg acceptors with hydrogen complexes was theoretically verified by J. Neugebauer and C. G. Van de Walle as well in 1995 [50, 51]. The output power of 42 μW was measured from these LEDs operating at 20 mA and 4 V, with a peak wavelength at 430 nm [52]. Activation of p-dopants to achieve p-type GaN is now a well-established process.

As the development of p-n homojunction became a success, researchers started working with mixed alloys for bandgap engineering. Nagamoto et al. grew indium gallium nitride ($InGaN$) on sapphire at 500 $^{\circ}C$ [53] and Yoshimoto grew $InGaN$ layers at 800 $^{\circ}C$ using MOCVD [54]. However, the grown $InGaN$ crystal showed poor quality during room temperature photolumi-

nescence (PL) measurements. A high-quality *InGaN* layer on a *GaN* template grown on sapphire was demonstrated by Nakamura and Mukai in 1992 [55]. Depending on the *In* concentration, band-to-band emission from violet to blue was observed in room temperature PL measurements which was the first report of band-to-band emission from *InGaN* layers [55].

Double-heterostructure (DH) 440 nm peak wavelength blue LEDs with layer structure of *p-GaN/n-InGaN/n-GaN* were first demonstrated by Nakamura et al. in 1993 [56]. These LEDs were capable of generating a power of 125 μW while operating under a forward bias of 20 mA. Commercial 450 nm blue LEDs with an output power of 1.5 mW were introduced by Nakamura et al. in 1994 [57]. A 45 nm thick Zn-doped *InGaN* active layer was used to improve the luminous efficacy, and for the first time, the p-type aluminium gallium nitride (*p-AlGaN*) electron blocking layer was introduced in the structure in between *p-GaN* and active layer to prevent electron carrier overflow from the active region. The layer structure for the same 440 nm LED was *p-GaN/p-AlGaN/Zn-doped InGaN/n-GaN*, and external quantum efficiency (EQE) was measured as 2.7%. High-brightness DH LEDs with an optical power of 1.5 mW and brightness of more than 100 mcd were also commercialized around the same time by Nichia Chemical Industries Ltd. [58].

All this work led towards the foundation for *GaN* LEDs, and single quantum well (SQW) green *GaN*-based LED was discovered by Nakamura in 1995 [59]. Due to the contribution "for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources" I. Akasaki, H. Amano and S. Nakamura were awarded the Nobel Prize in Physics in 2014 [60].

1.2 Fundamentals of GaN LED operation

A *GaN*-based LED is an III-V semiconductor diode that generates photons (light) by recombination of holes (positive carriers) and electrons (negative carriers) when a forward bias is applied. An LED is a p-n junction diode where the p-type material has free holes, and the n-type material has free electrons and two metal contacts, one for p-type material and one for n-type material. When a forward bias is applied, the potential barrier is reduced, and the electrons and holes diffuse towards the p-n junction and recombine (radiatively) by emitting a photon with energy the same as the bandgap.

To improve the recombination rate, the p-n junction is usually made with a single or a series of *InGaN* quantum wells (QW) sandwiched between p-type and n-type *GaN* material to form the active region. As the band gap of the active region is lower than the surrounding p-type or n-type material, a high concentration of carriers can be confined in the QW region. Figure 1.1(a) shows a basic p-n junction diode operating under forward bias. The electrons and holes are separated by the potential barrier at the p-n junction and do not recombine without bias. When a forward bias is applied [Figure 1.1(b)], the potential barrier reduces, and the carriers diffuse to the other side and recombine in the junction where the QWs are located, which emit photons. The band diagram of an *InGaN* QW sandwiched between p-type and n-type material and the effect of the polarization-induced field is shown in subsequent figures. Theoretically, when there is no in-built electric field, the energy band-diagram of the QW is flat with direct overlap between hole-electron wavefunction as shown in Figure 1.1(c). However, the *InGaN* structure grown on c-plane substrate suffers from a strong polarization-induced built-in electric field, causing the band bending in the QW, which reduces the spatial overlap between electron and hole wavefunction, and the internal quantum efficiency (IQE) is reduced [Figure 1.1(d)]. When a bias is applied, a high number of carriers in the QW can screen the effect of the piezoelectric field, which causes band flattening and the spatial overlap between electron and hole wavefunction is increased as shown in Figure 1.1(e).

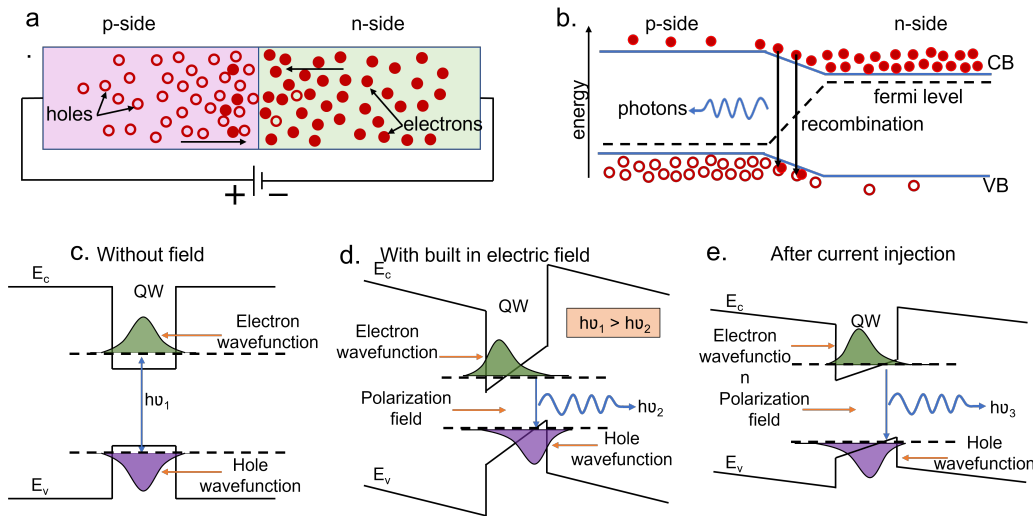


FIGURE 1.1: Schematic representation of the basic operating principle of an LED. Figure (a) shows the recombination of electrons and holes in a p-n junction diode when a forward bias is applied, and (b) shows the corresponding energy band diagram. The energy band diagram of a QW sandwiched between the p and n junction is shown in the following figures. Figure (c) shows the band diagram when there is no built-in electric field in the QW and (d) shows the band bending due to the presence of the strong piezoelectric field, and (e) shows that applied forward bias screens the built-in piezoelectric field and the band starts flattening.

The p-type layer of *GaN* LEDs is doped with *Mg* [61] (other p-dopants are zinc (*Zn*) [62] beryllium (*Be*) [63]) to create a free hole concentration and the n-type layer is doped with *Si* to create a free electron concentration. The QW region of *GaN* LEDs is generally made with *InGaN* material which has a lower bandgap than both p-type and n-type material and is sandwiched between them. As the thickness of the QWs typically varies between 1-3 nm typically, the carriers can only have discrete energy values. This is also known as the quantum confinement of carriers. By varying the *In* alloy concentration in the QW region, the bandgap energy is varied and, thus, the variation of the emitted wavelength. A deeper analysis of mechanisms that reduce the efficiency of *GaN* LEDs is presented below.

1.3 Efficiency of GaN LEDs

Since the demonstration and commercialization of blue *InGaN* LEDs in 1993 [56], researchers have been working to improve the light output power (P_{out}) and efficiency. The efficiency of a LED is mainly measured by four parameters: Internal Quantum Efficiency (IQE), Extraction Efficiency (EE), External Quantum Efficiency (EQE), and Wall-Plug Efficiency (WPE). The IQE refers to the number of photons ($\frac{P_{in}}{hv}$) emitted from the active region of the LED per second due to the number of injected electrons per second. In an ideal active region, the IQE should be unity. However, different loss mechanisms come to play, restricting the IQE to be less than 100%.

$$IQE = \frac{P_{in}/(hv)}{I/e}, \quad (1.1)$$

Where P_{in} is the optical power of the LED emitted from the active region that defines the internal optical power, and I is the injected current. In an ideal situation, all the photons generated by the active region should come out of the LED chip. However, losses such as material absorption, total internal reflection, and non-radiative recombination limit the light escape reducing the EE. The EE is defined as the number of photons emitted per second into free space (P_{out}) due to the number of photons emitted per second from the active region P_{in} .

$$EE = \frac{P_{out}/hv}{P_{in}/hv}, \quad (1.2)$$

The EE is one of the main limitations for achieving high-power blue LEDs as EE higher than 50% is difficult to achieve mainly due to material absorption, and total internal reflection. It

often requires specific-costly engineering processes to enhance the EE. The EQE of an LED is defined as the number of extracted photons due to the injection of electrons.

$$EQE = \frac{P_{out}/h\nu}{I/e} = EE \times IQE, \quad (1.3)$$

The WPE is defined as the ratio of optical power in free space and supplied electrical power.

$$WPE = \frac{P_{out}}{I \times V}, \quad (1.4)$$

Where $I \times V$ is the applied electrical power to the LED. It is quite evident from the definitions that the more the IQE and EE, the more will be the EQE and WPE.

1.3.1 Reasons for efficiency reduction

At room temperature, *GaN* has a peak wavelength of 365 nm (the near UV range of the electromagnetic spectrum). It is possible to get longer wavelengths part of the spectrum by tuning the bandgap to lower energy by varying the percentage of *In* into the *GaN* crystal. Figure 1.2 shows the bandgap energy of *AlN* (6.015 eV), *GaN* (3.41 eV), and *InN* (0.7 eV) as a function of lattice constant where the lattice constant is the physical dimensions and angles that determine the geometry of the unit cells in a crystal lattice. Theoretically, it is possible to tune the bandgap between UV and IR while maintaining direct recombination. It was initially challenging to achieve high *In* content in *InGaN* layers due to strain and piezoelectric effect, leading to poor quality material for their different optimized growth conditions, which was one of the reasons for having a lower efficiency in *GaN* LEDs. Although, it is now possible to grow high-quality *AlN* layers. Higher *In* percentage creates *In* clusters, which are efficient non-radiative recombination centers [64].

It is important to understand the *GaN* crystal structure to recognize the efficiency loss mechanisms better. The wurtzite structure is thermodynamically more stable than the zinc blende structure. The wurtzite structure is hexagonal with strong covalent bonds between gallium and nitrogen atoms. Each atom has four tetrahedral bonds, and the electronegativity of nitrogen is stronger than that of gallium, indium, and aluminum, providing strong ionic properties.

InGaN quantum well-based *GaN* LED structures are mainly grown as c-plane [0001] as they can be easily grown on [0001] sapphire or [0001] *SiC* substrates. The wurtzite *GaN* structure

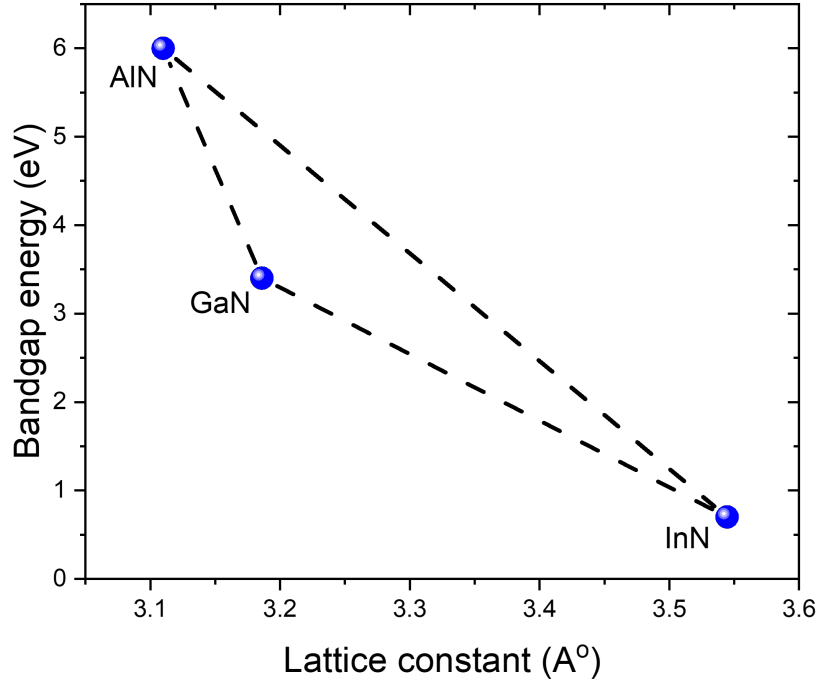


FIGURE 1.2: Bandgap energy of AlN, GaN, and InN as a function of lattice constant.

is non-centrosymmetric, meaning it does not have inversion symmetry. Also, Ga and N atoms have different electronegativity, which makes each Ga-N bond partially ionic with certain dipole moment, unlike centrosymmetric structures where these dipole moments cancel out each other. In the wurtzite GaN structure, the bond is nearly perpendicular to the c-axis, giving rise to a net dipole moment along the c-axis, and a spontaneous polarization field is generated perpendicular to the growth plane. Therefore, the strong ionic character of the covalent bond between Ga and N atoms and the deviation of the GaN unit cell from the ideal wurtzite structure is the reason for the generation of spontaneous polarization on the GaN structure.[65] InGaN devices also suffer from a large strain-induced piezoelectric polarization. A tilting of the band edges takes place due to the presence of piezoelectric polarization and spontaneous polarization (mainly due to piezoelectric polarization) fields, which causes spatial separation between hole and electron wave function and hence a reduction of the IQE of the device, which is known as quantum confined Stark effect (QCSE) [66]. Tilting of the energy bands reduces the quantum barrier (QB) height as well, which increases the carrier leakage.

The efficiency droop mechanism in the GaN-LED structure is described by a simple and well-known model known as the ABC model. The ABC model describes three main principles of

the electron-hole recombination process in the active region, non-radiative Shockley-Reed-Hall (SRH) recombination, radiative recombination, and non-radiative Auger recombination. The SRH recombination is a trap or defect-assisted non-radiative recombination process, dominant at low bias but saturates at higher currents [67–69]. The Auger recombination occurs only at high current densities where the energy dissipated by electron-hole recombination is transferred to another free electron to move it high into the conduction band or to a hole into the valence band. This third carrier loses its excess energy as thermal vibrations [67, 70].

The ABC model is based on some strict simplification, such as the electron leakage from the active region of the LED is assumed to be negligible. SRH recombination constant A , radiative recombination constant B , and Auger recombination constant C are assumed to be independent of carrier concentrations, and finally, non-equilibrium hole-electron concentration in the active region is equal to each other [71, 72]. The IQE in the ACB model is defined as,

$$IQE = \frac{Bn^2}{An + Bn^2 + Cn^3}, \quad (1.5)$$

Where n is the carrier concentration. As the fabricated LEDs described later in this thesis are targeted to operate at a low bias ($\leq 3 \text{ mA}$) where the carrier density is low as well, the non-radiative Auger recombination process will not have a significant impact on the efficiency of the LEDs and is not discussed further. Defect-assisted SRH non-radiative recombination is one of the major contributors to the reduction of the IQE. Such defects can arise due to lattice dislocations, foreign atoms, native defects, etc. Dislocation density can be reduced by choosing a suitable substrate for the epitaxial growth of GaN . Sapphire is one of the most common substrates for growing GaN -LEDs, although a high lattice mismatch of $\sim 13\%$ between sapphire and GaN leads to a high density of dislocations [73]. Researchers have been working on different substrates to replace sapphire over the years, which include a patterned sapphire substrate (PSS), a low-cost silicon substrate, a free-standing GaN substrate, a low lattice mismatch unconventional oxide substrate, and a metallic substrate.

1.3.2 Increasing light extraction efficiency

Since all the LED wafers used in this work are purchased from commercial vendors, the IQE of the LED is not in our control. Whereas the EQE or WPE of the μ LEDs could be increased by

increasing the light extraction efficiency. There are several factors that can contribute to improving the EE, such as choice of substrate, metal contacts (metal reflector, omnidirectional reflector(ODR), Bragg-reflector, anti-reflection coating), surface roughening, mesa design, encapsulation and discussed later in this section.

By choosing PSS (PSS has micro cone patterns on the buried surface) instead of the conventional plane sapphire substrate, EE can be improved by several factors [74–76]. *GaN* film grown on PSS has a much lower density of dislocations (dislocation density: $10^6 \text{ cm}^{-2} \sim 10^7 \text{ cm}^{-2}$) [77–79] than the conventional sapphire substrate (dislocation density: $10^9 \text{ cm}^{-2} \sim 10^{10} \text{ cm}^{-2}$) [78, 80], hence higher IQE. Before growing *GaN* on PSS, a low-temperature MOCVD-grown AlN (10 - 100 nm thick) buffer layer is grown on the PSS, which effectively improves the crystalline structure of *GaN* films. In addition, the presence of patterned sapphire enhances the scattering of light, and hence the out-coupling of light from the LED chip is improved. The PSS is one of the main reasons for having high extraction efficiency.

The engineering of p-metallization contact is another important factor for achieving higher efficiency. The contact optimization is done through voltage management and reflectivity of the metal contact. The better (more ohmic) the contact, the lower will be the power loss which increases the WPE of the device. The higher the reflectivity of the metal contact, the less light will be absorbed by the metal contact itself, increasing the EE. Generally, the p-contact is chosen such that it creates an ohmic contact with the p-*GaN*, and the current-voltage characteristics become linear. A specific contact resistivity (ρ_c) of the order of a minimum $10^{-2} \Omega\text{cm}^2$ is required to achieve an ohmic contact. The ρ_c defines the resistance at the metal-semiconductor interface. The lower the ρ_c , the easier the carriers will flow from metal to semiconductor, and the turn-on voltage of the LED will be lower. In μLEDs the contact area between metal and semiconductor is much lower, which already adds high resistance. Therefore, the ρ_c needs to be as low as possible for the μLEDs to have an efficient device. High-quality ohmic contacts have been a centre of attraction for researchers for a long time [81–83]. The main challenge arises due to a lack of metals or conducting oxides with work function (ϕ_B) higher than p-*GaN* [84]. The ϕ_B of a metal is the minimum amount of energy that is required to remove the electron from the metal surface to the vacuum level. Metals such as palladium ($\phi_B = 5.22 - 5.60 \text{ eV}$), nickle ($\phi_B = 5.04 - 5.35 \text{ eV}$), gold ($\phi_B = 5.10 - 5.47 \text{ eV}$), silver ($\phi_B = 4.26 - 4.74 \text{ eV}$) and their alloys are suitable for such applications. Alloys such as bare-*Pd*, *Pd/Ni/Au*, and *Ni/Ag/Ni* metallization have been used as p-contact in this thesis,

and are discussed in later chapters. Before the deposition of p-metal, the surface of p-*GaN* is usually treated with specific cleaning processes to get rid of different contaminants. A high-quality ohmic contact ensures low ρ_c , which reduces the forward voltage of the LED and improves the WPE. The use of reflective metals such as Ag as p-contact could improve the light EE further. Ag is a difficult metal to control and requires passivation to control the agglomeration and annealing for contact optimization.

Research has proven that introducing different reflectors could have a significant improvement on light EE. Reflectors such as metallic reflectors, distributed Bragg reflectors (DBR), and omnidirectional reflectors (ODR) can be used to have more EE, depending on the application. Metallic reflectors are one of the oldest and most popular reflectors that use metals like Ag or Al that have higher reflectivity in the visible range of the spectrum and work as a mirror [85–87]. A DBR consists of several alternate pairs of high refractive index (RI) and low RI material where the thickness of the two alternate layers is chosen in such a way that constructive interference takes place for reflective waves. While metallic reflectors have a broad-band high reflectivity ($\sim 85\text{--}94\%$)[88, 89], DBR can achieve a narrow-band higher reflectivity ($\sim 99\%$)[90, 91] by engineering the number of layers [92, 93]. An ODR is a type of reflector engineered to have high-angle-insensitive reflectivity. ODR mainly comprises of series of alternate high and low RI materials with thicknesses of a quarter wavelength which also include metal layers. General ODR modelling for different wavelengths was developed by Fink et al. [94] A high reflectivity of 98% from an ODR consisting of AlGaInP-quarter wavelength thick SiO₂-Ag layers was demonstrated in late 2003 [95].

Another useful method to increase the EE of a substrate emitting/bottom emitting LED is to modify the mesa into a slope rather than a vertical side wall [96]. Sloped sidewall could be achieved by re-flowing the photo-resist at higher temperatures ($\sim 120^\circ\text{C}$ for 5 minutes) and then dry etching of p-*GaN* into n-*GaN*. Also, encapsulating the LED chip into a high refractive index optically transparent material, roughening or patterning the top-bottom surface of the LED chip [97–99] could have further improvement of light EE. Encapsulation is another useful technique to enhance EE. Generally, LED chips are encapsulated with higher refractive index material such as silicone in the shape of a dome to minimize total internal reflections and to uniformly distribute the light. Researchers have shown that by encapsulating the LED and patterning the substrate with 30° pyramid arrays, one could achieve about 200% higher EE than a bare LED without encapsulation and patterned substrate.[100].

1.4 Thesis outline

The objective of this thesis is to realize highly-efficient μ LEDs wirelessly powered by ultrasound for optogenetic applications. Optogenetics is an emerging field where light is used to investigate the complex behaviour of neural circuits or to control genetically engineered cell populations or neurons. The work presented here in this thesis is targeted to realize a novel wireless implantable micro-scale device, ultimately enabling in-vivo electrophysiology, optogenetics, and ultra-localized drug delivery in freely moving animals. The proposed device is intended to be used to target specific neural circuits of the brain and test a new therapeutic approach for Parkinson's disease (PD). Due to the advantages of US-powering over RF-powering, the envisioned device will be based on highly efficient ultrasound powered μ LED, which will excite specific ChR-2 transfected neural cells.

The proposed US-powered neural implant (also known as the neural DUST) needs to be in the sub-millimeter range and to be powered at a few centimeters below the skin. The DUST needs to be capable of generating $\sim 5 \text{ mW/mm}^2$ of optical power while operating at 1 mA and needs to result in less than 1°C temperature rise to prevent damage to cells. The peak wavelength should be in the range of $470 \text{ nm} - 480 \text{ nm}$ which is suited to excite ChR-2 transfected cells. Also, to utilize an ultra-localized localized optically-triggered (by 370 nm UV LED) drug delivery system (DDS) to counter the spontaneous inflammatory reaction of the body in the advanced version of the DUST due to surgical insertion of the foreign implant. Finally, red LED (650 nm) combined with UV called dual-wavelength chips to achieve activation of red-sensitive ChR with DDS for the advanced DUSTs. To achieve the neural DUST a minimum of three active components are required, namely a PZT harvester, a CMOS chip, and a highly efficient μ LED. The PZT harvests the incoming US power and converts it to alternating current (AC), and then the CMOS rectifier chip converts the AC into direct current (DC) and delivers it to the load (μ LED). Finally, the μ LEDs deliver specific optical power for neural stimulation or activation of localized drug delivery systems.

- **Chapter 2: An overview of Optogenetic applications**

This chapter presents a high-level overview of the recently emerging neuroscience technology named optogenetics. A brief introduction is given to channelrhodopsin-2 which is the first optogenetic tool for making the cells or neurons sensitive to light. An outline of some wireless optogenetic devices and a comparison among different wireless power tran-

sfer technologies show the requirement for ultrasound-powering solutions. A study in some recent articles shows a successful demonstration of ultrasound-powered neural implants and the need for highly efficient μ LEDs for optogenetic stimulation.

- **Chapter 3: Design, fabrication, and characterization of efficient blue and UV LEDs**

In this chapter, specific designs, including geometry and size of the blue (480 nm) and UV (370 nm) μ LEDs compatible with micro-electronic chips and targeted for optogenetic applications, are presented. Fabrication of the μ LEDs starting from the selection of wavelength, wafer material, and process flow to back-end processing, is discussed in detail. Special importance is given to the electrical and optical characterization of μ LEDs. Simulation and implementation of ARC coating and its effect on the enhancement of external quantum efficiency of blue μ LEDs are also examined. A high wall-plug efficiency of about 40.7% and 25.4% was measured from 100 μ m mesa blue and UV μ LEDs, respectively, with a low turn-on voltage of 2.3 V for the blue and 3.1 V for the UV μ LED using Pd/Ni/Au based p-contact. For further improvement of EQE, an Ag-based reflective metal contact was evaluated, which showed about 20% improvement in extraction efficiency over Pd/Ni/Au-based contacts. A low turn-on voltage was observed for both blue and UV μ LEDs, which is below the bandgap energy corresponding to peak wavelength, which could be the result of high carrier temperature at low current densities.

- **Chapter 4: Characterization and optimization of drug delivery system**

This chapter presents the work carried out for the characterization and development of an optically triggered drug delivery system. Spiropyran (SP), a photochromic polymer that changes its physical and chemical properties upon UV exposure, is a suitable candidate for DDS. With UV exposure, the hydrophobic drug-embedded SP can change its form to its isomer called merocyanine (MC), which is hydrophilic and enables the drug release. The dependence of SP activation on wavelength was determined by measuring the absorption spectra. Exposure under different wavelengths ranging from 370 nm to 405 nm shows SP has a high wavelength selectivity and does not respond to wavelengths above 380 nm. With the increase in SP thickness, the required energy density for the activation of SP also increases. To activate 40 μ m thick SP with 370 nm UV LED, a minimum of 0.32 J/cm² energy density is required. Finally, the activation of SP with ultrasound-powered μ LED was demonstrated in this chapter.

- **Chapter 5: Dual wavelength μ LED assembly for optogenetics**

Integrating the DDS into neural DUST requires two different wavelengths where one wavelength (blue/red) can be used for optical stimulation, and the other wavelength (UV) would be used for activating the DDS. In this chapter, the development of dual-wavelength μ LEDs on a single chip compatible with an electronic chip and neural DUST is described. The layout and process flow of the dual-wavelength μ LEDs were designed based on the electronic die layout and minimum requirements of the DUST. It was targeted to achieve different combinations of dual-colour chips, namely red + blue, red + UV, and blue + UV. Several engineering challenges, including μ LED release, SiN edge rim, InterVia undercut, and metal delamination, were encountered during fabrication and were successfully addressed. Although, the backend processing of the dual-colour chips needs further optimization to have better yield. The electro-optical characteristics of the dual-wavelength μ LED assemblies presented here in this chapter show the viability of the chips to be used in neural DUSTs.

- **Chapter 6: Integration and packaging of neural DUSTs and its miniaturization**

The integration and packaging of the DUST and its path to further miniaturization to achieve a wireless neural implant are presented in detail in this chapter. In the initial phase, a basic version of the DUST (basic-DUST) was integrated on an Au-patterned $1.5 \times 3.0 \text{ mm}^2$ glass substrate by a heterogeneous integration process and encapsulated by PDMS. A total volume of 2.85 mm^3 was achieved in this case, and the working principle by ultrasound-powering was demonstrated. The optical power density from the blue μ LED was calculated to be about 103 mW/mm^2 by ultrasound operation, which is more than the minimum specification required for activation of blue-sensitive ChR-2. In the second phase, a different monolithic and heterogeneous approach was investigated to achieve a more compact version of the DUST. The compact-DUST was integrated on an Au-evaporated Si substrate. A total volume of 0.33 mm^3 was achieved in this case which is a reduction of more than 85% from the basic-DUST version. The working principle of the compact-DUST by ultrasound was also demonstrated, and to the best of our knowledge, this compact-DUST is the smallest wireless ultrasound-powered neural-DUST with integrated μ LED.

- **Chapter 7: Conclusion and future work**

The key results of the thesis are summarized here in this chapter, and recommendations for future development were outlined.

- **Appendix** Appendix [A](#) includes details of UV and blue materials used in the device fabrication. The experimental results for the optimization of high-quality ohmic p-contact using bare Pd and Pd/Ni/Au-based metallization on UV material are presented in appendix [B](#). The results for the optimization of Ag-based reflective p-contact are discussed in appendix [C](#) with the details of agglomeration and the stabilization of Ag upon annealing. Finally, appendix [D](#) gives an overview of the grinding, polishing and dicing processes used in this thesis.

Chapter 2

An overview of Optogenetic applications

2.1 Introduction

The field of optogenetics is a newly emerging technology and a strong tool that combines genetic engineering with a light source for monitoring and precisely controlling the functions of targeted and genetically-modified cells or neurons.[101–105] Natural and engineered photoreceptors, typically harvested from microbial origin, are genetically inserted selectively into the cells of interest via optogenetics. As a consequence, cells or neurons that are generally unresponsive to light become photosensitive, addressable by specific wavelength, and precisely adjustable in time and space. [102, 106–108]

Optogenetics has achieved great results in the precise control of neurons and decoding neural circuitry in both in-vivo and in-vitro animal studies, and in 2010 optogenetics was chosen as the "*Method of the Year*" across all fields of science and engineering by the interdisciplinary research journal Nature Methods.[109]

In this chapter, a brief introduction to an optogenetic tool named channelrhodopsin is provided, along with an overview of newly developed wireless optogenetic implantable devices. These wireless implants require a suitable wireless power supply technology that can deliver enough power while having a smaller volume. A comparison between different wireless power supply mechanism shows several advantages of ultrasound (US) powering technology over battery-

powered or radio frequency (RF) powered technologies. A few neural implants driven by US-powering are shown here, highlighting their capabilities in the different optogenetic applications. Lastly, the need for a highly efficient μ LED for optical stimulation in optogenetics is explained. Based on the knowledge gained from previous research on neural implants, the idea of a new wireless US-powered neural implant with integrated μ LED for optical stimulation is proposed here, which could be able to meet the minimum requirements for a miniaturized fully-implantable optogenetic device.

2.2 Channelrhodopsin: an optogenetic tool

The optogenetics field combines light with genetic engineering to measure, control, or detect molecular signals and cells to have a better understanding of their functions. The most studied genetic engineering is based on the use of different opsins. Opsins are fundamentally light-gated ion channels that absorb a specific wavelength. The channels activate (open) or deactivate (close) upon absorption of light that controls ion flow in or out of the cells, and also different opsins causes various electrochemical response.[110] Among different opsins, channelrhodopsins (ChR) is one of the most studied and popular optogenetic tools that allow fast depolarization of neurons upon light exposure.[111] In 2001, Peter Hegemann's group discovered the foundation of the new channelrhodopsins [112], and demonstrated channelrhodopsin-1 (ChR-1) in 2002 [113] and in 2003, channelrhodopsin-2 (ChR-2) [114] in collaboration with Georg Nagel's group. ChR-1 allows nonspecific cation influx in the cell when exposed to blue light whereas ChR-2 also activates cation channels by blue light with much higher conductance at physiological pH and trafficks [115] well to the membrane. Hence ChR-2 is the adopted optogenetic tool and is preferred over ChR-1.[116]

2.3 Application of optogenetics in neural implants

Optogenetics has shown great potential beyond fundamental research in improving human well-being and disease treatment. Although, at this point, it is still not approved to be used on humans except in exceptional circumstances. The advancement in the miniaturization of optoelectronics devices creates an opportunity to combine with optogenetics for the study of implantable devices. Such optogenetic implants could be remotely powered by the fibre-coupled

light source (also known as tethered systems) or could be wirelessly powered. Wireless optogenetic devices are more desired over tethered devices due to their fully implantable capabilities, compactness, and light delivery deep inside tissue. Research on the application of such optogenetic devices is not only limited to therapeutic studies for neurological diseases but expanded its domain from the brain to the spinal cord and organs.[117–119]

An overview of some optogenetic systems is presented in Table 2.1, showing different power transfer methods where the peak wavelengths were selected based on the targeted opsins. These optogenetic systems were capable of generating $> 5 \text{ mW/mm}^2$ optical power density while operating between 1 mA to 5 mA and briefly discussed in this section.

TABLE 2.1: An overview of different optogenetic systems highlighting their powering technologies with optical power density at a specific wavelength depending on the opsin used.

Publication	Yu et al., 2018 [120]	Seung et al., 2018 [121]	Xue et al., 2022 [122]	Park et al., 2015 [123]	Kathe et al., 2022 [124]
Wireless powering	RF	NA,Wired	RF + Battery	RF	RF + Battery
Operating frequency	2.4 GHz	10 Hz	2.4 GHz	$\sim 2.3\text{-}2.4$ GHz	2.44 GHz
Targeted opsin	ChR-2	Chrimson	ChR-2	ChR-2	ChR-2, Chrimson
Wavelength (nm)	471	638	470	470	470, 620
Optical power	82 mW/mm^2 at 5 mA	17 mW/mm^2 at 1 mA	10-15 mW/mm^2 at 1-5 mA	10 mW/mm^2 at 2.7 V	20-50 mW/mm^2 at 5 mA

A wireless RF powered (at 2.4 GHz) brain-implantable optoelectronic probe integrated with 471 nm InGaN μ LED was demonstrated by researchers from Tsinghua University for in-vivo optogenetic modulation of locomotive behaviours.[120] Another team of researchers successfully demonstrated whisker movements in mice using optogenetic photo-stimulation by surgically placing the implant in the motor cortex.[121] A red-emitting AlGaInP-based flexible LED was used for optical stimulation, and the brain was transfected by chrimson opsin in this case.[121]

A recent study published in 2022 showed a battery-powered wireless dual-channel optogenetic system for selectively modulated precise defensive behaviour.[122]

A soft stretchable RF-powered fully implantable optoelectronic implant was illustrated for optogenetic modulation of the mice's spinal cord and peripheral nervous system.[123] Wireless battery power and closed loop optogenetic implant integrated with 470 nm μ LED was demonstrated for manipulation of neurons and pathways over the entire dorsoventral spinal cord of the mice.[124] Optogenetic implants have captured attention for the control and study of organs. In a study, researchers have shown an optogenetic system for the modulation of smooth muscle to control unitary bladder contraction.[125] An organ-specific RF-powered wireless optogenetic system integrated with μ LED was demonstrated for the study of the feeding behaviour of mice. It showed that during optical stimulation the food intake of the mice was reduced when the μ LED was implanted inside the stomach.[126] There is a lot of other research currently ongoing in the domain of fully implantable wirelessly-powered neural implants than the above-mentioned ones. Although, there are several critical parameters depending on the optogenetic application that need to be addressed, such as implant powering system, volume, the efficiency of the light source and electronics, biocompatibility, etc.

2.4 Comparison of different wireless powering technologies for implants

One of the most critical factors for the stable operation of optogenetic implants without any behavioural or environmental negative effects is to have a suitable and steady power supply.[127–130] In the early stage, researchers investigated remote optical power supplies such as lasers coupled into fibre for light delivery, known as tethered approach.[131–134] The tethered approach is still considered one of the main methods for optogenetic stimulation. Unfortunately, this approach restricts the movement of the animals. To obtain a free movement and fully implantable optogenetic implant it was required to utilize a wireless power supply technology. Various wireless powering technologies have been investigated for wireless optogenetic implants including battery-powered, radio-frequency (RF) powered, hybrid-powered (battery+RF), light-powered, ultrasound powered, etc.[135–141]

Batteries have been studied as a power source in optogenetic implants for their stability.[138, 142, 143], But it requires suitable light-weight batteries to avoid brain damage resulting from behavioural disturbances.[138] Even though battery-powered implants are capable of wireless functioning, the need for intermittent battery replacement requires repetitive brain surgeries, which becomes an obstruction for continuous and long-term usage.[142, 144–148] Also, these type of systems often end up as bulky head-mounted configuration which is susceptible to external stress and cannot be utilized as fully implantable optogenetic implant.[142, 146–148]

Another way to utilize wireless powering for optogenetic implants is to harvest RF energy which provides the opportunity for a fully implantable and wireless battery-free approach.[136, 140, 149–151] Recent research have shown RF-powered wireless and independently controlled μ LED-based implants achieved by near field communication (NFC) chip, a microcontroller, and an analog filter for multiple stimulation modes in freely moving animals and regulation of individual animals in a restricted physical space.[136] This work opens an opportunity for studying the social behaviour of animals by optogenetics. Another research work demonstrated flexible wireless RF power transfer technology for stable optical stimulation using 13.56 MHz frequency to reduce physical interference during in-vivo optogenetics.[152] Although the RF power transfer system is vulnerable to angular orientations and physical obstacles,[152–154] and has high propagation loss in soft tissue.[139, 155] Also, it is required to design a specific antenna system based on the resonant frequency to harvest the RF power which leads to a bulky receiver coil system restricting the overall volume-miniaturization of the implant.[156, 157]

In some cases, researchers have investigated a hybrid wireless power transfer technology by combining RF power transfer with a battery in wireless implantable systems.[158] However, this kind of rigid and bulky system restricts biomechanically compatible long-term use within the body.[159] In recent work, a soft subdermal hybrid neural implant with wireless battery charging capabilities and programmable controls was demonstrated for optogenetic applications.[160] Such wireless battery charging capability in a neural implant was not demonstrated before. This allows a stable and long-term operation for the optogenetic implant. Although, the system demonstrated in this case, achieved a volume of $19 \times 12 \times 5 \text{ mm}^3$, which is considered a bulky device compared to the recent miniaturized implants.

As RF energy harvesting systems are bulky because of their requirement for large antennas and have high propagation loss in propagating deep tissue, alternate power sources such as solar power [161], photovoltaic-powered [162], and US-powered systems were investigated. Table

2.2 shows a basic comparison of different RF powering systems where the power conversion efficiency drops rapidly when the antenna size is limited to a few mm^2 .

US powering systems are useful due to several reasons. Firstly, the American Food and Drug Administration limits the deliverable US power to $7.2 \text{ mW}/mm^2$, whereas Federal Communications Commission and IEEE limit the RF exposure power to $10\text{-}100 \text{ }\mu\text{W}/mm^2$. [163] As a consequence of that, the US can deliver a much higher magnitude of power than RF, which is advantageous for optogenetic devices implanted deep inside the tissue. Like RF, US waves are also capable of power and data transfer simultaneously like RF. [164–167]

TABLE 2.2: A comparison of the power conversion efficiency of different RF-powered systems based on the size of the antenna.

Publication	Hucheng et al., 2012 [168]	Sun et al., 2015 [169]	Sun et al., 2015 [170]	Zhang et al., 2015 [171]	Kate L et al., 2015 [118]	Jian-Yu et al., 2014 [172]
Antenna area (mm^2)	80 $\times$ 87	70 $\times$ 70	70 $\times$ 100	40 $\times$ 40	6	2.3
Operating frequency	2.45 GHz	2.45 GHz	2.45 GHz	1.9-3.2 GHz	1.5 GHz	10 MHz
Incident power density	1.95 $\mu W/cm^2$	295.3 $\mu W/cm^2$	207 $\mu W/cm^2$	50 $\mu W/cm^2$	262 mW/cm^2	9 mW/cm^2
Power conversion efficiency	80.3%	78%	73.9%	70%	0.5%	15.2%

Moreover, US waves have a much lower attenuation rate of about $0.5\text{-}1 \text{ dB}/cm/MHz$ in soft tissue and have smaller wavelengths in tissue (e.g. 1.5 mm at 1 MHz), which enables focusing down to 1 mm spot to a longer depth. [165, 173] As US can be focused on a small region, the coupling efficiency gets much higher, and very high acoustic-to-electrical conversion efficiency can be achieved with a sub-millimeter-sized receiver (such as PZT) in that case. Such a US-powered wireless implantable system of millimeter size was demonstrated, consisting of a PZT harvester, recording electrodes, and a transistor that works as a sensor for the muscle or nerve implants. [174]

2.5 Ultrasound-powered optogenetic implants for optical stimulation

The comparative discussion on different implant-powering technologies described in section 2.4 clearly shows that US-powering technology has several critical advantages over RF powering in realizing fully-implantable wireless neural implants. In contrast to conventional optical fiber-based light delivery systems, μ LEDs also have received significant recognition in the field of wireless optogenetics as the main light source due to their smaller chip size, higher efficiency, and better accuracy on light delivery at a specific location deep inside the body of freely moving animals.

A US-powered implant integrated with commercially available surface-mounted blue 470 nm and red 640 nm μ LED was demonstrated for the application in photodynamic therapy, which is capable of generating 0.048 mW/cm^2 to 6.5 mW/cm^2 optical power (based on the size of the PZT and LED wavelength) while exposed to 1.85 mW/mm^2 acoustic power at 0.72 MHz frequency.[175] Another reported work showed a US-powered implantable device with integrated optical stimulators, which are driven and controlled by a programmable US transmitter of an external area of 15 mm^2 for optogenetics.[176] An optical power density of 15 mW/mm^2 was achieved from the 460 nm blue LED when driven by 1.9 mW/mm^2 acoustic power in this case. In 2021, a group from Columbia University demonstrated the smallest sub 0.1 mm^3 wireless US-powered implantable mote (This sub-0.1- mm^3 , sub-1-nW device was referred to as a mote) for temperature sensing in real-time. The device consists of a CMOS chip, and PZT (without any optical source) was achieved by monolithic integration showing that further miniaturization can be achieved.[177] Over the years, there have been many research papers that successfully demonstrated miniaturized US-powered implants for applications in optogenetic studies.[139, 155, 178–181] Although, US-powered neural implants are still not that matured in comparison to RF-powered implants and require more attention.

2.6 Importance of high-efficiency micro-LEDs for optogenetic applications

Further miniaturization of optical stimulation-based neural implants requires a higher efficiency and smaller light source for in-vivo studies to eliminate the need for fiber-optic-based laser systems or other bigger light sources. As the biological tissue has high absorption and scattering, it is difficult to have an efficient light delivery system in the visible range deep in the tissue.[182, 183] Commercial LEDs generally comes in different packaging, which becomes bulky and impacts the volume of the implant. Micro-LEDs offer a significant advantage in this case due to their smaller volume and the capability of deep tissue implantation.

Activation or inhibition of neural channels typically requires a power density of about 1-5 mW/mm^2 at a specific wavelength transfected with ChR-2.[184–187] Also, different wireless implant powering technologies can generate only a limited amount of electrical power ($< 2-3 mW$) and supply to the LED. Therefore, it restricts the amount of optical power that can be achieved from the LED which implies that the higher the efficiency of the LED, the more power achieved. Hence, the efficiency of μ LEDs plays an important role in optogenetic implants. Table 2.3 shows a list of different variants of opsins along with their peak wavelength responsivity and required minimum power density for channel activation.[116, 188, 189] Although some newer opsin such as ChEF requires less power density at 470 nm than ChR-2 for activation, the channel closing rate is longer [see Table 2.3].

Also, it is required that the LEDs are highly efficient so that they do not generate much heat during in-vivo operation, as a temperature increase of more than 1 $^{\circ}C$ could result in damage to the tissue.[190, 191] The design, dimensions, and metallization contacts of the light source need to be compatible with corresponding electronics and other components of the implants. Hence, custom-made and high-efficiency μ LEDs have immense importance in the realization of fully implantable wireless neural implants with an integrated light source. It is challenging to fabricate a blue μ LED (for blue-sensitive ChR-2) with a mesa diameter of less than 150 μm that can generate more than 5 mW/mm^2 power density while operating at a low bias of < 1 mA. Also, this power density depends on the distance from the LED surface; as the distance increases, the power density decreases following the inverse square law ($I_p \propto 1/d^2$), where I_p is the power density and d is the distance from the LED surface.

TABLE 2.3: Comparison between different channelrhodopsins with respect to peak wavelength responsivity, required activation power, channel opening rate, and closing rate.

Channel variant	Peak response wavelength (nm)	Minimum activation power density (mW/mm^2)	Channel Opening rate (τ_o) at 19.8 mW/mm^2	Channel closing rate (τ_c) at 19.8 mW/mm^2
VChR-1	~ 570	not tested	$\sim 2.80\ ms$	$> 90\ ms$
ChR-2	~ 470	~ 1.10	$\sim 1.21\ ms$	$\sim 13.5\ ms$
ChR-2/H134R	~ 450	~ 1.07	$\sim 1.92\ ms$	$\sim 17.9\ ms$
ChETA	~ 490	~ 5.02	$\sim 0.86\ ms$	$\sim 7.9 - 8.5\ ms$
ChEF	~ 470	~ 0.72	$\sim 1.56\ ms$	$\sim 24.9\ ms$
ChIEF	~ 450	~ 1.65	$\sim 1.62\ ms$	$\sim 12.0\ ms$
ChD	~ 450	~ 3.32	$\sim 1.49\ ms$	$\sim 7.82\ ms$
ReaChR	$\sim 590 - 630$	~ 5.00	$\sim 0.50\ ms$	$\sim 137\ ms$

2.7 Summary and motivation

The advancement in the field of optogenetics and its contribution to realizing neural implants shows excellent prospects for the future of neuroscience. Optogenetics not only requires sophisticated genetic engineering but also needs highly efficient μ LEDs for optical stimulation in advanced neural implants. The study of different implant-powering technologies establishes the advantage of ultrasound powering in wireless neural implants for in-vivo applications.

These foundational works give the motivation to develop a new ultrasound-powered neural implant integrated with high-efficiency μ LEDs for optogenetic applications. The proposed neural implant required mainly three functioning components, namely a PZT harvester, a μ LED, and a CMOS chip. The design and development of the CMOS chip were done by our collaborators from Aarhus University, as well as the study of PZT. In this thesis, one of the main focuses is the development of high-efficiency μ LEDs in blue, UV wavelength, and dual-wavelength chips starting from the design and fabrication to characterization. Also, integration and packaging of the development of neural DUST is another focus of this thesis.

In the later chapters, the design and fabrication of highly efficient blue, UV, and dual-wavelength μ LED chips are discussed in detail, highlighting the electro-optical characteristics and engineering challenges addressed to enhance EQE. A detailed discussion was provided in this thesis to show the development of a potential ultra-localized implant-compatible drug delivery system. Finally, a chapter dedicated to the integration and packaging of the US-powered neural DUST for optogenetic applications and its demonstration. With further research, this work holds immense potential for the future of wireless and fully-implantable systems in the field of neuroscience.

Chapter 3

Design, fabrication and characterization of efficient blue and UV micro-LEDs for neural DUSTs

3.1 Introduction

The aim of this chapter is to present the design, fabrication, and characterization of highly efficient blue and UV μ LEDs compatible with the neural DUST. The design of the μ LEDs directly depends on the custom-designed and fabricated electronic chips and PZT harvester. The dimensions of the μ LEDs are optimized such that they can be integrated directly with the available electronic die. Three different mesa sized μ LEDs were designed to determine the most suitable device for the application.

The electronic CMOS chip containing an active bridge rectifier with an external dimension of $300 \times 300 \times 300 \mu m^3$ was used to convert the incoming AC power from the PZT crystal into DC power which is supplied to the μ LED load at the output of the bridge. A maximum of $2.2 mW$ of power can be delivered to the μ LED by the electronic die. As the voltage limit of the electronic die is $3.3 V$, it can deliver a maximum of $1 mA$ to the μ LED. Therefore the μ LEDs need to be highly efficient while operating below $1 mA$ depending on the turn-on voltage. Several factors can influence the efficiency of the μ LED, including the wafer quality, geometry, ohmic contact, Anti-Reflection Coating (ARC), and reflective metal contact, which will be discussed in this chapter.

The results of characterizing the blue and UV μ LEDs are presented in this chapter. The characterization was performed to measure the performance of the devices in the key areas of μ LED performance: I-V characteristics, ideality, optical power, spectral quality, and efficiency. A low turn-on voltage below wavelength bandgap was observed in both blue and UV μ LEDs and discussed in section 3.4.6. A high WPE of 40.7% from the blue and 25.4% from the UV μ LEDs were achieved in this case.

3.2 Design of blue and UV LED

It is essential to engineer the devices for the application, and here, the design of the blue μ LED involves several key parameters:

1. Capable of generating $> 5 \text{ mW/mm}^2$ power density with a peak wavelength of 470 nm - 480 nm , which is the minimum requirement for activating blue light-sensitive protein (ChR-2)
2. Have an operating voltage below 3.3 V , the supply limit of the electronic die
3. Highly efficient while operating at a low forward bias ($\approx 1 \text{ mA}$)
4. The physical dimension is matched with the electronic die so that it can be integrated directly with the electronic chip
5. A UV μ LED (370 nm) for activating the localized DDS based on UV-sensitive photochromic polymer.

The μ LEDs were designed based on the layout of the electronic die. The $300 \times 300 \text{ }\mu\text{m}^2$ electronic chip has two $50 \times 100 \text{ }\mu\text{m}^2$ pads for the μ LED with a gap of $200 \text{ }\mu\text{m}$ between them. The layout of the electronic chip is presented below in Figure 3.1(a).

Based on the electronics, bottom-emitting μ LEDs were designed with the external dimensions of $130 \times 300 \text{ }\mu\text{m}^2$ having p and n contacts of size $100 \times 72.5 \text{ }\mu\text{m}^2$ and the mesa size was varied from $90 \text{ }\mu\text{m}$ to $120 \text{ }\mu\text{m}$ diameter 3.1(b). Mesa sizes lower than $90 \text{ }\mu\text{m}$ was not taken into consideration as that gives a lesser metal-semiconductor interface area, which results in higher resistivity. Though a mesa area higher than $120 \text{ }\mu\text{m}$ would be better in terms of contact resistivity and light output power but is not permitted due to dimension restrictions of the ele-

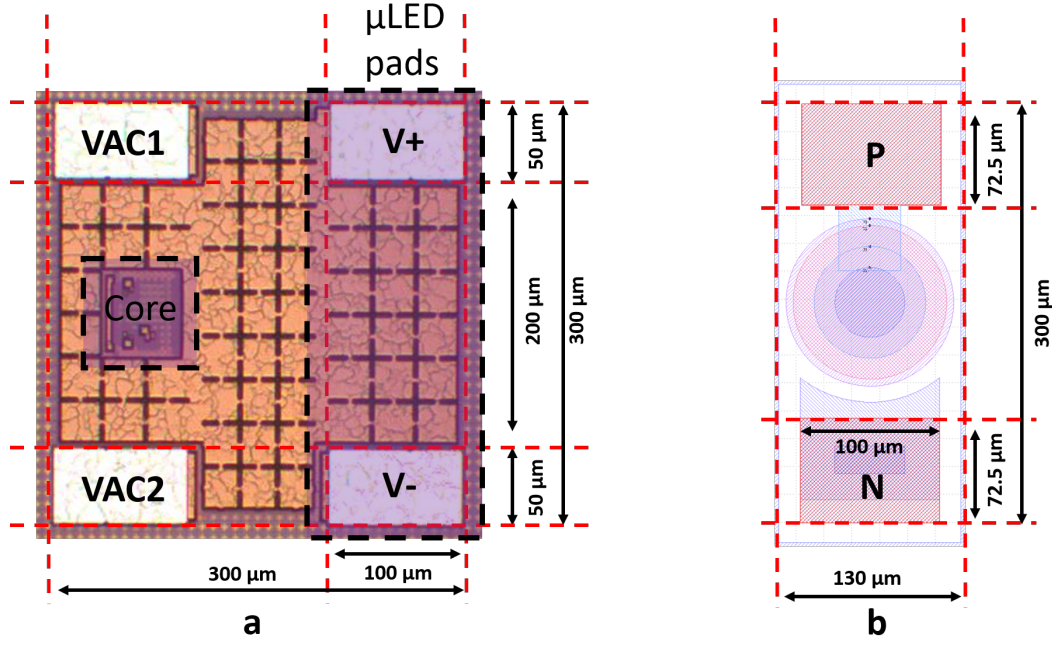


FIGURE 3.1: Layout of the (a) electronic die and (b) compatible μ LED.

electronic chip. The mesa was designed to be 5 μm wider than the p-metal. 30 μm wide lines around the μ LED were designed, which will be formed during the oxide etch step to assist mechanical dicing into individual LED chips.

3.3 Fabrication of BLUE and UV micro-LED

A detailed outline of the fabrication process flow is described here, from the choice of wafer material and wafer cleaning to the fabrication steps.

Commercially sourced *InGaN*-based blue and UV LED materials grown on a PSS were used to aid the out-scattering of the light and the epi-structure of both the LED wafer are presented in Appendix A.

3.3.1 Surface preparation

To achieve a high-quality ohmic contact between metal and semiconductor, the wafer surface must be cleaned before the p-metal is deposited. Initial tests showed that metal deposited on an uncleaned wafer has higher contact resistivity than on a cleaned wafer due to the presence

of different contaminants. During the epitaxial growth process of GaN, there is a likelihood of forming carbon (C) and oxides on the p-GaN surface, which act as a barrier to hole transport and increase the p-contact resistivity [192]. There is also a possibility of having some residual metal contaminants on the surface.

To remove the oxide from the surface, the samples were first cleaned with buffered oxide etchant (BOE) as BOE can effectively etch silicon dioxide (SiO_2) and silicon nitride (Si_3N_4). Then 1 : 1 = HCl : DI solution was used to remove metal contaminants. Finally, the samples were cleaned with 45% potassium hydroxide (KOH) solution as KOH is highly effective in removing C. The detailed cleaning process was:

- Initial cleaning with acetone and IPA followed by DI rinse
- 5 minutes in BOE followed by DI rinse
- 5 minutes in HCl : DI = 1 : 1 and rinse with DI
- 30 seconds in 45% KOH at 90 degrees and thoroughly rinse with DI

Once the samples were thoroughly rinsed with DI water, they were dried with oxygen-free nitrogen (OFN).

3.3.2 LED fabrication process flow

The fabrication process begins with a p-metal deposition. Initial tests on different p-metals showed that $Pd/Ni/Au$ contacts provide a lower resistance ohmic contact than $Ni/Ag/Ni$ contact with a low ρ_c of the order of $< 10^{-4} \Omega cm^2$ and, were more stable under higher temperatures than bare Pd or $Ni/Ag/Ni$ [see Appendix B and Appendix C]. Therefore, $Pd/Ni/Au$ metallization was chosen as p-contact for the final devices.

The detailed fabrication process flow is schematically presented in Figure 3.2. A two-level lift-off resists lithography was done to pattern the cleaned semiconductor surface. First, the samples were baked at 150 °C for 5 minutes to dehydrate the samples, and adhesion promoter ($HMDs$) were spray coated at 120 °C. Pre-exposed photoresist ($PMGI SF11$) was then spun on the samples and cured for 5 minutes at 170 °C. Then an imaging resist ($S1813$) was spun at 4000 rpm for 50 seconds and baked at 115 °C for 3 minutes. The patterns were developed

by exposing the samples through a chrome-quartz mask and dipping into developer (*MF319*). The final bake was done by placing the samples on the hotplate for 5 minutes at 120 °C.

Just before loading the samples for metal evaporation, they were dipped in aqua-regia (3 *HCl* : 1 *HNO*₃) for 30 seconds to remove any oxide from the surface. *Pd/Ni/Au* of 10/20/30 nm was then E-beam evaporated onto the samples and left for a few hours in photoresist remover (*RR 1165*).

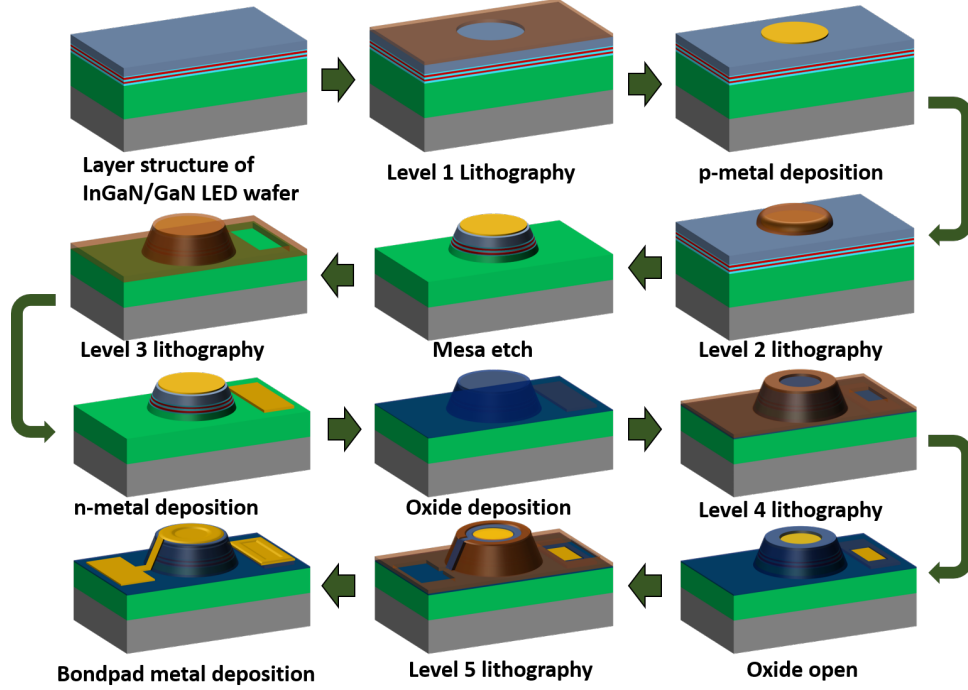


FIGURE 3.2: Schematic of fabrication process flow of blue 480 nm and UV 370 nm μ LED.

Pd/Ni/Au p-contact on the blue LED wafer was ohmic as deposited, whereas on the UV LED wafer, it was highly non-ohmic. The annealing condition for the UV wafer was optimized, and the best ohmic contact ($\rho_c=10^{-4} \Omega \text{ cm}^2$) was achieved when the sample was furnace annealed in N_2 for 10 minutes at 500 °C. The details of the optimization of the annealing conditions are provided in Appendix B.

In order to form the mesa, the samples need to be etched through p-GaN and MQW into n-GaN. A thick photoresist (*S1828*) was spun and developed to expose the regions to be etched. After developing the pattern, the samples were baked at an elevated temperature (150 °C) for 3 minutes to cure and re-flow the photoresist. The reflow helps to form sloped mesa during inductive coupled plasma (ICP) etch. About 1.2 μm was etched to form the mesa by Cl_2 assisted ICP etch. The photoresist cross-links during ICP etch which makes it harder to

remove by 1165. For this purpose, the samples were treated with O_2 plasma at 50 W for 5 minutes and then dipped into 1165 and kept overnight to strip the resist.

A third lithography step was done by two-layer lift-off resist using *PMGI SF11* and *S1828* to define regions for n-metal deposition. Before loading for evaporation, the samples were treated with O_2 plasma. *Ti/Al/Ti/Au* of 20/170/50/150 nm was then deposited by e-beam evaporation at a chamber pressure of 10^{-7} torr and finally, lifted-off the resist by 1165. At this point, the basic LEDs were ready for testing to validate the functionality of the device.

To passivate the surface, a blanket 300 nm SiO_2 was then deposited by sputtering. Another lithography level was done to open sections for bondpad and etched by C_4F_6 assisted plasma etch. A final two-layer lift-off lithography was done to deposit bondpad metal. 20/200 nm thick *Ti/Au* was deposited by 360° e-beam evaporation as bondpads.

3.3.3 Back-end processing

It is necessary to separate out the individual μ LED chips so that they can be integrated with the compatible electronic dies. The back-end processing of the wafer involves grinding-polishing of the sapphire substrate, deposition of ARC on the back surface to enhance the out-coupling of light, and finally, dicing.

3.3.3.1 Grinding and polishing

Grinding of the sapphire substrate is much more difficult than free-standing GaN or Si substrate and is a relatively slow process. The samples were mounted on a circular glass disk by OCON-200 wax (melting point 70 °C). A weight was applied to flatten the samples. Boron Carbide (*BC*) in DI (*BC* : *DI* = 1 : 6) and 9 μ m fused aluminium oxide powder was used during mechanical polishing. The samples were thinned down to 110 μ m from 350 μ m. As mechanical grinding is a crude process, it leaves severe scratch marks on the sapphire surface. A semi-polishing was done on the samples using 3 μ m sapphire powder and Logitech's SF1 polishing solution. Once the polishing was done, the samples were removed from the glass holders with acetone. [see Appendix D]

3.3.3.2 ARC coating

Once the samples are thinned down, an ARC coating was applied to the back surface of the Blue LED samples. No coating was applied on the UV LED wafers as UV is absorbed by most materials. The simulation for ARC coating using SiO_2 is presented in Figure 3.3. The simulation clearly shows that 83 nm thick SiO_2 has highest transmittance of 87% at 480 nm. Therefore 83 nm SiO_2 was sputtered deposited on the back of the semi-polished sapphire substrate as ARC.

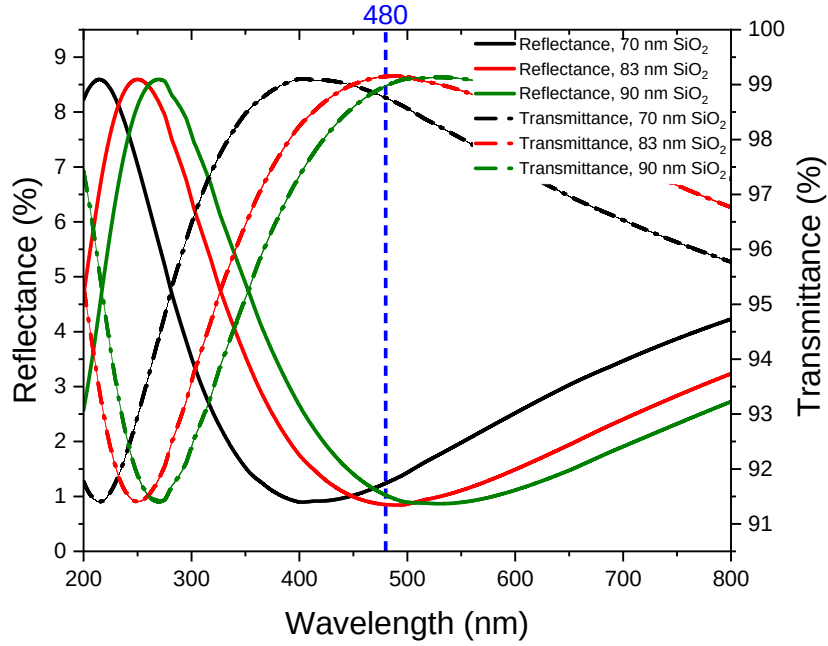


FIGURE 3.3: Simulation for SiO_2 -based anti-reflection coating.

3.3.3.3 Dicing

Finally, the μ LEDs were diced into individual chips by a semi-automatic dicing machine. Specialized dicing blades with 25 μm kerf width was used for this purpose. The dotted red line indicated in Figure 3.4 represents the line/kerf for dicing. See Appendix D for details of the dicing process.

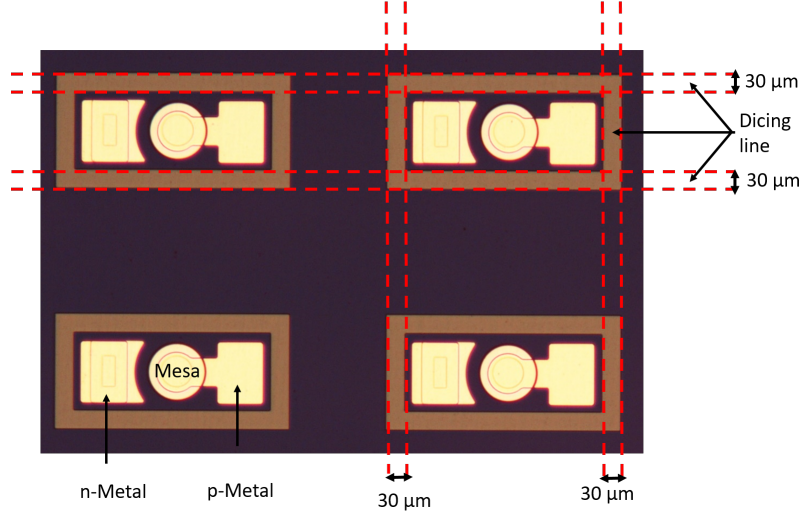


FIGURE 3.4: dicing indicator.

3.4 Characterization of BLUE and UV LEDs

The light-current-voltage (LIV) characterization of the μ LEDs was measured by probing devices on the wafer. The light output power from the probed devices was measured by silicon photo-detectors at a numerical aperture of 0.5, 1 and using an integrating sphere. The significance of different NA and integrating sphere measurements are discussed later in subsection 3.4.4.

3.4.1 Current-Voltage characteristics

The I-V characteristics of the fabricated μ LEDs were measured by driving with a Keithley 2400 sourcemeter and measuring the corresponding voltage with a Keithley 2000 multimeter as schematically shown in Figure 3.5. The I-V characteristics of 90 μm , 100 μm and 120 μm mesa sized blue and UV μ LEDs are shown in Figure 3.6.

The blue and UV μ LEDs have a low turn-on voltage of 2.3 V (photon energy 2.5 eV) and 3.1 V (photon energy 3.3 eV), respectively while operating at a forward bias of less than 50 μA . Both of these voltages are lower than the corresponding photon energy and a possible explanation for such behaviour is highlighted later in subsection 3.4.6. It is evident from the figure that the series resistance of 90 μm mesa blue μ LED is slightly higher than 100 μm and 120 μm device which is the result of a smaller metal-semiconductor contact area and reduces the WPE (light output power/ electrical power) of the 90 μm mesa μ LED. The UV μ LEDs also showed similar

behaviour with the variation of mesa size. These results suggest that 100 μm and 120 μm mesa μ LEDs are more suitable for neural DUSTs due to relatively lower power consumption.

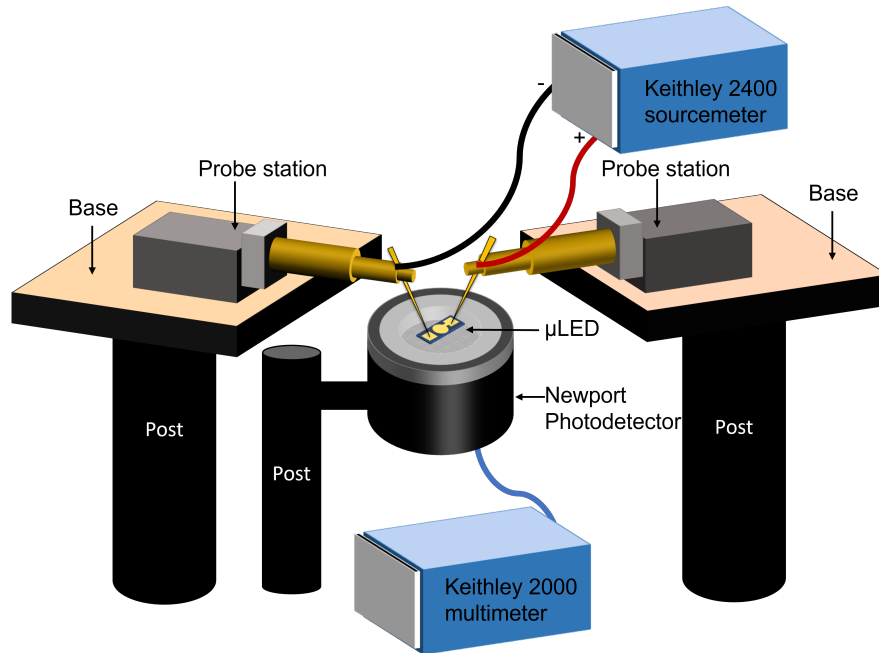


FIGURE 3.5: Schematic of the experimental setup used to measure the LIV characteristics by probing the μ LED with Keithley 2400 sourcemeter and measuring the optical power using a photodetector connected to Keithley 2000 multimeter.

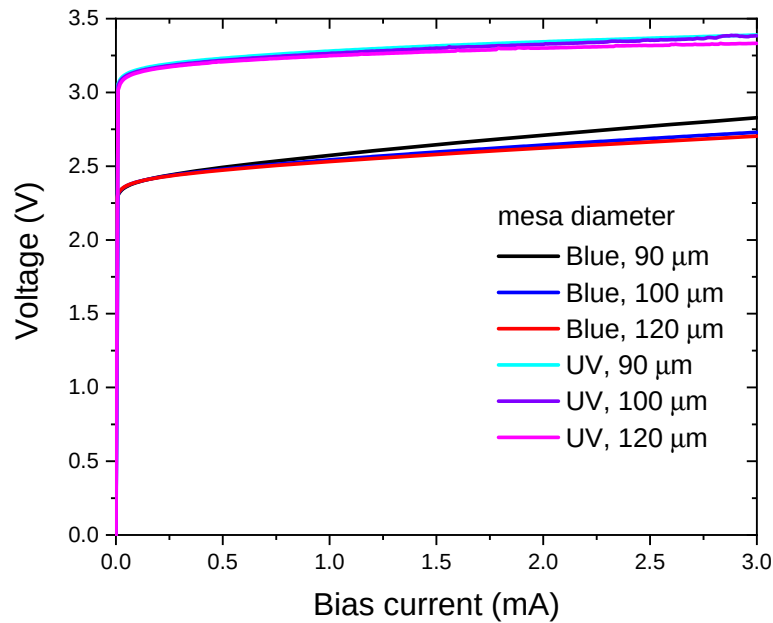


FIGURE 3.6: I-V characteristics of blue and UV μ LEDs driven in DC mode.

3.4.2 Ideality factor

The ideality factor (η) is the electrical measure of a diode to determine how closely the current-voltage follows the ideal diode equation. The ideal diode equation is as follows,

$$I = I_s \exp[eV/\eta_i KT] \quad (3.1)$$

Where η_i is the ideality factor. For the ideal diode, $\eta_i = 1$, corresponds to both diffusion current and radiative recombination and increases as the diode deviates more from the ideal diode. Whereas the $\eta_i = 2$ corresponds to non-radiative recombination. [67]

Figure 3.7 shows that the ideality of the blue μ LED reaches a very low value of 1.26 at 2.3 V, indicating highly efficient radiative recombination. Figure 3.8 shows that the UV μ LEDs reaches a very low ideality of 1.49 and 1.52 for a 120 μ m and 100 μ m mesa devices respectively at a voltage of 3.12 V, whereas the 90 μ m mesa UV-device has the ideality of 1.57 at 3.13 V.

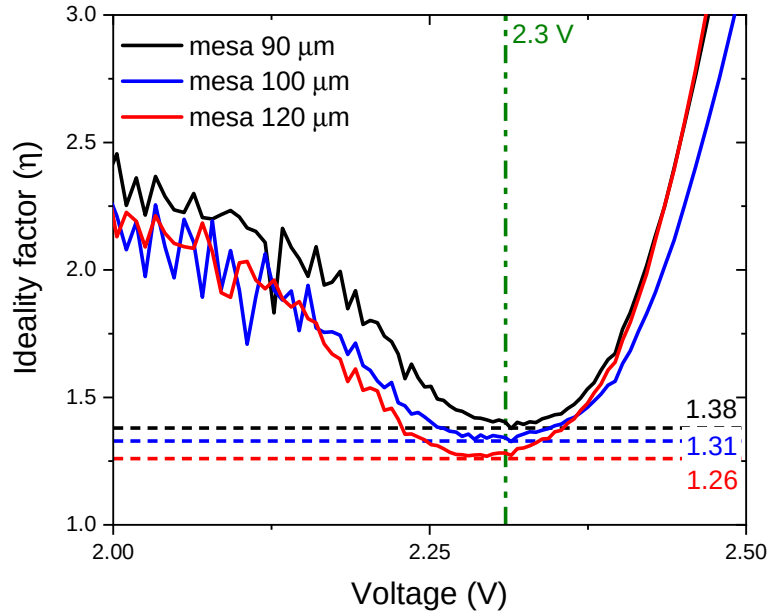


FIGURE 3.7: Ideality factor comparison among different mesa sized blue μ LEDs as a function of applied voltage.

It can be seen from Figure 3.7 and 3.8 that the ideality was measured to be lowest near the turn-on voltage of the LEDs, which is the region where the radiative recombination process dominates. The ideality factor between 1.0 and 2.0 is mainly due to the carrier drift-diffusion and generation-recombination process.[193] As the ideality of the blue and UV μ LEDs were measured to be below 2.0, it represents efficient radiative recombination.

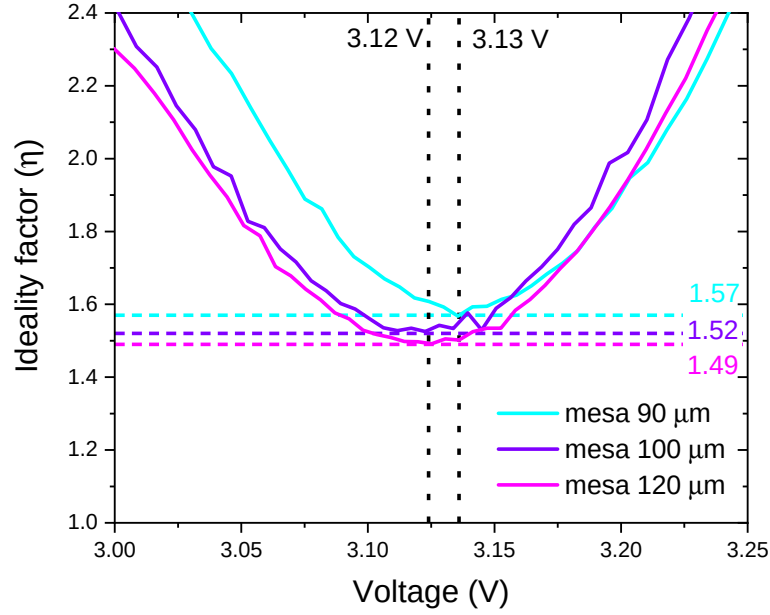


FIGURE 3.8: Ideality factor comparison among different mesa sized UV μ LEDs as a function of applied voltage.

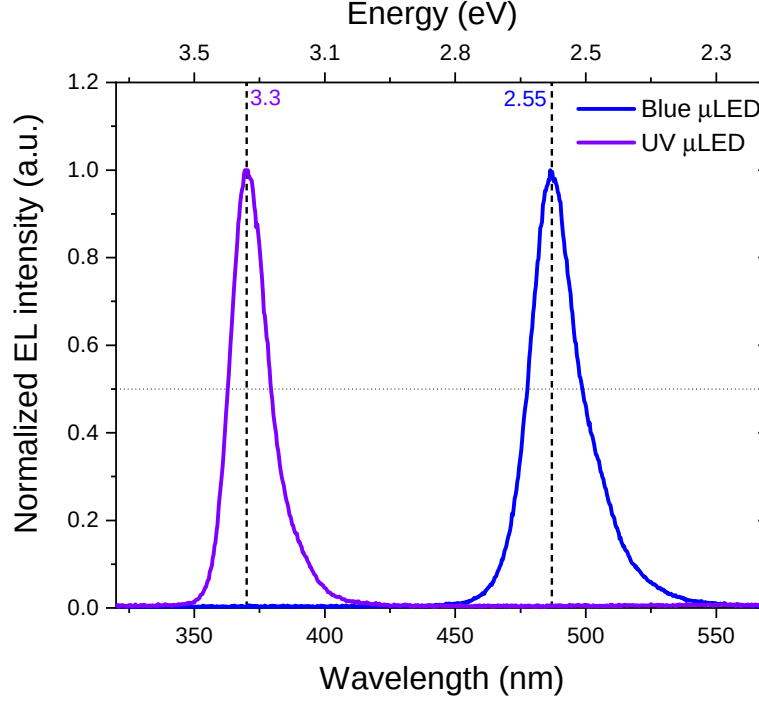
Good quality GaN-based epi-materials in the UV range (≤ 380 nm) are challenging to grow, which could be one of the main reasons for having a high ideality factor in UV devices than in Blue.

As expected from the I-V characteristics [Figure 3.6], the 120 μ m mesa blue μ LED has the lowest ideality than 100 μ m ($\eta = 1.31$) and 90 μ m ($\eta = 1.38$) devices. These electrical characteristics suggest that the 120 μ m mesa μ LED is more suitable for the neural DUST. However, these bigger-sized devices are incompatible with the electronic die and prone to damage during dicing. Therefore 100 μ m mesa μ LEDs were chosen for the integration with the DUSTs.

3.4.3 Electroluminescence Spectra

The electroluminescence (EL) spectra of the μ LEDs were shown in Figure 3.9, which was obtained by probing the devices and collecting the light with a fiber-coupled UV-Vis spectrometer at a bias current of 3 mA.

The EL spectra of the blue LED peaked around 483 nm, which is perfectly suited for the excitation of channelrhodopsin transfected cells. Whereas, the UV LED peaked at 371 nm which is rightful for activating the drug delivery system. An FWHM of 16.8 nm and 21 nm was measured from UV and blue μ LEDs, respectively.

FIGURE 3.9: Normalized electroluminescence spectra of UV and Blue μ LED.

3.4.4 Optical power

The optical power from the bottom-emitting 100 μm mesa blue μ LEDs was measured at $NA=0.5$, $NA=1$ and using an integrating sphere and the schematic setup is shown in Figure 3.10. Here, NA of 0.5 corresponds to the collection of light at a solid angle of 30° [Figure 3.10(a)] whereas, NA of 1 represents the collection of all the light coming only from the bottom surface (through the sapphire substrate) of the μ LED chip [Figure 3.10(b)]. The Optical power measured in an integrating sphere corresponds to the collection of light from all the surfaces of the μ LED respectively [Figure 3.10(c)]. The optical powers measured from the blue μ LEDs are presented in Figure 3.11.

At 1 mA , an optical power of 0.11 mW was measured at an NA of 0.5 (black line), whereas 0.71 mW when measured at a NA of 1 (red line). Theoretical calculations showed that a power of 7 times more can be achieved in $NA = 1$ than in $NA = 0.5$ which is in good agreement with the measured power. Assuming the LED as a point source and the emission profile of the LED is Lambertian, the optical flux measured at a numerical aperture θ is given as,

$$\Phi = \int_0^\theta \Phi_o 2\pi r^2 \sin \theta d\theta = 2\pi r^2 \Phi_o [-\cos \theta + \cos 0] \quad (3.2)$$

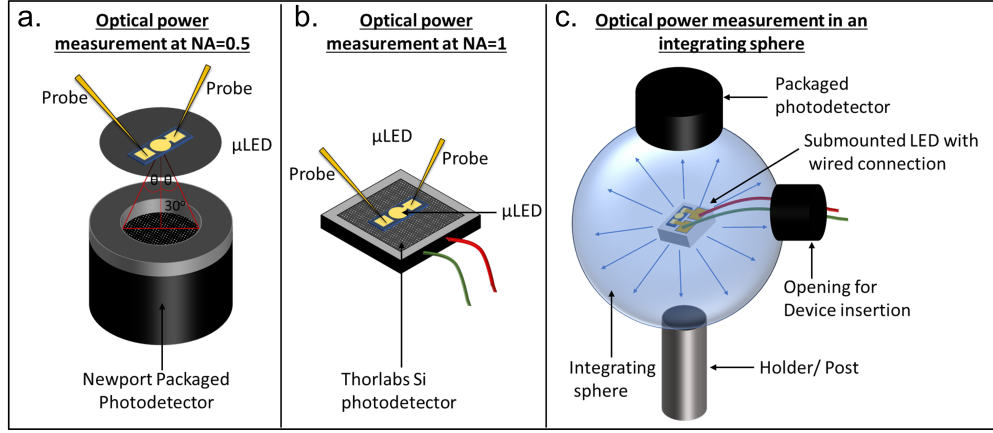


FIGURE 3.10: Schematic illustration of measuring optical power at (a) NA of 0.5, (b) NA of 1 and, (c) using an integrating sphere.

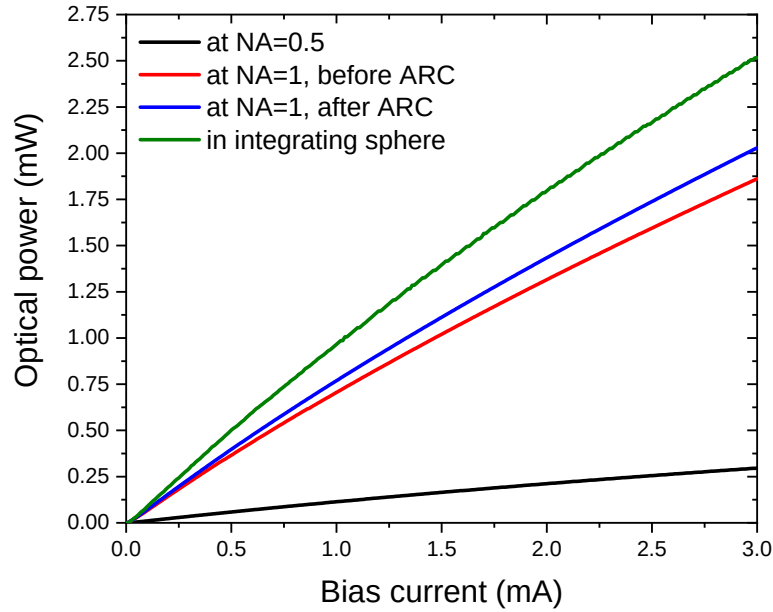


FIGURE 3.11: Optical power measured from the fabricated blue μ LEDs as a function of bias current. The black line shows the power measured at a solid angle of 30° , the red and blue line represents power measured at a numerical aperture of 1 with and without anti-reflection coating, respectively, and the green line represents the power measured in an integrating sphere.

When, the NA=1 indicates $\theta = 90^\circ$ and NA=0.5 implies $\theta = 30^\circ$. Supplementing these values in equation 3.2 we get $\Phi_{90} = 2\pi r^2 \Phi_o$ and $\Phi_{30} = 0.26\pi r^2 \Phi_o$. Dividing Φ_{90} by Φ_{30} a factor of 7.5 calculated which means about 7 times higher power can be achieved when measured at NA=1 than at NA=0.5. A 10% power improvement was achieved by ARC coating (blue line) than in non-ARC coated samples (red line). When measured using an integrating sphere, a total power of 1 mW was measured by the same 100 μ m mesa blue μ LED operating only at 1 mA, 2.5 V. A power density of 127 mW/mm² was calculated in this case when the mesa area (7850 μ m²) was considered as the main light generating area. which is more than the requirement

for activating light-sensitive proteins.

The optical power from the $100\ \mu\text{m}$ UV μ LEDs was measured at $NA=1$ and in integrating sphere, presented in Figure 3.12. At $1\ \text{mA}$ an optical power of $0.28\ \text{mW}$ was measured at $NA=1$ (pink line). When measured using an integrating sphere, a total power of $0.66\ \text{mW}$ was measured under the same driving current, $3.26\ \text{V}$ (violet line). Note that during the measurement in the integrating sphere, the UV μ LEDs were mounted on patterned glass substrates and encapsulated by UV curable epoxy, which includes absorption depending on the thickness of the epoxy at $370\ \text{nm}$. Therefore, we can expect the output power to be slightly higher than measured.

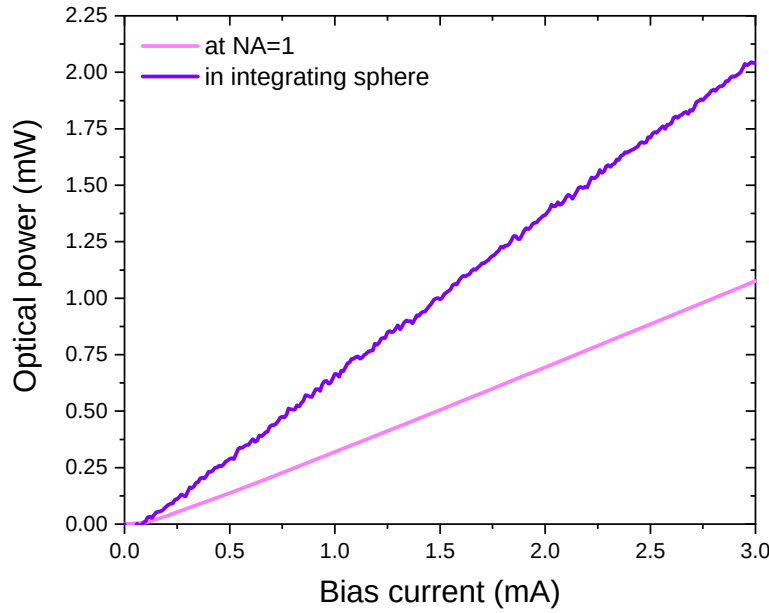


FIGURE 3.12: Optical power measured from the fabricated UV μ LEDs as a function of bias current. The magenta line shows the power measured at a numerical aperture of 1, and the violet line represents the power measured in an integrating sphere.

3.4.5 Efficiency

The efficiency of the μ LEDs plays a crucial role in evaluating the performance of the neural DUSTs. The efficiencies of the μ LEDs were measured in terms of external quantum efficiency (EQE) and wall-plug efficiency (WPE), where EQE refers to the ratio of the number of photons coming out of the μ LED chip with the number of injected electrons, and WPE refers to the optical power out for input electrical power.

The highest EQE was for the blue μ LEDs measured at 0.4 mA, where an EQE of 31% was obtained at NA of 1 and 39% when measured in the integrating sphere. A record EQE of 48.6% was demonstrated from a $100 \times 100 \mu\text{m}^2$ blue LED by a group from California.[194] A high WPE of about 41% was achieved from the blue μ LEDs when optical power was measured in an integrating sphere. Note that a WPE of 2% higher than EQE was achieved at 0.4 mA [Figure 3.13]. As the current density increases, carrier leakage and non-radiative Auger recombination mechanisms start to come to play, causing the efficiency droop of about 6% at 3 mA. A high EQE of 24.9 % with WPE of 25.4 % is achieved for the UV μ LEDs when measured in an integrating sphere as shown in Figure 3.14. These achieved EQE is higher compared to some recent literature published in [195–198].

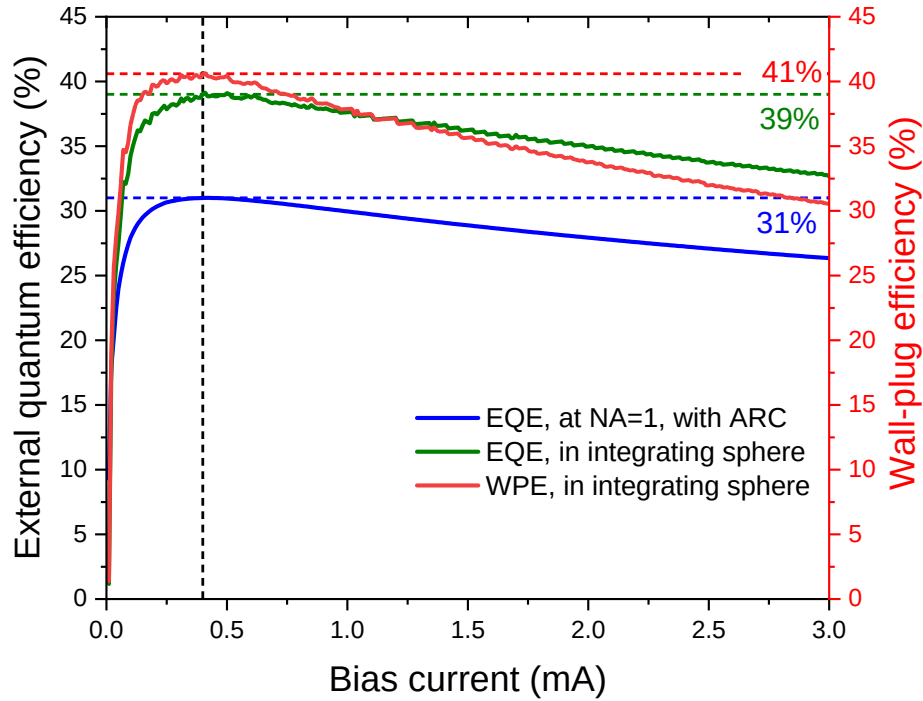


FIGURE 3.13: Shows external quantum efficiency and wall-plug efficiency of the blue μ LEDs as a function of bias current.

It was observed that the blue and UV μ LEDs have a turn-on voltage of 2.3 V and 3.1 V, respectively, which is lower than the band-gap energy of the corresponding peak wavelength ($V_{peak} = 2.567 \text{ eV}$, $\lambda_{blue} = 483 \text{ nm}$ and $V_{peak} = 3.334 \text{ eV}$, $\lambda_{UV} = 371.9 \text{ nm}$). As a result of this sub-bandgap turn-on, the WPE is measured about 2% and 1 % higher than EQE for the blue and UV μ LEDs, respectively.

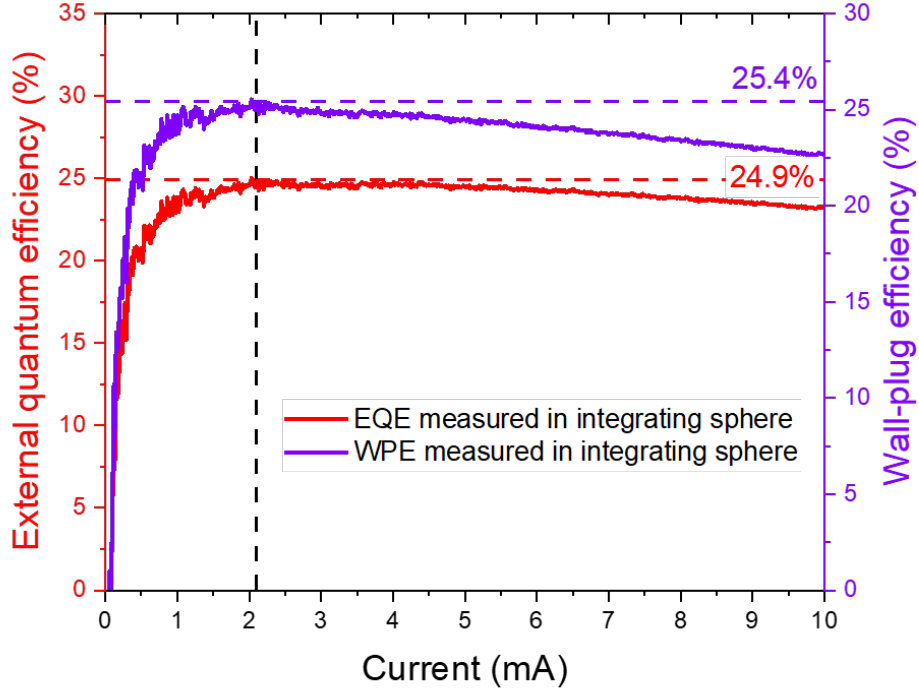


FIGURE 3.14: Shows external quantum efficiency and wall-plug efficiency of the UV μ LEDs as a function of bias current.

3.4.6 Sub-bandgap voltage analysis

To investigate the sub-bandgap voltage and the fact that the WPE is higher than EQE at low current density, semi-logarithmic I-V curve [Figure 3.15 A, B], Optical power on a semi-log scale with EQE on a linear scale as a function of V_{appl} [Figure 3.15 C, D] and normalized intensity as a function of energy (eV) [Figure 3.15 E, F] is plotted for blue and UV μ LEDs respectively.

The effect of SRH non-radiative recombination was observed in the semi-logarithmic I-V curve from bending of the curves at the low voltage of the plots Figure 3.15 A, B], whereas the central linear region is the part where radiative recombination starts to dominate. It is observed that the junction voltages (V_{junc}), which is the voltage across the p-n junction, were measured at 2.43 V and 3.239 V when the applied voltage (V_{appl}) were 2.48 V and 3.267 V for the blue [Figure 3.15 A] and UV [Figure 3.15 B] μ LEDs respectively. An excess voltage of 50 mV and 28 mV was measured in V_{appl} than the V_{junc} , which is the effect of series resistance induced by the metal contacts. The relationship between the V_{junc} and V_{appl} is that $V_{appl} = V_{junc} + IR_s$, where IR_s is the voltage induced by the metal contacts of the LED. The comparison between

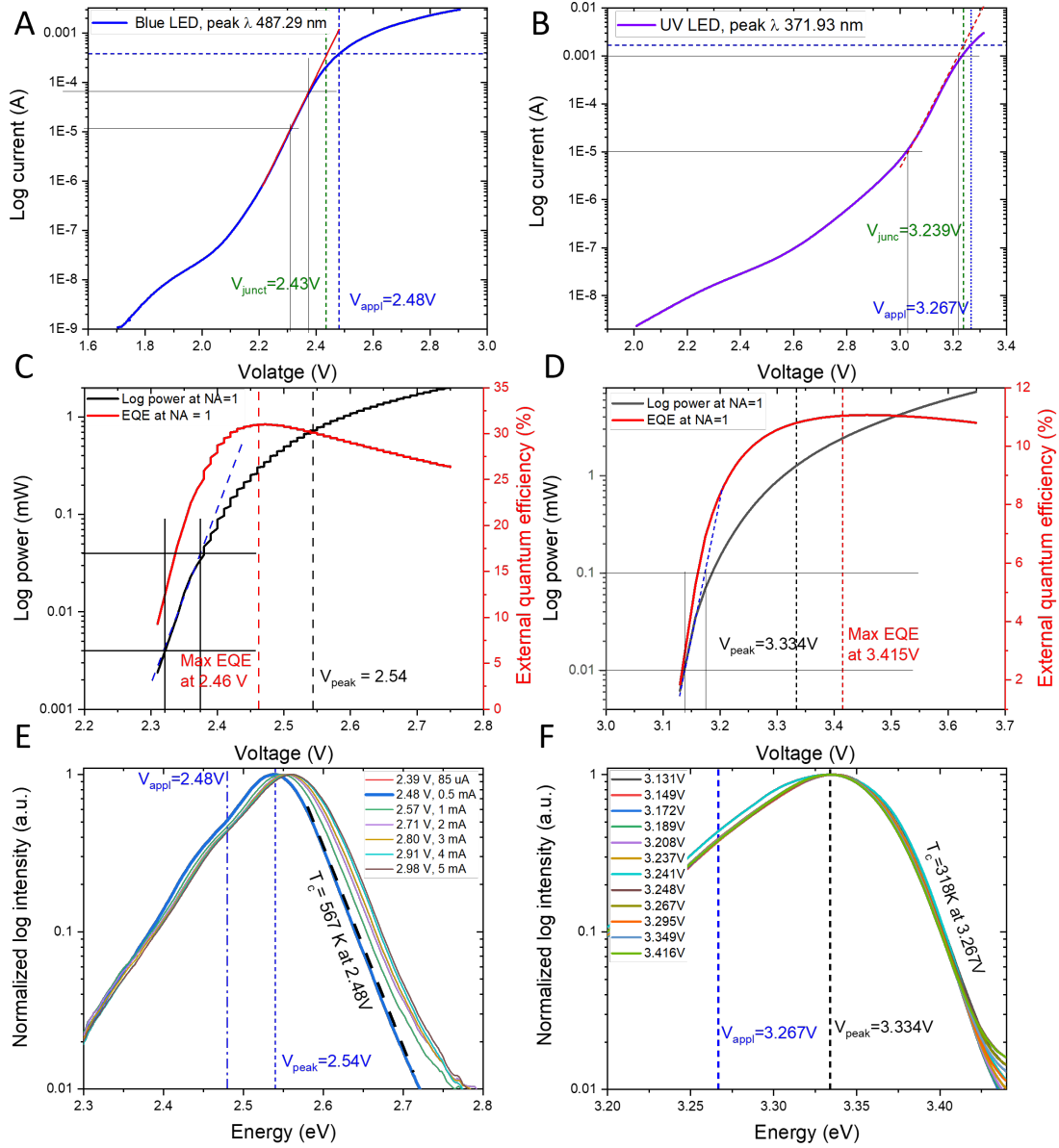


FIGURE 3.15: Sub bandgap voltage analysis.

the V_{junc} and V_{appl} clearly shows that for radiative recombination, an excess voltage than V_{junc} is needed to overcome the resistance due to the metal contacts.

Figure 3.15 C shows that the peak efficiency of the blue devices is at a voltage of 2.46 V whereas the voltage corresponding to the peak wavelength (V_{peak}) is 2.54 V and for the UV device [Figure 3.15 D] the peak efficiency is measured at 3.415 V when the V_{peak} is measured at 3.334 V. A stronger efficiency droop is observed at higher current densities for the blue devices than for UV devices. Note that the power (log scale) was measured here at a NA of 1.

The normalized μ LED spectra from blue and UV devices are plotted in a semi-log scale taken at different V_{appl} as a function of energy (eV) in Figure 3.15 E and Figure 3.15 F respectively. It can be observed that the applied voltage is lower for both the blue and UV μ LEDs than the energy of the corresponding peak wavelength. An energy offset of about 60 meV and 67 meV between V_{appl} and V_{peak} was measured in this case for the blue and UV μ LEDs, respectively. This suggests at low current densities, an excess energy in emission than the applied energy was measured. To evaluate the reason behind this phenomenon, the carrier temperatures were calculated from the slope at the higher energy side of the spectra. The carrier temperature (T_c) was calculated to be about 567 K for the blue μ LEDs and 318 K for UV μ LEDs, which is higher than the junction temperature ($\approx 300\text{ K}$). In general, the carrier energies are distributed following Boltzmann distribution [$P(E) \sim e^{-E/kT}$] from below kT to above kT even at room temperatures, where k is Boltzmann's constant. Only a few carriers will have high energy, like for blue $k \times 567\text{ eV}$ and for UV $k \times 318\text{ eV}$ as calculated here. These higher energy carriers overcome the energy barriers and diffuse into the QWs where they combine. Which is also the main reason for having higher WPE than EQE at low current density. Although most of these high-energy carriers recombine non-radiatively, a low concentration of such hot carriers recombines radiatively and emits photons.[199] In a perfect LED where no nonradiative recombination takes place, this low current operation would actually cool the device and is analogous to the evaporation of the hot water molecules cooling off a cup of water or the operation of a thermal electric cooler.

3.4.7 Effect of reflective metal contacts

The use of Ag-based reflective metallic p-contacts can improve the extraction efficiency further and has been a point of interest in this field [200, 201]. Pd/Ni/Au-based contacts have a reflectivity of around 44% due to the high absorption of the Pd itself, whereas Ag-based p-contacts have been reported to achieve a high reflectivity of over 90%, which offers the potential to achieve higher extraction efficiency than Pd/Ni/Au contacts. Unfortunately, Ag has a low work function ($4.1 - 4.2\text{ eV}$) and difficult to achieve ohmic contact with p-GaN without annealing. Also, Ag tends to agglomerate when exposed to high temperature or plasma-assisted processes and leads to poor adhesion. It often requires a thin under-layer and over-layer to minimize the diffusion of Ag.

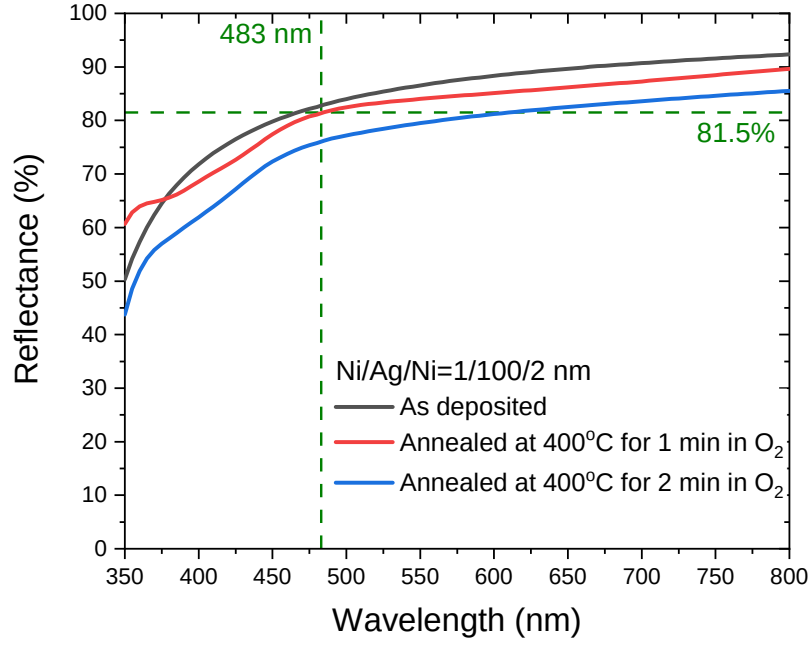


FIGURE 3.16: Reflectance of Ni/Ag/Ni as-deposited and after annealing at 400 °C in O_2 for 1 minute and 2 minutes.

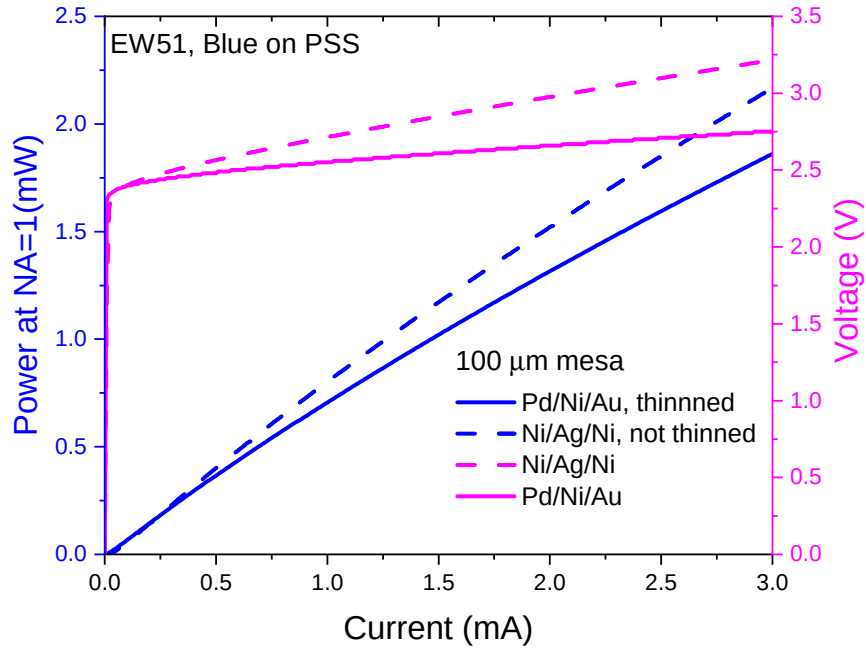


FIGURE 3.17: Current-voltage characteristics and optical Power measured at NA=1 of Ni/Ag/Ni based p-contact.

A $Ni/Ag/Ni = 1/100/2 \text{ nm}$ metallization p-contact was deposited on the blue LED wafer in this case. The contact was measured ohmic as-deposited, and the contact resistivity was improved dramatically ($\rho_c > 10^{-4} \Omega \text{ cm}^2$) upon annealing in O_2 . The details of the optimization of the annealing condition are presented in Appendix C.

Figure 3.16 shows the reflectance spectra of as-deposited Ni/Ag/Ni contact after annealing in O_2 for 1 minute and 2 minutes. As deposited, a high reflectance value of about 82% was achieved, whereas upon annealing for 1 minute, a reflectance of 81.6% was achieved at 483 nm. Annealing for a longer duration seems to reduce the reflectance of Ag.

The L-I-V characteristics were measured at an NA of 1 from the devices and presented in Figure 3.17. Note that in these devices, there is no n-contact metallization; only mesa was etched and probed onto p-metal and n-GaN to extract the power. The I-V characteristics show that the turn-on voltage was the same as Pd/Ni/Au contact with slightly higher series resistance which is due to the absence of n-contact. A 20% improvement in output power was measured in this case. As the substrate was not thinned and there is no ARC coating on the devices, it can be assumed that the extraction efficiency could be further improved by thinning down the substrate with ARC coating. The Pd/Ni/Au p-contact μ LEDs had a WPE of 41%, whereas a Ni/Ag/Ni p-contact showed a 20% improvement suggesting a WPE nearly about 60%, which leads to an extremely high-efficient μ LED.

3.5 Summary

The results presented in this chapter show the detailed fabrication process of highly efficient blue and UV μ LEDs compatible with neural DUSTs where the blue is responsible for the activation of blue-sensitive ChR-2 and the UV is responsible for activating the drug delivery system. The physical layout of the μ LEDs was designed to be compatible with the electronic die, whereas the optical and electrical performance of the μ LEDs was measured to be better than the minimum specifications.

The detailed electro-optical performance of the μ LEDs was presented here. A low turn-on voltage of the devices below the peak-wavelength voltage was achieved due to the presence of sub-bandgap voltage at lower current densities. A low electrical ideality of 1.3 and 1.5 was measured from the blue and UV devices, respectively, suggesting efficient radiative recombination. Very high optical power from the blue 100 μ m mesa μ LED of 1 mW was achieved while operating at a low 1 mA, 2.5 V. The UV μ LEDs of the same mesa size were capable of generating 0.66 mW of power operating at 1 mA, 3.26 V, which is sufficient to activate the DDS.

The WPE and EQE from the μ LEDs were measured both at a NA of 1 and in an integrating sphere. A very high WPE of 40.7% from the blue μ LEDs and 25.4% from the UV μ LEDs were achieved when measured in an integrating sphere defining the total power of the devices. A sub-bandgap turn-on voltage was observed at low current densities. It was measured that the carrier temperature is much higher ($> 300\text{ K}$) than lattice temperature at such low currents and hence has much higher energy. Such high-energy carriers can cross the barrier at a low applied voltage and recombine. Due to this sub-band gap turn-on, the WPE was measured higher than the EQE at low current densities. Although most of the high energy carriers combine non-radiatively and generated heat. Only a few numbers of these high-energy carriers participate in radiative recombination and emit photons.

Further, the effect of SiO_2 ARC coating showed a 10% improvement in extraction efficiency. Also, the potential to improve extraction efficiency by choosing suitable Ag-based reflective p-contact is presented here. The results showed about 20% improvement in power extraction due to Ni/Ag/Ni p-contact which suggests the possibility to get an extremely high WPE of about 60%. The extraction efficiency can be increased by about 5% to 8% more by encapsulating the device with suitable refractive index matching material.

The blue and UV μ LEDs designed and fabricated here in this chapter are targeted for optogenetic application. An optical power density (the mesa area is considered as the emitting area) of 127 mW/mm^2 was calculated from the blue μ LEDs while operating at a low electrical power of 2.5 mW . Based on the power density specifications for activating blue-sensitive ChR-2, the fabricated μ LEDs were well above the minimum requirement and are capable of operating below the CMOS voltage limit. As the μ LEDs will be operating near 1 mA under pulsed operation, which also is the region of peak efficiency, the heat generated by the LEDs is expected to be low. The wavelength and power from the UV μ LEDs are perfectly suitable for activating the DDS and will be discussed thoroughly in the next chapter. Since the turn-on voltage of the UV μ LEDs was measured below 3.3 V while operating at 1 mA , the CMOS chip driven by ultrasound will be able to turn on the UV LEDs as well. This shows the electro-optical performances of the fabricated UV LEDs are perfectly suitable to be used in neural DUSTs.

Chapter 4

Development and characterization of a UV activated drug delivery system

4.1 Introduction

The use of wirelessly powered micron-sized electronic neural devices (also called DUSTs) has attracted significant interest for neural implants [202–205]. Of particular interest is their use in the new field of light-induced selective nerve stimulation, also called optogenetics [104, 105, 206, 207]. Despite recent remarkable progress, traditional fully implantable neural modulating systems are still not sufficiently bio-compatible to maintain implanted in-vivo functioning [127, 208–211]. Biocompatibility is defined as a bio-material’s ability to perform its ideal function in relation to a medicinal treatment without inflicting any harmful immunomodulatory effects on the recipient while producing the most appropriate cell or tissue reaction in that specific circumstance and improving the treatment’s clinically applicable presentation [212]. The main side effect of brain implants is providing dangerous toxic chemicals to the brain, so increasing the immunological response or triggering tissue damage [213]. Despite initial tissue injury caused by a neural implant’s placement, the brain may recover quickly, it is the long-term tissue reaction, as well as the resulting inflammation at the implant site, that effectively degrades probe/tissue bio-integration [214, 215]. The immune system’s neuro-inflammatory reaction in the brain’s central nervous system is comprised of a mix of cellular and molecular processes that detach foreign components, such as a brain implant, from the tissue. As a result, it is highly important to use chemically stable and bio-compatible encapsulation with a localized

drug delivery system (DDS) containing anti-inflammatory drugs in realizing a fully implantable neural DUST.

The method by which a drug is being delivered can have a significant influence on its efficacy. Many of the drugs have an optimum concentration range, and a controlled release of the drug in the body is required. The concentrations above or below the concentration range can be toxic or can produce no therapeutic benefits at all. One of the most important specifications is drug release kinetics. Depending on the application, different release kinetics can be relevant. Sometimes a constant dose per unit of time is desired, other times, a burst release with a fast decay is the target. Therefore, it is desired to have a triggered drug delivery system on the top of the DUST system that can deliver a corticosteroid like prednisone or hydrocortisone on demand to suppress the inflammatory response of brain immunocompetent glial cells, and therefore decrease cell damage.

Different photochemical trigger mechanisms have been explored to find the most suitable for the DUST: (1) photoisomerization and oxidation, (2) surface plasmon absorption and photo-thermal effects, (3) photochemical hydrophobicity changes, (4) polymer backbone photo-degradation and (5) photo de-crosslinking.[216] The evaluation showed that the spiropyran (SP) photochemical group is near ideal for designing a triggered drug delivery system for the DUSTs. SP has attracted a lot of attention among researchers due to its different remarkable properties and wide range of applications.[217–227]

The closed-ring isomer of the SP molecule comprises an indoline and a chromene moiety bound together via a spiro junction and oriented perpendicular with respect to one another. Photo irradiation of SP gives rise to the open-ring isomer, merocyanine (MC), following first-order kinetics. Interestingly, the $SP \rightarrow MC$ isomerization can also be accomplished using near-infrared (NIR) radiation (via two-photon excitation) [219]. The $MC \rightarrow SP$ reverse isomerization usually occurs spontaneously, again following first-order kinetics, and can be accelerated by visible light. The uniqueness of SP is due to the fact that the two isomers, SP and MC, have extremely different physicochemical properties; moreover, the response to light as an external stimulus is rapid and reversible. In the dark or under visible light, the molecule is in its SP form, which is hydrophobic, colourless, uncharged, nonpolar, and insoluble in water. Under photo irradiation, it isomerizes to the MC form, which is hydrophilic, coloured (violet), zwitterionic, polar, and soluble in water. The MC form comprises a zwitterionic group, which significantly increases the hydrophilicity, and allows uptake of cerebrospinal fluid (CSF) and, thus release of

the anti-inflammatory drug. So, the drug delivery system could be realized by adding a coating of drug-loaded SP on the DUST system to provide the least necessary invasive impact on the brain tissue and ensure ultra-local drug delivery.

The objective of this chapter is to develop and characterize the optically triggering of localized DDS for neural implants as a countermeasure for the body's inflammatory reaction. Firstly, the wavelength dependence of SP upon exposure was measured to determine the high absorption regions of the spectra. Also, the activation time dependence on the thickness of SP was evaluated. High-efficiency UV μ LEDs presented in chapter 3, were used to show the activation of SP upon exposure. The UV μ LEDs were first integrated with basic DUST (see chapter 6), and activation of SP by ultrasound-powered UV μ LED was demonstrated. Drug-loaded SP was prepared by dissolving hydrocortisone in SP solution. Electrically pumped UV μ LEDs were integrated on a patterned glass substrate and coated with drug-loaded SP to investigate the drug release upon UV exposure.

4.2 Dependence of SP-activation on exposure wavelength

4.2.1 Transmittance and absorbance of spiropyran

To determine the wavelength having the highest photo-switching responsivity of SP under optical exposure, SP dissolved in tetrahydrofuran (THF) (2% wt) was first spin-coated on 20 mm diameter cover slides of a thickness of 7 μ m. The transmission spectra of both the blank cover slide and SP-coated cover slide were measured by a UV-Vis spectrometer.

Figure 4.1 shows that the absorption band of the blank cover slide was in the deep UV region ($\approx$ below 330 nm), representing any change due to light passing through polymer above 330 nm coated glass slide, was because of the SP. Further analysis showed that the transmission through the blank slide does not shift for different LED peak wavelengths, and about 10% of the intensity was lost while passing through the blank slide due to reflection. Strong absorption was seen for wavelengths shorter than 400 nm, increasing as the wavelength decreases. The sharp feature near 550 nm shows that SP has high absorption at that wavelength, and later experiments proved that 550 nm can be used to deactivate (reverse-isomerization of MC $\rightarrow$ SP) the polymer.

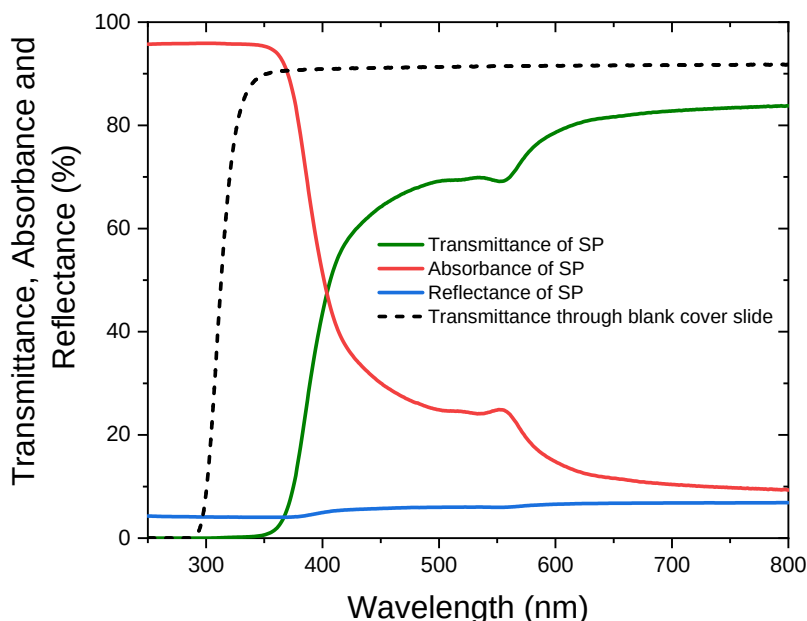


FIGURE 4.1: The dotted black lines shows the transmittance through the blank cover slide. The solid green and red lines represent transmittance and absorbance through the SP-coated cover slide respectively where the blue line shows the reflectance of SP.

4.2.2 Characterization of reference LEDs

Four commercial LEDs emitting at four different peak wavelengths namely 370 nm , 380 nm , 397 nm , and 405 nm were used to determine the transmission response of SP upon exposure through $40\text{ }\mu\text{m}$ thick (10% wt solutions in THF) SP coated cover slide.

The Current-Voltage (I-V) characteristics with the output powers of the commercial LEDs were measured using a setup schematically shown in Figure 4.2(a) and the results are presented in Figure 4.3. The optical power was measured by placing the LEDs on top of the detector such that it creates about a 5 mm spot diameter on the detector. The spot diameter was kept fixed at 5 mm while measuring transmittance through SP to provide the same power density as measured in Figure 4.3. From the normalized spectra of the four commercial LEDs, full width at half maximum (FWHM) was measured as 19 nm , 13 nm , 18 nm , and 20 nm for 370 nm , 380 nm , 397 nm , and 405 nm LEDs respectively [Figure 4.3(b)].

4.2.3 Activation of SP coated samples by reference LEDs

To measure the wavelength dependence of the SP-coated samples, the LEDs were placed emitting vertically downwards using a holder on the top of the SP-coated sample such that it crea-

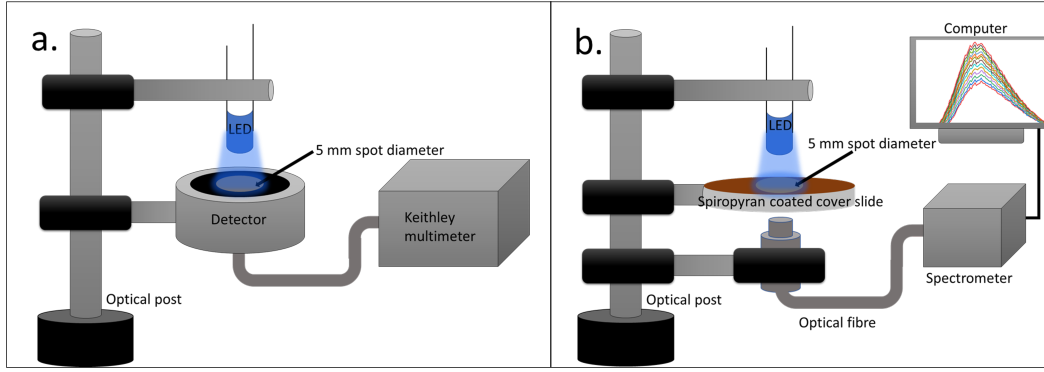


FIGURE 4.2: Schematic illustration of the measurement setup for (a) measuring the L-I-V characteristics of the reference LEDs and (b) measuring the wavelength dependence of SP upon exposure with reference LEDs with the same 5 mm spot diameter.

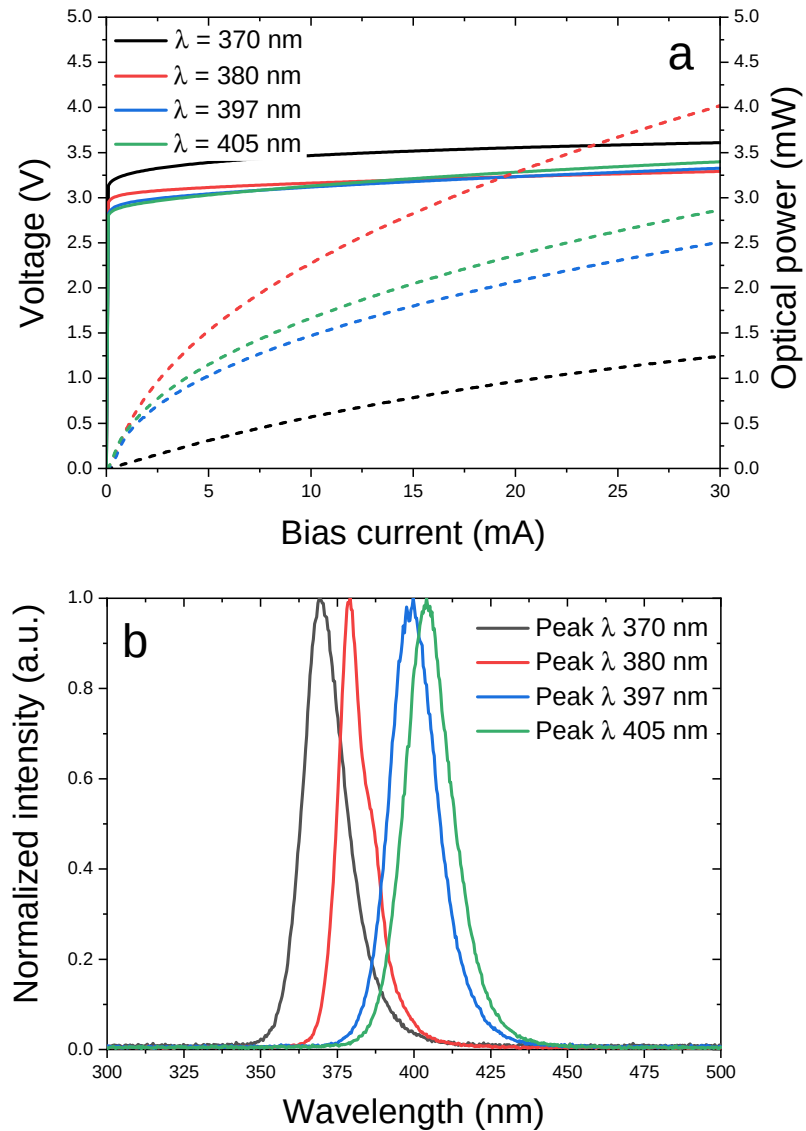


FIGURE 4.3: Shows the (a) Current-Voltage characteristics and output optical power at a numerical aperture of 1 of the reference LEDs with respect to the applied bias current. and (b) normalized spectra of the reference LEDs

tes the same 5 mm spot diameter of the sample and was driven by a Keithley source meter. A UV-Vis spectrometer was placed below the sample to collect the transmitted intensity through the SP-coated cover slide. The measurement setup is schematically presented in Figure 4.2(b). The LEDs are driven by a specific current to provide power ranging from 1.15 mW to 1.51 mW to the sample and the changes in the transmission peak were observed as a function of time and wavelength.

Figure 4.4 shows activation of SP under exposure with different peak wavelengths as a function of time. The results are presented in Table 4.1. It shows that the transmitted intensity decreases as the sample gets darker under exposure by 370 nm [Figure 4.4(a)] and 380 nm [Figure 4.4(b)] and stopped when SP was fully activated. As the SP starts to activate (SP $\rightarrow$ MC), it gets darker with time, and the transmitted intensity starts to decrease. The lowest intensity transmitted through SP was captured when the SP was completely activated, indicating dark MC form. After activation, the MC starts to self-recover, and the intensity peak starts to rise again by absorbing the green wavelength from the room light and changes from MC $\rightarrow$ SP. The dark spot was the exposed area indicating the photo-activated region. It is observed from Figure 4.4(a) and (b) that the transmitted intensity peak through SP appears at 400 nm, whereas in the LED spectrum shown in Figure 4.3(b) the peak appears around 370 nm.

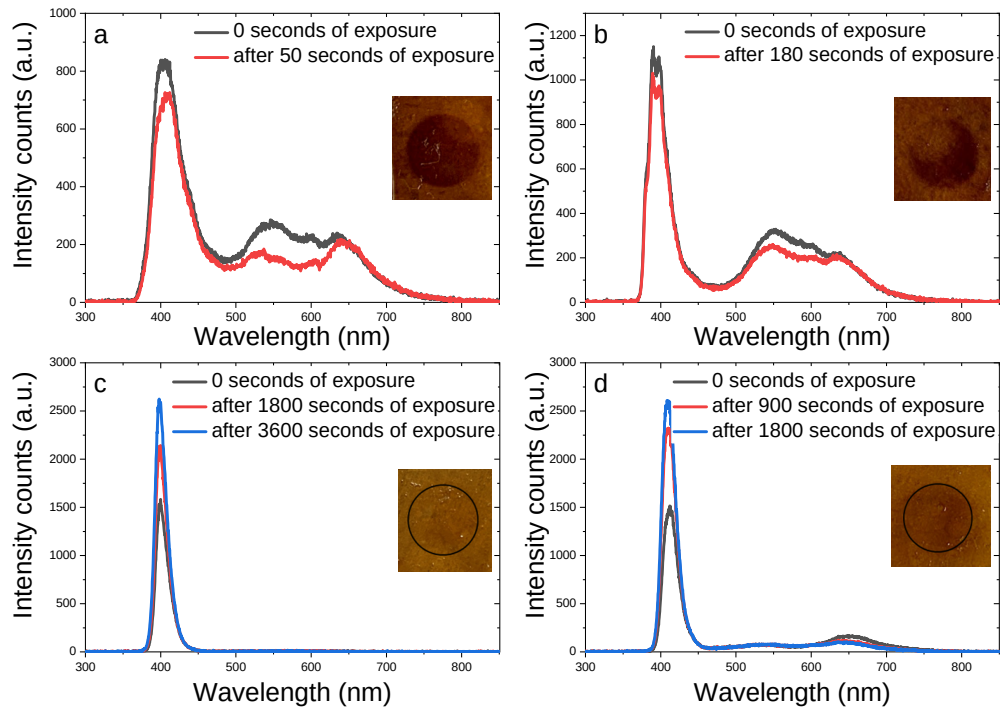


FIGURE 4.4: Activation of 40 μm thick SP as a function of wavelength and time when exposed by (a) 370 nm, (b) 380 nm, (c) 397 nm, and (d) 405 nm commercial LEDs and corresponding images of the exposed region.

The difference between these two measurements is that the transmitted intensity was measured through SP coated glass slide. From Figure 4.1, it is seen that the glass is highly absorptive only below 350 nm and above that, it has high transmission. Therefore, it can be concluded that the SP absorbs the majority of the UV and hence the wavelength shift during measurements through SP-coated samples.

TABLE 4.1: Activation parameters obtained for exposure under different wavelengths.

Thickness of SP 40 μm	Peak wavelength (nm)	Optical power (mW)	Duration (s)	Energy density (J/cm ²)
	370	1.24	50	0.32
	380	1.51	180	1.38
	397	1.46	3600	27.18
	405	1.15	1800	10.54

In addition, emission in the 500 nm to 650 nm range was observed whereas, in the LED spectra the emission intensity goes to zero at wavelengths above 420 nm. The exposure by 370 nm and 380 nm induces luminescence in the SP resulting in these features. Luminescence also decreases as the polymer activates similar to the transmitted intensity. It takes approximately 20 to 30 minutes for the sample to turn back to approximately the original colour (MC $\rightarrow$ SP) after it has been exposed under room lighting conditions showing the photo-switching mechanism.

When SP of the same thickness was exposed with 397 nm [Figure 4.4(c)] and 405 nm [Figure 4.4(d)], even with higher energy density, SP does not activate because of low absorption in that range [see Table 4.1]. It was observed that the transmitted intensity through SP increases with time instead of decreasing in this case. Because the recovery time of the polymer being 30 minutes, the material is changing back at the same time as it is being activated.

4.3 Dependence of SP-activation on the thickness of SP

In the previous section, it was demonstrated that the activation of SP was highly dependent on exposure wavelength, and wavelengths below 380 nm were required. To determine the dependence of SP-activation on the thickness of the polymer, initially, 80 μm thick SP-coated (10% wt solution in THF) cover slide was used and placed under a similar setup mentioned in subsection 4.2.3. and exposed by 370 nm commercial LED. Note that the thickness measured here is not accurate ($\pm 10 \mu m$) as the spin coating of thick SP was distributed non-uniformly over the cover slide.

From Figure 4.5, it was observed that exposure by 370 nm peak wavelength with the same optical power of 1.24 mW [see Table 4.1], this time it took about 100 seconds for the SP to activate which corresponds to an activation energy density of 0.63 J/cm^2 . Hence, under the same exposure condition (370 nm, 1.24 mW), a two times thicker SP requires about two times more energy density than for activation. Although, the thickness of SP across the cover slide was not uniform and the values obtained here were not accurate. A very strong luminescence was observed ranging from 400 nm to 800 nm which suggests that the higher the thickness of SP, the higher the absorption of the UV spectrum, resulting in higher photoluminescence.

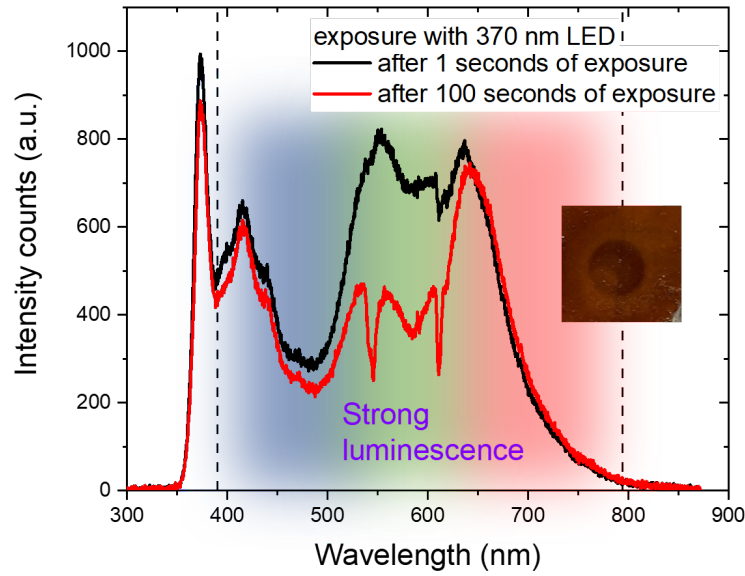


FIGURE 4.5: Activation of 80 μm thick SP as a function of exposure time when illuminated by 370 nm commercial LED and corresponding images of the corresponding exposed region.

To understand the relationship between SP-thickness and activation energy density more clearly, UV 370 nm top-emitting μLED integrated submounts were prepared. Custom-made top-emitting μLEDs were fabricated with square mesa area ranging from $50 \times 50 \mu\text{m}^2$ to $250 \times 250 \mu\text{m}^2$ following the process steps mentioned in Chapter 3. The submounts were prepared by dicing 4" Si wafer into $20 \times 20 \text{ mm}^2$ pieces. Then the samples went through 30 seconds of argon ion etch before evaporation to enhance adhesion and 300 nm of Al was evaporated onto the Si pieces at a rate of $1.5 \text{ \AA/sec}$ to act as a reflective metal. 370 nm SiO_2 was sputter deposited to passivate the Al. Then a lithography level was defined to put down 20/30/200 nm of Ti/Pt/Au at a chamber pressure of $2 \times 10^{-7} \text{ torr}$ as bond pad metal.

Five μ LEDs of size $50 \times 50 \mu\text{m}^2$, $100 \times 100 \mu\text{m}^2$, $150 \times 150 \mu\text{m}^2$, $200 \times 200 \mu\text{m}^2$, and $250 \times 250 \mu\text{m}^2$ were epoxy bonded onto each Si substrate, and interconnections were made by *Au* wire bonding between the pads of the substrate and μ LEDs and schematically shown in Figure 4.6(a). Finally, 2% wt solution of SP dissolved in THF was spin-coated onto the LED-integrated submounts 4.6(b).

Figure 4.6(c) presents the dependence on activation time as a function of current supplied to the $200 \times 200 \mu\text{m}^2$ LED for different thicknesses of SP. The optical power corresponding to each current value was measured beforehand and the activation time was determined by recording the time taken for the transmitted intensity to reach a minimum value which was visually seen as a darkening of the SP. For each thickness value of SP similar decreasing trend in activation time was initially observed. Figure 4.6(d) shows the activation energy as a function of the thickness of SP representing the increase in SP thickness requires a proportionate increase in activation energy.

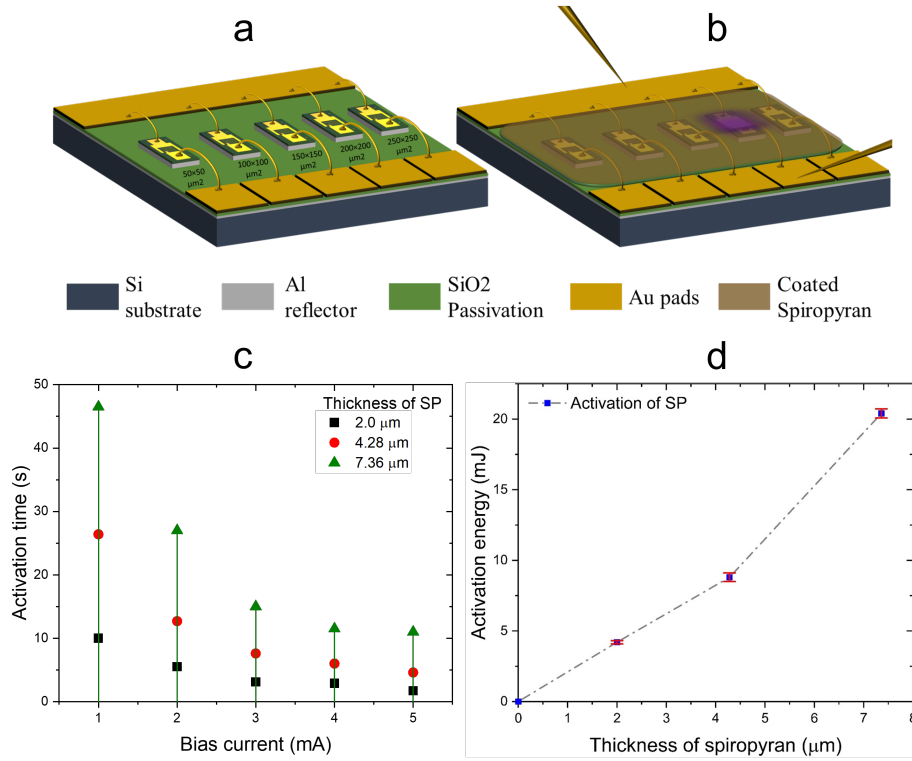


FIGURE 4.6: Fabrication process flow of submounted UV μ LEDs on Si wafer. (a) μ LEDs integrated onto a Si wafer with Al reflector, and interconnection between μ LEDs and submount pads by wire bonding, (b) submount coated with different thicknesses of spiropyran namely 2, 4.28 and 7.36 μm . Graph (c) shows the activation time of different thicknesses of SP as a function of bias currents supplied to the $200 \times 200 \mu\text{m}^2$ mesa LED and (d) shows the relationship between SP-thickness and activation energy

Although, further measurements proved that this type of experiment is not repeatable and the values obtained here are not accurate. The main reasons behind this failed experiment were due to the non-uniform thickness of the coated SP and the contribution of light that is coming out from the side of the LED chip activating the pooled SP on the sides of the LED. As there was severe topology involved in the submount design [Figure 4.6(b)], the spin-coated SP was non-uniformly distributed over the submount. On the top of the LED chip the thickness visually looks quite thin whereas, around the bottom edge of the LED, a pool of SP was observed. The thickness of the SP measured here was on the substrate and not on top of the LED due to the limitations of the surface profilometer. Also, as the refractive index of the SP was unknown, the thickness of the SP by reflection method using nanospec tool was not feasible. Therefore the thickness measured here was not precise and led to inaccurate data. Another issue was that the LED chip emits light from all directions and when the transmitted intensity was captured by coupling into an optical fibre, it was difficult to determine exactly which area was contributing to the measurements. Figure 4.7(a) shows the SP-coated LED before activation and Figure 4.7(b) shows the microscope image after activation. It is clear from Figure 4.7(b) that the dark purple colour around the bottom edge of the LED defines the higher thickness of activated SP. The microscope image shows that there is almost no darkening of SP on top of the LED which is possibly due to a low thickness of SP on top of the LED which the microscope image cannot capture. Although, this failed experiment strongly indicates that with a higher thickness of SP, higher activation energy density was required. A more precise SP coating tool is required such as coating only the mesa area with a micro-droplet dispenser, then it would be easier to determine the effect of a specific volume of SP on activation time and energy density.

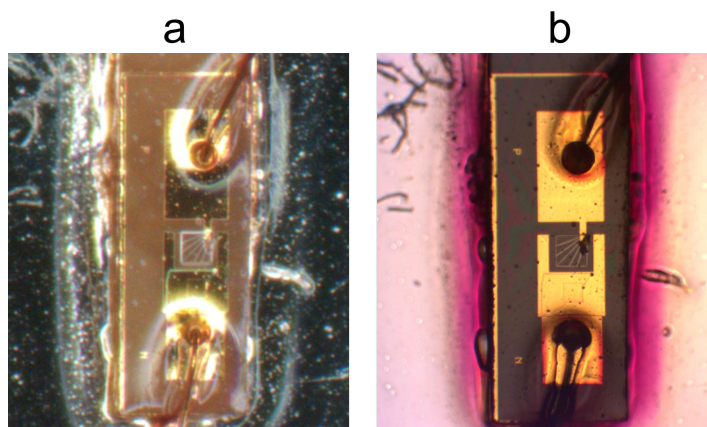


FIGURE 4.7: Microscope image of the SP coated LED (a) before activation showing non-uniform distribution of coated-SP and (b) after activation showing the pool of SP activated (dark purple colour) around the bottom edge of the LED.

4.4 Demonstration of SP-activation by ultrasound powering

In the real scenario, it is required to activate SP by UV μ LED powered by ultrasound. To demonstrate such capabilities, an ultrasound-powered implant-compatible system integrated with custom-designed and fabricated top-emitting UV μ LEDs called basic-DUST was integrated by the integration process described in chapter 6. The UV μ LED-integrated basic-DUST was then dip-coated into 10% SP solution dissolved in THF. Once the THF was evaporated, the basic-DUST was left with a coating of SP, acting as an encapsulation layer for the DUST.

For the US-powered activation, the SP-coated DUSTs were sent to our collaborators at Aarhus University. The SP-coated basic-DUST was mounted on a PCB strip and submerged in water to deliver the ultrasound at a frequency of 2.9 MHz. Ultrasonic bursts of 2 ms, at 5 Hz were delivered to the PZT harvester by the transducer with an acoustic intensity of 33 mW/mm². As the (500 μ m)³ PZT crystal harvests about 33% of the incoming power, the power delivered to the load (μ LED) was calculated to be 2.5 mW. As the turn-on voltage of the UV μ LEDs was measured at about 3.1 V, the operating current was calculated to be 0.8 mA. The operation of the μ LEDs by the US was visually confirmed by lighting up the μ LED.

Figure 4.8(a) shows the microscope image of the SP-coated DUST before activation of the SP by US-powering of the UV μ LED. After about 10-15 minutes of US powering, the DUST was imaged again under a microscope. This time a clear darkening of the SP was observed over the active region of the UV μ LED and shown in Figure 4.8(b). Based on the previous experiments with SP, the darkening represents the activation of the polymer. Hence activation of SP by ultrasound-powering wireless implant-compatible neural-DUST was successfully demonstrated in this experiment.

4.5 Integration, and demonstration DDS by electrically driven UV LEDs

In order to demonstrate ultrasound-powered drug release and avoid complications of handling individual sub-mm sized DUST, a number of electrically driven submounted UV- μ LED systems were prepared and coated with hydrocortisone (anti-inflammatory drug) loaded SP.

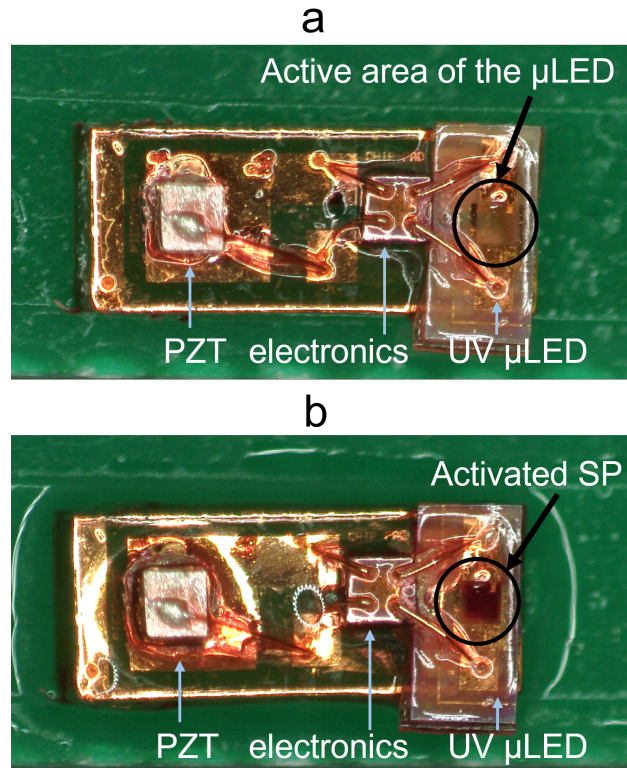


FIGURE 4.8: Microscope image of the SP coated basic-DUST (a) before US-powering showing non-activated SP on the mesa region of the UV- μ LED and (b) after US-powering of the DUST showing activated-dark SP on the mesa region of the UV μ LED.

4.5.1 Integration electrically driven submounts with UV micro-LED

To demonstrate drug delivery by exposure to UV wavelength, small μ LED systems were developed on a $2 \times 2 \text{ mm}^2$ Au patterned glass substrate. A top-emitting UV μ LED of sized $200 \times 200 \mu\text{m}^2$ mesa was glued on the top side of the substrate as shown in Figure 4.9(a). First, wire bonding between μ LED pads to the submount pads was done and then two long wires were soldered onto the submount pads to drive the system electrically. Figure 4.9(b) shows the sub-system after interconnection without power supply and Figure 4.9(c) shows the image of the μ LED turned on by DC power supply. Figure 4.9(d) and 4.9(e) shows the microscope image of the SP-coated sub-system before UV-activation and after UV-activation of SP at 1 mA bias respectively. Since the device was dip coated into SP, it was not possible to measure the thickness of coated SP. Hence, the activation time or the required energy density was not measured this time.

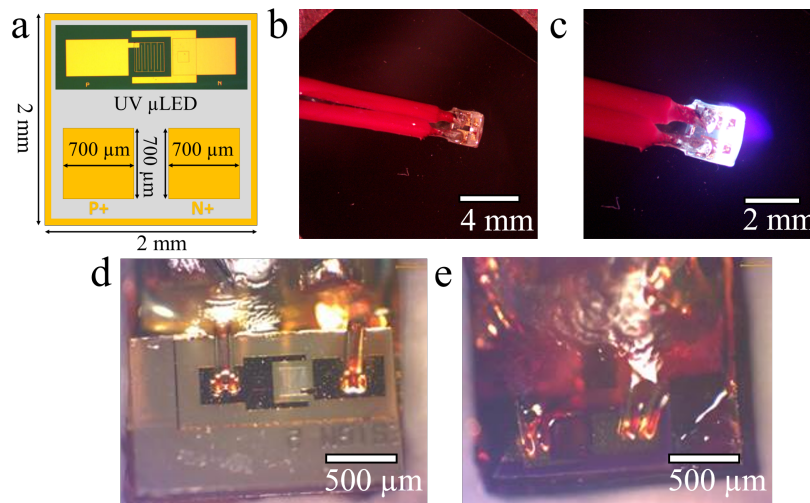


FIGURE 4.9: Figure (a) Shows the schematics of the submount prepared for an electrically driven sub-system. Shows the image of the integrated system (b) without bias and (c) with bias. Microscope image of the SP-coated sub-system (d) before activation of SP and (e) after activation of SP.

4.5.2 Demonstration of UV-activated drug delivery

The entire measurements of drug delivery demonstration were done by our collaborators from VIB and Biomodics. The DDS was prepared by adding 2 *mg* of SP to dissolve into 98 *mg* of THF and then 2 *mg* of hydrocortisone was dissolved in it. A 50 : 50 ratio of SP: hydrocortisone was thus prepared and the UV- μ LED integrated systems were dip coated in the solution.

The drug release test was performed using a commercially available ELISA (Enzyme-Linked Immunosorbent Assay) kit designed for hydrocortisone detection and provides a quantitative measurement of the drug levels in biological fluid. Initially, a strong background drug release was found without UV activation, which saturated the ELISA kit. The main reason for such background release was the free drug molecules on the surface of the SP, which dissolves into saline. To overcome such strong background release and get results within the range of the ELISA kit, the drug-loaded SP was diluted in two concentrations of 100 times (100x) and 1000 times (1000x) respectively. Then vortexing and pre-soaking into saline were done as shown in Figure 4.10.

Figure 4.10 shows the process of vortexing and pre-soaking for both 100 times and 1000 times diluted drug-loaded SP. A 100 μ l of saline was collected after each vortexing (2 minutes) with a coated μ LED inside a 1.5 *ml* tube (with 1 *ml* saline inside). The μ LED was then moved to another 1.5 *ml* tube collect (with 1 *ml* saline inside) for each vortex test (vortex 1, vortex

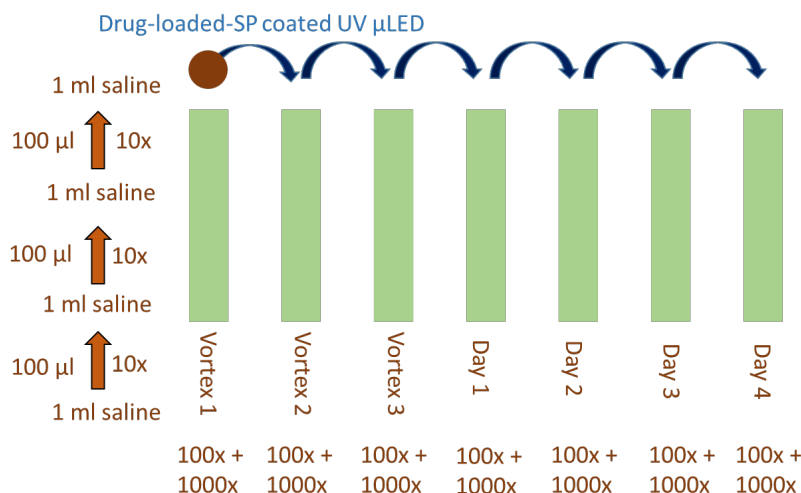


FIGURE 4.10: Experimental steps to reduce background drug release by vortexing and pre-soaking.

2, and vortex 3). For the pre-soaking test, each day, 100 μ l of saline again was collected and the μ LED was moved to another tube. The same procedure was repeated for another 3 days (day 2, day 3, and day 4). The results showed that both vortexing and pre-soaking reduced the background hydrocortisone release but did not eliminate it. In addition, the experiments showed that now the release is well within the limit of the ELISA kit. Pre-soaking release from day 1 to day 4 showed a gradual decrease in drug release from 2 μ g/ml (day 1), 1.5 μ g/ml (day 2), 0.9 μ g/ml (day 3), and 0.75 μ g/ml (day 4) for the 1000x dilution.

Based on the previous result, it was targeted to detect the additional light-triggered release of hydrocortisone on top of the high background release. 100 μ l of saline was collected after each of the three vortex cleaning steps with another submounted and coated-UV μ LED, inside a 1.5 ml tube (with 1 ml saline inside). The submounted- μ LED was moved to another 1.5 ml tube collect (with 1 ml saline inside) for each test (vortex 1, vortex 2, and vortex 3). To test light-triggered release, hydrocortisone release during 2-minute periods was sampled either with the light off (baseline) or with light (2 mA for 10, 15, and 25 seconds respectively)[Figure 4.11 (a)]. Again, the samples were diluted 100 times and 1000 times for the ELISA test. A standard concentration curve was included in the ELISA to calibrate the optical density measurements.

As shown in Figure 4.11(b), it appears that turning the UV μ LED on, increased the hydrocortisone release relative to the preceding baseline for all three light-on tests (green arrows). An additional drug release of 0.3 μ g/ml, 0.2 μ g/ml, and 0.44 μ g/ml for the three tests on 1000x sample when the μ LED was on for 10 s, 15 s and 20 s respectively at 2 mA. Thus, a

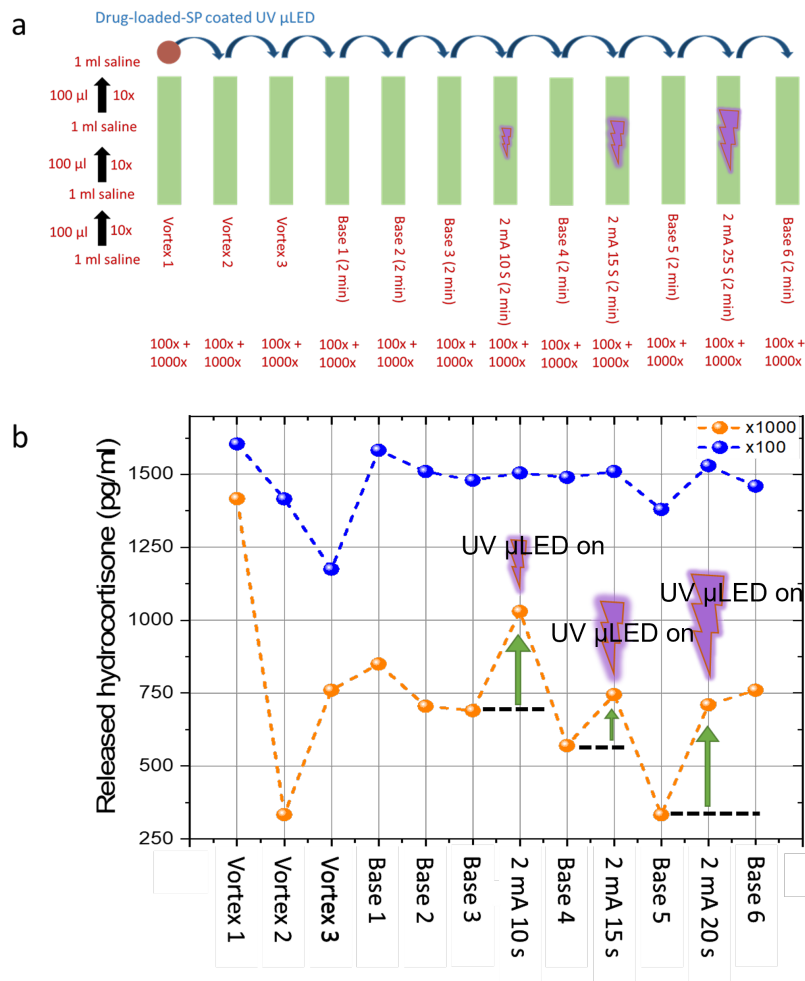


FIGURE 4.11: (a) Shows the experimental process to obtain the additional light-triggered release of hydrocortisone over background release and (b) shows the result of the experiment where the additional release was measured by turning on the UV μ LED. The lightning strike symbol here in the picture indicates when the UV μ LED was turned on.

light-triggered additional drug release was demonstrated even though the background leakage was high.

4.6 Summary and discussion

In this chapter, the development and characterization of a DDS based on the photochromic property of SP were demonstrated. The measurements of the transmission and absorption spectra through SP showed a high absorption below 400 nm with an additional absorption peak near 550 nm which can be used for reverse isomerization of MC $\rightarrow$ SP. Exposure to commercial LEDs ranging from 370 nm to 405 nm showed that SP has high wavelength selectivity on activation and wavelengths above 385 nm do not contribute to activation of the polymer. To

determine the dependence on the thickness of SP upon activation, experiments were conducted using 370 nm emitting LEDs. It was observed with higher thickness, it was required to have higher energy density for the activation of SP. Although, due to the uneven thickness of coated SP onto the submounted-LEDs and the contribution of the different regions of the LED chip, the quantitative measurement of the required activation energy density with respect to the thickness of SP was not successful. Further investigations are required to determine the refractive index and thickness of SP more accurately to quantify the relationship. Also, target-specific coating methods such as micro-droplet dispenser would be more useful for this type of experiment but needs more attention.

To demonstrate the activation of SP-based DDS, a basic-DUST module with 370 nm UV μ LED was integrated using the integration process mentioned in chapter 6 and dip coated with 2% SP in THF solution. The module was sent to Aarhus University to evaluate the activation of DDS by ultrasound operation. When ultrasound was delivered to the PZT, the blinking of the UV μ LED was observed, and the activation of the SP was visually confirmed by the darkening of the activated SP over the mesa region of the μ LED. This confirms the capability of the basic-DUST in driving the UV μ LED while activating the SP.

Electrically injectable UV μ LED systems were integrated separately and sent to our partners in VIB and Biomedics for demonstration where they were coated with hydrocortisone-infused SP to demonstrate optically triggered drug release. Even though a high background release was observed, an additional drug release of 0.3 $\mu\text{g/ml}$, 0.2 $\mu\text{g/ml}$, and 0.44 $\mu\text{g/ml}$ was clearly measured when the UV μ LED was turned on for 10 s, 15 s and 20 s at 2 mA respectively. Although the optically triggered drug release system was demonstrated, the amount of the released drug measured was not an exact value due to the large background release.

In this chapter, the activation of SP by US-powering of the DUST and the drug release by electrically-driven submounted- μ LED systems was demonstrated separately. Although, the drug release by the ultrasound-powered DUST system itself was not demonstrated here due to the limitations of the US-driving set-up and drug detection systems, and needs further investigation. This preliminary work on SP-based DDS holds a lot of potential for the future of neural implants in achieving bio-compatible encapsulation with integrated photo-activated drug delivery capabilities.

Chapter 5

Dual wavelength micro-LED assembly for optogenetics

5.1 Introduction

In this phase of the DUST development, it was envisioned to have two wavelengths integrated with the updated electronic chips (the modified electronic chip from Aarhus University includes a circuit for load regulatory that shares the available power budget between two μ LEDs in a power-efficient and controlled way while suppressing the need for adaptive matching and over voltage protection circuits), where one wavelength (UV) will be used to trigger the drug release mechanism and the other wavelength (blue/red) will be used for optogenetic stimulation (blue activates ChR-2 which suppresses the nerve action, whereas the red activates different opsins such as Crimson, Carmine, etc., which increase the nerve action). Hydrocortisone embedded in spiropyran will be used as a drug delivery system which can be triggered by exposing the UV μ LED (375 nm) [see Chapter 4], and a red μ LED (630 nm for red sensitive opsins) or blue μ LED (480 nm/ 450 nm for different blue-sensitive opsins) will be used for optogenetics. Also, the red and blue dual colour system has the potential to be used in dual excitation and suppression in optogenetics. Hence, dual colour μ LED system on a single chip capable of direct integration with electronic dies is required.

There are a handful number of research papers which showed the fabrication of dual-wavelength μ LEDs on a single chip where in most of the cases, two *InGaN* QWs were grown on sapphire

or silicon carbide substrate varying the well and barrier widths and In concentration to facilitate blue/green emission.[228–231] Such dual colour (blue/green) fabrication is possible due to the lattice match between blue and green epi-structure. Whereas growth of red material on blue material is not possible due to entirely different materials and different crystal structures between those two materials. In that case, people have used phosphor coating on blue LEDs for down-conversion to have emission in green and red wavelengths.[232] Nevertheless, the efficiency of the LEDs using such down-converting phosphor material is much lower than that of pure red/green LED material. Presently, industrial LEDs with different wavelengths are mainly obtained by coating phosphor material on blue LEDs, as blue LEDs are the most efficient LEDs among other wavelengths.

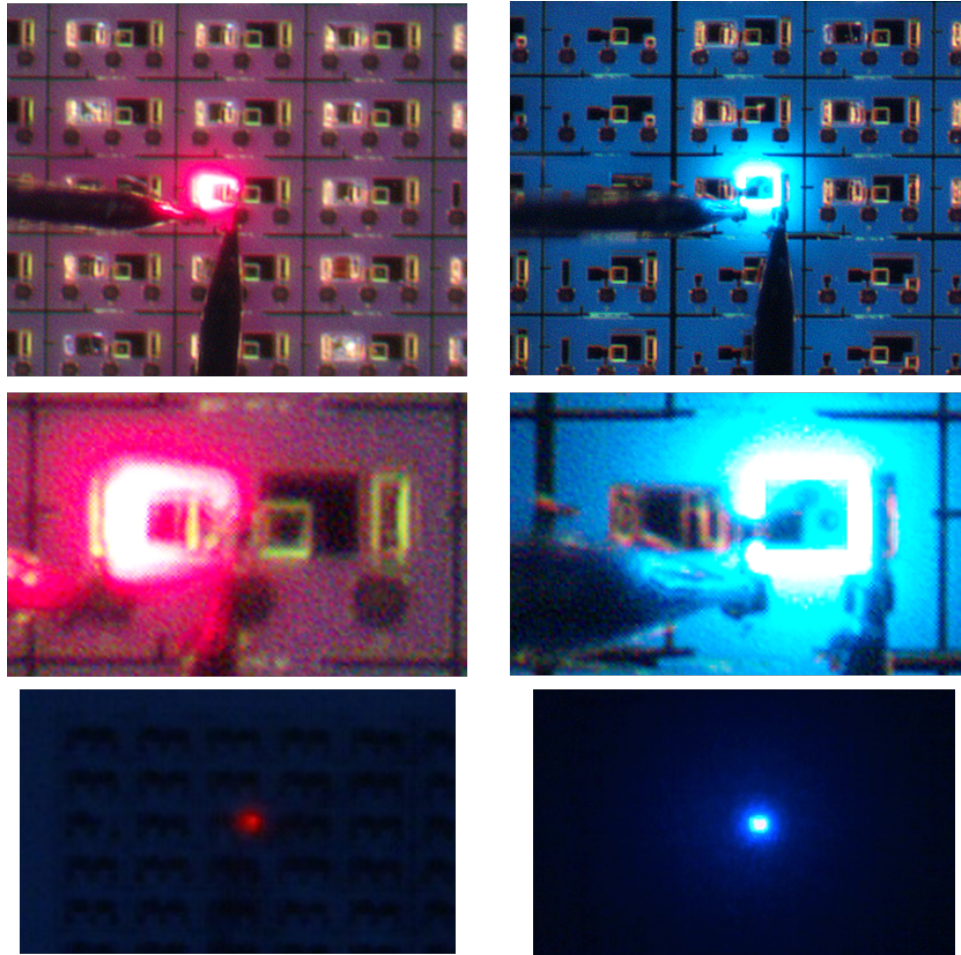


FIGURE 5.1: Camera image of the dual wavelength (Red+Blue) μ LED assembly under CW operation.

The development of transfer printing technology creates an opportunity for the fabrication of dual-wavelength μ LEDs for different applications. In this case, one of the μ LED is fabricated on the native wafer and undercut chemistry is used to release from the substrate. Then the transfer

printer then can pick up the LED coupon from the native substrate and print the coupon onto the foreign substrate.[233] With this approach, it is possible to combine a wide range of wavelengths onto a single chip with much lower complexity and lower time consumption.

This chapter discusses the fabrication process and characterization of dual colour μ LEDs on a single chip in detail. The process development, fabrication challenges, and measures taken to overcome such challenges are discussed in detail. Transfer printing technology is used with conventional GaN-on-sapphire μ LED fabrication technology to achieve different combinations of dual-wavelength μ LEDs on a single chip. Figure 5.1 shows the fabricated dual-wavelength (red+blue) μ LED on a single chip operating under CW where the red μ LEDs were transfer printed on GaN-blue LED wafer. The electrical and optical characterization of the dual colour μ LEDs was performed to highlight the key areas: I-V characteristics, optical power, spectral quality, and efficiency.

5.2 Design and process development

The dual colour μ LEDs were designed in conjugation with the layout of the electronic die, which was designed by our partners at Aarhus University. Two different electronic die of size $400 \times 400 \mu m^2$ [Figure 5.2 a] and $400 \times 425 \mu m^2$ [Figure 5.2 c] were used here. Based on the layout of the electronic dies, two separate dual-colour chips were designed. The first layout was designed to have a common-p contact configuration with external dimensions of $200 \times 300 \mu m^2$ as shown in Figure 5.2 b. Whereas the second layout had 4 separate pad configurations with the external dimensions of $200 \times 425 \mu m^2$ as schematically shown in Figure 5.2 d. In both designs, the bond-pads of the μ LED assembly chips ($50 \times 40 \mu m^2$) were designed to be slightly smaller than the pads on CMOS chip ($100 \times 50 \mu m^2$) to accommodate bigger active area of the μ LEDs. The mesa area on the common-p configuration was designed to $105 \times 90 \mu m^2$, and on the 4-pad configuration, it was $125 \times 100 \mu m^2$. Other than the pads for the LEDs, both the chips have two input pads (each pad $50 \times 100 \mu m^2$) for PZT and two extra pads for integrating external capacitor of size $50 \times 207 \mu m^2$ each. The wider capacitor pads are the main limiter on the space available for the μ LED assembly.

The fabrication process was designed by combining two different process flow steps and schematically presented in Figure 5.3. In the first step, blue and UV were fabricated on GaN-on-PSS with a reserved 'open-space' acting as a dual assembly carrier. In the second step, releasable

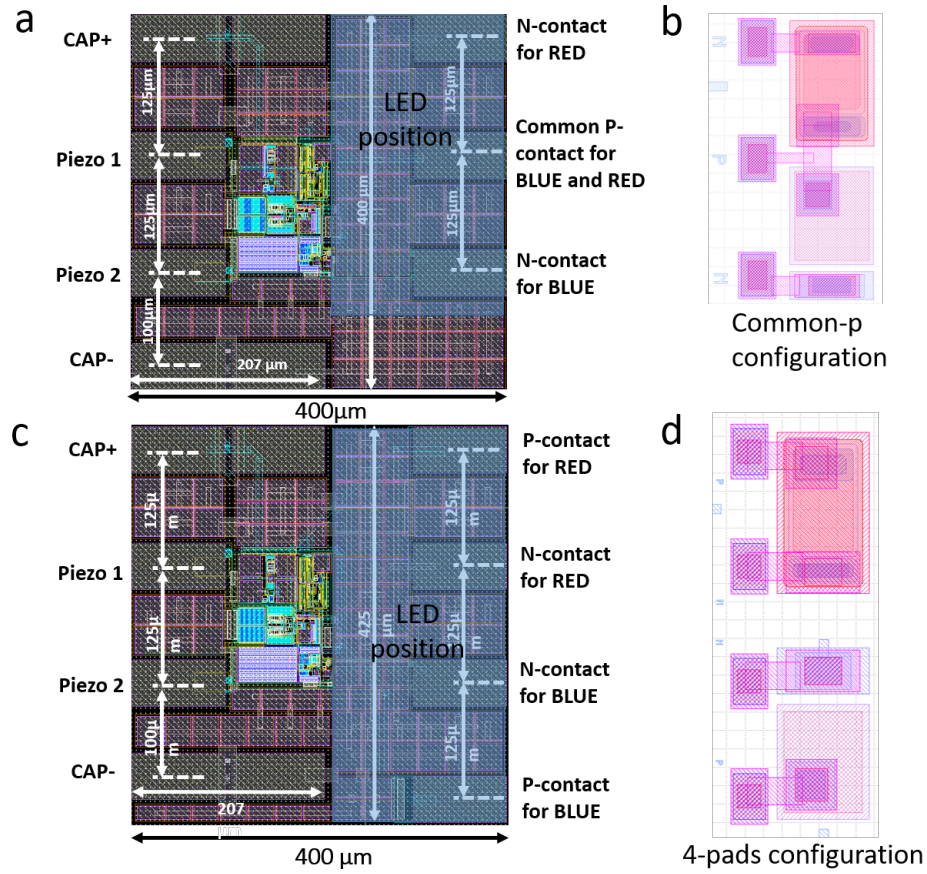


FIGURE 5.2: Layout of the (a) common-p type electronic die and (b) corresponding dual colour μ LED assembly, (c) 4 separate LED pad electronic die and (d) corresponding 4-pad dual colour μ LED assembly, designed to support flip-chip bonding.

blue (GaN-on-Si) and red (AlInGaP-on-GaAs) μ LEDs were fabricated on native substrates. After the undercut, the released μ LEDs were picked up from the native wafer and transfer printed on the 'open-space' of the carrier wafer with the help of a thin adhesion layer (Inter-Via). Finally, suitable interconnection methods were applied while considering challenges such as side-wall coverage, adhesion, different topology, and coverage on narrow space to obtain the final dual-colour chips.

5.3 Fabrication of dual colour assembly

The dual-colour on a single-chip fabrication process utilizes patterned sapphire as the carrier substrate. Since the sapphire substrate carries both the native μ LED (UV/blue) and transfer printed μ LED (red/blue) in the final dual colour chip, it is termed as the carrier wafer. The target is to achieve three different dual colour systems: a. UV+Red, b. UV+Blue and c.

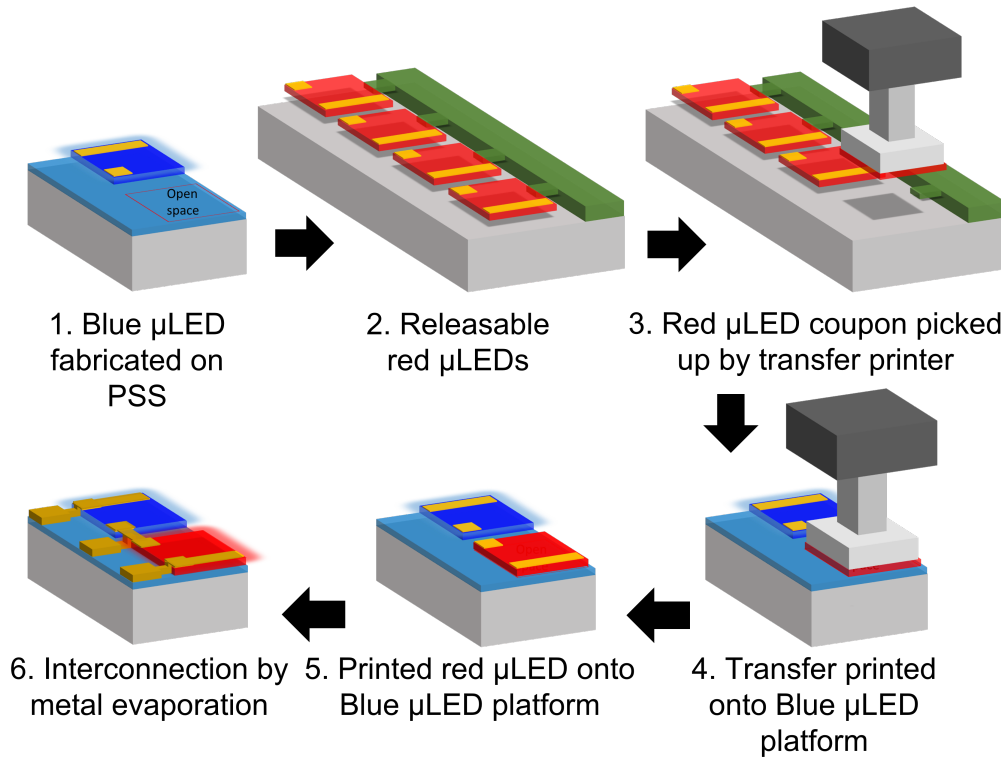


FIGURE 5.3: Schematically presents the process flow for fabricating the dual-wavelength μ LEDs on a single chip.

Blue+Red. UV and blue LED epilayers on sapphire substrates were used as the base carriers for the processing.

Transfer printing is a new technology where LEDs or coupons are initially fabricated on the native substrate and then undercut chemistry is used to release the coupons from the substrate. Though, the released coupons are held with the native wafer by a dielectric (such as $SiNx$) anchor-tether system. A patterned PDMS is then used to press on the released coupon to break the tether and pick it up. The target wafer is separately prepared by spinning adhesive polymer (such as *intervia*), which also can be patterned. Finally, the coupon stuck on the PDMS stamp is pressed on the *intervia* in the designated area and slowly picked up using a lateral sheering force. This process prints the coupon on the target wafer. Note, the speed of the PDMS stamp is generally fast (< 1 second) for pickup, while the printing speed is slow ($\sim 2-3$ seconds). The high-level flow of transfer printing is shown schematically in Figure 5.4(a) and the detailed process flow is presented in Figure 5.4(b). Once the printing is done, the *intervia* on the target wafer is hard-cured in the oven which makes the adhesion even stronger and the bonding more robust to allow subsequent processing steps.

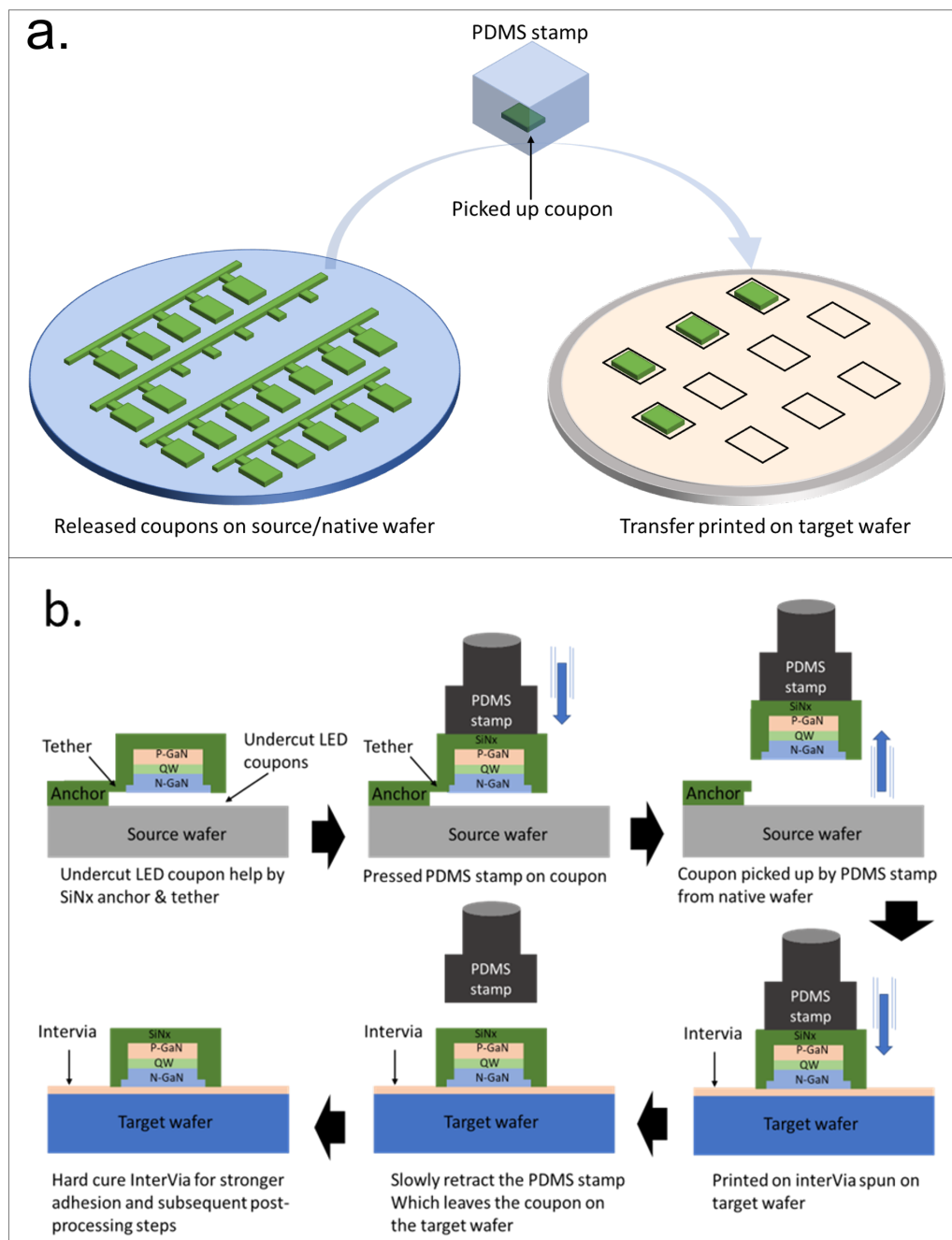


FIGURE 5.4: Schematically presents the process flow for the transfer printing. (a) Show a high-level flow where the released coupons are picked up by the PDMS stamp of the printer and printed onto the target wafer in the designated area, whereas (b) show the schematic process flow of transfer printing technology in detail.

The process needs suitable wafer materials, lithographic masks, and the development and implementation of the process steps. For this purpose, high-quality UV and blue LED wafers were sourced from commercial vendors. The process flow involves the fabrication of four different μ LEDs, namely:

1. 373 nm UV μ LEDs on patterned sapphire substrate
2. 480 nm Blue μ LEDs on patterned sapphire substrate
3. 630 nm releasable Red μ LEDs on GaAs
4. 450 nm releasable Blue μ LEDs on Si

The releasable red μ LEDs were fabricated by my colleague Jack Browne here at Tyndall National Institute and will not be discussed in detail in this thesis.

5.3.1 Fabrication of UV and Blue LEDs on carrier wafer

The cleaning process of the carrier wafers was done by following the steps mentioned in subsection 3.3.1, and the fabrication of the μ LEDs on the GaN-on-PSS carrier wafer was done by the process mentioned in subsection 3.3.2 except for some extra steps necessary for the integration of extra colour. The 'open space' on SiO_2 -passivated n-GaN was created for the integration of the red (on blue/UV carrier) or blue (UV carrier) devices. Figure 5.5 shows the microscope image of the fabricated blue and UV μ LEDs on the carrier wafer for both common-p type and 4-separate pad type configuration.

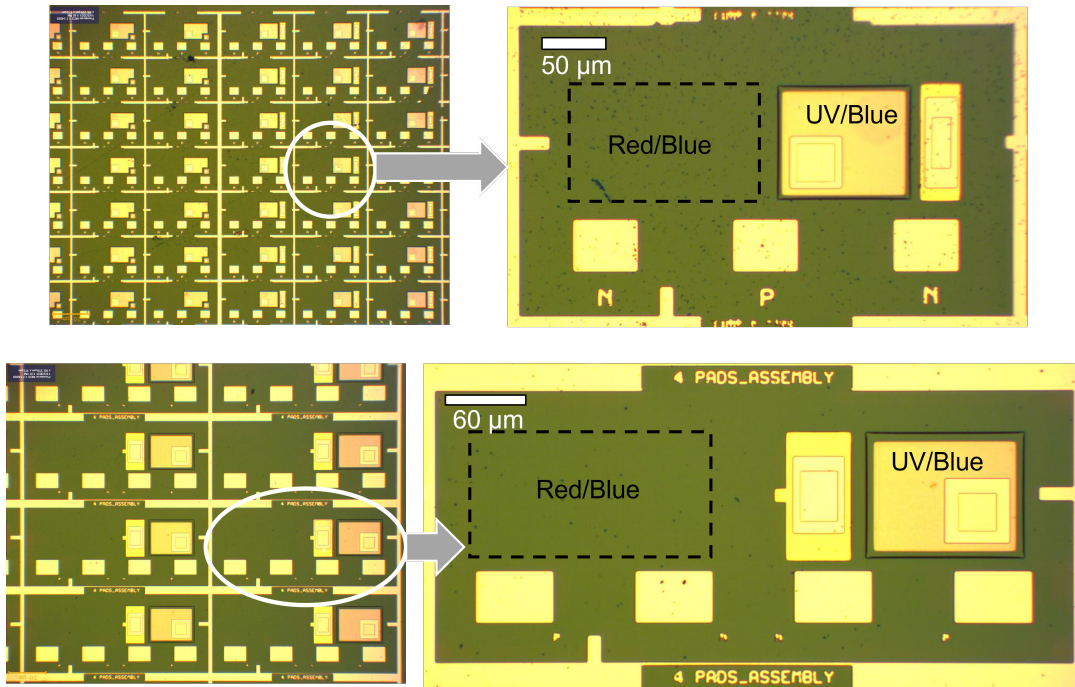


FIGURE 5.5: Microscope image of the fabricated UV and Blue μ LED on PSS carrier where the top picture shows the common-p type configuration and the bottom one shows the 4-separate pad configuration.

5.3.2 Fabrication of releasable Blue LEDs

To fabricate releasable Blue μ LEDs, 450 nm LED wafers grown on $\langle 111 \rangle$ Si substrates were used. The cleaning process was followed as mentioned in sub-section 3.3.1 except the KOH treatment was not done as it can etch Si.

5.3.2.1 Fabrication of blue LED for undercut

The process begins with the formation of a p-contact ($60 \times 80 \mu\text{m}^2$) using a 10/20/30 nm Pd/Ni/Au layer by lift-off lithography, followed by etching a mesa of depth 900 nm with the size of $70 \times 90 \mu\text{m}^2$ by inductive coupled plasma (ICP) etching to expose the n-GaN layer. Ti/Au of 20/300 nm metallization layer was evaporated onto n-GaN, serving as the n-contact. After that, a 350 nm thick SiO_2 passivation layer was deposited by plasma-enhanced chemical vapour deposition (PECVD) and then patterned to expose areas above the p & n contacts. Subsequently, a Ti/Au of 20/200 nm layer was evaporated onto these open areas, serving as the bond pad of the μ LED. Note that the commonly-used Al-containing n-metal contact was avoided here as Al could be attacked by the TMAH during the Si undercut process. The cross-section of the releasable μ LED is schematically shown in Figure 5.6 following the fabrication flow.

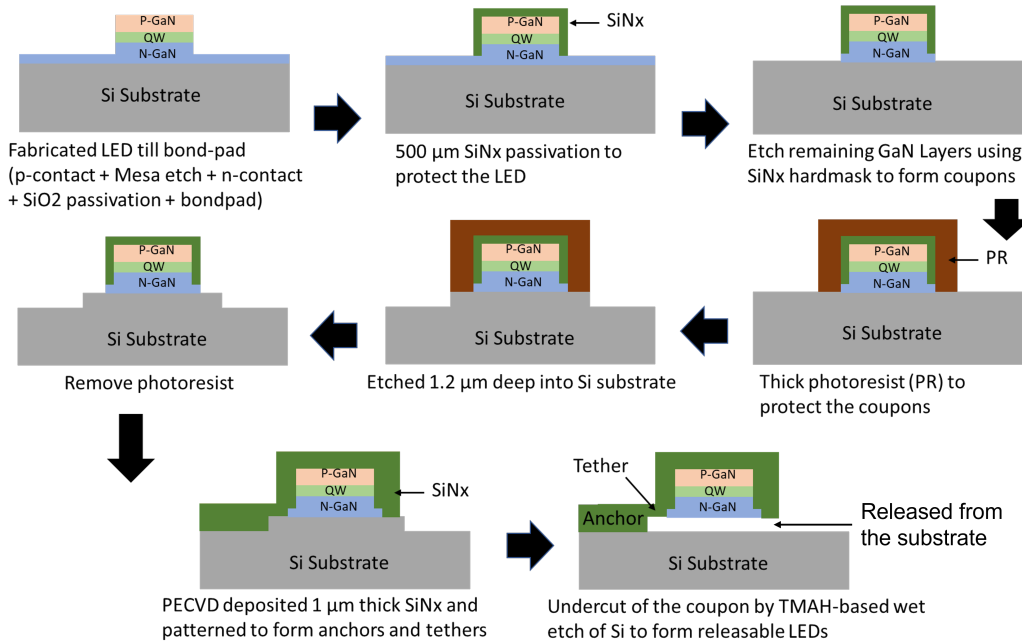


FIGURE 5.6: Cross-section view of the schematic illustration of the fabrication flow of releasable blue μ LEDs.

A SiN_x layer of thickness 500 nm and area of $77.5 \times 122.5 \mu\text{m}^2$ was deposited by PECVD to passivate the whole device and then dry etched to Si substrate through GaN epi-layers to form the coupons. A larger Si platform of size $135 \times 90 \mu\text{m}^2$ was defined by photolithography and then further etched deep ($1.2 \mu\text{m}$) into Si. Finally, to prepare the μ LEDs for releasing and the following transfer printing, 1 μm -thick SiN_x was deposited by PECVD and then patterned to form anchors along the $\text{Si} \langle 1 - 10 \rangle$ and tethers perpendicular to this direction [Figure 5.7].

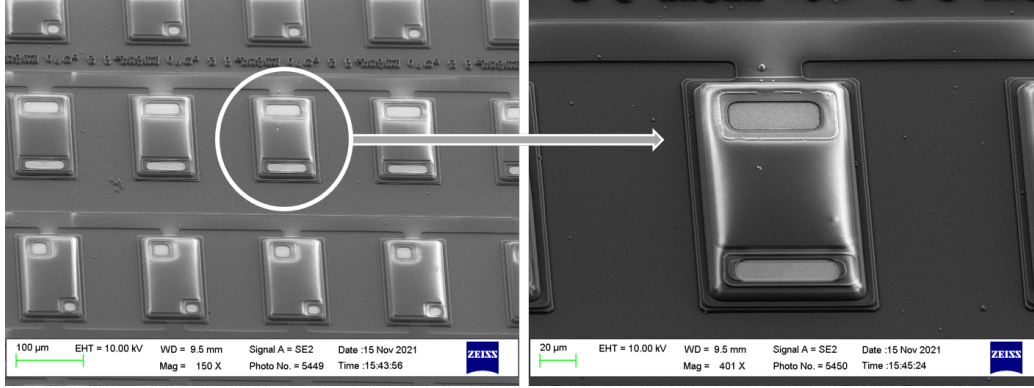


FIGURE 5.7: SEM image of the fabricated Blue μ LED ($\lambda = 450 \text{ nm}$) of size $125 \times 100 \mu\text{m}^2$ on Si wafer before undercut process showing the anchor-tether support system.

The anchor/tether system is used to support the suspended devices, preventing them from collapsing after releasing from the substrate. The stress of the PECVD deposited SiN_x layers was controlled by changing the plasma frequency between high and low to deposit SiN_x with compressive stress. The residual stress (tensile) within devices, when released from the substrate, could be then compensated by the SiN_x layer resulting in a completely flat surface after undercut.

5.3.2.2 Undercut of blue LEDs from the native substrate and transfer printing to carrier substrate

Just before the undercut, the sample was dipped into BOE for 10 seconds to remove any presence of oxide from the surface. The devices were released from the Si substrate by removing a thin layer of Si underneath the GaN epi-layers using TMAH-based wet etching. The wet etching of Si with TMAH is highly anisotropic on $\langle 111 \rangle$ oriented Si substrates, i.e., the etching rate of the $\langle 1 - 10 \rangle$ planes is much faster than that of the $\langle 111 \rangle$ planes or their projections. As shown in Figure 5.8, during the etching process, anchors oriented along the Si $\langle 1 - 10 \rangle$ direction were minimally etched while the etching under the devices was fast. To initiate the undercut process, at first the sample was immersed into 5% TMAH solution at 75

$^{\circ}\text{C}$ for 15 minutes (etch rate: $1.1 \mu\text{m}/\text{min}$), and then once the process is started (etch start process can be visually observed by rapid bubble formation) the temperature is reduced to 50°C and it took another 55 minutes (etch rate: $0.5 \mu\text{m}/\text{min}$) to fully undercut the μ LEDs.

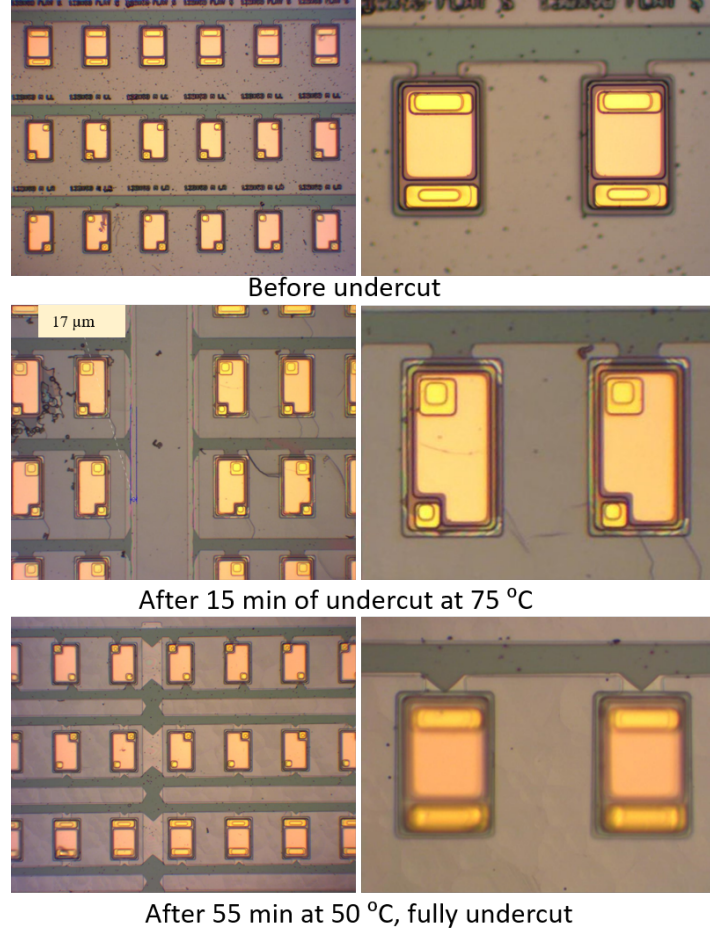
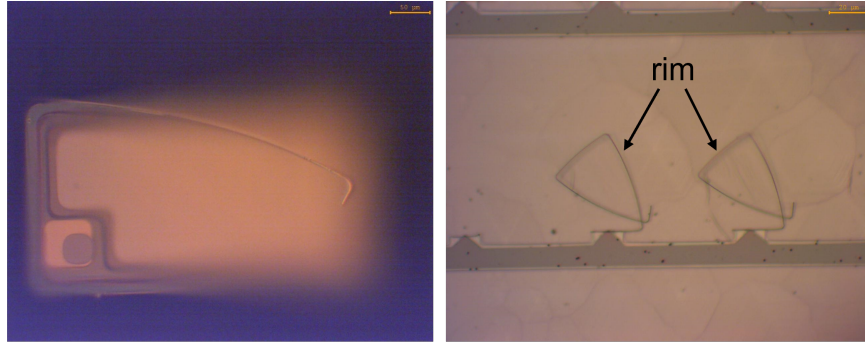


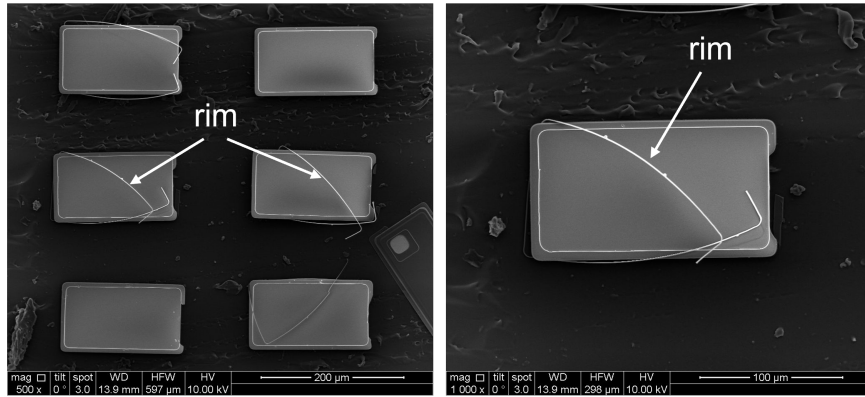
FIGURE 5.8: Microscope image of the μ LEDs during undercut process in 5% TMAH solution.

To show that the devices are ready for transfer print, 450 nm thick Intervia was first spun on a Si wafer. A PDMS stamp was used to pick up the LEDs from the native substrate and then printed on the Intervia of the Si wafer. A rim along the perimeter of the μ LED was observed during printing, which came between the LED and Intervia during the printing process resulting in an extremely low transfer printing yield. To investigate the origin of this rim, μ LEDs were manually picked up by a small PDMS piece and imaged by both microscope and SEM as shown in Figure 5.9. To determine the rim material, the process was carefully studied again, and SEM-EDX was done.

The SEM-EDX showed a high concentration of Si and N in the rim, confirming that the rim is SiN_x . A possible reason could be that during etching deep into Si , micro trenches were formed



Microscope image of the back surface of the LED and the rim trace on the native wafer



SEM image on the back surface of the LEDs showing the rim

FIGURE 5.9: Microscope image (top) and SEM image (bottom) of the back surface of the undercut μ LEDs show the trace of a rim around the edge of the device.

around the device. Which was then filled up with SiN_x during PECVD and was not removed during the etching of SiN_x to form anchors and tethers.

To remove the SiN_x rim, at first the previously released μ LEDs were dipped into BOE for 3-4 minutes. As the released devices are held by SiN_x tether, which also etches in BOE, and the formation of bubbles during etching in BOE between the released LED and Si wafer pushes the LED upwards, most of the devices collapsed during the process, and the microscope image of the collapsed devices is shown Figure 5.10(a). Therefore, the undercut chemistry was optimised by introducing BOE several times in between TMAH undercut steps. BOE has a slower etch rate of SiN_x than SiO_2 . Before undercut, the wafer was dipped into BOE for longer (30 seconds) than usual. After 15 minutes of undercut at a higher temperature, the sample was dipped into BOE for another 50 seconds, and after 43 minutes, the dip in BOE was done for 60 seconds. This process completely etches the rim away without compromising the anchor/tether system [Figure 5.10(b)]. The rim-free Blue μ LEDs were again printed onto Intervia coated Si,

and more than 90% printing yield was achieved.

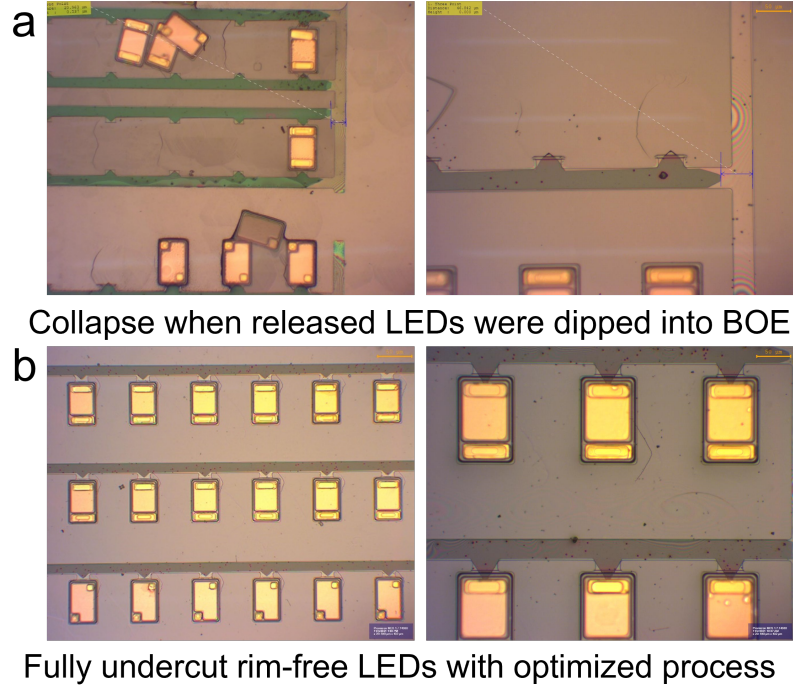


FIGURE 5.10: Microscope image of the μ LEDs showing (a) collapse of the devices when previously released devices were dipped into BOE to remove the rim and (b) rim-free devices obtained by the optimized undercut process without collapse.

5.3.3 Integration of dual-wavelength assembly

To integrate the dual-wavelength μ LEDs on a single chip, Intervia of thickness 450 nm was spun onto the carrier wafer (GaN-on-PSS) with pre-fabricated UV and Blue μ LEDs. Intervia acts as an adhesive layer for the transfer-printed devices. Intervia is a sticky-gel-like photoresist, but when baked at high temperatures, it becomes hard, and the printed devices would be strongly adhered by Intervia onto the carrier.

5.3.3.1 Transfer printing of released devices onto carrier wafer

The released red and blue μ LEDs were picked up by PDMS stamp using the transfer printer (TP) and printed onto the designated 'open space' of the UV and UV carrier wafer as schematically shown in Figure 5.3. A high transfer printing yield has been achieved in this case, as the issues with SiN_x were previously resolved. Figure 5.11 shows that most of the devices were successfully transfer-printed on the carrier with high alignment accuracy.

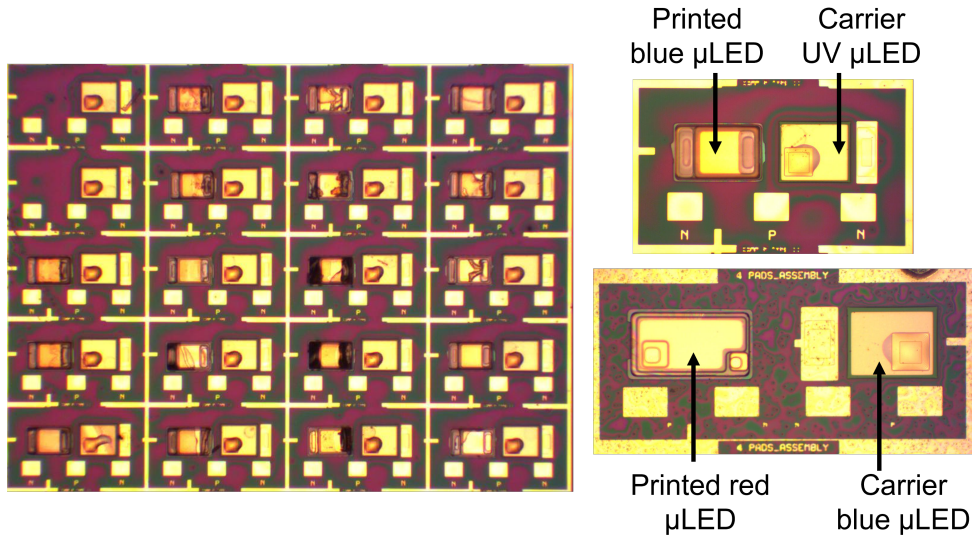


FIGURE 5.11: Microscope image of the transfer printed red and blue μ LEDs on to 450 nm thick Intervia spun on the UV μ LED carrier.

Once the TP was done, the Intervia was etched into an isotropic O_2 plasma chamber. The target was to etch Intervia from everywhere else other than the bottom of the printed LED. It was observed that during the etch process, the Intervia was also etched completely from underneath the printed μ LEDs as well, resulting in a failure in the process [Figure 5.12]. It suggests the etch rate of Intervia in an isotropic O_2 plasma chamber is higher in the lateral direction than in the vertical direction which could be possibly due to plasma crowding around the edges of the wafer.

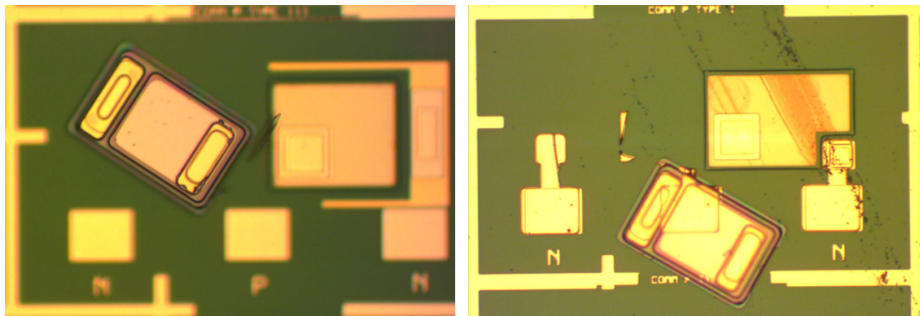


FIGURE 5.12: Microscope image of the carrier wafer showing the undercut of Intervia during isotropic O_2 plasma etch process.

To overcome the lateral etch of Intervia, it was required to have a directional O_2 plasma rather than an isotropic plasma. Two ICP etch recipes were developed and tested for this purpose. Intervia of thickness 840 nm were spun on Si pieces, and a few test μ LED coupons were transfer printed onto that to determine the best etch recipe. In one case, the etch recipes were used on Intervia before curing [Figure 5.13] and on the other after curing [Figure 5.14].

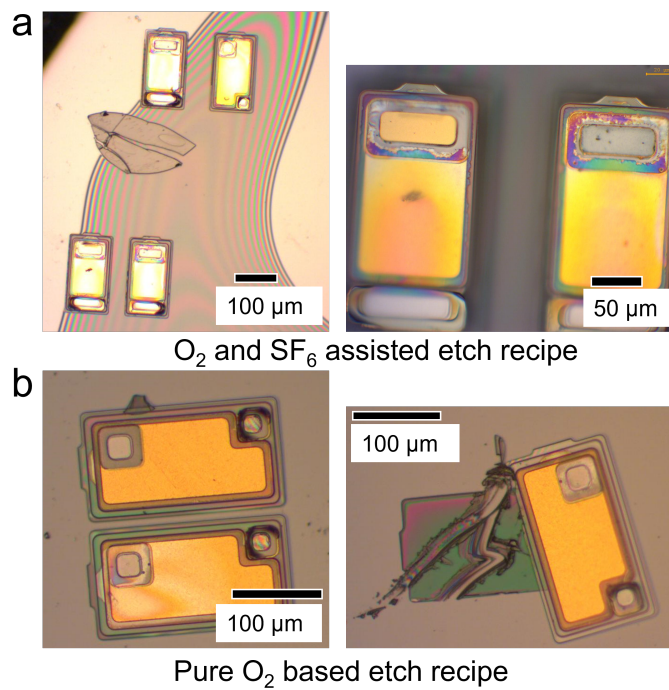


FIGURE 5.13: Microscope image of the μ LEDs demonstrating different ICP etch recipes used on uncured Intervia. (a) shows the effect of the recipe that contains a mixture of O_2 with SF_6 , and (b) shows the effect of pure O_2 etch recipe.

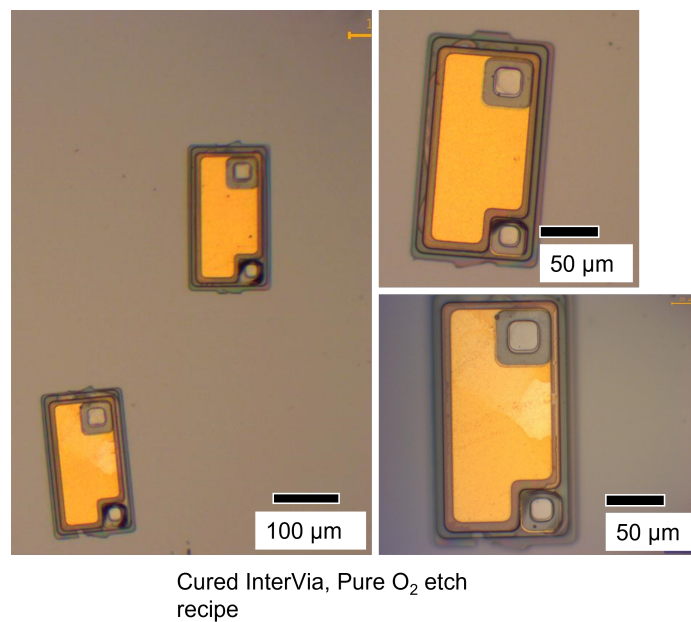


FIGURE 5.14: Microscope image of the printed μ LEDs of size $125 \times 100 \mu m^2$ demonstrating pure O_2 dry etch recipes used on cured Intervia.

The first recipe contains a gas mixture of O_2 (86%) and SF_6 (14%), and the results of the etch are presented in Figure 5.13(a). The etch rate was 230 nm/min measured by the endpoint monitor. Though this recipe seems to affect the Cr bondpad of the red LED slightly. The

second recipe contains 100% pure O_2 , and the results are shown in Figure 5.14. The etch rate obtained in this case was $1.7 \mu m/min$ and does not affect the device. Note in both cases, the Intervia was not cured before the etch.

Since Intervia is a kind of negative photo-resist, when the same O_2 etch recipe was used on the UV-exposed Intervia, the etch rate was slightly decreased to $1.5 \mu m/min$. After the pure O_2 etch was done, one of the μ LEDs was moved by forcing with tweezers to confirm the presence of Intervia at the back of the device. After the hard cure of the etched devices in the oven for 30 minutes at $90^\circ C$ followed by 3 hours at $175^\circ C$ in N_2 , the Intervia showed desired strength, and the LEDs were firmly attached to the Si wafer. The etch rate of Intervia measured from different etch recipes is presented in Table 5.1.

TABLE 5.1: Directional plasma etch test to remove Intervia.

Recipe (Gas flow)	Source power	Chamber pressure	Intervia condition	etch rate
Mix etch (86% O_2 and 14% SF_6)	400 Watt	5 mTorr	not hard cured not UV exposed	230 nm/min
O_2 etch (100% O_2)	1500 Watt	10 mTorr	not hard cured not UV exposed	1.7 $\mu m/min$
O_2 etch (100% O_2)	1500 Watt	10 mTorr	not hard cured UV exposed	1.5 $\mu m/min$
O_2 etch (100% O_2)	1500 Watt	10 mTorr	hard cured UV exposed	1.4 $\mu m/min$

In the final device, the Intervia was cured before the etch. As the Intervia shrinks upon curing, the measured thickness was $808 nm$ after curing (before curing Intervia thickness was $840 nm$). A slightly slower etch rate of $1.4 \mu m/min$ was obtained in this case which was expected as the Intervia hardens upon curing.

In the dual-colour device process, $1 \mu m$ thick Intervia was spun and cured before etching in order to secure the μ LEDs in position. Figure 5.15 shows the microscope image of the transfer printed μ LEDs onto hard-cured and pure O_2 ICP etched Intervia spun on the GaN-on-PSS carrier wafer.

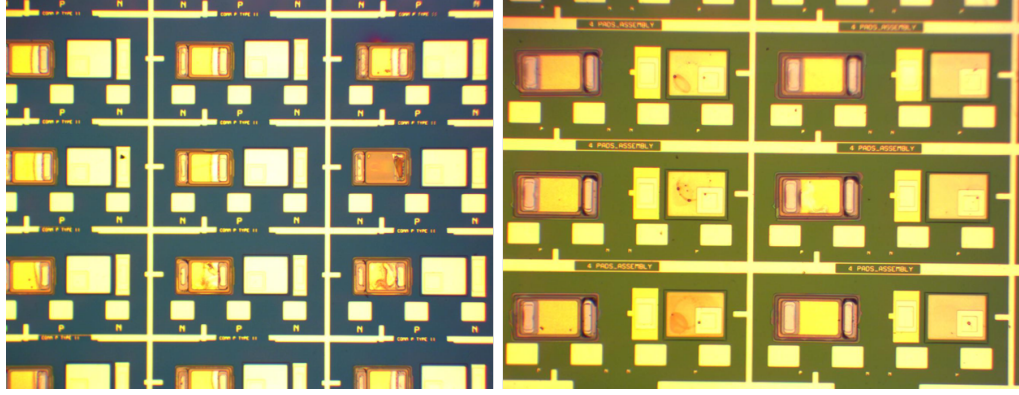


FIGURE 5.15: Microscope image of the μ LEDs showing successful transfer printing and etching of cured Intervia without undercut.

5.3.3.2 Interconnection between LEDs to carrier pads

The microscope image of the interconnection process steps is shown in Figure 5.16. Once the issues with Intervia undercut were resolved, red and blue μ LEDs were transfer printed onto 1 μ m thick Intervia on the blue and UV carrier wafer. Since the thickness of the printed blue or red μ LEDs were about 5 μ m and 3 μ m, respectively, a thick interconnection layer was required for sidewall continuity. Ti/Au of 25/500 nm were 360° evaporated to connect between μ LED pads to the bond pads. After that, a blanket of 500 nm SiO_2 was sputter deposited, and lithography was done to open sections only on the bondpad region by dry etching. To make the bondpads higher than the top surface of the transfer printed μ LEDs, so that during flip-chip bonding, the pads create better contact with the CMOS pads, a thicker pad metal was required. Bi-layer of photoresist PMGI SF19 (4.5 μ m) and SPR220 (4 μ m) were spun and patterned. A thick metal combination of $Ti/Ag/Au$ of thickness 20/4000/300 nm was evaporated onto the bondpads.

At this point, the wafer processing part of the integration process was completed. Next, the wafers were ground and semi-polished to reduce the PSS thickness to 120 μ m and mechanically saw-diced out into individual chips. Both the grinding and dicing processes were optimized for sapphire substrates and are extremely time-consuming processes. During the investigation of wire bonding, it was found that the adhesion of the thick metal stack with bottom Ti/Au layers was relatively poor and leads to peel-off. Although this peeling of thick metals does not affect the optoelectrical performance of the device, it might pose challenges during the bonding step with CMOS.

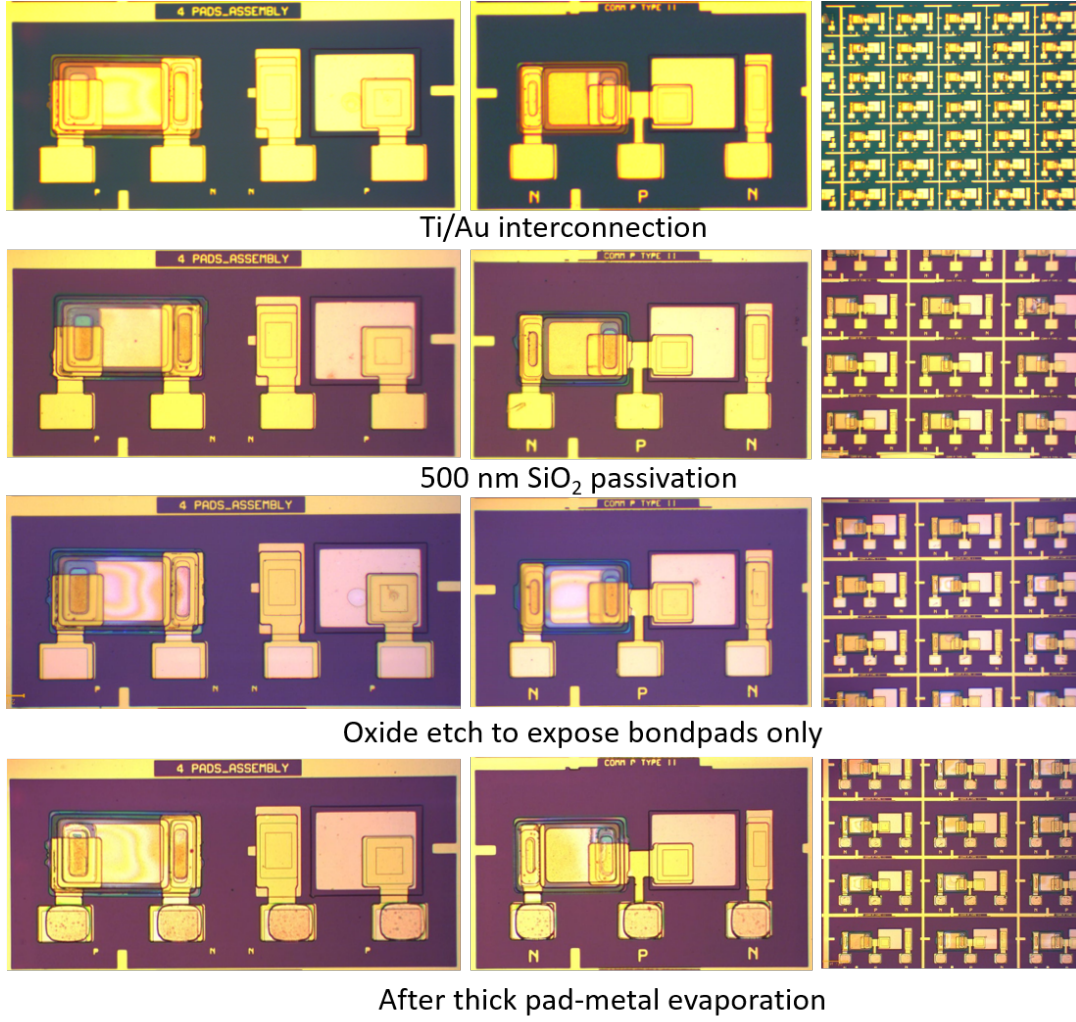


FIGURE 5.16: Microscope images of the interconnection process flow showing Ti/Au metal interconnection (1st image), after 500 nm sputtered SiO_2 (2nd image), after oxide etch to open pads on the bondpad (3rd image) and after thick metal evaporation on the bondpads (4th image)

5.4 Characterization of dual colour assembly

5.4.1 Electrical characteristics

The I-V characteristics of the blue (480 nm) and UV (370 nm) μ LEDs were measured from 0 mA to 3 mA and presented in Figure 5.17, whereas the I-V characteristics of released blue (450 nm) and released red (650 nm) μ LEDs are presented in Figure 5.18. Measurements at a higher forward bias (> 3 mA) was not investigated as the devices will be operated in the range of ≤ 1 mA due to limitations of the electronic die. Figure 5.17 shows that turn-on voltage of both carrier blue μ LEDs is about 2.33 V with a small increment in voltage due to the series resistance. Although both carrier-UV μ LEDs have the same turn-on voltage of 3.12 V, the

smaller mesa UV μ LED has a higher voltage increase with the current. This is due to higher contact resistance originated by smaller semiconductor-metal contact areas. About 1.5 times higher series resistance was measured for the smaller mesa ($105 \times 90 \mu\text{m}^2$) UV μ LEDs than the bigger mesa ($125 \times 100 \mu\text{m}^2$) UV device.

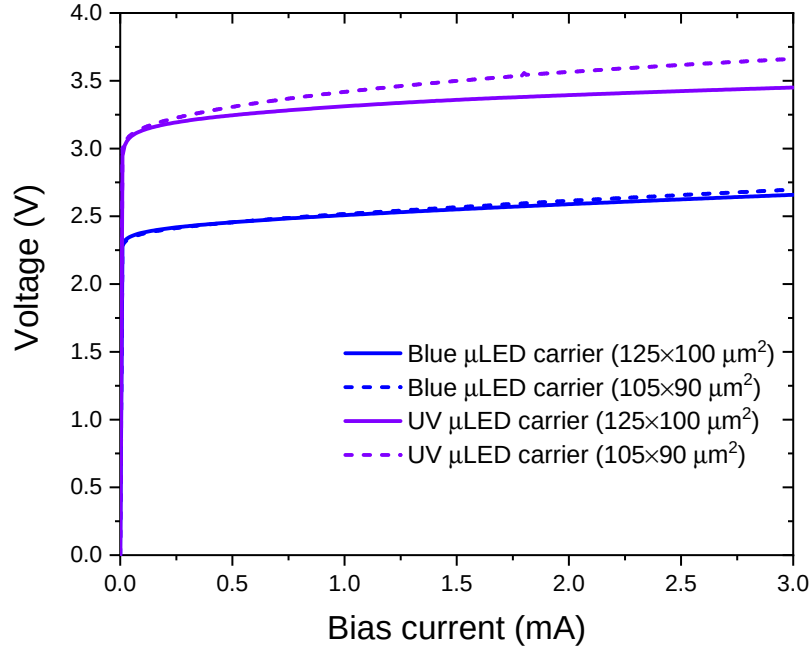


FIGURE 5.17: Forward bias current-voltage characteristics of the blue and UV μ LEDs on the carrier wafer.

Figure 5.18 shows the turn-on voltage of the released and transfer printed blue and red μ LEDs were measured at 2.51 V and 1.25 V respectively. Blue μ LEDs showed similar I-V characteristics before and after release, which shows that the release process does not affect the electrical performances of the device. On the other hand, the red μ LED had a sharp rise in voltage with increasing current, which is typical behaviour of AlGaInP-based material.

The electrical ideality (η) of the μ LEDs in the dual colour chip was measured to be 1.42, 1.52, 1.35, and 2.09 for released red, released blue, carrier blue, and carrier UV μ LEDs respectively, and presented in Figure 5.19. It can be seen from Figure 5.17 and 5.18 that the ideality was lowest near the turn-on voltage of the LEDs and is between 1.0 and 2.0, which implies a highly radiative recombination process. As the ideality of released red, released blue, and carrier blue was measured below 2.0, it represents efficient radiative recombination. On the UV μ LED, the ideality was found slightly above 2.0 as the GaN-based UV epi-material is not as efficient as the blue material.

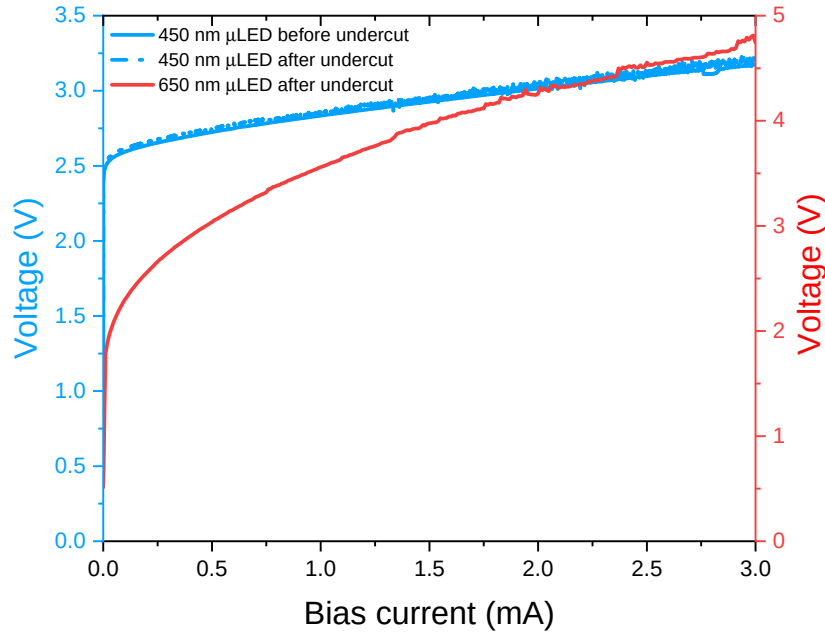


FIGURE 5.18: Forward bias current-voltage characteristics of the released blue and red μ LEDs transfer printed onto the carrier wafer.

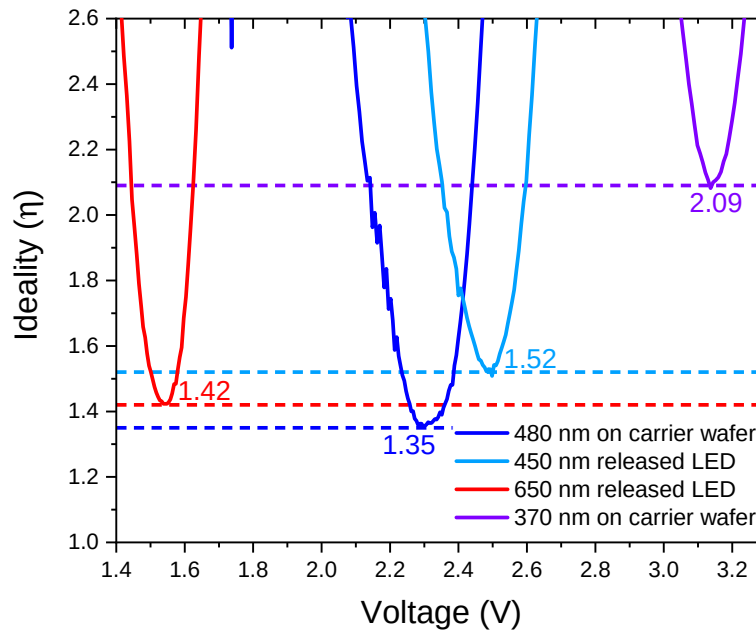


FIGURE 5.19: Electrical ideality of all four μ LEDs as a function of voltage measured after interconnection layer.

5.4.2 Electroluminescence spectra

The normalized EL spectra from the dual wavelength chips were measured by the fiber-coupled UV-Vis spectrometer and presented in Figure 5.20 as a function of wavelength. The peak wavelength and corresponding energy are indicated in the figure. It can be seen from the plot that UV μ LED has the narrowest FWHM of about 10 nm while the released blue μ LED has

18.7 nm, blue μ LED on carrier wafer has 21 nm and released red μ LED has the FWHM of about 28 nm. Although the red μ LED has the broadest FWHM, the peak wavelength of 650 nm is perfectly suitable for the activation of red-sensitive ChR-2. Although, it is not highly required to have a narrow FWHM for optogenetic applications, as long as the peak wavelength variation is within ± 10 nm range for the red/blue. For the UV, the peak wavelength should be strictly less than 375 nm for activation of the DDS, and the FWHM should be narrow (± 5 nm) for the requirement of high energy density for the DDS activation.

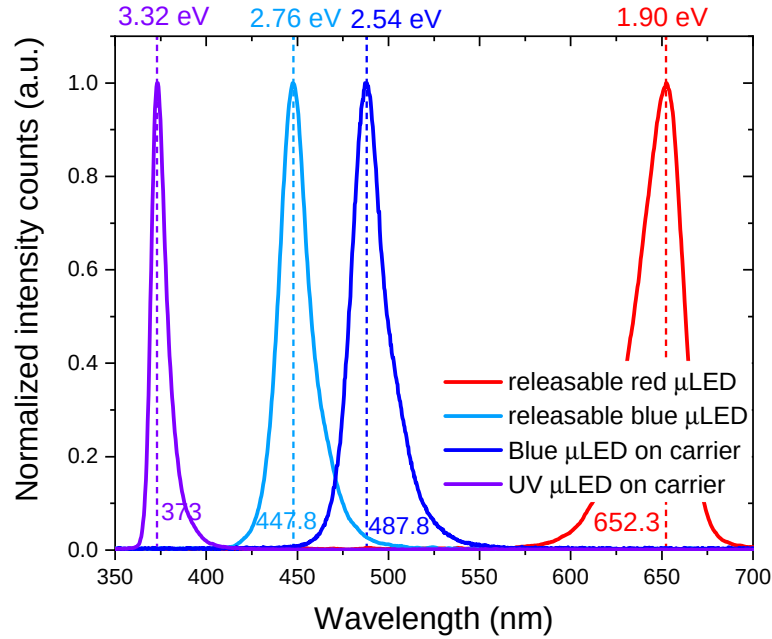


FIGURE 5.20: Normalize EL spectra obtained from fully integrated dual-colour on single chip μ LED assembly.

Compared with Figure 3.9, a small red shift in peak wavelength was observed in the dual colour carrier UV (2 nm shift) and blue (4 nm shift) even though both devices were fabricated from the same epi-material. As both times, the EL spectra were measured at a low current density (< 15 A/cm²), and a red shift is observed, which could be attributed to stress induced by the dual-colour fabrication process or the generation of heat in the device and requires further investigation.

5.4.3 Optical power and efficiency

Figure 5.21 and 5.22 show the optical power and EQE respectively measured from the fully integrated dual colour μ LEDs at a NA of 1. Note that the power measured here shows represents the power coming out only from the bottom surface of the dual-colour chip. Due to the limited

availability of the dual colour chips, measurement of the absolute power in the integrating sphere was not carried out in this case.

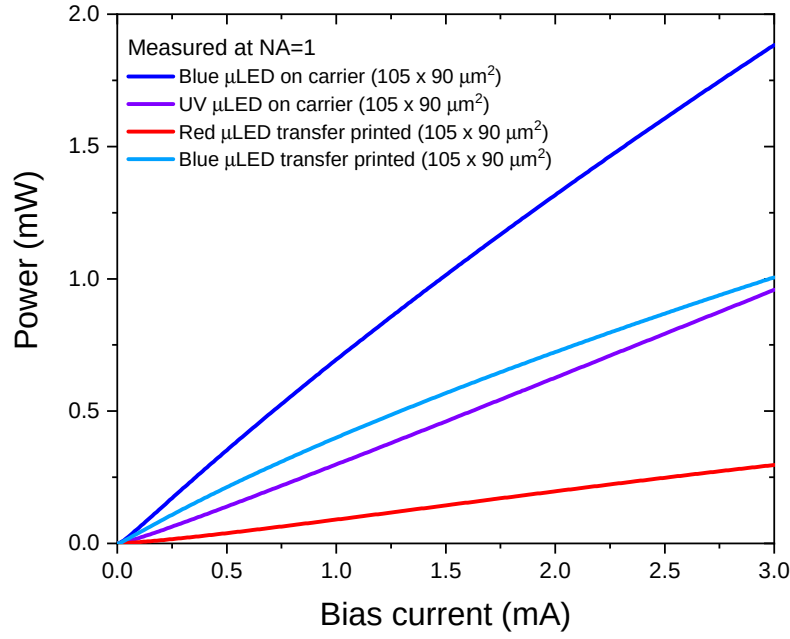


FIGURE 5.21: Optical power measured at NA of 1 from the fully integrated dual-colour on single chip μ LED assembly.

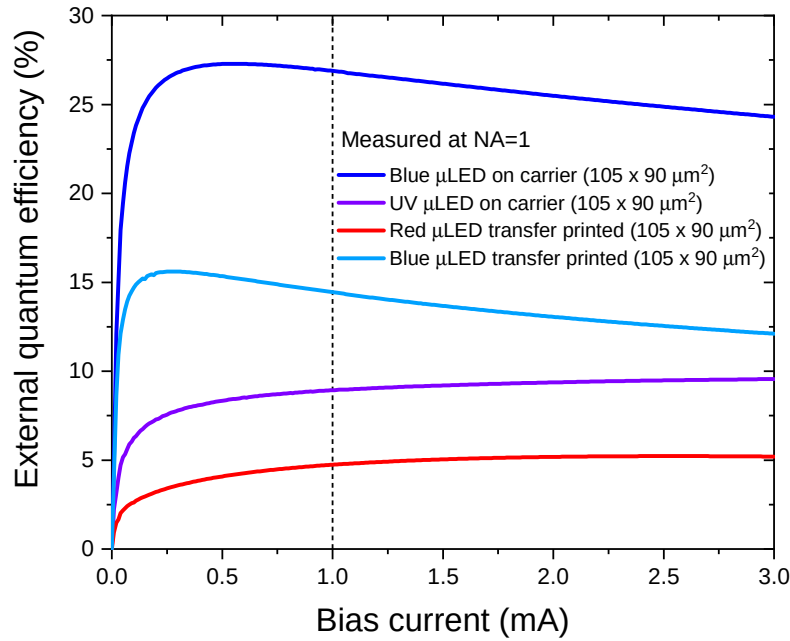


FIGURE 5.22: Shows the external quantum efficiency of all four different wavelength μ LEDs measured at NA of 1 as a function of current.

For ease of comparison, the optical power presented here were measured from the devices that had the same active area of $105 \times 90 \mu\text{m}^2$ and operating between 0 to 3 mA. By comparing all four devices, it is evident that the blue devices on the carrier wafer are the most efficient of all.

At 1 mA blue LED on the carrier wafer generates a power of 0.69 mW while the power from the blue released LED was measured as 0.40 mW at 1 mA . A maximum EQE of 27.4% from the blue device on the carrier wafer and 15.6% for the release blue μ LED were measured from these devices while the power was measured at NA=1. Compared with the blue devices in Chapter 3, at NA=1, about 3% less EQE was measured here. There was no ARC coating on these dual-colour chips, so about 10% less light extraction was achieved, which is the main reason for the lower EQE. The lower efficiency from the released-blue device than carrier-blue μ LED is mainly due to low-quality epi-material growth on Si wafer than PSS. Also, the absorption and refractive index mismatch-related loss of 1 μm thick Intervia layer between blue released device and carrier wafer could be another potential reason for such lower EQE. Also, there was no surface roughening on the blue-released LEDs, which also lowers the light extraction. Note that these dual-colour devices do not have any ARC on the PSS substrate. When compared between Figure 3.13 and Figure 5.22, it is clearly observed that about 10% less efficiency at NA=1 was achieved from the blue 480 nm LEDs in this case due to absence of ARC. This measurement matches with the previous observation mentioned in subsection 3.4.4.

The optical power from the UV on the carrier wafer and the transfer printed red μ LEDs were measured about 0.3 mW and 0.1 mW [Figure 5.21] respectively while operating at 1 mA . Compared with the UV LEDs mentioned in Chapter 3, the same amount of optical power is achieved here as well. The power measured from the red LEDs was low due to the high refractive index mismatch between AlInGaP (RI=3.5) and Intervia interface. Although the power from the blue and UV μ LEDs are measured more than the minimum specifications, the power from red μ LEDs will be an issue while restricted by the voltage limit of the CMOS chip.

5.5 Summary and discussion

In this chapter, the process flows to achieve a dual-colour μ LED assembly on a single chip were developed, and the fabrication steps were described in detail. Three different configurations of dual-colour μ LED assemblies were developed here with combinations of 1. BLUE + UV, 2. RED + UV, and 3. RED + BLUE, where the red and blue wavelengths will be targeted for activation of red and blue sensitive ChR-2, respectively and the UV will be used to trigger SP-based localized DDS. The process flow consisting of design, process development, device fabrication, and electro-optical characterization are presented here in detail.

The dual colour μ LED assemblies had two different physical layouts and were designed based on the CMOS layout: common p-contact configuration and 4-separate pad configuration [Figure 5.2]. As the dual colour compatible CMOS chip had two $207 \times 50 \mu\text{m}^2$ pads for external capacitor out of $400 \mu\text{m}$ length, it leaves less than $200 \mu\text{m}$ width for the μ LED. Therefore, the external dimension available for the μ LED was less than $200 \times 400 \mu\text{m}^2$, which leads to a smaller dimension on each individual colour μ LED. In order to reduce the power consumption by the loads (μ LEDs) and achieve higher optical power from the μ LEDs, a more optimized CMOS and μ LED assembly design is required to achieve a bigger area for the μ LEDs while accommodating all other connections and components.

The dual colour μ LEDs were achieved by fabricating blue and UV μ LEDs on GaN-on-PSS wafer and then transfer printing of red and blue released μ LEDs from native Si wafer to carrier PSS wafer. This process requires processing four separate wafers (blue on Si, red on GaAs, and finally blue and UV on PSS) with different process flow and finally integrating them together to achieve a single unit. Thus, the process is much more complicated than the fabrication of μ LEDs on a single wafer. On the other hand, the requirement of a higher number of masking layers increases the alignment complexity. Several unexpected issues were encountered downstream on the process flow, such as undercut of blue and red μ LEDs from Si and n-AlGaAs, respectively, SiNx rim, intervia adhesion, intervia undercut, and successfully addressed. Although there are still some issues that need further investigation, such as stress due to thick nitride layers on transfer printed devices, adhesion of metals on SiO_2/SiNx , and back-end processing (grinding, dicing, and breaking). In the final phase of the process flow, the issues with adhesion and back-end processing dominated, resulting in the failure of most of the devices. It was observed that after dicing the interconnection metal and the top layer of red μ LED p-contact metal was peeled off. The main reason for interconnection metal (Ti/Au=25/500 nm) peeling is poor adhesion of metals on SiNx , which could be resolved by using a thicker Ti layer ($\approx 50 \text{ nm}$) and using Ar ion etch just before metal evaporation. Also, changing the metal stack could potentially be effective but requires a more detailed investigation. Whereas the main reason behind the peeling of the top metal layer of the p-contact could be due to both stress and adhesion. It was observed that after dicing, the top metal layer was peeled off mainly from the region on the metal interconnection. It is unlikely to have such poor metal-to-metal adhesion, although the mechanical grinding and dicing process is done by brute force and could contribute to the peeling.

Another critical issue is the dicing of sapphire to get individual chips. To accommodate mechanical dicing, the sapphire substrate was ground manually to thin down to $120\ \mu\text{m}$. During dicing, most of the devices break or chip away, resulting in low yield. To overcome these issues, laser dicing was investigated, but the available laser dicing tool was not optimized enough for this job. More than $\pm 30\ \mu\text{m}$ spread of the burnt material on either side of the laser diced groove was observed, damaging the μ LEDs. Currently, a lot of industry-level tools are available that can laser dice full sapphire without damaging surrounding devices ($\leq 25\ \mu\text{m}$ kerf width). A combination of semi-laser dicing and mechanical breaking could be the best way to achieve nice & clean diced devices but was not feasible within the scope of the project.

It is observed from the current-voltage characteristics that the UV and blue μ LEDs on carrier wafers show similar behaviour as measured in Chapter 3. The blue transfer printed μ LED has a higher turn-on voltage which is reasonable due to higher bandgap energy at shorter wavelength. If the mesa area is considered as the light emitting area ($105 \times 90\ \mu\text{m}^2$), then at $1\ \text{mA}$, a power density of $73\ \text{mW}/\text{mm}^2$ (power: $0.69\ \text{mW}$) from the blue carrier μ LED and $42.3\ \text{mW}/\text{mm}^2$ (power: $0.4\ \text{mW}$) from the transfer printed blue μ LED were measured at an $\text{NA} = 1$. It is expected that when measured in an integrating sphere, the total power density should be more than measured here at $\text{NA}=1$. For the activation of blue-sensitive ChR-2, this power density is still more than the minimum criterion ($\geq 20\ \text{mW}/\text{mm}^2$). For the red μ LED at $1\ \text{mA}$, a power density of $10.6\ \text{mW}/\text{mm}^2$ was measured at $\text{NA} = 1$. It has been observed in Chapter 3 that about 35% - 40% more power was achieved for the blue μ LEDs when measured in integrating sphere than $\text{NA}=1$. This suggests a maximum power density of about $15\ \text{mW}/\text{mm}^2$ could be achieved from the red μ LED, which should be sufficient for activation of the red-sensitive proteins [see Table 2.3]. Further research is required to improve the efficiency of the red μ LEDs.

Despite the successful process flow development for the integration of dual colour μ LED assemblies on a single chip, only a few devices were achieved due to issues with metal peeling and dicing. A thorough investigation is required to optimize the best dicing method along with strong metal-to-oxide/nitride adhesion for higher yield. Although these dual-colour devices were developed targeting applications for dual-colour optogenetics, integration with CMOS was not done in this scope of work due to the limited number of devices. Integration of single colour μ LEDs with CMOS is discussed in the next chapter which shows the integration of dual colour would be more challenging than single colour chips. This work could open a new therapeutic approach in the field of optogenetics and requires in-vivo testing with animals. This

process flows for the integration of dual colour μ LEDs on a single chip has the potential to be used for RGB-on-a-single chip which could be used in RGB display technologies.

Chapter 6

Integration of the ultrasound-powered implantable systems for optogenetics

6.1 Introduction

Recent technological advancement in implantable devices by combining optics and electronics with genetics has triggered significant interest among researchers.[234, 235] The idea of the miniaturized electronic ultrasound-powered micro system called the neural DUST has shown promise for future bio-electronics-based treatments.[139] Conventional optogenetic systems use long optical fibres for light delivery [132, 134], restricting movements and inducing a higher chance of soft tissue inflammation. A better solution is necessary for in-vivo applications requiring a compact light source with wireless power. Some recent wireless systems showed battery-powering or radio frequency (RF) powering solutions for optogenetic applications. While battery-powered devices are able to supply stable power, they require replacement after a certain amount of time and often end up as large head-mounted systems for the requirement of intermittent battery replacement.[142, 146–148] RF-powered systems are able to overcome the limitations of battery-powered systems, but they have severe limitations with the volume of the implant and power conversion efficiency (PCE) due to requirement of large antennas to achieve efficient coupling to RF [see Table 2.2]. In addition, RF has high propagation loss in soft tissue and is susceptible to angular orientations. Some recent research has combined

batteries with RF harvesters for wireless battery charging capabilities, but they have larger volume displacement.[160] To overcome such limitations, ultrasound has been used as it offers several noticeable advantages over RF for powering optogenetic systems. Ultrasound has higher coupling efficiency when the power is harvested with a piezoelectric transducer, e.g. lead zirconate titanate (PZT) and able to generate more than 2 mW of power by a small 0.125 mm³ PZT crystal.[236, 237] Ultrasound also has a low attenuation rate of $\approx 0.5 - 1 \text{ dB}/(\text{cm.MHz})$ in soft tissue compared to RF.[139, 155] The use of ultrasound-powered micron-sized electronic neural devices has attracted significant interest for neural implants.[139, 156, 157, 237–240]

Integration plays the most important role in terms of the miniaturization of implantable devices to achieve higher volume efficiency. Recent reports of ultrasound-powered implants [155, 179–181] have 10-fold larger displacement volume than in the best scenario where a volume of 0.8 mm³ was achieved [178]. A comparison among battery [241], RF [242], RF with the battery [160], and an ultrasound powered [177] implantable devices showed that the smallest integration volume was achieved in the ultrasound powering system.

The work presented here is to integrate a novel wireless implantable micro-scale device, ultimately enabling in-vivo electrophysiology, optogenetics, and ultra-localized drug delivery in freely moving animals. The proposed device will be used to target specific neural circuits of the brain and test a new therapeutic approach for Parkinson’s disease (PD). The device is based on highly efficient ultrasound powered μ LEDs which will be used to excite specific channelrhodopsin transfected neural cells.

The proposed DUST size needs to be in the sub-millimeter range and to be energized at a few millimeters or so below the skin. A much larger implant was shown in [155] where a fully integrated ultrasound-powered electrical device capable of operating 10.5 cm below the skin. The DUST needs to generate 10 – 20 mW/mm² of optical power at 1 mA and needs to result in less than 1 °C temperature rise to prevent damage to cells. The peak wavelength should be around 480 nm which is suited to excite channelrhodopsin transfected cells.[243, 244]

The integration processes of two different US-powered implant-compatible systems with integrated custom-made μ LED are described in this chapter. The first prototype was integrated on a custom-made Au-patterned glass slide with a total volume of 2.85 mm³ and is termed the basic-DUST. To achieve a further reduction in the volume of the implantable system, the integration process was modified and optimized. The second version of the prototype called as

the compact-DUST, was able to achieve a volume of 0.33 mm^3 , which was about $1/10\text{th}$ of the size compared to the basic-DUST. All the challenges for integration of both the basic-DUSTs and compact-DUSTs were explained in detail, and finally, the working principle was demonstrated. The optical power from the μLEDs during US operation was roughly calculated based on the power delivered to the LED by CMOS, and the corresponding L-I-V curve of the μLED shows more than 20 mW/mm^2 power density could be achieved from both the DUSTs.

6.2 Integration of basic-DUST

The basic-DUST system is composed of a piezoelectric harvesting cube (PZT), an electronic chip, and a custom-designed μLED emitting at a peak wavelength of 480 nm , and envisioned to be used as a proof-of-concept. The operating principle is based on ultrasound power conversion to DC power, where the PZT will convert the ultrasound power into AC, and the electronic die will convert the AC into DC and will be supplied to the load μLED for generating optical power to stimulate the neural channels.

6.2.1 Integration challenges

The integration poses several engineering challenges that should be taken care of. Firstly, all the components come as individual $100 \text{ }\mu\text{m}$ -level chips, which are difficult to work with and limit any wafer-scale integration at this point. Secondly, each component has different dimensions and is finished with different contact metallization pads which are not readily compatible with each other. The PZT was a cube of $(500 \text{ }\mu\text{m})^3$ with two top-bottom silver (Ag) contact pads. The electronic die had an external dimension of $(300 \text{ }\mu\text{m})^3$ with four $50 \text{ }\mu\text{m}^2$ Al contact pads for interfacing the PZT harvester and the μLED . The Al contact pads tend to oxidize under an uncontrolled environment and need to be dealt with during integration. Finally, the μLEDs have Au finished bond-pads with dimensions of $(130 \times 330 \times 110) \text{ }\mu\text{m}^3$. Also, the components have a severe surface topology of about $3.5 \text{ }\mu\text{m}$, which causes problems with direct flip-chip bonding. Different limits on thermal exposure are another issue, such as the PZT can easily be damaged if exposed over $110 \text{ }^\circ\text{C}$, and the electronic die does not come with any electrostatic discharge (ESD) protection circuits due to size limitations.

6.2.2 Integration process flow

An integration process was developed in order to fabricate the basic-DUST onto a custom-designed glass substrate and to overcome the integration challenges. The detailed integration process flow is schematically presented in Figure 6.1. The glass submounts of size ($3.0 \times 1.5 \text{ mm}^2$) were prepared by patterned $Ti/Au = 20/200 \text{ nm}$ evaporation. Just before the evaporation, the glass substrate went through 1 minute of argon (Ag) ion etch to improve the adhesion of the metal. The submount has two pads of a dimension of $500 \times 500 \mu\text{m}^2$ for the μLED , one 1 mm^2 pad for the PZT crystal, and one open space in the middle for the integration of the electronic die.

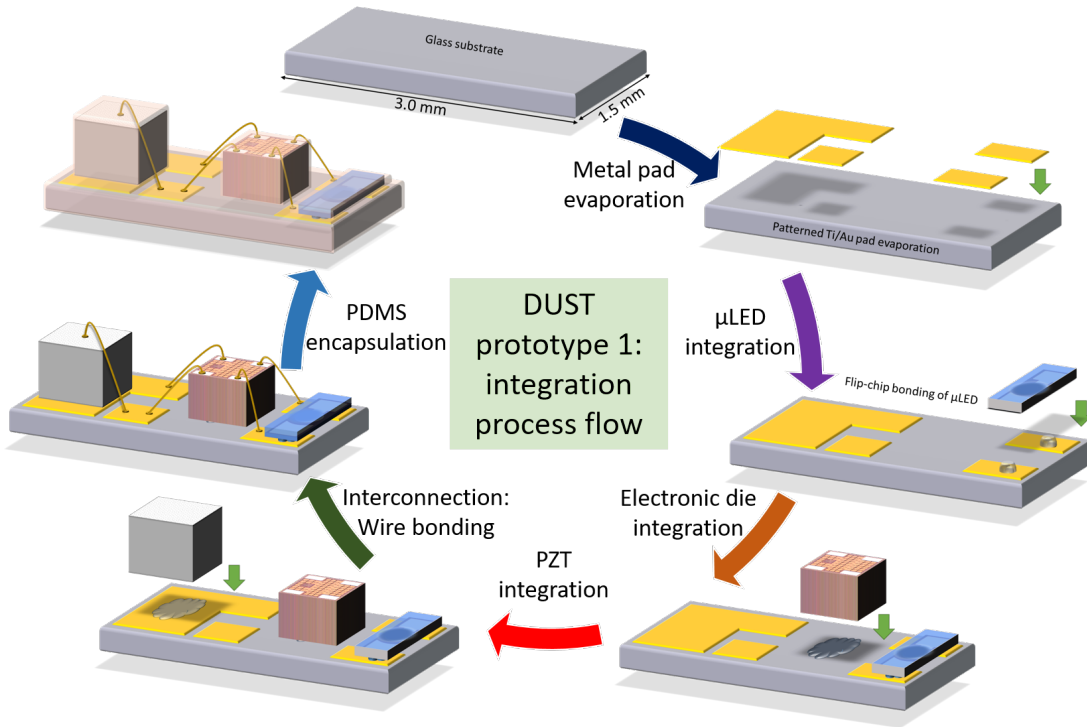


FIGURE 6.1: Schematic integration process flow of the basic-DUST.

First, the μLED was integrated into the submount as it is the most robust component. Two Au studs were deposited on each of the pads of the submount designed for μLED , and a single solder bump on top of that and then the bumps were flattened by compressing with a smooth silicon piece. Similarly, a single Au stud was deposited on each of the μLED pads and flattened. The flattening generally helps the components to maintain the angular or rotational alignment during bonding. The μLED was then bonded to the submount using the flip-chip bonder using thermal compression at 300°C for 20 seconds. A small amount of non-conductive epoxy was used on the edges of the μLED to strongly secure it to the submount.

The electronic die was bonded to the open space of the submount by non-conductive epoxy while taking precautions needed for non-ESD protected chip. After that, PZT crystal was then bonded to the submount by using room temperature-curable silver epoxy, which was left to harden for 18 hours. The interconnection between the devices was made by Au wire bonding, and all the Au-bonded sections were secured by conductive epoxy.

Finally, the integrated device was encapsulated by spin coating of a thin layer of polydimethylsiloxane (PDMS). PDMS was chosen because of its bio-compatibility and acoustic impedance matching between tissue and water. Figure 6.2(a) shows a top-view microscope image of the integrated basic-DUST. A size comparison is presented by placing the basic-DUST beside a 20 mm euro coin [Figure 6.2(b)] and on a fingertip [Figure 6.2(c)]. A total volume of 2.85 mm^3 was achieved on the fully packaged basic-DUST with this integration scheme presented here.

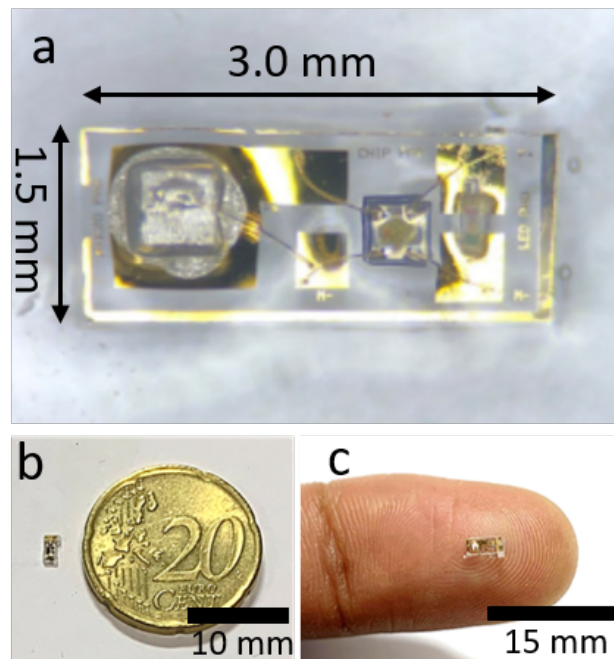


FIGURE 6.2: Shows (a) the microscope image of the integrated and packaged basic-DUST, a size comparison by placing the basic-DUST (b) beside a coin and (c) on a fingertip.

6.2.3 Demonstration of the basic-DUST

To demonstrate the complete ultrasonically-powered microsystem, the integrated basic-DUST, is mounted on the end of a narrow PCB and submerged in water in front of a transducer as seen in Figure 6.3. The entire work on demonstration was performed by our project collaborators at Aarhus University.

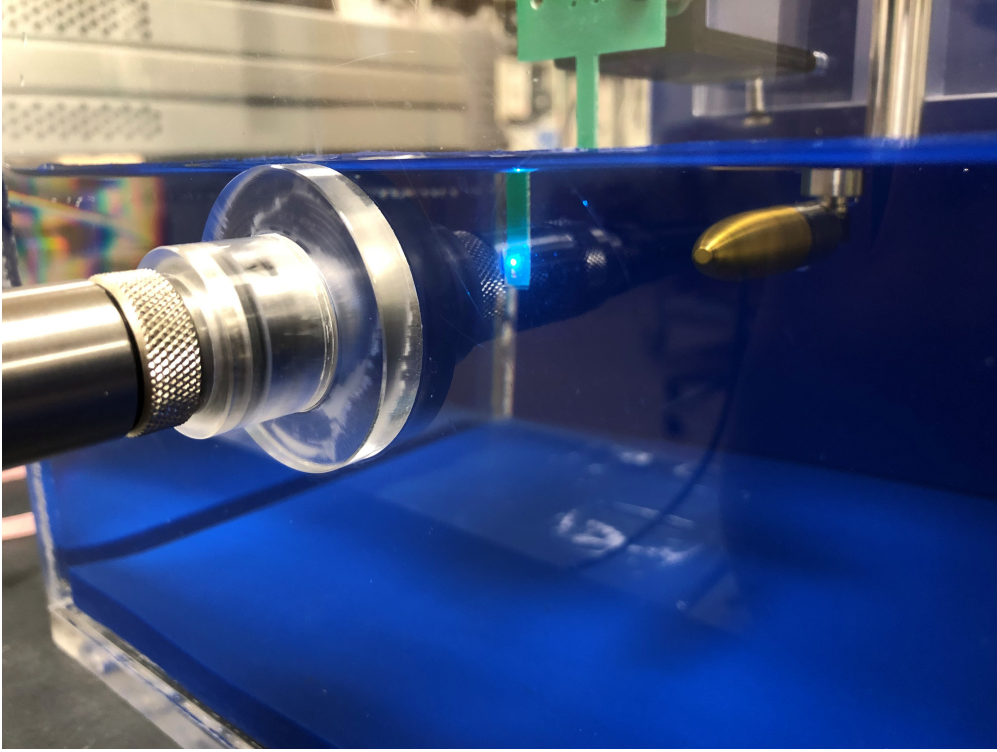


FIGURE 6.3: Picture of the basic-DUST under ultrasonic stimulation that in turn powers up and drives the μ LED demonstrated by collaborators at Aarhus University.

An acoustic intensity of 7.2 mW/mm^2 at a frequency of 3.14 MHz was delivered to the PZT crystal. Given the integrated nature of the prototype dust and its complete electrical isolation, the only available feedback of successful ultrasonic power transfer is to visually observe that the μ LED turns on. This can be seen successfully achieved in Figure 6.3 where the blue light emitted from the μ LED can be seen. Based on the previous measurements on PZT and CMOS chips conducted at Aarhus University, an electrical power of about 2.2 mW was estimated to have been delivered to the μ LED. The optical power density can be estimated from the pre-measured L-I-V plot and WPE of the μ LED to be 103.5 mW/mm^2 , which is more than required for the activation of blue-sensitive proteins.

This experiment successfully demonstrates the working principle and a proof-of-concept of the ultrasound-powered basic-DUST. Once the working principle was demonstrated, the next step was to further improve the integration method to reduce the size of the DUST, which is also termed the compact-DUST in this thesis.

6.3 Integration of compact-DUST

Previously, blue emitting (480 nm) μ LEDs were fabricated with a very high wall-plug efficiency of $\approx 41\%$ with an active emitting diameter of only 100 μm as described in Chapter 3 and was used to integrate the basic-DUST. In the next phase, a more compact version of the DUST was required to enable in-vivo testing.

6.3.1 Process development and challenges

A new process is required for the co-integration of the μ LED with the control circuit and PZT harvester to achieve further miniaturized DUST. The new process was developed where instead of using a patterned glass substrate, the DUST will be integrated by stacking all the components using an optimized bonding technique onto an Au-coated thin Si substrate. The planned process goes as follows:

- I . Flip-Chip bond μ LED directly on top of the electronic chip
- II . Prepare thin conductive submounts enabling maximum power transfer to the PZT through submounts by ultrasound
- III . Integrate PZT onto the submount and then co-integrate the μ LED-bonded electronics
- IV . Wire bond to complete the interconnection
- V . Encapsulation for driving the DUST inside liquid environment

I. To integrate the μ LED directly onto the electronics, several challenges needed to be resolved. The aluminium (Al) pads of electronic die oxidize quite easily. The rectifiers were first cleaned with 30 seconds of dip into photoresist developer (contains a small percentage of TMAH) to remove the oxides from the pads. Secondly, the pads were about 3.5 μm recessed from the surface of the electronic die [Figure 6.4]. The mesa region of the μ LED is also 1.2 μm above the contact pads. This creates a gap between the μ LED and electronic bond-pads of around 4.7 μm [Figure 6.5] preventing it from direct bonding.

Different methods were experimentally tested to optimize the best integration technique and presented in Figure 6.6. Three Au studs were put down onto the output pads of the electronic

driver and coined using a silicon piece [Figure 6.6(a)]. Then one $50\ \mu\text{m}$ solder bump was put down by a laser-assisted solder ball dispenser [Figure 6.6(b)]. The solder ball was not coined as it has been observed that solder re-flows more towards each other while coined and causes a short circuit. A single Au stud was then put down on each of the pads of the μLED . The μLED was then flip-chip bonded to the rectifier by thermal compression at $300\ ^\circ\text{C}$ for 20 seconds [Figure 6.6(c)]. Precautions were taken throughout the integration while handling the electronic die to prevent any ESD (Electrostatic Discharge) damage.

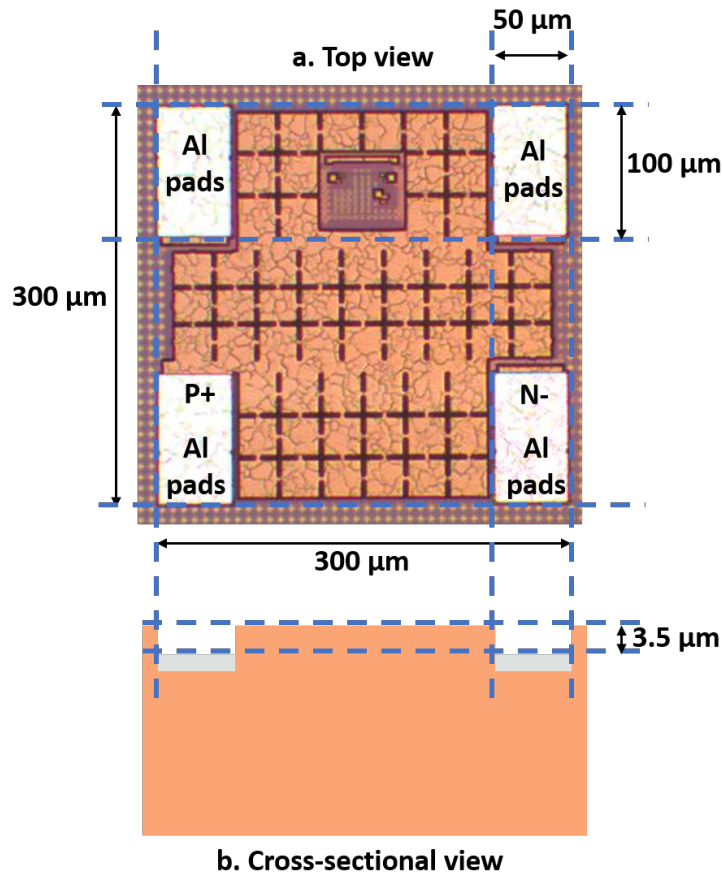


FIGURE 6.4: (a) Top view and (b) schematic cross-sectional view of the electronic die showing the dimensions and recess in the pads.

II. The next step was to determine a suitable substrate of low thickness and conductive surface. Initially, the copper tape was tested with wire bonding for the substrate. The results were not promising as the wire was not bonding with the copper tape due to its flexibility. Cleaning the copper tape with IPA and $2\ \mu\text{m}$ Au plating onto the copper tape was also investigated but did not improve the yield of wire bonding. Hence, in the final approach, a Si substrate was thinned down to $80\ \mu\text{m}$, and with Ti/Au ($20/300\ \text{nm}$), metallization was used as the substrate

to assist wire bonding. Before the metal evaporation of 1 minute of Ar ion, etch was done onto Si to improve the metal adhesion.

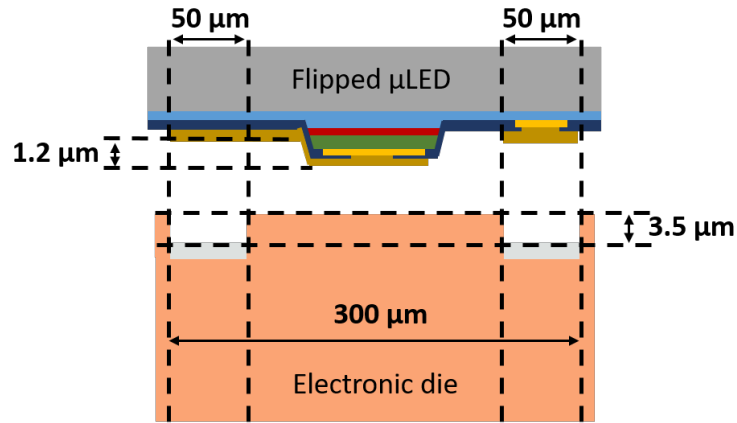


FIGURE 6.5: Schematic illustration of the gap between μ LED and rectifier pads.

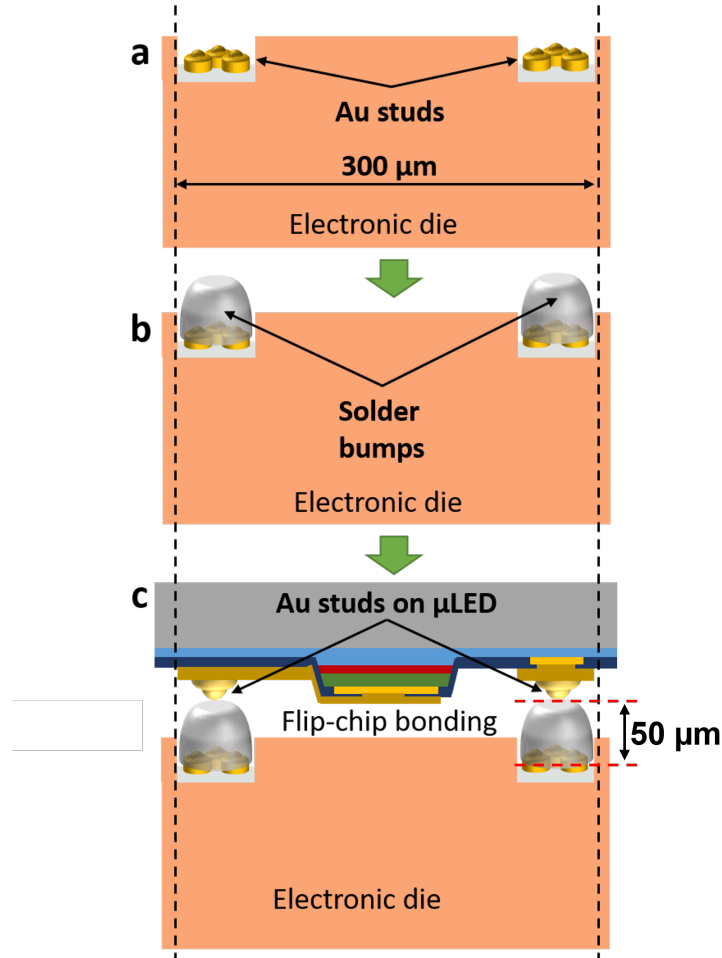


FIGURE 6.6: Schematics of flip-chip process. (a) Au stud on the electronic driver's pad, (b) 50 μ m single solder bump on the Au stud of the electronic driver, and (c) flip-chip thermal compression to bond the electronic die with μ LED.

The size of the substrate was designed such that it allows just enough space for wire bonding. The above schematic represents that the substrate needs to be at least $200\ \mu\text{m}$ larger on one side such that the capillary of the wire bonder can reach the substrate without damaging the stacked components [Figure 6.7]. Therefore, the minimum substrate dimension was optimized to $700 \times 500\ \mu\text{m}^2$, which was achieved by mechanical dicing.

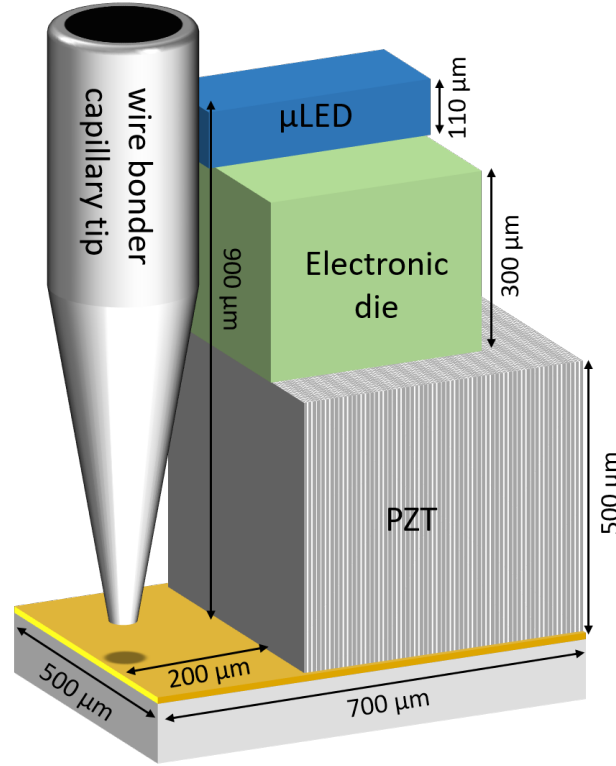


FIGURE 6.7: Schematics for determining the area of the substrate to allow space for wire bonding.

III. & IV. A room-temperature curable conductive silver epoxy was used to integrate the PZT crystal ($500\ \mu\text{m}$)³ onto the substrate and left for 12 hours at room temperature to cure. Non-conductive epoxy was used to mount the μLED -bonded electronics onto the PZT harvester. The electronic die was placed carefully on the edge of the PZT crystal by using the pick-up tool of the flip-chip bonder to allow wire bonding between the cathode of the electronic die and the top side of the PZT. The interconnections between the anode of the electronics and the bottom of the PZT pads were completed by another Au wire bonding.

V. Finally, the DUST was encapsulated by UV-curable epoxy. Thus, a compact version of the DUST was integrated by stacking all the active components with optimized bonding mechanisms to obtain a sub-mm sized system with external dimensions of $500 \times 700 \times 950\ \mu\text{m}^3$ as shown in Figure 6.8.

6.4 Integration and demonstration of compact-DUST

The compact-DUST was integrated by using the methods described in subsection 6.3.1 and shown in Figure 6.8. A volume of 0.33 mm^3 was achieved by this stacked monolithic heterogeneous integration process in this case. To the best of our knowledge, this compact-DUST demonstration is the smallest stand-alone remotely powered implant-compatible light source.

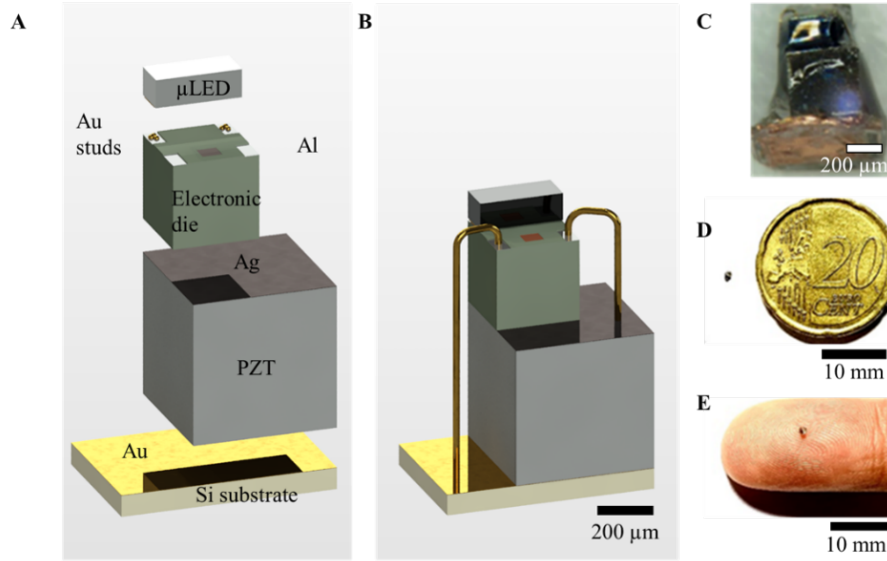


FIGURE 6.8: Schematics of the integrated compact-DUST. Figure (a) shows the exploded view of the DUST (b) integrated compact-DUST (c) microscope image of the fully integrated and encapsulated DUST. A size comparison is presented by placing the compact-DUST (d) beside a 20-cent coin and (e) on the fingertip. Figure (f) shows the schematic of the experimental test setup used for measurements.

A volume comparison between recently published such US-powered implant-compatible systems presented in Table 6.1 shows that the compact-DUST was able to achieve the smallest volume. Figure 6.8(a) shows the exploded view of the integration process, and Figure 6.8(b) shows the schematics of the integrated compact-DUST. Figure 6.8(c) shows the side-view of the fully integrated and encapsulated DUST taken by a microscope. To demonstrate the compactness of the DUST, a size comparison was presented in Figure 6.8(d) & (e) by placing the DUST beside a 20 cent coin having a diameter of 20 mm and on the fingertip respectively.

To demonstrate the working principle, the DUST was placed on a small glass substrate while submerged in water and exposed to ultrasound power at CNRS (Centre national de la recherche scientifique), France. An acoustic power was provided by the ultrasound transducer to the DUST, and blinking of the μLED was visually observed [Figure 6.9]. An optical power density of 47 mW/mm^2 was calculated in this case. Note that to drive the DUST the transducer was

placed on the top side of the DUST, which reduces the ultrasound coupling efficiency to the PZT as the ultrasound has to travel about $400\text{ }\mu\text{m}$ through the μLED and electronic die to reach the PZT. Hence, a lower power density than the basic-DUST was achieved in this case.

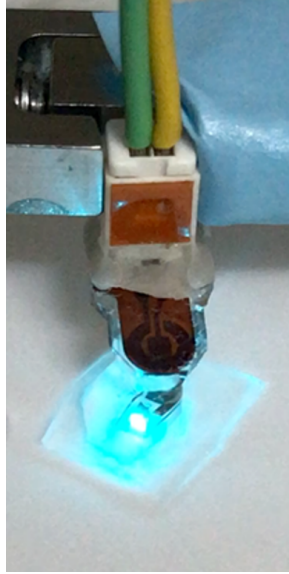


FIGURE 6.9: Picture of the compact-DUST under ultrasonic stimulation that drives the μLED demonstrated at CNRS by our collaborators.

TABLE 6.1: A comparison of the volume of different ultrasound-powered implant-compatible systems with integrated light-source.

Publication	Weber et al., 2016 [176]	Charthad et al., 2018 [155]	Kim et al., 2019 [175]	Sonmezoglu et al., 2021 [245]	This work Basic DUST, 2020 [237]	This work, Compact DUST
Implant Powering method	US	US	US	US	US	US
Power harvester module	PZT	BaTiO_3 piezo	PZT	PZT	PZT	PZT
Main elements	PZT, IC, LED	Piezo, IC, IC, Capacitor, LED	PZT, IC, LED	PZT, IC, LED, O_2 sensor, Fiber	PZT, CMOS μLED	PZT, CMOS μLED
LED	blue (460 nm)	blue (470 nm)	red & blue (640 nm & 470 nm)	blue (470 nm)	Custom made blue (480 nm)	Custom made blue (480 nm)
Optical Power density (mW/mm^2)	15	23	Max 0.65	Not available	103.5	47
Implant volume (mm^3)	16.5	39	> 9 & 18	16.2	2.85	0.33

6.5 Summary and discussion

The integration of ultrasound-powered neural DUST is presented in this chapter with a detailed outline of the encountered challenges and integration process. In the first section, the integration of a larger version of the DUST called the basic-DUST was presented. An optical power density of 103.5 mW/mm^2 was achieved in this case when the DUST was driven by acoustic power of 7.2 mW/mm^2 at a frequency of 3.14 MHz . A total volume of 2.85 mm^3 was inferred on the basic-DUST, which is relatively bigger for a neural implant but needed for proof-of-concept.

Once the proof-of-concept was established, a new integration process was developed and optimized to achieve a more compact version of the DUST. A total volume of 0.33 mm^3 was achieved using the newly developed monolithic-heterogeneous integration process, which stands out as the smallest ultrasound-powered DUST with the integrated light source. As ultrasound was delivered to the DUST from the top side, the coupling efficiency of ultrasound with the PZT was reduced. Hence a lower optical power density of 47 mW/mm^2 from integrated blue μLED was inferred in this case. Note that both basic-DUSTs and compact-DUSTs with UV μLED s were also integrated to verify DDS. Different integration challenges were successfully addressed to achieve the compact-DUST and presented in detail in subsection 6.3.1.

The definition of the required power density from the μLED for the activation of the channelrhodopsin is ambiguous. It is not precisely defined where one measures the power, i.e. on the surface or at a certain distance. Although, for in-vivo applications, the LED should be placed really close to the targeted region as inside the body lies a high scattering and absorptive medium. Also, the consideration of LED emitting areas during power density calculation varies largely among different researchers. In this case, the emitting area is considered as the mesa of the μLED ($100 \text{ }\mu\text{m}$ diameter) as that includes the quantum wells and at low bias ($\leq 1 \text{ mA}$) light is mostly distributed in the mesa region.

Although the integration process for the compact-DUSTs was optimized, the yield of producing a working device is still limited to $\sim 40\%$. The main issue was to successfully integrate the μLED s with the electronic die. Initially, silver epoxy was used for the bonding. Unfortunately, silver epoxy is hard to control, causing higher resistance with lower bonding strength and a higher rate of short circuit ($\sim 90\%$). Flip-chip bonding using a solder re-flow process was certainly a better choice over silver epoxy. The minimum solder ball size available in the solder

dispensing tool was $50\ \mu\text{m}$, which is quite large in comparison to the pads of the devices. During flip-chip thermal compression, the solder tends to re-flow towards each other and causes a short circuit. Therefore one must be careful not to apply more than $1\ \text{N}$ force during thermal compression.

The integration processes described here lack scaleable integration as the process is manual and depends on individual skills in most steps. The best way to achieve a wafer-scale integration process is by using photo-lithography and evaporation solder-able material (alternate layers of Sn/Au). Unfortunately, current electronic dies come as individual chips, and lithography on them is not possible. To enable lithography, electronic chips on full wafers are required, which induces a cost factor to the work. Another possible way for bonding is to use anisotropic conducting films (ACF), which offer only vertical conductive connection when laterally the film is insulated and higher bonding strength with lower re-flow temperature. The minimum bonding area needed for ACF is about $0.1\ \text{mm}^2$ with a space between pads of $250\ \mu\text{m}$ according to the specifications mentioned on the website of commercial vendors (such as 3M). In our case, the maximum pad size is $0.005\ \text{mm}^2$ with a pitch width between pads of only $200\ \mu\text{m}$; hence the use of ACF is not feasible for our integration. The best way to achieve a clean and precise bonding between μLED and the electronic driver would be to evaporate a very thick layer ($> 5\ \mu\text{m}$) of Sn/Au alternate layer as solder-able material onto the μLED bond-pads and use flip-chip bonding. Nevertheless, evaporating that thick layer of Sn/Au is highly costly and also requires further investigation.

Biocompatibility is one of the most important parameters when it comes to implantable systems. Though PZT has the highest PCE, it lacks biocompatibility due to lead in the material and silver (Ag) electrodes. A solution to this problem could be achieved by using suitable biocompatible encapsulation with PZT based system or using lead-free Potassium-sodium niobate ($K_{1-x}Na_xNbO_3$) piezoelectric material known as KNN. Bio-compatible encapsulation is another important aspect of neural implants for protection against liquid environments and long-term in-vivo functioning. The basic-DUSTs were encapsulated by spin coating of PMDS, which is a good candidate for bio-compatible material but lacks long-term viability.[246] Also, PDMS is porous and absorbs water while showing micro-cracks upon long-time operation, which shortens the lifetime of the implants.[247] The compact-DUSTs were coated with UV-curable epoxy for encapsulation. PDMS was not used as a spin coating on such small devices was not possible. Parylene-C is the most promising candidate for long-term bio-compatible encapsula-

tion. Previous studies showed that Parylene-caulked PDMS offers even more stability and robustness, making it a better material for encapsulation.[248] Investigation on parylene-C coating of thickness $5\ \mu\text{m}$ on the basic-DUSTs showed conformal coating but requires further testing for long-term reliability and 360° coating of the compact-DUSTs. But the main issue is to figure out how to hold the device in the coating chamber during 360° coating. In our case, spiropyran gives an excellent opportunity to be used as encapsulation due to its superior bio-compatibility and capability to be used as DDS. In the future, a thorough investigation is needed to validate SP's reliability.

In the future, the integration of dual colour μLEDs with new electronic chips needs to be investigated. Integration of dual colour μLEDs to achieve an advanced neural implant for both optogenetics and localized on-demand DDS is not presented in this thesis due to the limited time frame. Interconnection using flex-wrap technology can add a more precise and wafer-scale solution but needs further investigation. Moreover, in-vivo animal testing is required in the future to demonstrate optogenetic stimulation.

Chapter 7

Conclusion and future work

The objective of the research presented in this thesis was to realize a fully-implantable ultrasound-powered neural DUST integrated with high-efficiency μ LEDs for optogenetic applications, specifically, to enable in-vivo electrophysiology, optogenetic stimulation of neurons and ultra-localized drug delivery in freely moving animals. The envisioned device will target specific neural circuits of the brain to test a new therapeutic approach for Parkinson's disease (PD). The device is based on highly efficient ultrasound powered μ LEDs which will be used to excite specific ChR-2 transfected neural cells.

The volume of the proposed neural-DUST should be in the order of sub-mm range ($< 1 \text{ mm}^3$), capable of generating a minimum of 5 mW/mm^2 optical power for stimulating ChR-2 transfected cells while operating a few millimeters below the skin. The functioning components (PZT harvester, CMOS chip, and the μ LEDs) of the DUST should be highly efficient so that not enough heat is generated to damage the brain cells. Commercially available $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ PZT material was used as that has the highest US-to-electrical power conversion efficiency than other piezo materials. A highly efficient (91.2%) CMOS chip, designed by our collaborators from the Aarhus University, was used for AC $\rightarrow$ DC conversion, which was able to deliver only about 2.2 mW power to the μ LED when driven by an acoustic intensity of 7.2 mW/mm^2 at 3.14 MHz . One of the main challenges was to fabricate high efficiency μ LEDs for this application as GaN μ LEDs (blue) of efficiency above 40% is challenging to achieve. The fabrication of highly efficient blue and UV μ LEDs was demonstrated in this thesis and also presents the successful development of dual-wavelength μ LEDs on a single chip for optogenetics. Integration of the efficient μ LEDs with PZT and CMOS chip was also shown in realizing a fully implantable neu-

ral DUST. This thesis also presents the process steps to fabricate high efficiency μ LEDs that can be applied generally to the fabrication of GaN-based μ LEDs along with the optimization of neural DUST-integration steps which can be used for achieving a smaller volume of the implant. The following section summarizes the main results from chapters 3, 4, 5, and 6 and the recommendations for future work in section 7.2.

7.1 Overview of the results

Chapter 3 is focused on the design and development of highly efficient blue and UV μ LEDs targeted for optogenetic applications. The physical layout and dimension of the μ LEDs were designed in such a way that they can be directly integrated with the CMOS electronic chips. The circular mesa diameter was optimized to 100 μm to have higher light output and also to accommodate interconnection with other components. Commercially sourced InGaN-QW-based blue and UV LED wafers grown on PSS were used for better light extraction. Specific surface treatments were used, and annealing conditions were optimized to have high-quality ohmic contact (of the order of $10^{-4} \Omega cm^2$) with Pd/Ni/Au p-contact. An anti-reflection coating based on SiO_2 was simulated and applied on the back of the ground and semi-polished sapphire substrate, showing 10% improvement on extracted power. A low turn-on voltage of 2.3 V for blue and 3.1 V for UV μ LEDs was measured which is below the bandgap energy of the corresponding peak wavelength (Blue 483 nm and UV 371 nm). This sub-bandgap turn-on is the effect of high carrier temperature observed at low current densities. A very high EQE of 39% and WPE of 40.7% for the blue, while an EQE of 24.9% and WPE of 25.4 % for the UV was measured respectively when measured in an integrating sphere. An investigation on Ag-based reflective p-contact showed a further 20% improvement on extracted power from the same mesa-sized devices indicating a WPE of nearly 50% could be achieved from the μ LEDs. Nevertheless, the current power achieved with Pd/Ni/Au-based p-contact was well above the minimum requirement for optogenetic applications.

Chapter 4 represents the work on the development and characterization of an optically triggered drug delivery system (DDS). The DDS is required for the implants to enable in-vivo functioning by protecting against the body's spontaneous immuno-inflammatory reaction due to the insertion of a foreign object. Photochromic spiropyran (SP) was used as the carrier to load anti-inflammatory drugs such as hydrocortisone. It was reported that SP, upon exposure

to a specific wavelength, goes through an isomerization process and becomes merocyanine (MC), which has different physical and chemical properties than SP. Initially, the spectral absorption characteristics of SP were measured and high absorption below 400 nm was observed. Exposure by a shorter wavelength ranging from 370 nm to 405 nm showed that SP has high wavelength selectivity. Experimental results showed that SP can be activated (SP $\rightarrow$ MC) with lower energy density at 370 nm whereas, even with higher energy density at wavelengths above 385 nm, the polymer does not respond. A study on the dependence of SP activation on thickness was conducted. Although it was observed that higher thickness requires higher energy density for SP activation, due to severe topology of the submounted- μ LED system, the exact thickness values were not able to be quantified. The fabricated UV μ LEDs mentioned in chapter 2 were integrated with the basic-DUST system, and the activation of SP was visually confirmed by ultrasound powering. Some electrically injectable μ LED integrated submounts were prepared and coated with drug-loaded SP. Finally, the drug release by exposure to UV was verified. This work outlines the proof-of-concept for UV-triggered DDS suitable for neural DUSTs.

The development of UV-sensitive DDS, blue-sensitive ChR-2, and red-sensitive chrimsonChR demands a dual-wavelength μ LED system on a single chip for dual-colour optogenetic applications. Chapter 5 was reported on the design and development of dual-wavelength μ LEDs on a single chip with combinations of red + blue, blue + UV, and red + UV for dual colour optogenetics. The design of dual colour chips was optimized based on the two advanced CMOS layouts to match the pad positions while accommodating two different colours on the same chip. The mesa side of both the μ LEDs was designed bigger in order to have a larger active region. Two different process flows were combined to achieve such dual-colour chips. Blue and UV μ LED wafers grown on PSS were used to fabricate the blue and UV μ LEDs till the oxide passivation step and an 'open space' were designed to integrate the other colour. This PSS wafer will act as a carrier for dual colours. Then releasable red and blue μ LEDs were fabricated on n-GaAs and Si wafers, respectively. Finally, the released μ LEDs were picked up by PDMS stamp and transfer printed onto the open space, and interconnections were done for the dual colour. Issues such as the undercut process, post-undercut SiN_x rim, and InterVia etch were successfully resolved, and the electro-optical performances of the developed dual-wavelength chips were presented in this chapter. Although, oxide-to-metal adhesion and the dicing process need more attention as severe delamination of the interconnection-metal layer deposited on SiO_2 was observed in this step, making a low yield of working devices.

Chapter 6 was dedicated to the integration and development of wireless ultrasound-powered neural DUST with integrated μ LED for optogenetic stimulation. To realize a fully implantable DUST, the minimum requirements must be met, such as the μ LED must be able to generate more than 5 mW/mm^2 of power density while operating at a bias as low as 1 mA , the device should be highly efficient so that it does not generate heat more than 1°C and should be able to operate below few mm inside the skin. The first device, called the basic-DUST comprises a PZT harvester, CMOS chip, and blue μ LED was integrated into an Au-patterned $1.5 \times 3.0 \text{ mm}^2$ glass substrate. All the components were integrated with different bonding technology and encapsulated by PDMS. A total volume of 2.85 mm^3 and the operating principle by ultrasound were demonstrated by Aarhus University. Ultrasound waves with the acoustic intensity of 7.2 mW/mm^2 at a frequency of 3.14 MHz were delivered to the DUST while submerged in water, and the working principle was visually verified by blinking of the μ LED. Based on the electrical power (2.2 mW) delivered to the μ LED, the optical power density can be estimated to be 103.5 mW/mm^2 , which was more than required for activation ChR-2. To further reduce the volume of the DUST, another monolithic and heterogeneous integration approach was evaluated. Due to the different thermal budgets of each component, non-compatible contact metallization, non-ESD protection, and micron-level individual chips, it was extremely difficult to integrate the DUST. Finally, the processes were optimized, and a compact-DUST of total volume 0.33 mm^3 encapsulated by UV epoxy was integrated. A volume reduction was achieved in compact-DUST which is about 1/10th of the size of basic-DUST. To demonstrate the functionality of the compact-DUST, an ultrasound power at 3.14 MHz was delivered to the DUST and again visually verified by blinking of the μ LED. Although a low optical power density of 47 mW/mm^2 was calculated in this case as there were losses due to US exposure from the top side of the compact-DUST, making US travel about $400 \mu\text{m}$ through LED and CMOS before coupling to PZT. Nevertheless, the measure of optical power density is sufficient enough for ChR-2. In the real scenario, ultrasound will be delivered to the back side of the compact DUST; hence a higher coupling efficiency (US $\rightarrow$ PZT) should be achieved. Referring to the previous literature, this compact-DUST demonstration is the smallest stand-alone ultrasound-powered implant with an integrated optical source.

7.2 Future prospects

The work presented here shows the fabrication of highly efficient blue and UV μ LEDs targeted for optogenetic applications and the integration of the smallest wireless ultrasound-powered neural-DUST. The achieved compact-DUST had a volume of 0.33 mm^3 , and so far, none of the previous research has developed such a small implantable system integrated with a light source.

The efficiency of the μ LED is important not only for optogenetics but all other applications as well, and research is still ongoing to improve the efficiency further. In chapter 3, high-efficiency blue and UV μ LEDs were demonstrated, and the investigation on Ag-based reflecting metal contact showed promising improvement. Metal mirrors such as Ag and Al were investigated by many research groups. Although Al has high reflectivity, it is susceptible to quick oxidation and incompatible with metals used in III-V semiconductors. On the other hand, Ag shows much better compatibility and higher reflectivity in the blue-red range. But Ag is very hard to control due to high agglomeration issues. Further investigation on Ag-based contacts to have higher extraction efficiency is required. DBR mirrors are another point of interest in achieving much higher reflectivity, but they need the deposition of multiple alternate stacks of high and low-index material, which is a costly process. Integration of Ag-based metal contact with DBR mirrors on top has the potential to achieve the highest reflectivity but needs further investigation. Not only the top side of the LED chip but proper engineering of the bottom substrate also improves the light extraction, such as the use of the patterned sapphire substrate, anti-reflection coating, and integration of micro-lens. Results presented in Chapter 3 showed a 10% improvement in extracted power by putting down a simple SiO_2 based ARC coating on the back side of the LED chip. Similarly, the integration of micro-lenses could be another factor in improving the directionality and extraction efficiency. Also, proper engineering of the mesa slope and smoothening the mesa sidewall improves light extraction and hence the efficiency of the device.

The investigation on DDS showed promising results where light-activated DDS was achieved using the photochromic property of SP. Although the dependence on activation energy density with the thickness of SP was not quantified in this thesis due to time constraints. The refractive index of SP needs to be measured, which is difficult as it changes depending on the concentration of SP dissolved in THF. It was also observed that spin coating of SP, even on bare circular co-

ver slides, creates non-uniform thickness. Therefore, where coated on μ LEDs, due to severe topology, the thickness was even more non-uniform. In the future, a thorough study is needed to quantify the dependence. Also, in this thesis, the activation of the SP by ultrasound-powered μ LED and the drug release by electrically powered μ LED were presented separately. In the future, the drug release from SP by ultrasound-powered neural DUST should be investigated. This work holds immense potential for the future of implantable devices to counter the body's spontaneous immune-inflammatory response and to provide a stable long-term operation.

The development of dual-wavelength μ LEDs on a single chip has high importance for future optogenetic implants. The development of blue-sensitive ChR-2 and red-sensitive chrimsonChR could be utilized for dual-channel activation if integrated with dual-wavelength μ LEDs. Also, dual colour μ LEDs having a UV and blue/red wavelength can be used for single colour stimulation with the capability of localized drug delivery. Although, the dual-wavelength on single chip μ LED fabrication process steps require further optimization. The metal interconnection deposited on sputtered- SiO_2 shows severe delamination which needs a thorough investigation to resolve. Surface treatment of SiO_2 by Ar plasma prior to Ti/Au deposition or increasing the thickness of Ti should be investigated. One of the main issues was to have an optimized μ LED chip singulation process. Before the mechanical dicing process, the wafer was coated with a photoresist to protect damage from brute force induced by the blade and water jet. Even though severe metal delamination, chipping, and device breakage were observed. Further investigation on mechanical dicings, such as dicing parameters and the use of smaller kerf width blades with higher diamond concentration, should be conducted. Also, the use of laser dicing or a combination of laser + manual dicing could resolve the issue but requires thorough investigation. The developed technology for dual-wavelength μ LED on a single chip can be used to utilize RGB on a single chip which has many other applications, such as in display technologies.

The integration of the neural DUST plays one of the most important roles in this scope of work. Although the integration of the smallest implant-compatible neural-DUST was demonstrated here in this thesis, it was a highly time-consuming process and involves complex manual integration steps. Therefore, the integration process described here is a highly manual process and lacks wafer-scale integration. Future investigation on a smarter and much simpler scalable integration process is required for the neural DUSTs such as flex-wrap technology, where all the components of the DUST will be integrated on the metal pads of a specially designed flex

material, and the specific tool can be used to wrap around the flex. The easier way is to obtain wafer-scale CMOS chips instead of singulated chips, so that lithographic processes can be utilized for metal or dielectric deposition. Unfortunately, wafer-scale CMOS is highly costly. The current DUST integration process utilizes different bonding techniques, such as wire bonding and silver epoxy bonding, which are susceptible to external stress. A monolithic integration process was presented in [177] showing the use of anisotropic conductive film (ACF) for bonding. Such bonding technology could be more useful than conventional wire bonding or epoxy bonding but requires further investigation. Moreover, the capabilities of the DUST presented here for in-vivo animal testing were not demonstrated. In the future, it is required to demonstrate the DUST for optogenetic stimulation of ChR-2 transfected neural cells on live animals to demonstrate its full potential. Also, the integration of the dual-wavelength μ LED chips on neural DUSTs was not evaluated due to time constraints. It should be targeted to efficiently integrate the dual-wavelength μ LEDs on neural DUSTs as that holds immense potential for the future of optogenetic implants.

Appendix A

Blue and UV wafer material

The *InGaN*-based blue and UV LED materials grown on a PSS were used to aid the out-scattering of the light. Commercially sourced epi-material of blue and UV LED wafers are schematically presented in Figure A.1.

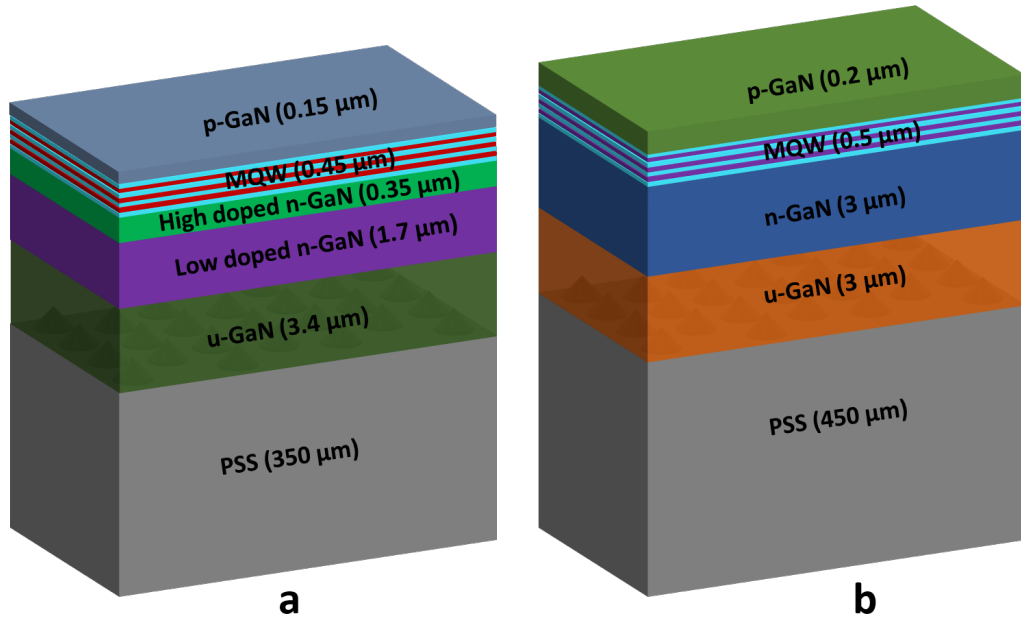


FIGURE A.1: Schematic epi-layer structure of the (a) Blue 480 nm and (b) UV 370 nm μ LED wafer.

The epitaxial layers were grown on c-plane (0001) 350 μ m and 450 μ m thick PSS for blue and UV, respectively by MOVPE followed by 3.0 – 3.4 μ m thick undoped GaN/buffer layer. The blue LED wafer had about 2 μ m thick Si-doped n-GaN layer, whereas, in the UV structure, about 3 μ m thick n-GaN layer was grown. Both wafers consist of thin MQW structures of a

total thickness of about $0.45 - 0.50 \mu m$ to form the active layer, and the In concentration was varied to tune the wavelength. A thin p-GaN layer doped with Mg of thickness $\sim 0.15 - 0.20 \mu m$ was grown and activated by high-temperature annealing.

The basic physical properties and epi-layer thicknesses of the UV wafer were provided by the commercial vendor and presented in Table A.1.

TABLE A.1: Epi-layers of commercial 2-inch *GaN* UV LED wafer.

Substrate	1.1	C plane (0001) off angle toward M-axis 0.2 ± 0.1 degree
	1.2	Diameter: $50.8 \pm 0.1 mm$
	1.3	Thickness: $430 \pm 25 \mu m$
	1.4	Patterned sapphire
	1.5	Sapphire substrate
GaN	2.1	Epi-layers: p-GaN $0.2 \mu m$, MQW $0.5 \mu m$, n-GaN $3 \mu m$, and u-GaN $3 \mu m$
	2.2	Wavelength: $370 nm$
	2.4	Defect density: $5 \times 10^8 / cm^2$

Note that the epi-structure of both UV and blue LED wafers presented here was provided by the vendor and does not include all the details. The basic information that is required to fabricate the device, such as the thickness p-GaN + QW required to etch mesa to reach n-GaN, was provided. More detailed information can be obtained by doing a cross-section transmission electron microscopy (TEM) analysis.

Appendix B

Optimization of ohmic contact

It is important to achieve low resistance metal-semiconductor ohmic contact for an efficient semiconductor device. Ohmic contacts exhibit linear current–voltage (I–V) characteristics and are fundamental building blocks of any semiconductor device. The contact resistance is an important parameter characterizing the metal-semiconductor interfaces. It is the total resistance of the metal/semiconductor junction (expressed in Ω) and hence, it depends on the area of the contact. A more useful physical parameter describing the performance of Ohmic contacts is the specific contact resistivity (ρ_c), which is independent of the contact geometry and is typically expressed in $\Omega\text{ cm}^2$.^[249]

Metals are chosen according to their work function such that they do not pose barriers for the majority carriers. To achieve ohmic contact, the work function of the metals should be equal to or higher than the p-type semiconductor. In terms of $p\text{-Ga}N$, Ni , Au , Pt , and Pd are the most suitable metals for ohmic contacts. In this section, the work on the optimization of two different metallizations for achieving ohmic p-contacts is discussed. Comparison between bare Pd : 40 nm and $Pd/Ni/Au$: 10/20/30 nm as p-contact on UV (370 nm) LED wafer were investigated as-deposited and under various annealing conditions.

B.1 Circular Transmission Line Measurement (c-TLM)

Achieving high-quality ohmic contact between p-metal and $p\text{-Ga}N$ has always been one of the key issues relating to GaN -based LEDs. The key parameters for optimization are ρ_c and R_{sh} ,

which can be evaluated by analyzing circular transmission line measurement (c-TLM). The ρ_c and R_{sh} can be extracted from c-TLM arrangements using the following equation,

$$R_{pp} = \frac{R_{sh}}{2\pi} \ln \frac{r_o}{r_i} + \frac{\rho_c}{2\pi L_s} \left(\frac{r_i + r_o}{r_o r_i} \right) \quad (\text{B.1})$$

where R_{sh} is the sheet resistance, L_s is current spreading length, R_{pp} is the point-to-point resistance, r_o and r_i defines the outer and inner radius of the c-TLM.[250] The ρ_c was determined using the I-V data measured from c-TLM and then fitting the data in Equation B.1. In this case, all the c-TLM patterns had an inner diameter of 50 μm while the outer diameter was varied from 56 μm to 400 μm (Pattern name with outer diameter: A= 400 μm , B= 280 μm , C= 220 μm , D= 140 μm , E= 120 μm , F= 100 μm , G= 80 μm , H= 60 μm , and I= 56 μm)

B.2 Optimization of ohmic contacts on UV LED material

Once the surface cleaning was done according to the process steps mentioned in Chapter 3, lithography level was done to deposit c-TLM patterns. Just before loading the samples for metal evaporation, they were dipped into Aqua Regia (3 HCl : 1 HNO_3) for 30 seconds to remove any kind of inorganic contaminants from the surface. Both 40 nm thick Pd and 10/20/30 nm thick $Pd/Ni/Au$ metallizations were deposited on $p-GaN$ at high vacuum (10^{-7} torr) at a chamber temperature of 80 $^{\circ}C$.

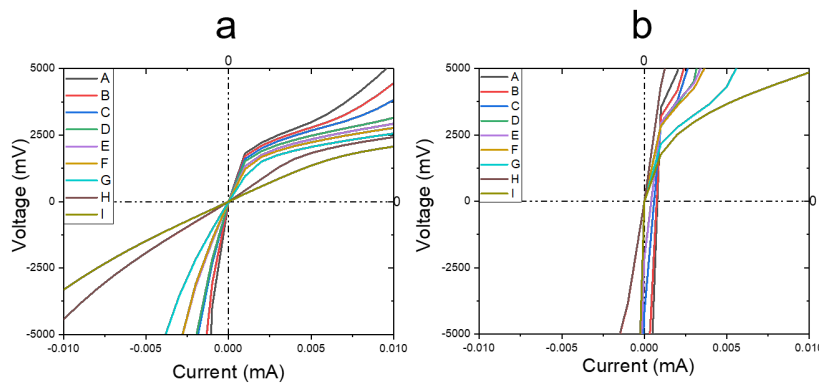


FIGURE B.1: Current-Voltage characteristics measured from c-TLM patterns for as-deposited (a) bare Pd contact and (b) $Pd/Ni/Au$ contact. Both show highly non-ohmic behaviour as deposited.

Figure B.1(a) shows the current-voltage measurements from the c-TLMs for Pd , and Figure B.1(b) $Pd/Ni/Au$ p-Contacts as-deposited condition. Although both the contacts were

non-ohmic as deposited, *Pd* showed slightly better behaviours than *Pd/Ni/Au* p-contact. To optimize the annealing conditions, the samples were diced into several pieces and investigated further under different annealing conditions by varying annealing temperature and annealing time. All the annealing was done using the furnace in N_2 ambience while varying the temperature ranging from 300 °C to 500 °C. The annealing duration also varied between 10 minutes and 20 minutes for optimization.

Figure B.2 shows the results of all the annealing conditions. After annealing both *Pd* [Figure B.2(a)] and *Pd/Ni/Au* [Figure B.2(b)] were annealed at 300 °C, both metallization showed a small improvement than as-deposited. As both contacts were still non-ohmic, higher temperature annealing was evaluated. When *Pd* [Figure B.2(c)] and *Pd/Ni/Au* [Figure B.2(d)] were annealed at 400 °C for 10 minutes, both became quasi-ohmic. At this point, the measured R_{sh} for both p-Contacts were over 320 $k\Omega/\square$, which indicates that the quality of the p-Contacts is still poor and requires further investigation.

To determine the effect of annealing duration, *Pd* [Figure B.2(e)] and *Pd/Ni/Au* [Figure B.2(f)] were annealed at 400 °C for 20 minutes. In this case, a degradation in I-V characteristics was observed. Also, annealed for 20 minutes at 400 °C, increased the R_{sh} over $\sim 400 k\Omega/\square$ for the *Pd/Ni/Au* contacts. Whereas, for bare *Pd* contact, it was more than two times than when annealed for 10 minutes. Also, inspection under the microscope reveals lots of dark spots (probably voids) on the metal surface, which were not present when annealed for 10 minutes. The degradation of *Pd* contact was more severe than *Pd/Ni/Au*, which indicates that the annealing time should not be over 10 minutes for higher temperature (> 400 °C) annealing. Therefore, only the temperature was increased for the later annealing conditions while keeping the annealing duration fixed at 10 minutes.

When annealed at 450 °C for 10 minutes in N_2 ambience, both *Pd* [Figure B.2(g)] and *Pd/Ni/Au* [Figure B.2(h)] showed ohmic contact with linear I-V characteristics. The measured values of R_{pp} from the c-TLM, were plotted against outer radii (r_o) of the c-TLMs [Figure B.3(a)] and $\ln(r_o/r_i)$ [Figure B.3(b)] and by solving them a R_{sh} of $\sim 146 k\Omega/\square$ and $\sim 132 k\Omega/\square$ were measured for *Pd* and *Pd/Ni/Au* contacts respectively. The ρ_c for *Pd* contact was measured in the order of $10^{-4} \Omega cm^2$ while for *Pd/Ni/Au* contact it was in the order of $10^{-3} \Omega cm^2$.

Figure B.2(i) and Figure B.2(j) shows the results of annealing *Pd* and *Pd/Ni/Au* p-contacts at 500 °C for 10 minutes in N_2 . The graphs show linear I-V characteristics with a further

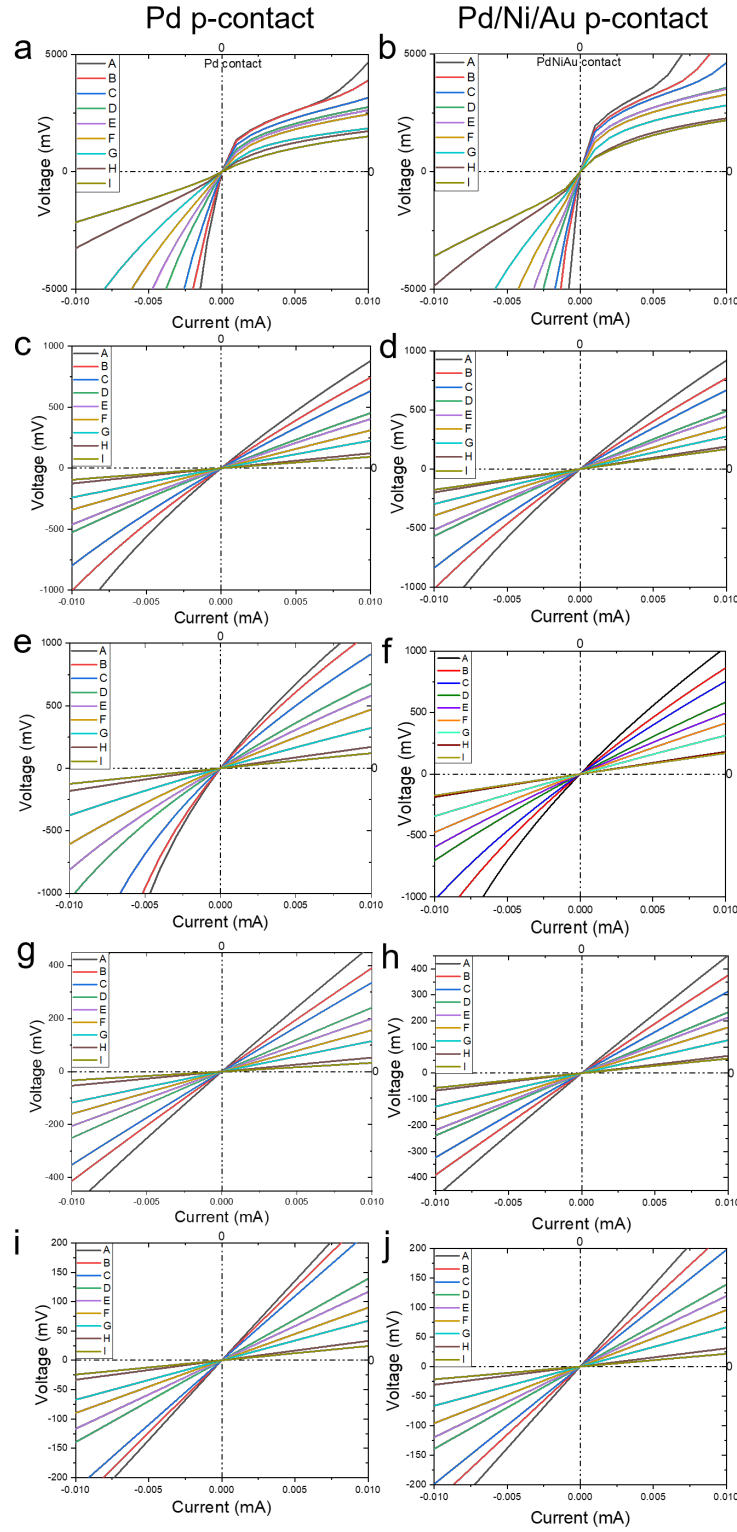


FIGURE B.2: Current-Voltage characteristics measured from c-TLM patterns after annealing in N_2 ambient for Pd contact at (a) $300^\circ C$ -10 min, (c) $400^\circ C$ -10 min, (e) $400^\circ C$ -20 min, (g) $450^\circ C$ -10 min, (i) $500^\circ C$ -10 min and $Pd/Ni/Au$ contact at (b) $300^\circ C$ -10 min, (d) $400^\circ C$ -10 min, (f) $400^\circ C$ -20 min, (h) $450^\circ C$ -10 min and (j) $500^\circ C$ -10 min respectively.

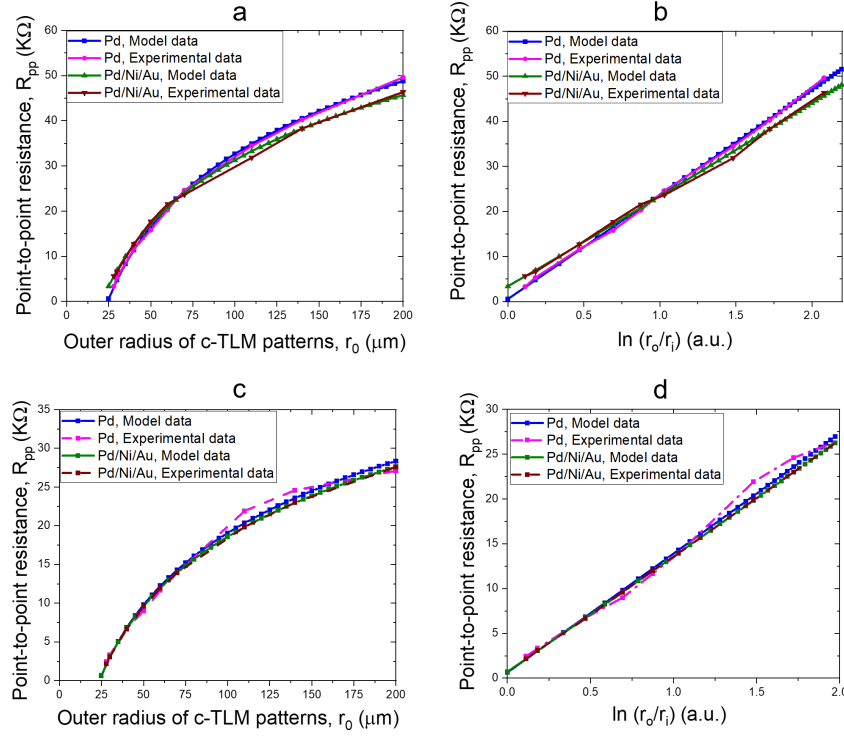


FIGURE B.3: Fitting of c-TLM measured data with model data to calculate the specific contact resistivity (ρ_p) and sheet resistance (R_{sh}). Fitting of point-to-point resistance (R_{pp}) with (a) outer radii of c-TLM and with (b) $\ln(r_o/r_i)$ for annealing at 450 °C. Similarly, fitting of R_{pp} with (c) outer radii of c-TLM and with (d) $\ln(r_o/r_i)$ for annealing at 500 °C.

decrease in corresponding measured voltage, indicating further improvement of the p-contacts. Similarly, the ρ_p and R_{sh} were calculated by fitting R_{pp} from the c-TLM with the model data against outer radii (r_o) of the c-TLMs [Figure B.3(c)] and $\ln(r_o/r_i)$ [Figure B.3(d)]. The lowest R_{sh} was obtained for both the metal contacts with *Pd* at 84 k $\Omega/\square$ and *Pd/Ni/Au* at 82 k $\Omega/\square$. Whereas ρ_c for both contacts was measured in the order of $10^{-4} \Omega \text{ cm}^2$. This was the best-optimized condition for ohmic p-contacts on the UV material. However, the dark spots on the bare *Pd* contacts became severe and had higher density spots on the metal surface. This shows the degradation in the bare *Pd* metal contacts. Since both the metal contacts were ohmic and had low contact resistivity, *Pd/Ni/Au* would be a better choice over bare *Pd* when a higher annealing temperature is required.

Figure B.4 shows the improvement of the R_{sh} of the *p* – *GaN* for both *Pd* and *Pd/Ni/Au* p-contacts with increasing annealing temperatures. Also, upon annealing for 20 minutes, a degradation in R_{sh} was observed, which is more prominent on *Pd* than *Pd/Ni/Au* contact.

Although, the sheet resistance should not vary with p-contact annealing temperature as the epi should be pre-annealed for activating *Mg* dopants at much higher temperatures. The

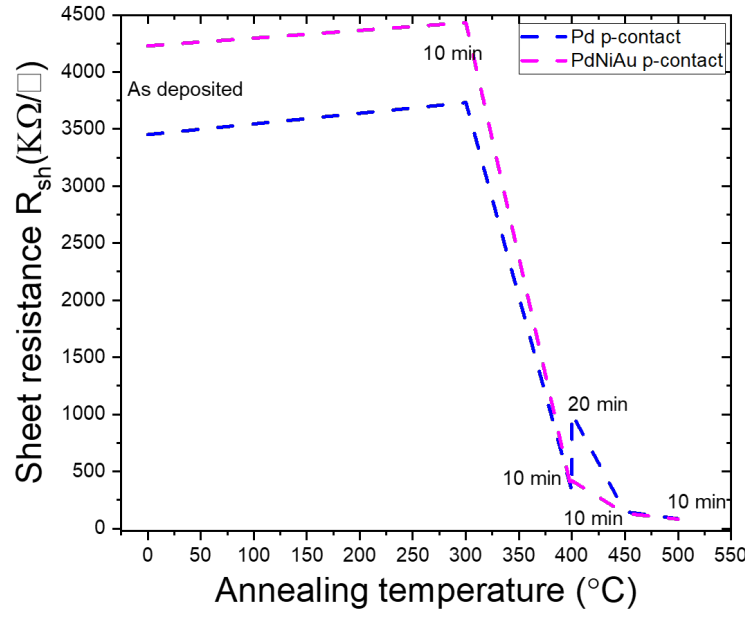


FIGURE B.4: Comparison of sheet resistance $k\Omega/\square$ with annealing temperature for both Pd and $Pd/Ni/Au$ contacts.

improvement in R_{sh} might be the result of an unoptimized epi-annealing condition which might cause the dopants to still activate during the p-contact annealing process. Annealing at even high temperatures of $550\text{ }^{\circ}C$ was also investigated (not shown in this thesis), which showed degradation of ρ_c , and therefore annealing at higher temperatures than $550\text{ }^{\circ}C$ was not evaluated any further. In summary, the best ohmic p-contact was achieved when $Pd/Ni/Au$ of thickness $10/20/30\text{ nm}$ was deposited on UV material and furnace-annealed at $500\text{ }^{\circ}C$ for 10 minutes under N_2 ambience with a low ρ_c of the order of $10^{-4}\text{ }\Omega\text{ cm}^2$.

Appendix C

Optimization of Ag-based reflective p-contact

Highly reflective *Ag*-based metal had always been a point of immense interest as p-contact or mirror material on LED devices for achieving higher extraction efficiency. Although, there are several issues that need to be addressed to enable good p-contact, such as lower adhesion of *Ag* with GaN/oxides, high agglomeration that makes it hard to control, low work function, and generally non-ohmic as deposited.

This section presents the work on Ag-based p-contact deposited on 480 nm *GaN* LED wafer for achieving high-quality ohmic contact with some investigation for overcoming *Ag* agglomeration. The surface of the wafer was initially cleaned using the process described in chapter 3. A 1/100/2 nm *Ni/Ag/Ni* metal stack was evaporated at a chamber pressure of 10^{-7} torr onto *p-GaN* as p-contact. Here, the 1 nm *Ni* was deposited as an underlayer to stop the diffusion of *Ag* into the semiconductor, and the 2 nm *Ni* overlayer should stop the agglomeration to some extent. A thicker *Ni* underlayer was not used as it decreases the *Ag* reflectivity. The *Ag* layer thickness was chosen to be 100 nm, as a lower thickness than that decreases the reflectivity, and a higher thickness will cause severe agglomeration issues.

To determine the quality of the p-contact, c-TLM measurements were done on as-deposited *Ag* contact. It was found the *Ni/Ag/Ni* p-contact was ohmic as deposited with a ρ_c of $> 10^{-4} \Omega \text{ cm}^2$ and R_{sh} was measured as $169 \text{ k}\Omega/\square$. Although the *Ag*-contact was ohmic as deposited, it still requires annealing to stabilize *Ag* so that there is no agglomeration issue in the subsequent downstream process.

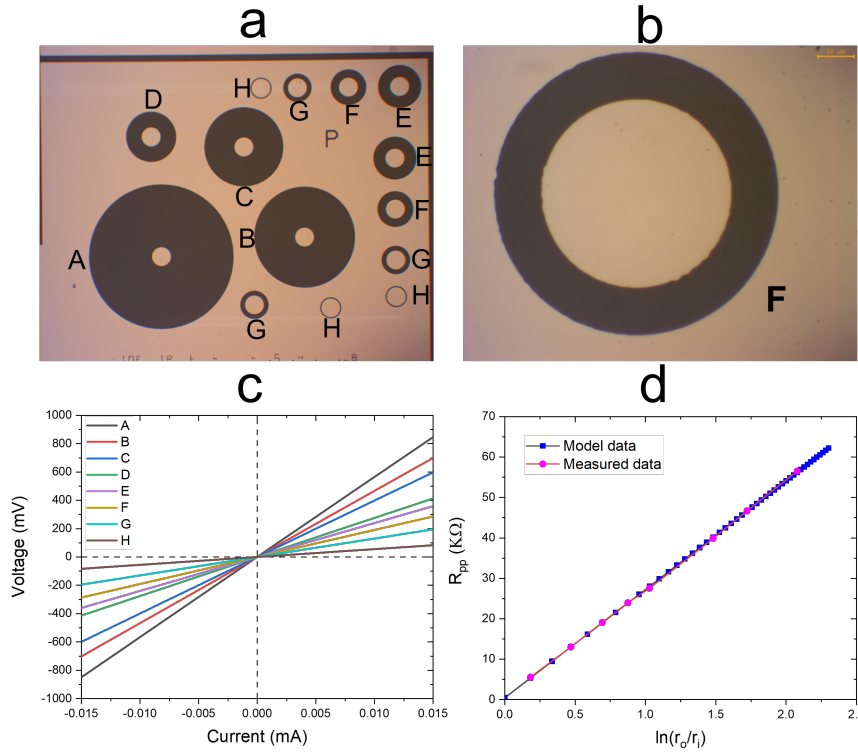


FIGURE C.1: Ni/Ag/Ni as-deposited on p-GaN of peak wavelength 480 nm blue LED wafer grown on PSS, where (a) shows the c-TLM patterns as-deposited and (b) zoomed-in image of c-TLM pattern F showing no indication of Ag agglomeration. Figure (c) represents the measured I-V from the c-TLM showing linear characteristics, and (d) shows the match between model data and measured data when point-to-point resistance is plotted as a function of $\ln(r_o/r_i)$.

Figure C.1(a) shows the microscope image of the as-deposited *Ni/Ag/Ni* c-TLM patterns by identifying each pattern number. All the patterns had a fixed inner radius of (r_i) 25 μm while the outer radius (r_o) varies from 200 μm to 28 μm . A zoomed-in image of pattern F in Figure C.1(b) shows that as-deposited Ag shows no signs of agglomeration. The measurements of the c-TLM current-voltage characteristics show a linear behaviour in Figure C.1(c) and the overlap between model data and measured data in R_{sh} vs $\ln(r_o/r_i)$ plot shown in Figure C.1(d) represents a high-quality ohmic contact was achieved with *Ni/Ag/Ni* p-metal.

As investigation on annealing conditions was required, a 100 nm SiO_2 was deposited onto the Ag contacts by the Leybold system as a stop layer for Ag migration during annealing. The argon plasma source (APS) was turned off during Ag deposition by the Leybold system so that Ag does not migrate during oxide deposition itself. Rapid thermal annealing (RTA) was done for 1 minute with O_2 supply for temperatures ranging from 400 $^\circ\text{C}$ to 550 $^\circ\text{C}$ with a step of 50 $^\circ\text{C}$ and the results were presented in Table C.1.

TABLE C.1: Annealing of *Ag* deposited on 480 nm blue LED wafer grown on PSS to achieve stabilization for the downstream processes with highly ohmic p-contact.

Oxide protection	Annealing condition	Contact quality	Contact resistivity (ρ_c)	Sheet resistance (R_{sh})
No oxide	As deposited no anneal	ohmic	$< 10^{-4} \Omega cm^2$	169 k $\Omega/\square$
With oxide on top	RTA, 400 °C 1 min in O2	ohmic	$< 10^{-4} \Omega cm^2$	73.2 k $\Omega/\square$
With oxide	RTA, 450 °C 1 min in O2	ohmic	$< 10^{-4} \Omega cm^2$	77.2 k $\Omega/\square$
With oxide on top	RTA, 500 °C 1 min in O2	ohmic	$1.23 \times 10^{-3} \Omega cm^2$	87.3 k $\Omega/\square$
With oxide on top	RTA, 550 °C 1 min in O2	ohmic	$5.54 \times 10^{-4} \Omega cm^2$	87.9 k $\Omega/\square$
oxide removed	RTA, 400 °C 1 min in O2	ohmic	$< 10^{-4} \Omega cm^2$	71.5 k $\Omega/\square$

It was observed that upon annealing at 400 °C, the sheet resistance decreases by more than 50% while the contact resistivity still was higher than $10^{-4} \Omega cm^2$ [Table C.1]. annealing at higher temperatures showed a further increase in both sheet resistance and contact resistivity. Note that during annealing and c-TLM measurements, the oxide was still on top of the *Ag* contacts. Initially, it was concluded that the probe tips were easily able to penetrate the thin layer of oxide during c-TLM measurements, so the removal of oxide was not necessary. Although, when the oxide was removed by wet BOE chemistry, a small improvement in sheet resistance was observed. The possible reason behind this phenomenon could be that the *Ag* diffused into oxide through 2 nm *Ni* overlayer making the oxide layer conductive. Hence the previous values of the sheet resistance (with oxide on top) was incorporating resistance of oxide as well in the measurement, and when oxide was removed, the sheet resistance was decreased from 73.2 k $\Omega/\square$ to 71.5 k $\Omega/\square$. Further investigation with SEM and EDX is required to verify this theory.

Even though a high-quality ohmic contact was achieved with 1/100/2 nm *Ni/Ag/Ni* contact on p-GaN showing excellent electrical performance and in chapter 3, it was shown enhancement in optical performances with *Ag*, the main issue with *Ag* migration still remains. Figure C.2 shows that after annealing (AA) at 400 °C *Ag* diffuses out through *Ni* and *SiO2* layer and

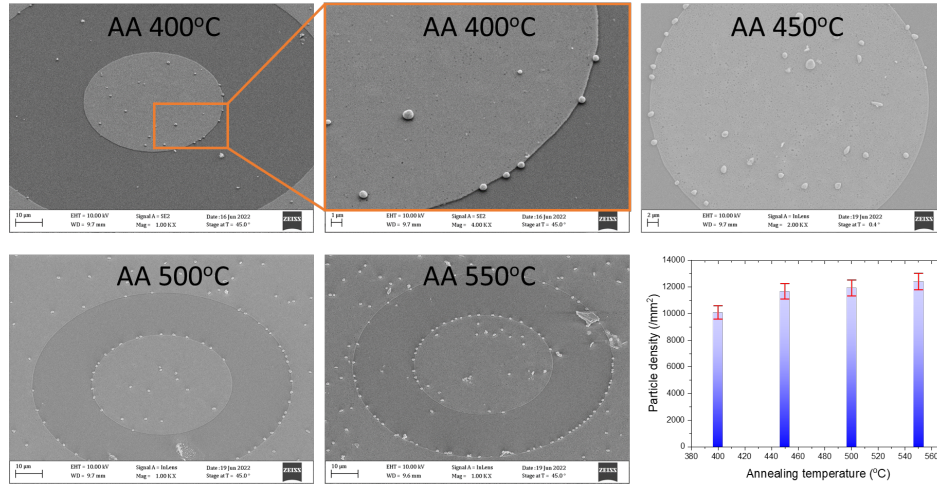


FIGURE C.2: Shows the SEM image of Ni/Ag/Ni p-contact buried inside thin SiO_2 layer after RTA at temperatures of 400 °C (top-left), 450 °C (top-right), 500 °C (bottom-left and at 550 °C (bottom-middle). The top-middle picture shows the zoomed-in 400 °C annealed sample showing about 1 μm diameter Ag balls migrated to the surface. The bottom-right graph shows that with increasing annealing temperature, the density of agglomerated Ag balls also increases.

forms balls of sized upto 1 μm diameter. The migration of Ag becomes more severe when exposed to higher temperatures [Figure C.2]. It is considered a potentially high risk as such Ag balls might end up in the mesa sidewall during LED processing, causing leakage or a worse, short circuit.

Investigation on thicker SiO_2 layer or SiN_x layer or a combination of both might be a way to resolve this migration issue. Another way could be to use a thicker Ag layer ($> 130 \text{ nm}$) with a thick Ni or Ti overlayer as a barrier to Ag migration. All these concepts require more thorough investigations.

Appendix D

Grinding, polishing, and dicing

D.1 Grinding and polishing

This section highlights the process for grinding-polishing of sapphire substrate with detailed parameters. The grinding and polishing were done with Logitech PM5 semi-automatic tool. Firstly the sapphire wafer was glued onto a circular glass slide with OCON-200 wax which has a melting point of 70°C , and a block of weight was applied to flatten the wafer onto the glass slide. After that, the glass slide was mounted onto the PM5 jig by vacuum, as illustrated in Figure D.1. It is essential to make the wafer as flat as possible during the glueing process to the glass slide with wax, as any tilt will make the edges of the wafer thinner than the central region or, in the worst case, break.

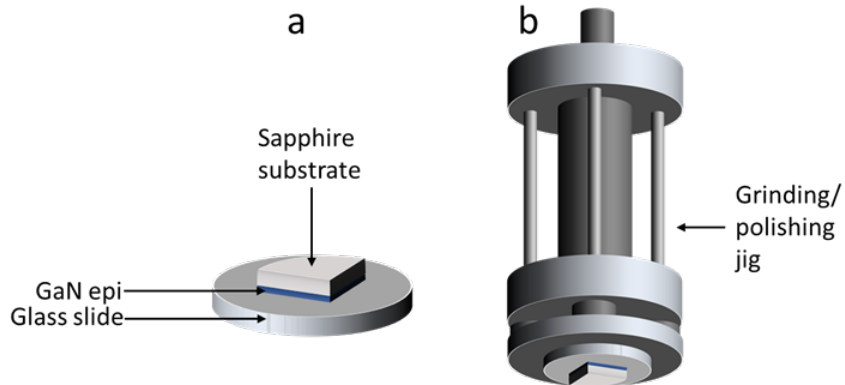


FIGURE D.1: Schematically shown the process of (a) mounting the GaN-on-Sapphire substrate onto the glass slide by crystal wax and then (b) mounting the glass slide onto the grinding jig by vacuum.

To grind sapphire, OCON-400 boron carbide (BC) powder and calcinated aluminium oxide powder ($9\ \mu m$ particle size) dissolved into water with a ratio of DI : BC/sapphire powder = 6 : 1 were used along with pure DI water. Initially, an rpm of 40 was used to thin the sapphire down to $200\ \mu m$. After that, the rpm was reduced to 30 till the remaining thickness reached $150\ \mu m$. Finally, the sapphire was thinned down to $110\text{-}120\ \mu m$ with an rpm of 20. Note when the thickness is below $150\ \mu m$, rpm above 20 has a high probability of breaking the substrate. During the grinding process, the thickness was measured every 30-minute interval as the tool could not monitor the thickness during the process. The entire grinding process may take more than 4 hours to thin it down to $100\text{-}120\ \mu m$.

Once the grinding was done and desired thickness was achieved, the grinding plate was changed with the polishing plate. Calcinated aluminium oxide powder of $3\ \mu m$ particle size, SF1 slurry from Logitech, and DI water were used for polishing. Polishing can take 3 hours or more, depending on the desired level of the polished surface. For the first 1 hour, the polisher was run at an rpm of 50, and after that, the speed was reduced to 30 rpm for another 1.5 hours and finally to 20 rpm. Once the polishing was done, the wafer was removed from the glass substrate with acetone. The wax residue was cleaned by immersing the wafer in acetone and placing it into an ultrasonic bath.

D.2 Dicing

The dicing of the μ LEDs on the sapphire substrate into individual devices is difficult due to the hardness of the sapphire. Several iterations and combinations of dicing parameters were evaluated for dicing with a semi-automatic Disco-DAD dicing tool. As mechanical dicing uses brute force, it is required to have a suitable wax to bond the wafer strongly onto a Si wafer so that it will not de-bond during dicing. A black wax that dissolves in toluene was used to bond the wafer to Si for having a better adhesion than crystal wax or blue sticky tape.

A specialized dicing blade from DISCO was purchased with a kerf width of $20 \pm 5\ \mu m$ and a diamond concentration of 110. The rpm of the blade was fixed by the tool at 30000 rpm. The dicing speed for sapphire was optimized to $0.3\ mm/s$. To dice $120\ \mu m$ of thick sapphire, first, a line was diced with a depth of only $10\text{-}15\ \mu m$. Then at each cut, the dicing depth was kept fixed at $30\ \mu m$ until about $30\text{-}40\ \mu m$ substrate is left. As the minimum dicing distance limited by the tool is 25 mm, dicing 1 line at $0.3\ mm/s$ takes about 84 seconds. Also, at each

position, it is needed to cut about 4 times, which equals to about 6 minutes per cut. Therefore the dicing process is a time-consuming process. Once the dicing is done, the wafer was removed from Si by toluene, and the remaining 30 μm was separated by manually breaking the wafer by putting pressure on the opposite side. It was observed that either increasing the dicing speed or dicing depth increases the probability of chip or blade breakage.

Although the yield of getting diced μ LEDs by mechanical dicing was not fully optimized. There are several issues that still require further attention. During dicing, some of the diced chips delaminate from the wax or break, which gets lost with the DI water flow. Once the diced chips were removed from the wax, they started to auto-break along the diced lines and float in the toluene solution. During the manual collection of all such chips and again cleaning them with acetone, a large number of chips get lost. As the chips are micron level, finding individual chips floating or submerged in a liquid is not an easy task. Also, during the manual breaking of the chips, a lot of them either break or get lost due to the limitations of the manual handling process.

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