

國立交通大學

光電工程研究所

博士論文

奈米製程技術在氮化鎵相關發光元件之研究

**Study of Nano-Processing Techniques
for GaN-based Light Emitting Devices**

研究生：黃泓文

指導教授：王興宗 教授

郭浩中 教授

中華民國九十六年五月

國立交通大學

光電工程研究所

博士論文

奈米製程技術在氮化鎵相關發光元件之研究

**Study of Nano-Processing Techniques
for GaN-based Light Emitting Devices**

研究生：黃泓文
指導教授：王興宗 教授
郭浩中 教授

中華民國九十六年五月

奈米製程技術在氮化鎵相關發光元件之研究

**Study of Nano-Processing Techniques for
GaN-based Light Emitting Devices**

研究生：黃泓文

Student : Hung-Wen Huang

指導教授：王興宗 教授

Advisor : Prof. Shing-Chung Wang

郭浩中 教授

Prof. Hao-Chung Kuo

國立交通大學 電機學院
光電工程研究所
博士論文

A dissertation

Submitted to Institute of Electro-Optical Engineering

College of Electrical Engineering

National Chiao Tung University

in partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

in

Electro-Optical Engineering

May 2007

Hsinchu, Taiwan, Republic of China

中華民國九十六年五月

國立交通大學

論文口試委員會審定書

本校光電工程研究所博士班 黃泓文 君

所提論文 奈米製程技術在氮化鎵相關發光元件之研究

合於博士資格標準、業經本委員會評審認可。

口試委員：張振雄
(張振雄)

張守進
(張守進)

彭隆翰
(彭隆翰)

盧廷昌
(盧廷昌)

許進恭
(許進恭)

指導教授：王興宗 郭浩中
(王興宗) (郭浩中)

所長：趙丁水 教授

系主任：黃中堯 教授

中華民國 96 年 5 月 24 日

Institute of Electro-Optical Engineering
National Chiao Tung University
Hsinchu, Taiwan, R.O.C.

Date : 5/24/2007

We have carefully read the dissertation entitled Study of Nano-Processing technique for GaN-Based Light-Emitting Devices

submitted by Hung-Wen Huang in partial fulfillment of the requirements of the degree of DOCTOR OF PHILOSOPHY and recommend its acceptance.

Chen-Shiung Chang
(Chen-Shiung Chang)

Shoou-Jinn Chang
(Shoou-Jinn Chang)

Lung-Han Peng
(Lung-Han Peng)

Tien-Chang Lu
(Tien-Chang Lu)

Jinn-Kong Sheu
(Jinn-Kong Sheu)

Thesis Advisor : Shing-Chung Wang
(Shing-Chung Wang)

Hao-chung Kuo
(Hao-chung Kuo)

Director of Institute of Electro-Optical Engineering : Yu-Fang Chen

Chairman of Department of Photonics : Jung-J. Huang

博碩士論文授權書

本授權書所授權之論文為本人在國立交通大學(學院)光電工程系所
組九十五學年度第二學期取得博士學位之論文。

論文名稱：奈米製程技術在氮化鎵相關發光元件之研究

指導教授：王興宗 教授、郭浩中 教授

1. 同意 不同意

本人具有著作財產權之上列論文全文(含摘要)資料，授予行政院國家科學委員會科學技術資料中心(或改制後之機構)，得不限地域、時間與次數以微縮、光碟或數位化等各種方式重製後散布發行或上載網路。

本論文為本人向經濟部智慧財產局申請專利(未申請者本條款請不予理會)的附件之一，申請文號為：_____，註明文號者請將全文資料延後半年再公開。

2. 同意 不同意

本人具有著作財產權之上列論文全文(含摘要)資料，授予教育部指定送繳之圖書館及國立交通大學圖書館，基於推動讀者間「資源共享、互惠合作」之理念，與回饋社會及學術研究之目的，教育部指定送繳之圖書館及國立交通大學圖書館得以紙本收錄、重製與利用；於著作權法合理使用範圍內，不限地域與時間，讀者得進行閱覽或列印。

本論文為本人向經濟部智慧財產局申請專利(未申請者本條款請不予理會)的附件之一，申請文號為：_____，註明文號者請將全文資料延後半年再公開。

3. 同意 不同意

本人具有著作財產權之上列論文全文(含摘要)，授予國立交通大學與台灣聯合大學系統圖書館，基於推動讀者間「資源共享、互惠合作」之理念，與回饋社會及學術研究之目的，國立交通大學圖書館及台灣聯合大學系統圖書館得不限地域、時間與次數，以微縮、光碟或其他各種數位化方式將上列論文重製，並得將數位化之上列論文及論文電子檔以上載網路方式，於著作權法合理使用範圍內，讀者得進行線上檢索、閱覽、下載或列印。

論文全文上載網路公開之範圍及時間-

本校及台灣聯合大學系統區域網路：2008年7月1日公開

校外網際網路：2008年7月1日公開

上述授權內容均無須訂立讓與及授權契約書。依本授權之發行權為非專屬性發行權利。依本授權所為之收錄、重製、發行及學術研發利用均為無償。上述同意與不同意之欄位若未鈎選，本人同意視同授權。

研究生簽名：
(親筆正楷)

黃泓文

學號：9224806
(務必填寫)

日期：民國 96 年 5 月 24 日

1. 本授權書請以黑筆撰寫並影印裝訂於書名頁之次頁。

國家圖書館博碩士論文電子檔案上網授權書

本授權書所授權之論文為本人在國立交通大學(學院)光電工程系所
組九十五學年度第二學期取得博士學位之論文。
論文名稱：奈米製程技術在氮化鎵相關發光元件之研究

指導教授：王興宗 教授、郭浩中 教授

同意 不同意

本人具有著作財產權之上列論文全文(含摘要)，以非專屬、無償授權國家圖書館，不限地域、時間與次數，以微縮、光碟或其他各種數位化方式將上列論文重製，並得將數位化之上列論文及論文電子檔以上載網路方式，提供讀者基於個人非營利性質之線上檢索、閱覽、下載或列印。

上述授權內容均無須訂立讓與及授權契約書。依本授權之發行權為非專屬性發行權利。依本授權所為之收錄、重製、發行及學術研發利用均為無償。上述同意與不同意之欄位若未鈎選，本人同意視同授權。

研究生簽名：
(親筆正楷)

黃泓文

學號：9224806
(務必填寫)

日期：民國 96 年 5 月 24 日

1. 本授權書請以黑筆撰寫，並列印二份，其中一份影印裝訂於附錄三之一(博碩士論文授權書)之次頁；另一份於辦理離校時繳交給系所助理，由圖書館彙總寄交國家圖書館。

奈米製程技術在氮化鎵相關發光元件之研究

學生：黃泓文

指導教授：王興宗 教授
郭浩中 教授

國立交通大學光電工程研究所

摘 要

本論文旨在於探討氮化鎵族奈米發光元件及結構之製作、材料特性、及光電特性。主要分為四個部分，第一部份為研究氮化鎵銻表面奈米粗化發光二極體之光輸出特性，其包含了元件的製作、電性的探討以及光輸出的特性研究，並搭配ASAP模擬軟體分析其元件性能的實驗結果。接著，使用TiO₂ particles在氮化鎵發光元件平台之側壁做粗化製程，並搭配ASAP模擬軟體分析其元件性能的實驗結果。接下來介紹直徑約為50到250奈米的氮化鎵銻多重量子井奈米柱，包含兩種製作方式，一種為利用奈米點狀的鎳金屬作為蝕刻奈米柱的遮罩，另一種為透過奈米點狀的鎳金屬/氮化矽(Si₃N₄)薄膜作為蝕刻奈米柱的遮罩，並利用光激發光譜技術以及高解析穿透式電子顯微鏡研究其光學物理及結構特性，並更進一步討論有關存在於氮化鎵銻多重量子井的壓電場在此結構下的影響。最後，更利用光增強型化學式蝕刻技術，將氮化鎵銻多重量子井奈米柱作成電激發發光元件，並利用高解析穿透式電子顯微鏡研究其結構特性，以及分析其多重量子井之光激發光譜及電激發光光譜等特性，並與一般氮化鎵銻之元件作比較。

Study of Nano-Processing Techniques for GaN-based Light-Emitting Devices

Student: Hung-Wen Huang

Advisor: Prof. Shing-Chung Wang
Prof. Hao-Chung Kuo

Institute of Electro-Optical Engineering
National Chiao Tung University

Abstract

This dissertation explores the fabrication, structural properties, physical features, optical and electronic properties of GaN-based nano-processing light emitting devices. The main focus of this dissertation can be divided into four parts. First, the enhancement in the light output of GaN-based top-surface nano-roughened light emitting diodes (LEDs) with self-assemble nickel (Ni) nanomasks formed by rapid thermal annealing is studied, including device fabrication, electronic properties and light output performance. The experimental results measured from the top-surface nano-roughened LEDs are analyzed with the ASAP simulation. Next, the enhancement in the light output of GaN-based sidewall nano-roughened light emitting diodes (LEDs) with nano-masks by TiO₂ particles also is studied. The following part presents the optical properties of InGaN/GaN multiple quantum well nanorods with diameters from 50 to 100 nm. The formation of the nanorods is employed by ICP etching with self-assemble nickel (Ni) nanomasks formed by rapid thermal annealing. The optical and structural properties are investigated by using varied temperature photoluminescence (PL) measurement, high resolution transmission microscope (HRTEM) and scanning electron microscope (SEM). The last part is fabrication of InGaN/GaN nanorod LEDs with self-assemble nickel (Ni) nanomasks and photo-enhanced chemical (PEC) etching. This part focus on the fabrication, optical and electrical properties are investigated on the InGaN/GaN nanorod LEDs by using room temperature PL, EL (electroluminescence) and HRTEM measurements compared with that of the conventional devices.

誌謝

四年的博士生生涯，心中有無限的感謝，一路走來從跌跌撞撞而今成長茁壯，首先要感謝指導老師王興宗和郭浩中教授對我耐心的指導與教誨，讓我學習到在求學上應有的態度與精神，更別提在專業知識領域上的精進以及學習待人處世的哲學。老師，謝謝您！

在眾人的協助下，才能造就今日順利畢業的我。感謝這幾年跟我一起努力的同學與學弟小強、小朱，你們是我的好伙伴、好朋友，我們共同完成了許多不可能的任務，謝謝你們；感謝盧廷昌教授、林佳鋒教授、賴芳儀教授、余長治博士、薛道鴻博士、蔡睿彥博士、姚炘宏博士、黃根生博士從旁的指導與討論；實驗室博士班學弟小賴、清華，感謝你們在實驗上給予的協助，與你們合作的時間雖不長，但也建立的良好默契與不錯的成果。感謝學弟妹宗憲、德宗、士偉、明華、碩均、剛帆、宗鼎、立凡、孟儒、維志、潤琪為實驗室的付出以及營造愉快的實驗室氣氛，讓我在實驗室感受到愉悅與歡笑。感謝口試委員彭隆瀚老師、張振雄老師、張守進老師、許進恭老師、盧廷昌老師對我論文上的指導。感謝所有幫助過我的朋友們！

最後，特別感謝我的家人給我全力的支持與無怨無悔的付出，不會讓我因學業與工作需兼顧的情況下，導致減少對家裡的關心而有所抱怨，使我無後顧之憂順利完成學業，爺爺、奶奶、爸、媽、哥哥、姐姐、妹妹、老婆佳琪謝謝你們。

謝謝大家！

泓文 于 96 年 6 月 14 日
交通大學光電所

Content

Abstract (in Chinese).....	i
Abstract (in English).....	ii
Acknowledgement.....	iii
Content.....	iv
Table Caption.....	vi
Figure Caption.....	vii
Chapter 1 Introduction.....	1
1.1 Overview.....	1
1.2 Outline of this dissertation.....	2
Chapter 2 GaN-Based Nano-Roughened Light-Emitting Diodes.....	5
2.1 Progress in GaN-based nano-roughened LEDs with wet etching.....	5
2.2 Fabrication of nano-roughened LEDs with wet etching.....	6
2.3 Characteristics of GaN-based nano-roughened LEDs with wet etching.....	6
2.4 Fabrication of GaN-based nano-roughened LEDs with laser etching.....	9
2.5 Characteristics of GaN-based nano-roughened LEDs with laser etching.....	13
Chapter 3 GaN-Based Sidewalls Roughened Light-Emitting Diodes.....	36
3.1 Progress in GaN-based sidewalls roughened LED device by natural lithography.....	36
3.2 Fabrication of GaN-Based sidewalls roughened LED device by natural lithography.....	36
3.3 Characteristics of GaN-Based sidewalls roughened LED device by natural lithography.....	37
3.4 Fabrication of GaN-Based sidewalls roughened power chip LED device by natural lithography.....	39
3.5 Characteristics of GaN-Based sidewalls roughened power chip LED device by natural lithography.....	39
Chapter 4 InGaN/GaN Multiple Quantum Wells Nanorods.....	56

4.1 Introduction.....	56
4.2 Fabrication of InGaN/GaN MQWs nanorods.....	57
4.3 Optical properties of the InGaN/GaN MQWs nanorods.....	59
Chapter 5 GaN-Based MQW Nanorods Light-Emitting Diodes.....	78
5.1 Introduction.....	78
5.2 Experiments.....	79
5.3 Photoluminescence measurement.....	81
5.4 Electroluminescence measurement.....	82
Chapter 6 Summary.....	89
Publication List.....	91
Curriculum Vita.....	95

Table Caption

Table 3.1 Parameters of structure layer in the stimulated power-chip LEDs.

Figure Caption

Chapter 2

- Fig. 2-1 AFM images presenting the top surface morphology of a LED sample. (a) Image taken from the top surface of a LED sample after the formation of Pt clusters. (b) Image taken from the top surface of a LED spectrum, respectively.
- Fig. 2-2 Showing the process flowchart of the GaN-based top-surface nano-roughened LEDs using wet etching.
- Fig. 2-3 Showing the standard process flowchart of GaN-based LEDs.
- Fig. 2-4 AFM images of the top surface morphology of a LED sample. (a) Conventional LED p-GaN surface image. (b) Ni nano-mask on p-GaN surface image. (c) Nano-roughened LED top p-GaN surface image.
- Fig. 2-5 I-V (a)forward (b) reverse curves of conventional and nano-roughened LEDs fabricated in this investigation. (c) I-V characteristics of the nano-roughened and conventional p-GaN measured by the Circular Transmission Line Method (CTLM). (d) Total resistance (Y) measured by CTLM is linearly related to the pad distance (X).
- Fig. 2-6 (a) Room temperature EL spectrum of conventional and nano-roughened LED at a current of 20 mA. (b) Light output power-current (L-I) characteristics of conventional and nano-roughened LEDs.
- Fig. 2-7 Photons of (a) conventional LED and (b) nano-roughened LED at a dc injection current of 20 mA.
- Fig. 2-8 Schematic diagram of the nano-roughened LED structure.
- Fig. 2-9 Simulation describes the light extraction efficiency of LEDs with and without rough top surface as a function of absorption coefficient of the p-GaN.
- Fig. 2-10 The schematic diagram of laser etching process setup.
- Fig. 2-11 The etching rate as a function of laser fluence.
- Fig. 2-12 (a)SEM and (b)AFM images of the Ni nano-mask on p-GaN surface morphology of a nano-roughened LED sample.
- Fig. 2-13 AFM images of the top surface morphology of a LED sample. (a) Conventional LED p-GaN surface image. Nano-roughened LED top p-GaN surface applied laser etching energy of : (b) 300 mJ/cm², (c) 400mJ/cm², (d) 800mJ/cm².
- Fig. 2-14 forward I-V curves of conventional and nano-roughened LEDs.

Fig. 2-15 (a) Room temperature EL spectra of conventional and nano-roughened LEDs with laser etching energy of 300 mJ/cm^2 at a current of 20 mA. (b) Light output power-current (L-I) and RMS surface roughness characteristics of conventional and nano-roughened LEDs.

Chapter 3

Fig. 3-1 A schematic diagram of InGaN-GaN MQW LED structure with nano-scale textured sidewalls.

Fig. 3-2 SEM images of InGaN-GaN MQW LED structure with nano-scale textured sidewalls. (a) cross-section of nano-scale textured sidewalls and (b) nano-rods density of nano-scale textured sidewalls.

Fig. 3-3 (a) current-voltage (I-V) and (b) intensity-current (L-I) characteristics of conventional and LED with nano-scale textured sidewalls LEDs fabricated in this investigation.

Fig. 3-4 Light output patterns of the LED with nano-scale textured sidewalls and the conventional LED.

Fig. 3-5 Top-view ray tracing images of the (a) conventional LED. and the (b) LED with nano-scale textured sidewalls.

Fig. 3-6 Top-view of power chip LED.

Fig. 3-7 (a) current-voltage (I-V) and (b) intensity-current (L-I) characteristics of conventional power chip LED and power chip LED with sidewall roughness fabricated in this investigation.

Fig. 3-8 Light output wavelength peak of the power chip LED with sidewall roughness.

Fig. 3-9 Light output far-field patterns of the power-chip LED with sidewall roughness and the conventional LED.

Fig. 3-10 Top-view ray tracing images of the (a) conventional power chip LED. and the (b) power chip LED with sidewall roughness.

Fig. 3-11 Power chip LEDs with sidewall roughness were driven by 350 mA current injection at room temperature.

Chapter 4

Fig 4.1 Schematic illustration of GaN-based nanorod LEDs' process: using (a) Ni (first set) and (b) Ni/Si₃N₄ (second set) as nano-masks formation. The reaction products after RTA and ICP-RIE etching, leading to the formation of GaN-based nanorod LEDs.

Fig. 4.2 The SEM images of GaN-based nanorod LEDs samples : (a) only Ni/Si₃N₄ nano-masks, (b) etching first set sample, and (c) etching second set sample at fixed the same RTA temperature 850°C, annealing time 1min, Cl₂/Ar flow rate of 50/20 sccm, ICP/Bias power of 400/100 W, and chamber pressure of 5mTorr for 3 min of etching time.

Fig. 4.3 The mean dimension and density of GaN-based nanorod LEDs on first and second set samples as

a function of the RTA temperature varies from 800 to 900°C for 1min with Cl₂/Ar flow rate of 50/20 sccm, ICP/Bias power of 400/100 W, and chamber pressure of 5mTorr for 3 min of etching time.

Fig. 4.4 The mean dimension and density of GaN-based nanorod LEDs on second set samples as a function of the Ni film thickness varies from 50 to 150 Å at the same RTA 850°C for 1min with Cl₂/Ar flow rate of 50/20 sccm, ICP/Bias power of 400/100 W, and chamber pressure of 5mTorr for 3 min of etching time.

Fig. 4.5 TEM image of a single InGaN/GaN MQW nanorod.

Fig. 4.6 (a) A schematic diagram of In_{0.3}Ga_{0.7}N/GaN MQWs green emission nanorods structure. (b) Tilted 45° SEM and (c) TEM images of In_{0.3}Ga_{0.7}N/GaN MQWs green emission nanorods.

Fig. 4.7(a)The Arrhenius plot of an integrated PL intensity obtained from the In_{0.3}Ga_{0.7}N/GaN MQWs active layer emission over a temperature range from 20 to 300 K. (b)Comparing the PL spectra from as-grown and green nanorods of excited by a 325 nm He-Cd laser from 20 to 300K.

Fig. 4.8 TRPL life time curves of the In_{0.3}Ga_{0.7}N/GaN MQW as-grown and green nanorod samples for the main InGaN emission peak measured at 10K and 300K.

Fig. 4.9 Radiative recombination rates of the structures with the two different polarization charges in the special location of single-QW.

Chapter 5

Fig. 5.1 schematic illustration of InGaN/GaN MQW nanorods LED process flowchart.

Fig. 5.2 the SEM images of (a) Ni nano-masks on p-GaN top surface after RTA process, (b) InGaN/GaN MQW nanorods LED after ICP-RIE etching. (c) InGaN/GaN MQW nanorods LED after PEC process. (d) InGaN/GaN MQW nanorods LED after deposited contact metal.

Fig. 5.3 normalized PL intensity spectra for as-grown LED and nanorods LED with/without PEC at room temperature.

Fig. 5.4 normalized EL intensity spectra for as-grown LED and nanorods LED with PEC at room temperature. Insets show the top-view photograph image of a blue emission from InGaN/GaN MQW nanorods LED at 1 mA dc current. The inset shows the top-view photograph image of nanorod LED with PEC.