

Contents

Contents.....	I
致謝詞.....	III
Abstract.....	IV
中文摘要.....	VI
Figure Captions.....	VIII
Table Captions.....	X I

Chapter 1: Introduction

- 1-1 Blue light-emitting materials and GaN
- 1-2 Nanomaterial and quantum confinement effect
- 1-3 Carbon nanotube
- 1-4 Motivation

Chapter 2: Experimental Method

- 2-1 Introduction
- 2-2 MOCVD system
 - 2-2-1 Gas and Metal-Organic sources
 - 2-2-2 Deposition chamber

2-2-3 Pumping system

2-3 Substrate preparation

2-4 Analysis equipments

Chapter 3: Synthesis of one-dimension GaN

**nanostructure encapsulated inside
carbon nanotube**

3-1 Experiment Method

3-2 Results and Discussion

Chapter 4: Synthesis of GaN nanowire

4-1 Experiment Method

4-2 Results and Discussion

Chapter 5: Conclusion

References

致謝詞

這篇論文的完成所先要先感謝蕭錫鍊老師以及楊安邦老師的悉心指導，在這兩年的時間裡因為有你們的指導，讓我學到了實驗該有的精神與態度，以及發現問題、解決問題的能力，也因此這篇論文才能順利的產生。

其次要感謝盧明昌、許瀚恭、林博文學長和李姿青學姊，當我實驗遇到瓶頸時因為有你們的一句話，讓我頓時茅塞頓開，也因為有你們的指導讓我能夠順利解決問題，另外要感謝黃豐欽同學在 X-ray 量測上的幫助，惟淳學弟(同學)在 PL 量測上的幫忙，東嘻學弟、介良學弟(同學)平時在實驗上的支援，以及當我無暇分身時的適時幫助都令我感謝萬分。

最後要感謝我的女朋友，惠如，以及我的家人，奶奶、媽媽、姑姑們的支持，也因為有你們的付出與支持才能讓我順利的完成學業，謹以此論文獻給你們。

Abstract

In this thesis, combining low-pressure metal-organic chemical vapor deposition technology with metal-catalyzed the growth of nanowire onto silicon substrate is the main purpose. We hope to synthesize GaN nanostructure possesses quantum confinement effect.

In this study, 5nm-thick Au thin film used as catalyst for synthesizing nanowires sputtered onto monocrystalline silicon (100). TMG, NH_3 and C_2H_2 gases were used as Ga, N and C precursors respectively. The structural characteristic of the material was examined with scanning/transmission electron microscope, Raman spectra and X-ray powder diffraction. On the side, the optic characteristic and quantum confinement effect were measured by Photoluminescence spectra.

First, carbon nanotubes (CNT) were used to confine the radial growth simultaneously growth of GaN and carbon nanotube. The presence of the wurtzite structure GaN nanowires encapsulated inside the cavity along the length of a multi-wall carbon nanotube by experiment result. In the experiment, the inner and outer diameters and GaN nanowire encapsulated inside the carbon nanotube were changed with the flow rate of C_2H_2 was controlled. The outer diameter of CNT is about 20-50 nm and the diameter of GaN nanowire is about 10-15nm while the flow rate of C_2H_2 was controlled to be 50sccm. The outer diameter of CNT is about 15-20 nm and the diameter of GaN nanowire is about 6-8nm while the flow rate of C_2H_2 was controlled to be 25sccm. The diameter of GaN nanowire is decreasing with the flow rate of C_2H_2 reduced and conforms with the inner diameter of CNT as well as the band-gap has blue-shift. Gold can not catalyze the growth of CNT is already knew ago, but we

find that the carbon nanotube can be catalyzed by Ga in documents. Hence we suppose the growth of CNT was catalyzed by Ga-Au alloy and the sections of GaN nanowire were caused by the different speed of growth.

On the side, we synthesize GaN nanowire by 2-step method. The first part of GaN nanowire was synthesized at 750°C and the second part was synthesized while the temperature cooling down. The GaN nanowire was defined to be wurtzite structure from experiment result. The first part of the wire was observed from TEM image that has triangular cross section with 36 nm diameters and the second part of the wire was observed from TEM image that has 5nm diameter. We can not observe obviously the quantum confinement effect from the analysis of spectra due to the second part GaN nanowires are too short. Hence we suppose that the synthesis of second part of GaN nanowire was catalyzed by using the minority of Au was not covered by nitrides as catalyst during cooling down.

In this study, the way of synthesizing GaN@CNT is efficiently to control the diameter of GaN nanostructure. That is efficiently and simply to synthesize a large amount of semiconductor materials possess quantum confinement effect.

中文摘要

本論文中主要的目的為結合低壓有機金屬化學氣相沉積技術以及金屬觸媒催化作用在矽基板上成長奈米線，希望製造出具有量子侷限效應的氮化鎵奈米結構。

本研究中我們利用濺鍍的方式在單晶矽(100)基板上鍍上約 5nm 厚的金薄膜作為合成奈米線的催化劑。另外利用 TMG, 氮氣及乙炔氣體作為成長所需鎵、氮、碳等元素的來源。藉由掃描式/穿透式電子顯微鏡，拉曼光譜, X-ray 繞射圖形來觀察材料的結構與組成，另外材料的量子侷限效應藉由光激光譜的量測來確認。

首先我們利用碳管小內徑的特性來限制氮化鎵的徑向成長, 由實驗結果顯示所成長出奈米線是一個多層奈米碳管包覆 wurtzite 結構氮化鎵的奈米線。實驗結果顯示改變乙炔的流量，碳管的內徑外徑與內層的氮化鎵奈米線也會隨著流量而改變，在乙炔為 50sccm 時碳管的外徑約為 20-50nm 氮化鎵奈米線直徑約為 10-15nm，乙炔為 25sccm 時碳管外徑約為 15-20nm 氮化鎵奈米線直徑約為 6-8nm，因此氮化鎵奈米線的直徑也隨著變大，同時由光激螢光光譜也發現隨著氮化鎵奈米線直徑的變小，氮化鎵的能階也有藍位移的趨勢。由於金對於碳管並沒有催化能力，但由文獻顯示鎵具有催化成長奈米碳管的能力，因此我們推測碳管是藉由鎵與金的合金催化而成長，並且由於碳管成長

速度較快也就造成氮化鎵奈米線形成一節一節的結構。

此外，我們利用 2 階段成長的方式，先成長一段氮化鎵奈米線並且在降溫同時持續成長，實驗結果顯示所長成之氮化鎵奈米線是具有 wurtzite 結構的 2 段式結構，第一段是直徑約 36nm 的三角形橫切面的氮化鎵奈米線以及第二段直徑約 5nm 量子尺度的氮化鎵奈米線，由於 2 段式氮化鎵奈米線的第二段極短因此在光譜分析上並沒有很明顯的量子侷限效應，由實驗結果顯示極細氮化鎵奈米線可能是由於在降溫同時金觸媒逐漸被氮化物包覆僅存極小部分可持續催化，因此而成長出第二段的奈米線。

在本研究中所發展出氮化鎵/碳管的製程方法可以快速且大量的成長半導體量子結構。

Figure Captions

Fig.1-1 Gallium nitride nanorods were prepared through a carbon nanotube-confined reaction.

Fig.1-2 A method using an arc discharge in a nitrogen atmosphere for synthesizing large quantities of GaN–Carbon composite nanotubes and GaN nanorods.

Fig.1-3 Laser-Assisted catalytic growth of single crystal GaN nanowires

Fig.1-4 Formation of GaN nanorods by a sublimation method

Fig.1-5 Straight and Smooth GaN Nanowires

Fig.1-6 Pyrolysis approach to the synthesis of gallium nitride nanorods

Fig.1-7 Catalytic growth and characterization of gallium nitride nanowires

Fig.1-8 Strained gallium nitride nanowires

Fig.1-9 Growth of GaN nanorods by a hydride vapor phase epitaxy method

Fig.1-10 A HRTEM image and Photoluminescence spectra of the 1-D GaN-SiO₂ nanocable

Fig.1-11(a) Radiation from a forward biased p-n junction at 78°k

Fig.1-11(b) The band edge radiation at 1.47eV

Fig.1-12 Low-temperature catalytic synthesis of Gallium nitride nanowires

Fig.1-13 The development of various type LEDs

Fig.1-14 Arrays of ZnO nanowires and GaN nanotubes

Fig.1-15 Gallium nitride nanowire nanodevices

Fig.1-16 Electron microscopy images of synthesized GaN nanowires and

individual,isolated GaN nanowire laser.

Fig.1-17 Change of energy-level of atom, molecular, nanomaterial and bulk

Fig.1-18 The relationship between the form and density of state

Fig.1-19 The different shape of carbon

Fig.1-20 Multi-wall carbon nanotube

Fig.1-21 Single-wall carbon nanotube

Fig.1-22 The direction of graphite rolled into a cylinder

Fig.2-1 (a)Sketch map of MOCVD system (b) Photography of TMGa source and high temperature furnace.

Fig.3-1 Schematic diagram of the setup for preparing the GaN@CNT and needly GaN nanowires

Fig.3-2 SEM images of GaN@CNT with the relatively much amount of C_2H_2 (a) a tilt of plane view (b) cross-section (c) high-magnification images

Fig.3-4 (a) GaN nanorod is coated several sheets of the graphitic lays; the inset is the corresponding diffraction patterns (b) high-magnification of a section of GaN nanorod, (c) The interface of GaN and CNT.

Fig.3-5 Typical PL spectra from GaN@CNT nanowires

Fig.3-6 Temperature dependence of photoluminescence spectrum

Fig.3-7 Typical SEM image (a) high-density nanowires (b) coress-section of GaN@CNT nanowire (c) high-magnification image and the range of circle shown the nanostructure within the CNT

Fig.3-8 The X-ray diffraction pattern of the nanowire

Fig.3-9 HRTEM image of GaN@CNT (a) low-magnification image; the

diffraction pattern of nanowire in inset (b)(c) the diameter of GaN core is about 8nm (d) the atomic resolved lattice

Fig.3-10 An individual GaN@CNT nanowire HRTEM image

Fig.3-11 Typical PL spectra from GaN@CNT nanowires

Fig.3-12 Temperature dependence of photoluminescence spectrum

Fig.3-13 Blue-shift of photon energy

Fig.3-14 Raman spectra at two samples with different conditions

Fig.4-1 SEM images of GaN nanowire (a) morphology view (b) (c) high-magnification images of triangular GaN nanowires.

Fig.4-2 SEM images of GaN nanowires cross section (a) a large amount of GaN nanowire (b)(c) a needle-like structure upon the nanowire

Fig.4-3 A range from 20 to 80° XRD pattern taken from the GaN nanowire.

Fig.4-4 TEM image of full view; the inset is the diffraction pattern of the nanowire.

Fig.4-5 (a) An individual GaN nanowire image (b)(c)high-magnification image of GaN nanowire

Fig.4-6 EDS of single GaN nanowire

Fig.4-7 PL spectrum of GaN nanowire at room temperature

Fig.4-8 PL spectrum of GaN nanowires with diameter of 36 nm and 2-step GaN nanowires

Fig.4-9 Raman scattering spectrum of needly GaN nanowires

Table Captions

Table 1-1 Different types of LEDs are grown with different techniques and have different characteristics.

Table 1-2 The develop of III-nitride materials.

Table 1-3 The comparison of carbon nanotube, steel and wood