

缺陷對氮化物藍光二極體光電特性之影響

學生：許晉源

指導教授：吳耀銓 博士

共同指導教授：藍文厚 博士

國立交通大學材料科學與工程研究所博士班

摘 要

本論文主要是研究氮化物藍光二極體的缺陷和其光電特性。我們會探討熱回火對金屬接觸在氮化鎵二極體上的效應，也會觀察貫穿式差排（threading dislocation）對氮化鎵二極體的影響，並對這兩者間的相互關係進行討論。在金屬接觸的實驗上，我們使用了鎳-金系和氧化銦鎵系金屬作為 p 型的透明接觸層。在經過不同溫度的熱回火處理之後，我們會量測元件的光電特性，例如特徵性接觸電阻、電流-電壓性質，電致激發光譜和光致激發光譜等等。在微觀結構分析方面，藉由穿透式電子顯微鏡、掃描式電子顯微鏡的影像與能量散佈光譜，我們可以清楚的觀察到缺陷與差排的存在與形態。因此我們將進一步的討論差排對氮化鎵二極體的影響。

首先，我們會先探討熱回火對鎳金屬層接觸 p 型（鎂摻雜）氮化鎵的影響。藉由鎳金屬層的催化來熱活化氮化鎵晶片，可以得到較高的有效載子濃度。在活化溫度低於 500 °C 時，鎳金屬層可能是扮演催化的角色來熱活化氮化鎵晶片。可是在活化溫度高於 600 °C 時，鎳金屬層可能會和 p 型（鎂摻雜）氮化鎵晶片的表面進行化學反應而形成氮化鎳。此結果可能導致有效載子濃度的增加。

我們使用鎳-金系和氧化銦鎵系金屬作為 p 型的透明接觸層製作了多種氮化物藍光二極體元件，並對熱回火在其電性上的影響做了探討。根據穿透式電子顯微鏡、掃描式

電子顯微鏡與能量散佈光譜儀的分析，我們發現金屬會沿著缺陷（例如貫穿式差排或 V 型凹洞）而擴散進入二極體元件的結構內。包含金屬元素的差排會形成一條具有導電性的路徑，並且會導致 p-n 接面在較高的回火溫度時產生短路的現象。另外我們也發現，熱回火溫度在 600 °C 時，氧化銻錫的透明接觸層會與 p-型氮化鎵的表面發生反應，而在兩者之間的介面產生含銻、錫的金屬化合物，銻，錫元素亦會往 p-型氮化鎵的表面擴散。然而，為了改善使用氧化銻錫透明接觸層的氮化鎵二極體的可靠度，我們建議可以在氧化銻錫透明接觸層與氮化鎵二極體之間先製作一層氧化鎳薄膜，用以防止氧化銻錫與氮化鎵二極體之間的反應與阻擋金屬擴散的發生。

最後，我們製作了具有表面自然粗糙結構的氮化鎵二極體，並研究熱回火對其電性的影響。在熱回火溫度高於 800 °C 時，具有表面自然粗糙結構的氮化鎵二極體依然保持著二極體的電流-電壓行為。而且其在高電流應力注入時仍有很好的可靠度。藉由穿透式電子顯微鏡的分析，我們觀察到具有表面自然粗糙結構的氮化鎵二極體其結構內之貫穿式差排並沒有如傳統結構的氮化鎵二極體一樣延伸至元件表面。這是因為具有表面自然粗糙結構的氮化鎵二極體多成長了第二層 p 型氮化鎵，而此第二層 p 型氮化鎵正是具有這自然粗糙的表面結構。因此，我們認為此第二層 p 型氮化鎵不但增加了光輸出的效率，亦阻擋了金屬擴散進入氮化鎵二極體的路徑而增加元件的可靠度。

Effects of Defects on the Optoelectronic Properties of III-Nitride Based Light Emitting Diodes

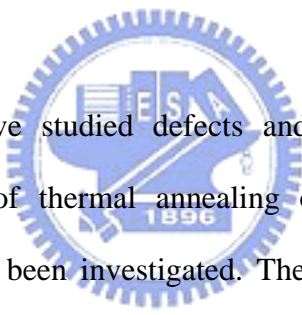
Student : Chin-Yuan Hsu

Advisor : Dr. YewChung Sermon Wu

Co-Advisor : Dr. Wen-How Lan

Department of Materials Science and Engineering
National Chiao Tung University

ABSTRACT



In this dissertation, we have studied defects and optoelectronic characteristics on III-nitride based LEDs. Effect of thermal annealing of metals contact on GaN based light-emitting diodes (LEDs) has been investigated. The effect of threading dislocation on GaN based LEDs were also discussed. In the metals contact, we used Ni/Au and indium tin oxide (ITO) based metals for *p*-type transparent contact layer (TCL). After thermal annealing, the optoelectronic characteristics were measured such as the specific contact resistance (ρ_c), current-voltage (*I-V*) characteristics, electroluminescence (EL), and photoluminescence (PL). In the microstructure analyses, the defects and dislocations were observed by transmission electron microscopy (TEM), scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometer (EDS). Thus, the influences of dislocations on GaN based LEDs would be discovered and discussed.

Effect of thermal annealing on Ni film/Mg-doped GaN layer has been investigated. The wafers activated with Ni film obtained higher effective carrier concentrations than activated without Ni film. The Ni film may react as a catalyst for activation of Mg-doped GaN with

temperature below 500 °C. While temperature above 600 °C, the Ni film may react with Mg-doped GaN to transform nickel nitride (Ni_3N), and result in the increase of the effective carrier concentrations.

The effect of thermal annealing on I - V properties of GaN based LEDs with Ni/Au and ITO p -type layer have been studied. According to TEM, SEM and EDS analyses, it was found that metals diffused into the LED structure with defects such as threading dislocations (TDs) or V-pits. The conducting paths formed by the metal containing dislocation cores are believed to be the cause for the observed short circuit behavior of p - n junctions at high annealing temperatures. Using TEM and EDS analyses, we also observed In-contained metallic interface between the p -GaN layer and the pure ITO contact layer after annealing at 600 °C. It revealed that ITO would react at interface or indiffuse near interface at 600 °C. To improve the reliability of GaN-based LEDs with the ITO contact layer, we suggest that the NiO layer be used to prevent the reaction and block the leakage pathway.

The influences of TDs on electrical properties of GaN based LEDs with naturally textured surface have been investigated. After annealing above 800 °C, the normal I - V behavior of the GaN based LEDs with naturally textured surface still has been observed. It can achieve good reliability at high current injection life tests. The TEM images are clearly indicated that the straight TDs of the LED with naturally textured surface can't extend to top surface during growth of the second p -GaN layer. These results imply evidences that the second p -GaN layer (the naturally textured surface) block the leakage pathway and prevent metals indiffusion along defects or dislocations.

誌 謝

經歷了這六年在博士班的學習、研究與成長，讓我的人生進入了一個更成熟的階段。而隨著這博士論文的完成，我也即將告別博士班的求學生涯，而邁入下一個更嚴峻的挑戰。在此要感謝許多人，在這求學階段不斷的幫助我、鼓勵我和支持我，使我能順利完成博士學業。

首先，感謝指導教授吳耀銓老師的關懷與指導，在老師充分的支持與完全的信賴下，讓我有更寬廣的空間盡情揮灑。在此要特別感謝共同指導教授藍文厚老師長久以來的提攜與教誨，不論是在理論基礎上或是在實驗研究上都給我很大的指點與啟發，而且在待人處事與心靈成長上亦是我的心靈導師，此外亦感謝藍文厚老師在生活上對我的支持與關懷。古有銘言：「一日為師，終生為父」，我想對兩位指導教授的感謝與敬重，並不會隨著論文的完成而終止或有所遞減。感謝本校材料系系主任張翼老師與北科大光電所陳隆建老師於百忙中抽空對本論文給予寶貴的意見與指導。

接著，感謝璨圓光電董事長簡奉任博士一直以來的支持、教導與關懷，並提供各項研究與實驗的資源。亦感謝璨圓光電全體同仁的幫助（特別是朱胤丞、鍾勝時、游正璋...等），讓我的實驗得以進行與完成。此外，我要感謝趙志偉學長、劉柏均同學、侯智元、胡國仁、彭韋智、林沛彥和盧昶鳴等學弟、交大電物所黃國欽學弟與清大材料所邱建超同學這幾年來的協助與鼓勵，有他們的陪伴這段求學路程走的才會順暢。還有感謝其他我無法述及的好朋友們，謝謝你們的加油打氣。

最感謝永遠都支持我的父母，沒有你們的栽培與教養，我無法完成這博士學業。感謝我的弟弟峰銘分擔我的家庭責任，讓我無後顧之憂。最後，感謝我的妻子沈姿慧小姐與我的可愛寶貝郁欣與任承小朋友，感謝你們這一路在背後默默的支持與鼓勵，你們是我的動力來源，有你們的陪伴我才能勇敢的面對挑戰。最後僅以本博士論文獻給我最摯愛的家人們，我的成就願與你們一起分享。

~ 2006 年 6 月 新竹 ~

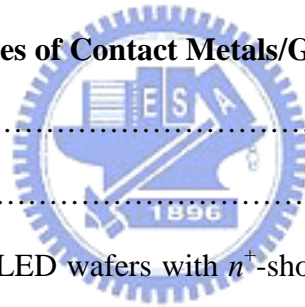
Contents

中文摘要.....	i
Abstract.....	iii
誌謝.....	v
Contents.....	vi
Table Lists.....	x
Figure Lists.....	xi
Chapter 1 Introduction.....	1
1.1 Light-Emitting Diodes.....	1
1.2 III-V Nitride Based LEDs.....	2
1.3 History of Gallium Nitride.....	5
1.4 Major Issues of Gallium Nitride.....	8
1.4.1 Issues of GaN substrates.....	8
1.4.2 Issues of <i>p</i> -type GaN.....	9
1.4.3 Issues of <i>p</i> -type ohmic contact.....	11
1.5 Overview of This Dissertation.....	13
1.6 References.....	15
Chapter 2 Theory and Background.....	26
2.1 Principles of the Formation of Ohmic Contacts.....	26
2.2 Current Flow in Metal-Semiconductor Junctions.....	28
2.3 Current-Voltage Characteristics of <i>P-N</i> Junction Diodes.....	29
2.3.1 The case of a forward-biased <i>p-n</i> junction.....	30
2.3.2 The case of a reverse-biased <i>p-n</i> junction.....	31
2.3.3 Leakage current.....	34

2.4 Basics of Degradation and Reliability for LEDs.....	34
2.5 The Role of Threading Dislocations in GaN Based LEDs.....	35
2.6 References.....	39
Chapter 3 Experiments and Analyses.....	51
3.1 Epitaxial Wafers of GaN Based LEDs.....	51
3.2 Processes of GaN Based LEDs.....	51
3.3 Circular Transmission Line Model (CTLM).....	52
3.4 Measurement of Carrier Concentration by Capacitance-Voltage Method.....	54
3.5 Field Emission Scanning Electron Microscopy.....	55
3.6 Transmission Electron Microscopy.....	55
3.7 Photoluminescence.....	56
3.8 Hall Effect Measurement.....	56
3.9 References.....	58
Chapter 4 Effect of Thermal Annealing on Ni Film/Mg-Doped GaN Layer.....	63
4.1 Introduction.....	63
4.2 Experiments.....	64
4.2.1 Preparation of Mg-doped GaN wafers.....	64
4.2.2 Activation of Mg-doped GaN wafers.....	65
4.2.3 Measurements and analyses.....	65
4.3 Results and Discussions.....	66
4.3.1 Results of XRD analysis.....	66
4.3.2 Effective carrier concentrations and mobility by Hall effect measurement.....	67
4.3.3 Effective carrier concentrations by $C-V$ method.....	67
4.3.4 Results of photoluminescence measurement.....	68
4.4 Conclusions.....	69
4.5 References.....	70



Chapter 5 Effect of Thermal Annealing of Metals Contact on GaN Based LEDs.....	83
5.1 Introduction.....	83
5.2 Experiments.....	84
5.2.1 Growth of GaN based LED wafers.....	84
5.2.2 Fabrication of GaN based LEDs.....	85
5.2.3 Measurements and analyses.....	85
5.3 Results and Discussions.....	86
5.3.1 Effect of thermal annealing on GaN based LEDs with Ni/Au contact layer.....	86
5.3.2 Effect of thermal annealing on GaN based LEDs with ITO contact layer.....	88
5.4 Conclusions.....	90
5.5 References.....	91
Chapter 6 Influences of Interfaces of Contact Metals/GaN on LED Properties.....	109
6.1 Introduction.....	109
6.2 Experiments.....	111
6.2.1 Growth of GaN based LED wafers with n^+ -short period superlattice tunnel contact layer.....	111
6.2.2 Fabrication of GaN based LEDs with various TCL conditions.....	112
6.2.3 Measurements and analyses.....	112
6.3 Results and Discussions.....	113
6.3.1 Electrical properties of GaN based LEDs with various TCL conditions after thermal treatment.....	113
6.3.2 Life tests of GaN based LEDs with various TCL conditions by current injection.....	115
6.3.3 Observation of interfaces between contact metals and GaN based LEDs.....	116
6.4 Conclusions.....	118
6.5 References.....	120



Chapter 7 The Effect of Threading Dislocation on GaN Based LEDs with Naturally Textured Surface	144
7.1 Introduction.....	144
7.2 Experiments.....	146
7.2.1 Growth of GaN based LED wafers with naturally textured surface.....	146
7.2.2 Fabrication of GaN based LEDs with naturally textured surface.....	147
7.2.3 Measurements and analyses.....	148
7.3 Results and Discussions.....	148
7.3.1 Electrical properties of GaN based LEDs with naturally textured surface after thermal treatment.....	148
7.3.2 Electroluminescence characteristics of GaN based LEDs with naturally textured surface after thermal treatment.....	150
7.3.3 Life tests of GaN based LEDs with naturally textured surface by current injection	151
7.3.4 Microstructure of GaN based LEDs with naturally textured surface.....	151
7.4 Conclusions.....	152
7.5 References.....	154
Chapter 8 Conclusions and Future Works	169
8.1 Conclusions.....	169
8.2 Future Works.....	171

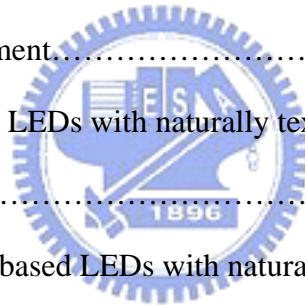


Table Lists

Table 1-1 Properties of GaN substrates.....	24
Table 1-2 Work functions and electronegativity of some elements.....	25
Table 2-1 Main causes of and factors enhancing the failure of laser diodes and LEDs (forward bias devices).....	48
Table 6-1 The various transparent contact layer conditions.....	122
Table 6-2 The conditions of the LED samples.....	123
Table 6-3 The minimum specific contact resistances of the metals contact.....	125



Figure Lists

Figure 1-1 Bandgap energy of various materials for visible emission devices as a function of their lattice constant.....	20
Figure 1-2 Chromaticity diagram where blue InGaN/AlGaIn LEDs, blue-green InGaN/AlGaIn LEDs, green GaP LEDs and red GaAlAs LEDs are shown.....	21
Figure 1-3 Chromaticity diagram in which blue InGaN SQW LED, green InGaIn LED, green GaP LED, green AlInGaP LED and red GaAlAs LED are shown.....	22
Figure 1-4 Structure of GaN M-I-n LED.....	23
Figure 2-1 Surface-included energy band diagrams for (a) a metal and (b) <i>n</i> -type semiconductor.....	40
Figure 2-2 Energy band diagrams for ideal MS contacts between a metal and <i>p</i> -type semiconductor: $\Phi_M < \Phi_S$ system (a) band diagram before contact (b) under equilibrium condition after contact; $\Phi_M > \Phi_S$ system (c) band diagram before contact (d) under equilibrium condition after contact.....	41
Figure 2-3 Schematic description of (a) the thermionic emission, (b) thermionic field emission, and (c) field emission (tunneling) mechanisms in an <i>n</i> -type semiconductor.....	42
Figure 2-4 Methods of making ohmic contacts to <i>p</i> -type semiconductors (a) Use a high work function metal to minimize the Schottky barrier height. (b) Dope the semiconductor heavily to make a tunneling contact. (c) Reduce the bandgap of the semiconductor at the contact by the formation of the interfacial semiconductor layer.....	43
Figure 2-5 (a) Equivalent circuit of a diode, (b) $\log(I)$ versus V for a diode with series resistance, the upper dashed line is for $r_s = 0$	44
Figure 2-6 Reverse-biased in a <i>p-n</i> junction.....	45
Figure 2-7 Breakdown mechanisms in a <i>p-n</i> junction diode (a) tunneling, (b) avalanche multiplication, and (c) carrier lose the gained energy to phonons and remain too cold to	

ionize.....	46
Figure 2-8 Failure modes and causes for laser diodes and LEDs (forward bias devices).....	47
Figure 2-9 Cross-section view of V-defects in InGaN/GaN multiple quantum well structures and schematic structure of the V-defect.....	49
Figure 2-10 $I - V$ characteristics for several diodes on LEO GaN and on the window region (dislocated GaN).....	50
Figure 3-1 The epitaxial structure of the GaN based LEDs.....	59
Figure 3-2 The flow chart of GaN based LEDs process.....	60
Figure 3-3 The chip structure of the GaN based LEDs.....	61
Figure 3-4 Circular transmission line geometry test structure.....	62
Figure 4-1 Schematic diagram of hydrogen desorption process of Mg-doped GaN with the Ni catalyst.....	72
Figure 4-2 SIMS profiles of H concentration for the samples annealed at various temperatures with and without Ni film.....	73
Figure 4-3 XRD spectra of Mg-doped GaN structure after activation with Ni film at 400, 500 and 600 °C in air ambient.....	74
Figure 4-4 XRD spectra of Ni film on glass after annealing in air ambient.....	75
Figure 4-5 XRD spectra of Ni/Mg-doped GaN for cases of as deposited Ni film, after activation with Ni film at 600 °C in air, and immersed in aqua regia for 30 min after activation with Ni film at 600 °C, respectively.....	76
Figure 4-6 (a) Effective carrier concentrations as a function of annealing temperature for activation without and with Ni film (b) mobility as a function of annealing temperature for activation without and with Ni film.....	77
Figure 4-7 Profiles of effective carrier concentrations vs. depth from surface. Mg-doped GaN samples were activated without and with Ni film at 600 °C.....	79
Figure 4-8 SIMS depth profiles of Ni.....	80

Figure 4-9 SIMS depth profiles of Mg.....	81
Figure 4-10 Typical PL spectra at 15K for Mg-doped GaN film after activation with and without Ni film.....	82
Figure 5-1 <i>I-V</i> characteristics of GaN based LEDs with Ni/Au contact layer at various annealing temperatures.....	93
Figure 5-2 <i>I-V</i> characteristics of GaN based LEDs. The LED structure wafers without thermal treated and with thermal treated at 500 and 700 °C.....	94
Figure 5-3 SEM image of Ni/Au on <i>p</i> -GaN contact surface after annealing at 900 °C.....	95
Figure 5-4 Schematic drawing illustrating decomposition of GaN along a dislocation line and resulting in the formation of N ₂	96
Figure 5-5(a) Cross-section bright-field TEM micrograph of the LEDs structure with Ni/Au contact layer after annealing at 900 °C (b) at 600 °C.....	97
Figure 5-6(a) EDS spectrum of EDS-1 region at metallic bubble of Fig. 5-5(a), (b) EDS-2 region at threading dislocation of Fig. 5-5(a), (c) EDS-3 region at <i>p</i> -GaN layer of Fig. 5-5(a), and (d) EDS-4 region at threading dislocation of Fig. 5-5(b).....	99
Figure 5-7(a) SEM image of as-deposited ITO contact layer on <i>p</i> -GaN (b) SEM image of the ITO contact layer on <i>p</i> -GaN after annealing at 700 °C.....	103
Figure 5-8 <i>I-V</i> characteristics of GaN-based LEDs with ITO contact layer after different thermal treated temperatures.....	105
Figure 5-9(a) SEM image of etched <i>n</i> -GaN surface with device after 600 °C annealing (b) after 700 °C annealing.....	106
Figure 5-10 EDS spectra obtained from different regions: (a) “1” at pinhole in Fig. 5-9(a), (b) “2” at pinhole in Fig. 5-9(b), and (c) “3” at flat <i>n</i> -GaN surface in Fig. 5-9(b).....	108
Figure 6-1 The specific contact resistances of all the samples as a function of annealing temperature.....	124
Figure 6-2(a) SEM image of as-deposited Ni film on GaN surface (b) SEM image of Ni film	

on GaN surface after annealing at 550 °C in air for 15 min, and (c) XRD spectra of as-deposited Ni film and after annealing at 550 °C on GaN surface respectively.....	126
Figure 6-3 <i>I-V</i> characteristics of GaN based LEDs with various TCL conditions.....	129
Figure 6-4 <i>I-V</i> characteristics of GaN based LEDs with various TCL conditions after thermal treated at 600 and 700 °C.....	130
Figure 6-5 Life tests of reverse leakage current variation (at -5 V) from GaN based LEDs with various TCL conditions by stressed at 50 mA and 25 °C.....	131
Figure 6-6 Life tests of light output variation from GaN based LEDs with various TCL conditions by stressed at 50 mA and 25 °C.....	132
Figure 6-7 Cross-section bright-field TEM micrograph of the LED structure before coating contact metal (TCL).....	133
Figure 6-8 Cross-section bright-field TEM micrograph of the LED-E structure.....	134
Figure 6-9 Cross-section bright-field TEM micrograph of the LED-E structure with higher magnification image.....	135
Figure 6-10(a) EDS spectrum obtained at “a” of Fig. 6-9 (b) at “b” of Fig. 6-9.....	136
Figure 6-11 Ga-In phase system.....	138
Figure 6-12 Schematic drawing illustration of (a) ITO and <i>p</i> -GaN interface and (b) NiO/ITO and <i>p</i> -GaN interface.....	139
Figure 6-13 Cross-section bright-field TEM micrographs of LED-D after thermal treated at 700 °C.....	140
Figure 6-14(a) EDS spectrum obtained at “a” of Fig. 6-12, (b) at “b” of Fig. 6-12, and (c) at “c” of Fig. 6-12.....	141
Figure 7-1 Schematic cross-section view of GaN based LEDs with truncated pyramids on the surface.....	156
Figure 7-2 The specific contact resistances of <i>p</i> -GaN with and without naturally textured surface as a function of annealing temperature.....	157

Figure 7-3 The specific contact resistances of <i>n</i> -GaN with and without naturally textured surface as a function of annealing temperature.....	158
Figure 7-4 The <i>I-V</i> characteristics of the LED-conv and LED-Mg chips with different annealing temperatures.....	159
Figure 7-5 <i>L-I</i> characteristics of GaN based LEDs without naturally textured surface (LED-conv) after different annealing temperatures.....	160
Figure 7-6 <i>L-I</i> characteristics of GaN based LEDs with naturally textured surface (LED-Mg) after different annealing temperatures.....	161
Figure 7-7 Life tests of reverse leakage current variation (at -5 V) by stressed at 50 mA and 25 °C.....	162
Figure 7-8 Life tests of light output variation by stressed at 50 mA and 25 °C.....	163
Figure 7-9(a) SEM image of LED-Mg before metals deposition (cross-section) (b) after metals deposition (tilted).....	164
Figure 7-10(a) Cross-section bright-field TEM micrograph of the LED-Mg structure with low magnification image, (b) with higher magnification image, and (c) the LED-conv structure.....	166