

行政院國家科學委員會專題研究計畫 成果報告

奈米結構性寬能隙氮化物暨其他發光器件用半導體材料的
磊晶和缺陷工程

計畫類別：個別型計畫

計畫編號：NSC93-2215-E-002-035-

執行期間：93年08月01日至94年10月31日

執行單位：國立臺灣大學光電工程學研究所

計畫主持人：馮哲川

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主持人：台灣大學光電工程研究所 馮哲川教授

一、中文摘要

本報告總結國科會計畫 NSC93-2215-E-002-035-「奈米結構性寬能隙氮化物暨其他發光器件用半導體材料的磊晶和缺陷工程」(93年8月1日至94年10月31日)的執行成果。在這段時間之內，計畫主持人(暨合作者和學生)已經發表了1本專業書籍，1章專書著作以及9篇發表(或已接受發表)在SCI上的期刊論文。主要的結果及成就包含了以下幾項：(A)藍寶石基板上金屬氧化物化學氣相磊晶成長的氮化銦鎵/氮化鎵多量子井結構的發光復合機理與缺陷，(B)以氮化鎵為基礎金屬氧化物化學氣相磊晶成長的藍綠發光二極體的缺陷和影響，(C)以金屬氧化物化學氣相磊晶成長的氮化鎵中P型摻雜與退火的影響，(D)在金屬氧化物化學氣相磊晶成長以矽為基板的氮化鎵龜裂現象的控制與改善，(E)以金屬氧化物化學氣相磊晶成長低銦濃度之氮化銦鎵合金的光致發光性質，(F)以金屬氧化物化學氣相磊晶成長在砷化鎵基板上之銻化銦的缺陷性質和光學特性，(G)在化學氣相磊晶生長以矽為基板的立方結構碳化矽薄膜的光學特性，(H)應用於可見光範圍發光二極體且以金屬氧化物化學氣相磊晶成長的磷化銦鋁鎵材料的缺陷性質和光學特性，(I)出版碳化矽功率材料及元件專業書籍，(J)提供十多名研究生的良好訓練。

關鍵詞：金屬氧化物化學氣相磊晶, 缺陷工程, 氮化物, 量子井, P型摻雜, 碳化矽, 磷化銦鋁鎵, 銻化銦, 砷化鎵

Abstract

This report reviews the performance on the project NSC 93-2218-E-002-011, Epitaxy and Defects Engineering of Nano-structural Wide Gap III-Nitrides and Related Semiconducting Materials for Light Emitting Devices for 8/1/2004 - 10/31/2005. In this period, P.I. (and collaborators as well as students) have

published 1 specialized book [1], 1 review book chapter [2], 9 journal papers to be listed in SCI [3-11], and more conference/proceeding papers. Main results and achievements include: A) recombination mechanism and defects from InGaN/GaN multiple quantum well (MQW) grown on sapphire by MOCVD, B) defects and influence from the MOCVD-grown GaN-based blue-green LEDs, C) effects of p-type doping and annealing for GaN grown by MOCVD, D) cracking control and improvement of GaN films grown on Si by MOCVD, E) photoluminescence features of low indium composition InGaN alloys grown by MOCVD, F) defect features and optical/transport properties of epitaxial InSb on GaAs by MOCVD, G) optical properties of CVD-grown cubic SiC thin films on Si substrates, H) defects and optical properties of MOCVD-grown InAlGaP materials for visible LED application, I) the publication of a specialized review book on SiC power materials and devices, and J) good trainings for more than 10 graduate students.

Keywords: MOCVD epitaxy, defects engineering, GaN, InGaN, quantum wells, p-type doping, SiC, AlInGaP, InSb, GaAs

二、緣由與目的

該計畫為馮哲川教授於92學年加入台灣大學光電所暨電機系後申請的第二個國科會計畫。接續計畫主持人的新進人員92年度計畫：奈米結構性氮化物暨相關材料的磊晶和缺陷工程。本計畫是前計畫的延伸與深入，包含八項新技術項目，著重於研究金屬氧化物化學氣相磊晶(MOCVD)技術相關的缺陷工程，研究生長過程的缺陷和問題，

深入其物理機制,探索新路徑以控制生長過程的缺陷,以製成高質量的氮化物磊晶材料。此外也研究其他半導體,例如碳化矽的整體和磊晶材料,以及在半導體發光二極體和雷射產研中應用頗廣的 InAlGaP, AlGaAs 和 InSb 材料。這些材料均可由 MOCVD 技術製作。

磊晶是一種必要的技術,極其適用於生長氮化物暨其他半導體材料,並用於製作先進的光電器件,例如:發光二極體(LED),雷射二極體(LD),和紅外-超紫外檢測器。MOCVD 為極有用的工具,適合用於生產以上材料與器件。基於氮化物和發光二極體以及光電-電子器件的新工業正在形成,台灣的公司群已在此領域中佔據世界市場上的重要份額。然而仍然存在著一些技術障礙而妨礙進一步的發展。這種迄今為止的發展仍忽略了如何使得缺陷密度可降至其他如三五族半導體所具有的水平。摻雜,缺陷,異質特性,合金與介面,這些在氮化物中均是比通常的三五族砷化鎵,磷化銦等為之複雜得多的。似乎,氮化物中的晶體不完整性有其特殊的性能,使其減低其對晶體的電學和光學性能的影響。但是,許多科學和技術的問題仍是未知或尚未解決,這些問題又反過來妨礙了進一步的發展以製作高質量的材料和高性能的器件。這是本計畫(和前計畫)的主要目標:解決以上一些困難的問題和排除某些瓶頸。根據本總結報告(以及前計畫的總結報告),我們可看到,馮哲川教授暨研究團隊已朝此目標邁進並取得很好的成果,對於學術研究、國家發展及其他應用方面有極好之貢獻。當然長期的大目標是要探索與建立金屬氧化物化學氣相磊晶生長形成的各種缺陷與物理方法探測到的光學和材料特性之間的相關聯繫,以幫助成功的磊晶及研製新一代高性能的光電器件。

四名碩二學生和一名博士生以及多名碩一學生已積極參與本計畫工作並從事於不同的課題得到極好的訓練,獲取寬帶隙半導體的知識,各種量測技術,金屬氧化物化學氣相磊晶理論和實作經驗。四名碩二學生已畢業並加入了台灣的光電與電子公司。兩計畫的執行已給一年級研究生們打下堅實的基礎並有益於第二年及博士班的

進一步學習與深造。

三、研究結果與討論

In performing this project, we have produced 1 specialized book [1], 1 review book chapter [2], 9 journal papers which to be listed in SCI [3-11] and >10 conference and proceeding papers as more presentation in various international and national academic conferences. On the beginning, P.I. had planned 8-items of research work. All have been achieved with good results, which are reviewed and discussed one-by-one item (some contents modified according to the research results) as follows.

A] Recombination mechanism and defects from InGaN/GaN multiple quantum well (MQW) grown on sapphire by MOCVD.

We have grown, by MOCVD, a series of InGaN/GaN MQWs grown on sapphire with different indium composition and well thickness, and performed penetrating studies via a variety of characterization techniques, including high resolution X-ray diffraction (HRXRD), high resolution transmission electron microscopy (HRTEM), temperature (T) and excitation-dependent photoluminescence (PL), PL excitation (PL) and Raman etc., to obtain knowledge on the defects-related PL mechanisms in these MQWs. With increasing excitation power density, the PL peak position showed a blue shift followed by a red shift. It is believed that a screened quantum-confined Stark effect is responsible for the blue shift and the band gap renormalization due to many body effect is responsible for the red shift [3].

We have measured the shift of so-called quantum-confined Stark effect (QCSE) at room temperature (RT), which was done so by other researchers only at low-T. Through the optimization of growth parameters, we have achieved to high quality of InGaN/GaN MQW structures with excellent structural and optical characteristics [4].

B] Defects and influence from the MOCVD-grown GaN-based blue-green LEDs.

We have collaborated with different Nitride-LED companies and researchers to perform comprehensive investigations on blue-green Nitride-LEDs fabricated under different conditions and with different performance. The effects of defects and dependence of the temperature and excitation power on the characteristics of InGaN/GaN single quantum well (SQW) and multiple quantum well (MQW) light-emitting diodes (LED) has been investigated in-depth over a broad range of temperatures from 9 K to 300 K. It was found that the device with a stair-shaped SQW structure exhibited stronger localization effect, having higher internal quantum efficiency than did the conventional MQW and SQW LEDs. This is interpreted due to the stair-shaped SQW configuration, which offered a large contribution to the exciton capturing. The adoption of an appropriate hetero-structure in active region allows the achievement of improved LED performance. With increasing the excitation power intensity, QW PL line broadening and emission peak blueshifts were observed, which are assumingly caused by the disordering formed in the In-rich heterostructures of QW ensembles. We expect that distinct degree of carrier localization occurs in these samples. These results have been reported in an oral presentation at the 16th American Conference on Crystal Growth and Epitaxy and 12th US Biennial Workshop on Organometallic Vapor Phase Epitaxy, July 10-15, 2005, Montana, USA, which is going to publish in J. Crystal Growth [5].

C] Effects of p-type doping and annealing for GaN grown by MOCVD.

P-type doping in GaN is an important subject and currently achieved typically by Mg-dopings with proper annealing process. But the acceptor activation energy of Mg in GaN is high and hole carrier concentration is not easy to reach beyond 10^{20} cm^{-3} . Efforts have been pursued in searching new impurities. We have explored the P-type doping through Be implantation in GaN by a two-step annealing process. Combined photoluminescence-Raman measurements

showed Be-related band, indicating a low acceptor ionization energy of 140 meV, and resonance Raman features. X-ray diffraction revealed the lattice expansion due to Be-implantation. Scanning electron microscopy exhibited the surface defects morphology with hexagonal plane like inverse open pyramids. We have found that the crystal structure was almost recovered by annealing and some microstrains after growth relaxed [6].

D] Cracking control and improvement of GaN films grown on Si by MOCVD.

We have employed MOCVD to grow a series of GaN thin films on Si under different conditions and films were characterized by a variety of techniques. Nomarski microscopy (NM) showed different cracking patterns for GaN/Si depending on growth and source flow parameters. Film thicknesses were determined from optical reflectance. High resolution XRD, Raman scattering and photoluminescence measurements confirmed their wurtzite crystalline GaN structures, and the corresponding line shape analyses revealed their difference corresponding to the NM observations. It's found that one sample has the best shape of widest cracking distribution, the narrowest PL and Raman band, Another one takes the 2nd position while the 3rd one is with poor surface morphology. Other two have the high density of cracks. The high temperature AlN buffer growth with Si-doping and the Si-delta doping during the GaN layer growth are useful to realize the control and improvement of cracking in GaN/Si [7]. In Taiwan, there exists strong Si-based semiconductor industry. It is very significant to develop the GaN epitaxy on Si.

E] Photoluminescence features of low indium composition InGaN alloys grown by MOCVD.

We have grown a series of InGaN thin films with low indium composition (~3%) on sapphire substrates by MOCVD. The wavelength shifts in the major photoluminescence (PL) bands have been studied by a combination of experiment and theory. As temperature increases from 6 K, the PL peak energy red-shifts very slightly first, then blue-shifts to reach a maximum at near 100 K, and red-shifts again till room

temperature. This unique PL behavior, indicating the existence of the phase separation, is interpreted qualitatively from the spatial variation of band structure due to the In-compositional fluctuation. Theoretical calculation, based upon a model involving the band-tail states in the radiative recombination, explains the experimental data successfully [8].

F] Defect features and optical/transport properties of epitaxial InSb on GaAs by MOCVD.

We have grown a series of InSb thin films on GaAs by MOCVD under different growth conditions and performed the optical investigation on them by way of far infrared spectroscopy and theoretical simulation. Various mode parameters, e.g., the transverse optical (TO) mode frequency, carrier concentration, mobility, etc. were obtained from these InSb/GaAs materials. All the specimens were analyzed by a dielectric response model. It was found that the extra modes appear in infrared (IR) spectra due to the interface reaction between the film and substrate. Interesting splitting of the GaAs transverse optical phonon mode was observed and explained using the dielectric response model to fit the IR reflectance spectrum by varying the InSb film thickness. Effects of III/V source ratios were successfully studied by FIR spectroscopy and the optimized growth parameters have been obtained. The InSb film grown with an III-V ratio of 4.1 possesses the highest carrier concentration and mobility. The results of this study show that MOCVD technology is capable to produce high quality far infrared InSb epitaxial materials, and the Fourier transform infrared (FTIR) method is a very useful tool for non-destructive characterization of large size wafers in industrial mass production [9].

G] Optical properties of cubic SiC grown on Si substrate by chemical vapor deposition.

Silicon carbide (SiC), owing to its excellent electrical, mechanical and chemical properties, is experiencing a renewed wave of interest in electronic and optoelectronic applications with feasibility of use in extreme

environments. Continuing progress in the growth of bulk and epitaxial SiC films with defined doping levels and device processing has resulted in successful fabrication of several electronic devices with the same quality standards as of the Si technology. We have used chemical vapor deposition (CVD) to grow a series of 3C-SiC films on Si substrates with varied film thickness up to 17 μm . They were studied by photoluminescence (PL), Raman scattering (RS), Fourier transform infrared (FTIR) transmission and reflectance measurements. Typical key or main features on these optical spectra are obtained. It has shown that the thinner (less than 3 μm) 3C-SiC grown on Si have their PL, RS and FTIR optical spectral features, mainly associated with defects. After a certain thickness ($> 10 \mu\text{m}$) of CVD film growth, good and high quality of single crystalline cubic SiC films on Si were obtained, evidenced by PL, RS and FTIR spectra.

From comparative measurements for 3C-SiC grown on Si and with Si-substrate removed, the stress and strain effects on 3C-SiC/Si are exposed. Tensile stress in the 3C-SiC films grown on Si is identified and measured. A relation formula on two deformation potentials, a and b, for 3C-SiC is deduced from the PL and Raman data. Further interesting variations on the intensities from bound exciton lines of 3C-SiC due to layer tensile stress are described. These significant results have been reported in an invited presentation of an international conference [10] and in a book review chapter [2].

In additions, P.I. has published two authorized books on SiC materials and devices in 2004 [1] and 2003 [17], which further confirm his scientific positions in the SiC R&D field.

H] Defects and optical properties of MOCVD-grown InAlGaP materials for visible LED application.

The quaternary alloy $\text{In}_{0.5}(\text{Ga}_{1-x}\text{Al}_x)_{0.5}\text{P}$, lattice-matched to GaAs, has a direct band-gap transition in the wavelength range between green and red and is useful for

optoelectronic applications such as red-green LEDs, laser diodes (LDs) and heterojunction bipolar transistors (HBT). This material is expected to offer a high radiative recombination rate in the green-red region that cannot be realized with traditional semiconductors such as AlGaAs and GaAsP. InGaAlP has been used for bulk and quantum well (QW) active and confinement layers, layers in distributed Bragg reflectors for visible vertical cavity surface emitting lasers (VCSEL), high-power and reliable LDs for large-memory-capacity optical disk drives, and high brightness visible LEDs for large area displays.

We have grown two sets of $(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{In}_{0.5}\text{P}$ thin films on GaAs substrates with x near 24% and 18%, respectively, by low pressure MOCVD and performed a combined characterization by Nomarski microscopy, atomic force microscopy (AFM), photoluminescence (PL), and Raman spectroscopy. Nomarski microscopy observe the cracking line and twist defect line on the surface of the first set of AlGaInP films, while the second set of samples have almost clear surface. AFM revealed the cross-hatch dislocation patterns from the first set of films but no cross-hatch observed from the second set of films. Room temperature PL and Raman spectra showed corresponding variations. The degree of variations in compositions and film quality with the growth conditions were found from the spectral analyses. Raman spectral features are more sensitive to the sample growth parameter variations. The line shape analysis of line width, integrated intensity ratio and spatial correlation model fitting leads to information about the order of the sample crystalline quality. The optimum growth conditions have been obtained from our comprehensive analyses. The employment of these non-destructive techniques offers us a better understanding of MOCVD-grown $\text{In}_{0.5}(\text{Ga}_{1-x}\text{Al}_x)_{0.5}\text{P}/\text{GaAs}$ and a useful way to optimize the growth parameters of high quality quaternary semiconductor materials [11].

In additions, we have produced more conference and proceeding papers with some examples listed [12-16].

(四) 成果自評

P.I. has joint NTU since 2003 Fall and in performing the second NSC project, NSC93-2215-E-002-035 for 93 年 08 月 01 日至 94 年 10 月 31 日, P.I. (and collaborators as well as students) have published 1 specialized book, 1 book review chapter and 9 journal papers (SCI), plus more conference papers/reports that are not listed. All the works would stand among the world advanced class levels. Continual penetrating research will be further processed. The outstanding results and achievements include: A) recombination mechanism and defects from InGaN/GaN multiple quantum well (MQW) grown on sapphire by MOCVD, B) defects and influence from the MOCVD-grown GaN-based blue-green LEDs, C) effects of p-type doping and annealing for GaN grown by MOCVD, D) cracking control and improvement of GaN films grown on Si by MOCVD, E) photoluminescence features of low indium composition InGaN alloys grown by MOCVD, F) defect features and optical/transport properties of epitaxial InSb on GaAs by MOCVD, G) optical properties of CVD-grown cubic SiC thin films on Si substrates, H) defects and optical properties of MOCVD-grown InAlGaP materials for visible LED application, I) the publication of a specialized review book on SiC power materials and devices, and J) good trainings for more than 10 graduate students.

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出席國際學術會議心得報告及發表之論文

P.I. has attended the SPIE Symposium on Micro-technologies for the New Millennium 2005, 9-11 May, Sevilla, Spain. It has provided a forum for researchers to present their latest findings in a scientific environment, stimulating meaningful debate, enabling in-depth technical discussions, and allowing significant exchange of knowledge. P.I. has given an oral presentation for our research results in performing this project on the MOCVD InGaN/GaN MQW, which has been included in a SPIE proceeding book, “Photonic Materials, Devices, and Applications” [12].

P.I. has also attended 3rd International Conference on Materials for Advanced Technologies (ICMAT 2005), 3-8 July 2005, in Singapore, with partial support from 台灣大學資訊電子科技整合研究中心經費. Two invited presentations were given on MOCVD InGaN/GaN MQW LEDs and SiC power

materials, which will be published in two SCI journals [4,10]. Singapore side has put into a great amount of money on this 2-year series international conference on materials research. Many world well-known scientists have been invited. It is a great honor and the recognizing on our research achievements in the fields of GaN and SiC from their invitation on P.I.

We have also sent a Ph.D student of NTU-Materials Engineering (using a travel fund for Ph.D students) to give an oral presentation for a paper on InGaN/GaN LED, for which P.I. prepared, at the 16th American Conference on Crystal Growth and Epitaxy and 12th US Biennial Workshop on Organometallic Vapor Phase Epitaxy, July 10-15, 2005, USA, which is going to publish in J. Crystal Growth [5].

Through friendly exchanging and discussion with many scientists in these conferences, many knowledge and significant ideals have been obtained and raised. These are very helpful to us to open the eyes and deepen the scientific and technological sense. Indeed, some knowledge obtained from these conferences improve or deepen several important ideals in the research items listed in this research plan and for several papers or manuscripts.