Laser-Assisted Metal Organic Chemical Vapor Deposition of Gallium Nitride

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LASER-ASSISTED METAL ORGANIC CHEMICAL VAPOR DEPOSITION OF
GALLIUM NITRIDE

by
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Due to its unique properties, gallium nitride is of great interest in industry applications including optoelectronics (LEDs, diode laser, detector), high power electronics, and RF and wireless communication devices. The inherent shortcomings of current conventional deposition methods and the ever-increasing demand for gallium nitride urge extended efforts for further enhancement of gallium nitride deposition. The processes of conventional methods for gallium nitride deposition, which rely on thermal heating, are inefficient energy coupling routes to drive gas reactions. A high deposition temperature (1000-1100 °C) is generally required to overcome the energy barriers to precursor adsorption and surface adatom migration. However, there are certain limitations associated with deposition methods that require high temperatures. As an intensive, coherent and monochromatic light, laser is an ideal candidate for exploring alternative energy coupling pathways. The laser techniques, in some instances, may offer processing advantages that are not available with conventional deposition methods.

To address the challenges, the research efforts in this dissertation mainly focused on laser incorporation in metal organic chemical vapor deposition of gallium nitride films, which led to: 1) rapid growth of $m$-plane gallium nitride nanoplates 2) low-temperature growth of gallium nitride films 3) promotion of energy coupling efficiency; 4) enhancement of gallium nitride deposition; 5) fast growth of gallium nitride epilayers;
and 6) realization of high-performance ultraviolet photodetectors based on the as-grown gallium nitride epilayers.

The $m$-plane-oriented gallium nitride nanoplates were successfully grown on silicon substrates at 450 °C, using CO$_2$ laser-assisted metal organic chemical vapor deposition with perpendicular geometries.

Vibrational excitations of precursor molecules were realized using a kilowatt wavelength-tunable CO$_2$ laser with a spectrum range from 9.2 to 10.9 μm. The resonant excitation of the NH-wagging mode of ammonia molecules was demonstrated to be more efficient than nonresonant excitations in promoting the deposition rate and improving the gallium nitride quality attributed to a higher energy coupling efficiency.

Low-temperature growth of crystalline gallium nitride films on $c$-plane sapphire substrates was achieved by laser-assisted metalorganic chemical vapor deposition and coupling laser energy into the chemical reactions.

A CO$_2$ laser-assisted metal organic chemical vapor deposition approach was also successfully developed for the fast growth of high-quality gallium nitride epilayer on the sapphire (0001) substrate. By optimizing the growth parameters, the ~ 4.3 μm thick gallium nitride films showed excellent thickness uniformity and smooth surface with a root mean square. The ultraviolet photodetectors were also realized based on the as-grown laser-assisted metalorganic chemical vapor deposition gallium nitride layers, which exhibited a high responsivity and a fast response time.
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<th>Meaning</th>
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<tr>
<td>GaN</td>
<td>Gallium nitride</td>
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<tr>
<td>LMOCVD</td>
<td>Laser-assisted metal organic chemical vapor deposition</td>
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<tr>
<td>TMGa</td>
<td>Trimethylgallium</td>
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<td>NH₃</td>
<td>Ammonia</td>
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<td>α-Al₂O₃</td>
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<td>Silicon</td>
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<tr>
<td>CW</td>
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<td>CVD</td>
<td>Chemical vapor deposition</td>
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</tr>
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<td>3</td>
</tr>
<tr>
<td>sccm</td>
<td>Standard cubic centimeters per minute</td>
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<td>UV</td>
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CHAPTER 1 INTRODUCTION

1.1 Background and Motivation

1.2 Dissertation Outline

1.3 References
1.1 Background and motivation

Using of various advanced techniques for thin film and crystal growth has attracted increasing attentions and achieved significant progress. Laser chemical vapor deposition (LCVD) is a potential new method for material synthesis and processing, in which laser energy can be deposited into reactant molecules.\textsuperscript{1-6} In this process, the deposition occurred either by direct irradiating laser beam on the substrate, or the gas-phase chemical reactions are induced by laser irradiation in parallel configuration with the substrate. Depending on how the gas-phase reactions are affected by laser energy, the laser irradiation can lead to either pyrolytic or photolytic reaction.\textsuperscript{1-6} If the laser thermally heats up and dissociates the reactant precursors, the reaction is pyrolytic. In case that the reactant precursors are vibrationally or electronically excited towards dissociation by absorbing photons without heating, photolytic takes place. The use of lasers for deposition and processing of semiconductor including silicon, gallium arsenide (GaAs), indium phosphide (InP) has been studied by several research groups.\textsuperscript{1-6}

Gallium nitride (GaN) has attracted attentions for applications in light-emitting diodes (LEDs), short wavelength optoelectronics, and high-power high-frequency electronics, due to its excellent physical properties, such as wide direct bandgap, high thermal stability, and high electron velocities.\textsuperscript{7-9} High quality GaN are routinely grown by metal-organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE).\textsuperscript{10-13} These conventional growth techniques generally require a sufficiently high temperature to overcome the activation barriers to precursor chemisorption and adatom surface diffusion, which are inefficient energy coupling routes to drive gas reactions.
Additionally, high substrate temperatures cause severe adverse effects, such as biaxial stress within GaN films, nitrogen loss, and GaN decomposition, which affect the optical performance of the films and degrade the efficiency of GaN-based devices. As an intensive, coherent and monochromatic light, laser is an ideal candidate for selective promotion of GaN growth and exploring alternative energy coupling pathways. The laser techniques offer processing advantages that are not available with conventional deposition methods. For instance, Zhou et al. reported ultraviolet (UV) laser-assisted MOCVD growth of GaN at room temperatures, leading to films with (0002) preferential orientation and a broad x-ray diffraction (XRD) peak. However, the photolysis of the precursors with UV laser resulted in the low density of the reactive radicals, a low GaN growth rate and film quality. On the other hand, carbon dioxide (CO$_2$) laser-assisted MOCVD has been used successfully to prepare various kinds of thin films at high growth rates. For example, Iwanaga et al. reported the deposition of large-area silicon films using CO$_2$ laser CVD with a high growth rate in a relatively low laser power and low substrate temperatures. However, to date, there is no report of a comprehensive study on growth, growth mechanism, structural evolution, and optical/electrical properties of GaN grown by CO$_2$ laser-assisted MOCVD (LMOCVD).

The research projects in this dissertation address various challenges and goals which mainly focused on the following five tasks: 1) synthesis of semipolar m-plane oriented gallium nitride nanoplates; 2) the investigation of resonant and nonresonant vibrational excitation of ammonia (NH$_3$) molecules in the growth of gallium nitride; 3) low-temperature growth of crystalline GaN films using vibrational excitation of NH$_3$
molecules; 4) fast growth of high-quality GaN epilayers; and 5) performance evaluation of UV detectors realized based on as-grown LMCVD GaN epilayers.

1.2 Dissertation outline

The dissertation focused on controlling the crystallographic orientation of the GaN deposition, exploring alternative efficient energy coupling paths to obtaining low-temperature growth of GaN films and enhancing the GaN growth, optimizing experimental design for fast growth of high-quality GaN epilayers, and realizing high-performance GaN-based UV detectors. The dissertation is divided into nine chapters. Chapter 1 introduces the motivation and outline of this dissertation. Chapter 2 reviews the background of GaN, technological challenges for GaN growth, laser chemistry control, laser-assisted material synthesis and basic working principles of UV detectors. Chapter 3 describes the experimental methods adopted in the study, including the sample preparation procedure, GaN film characterizations and GaN-based UV detectors device characterization. Chapter 4 demonstrates the growth of m-plane-oriented GaN nanoplates on Si substrates using the LMCVD method. The high-resolution scanning and transmission electron microscopy images confirmed the formation of m-plane GaN nanoplates. The growth direction of GaN nanoplates was found to be the <10-10> direction. The A1(TO) mode of Raman further confirmed the m-plane orientation of the GaN nanoplates. Chapter 5 shows that the laser-assisted vibrational excitations of NH3 molecules promote the GaN deposition rate and improve the GaN film quality on Si (100). The NH-wagging mode (ν2, 1084.63, 968.32, 932.51 cm⁻¹) of NH3 has a strong infrared activity and the corresponding ro-vibraitional transitions match CO2 laser emission lines (9.219, 10.350, and 10.719 μm). The resonant vibrational excitation at
9.219, 10.350, and 10.719 \, \mu m were more efficient than the nonresonant excitation in dissociating NH$_3$ molecules and enhancing the GaN deposition rate and the film quality. The optical emission spectroscopy (OES) results showed the resonant excitation of the NH-wagging modes modifies the synthesis process in a way that increases the generation of NH, NH$_2$, N, N$^+$, and H intermediate species. This leads to the enhancement in the GaN deposition rates and the improvement in the crystalline quality. The extremely high GaN growth rate of $\sim 84 \mu m/h$ with an improved crystalline quality was achieved under the resonant excitation at 9.219 \, \mu m. Chapter 6 describes a novel strategy to realize low-temperature growth of crystalline GaN films on c-plane sapphire substrates by LMOCVD with laser energy coupled into the chemical reactions. Trimethylgallium and NH$_3$ were used as precursors for the growth of GaN films. Through the resonant excitation of rotational–vibrational transition (1084.71 cm$^{-1}$) of the NH-wagging mode ($v_2$) in NH$_3$ molecules using a wavelength-tunable CO$_2$ laser tuned at 9.219 \, \mu m, highly c-axis oriented GaN films were deposited on sapphire at low substrate temperatures from 250 to 600 °C. The GaN films deposited by LMOCVD showed a higher degree of crystallinity, higher growth rate, and lower defect densities as compared to those synthesized by MOCVD without resonant excitation of NH$_3$ molecules. Chapter 7 demonstrates a developed CO$_2$ LMOCVD approach for the fast growth of high-quality gallium nitride (GaN) epilayers on the sapphire (0001) substrate. By employing a two-step growth process, high-quality smooth GaN layers with a fast growth rate of 25.8 \, \mu m/h were obtained. The high crystalline quality was confirmed by a combination of different characterization techniques. By optimizing the growth parameters, the $\sim 4.3 \, \mu m$ thick GaN films grown for 10 min at 990 °C showed excellent thickness uniformity and
smooth surface with a root mean square surface roughness of \( \sim 1.9 \) nm, very narrow XRD peaks, and sharp GaN/sapphire hetero-interfaces. Chapter 8 illustrates high-performance UV detectors have been realized based on as-grown LMOCVD GaN epilayers. The devices exhibit a high responsivity of 0.12 AW\(^{-1}\) and a fast response time of 125 ns at 5 V reverse bias, indicating the excellent optical properties of GaN layers. The results demonstrate that LMOCVD technique can produce high-quality GaN epilayers and other nitride related materials with fast growth rates with potential application for next-generation electronics and optoelectronics. Chapter 9 concludes the projects with important results and suggests future research directions.
1.3 References


12. Boyd, A. R.; Degroote, S.; Leys, M.; Schulte, F.; Rockenfeller, O.; Luenenbuerger, M.; Germain, M.; Kaeppeler, J.; Heuken, M., Growth of GaN/AlGaN on 200 mm diameter silicon (111) wafers by MOCVD. physica status solidi (c) 2009, 6 (S2).


CHAPTER 2 BACKGROUND AND REVIEWS

2.1 Introduction to GaN
2.2 Introduction to Laser Chemistry Control
2.3 Introduction to Laser-assisted Material Growth
2.4 Challenges in Laser-Assisted GaN Growth
2.5 Basic Working Principles of UV Detectors
2.6 References
2.1 Introduction to GaN

2.1.1 GaN and properties

Gallium nitride (GaN) is very promising wide band gap semiconductor material for applications including optoelectronics, and high-temperature high power electronics. GaN is one of the most important semiconductor after silicon. The III-V nitride materials and their ternary and quaternary alloys are direct bandgap semiconductors. The energy band gap of these materials contains a wide spectral region from red to deep ultraviolet (1.9 - 6.2 eV).\textsuperscript{1-4} Fig. 2.1 illustrates the bandgap and lattice constant of nitride semiconductor materials.

![Figure 2.1 Bandgaps of nitride semiconductors with wurtzite and zincblende structure versus their lattice parameter at 300 °K. The right-hand scale gives the light wavelength λ, corresponding to the band gap energy.\textsuperscript{5}](image)

Various techniques have been employed for GaN synthesis. The GaN structure has two crystalline phases: wurtzite (WZ) structure with a hexagonal symmetry (the
thermodynamically equilibrium phase), and zincblende (ZB) structure with a cubic symmetry. The schematic image of these two structures is illustrated in Fig. 2.2. In both structures, the Ga and N atoms are tetragonally coordinated with 4 atoms of the opposite type.

![Fig. 2.2](image)

**Figure 2.2** (a) Wurtzite lattice structure of GaN and (b) zincblende structure of GaN.

Three important planes of the hexagonal GaN structure are illustrated in Fig. 2.3: the \{0001\} c-plane (green plane) which is basal plane, the \{1-100\} m-plane (orange plane), and \{11-20\} a-plane (blue plane) which is perpendicular to both the m-plane and the c-plane.\(^8\)-\(^11\) Due to the high surface free energy of the c-plane, the GaN films prefer to grow along the \{0001\} direction. Our work focuses on the synthesis of m-plane and c-plane-oriented films. The non-polar nitride and heterostructures (the layers grown in a- and m-orientation) do not suffer from the effects of the inbuilt polarization fields, which degrades the recombination efficiency and performance of GaN photonic devices.\(^8\)-\(^11\) However, the polar nitride films and heterostructures (layers grown in c-orientation) suffer from the effects of the inbuilt polarization fields. The inbuilt polarization fields are
not oriented along the heterostructure interface and do not affect its band gap in non-polar nitride films.

Figure 2.3 Wurtzite lattice structure of GaN with polar and non-polar planes.\textsuperscript{5}

GaN semiconductor has unique properties including high thermal, mechanical, and chemical stability compared to other semiconductor materials such as Si and GaAs. These unique properties are mostly because of strong bonding between the gallium and nitrogen atoms. Some reported material properties are as below:\textsuperscript{12-13}

- With wide direct band gap, it is useful for photonic devices;
- It is chemically stable at high temperatures;
- It has a good thermal conductivity;
- It has high room-temperature electron mobilities and high breakdown electric field.
Below the important physical properties of the GaN semiconductor have been summarized in Table 2.1.\textsuperscript{12-13}

<table>
<thead>
<tr>
<th>Properties</th>
<th>Wurtzite</th>
<th>Zinc-blende</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm(^3))</td>
<td>6.15</td>
<td>-</td>
</tr>
<tr>
<td>Band-gap (eV)</td>
<td>3.4</td>
<td>3.2</td>
</tr>
<tr>
<td>Bandgap type</td>
<td>direct</td>
<td>direct</td>
</tr>
<tr>
<td>Lattice Constants (Å)</td>
<td>a = 3.189</td>
<td>4.52</td>
</tr>
<tr>
<td></td>
<td>c = 5.186</td>
<td></td>
</tr>
<tr>
<td>Effective Electron Mass (m(_0))</td>
<td>0.2</td>
<td>0.13</td>
</tr>
<tr>
<td>Electron Affinity (eV)</td>
<td>4.1</td>
<td>4.2</td>
</tr>
<tr>
<td>Thermal conductivity (W/cm × C)</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Electron Mobility (cm(^2)/Vs)</td>
<td>&lt; 1000</td>
<td>&lt; 1000</td>
</tr>
<tr>
<td>Hall Mobility (cm(^2)/Vs)</td>
<td>&lt; 200</td>
<td>&lt; 350</td>
</tr>
<tr>
<td>Melting temperature</td>
<td>&gt; 1700 °C</td>
<td>-</td>
</tr>
<tr>
<td>Index of refraction (n)</td>
<td>2.67 @ 3.38 eV</td>
<td>2.91 @ 3.2 eV</td>
</tr>
<tr>
<td>Piezoelectric constant (C/m(^2))</td>
<td>0.375</td>
<td>-</td>
</tr>
</tbody>
</table>

\textit{2.1.2 Substrates for GaN heteroepitaxial growth}

Current commercial GaN-based devices are fabricated by epitaxy on foreign substrates because the GaN bulk and freestanding substrate technology is still immature.\textsuperscript{13-15} The choice of substrate for GaN growth depends on several factors such as the lattice mismatch between the substrate and the GaN (different lattice constants), the difference
in thermal expansion coefficients between the substrate and the GaN, and the substrate cost. The common substrates for GaN heteroepitaxial growth are as follows:\textsuperscript{13-15}

2.1.2.1 Silicon

The Si with the price of around $25 per 100 mm wafer is a low-cost substrate. The lattice mismatch between silicon and GaN is approximately 17\%, and the thermal expansion coefficient of silicon is 113\%. GaN films grown on silicon suffer from tensile stresses as cooling the sample from high growth temperature to room temperature, potentially leading to film cracking. Si has a reactive surface when exposed to ammonia at temperatures above 500 °C during the growth and a thin silicon nitride layer can be formed. From the point of view of integrating GaN devices with Si technology, the Si (100) substrate is preferred because Si (100) is the most widely used in silicon mainstream technology. In contrast to the Si (111), Si (100) does not show a 6-fold symmetry but a 4-fold symmetry which is more suitable for the epitaxial growth of a cubic GaN,\textsuperscript{15,16} however, the cubic phase is metastable. The thermodynamically stable hexagonal GaN phase could be also grown on the (100) plane.

2.1.2.2 Silicon carbide (SiC)

SiC substrate with a hexagonal structure is also used for GaN heteroepitaxial growth. With a lattice mismatch of 3.5\%, SiC is a very appropriate substrate for growth of high-quality GaN films with low dislocation density. Additionally, this substrate is very resistant to chemical reaction compared to Si. Therefore, a blocking layer is not formed during the GaN growth.\textsuperscript{13-16}
The thermal expansion coefficient of SiC is almost twice that of GaN and this substrate is extremely expensive with the cost around $1000 per 100 mm wafer. GaN layers grown on SiC suffer from significant compressive stress during cooling down, which can lead to film cracking.

2.1.2.3 Sapphire

Sapphire (Al₂O₃) as a transparent substrate is the most common substrate for GaN epitaxy growth with a reasonable price (~ $150 per 100 mm wafer) and performance. The lactic mismatch between sapphire and GaN is ~14% and the thermal expansion coefficient of sapphire is 33% larger compared to GaN. As an oxide compound, this dielectric substrate is fully stable to harsh growth environment even at high growth temperatures. Sapphire is resistant to forming an amorphous nitride when exposed to ammonia during GaN growth. Since sapphire is an insulator substrate with a bandgap of 10 eV, the fabrication of specific devices with a backside electrical contact on GaN/sapphire is impossible.¹³⁻¹⁶

2.1.3 - GaN growth techniques

2.1.3.1 HVPE

Hybrid Vapor Phase Epitaxy method (HVPE) is a growth technique for synthesis of III-V compound.¹²,¹⁷⁻²⁰ This technique is appropriate for high growth rate deposition (deposition rates ~ 10-200 µm/h and higher). Fig. 2.4 shows the schematic of a hot-walled HVPE system. Hydrochloric acid (HCl) passes over the gallium (Ga) upstream and reacts with Ga at 800 - 900 °C. A volatile gas-phase metal chloride (GaCl) forms as follows:
Ga + HCl → GaCl + 1/2H₂ \hspace{1cm} (2.1)

The volatile metal compound, then, is transported downstream to the substrate and reacts with NH₃:

GaCl + NH₃ → GaN + HCl + 1/2H₂ \hspace{1cm} (2.2)

Figure 2.4 A schematic diagram of a hot-walled HVPE reactor (a hot-walled reactor utilizes a tube furnace that heats the entire reactor to a more uniform substrate temperature).\(^{12}\)

The GaN films grown with HVPE method generally have rough surface morphology with hexagonal shaped hillocks and pyramids. This is because the HCl can chemically attack and etch the films during growth where the etching rate is higher in strained regions, such as the boundaries of coalesced grains.

In HVPE, the GaCl is transported to the substrate only after HCl passes over and reacts with the gallium; which an inherent latency occurs. Therefore, this technique is not appropriate for quick compositional changes during growth and synthesis of thin heterostructures with abrupt interfaces.\(^{17-20}\)
Because of the presence of reactive HCl and GaCl in the reactor, the choice of substrates for GaN growth using HVPE is more constrained compared to other deposition methods. For example, silicon substrates easily react with HCl and GaCl, forming several by-products including volatile silicon chloride, liquid gallium and H₂.¹⁷-²⁰ The liquid gallium remains on the silicon surface and affects the quality of epitaxial GaN films on substrate.

2.1.3.2 MBE

Molecular beam epitaxy (MBE) is another technique for the epitaxial growth of compound semiconductor films. MBE has a low growth rate of 0.1-1 μm/hr, and performs in a growth temperature of 800-1000 °C. These relatively low growth rates limit the applicability of MBE for growth of many GaN-based device structures.²¹-²³ The basic elements of an MBE growth system are UHV chamber, substrate heater part, individually shuttered and liquid nitrogen shrouded molecular beam effusion cells, and substrate exchange load-lock system, as shown in Fig. 2.5.²¹-²³
Figure 2.5 A schematic diagram of a typical MBE system.  

A base pressure of less than $5 \times 10^{-10}$ Torr is used in MBE process to obtain films with low impurity levels. The in-situ monitoring of growth conditions and growth rate is done by Fluorescent screen (FRHEED). Atomic layer-by-atomic layer deposition is achieved by using low beam fluxes, which are controlled by temperature variation of the source cells. By rotating substrates during the film deposition, a uniform growth is achieved. GaN growth proceeds according to following steps:\textsuperscript{21-23} (1) Atoms impinge on the sample surface, where they are adsorbed, (2) The atoms migrate along the surface towards atomic steps, where they are stabilized by the increased number of atomic bonds, (3) The atoms migrate along the step edges to a kink site, where they are incorporated into the lattice. Deposition involves the lateral motion of step edges or the growth of two-dimensional islands until an atomic layer is completed.\textsuperscript{21-23}

\textit{2.1.3.3 MOCVD}

Metal-organic chemical vapor deposition (MOCVD) is a common technique for growth of high quality epitaxial GaN layers with excellent surface morphology and a precise control over layer thickness and uniformity.\textsuperscript{13,24-27} Current commercial GaN devices including lasers, light emitting diodes, photocathodes, heterostructure bipolar transistors, photodetectors, and solar cells are usually synthesized by MOCVD. The MOCVD process involves a series of complex gas phase and surface reactions. The process contains following steps: (a) Evaporation and transport of precursors; (b) Pyrolysis of precursors leading to film deposition; and (c) Removal of the remaining fragments of the decomposition reactions from the reactor. This process often proceeds by the formation of steps on the surface, with the diffusion of adsorbed atoms across the surface and
attachment to a step. The basic growth steps in MOCVD are shown in Fig. 2.6 and are as follows:

Figure 2.6 Schematic of MOCVD growth mechanisms.\textsuperscript{13}

1. The transport of reactant precursors into the reactor.

2. The chemical gas-phase reactions which produce growth species and byproducts.

3. The transport of the growth species to the surface and absorption on the surface.

4. The diffusion of the growth species on the surface.

5. The incorporation of these species at kinks.

6. The desorption or evaporation some of species from the surface.
7. Phase change including vapor-phase condensation and solidification which leads to nucleation and step growth for film formation.

8. The exhaustion of the byproducts of reactions.

The most common chemical reactions in MOCVD process of GaN are driven by pyrolysis. Pyrolysis is the thermal decomposition of reactant species such as NH$_3$ and metal-organic radicals for material synthesis. Trimethylgallium (TMGa) is the most common gallium precursor for MOCVD growth of GaN. The major product of TMGa pyrolysis with H$_2$ or N$_2$ as carrier gases is methane (CH$_4$). Ammonia NH$_3$ is used as the most common nitrogen precursor for GaN growth. The growth of high-quality GaN requires very high growth temperatures. While the TMGa is fully pyrolyzed at 550 °C,$^{13,24-27}$ the decomposition of NH$_3$ occurs at much higher temperatures compared to the metalorganic precursors. It has been reported that the decomposition of NH$_3$ at atmospheric pressure starts at 600 °C and a complete decomposition occurs above 800 °C.$^{13}$

The formation of GaN in MOCVD includes four key steps:$^{13,28,29}$ (i) TMGa:NH$_3$ adduct formation, (ii) amide formation and methane elimination, (iii) trimer formation, and (iv) decomposition reaction and creating N and Ga to form GaN. The general related equations are given by:$^{13,28,29}$

\[
\begin{align*}
(CH_3)_3Ga + NH_3 & \rightarrow (CH_3)_3Ga:NH_3 \quad (2.3) \\
(CH_3)_3Ga:NH_3 & \rightarrow (CH_3)_2Ga:NH_2 + CH_4 \quad (2.4) \\
3[(CH_3)_2Ga:NH_2] & \rightarrow [(CH_3)_2Ga:NH_2]_3 \quad (2.5)
\end{align*}
\]
([CH₃)₂Ga:NH₂]₃ → 3GaN + 6CH₄ \hspace{1cm} (2.6)

The MOCVD growth of high-quality GaN is as follows: Substrate cleaning with annealing under H₂ at high temperature. A thin (20-30 nm) low-temperature (~550 °C) GaN is first grown as nucleation layer and this layer is annealed to be recrystallized. The islands formed during nucleation start to coalesce as the three-dimensional growth continues, converting to a two-dimensional surface. The step-flow growth of final GaN layer is typically performed at a temperature ~ 1020 °C with a growth rate of ~2-4 µm/h.¹³

The large thermal and lattice mismatch between common substrates including Si, sapphire and SiC with GaN is an issue in MOCVD growth of GaN on these substrates. Intrinsic defects in GaN are typically donor-like defects (nitrogen vacancy, V₉, and gallium interstitials, Gaᵢ). Therefore, undoped GaN films are n-type with a free carrier concentration around 10¹⁶ cm⁻³ and p-type doping of the films is typically difficult. Magnesium (Mg) is the common p-type dopant in GaN. However, Mg often incorporates during growth as a Mg-H complex, which is also a donor-type defect. To remove the hydrogen and activate the Mg as an acceptor, a subsequent annealing step under H₂ is required.¹³

2.2 Introduction to laser chemistry control

Controlling the outcome and product of the chemical reactions is an old dream in chemistry. We would like to steer the reactants into a desired outcome and product. Traditionally, control the dynamics of chemical reactions is done with temperature control or finding an appropriate catalyst.³⁰⁻⁴⁴ The energy is traditionally supplied into
the reaction as heat. With changing the temperature, the average energy of all molecules in the sample is changed and the energy is only controlled on an average macroscopic level. The energy is universally injected into all molecule modes including external and internal (electronic, vibrational, rotational) modes and affects the dynamics and the outcome of the reaction.

Laser chemistry concentrates the challenging objective of using lasers to control the outcome of chemical reactions by breaking particular bond in a large molecule. High intensity laser can supply energy into specific reactant bonds, leaving rest cold. For instance, using the infrared (IR) laser, we can selectively supply energy into the internal state (vibrational/rotational) of the reactants because the frequencies of vibrational modes of molecules fall in the IR region. A vibrational mode which is in resonance with an IR laser frequency can be selectively excited via single- or multi-photon processes.62

Several experimental studies have revealed the ability of vibrational excitation of molecules to control and promote the chemical reactions.45-53 S. Nave et al. showed the vibrational excitation of the methane molecule significantly enhances its reactivity when the molecule undergoes transitions to the ground or lower-energy vibrational states.45 They found the $v_1$ vibration has the largest efficiency for promoting reaction, however, the $v_3$ vibration has smaller efficiency, but significant.45 F.F. Crim et al. showed different vibrational modes, such as the symmetric and antisymmetric stretches in CH$_3$D, lead to very different reactivities.46,47 The symmetric stretching vibration excitation of molecules leads the molecules be 10 times more reactive than antisymmetric stretch excitation of molecules.46,47 Several other studies of laser chemistry control using vibrational excitations contain Cl + CHD$_3$,48 Cl + HCN,49 NH$_3$+ + ND$_3$,50 and C$_2$H$_2$+ + CH$_4$.51
2.3 Introduction to laser-assisted material synthesis

The use of lasers for synthesis of material and thin films has been obtained increasing interests. It is necessary to understand the species and molecule modes of excitation and energy relaxation during laser interaction with gases and precursors to know how lasers promote material deposition. Laser chemical vapor deposition (LCVD) is a suitable method for thin-film synthesis and enables us to study new reaction pathways. When metalloorganic compounds are used as reactants, LCVD is usually called laser metal organic chemical vapor deposition (LMOCVD).

The overall reaction mechanisms in laser material synthesis are generally complicated. The laser can induce thermal reactions on the substrate surface by heating the substrate and deposition occurs, which is known as pyrolytic or thermochemical deposition like that in conventional CVD synthesis of thin films. In pyrolytic process precursor gases are thermally activated.\textsuperscript{52-62} The energy is first deposited to the translational modes of reactant molecules, and then distributed to their internal modes. An enough internal energy is required for overcoming reaction barrier and gas dissociation. When high surface temperatures are required to induce deposition, the pyrolytic process can cause more structural damage in thin films due to high temperatures and thermally induced stresses. Additionally, pyrolytic process is inefficient in energy coupling to drive gas reactions and short of selectivity.

In another arrangement, the laser is absorbed directly by the reactants and dissociates gas-phase or surface-adsorbed molecules without heating the substrate surface. This method is known as photolytic or photochemical deposition. The monochromaticity of lasers
enables narrow-band excitations of selective reactants. Laser excitation can occur by stimulating molecule vibrational or electronic transitions by the absorption of infrared laser multiple-photons and ultraviolet photons. It can selectively control reactions in material synthesis processes. In some cases, the photodissociation products must be decomposed further by conventional heating of the substrate to achieve film depositions.

Two different irradiation geometries can be used in LCVD as shown in Fig. 2.7. In first configuration (Fig. 2.7a), the beam impinges on the surface at nearly normal incidence and gas and substrate surface are both excited. In second configuration, the laser travels parallel to and just above the substrate (Fig. 2.7b). In this case, the laser energy is directly coupled into the gas phase and possible heating of the substrate surface is eliminated. In this dissertation, both parallel and perpendicular irradiation geometries were employed.

Several semiconductor materials, including Silicon (Si), gallium arsenide (GaAs), cadmium telluride (CdTe), indium phosphide (InP), indium antimonide (InSb), and aluminum nitride (AlN), have been grown using the LCVD technique. The LCVD deposition of other films including metal films (W, Al, Cu, and Au), and insulators (Al₂O₃, SiO₂, Si₃N₄) have been also reported. Table 2.2 summarizes some typical LCVD processes of various materials.
Figure 2.7 (a) Perpendicular and (b) Parallel irradiation geometries employed in a LCVD process.

Table 2.2 Typical LCVD of various materials with specific lasers and precursors.63-92

<table>
<thead>
<tr>
<th>Material</th>
<th>Precursors</th>
<th>Substrate</th>
<th>Laser wavelength(nm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>WF₆/H₂</td>
<td>GaAs</td>
<td>ArF/193</td>
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<tr>
<td>Cu</td>
<td>Cu(hfac)tmvs/H₂/N₂</td>
<td>Si</td>
<td>Ar+/514.5</td>
<td>[66]</td>
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<tr>
<td>Au</td>
<td>(CH₃)₂Au(hfac)</td>
<td>Si</td>
<td>XeCl/308</td>
<td>[68]</td>
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<td>Al</td>
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<tr>
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<td>KrF/248</td>
<td>[74]</td>
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<td>GaAs</td>
<td>TMG/AsH₃</td>
<td>GaAs</td>
<td>Ar+/514</td>
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<tr>
<td>InN</td>
<td>HN₃/TMln</td>
<td>Si</td>
<td>XeCl/308</td>
<td>[77]</td>
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<tr>
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<td>DMZ/DMSe/H₂</td>
<td>GaAs</td>
<td>ArF/193</td>
<td>[78]</td>
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<td>SiO₂</td>
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<td>Si</td>
<td>ArF/193</td>
<td>[80]</td>
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<tr>
<td>Si₃N₄</td>
<td>SiH₄/NH₃</td>
<td>-</td>
<td>CO₂/10600</td>
<td>[81]</td>
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<tr>
<td>CNT</td>
<td>C₂H₂/NH₃</td>
<td>Si</td>
<td>CO₂/10600</td>
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<tr>
<td>Diamond</td>
<td>CH₄/H₂</td>
<td>Silica</td>
<td>Nd:YAG/532</td>
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<tr>
<td>Graphene</td>
<td>CH₄/H₂</td>
<td>Ni</td>
<td>Nd:YAG/532</td>
<td>[87]</td>
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</table>
2.4 Challenges in laser-assisted GaN synthesis

Gallium nitride (GaN) has attracted attentions for applications in light-emitting diodes (LEDs), short wavelength optoelectronics, and high-power high-frequency electronics, due to its excellent physical properties such as wide direct bandgap, high thermal stability, and high electron velocities. These conventional growth techniques generally require a sufficiently high temperature to overcome the activation barriers to precursor chemisorption and adatom surface diffusion, which are inefficient energy coupling routes to drive gas reactions. Additionally, high substrate temperatures cause severe adverse effects, such as biaxial stress within GaN films, nitrogen loss, and GaN decomposition, which affect the optical performance of the films and degrade the efficiency of GaN-based devices. As an intensive, coherent and monochromatic light, laser is an ideal candidate for selective promotion of GaN growth and exploring alternative energy coupling pathways. A more efficient energy coupling path can be achieved via directly activating internal motions of reactant molecules. Frequencies of molecular vibrational modes and electronic excitations locate in infrared range and UV-Vis range, respectively. The laser techniques may offer processing advantages that are not available with conventional deposition methods. Laser is a perfect energy source due to its high-energy intensity, wavelength capability from UV to IR, and monochromaticity. In this dissertation, we introduced CO$_2$ laser for IR-laser vibrational excitations in MOCVD growth of GaN films. We achieved an enhanced energy coupling efficiency and promoted GaN growth rate and crystalline quality.

NH$_3$ is the common nitrogen precursor used in MOCVD growth of GaN. It has six fundamental vibrational modes as shown in Fig. 2.8, which NH-wagging mode is
strongly infrared active.\textsuperscript{62,93} The NH\textsubscript{3} vibrational modes at 932.51 (\(v_2^+\)), 968.32 cm\textsuperscript{-1} (\(v_2^-\)) and 1084.63 cm\textsuperscript{-1} match to the emission lines of a CO\textsubscript{2} IR-laser at 10.719, 10.35 and 9.219 \(\mu\text{m}\), respectively. Therefore, NH\textsubscript{3} is an ideal candidate for studying the IR-laser vibrational excitations in GaN synthesis.

Figure 2.8 Schematic illustration of the NH\textsubscript{3} vibration modes.

2.5 Basic working principles of metal-semiconductor-metal (MSM) UV Photodetectors

Among GaN photodetectors with different device structures, the MSM structure is an attractive candidate for UV photodetector applications, because this type of detector has low dark current, low noise and high response speed characteristics. In addition, its growth and fabrication processes are simplified because n- and p-type doped layers are not required. With lateral and planar structure, these devices have very low capacitance,
suitable for high-speed performance detectors. Additionally, the fabrication process for MSM photodetectors is compatible with field effect transistors, which results an easy integration in an optical detection and amplifier. 

Figure 2.9 Schematic top view of MSM structure.

The schematic of an MSM structure is shown in Fig. 2.9. In this thesis, the finger spacing, \( t \), is equal to the finger width, \( w \). The MSM photodetector is made by forming Schottky diodes on GaN layer. Two contact pads and interdigitated fingers form the metal structure and the active area of the device. The energy band diagram of the MSM device under thermal equilibrium condition is shown in Fig. 2.10. The MSM photodetector is a two Schottky barriers connected back to back. The electron affinity of GaN is 4.1 eV and the work function of Au is \( \sim 5.1 \) eV which result in electron injection barrier of \( \sim 0.9 \) eV. Under the applied bias, one of the Schottky contacts is in reverse bias, and the other one is in forward bias. With the illumination to the active area of the device, electron-hole pairs are generated in this region. The photo-excited carriers are
collected by contact pads (Ni/Au) under the bias voltage. Responsivity, speed, and dark current are the important parameters of the MSM Photodetectors. The relative importance of each parameter depends on the application, and they are not independent of each other.

Figure 2.10 Energy band diagram of the GaN MSM photodetectors (a) under thermal equilibrium, (b) with applied voltage bias, (c) under photoexcitation with applied voltage bias. Devices are illuminated from the top.

The growth of high-quality nitride material is the primary obstacle in developing nitride-based UV photodetectors. The UV detectors with low dark currents require the films with very low defect density. In the sections 7 and 8, we introduce improvements in the GaN film crystalline quality and realize the high-performance photodetectors based as grown LMOCVD GaN epilayers.
2.6 References


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CHAPTER 3 THEORETICAL OVERVIEW AND CHARACTERIZATION TECHNIQUES

3.1 Sample Preparation

3.2 Structural Characterization

3.3 Surface Characterization

3.4 Optical Characterization

3.5 Electrical Characterization

3.6 Device Processing and Characterization

3.7 References
3.1 Sample preparation

We used two general types of irradiation geometries in laser-assisted metal organic chemical vapor deposition (LMOCVD) of gallium nitride (GaN), represented in Fig. 3.1. In first irradiation geometry used in chapter 6, large GaN films were formed at low temperatures by a laser-initiated homogeneous reaction above the surface. A wavelength-tunable carbon dioxide (CO₂) laser (PRC, wavelength range from 9.2 to 10.9 μm) was used as the irradiation sources. The laser beam, with a diameter of around 10-12 mm, was irradiated in parallel to the substrate surface inside the chamber through a zinc selenide (ZnSe) window, as shown in Fig. 3.1a. The laser was tuned at a wavelength of 9.219 μm to resonantly excite the wagging mode of ammonia (NH₃) molecules, couple the laser energy into the reaction. The distance between the laser beam and substrate surface was maintained at about 20 mm. In this case, the laser initiates chemistry in the gas only and not on the substrate surface. In another irradiation geometry and configuration of laser-assisted metal organic chemical vapor deposition of gallium nitride in chapters 4, 5, 7 and 8, the continuous-wave (CW) CO₂ laser beam irradiates on the substrate surface at nearly normal incidence (Fig. 3.1b). In chapter 4, the Si substrate was shined and heated with a CO₂ laser beam of diameter 2.5 ± 0.5 mm. In chapter 6, CW CO₂ laser (PRC, Inc., 9.2-10.9 μm) was used as the irradiation source at laser wavelengths of 10.719, 10.350, and 9.219 μm, achieving a reactant excitation of NH₃ molecules and substrate heating. In chapters 7 and 8, a continuous-wave wavelength-tunable CO₂ laser (PRC Inc., λ = 9.201 μm) was also used for substrate heating. However, in this new setup, a flat top laser beam shaper (Edmund Optics) was used for generating a wider beam with uniform power distribution (beam diameter ~ 20 mm) from
a Gaussian CO\textsubscript{2} laser beam (wavelength-tunable PRC CO\textsubscript{2} laser Inc., \(\lambda = 9.201\ \mu\text{m}\)). The temperature of the substrates during the deposition was monitored by a noncontact pyrometer (OS3752, Omega Engineering, Inc.).

Figure 3.1 (a) Illustration of the experimental setup for the CO\textsubscript{2} laser-assisted MOCVD growth of GaN films with: (a) parallel irradiation geometry and (b) perpendicular irradiation geometry.
In all experiments, the silicon and sapphire substrates (10 × 10 mm²) were cleaned and dried before loading into the LMOCVD chambers. Trimethylgallium (TMGa) and NH₃ were used as the Ga and N precursors, respectively. The experimental details were explained in each chapter.

The applications of GaN films are based on their remarkable properties. For these applications to be realized, the structural, optical and electronic qualities of films need to be more thoroughly characterized. Numerous techniques are useful in GaN characterizations.

3.2 Structural characterization

3.2.1 X-ray diffraction

X-Ray diffraction (XRD) is a non-destructive method used to characterize the structures of GaN film. The Bragg’s law describes the diffraction of X-rays from a crystal by:

\[ n\lambda = 2d \times \sin \theta \]  \hspace{1cm} (3.1)

where \( n \) is an integer, \( \lambda \) is the X-ray wavelength, and \( d \) is the spacing between atoms. With a given X-ray wavelength and the angle that X-rays are diffracted, \( \theta \), the atomic spacing \( d \) can be calculated, as shown in Fig. 3.2. Because the exact atomic spacing, \( d \), is unique for a material, the unknown materials can be identified by comparing their XRD spectrum with that of a known standard. The Fig. 3.2 illustrates the schematic illustration of the geometrical parameters of the XRD characterization.
3.2.1.1 $\theta$-2$\theta$ scan

The lattice constant and mole fraction of the materials can be identified using the XRD $\theta$-2$\theta$ scan measurement. In $\theta$-2$\theta$ scan, the X-ray source is fixed and the sample rotates a certain angle, $\theta$, with respect to the axis of X-ray beam. The detector rotates
twice of the angle $\theta$ as shown in Fig. 3.3, and collects the reflected X-ray beam. The material information such as orientation can be calculated from this type of XRD scan. For example, the (0002) reflection plane is indexed to the c-plane GaN. This reflection is perpendicular to the growth direction and is a good gauge of GaN crystal orientation and quality.\textsuperscript{1-3} Figs. 3.4a and b show a photo of Rigaku Smartlab, a multifunctional X-Ray diffractometer system, and XRD $\theta$-2$\theta$ spectrum of c-oriented GaN on sapphire, respectively.

![Figure 3.4](image)

\textbf{Figure 3.4} (a) A photo of Rigaku Smartlab, a multifunctional X-Ray diffractometer system. (b) XRD $\theta$-2$\theta$ spectrum of c-oriented GaN on sapphire.

### 3.2.1.2 Rocking curve scan ($\omega$-scan)

The XRD rocking curve (XRC) measurement is commonly used for quantitative measurement of the film quality while the $\theta$-2$\theta$ XRD only gives the information on the crystalline orientation of the thin films. The inter-planar spacing of the grown films is measured using XRC.\textsuperscript{4-7} In this experiment, the detector and the X-ray source are fixed at certain angle, which receive the x-ray signal in $\theta$-2$\theta$ scan. Then, the sample is rocked about $\omega$ axis. The strong diffraction peak is only observed when a particular crystal is
aligned at the angle matching to Bragg’s Law. The full width at half maximum (FWHM) of XRC is typically used to measure the film threading dislocation density and determine the film quality.\textsuperscript{4-7}

### 3.2.1.3 In-plane $\phi$-scan

The XRD $\phi$-scans are conducted to reveal the in-plane orientation and epitaxial details of films.\textsuperscript{4-7} The in-plane orientation can be measured by four-circle diffractometer. In $\phi$-scan experiment, first, a crystallographic plane inclined to the growth plane is identified. The $\theta$ and $2\theta$ angles are constant to corresponding to Bragg angle for the identified plane. The $\psi$, sample tilt, is set equal to the crystallographic angle between the growth plane and the identified plane for the $\phi$-scan. The diffraction spectra are collected with the sample rotation along $\phi$-axis. In an epitaxial film, the $\phi$ spectra have sharp diffraction peaks at certain $\phi$-angles.\textsuperscript{4-7}

### 3.2.2 Raman spectroscopy

Raman spectroscopy is a common technique for studying the quality and residual stress of thin films.\textsuperscript{8-10} In Raman spectroscopy, an incident beam with a single wavelength is irradiated on the sample and a photon with different energy from the incident photon is scattered. The different between the energy of scattered photon and incident photon is one vibrational energy unit which forms the basis of Raman scattering.

The theoretical studies show that the hexagonal structure has eight sets of phonon modes at $k \sim 0$ (Γ point in Brillouin zone), $2A_1 + 2E_1 + 2B_1 + 2E_2$. The $A_1$ and $E_1$ modes are acoustic and other six modes, $A_1 + E_1 + 2B_1 + 2E_2$, are optical.\textsuperscript{8-11} The schematic of the atomic displacement of the optical modes is seen in Fig. 3.5. The $A_1$ and $B_1$ modes represent atomic displacements along the $c$-axis and the $E_1$ and $E_2$ are atomic.
displacements perpendicular to the c-axis. The A₁ and E₁ modes are both Raman and infrared (IR) active, while the two E₂ modes are only Raman active, and the two B₁ modes are neither Raman nor IR active.

Raman configurations of allowed modes in hexagonal nitrides are shown in Table 3.1. The symbols from left to right outside the bracket show the direction of incident and scattered light, respectively, and the ones from left to right inside the bracket represent the polarization direction of the incident and scattered light, respectively. In wurtzite nitride structures studied under a z(x,x)-z geometry, E₂(high) mode is the strongest and is very sensitive to the inplane strain. The A₁(LO) phonon mode has atomic displacement parallel to the c-axis. If we suppose the c-axis is along the z direction and x and y directions are perpendicular to c-axis, the A₁(LO) mode can be detected from c-plane wurtzite nitrides under a z(x,x)-z backscattering geometry.8-10

In this work, Raman spectroscopic studies were conducted under a z(x,x)-z backscattering geometry, where z and -z represent the projection direction of the incoming and scattered light, and x represents the polarization direction of the incoming and scattered light. Figs. 3.6a and b show a picture of the Raman spectroscopy system (inVia Raman microscopy, Renishaw) and Raman spectrum of a wurtzite GaN film grown by LMOCVD, respectively.8-11

Table 3.1 Raman configurations of allowed modes in hexagonal nitrides11

<table>
<thead>
<tr>
<th>Configuration</th>
<th>x(y, y)-x</th>
<th>x(z, z)-x</th>
<th>x(z, y)-x</th>
<th>x(y, z)</th>
<th>x(y, z)</th>
<th>x(y, y)-z</th>
<th>z(y, x)-z</th>
<th>z(y, y)-z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode</td>
<td>A₁(TO), E₂</td>
<td>A₁(TO)</td>
<td>E₁(TO)</td>
<td>E₁(TO), E₁(LO)</td>
<td>E₂</td>
<td>E₂</td>
<td>A₁(LO), E₂</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.5. Atomic displacements of the Γ-point phonons in wurtzite GaN. Low-\(E_2\) (low-\(B_1\)) and high-\(E_2\) (high-\(B_1\)) represent the low- and high-frequency \(E_2\) (\(B_1\)) modes, respectively. The frequency numbers inside the parentheses are in THz obtained from previous studies.\(^{11}\)
Figure 3.6 (a) A picture of the Raman spectroscopy system (inVia Raman microscopy, Renishaw); (b) A Raman spectrum of a wurtzite GaN film grown by LMOCVD.

3.3 Surface characterization

3.3.1 Scanning Electron Microscopy (SEM)/Energy Dispersive X-ray Spectroscopy (EDS)

Using the interaction between a beam of high energy electrons and the sample, a thin film can be imaged. The interaction between the sample and the electrons has different types including transmitted electrons, secondary electrons, and backscattered electrons. In a SEM, high-energy beam of electrons scan the sample surface. Depending on the desired image, various types of the electrons can be detected. SEM images are very useful in investigating the microstructure of a GaN film surface. Incident a beam of high energy electrons can also generate X-rays with a specific wavelength which is used for the characterization of the thin film composition. In EDS, the relative intensities of these X-rays are measured to study the composition of sample surface.

3.3.2 Transmission Electron Microscopy (TEM)

TEM, a high-resolution imaging method, is known as a very powerful method for studying the crystal quality of thin films and interfaces. In TEM, a beam of electrons transmitted through a very thin sample (10-100 nm thickness). Very high magnification
images are obtained from the patterns produced from the interaction of the electrons with the sample. Electrons can be diffracted, absorbed or transmitted through the sample. The diffracted electron patterns can help for studying the crystal structure and quality, and the absorbed electron patterns are useful to create contrast in both bright-field and dark-field TEM images.

3.3.3 Atomic Force Microscope (AFM)

AFM is a simple and non-destructive method to determine the film surface roughness and average threading dislocations in gallium nitride. In AFM technique, a sharp tip runs over the surface to scan and takes AFM images. The AFM tips are typically from silicon nitride or silicon attached to a cantilever. A laser beam is used to detect cantilever deflections towards or away from the surface. A position-sensitive photo diode (PSPD) is used to detect these changes and generate an electric signal. This signal is sent via a feedback loop to a piezoelectric ceramic to control the height of the tip above the surface and maintain the position of laser constant. The interaction force around $10^{-11}$-$10^{-6}$ N between tip and film surface can detect the topography of sample.\(^\text{12}\)

The AFM measurements in GaN can be done either in tapping or contact mode. Since, the GaN is a very hard material compared to the tip, the dragging motion of the probe tip in contact mode can break the tip. The measurements in this work were done at Nebraska Center for Materials and Nanoscience using Bruker Dimension ICON SPM. The resonance frequency was set on 220-320 kHz, and a scan rate of 2 Hz was used for scanning GaN film surface using a silicon tip.
3.4 Optical characterization

The information about the quality, strain, impurities, and native defects of GaN can be obtained using optical characterization of films. The information about energy level of impurities can be also achieved form the temperature dependence of these properties. Photoluminescence spectroscopy and optical transmission/absorption spectroscopy are the common methods for investigating optical properties in semiconductors materials. Photoluminescence spectroscopy was employed in this work, along with optical transmission and absorption, to study the optical properties of the grown GaN layers.

3.4.1 Photoluminescence Spectroscopy (PL)

In photoluminescence process, a material absorbs photons of one wavelength and emits photons of another wavelength. The electrons are excited to higher energy states by absorbing photon energy from a photoexcitation source like laser.\textsuperscript{14-16} When the electrons return to their ground state through a radiative recombination, they emit photons. PL is the investigation of radiative recombination mechanisms in materials. Many semiconductor material properties including bandgap energy, electronic defects, strain, and optical quality can be determined using PL spectroscopy.

PL spectrum of a semiconductor material shows two prominent features, near-bandgap emission that gives the semiconductor band gap, and radiative transitions which involve semiconductor impurities and electronic defects.\textsuperscript{14-16} PL spectra of wide bandgap semiconductors typically contain several radiative transitions including near-band edge transitions, donor-acceptor pair transitions, defect levels to the bandedge transitions and
bandedge to defect levels transitions. Using the energy of such transitions, the defect levels in semiconductors are determined.

In our work, the PL spectroscopy of GaN films was studied using a photoluminescence spectrometer (a 325 nm Melles-Griot He-Cd laser as photoexcitation source and a iHR320 photoluminescence spectrometer with Si and indium gallium arsenide (InGaAs) detectors).

3.4.2 Optical transmission

Another useful technique to examine the optical properties of a material is optical transmission. The GaN is transparent throughout the visible spectrum, allowing light of a lower energy than the bandgap to pass through the material. Examining the percent transmission as a function of wavelength give information about the bandedge as well as electronic defects that are not visible in PL spectra.

Defects are often visible in a transmission spectrum as an absorption band that causes a drop in the transmission signal below the bandgap energy. Optical transmission also provides information about intra-atomic transitions. These measurements require a smooth surface on both top and bottom of the film, however, as a rough surface will scatter the transmitted light and decrease signal intensity significantly. Optical transmission data were collected using a Perkin-Elmer LAMBDA 1050 UV/Vis/NIR spectrophotometer.

3.5 Electrical characterization

Electrical characterization techniques are performed to measure the free carrier concentration, conductivity and resistivity of the thin films. This information helps to determine the impurity levels and quality of GaN films. For example, the important
impurities in GaN, such as oxygen, silicon, and carbon contribute to high carrier concentration and conduction.

3.5.1 Hall effect measurement

The Hall effect is measured with applying a magnetic field perpendicular to the flow of current in a semiconductor bar to deflect the path of the carriers.\textsuperscript{17,18} If we suppose that the magnetic field is applied in the $z$ direction in a right-handed coordinated system, and current flows in the $x$ direction, then the force applied to the carriers is given as:

$$F_y = q(E_y - V_x B_z)$$

(3.2)

where $E_y$ is the electric field ($y$ direction), $V_x$ is carrier velocity ($x$ direction), and $B_z$ is the magnetic field ($z$ direction). The carriers will face a net force $F_y$ ($-y$ direction) except an electric field with magnitude equal to $V_x B_z$ is caused to compensate. The compensating electric field is created with the shift of the carriers along the $y$-axis which it causes the carriers to keep the $x$-axis as their overall direction. The compensating electric field generated by the Hall effect is measured with the product of current density and magnetic flux density. The Hall coefficient is calculated by:\textsuperscript{17,18}

$$R_H = \frac{1}{qp_o}$$

(3.3)

where $p_o$ is the carrier density. With given the values of current and magnetic field, and measuring the induced voltage across the sample, the free carrier concentration can be computed. Hall effect measurements are useful to determine information, including the resistivity, conductivity, and carrier mobility of GaN films. In this work, Hall effect measurements were performed using the Van der Pauw technique with cloverleaf geometry at room temperature.
3.6 Optical emission spectroscopy

The optical emission spectra (OES) of laser irradiated NH$_3$ were taken in open air using a spectrometer (Shamrock SR-303i-A, Andor Technology) coupled with an intensified charged coupled device (ICCD) (iStar DH-712, Andor Technology). Fig. 3.7a and b show the schematic experimental setup for the OES measurements in open air and OES of the NH$_3$ under laser irradiation at wavelength of 9.219 µm in open air, respectively.

The IR laser beam was focused to a diameter around 1 mm using a ZnSe convex lens ($f = 25.4$ cm). A welding torch with a nozzle diameter of 1.5 mm was used to introduce the NH$_3$ gas at a flowrate of 50 sccm. The CO$_2$ laser beam was directed perpendicularly to the NH$_3$ flow. The laser incident power density was fixed at $1.4 \times 10^4$ W/cm$^2$ for all laser wavelengths. All spectra were taken with a vertical collecting length of 0.5 mm along the emission, centered at the tip of the emission, and with a horizontal slit width of 30 µm centered at the tip apex of the emission. A background spectrum captured before collecting the emission spectra was subtracted from all spectra.

![Figure 3.7](image.png)

Figure 3.7 (a) schematic experimental setup for the OES measurements in open air. b) OES of the NH$_3$ under laser irradiation at wavelength of 9.219 µm in open air.
3.7 Device processing and characterization

Once LMOCVD GaN films were grown, the metal semiconductor metal (MSM) device was fabricated on as-grown films. The interdigitated finger of MSM device was 50 µm long, with 10 µm finger width and 10 µm finger spacing, and a detection area of $10 \times 10 \, \mu m^2$. The devices were fabricated using standard photolithography with patterning photoresist for subsequent metallization of metal Schottky contacts on the GaN. With the high metal work function and the good adhesion with GaN, Ni and Au metals were chosen as the Schottky contacts.\textsuperscript{19,20} Schottky contacts were 100 nm Au/20 nm Ni, deposited using magnetron sputtering. To improve the Schottky characteristics, a pre-cleaning step was used to remove the oxide on the GaN surface prior to metallization. The film cleaning process has been done using hydrofluoric (HF) acid for 1 min and warm ammonium hydroxide (NH$_4$OH) for 15 min.

The current-voltage ($I-V$) measurements of the GaN UV photodetectors were carried out using a Keithley 237 electrometer. Photoresponse measurements were realized by using a Xe arc lamp with power of 150 W as UV light source. External quantum efficiency (EQE) measurement was performed by using an incident monochromatic light beam directed onto the photodetector and the data was collected via a Newport QE measurement kit. Transient response measurements were taken using a 337 nm, 4 ns pulsed laser as light source, and voltage variations were collected using an oscilloscope (LeCroy WaveRunner).
3.8 References


CHAPTER 4 GROWTH OF M-PLANE GAN NANOPlate USING LASER-ASSISTED METAL ORGANIC CHEMICAL VAPOR DEPOSITION

4.1 Introduction

4.2 Experimental Methods

4.3 Results and Discussion

4.4 Conclusions

4.5 References
4.1 Introduction

The growth of GaN nanostructures including nanowires and nanorods is predominant along the (0001) direction (c-plane) due to the high surface free energy of the c-plane.\textsuperscript{1-3} Several attempts were made to grow the gallium nitride (GaN) nanostructures oriented along the <10-10> direction (m-plane).\textsuperscript{1,2} The <10-10> oriented GaN nanostructures can be utilized to overcome the quantum-confined stark effect (QCSE) [i.e., separation of the electron and hole wave functions within the quantum wells (QWs)], which degrades the recombination efficiency of GaN-based photonic devices.\textsuperscript{4-6} However, the growth of <10-10> oriented GaN nanostructures requires expensive lattice-matched substrates, including lithium aluminate (\(\gamma\)-LiAlO\(_2\)), m- and r-plane sapphire (Al\(_2\)O\(_3\)), and m-plane silicon carbide (4H-SiC).\textsuperscript{4,5} In addition, the growth of GaN involves high-temperature methods, including metal organic chemical vapor deposition (MOCVD, \(\sim930\) °C), molecular beam epitaxy (MBE, \(\sim800\) °C), and hydride vapor phase epitaxy (HVPE, \(\sim750\) °C).\textsuperscript{7-9} All of these methods require a long processing time of \(\sim2\) h.\textsuperscript{1-10} The growth rates of GaN were reported to be 200, 4, and 1 \(\mu\)m/h in HVPE, MOCVD, and MBE techniques, respectively.\textsuperscript{10,11}

The potential applications of GaN demand a simple approach for the rapid and selective growth of GaN nanostructures. Laser-assisted MOCVD (L-MOCVD) is a suitable method for enabling the rapid growth of materials at a low temperature in a predefined area.\textsuperscript{12-16} In addition, another obvious advantage of the L-MOCVD over conventional MOCVD is the ability to generate patterned material deposition on substrates without involving complex lithography steps.\textsuperscript{14,17} Several semiconductor
materials, including gallium arsenide (GaAs), cadmium telluride (CdTe), indium phosphide (InP), indium antimonide (InSb), and aluminum nitride (AlN), were grown using the L-MOCVD technique. Similarly, GaN can be grown at low substrate temperatures using L-MOCVD compared to conventional growth methods. The growth rate can be remarkably enhanced due to the rapid processing nature of L-MOCVD. There are few reports available discussing the growth of GaN using L-MOCVD. In this study, the $m$-plane oriented GaN nanoplates have been successfully grown on lattice-mismatched (Si) substrates using L-MOCVD. The rapid growth of GaN was realized by pyrolytically decomposing the source precursors at 450 °C.

4.2 Experimental methods

GaN nanoplates were grown on Si substrates at 450 °C using a home-built L-MOCVD system. Fig. 4.1 shows the schematic diagram and real-time image of the L-MOCVD system. Initially, the vacuum chamber was evacuated to a base pressure of $1 \times 10^{-3}$ Torr. The TMGa and NH$_3$ were used as gas precursors in L-MOCVD. The flow rate of NH$_3$ was maintained at 2.2 mmol/min. The TMGa was carried into the growth chamber using nitrogen (N$_2$) as a carrier gas at a flow rate of 0.4 mmol/min. The chamber pressure was maintained at 450 Torr during the deposition process. Once the chamber pressure is stabilized, a CO$_2$ laser beam was shined on to the Si substrate. The power of the laser beam was fixed at 14 W. GaN nanostructures were grown at different deposition times from 1 to 5 min. The temperature of the growth region was monitored using a pyrometer (Omega, OS3752). After the growth process, the GaN nanoplates were characterized as follows. The morphology of the GaN films was examined using a field-emission scanning electron microscope (FESEM, S4700) and a high-resolution
transmission electron microscope (HRTEM, FEI Tecnai). The composition of the nanoplates was analyzed using an energy dispersive X-ray spectrometer (EDX, Oxford X-max 20 mm²). The crystallinity and structure of the GaN nanoplates was studied using a micro-Raman spectroscope (Renishaw Invia, Argon ion laser, $\lambda = 514$ nm) and a powder X-ray diffractometer (Rigaku D/Max B diffractometer, Co Kα1 $\lambda = 1.788$ Å). The optical properties of the nanoplates were examined using a home-built photoluminescence spectrometer (Spectra Physics, wavelength-tunable Argon ion laser, $\lambda_{ex} = 244$ nm).

4.3 Results and discussion

4.3.1 Morphological analysis

The morphology of the GaN films was examined using a field-emission scanning electron microscope (FESEM) and high-resolution transmission electron microscope (HRTEM). The FESEM images in Fig. 4.2a-d show the micrographs of GaN nanoplates grown at 1, 3, 5 and 7 min, respectively. The GaN film deposited at 1 min revealed the formation of nanoplates as shown in Fig. 4.2a. The shape of the nanoplates was similar to a semi-hexagonal and hexagonal. The arrows in Fig. 4.2a show the hexagonal shape of nanoplates. GaN nanoplates grown at 3 min had similar shape compared to the nanoplates grown at 1 min as shown in Fig. 4.2b. As the growth time was further increased to 5 and
7 min, the nanoplates overlapped with the adjacent nanoplates and formed interlinked GaN nanoplates as shown in Fig. 4.2c and d. The diameters of the GaN nanoplates were \( \sim 200 \pm 50, 250 \pm 50, 900 \pm 50, 1500 \pm 50 \) nm at 1, 3, 5 and 7 min, respectively. The thicknesses of the GaN nanoplates were 40 ± 10 nm, 50 ± 10 nm, 90 ± 10 nm and 900 ± 10 nm at 1, 3, 5 and 7 min, respectively. As the growth time increased the thickness of the nanoplates increases. The nanoplates join with the adjacent counterparts in all directions. The orientation of the GaN crystals on the Si substrate was similar to the GaN nanoplates, i.e., the c-axis of GaN was perpendicular to the substrate normal. The EDX results confirmed the presence of Ga and N elements in the nanoplates. The atomic concentrations of Ga and N were 52.63 and 43.42, respectively.

Figure 4.2 FESEM images of m-plane GaN nanoplates grown at (a) 1, (b) 3, (c) 5 min and (d) 7 min.
Figs. 4.3a and 4.3b show the selected-area electron diffraction (SAED) and high-magnification TEM images of a GaN nanoplate. SAED pattern of the GaN nanoplates revealed the array of spots indexed to the reflection of GaN with the wurtzite structure along the $m$-direction. The lattice fringes in Fig. 4.3b further confirm the single crystallinity of the GaN nanoplate. The interplanar spacing of 0.28 nm can be assigned to (10-10) plane, which corresponds to the m-plane of GaN.\textsuperscript{19}

Figure 4.3 TEM images of a GaN nanoplate: (a) SAED pattern of the GaN nanoplate, (b) lattice fringes of the GaN nanoplate.

4.3.2. Growth Mechanism

The growth rates of different planes of the hexagonal GaN crystals were reported to have the following tendency \([0001] > [01-1-1] > [10-10] > [01-11]\).\textsuperscript{20-21} Typically, due to high growth rate of c-plane, the GaN nanostructures grow along \(<0001>\) direction.\textsuperscript{20} However, in this study the GaN nanoplates were grown along \(<10-10>\) direction. The growth orientations other than (0001) can be achieved for the films deposited at low-temperature and/or high deposition rate.\textsuperscript{3,22,23} The estimated growth rate of GaN was $\sim 38$ $\mu$m/h. The high growth rate can be attributed to the three-dimensional (3-D) diffusion
path of the reactive gases in LMOCVD. In addition, in this study GaN nanoplates were grown at a low temperature (450 °C) compared to GaN nanostructures grown by MOCVD at 930 °C.

The schematic diagram in Fig. 4.4a represents the growth of $m$-plane GaN nanoplates. Once the substrate is completely covered by the nanoplates, the upcoming species have to nucleate either on c-plane or m-plane of the nanoplates.$^{24-29}$ The GaN nanoplates served as seed crystals for the subsequent growth of m-plane oriented interlinked nanoplates. At an increased growth time, the growth continued on the different facets of the GaN nanoplates. Due to the negligible lattice mismatch between the c-plane and m-plane of GaN, the m-plane oriented nanoplates were dominant at a longer growth time. At an increased growth time, the overlap of the nanoplates led to the formation of nanoplate networks whose m-plane was orienting parallel to the Si substrate as shown in Figs. 4.4a and b. The FESEM images in Fig. 4.4b clearly revealed the growth of m-oriented GaN nanoplates.
4.3.3. Structural and optical properties

According to the group theory the Raman active modes of GaN are $A_1+E_1+2E_2$, where two non-polar $E_2$ modes are Raman active, $A_1$ and $E_1$ modes are both Raman and infrared active.\(^{30-33}\) The vibrational modes of the GaN nanoplates were examined using a micro-Raman spectrometer under a $Z(X,X)-Z$ backscattering geometry. Where, $Z$ and -$Z$ represents the projection direction of the incoming and scattered light, while $X$ represents the polarization direction of the incoming and scattered light. Fig. 4.5 shows the micro-Raman spectra of the GaN nanoplates grown at 1 and 5 min, respectively.

The GaN nanoplates grown at 1 min showed strong $E_{2H}$ mode at 569 cm\(^{-1}\) and relatively weak $A_1$(TO), $E_1$(TO) and $A_1$(LO) modes at 530, 560, 738 cm\(^{-1}\), respectively.\(^{30-33}\) The strong $E_{2H}$ mode is characteristic of wurtzite GaN. The c-plane GaN showed strong $E_{2H}$ at 569 cm\(^{-1}\) as shown in Fig. 4.5a. The strong $A_1$(TO) mode was obtained for GaN nanoplates grown at 5 min as shown in Fig. 4.5b. The GaN nanoplates grown at 5
min did not show E$_{2H}$ mode. According to the Raman selection rule, the m-plane GaN will show strong A$_1$(TO) mode along the Z(X,X)-Z geometry. This can be attributed to the absence of E$_{2H}$ mode and presence of strong A$_1$(TO) mode for GaN film grown at 5 min.

Fig. 4.6 compares the XRD patterns of GaN nanoplates grown at 1 and 5 min. The XRD peaks including (10-10), (0002) and (10-11) can be indexed to wurtzite GaN with the hexagonal structure, which are in good agreement with Joint Committee on Powder Diffraction Standards (JCPDS) card no. 01-070-2546. GaN nanoplates grown at 1 min showed a strong (0002) peak which indicates the c-axis orientation of the nanoplates as shown in Fig. 4.6a.

![Figure 4.6 XRD patterns of GaN nanoplates grown at 1 and 5 min.](image)

The degree of orientation can be estimated by the relative texture coefficient which is given as:

$$\text{TC}_{0002} = \frac{I_{0002} / I_{0002}^0}{I_{10-10} / I_{10-10}^0}$$

where TC$_{0002}$ is the relative texture coefficient of (0002) peak over (10-10) peak. $I_{0002}$ and $I_{10-10}$ are the measured intensities of (0002) and (10-10) peaks, respectively.
\( I^0_{(0002)} \) and \( I^0_{(10-10)} \) are the intensity values of (0002) and (10-10) peaks of GaN powders obtained from the JCPDS card no. 01-070-2546, respectively. The textured coefficient of GaN powders with random crystallographic orientation is 0.5. The textured coefficient of GaN nanoplates grown at 1 min is 0.923, which indicates strong \( c \)-axis orientation of the GaN nanoplates. This is obvious from Fig. 4.2a which clearly showed the formation of GaN nanoplates and \( c \)-axis of most of the nanoplates are parallel to the substrate normal. On the other hand, GaN film grown at 5 min showed a strong (10-10) peak as shown in Fig. 4.6b which corresponds to the \( m \)-plane of GaN. The relative texture coefficient was used to estimate their degree of orientation using the following relation:\textsuperscript{19,34}

\[
TC_{10\bar{1}0} = \frac{I_{10\bar{1}0} / I^0_{10\bar{1}0}}{I_{10\bar{1}0} / I^0_{10\bar{1}0} / I^0_{0002} / I^0_{0002}}
\]  

where \( TC_{10\bar{1}0} \) is the relative texture coefficient of (10-10) peak over (0002) peak. The estimated \( TC_{(10-10)} \) of interlinked GaN nanoplates grown at 5 min was 0.563. This result indicates that the as grown interlinked GaN nanoplates are preferentially oriented along the \(<10-10>\) direction. The XRD data are in good correlation with the FESEM, HRTEM and Raman results.

The optical properties of the nanoplates were examined using a photoluminescence (\( \lambda = 244 \) nm) set up. The GaN nanoplates grown at 5 min showed near-band-edge (NBE) emission at 3.4 eV which is closer to the NBE emission of bulk GaN (3.47 eV).\textsuperscript{35,36} In addition, GaN nanoplates showed a broad deep level emission (DLE) at 2.21 eV. The DLE emission at 2.21 eV can be attributed to nitrogen vacancies and gallium interstitials of the GaN nanoplates.\textsuperscript{35,37} The NBE emission peaking at 3.4 eV confirmed the good optical quality of the GaN nanoplates.
4.4 Conclusions

The interlinked m-plane-oriented GaN nanoplates can rapidly be grown on a Si substrate using the L-MOCVD method. The FESEM and HRTEM images confirmed the formation of GaN nanoplates. The growth direction of GaN nanoplates was found to be the <10-10> direction. The $A_1$ (TO) mode of Raman further confirmed the m-plane orientation of the GaN nanoplates. The high deposition rate, low-growth temperature, and repeated growth on the different facets of the nanoplates resulted in the formation of m-plane-oriented interlinked GaN nanoplates. Therefore, the LMOCVD is a suitable technique for the rapid growth of m-plane-oriented GaN nanoplates on Si substrate at low-growth temperatures. This method can be extended to the rapid growth of other III-nitride materials.
4.5 References


CHAPTER 5 ENHANCED GAN FILMS GROWTH ON SILICON SUBSTATES WITH RESONANT VIBRATIONAL EXCITATIONS OF AMMONIA MOLECULES

5.1 Introduction

5.2 Experimental Details

5.3 Results and Discussion

5.4 Mechanism of the Resonant Vibrational Excitation

5.5 Conclusions

5.6 References
5.1 Introduction

In this chapter, the influence of exciting ammonia (NH$_3$) molecular vibration in the growth of gallium nitride (GaN) on silicon (100) substrates is investigated by using an infrared laser-assisted metal organic chemical vapor deposition (LMOCVD) method. High-quality commercial GaN films are usually grown by the metalorganic chemical vapor deposition (MOCVD) technique on expensive lattice-mismatched substrates such as sapphire and SiC substrates at a growth rate around 2 μm/h.$^{1-14}$ Recently, interests in the epitaxial growth of thick GaN films on Si (100) substrates arose for scalable production of power-switching devices at an affordable cost.$^6,8$ However, the MOCVD technique is accompanied with a parasitic reaction between the precursors at high temperatures, which restricts the growth rates and impairs the epitaxial growth of thick GaN films.$^{13-16}$ In addition, the high growth temperatures ($\sim$ 900 - 1200 °C) lead to GaN decomposition and nitrogen reevaporation therefore result in reduced GaN growth rates and degraded crystalline quality.$^{17,18}$ Moreover, there is a series of Ga-Si reactions at elevated temperatures that could directly deter the growth of GaN on Si.$^{19}$ However, a high reaction temperature is required for effective NH$_3$ decomposition and overcoming the energy barriers on precursor adsorption and surface adatom migration.$^{13-16}$

Ultraviolet laser-induced MOCVD growth of group-III nitrides was developed$^{20,21}$ with the potential to overcome these disadvantages and was principally intended to provide the reactive radicals Ga and N by photolysis of their precursors at low substrate temperature. However, the density of the reactive N-containing fragments from NH$_3$ was not very high even at high volume ratios and GaN growth rate was low. To address the challenges without introducing hetero catalysts, we have developed an infrared laser
LMOCVD method to achieve thick GaN on Si (100).\textsuperscript{22} Selective NH\textsubscript{3} decomposition at room temperatures is realized by resonantly exciting the rotational-vibrational transition of the NH-wagging modes using a CO\textsubscript{2} laser beam. The roles of vibrational excitation in NH\textsubscript{3} decomposition and GaN formation is discussed. There are six vibrational modes and numerous vibrational bands in NH\textsubscript{3} molecules. Will vibrational excitation of each mode contribute equally to the NH\textsubscript{3} decomposition and GaN growth? How will each mode impact the NH\textsubscript{3} decomposition and GaN growth?

Based on the available irradiation lines, the NH\textsubscript{3} NH-wagging modes at 932.51 (\(\nu_{2+}\)) and 968.32 cm\(^{-1}\) (\(\nu_{2-}\)), and the NH rotational-vibrational transition at 1084.63 cm\(^{-1}\) were resonantly excited leading to significantly improved GaN growth rates. Compared to laser-induced thermal heating at nonresonant wavelengths, the resonant excitations lead to more effective NH\textsubscript{3} decomposition, higher concentrations of active species, higher GaN deposition rates, and better GaN crystalline quality.

5.2 Experimental details

5.2.1 Sample preparation

The schematic experimental setup of a home-built LMOCVD system is shown in Fig. 5.1. GaN films were grown on p-type Si(100) substrates. From the point of view of integrating GaN devices with silicon technology, the Si(100) substrate is preferred because Si(100) is the most widely used in silicon mainstream technology. The Si substrates (10 \(\times\) 10 mm\(^2\)) were etched with 10% hydrofluoric to remove oxide layers, cleaned and dried before loading into the LMOCVD chamber. Trimethylgallium (TMGa) and NH\textsubscript{3} were used as the Ga and N precursors, respectively. The LMOCVD chamber was evacuated to a base pressure of 1 \(\times\) 10\(^{-3}\) Torr. Then, laser thermal cleaning of Si
substrates was carried out at 900 °C under H₂ flow for 5 min to remove the native oxide on the substrate surface followed by one step nitridation at 750 °C. The nitridation was lasted for 5 min under 54 mmol/min NH₃ flow at a reactor pressure of 100 Torr. It has widely been reported that a silicon nitride layer is formed due to the nitridation surface treatment process on the silicon substrate.²³,²⁴ Nitridation of Si surface helps to release strain in GaN-on-Si growth and favours the growth of wurtzite GaN.²⁵-²⁷

The molar flow rate of NH₃ was maintained at 54 mmol/min. The TMGa was carried into the growth chamber using a nitrogen carrier gas (N₂) at a molar flow rate of 88 μmol/min. The chamber pressure during the growth process was maintained at ~ 10 Torr. A continuous-wave wavelength-tunable CO₂ laser (PRC Inc., 9.2 - 10.9 μm) was used as the irradiation source, achieving reactant excitation and substrate heating. Based on the available emission lines of the CO₂ laser, the NH-wagging modes (ν₂, at 932.51, 968.32, and 1084.71 cm⁻¹) of NH₃ molecules were selected to be resonantly excited at corresponding laser wavelengths of 10.719, 10.350, and 9.219 μm. Two other wavelengths at 9.201 and 10.591 μm were selected as nonresonant wavelength references realizing only conventional laser heating. GaN nucleation layers (40 - 60 nm in thickness) were deposited at 500 °C for 30 seconds followed by epilayer growth at 750 °C for 5 min. The laser incident power was tuned to keep the substrate temperature same for all GaN samples grown at different laser wavelengths. The substrate temperature was monitored using a pyrometer (Omega, OS3752).
In order to find appropriate wavelengths achieving resonant vibrational excitation of NH$_3$ molecules, it is essential to found out available emission lines matching NH$_3$ molecular vibrational modes within the CO$_2$ laser wavelength range (9.2 - 10.8 µm). Due to the discrete emission lines of the CO$_2$ laser, effective NH$_3$ absorption spectrum within the CO$_2$ laser wavelength range was measured in a vacuum chamber with an absorption path length of 40.64 cm. The chamber was evacuated to a base pressure of 1 × 10$^{-3}$ Torr. Gaseous NH$_3$ was subsequently introduced into the chamber and reach a pressure of 10 Torr. The incident laser power was kept at 220 W. A power meter was used to measure the laser power before and after passing through the chamber. The drop in laser power was calculated as the absorption percentage.

Three strong absorption peaks were observed at 9.219, 10.35, and 10.719 µm (resonant wavelengths), corresponding to the NH-wagging modes ($\nu_2$) at 1084.63,
Among all six vibrational modes of NH$_3$ molecules, the NH-wagging mode is strongly infrared active. A NH$_3$ molecule in the NH-wagging mode vibrates in an umbrella inversion way. Due to the barrier that the nitrogen atom encounters on its travel through the proton plane, the vibrational level is split into two components at 932.51 ($v^{+2}$) and 968.32 cm$^{-1}$ ($v^{-2}$) which correspond to the observed absorption peaks at 10.719 and 10.35 µm, respectively. The strongest absorption peak at 9.219 µm is ascribed to the NH rotational-vibrational transition at 1084.63 cm$^{-1}$ [$5(J) \rightarrow 6(J'), K=0$].

5.2.3 Characterization

The Surface morphologies of the GaN films were studied using a field-emission scanning electron microscope (FESEM, Hitachi S4700). The qualities of GaN films were examined using a Raman microscope (Renishaw inVia H 18415, Argon ion laser, $\lambda = 514$ nm) and X-ray diffractometer (Rigaku D/Max B diffractometer, Co K$\alpha \lambda = 1.788$ Å). The doping type, carrier concentration and mobility of the GaN films were obtained via the Van der Pauw method at room temperature. The optical emission spectra (OES) of laser irradiated NH$_3$ were taken in open air using a spectrometer (Shamrock SR-303i-A, Andor Technology) coupled with an intensified charged coupled device (ICCD) (iStar DH-712, Andor Technology). The IR laser beam was focused to a diameter around 1 mm using a ZnSe convex lens ($f = 25.4$ cm). A welding torch with a nozzle diameter of 1.5 mm was used to introduce the NH$_3$ gas at a flowrate of 50 sccm. The CO$_2$ laser beam was directed perpendicularly to the NH$_3$ flow. The laser incident power density was fixed at $1.4 \times 10^4$ W/cm$^2$ for all laser wavelengths. All spectra were taken with a vertical collecting length of 0.5 mm along the emission, centred at the tip of the emission, and with a horizontal slit.
width of 30 µm centered at the tip apex of the emission. A background spectrum captured before collecting the emission spectra was subtracted from all spectra.

5.3 Results and discussion

5.3.1 FESEM images of the GaN films

The morphologies and grain sizes of the GaN films deposited at different laser wavelengths are shown in Figs. 5.2(a) – 5.2(e), respectively. Crystalline GaN films containing highly oriented grains along the c-axis with hexagonal facets are observed, indicating the formation of wurtzite GaN films on the Si(100) substrates. Generally, a mixture of cubic and hexagonal GaN tends to grow on Si(100) substrates because the (001) plane of Si possesses a fourfold symmetry.\textsuperscript{23-27} However, the nitridation process promotes the silicon nitride formation and prohibits cubic GaN nucleation. Therefore, hexagonal GaN dominates the GaN growth.\textsuperscript{23-27}

It is generally accepted that grain boundaries impact negatively on the electrical and optical properties of GaN films.\textsuperscript{33,34} Increasing grain sizes leads to reduced grain boundaries and results in a reduced amount of defects and stress. Therefore, the crystalline quality and optical properties of GaN films are improved accordingly.\textsuperscript{33,34} Fig. 5.2(f) compares the average grain sizes of the GaN films grown at different laser wavelengths. As shown in Figs. 5.2(a) and 5.2(d), GaN grains with average grain sizes of 1.0 and 2.1 µm are obtained at nonresonant wavelengths of 9.201 and 10.591 µm, respectively. The average grain sizes increase to 4.0, 3.8, and 3.1 µm at resonant wavelengths 9.219, 10.350, and 10.719 µm, respectively, as shown in Figs. 5.2(b), 5.2(c), and 5.2(e).
The cross-sectional SEM images of the GaN films deposited at non- (9.201 µm) and resonant wavelengths (9.219 µm) for 5 minutes are exhibited in Figs 5.3(a) and 5.3(b), respectively. The resonant deposition, Fig. 5.3(b), results in a thicker GaN film (7 µm) than the nonresonant deposition, Fig. 5.3(a), indicating a higher growth rate (around 2.7 times higher) at the resonant deposition. Fig. 5.3(c) compares the deposition rates obtained at all five wavelengths. It is obvious that resonant depositions result in higher GaN growth rates than nonresonant depositions. The highest growth rate (84 µm/h) is achieved at 9.219 µm, which is ~ 42 times higher than that of conventional MOCVD (2 µm/h).\textsuperscript{6,12,13} Although not as significant as those obtained under the resonant wavelengths, promoted GaN growth rates are also observed at nonresonant wavelengths, 9.201 and 10.591 µm, and are ascribed to the coupled energy via laser irradiation. However, the same amount of energy coupled at different wavelengths yields obviously divergent results as observed in Figs. 5.2(f) and 5.3(c).
Figure 5.2 (a) SEM images of GaN films deposited on Si (100) at excitation laser wavelength of (a) 9.201 µm, (b) 9.219 µm, (c) 10.350 µm, (d) 10.591 µm, and (e) 10.719 µm, respectively. (f) A chart showing average GaN grain sizes obtained at different laser wavelengths.
Figure 5.3 (a) SEM images of GaN films deposited on Si (100) at excitation laser wavelength of (a) 9.201 µm, (b) 9.219 µm, (c) 10.350 µm, (d) 10.591 µm, and (e) 10.719 µm, respectively. (f) A chart showing average GaN grain sizes obtained at different laser wavelengths.

5.3.2 Raman spectra of the GaN films

Raman spectroscopy is a powerful method evaluating the quality and residual stress of GaN films. Raman spectroscopic studies were conducted under a Z(X,X)Z̅ backscattering geometry, where Z and Z̅ represent the projection direction of the incoming and scattered light, and X represents the polarization direction of the incoming and scattered light. Fig. 5.4(a) shows the Raman spectra of the GaN films grown at different laser wavelengths. Two prominent Raman shifts at around 567 and 733 cm⁻¹ are observed from all samples, corresponding to the GaN E₂H and A₁(LO) phonon modes, respectively. These modes originate from allowed vibrational states in the wurtzite GaN epitaxial layer. The exact positions of the GaN E₂H phonon peak of the samples were summarized in Table 5.1.
It is well known that the E$_{2H}$ mode in the GaN Raman spectra reflects crystalline quality and stress of the crystals.$^{35}$ The E$_{2H}$ peaks were shifted to lower wave-numbers (red-shift) compared with the standard frequency value of the E$_{2H}$ phonon mode of strain-free GaN at 567.8 cm$^{-1}$. The peak positions of the E$_{2H}$ were observed to have red-shifts of about 1.7, 1, 1.3, 1.3 and 1.2 cm$^{-1}$ for the samples grown at laser wavelengths of 9.201, 9.219, 10.35, 10.591 and 10.719 µm, respectively. The red-shift in the position of E$_{2H}$ indicated that the GaN films suffered from tensile stress. The stress levels of the GaN epilayer can be calculated using the following equation:$^{36}$ $\sigma = \Delta\omega / 4.3 \text{ (cm}^{-1} \text{ GPa}^{-1})$, where $\sigma$ is the biaxial stress and $\Delta\omega$ is the E$_{2H}$ phonon peak shift. The estimated tensile stresses were calculated and summarized in Table 5.1. The Raman spectra indicated that the GaN films grown at laser wavelengths of 9.219 µm exhibited the lowest stress.

Moreover, as observed in Fig. 5.4(a), the E$_{2H}$ peak is much stronger in the resonant samples (9.219, 10.35, and 10.719 µm) than in the nonresonant samples (9.201 and 10.591 µm), indicating better crystalline quality of the resonant samples. The strongest E$_{2H}$ peak is observed when resonantly excited at 9.219 µm, denoting the highest GaN crystalline quality. The full-width-at-half-maximum (FWHM) values of the E$_{2H}$ peaks of the GaN samples were summarized in Table 5.1. A narrow E$_{2H}$ peak, i.e. a low FWHM value, indicates a better crystalline quality. According to Table 5.1., it is obvious that FWHMs of resonant samples are lower than those of nonresonant samples. The lowest FWHM, 9.3 cm$^{-1}$, is observed in the resonant sample excited at 9.219 µm, indicating the highest GaN crystalline quality.
Figure 5.4 Raman spectra of the GaN films grown at resonant (9.219, 10.35, and 10.719 µm) and nonresonant (9.201 and 10.591 µm) wavelengths.

Table 5.1 Summary of GaN films characterization grown on Si (100) substrates at different laser wavelengths.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Laser wavelength (µm)</th>
<th>Average grain sizes (µm)</th>
<th>Growth rate (µm/hr)</th>
<th>GaN $E_{2H}$ peak position (cm$^{-1}$)</th>
<th>GaN $E_{2H}$ peak FWHM (cm$^{-1}$)</th>
<th>$\sigma$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>9.201</td>
<td>1</td>
<td>32</td>
<td>566.1</td>
<td>19</td>
<td>0.395</td>
</tr>
<tr>
<td>II</td>
<td>9.219</td>
<td>4</td>
<td>84</td>
<td>566.8</td>
<td>9.3</td>
<td>0.233</td>
</tr>
<tr>
<td>III</td>
<td>10.350</td>
<td>3.8</td>
<td>66</td>
<td>566.5</td>
<td>10.1</td>
<td>0.302</td>
</tr>
<tr>
<td>IV</td>
<td>10.590</td>
<td>2.1</td>
<td>45</td>
<td>566.5</td>
<td>11.9</td>
<td>0.302</td>
</tr>
<tr>
<td>V</td>
<td>10.719</td>
<td>3.1</td>
<td>59</td>
<td>566.6</td>
<td>11.2</td>
<td>0.280</td>
</tr>
</tbody>
</table>

5.3.3 XRD characterization of the GaN films
Figs. 5.5(a) and 5.5(b) exhibit the XRD diffraction curves of the GaN films obtained at 9.219 (resonant wavelength) and 9.201 µm (nonresonant wavelength), respectively. The XRD peaks at around 40.2° and 87.02° are observed in both curves and attributed to the GaN {0001} family planes. These peaks correspond to the (0002) and (0004) orientations of wurtzite GaN, respectively, indicating a high c-axis orientation of the GaN films deposited on the Si(100) substrates. It is observed from Fig. 5.5(a) and 5.5(b) that the GaN XRD peaks are much stronger in the resonant sample than those in the nonresonant sample, which is attributed to the improved crystalline quality.

The GaN (0002) rocking curves of the GaN films deposited at the resonant (9.219 µm) and nonresonant (9.201 µm) wavelengths are exhibited in Figs. 5.5(c) and 5.5(d), respectively. FWHM values of the rocking curves of (0002) symmetric and (10-12) asymmetric diffraction peaks were summarized in Table 5.2. It is well known that the FWHM of XRD in the (0002) reflection reveals information about the out-of-plane misorientation of domains (tilt) while the FWHM of the GaN (10-12) peak is sensitive to both tilt and twist. Thus, the FWHM of the (0002) peak is usually used to evaluate the screw or mixed threading dislocations (TDs) density and the FWHM of XRD in the (10-12) reflection corresponds to the lattice distortion from all components of the TDs including edge, screw and mixed screw-edge dislocations. Low FWHM values indicate low TDs density and better crystalline quality.

As shown in Table 5.2, (0002) FWHM values of 92 and 60 arcmin and (10-12) FWHM values of 99 and 67 arcmin are observed for the GaN samples deposited at the nonresonant wavelengths of 9.201 and 10.591 µm, respectively. For the GaN film deposited with resonant excitation, the FWHMs of (0002) are 39, 45, and 55 arcmin and
the FWHMs of (10-12) are 43, 53, and 61 arcmin at resonant wavelengths of 9.219, 10.350, and 10.719 µm, respectively. The distinctive FWHMs decrease in resonant samples compared to those with nonresonant samples indicates improved GaN crystalline quality and reduced TDs density by using resonant excitation. However, the crystalline quality of GaN films are inferior to that reported for conventional MOCVD, which is attributed to the high growth rates of GaN, large crystal lattice mismatch (16.9%), and thermal coefficient of expansion mismatch (113%) between the GaN epilayer and the Si substrate.

Figure 5.5 X-ray diffraction curves of GaN films deposited at (a) resonant wavelength of 9.219 µm and (b) nonresonant wavelength of 9.201 µm (x-ray diffractometer: Rigaku D/Max B diffractometer, Co Kα λ = 1.788 Å). Rocking curves of (0002) diffraction peaks of
GaN films deposited at (c) resonant wavelength of 9.219 µm and (d) nonresonant wavelength of 9.201 µm.

Table 5.2 Summary of GaN films characterization grown on Si (100) substrates at different laser wavelengths.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Laser wavelength (µm)</th>
<th>GaN (0002) peak ω-FWHM (arcmin)</th>
<th>GaN (10-12) peak ω-FWHM (arcmin)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>9.201</td>
<td>92</td>
<td>99</td>
</tr>
<tr>
<td>II</td>
<td>9.219</td>
<td>39</td>
<td>43</td>
</tr>
<tr>
<td>III</td>
<td>10.350</td>
<td>45</td>
<td>53</td>
</tr>
<tr>
<td>IV</td>
<td>10.590</td>
<td>60</td>
<td>67</td>
</tr>
<tr>
<td>V</td>
<td>10.719</td>
<td>55</td>
<td>61</td>
</tr>
</tbody>
</table>

5.3.4 Hall measurement of the GaN films

Hall measurements using the Van der Pauw method were conducted to characterize carrier concentrations and mobilities of the GaN films deposited at resonant (9.219 µm) and nonresonant (9.201 µm) wavelengths. Both GaN films were demonstrated to be n-type semiconductors. Corresponding carrier concentrations and mobilities are $8.27 \times 10^{17}$ cm$^{-3}$ and 299.5 cm$^2$/Vs for the resonant sample, and $4.9 \times 10^{18}$ cm$^{-3}$ and 119.1 cm$^2$/Vs for the nonresonant sample. The relatively high carrier concentrations are indicative of high concentration of unintentionally doped impurities. However, the resonant sample possesses a lower carrier concentration but higher mobility, compared to nonresonant sample.

5.4 Mechanism of the Resonant Vibrational Excitation

According to above experimental results, two points are clearly demonstrated. The first is that resonant vibrational excitation can significantly promote GaN growth rates and improve GaN crystalline quality when comparing to conventional thermal heating and nonresonant laser irradiation. The second is that the same amount of energy coupled into different vibrational states lead to diverse results. In this study, the resonant
Excitation of the NH rotational-vibrational transition at 1084.63 cm\(^{-1}\) \([5(J) \rightarrow 6(J'), K=0]\) leads to the highest GaN growth rate, best crystalline quality, and highest carrier mobility. To understand the reasons behind the difference, optical emission spectroscopic (OES) investigations were carried out to study the evolution of NH\(_3\) molecules under laser irradiation at resonant and nonresonant wavelengths in open air. Fig. 5.6 shows optical images of the NH\(_3\) flows under laser irradiation at different wavelengths. Stronger emissions are observed from NH\(_3\) flows when irradiated at resonant wavelengths (i.e. 9.219, 10.350, and 10.719 \(\mu\)m) than those at nonresonant wavelengths (i.e. 10.591 and 9.201 \(\mu\)m). The shape and brightness of the laser-induced plasma reflect dissociation of NH\(_3\) molecules under the laser irradiation. According to Fig. 5.6, resonant excitations lead to NH\(_3\) flows of brighter colors and expanded diameters due to accelerated NH\(_3\) dissociation, promoted chemical reactions, and increased reactive species concentrations.\(^{39}\) The brightest and strongest NH\(_3\) flow is observed under the resonant excitation at 9.219 \(\mu\)m.

Figure 5.6 Optical images of NH\(_3\) flows when irradiated at different laser wavelengths in open air.
OES spectra of the laser-irradiated NH$_3$ are shown in Fig. 5.7. Emissions from OH, NH, N$^+$, H$_\alpha$, N, and H$_\beta$ are observed at 309, 336, 463, 486, 496, and 656 nm, respectively. Strong emissions from NH$_2$ radicals are observed at 525, 543, 569, 603, 629, and 663 nm in all OES spectra from resonantly excited NH$_3$ flows, indicating effective dissociation of NH$_3$ molecules. Obviously increased emission intensities of OH, NH, NH$_2$, N, N$^+$, and H are observed at the resonant wavelength of 9.219 µm. However, only very weak emission intensities of NH and NH$_2$ radicals are identified when irradiated at the nonresonant wavelength of 10.591 µm. No emission peak is observed at the nonresonant wavelength of 9.201 µm.

N, NH, and NH$_2$ are active nitrogen species for growing GaN.$^{20,21,40}$ Growth of high-quality GaN films requires a sufficient supply of active nitrogen and gallium species by cracking NH$_3$ and TMGa molecules, respectively, and transporting atomic N and Ga to proper lattice sites. The dissociation energies for dissociating TMGa into active gallium species has been reported to be much lower than that of NH$_3$.\$^{20,21}$ It is found that with the laser photons, the TMGa molecules undergo fragmentation with relative ease in analogy with their thermolytic instability.$^{20,21,41}$ However, effective decomposition of NH$_3$ molecules requires a high temperature around 1000 °C, which also leads to increased parasitic reactions, GaN decomposition and N escaping.$^{13}$ Therefore, decomposing NH$_3$ at an appropriate temperature is essential for growing high-quality GaN.
It is generally believed formation of GaN in MOCVD includes four key steps: \(^{13,40}\)

(i) TMGa:NH\(_3\) adduct formation, (ii) amide formation and methane elimination, (iii) trimer formation, and (iv) decomposition reaction and creating N and Ga to form GaN.

The first gas-phase reaction is a spontaneous reaction between TMGa and NH\(_3\) to form a stable adduct [(CH\(_3\))\(_3\)Ga:NH\(_3\)]. It is reported that the formation of the adduct as parasite reaction significantly degrades GaN film quality and growth rate at high temperatures. \(^{13,21,40}\) The amide formation, trimer formation and decomposition reaction can be expressed by equations (5.2), (5.3) and (5.4), respectively: \(^{13,40}\)

\[
(\text{CH}_3)_3\text{Ga} + \text{NH}_3 \rightarrow (\text{CH}_3)_3\text{Ga:NH}_3 \tag{5.1}
\]
(CH₃)_3Ga:NH₃ → (CH₃)_2Ga:NH₂ + CH₄  \hspace{1cm} (5.2)

3[(CH₃)_2Ga:NH₂] → [(CH₃)_2Ga:NH₂]₃  \hspace{1cm} (5.3)

[(CH₃)_2Ga:NH₂]₃ → 3GaN + 6CH₄  \hspace{1cm} (5.4)

The OES results indicate that the resonant vibrational excitation effectively dissociates NH₃ molecules and increases the concentrations of the active nitrogen species, i.e. N, NH, and NH₂. Based on the reported 4-step mechanism, effective decomposition of NH₃ is suggested to reduce the formation of the TMGa:NH₃ adduct²¹ in the first step and decrease the energy barriers for the rest of the steps, and therefore results in the increased GaN growth rate.

It is noteworthy that performance of a GaN-based device is limited by parasitic defect-induced emission, such as the yellow luminescence observed in GaN.⁴²,⁴³ Unintentionally doped GaN is generally a n-type semiconductor due to a high concentration of shallow donor Si_Ga and O_N.⁴³ It is reported that H radicals can form neutral complexes with shallow donors and acceptor dopants. These reactions help eliminating oxygen impurities, reducing impurity density and increasing in carrier mobility and resistivity of gallium nitride films.⁴² Considering the concentration of atomic hydrogen resulted from NH₃ decomposition, oxygen impurities in GaN are expected to be reduced. It is suggested that with the increments of H radicals, Fig. 5.7, the GaN crystalline quality and carrier mobility increase under resonant excitations, compared to those at nonresonant wavelengths.

Therefore, GaN films of better crystalline quality, lower impurity densities, and high deposition rates are obtained under resonant vibrational excitation. The results are in good accordance with the SEM, Raman, and XRD results.
5.5 Conclusions

In summary, vibrational excitations of NH₃ molecules were studied using a tunable CO₂ laser in growing crystalline GaN films on Si(100) substrates. The resonant vibrational excitation at 9.219, 10.350, and 10.719 µm were more efficient than nonresonant excitation in dissociating NH₃ molecules and enhancing the GaN deposition rate and quality. The OES results showed the resonant excitation of the NH-wagging modes modifies the synthesis process in a way that increases the supplies of NH, NH₂, N, N⁺, and H. This leads to the enhancement in GaN deposition rates and improvement in crystalline quality. The extremely high GaN growth rate of ~ 84 µm/h with an improved crystalline quality was achieved under the resonant excitation at 9.219 µm. The red-shift in the position of E₂H of Raman spectra indicated that the GaN films grown on Si suffered from tensile stress and the films grown at laser wavelengths of 9.219 µm exhibited the lowest stress. The FWHM value of the XRD rocking curves of GaN (0002) and GaN (10-12) diffraction peaks decreased at resonant depositions and reached its minimum values at 9.219 µm, indicating reduced TDs density. XRD ω-FWHMs of 45 arcmin for the GaN(0002) and of 53 arcmin for the GaN(10-12) reflection were measured for samples grown at laser wavelength of 9.219 µm; the FWHMs of the GaN(0002) and GaN(10-12) planes are about 3-5 times broader than those of the best GaN epilayer samples reported in literature. Further investigation are done in chapter 7 to improve the quality of the GaN films deposited via the LMOCVD techniques while maintaining high growth rates.
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CHAPTER 6 LOW-TEMPERATURE GROWTH OF CRYSTALLINE GALLIUM NITRIDE FILMS USING VIBRATIONAL EXCITATION OF AMMONIA MOLECULES

6.1 Introduction

6.2 Experimental Methods

6.3 Results and Discussion

6.4 Conclusions

6.5 References
6.1 Introduction

Gallium nitride (GaN), a III-V compound semiconductor with a wide, direct band gap of ~3.4 eV, has been utilized in widespread applications, such as optoelectronics and high-power electronic devices.\textsuperscript{1-3} High-quality crystalline GaN films are in demand for their ability to enhance the performance and reliability of GaN-based devices.\textsuperscript{4-7} However, growth of high-quality crystalline GaN films requires growth techniques using high temperatures, such as metalorganic chemical vapor deposition (MOCVD, \textasciitilde950-1100 °C), molecular beam epitaxy (MBE, \textasciitilde800 °C), and hydride vapor phase epitaxy (HVPE, \textasciitilde750 °C).\textsuperscript{6-8} A sufficiently high temperature is necessary to overcome the activation barriers to precursor chemisorption and adatom surface diffusion. However, high substrate temperatures can also cause adverse effects, such as biaxial stress within GaN films, nitrogen loss, and GaN decomposition, which degrade the efficiency of GaN-based devices.\textsuperscript{9-10} The biaxial stress is caused by the difference between thermal expansion coefficients of the GaN epitaxial layer and substrates (e.g., sapphire and silicon (Si)), and results in a poor light extraction in GaN-based light-emitting diodes (LEDs).\textsuperscript{10} To reduce the thermal stress in GaN films, substrates with a matching lattice, including lithium aluminate (LiAlO\textsubscript{2}), lithium gallate (LiGaO\textsubscript{2}), and silicon carbide (SiC), are preferred.\textsuperscript{11-13} However, such lattice-matching substrates are too expensive to be commercialized. A high growth temperature will also lead to nitrogen reevaporation and GaN decomposition, which limits the growth rate of GaN films.\textsuperscript{14} So far, the growth rates of GaN films synthesized by MOCVD and MBE were reported to be 4 and 1 µm/h, respectively.\textsuperscript{15-16} Therefore, a low-temperature synthetic technique is highly desired in growing crystalline GaN films.
In conventional GaN synthetic methods, energy is added into the gas precursors in the form of thermal heating. Energy is first deposited to kinetic energy of the reactant molecules and eventually makes its way into the internal modes (electronic, vibrational, and rotational) via collisions. However, universal thermal heating is short of selectivity in chemical reactions. Attempts at promotion of material synthesis have been investigated by exploring infrared (IR)-laser-assisted vibrational excitations of precursor molecules, in which energy is directly coupled into specific molecules towards selective reaction pathways. Highly efficient energy coupling through vibrational excitation provides reactant molecules with sufficient energy to surmount reaction barriers and influence reaction pathways. In our previous studies, substantial enhancement in diamond growth was observed with resonant vibrational excitation of ethylene molecules in IR-laser-assisted combustion CVD process.

In this study, low-temperature growth of highly c-oriented GaN films was achieved at a growth rate of up to 12 µm/h using laser-assisted metalorganic chemical vapor deposition (LMOCVD). Resonant excitation of the NH-wagging mode ($v_2$) in NH$_3$ molecules was realized using a wavelength-tunable carbon dioxide (CO$_2$) laser at a matching wavelength of 9.219 µm. GaN films were successfully deposited on sapphire at a substrate temperature as low as 250 °C. A GaN growth rate of up to 12 µm/h was achieved at 600 °C using the LMOCVD method, which is 4.6 times faster than that of conventional MOCVD (2.6 µm/h). The influence of laser resonant vibrational excitation of NH$_3$ on the GaN film growth was investigated.
6.2 Experimental Section

6.2.1 Measurement of laser power absorption by NH$_3$ molecules

The absorption spectra of CO$_2$ laser power by gaseous NH$_3$ were measured in a vacuum chamber with an absorption path length of 40.64 cm (Fig. 6.1). Absorption measurement of laser power at different laser wavelengths (9.2-10.9 µm) was performed at three different gas pressures of 1, 10, and 100 torr, respectively. In the experiments, the chamber was evacuated to a base pressure of 1 × 10$^{-2}$ torr. NH$_3$ gas was subsequently introduced into the chamber. The incident laser power was kept at 80 W. A power meter was used to measure the laser power before and after passing through the chamber. The drop in laser power was calculated as the absorption percentage.

6.2.2 Growth of GaN films

Fig. 6.1 shows the experimental setup of the LMOCVD system for the growth of crystalline GaN films at low temperatures. GaN films were grown on c-plane sapphire substrates at different temperatures (250-600 °C). The sapphire substrates, with a dimension of 10 × 10 mm$^2$, were ultrasonically cleaned with organic solvents (acetone and methanol) and deionized water, dried, and loaded into the LMOCVD chamber, sequentially. Then, the chamber was evacuated to a base pressure of 1 × 10$^{-2}$ torr using a mechanical pump. Trimethylgallium (TMGa) and ammonia (NH$_3$) precursors were used as gallium (Ga) and nitrogen (N) precursors, respectively. The gas flow rate of NH$_3$ was 1200 standard cubic centimeters per minute (sccm), and TMGa was carried into the reaction chamber using nitrogen as the carrying gas at a flow rate of 16 sccm. The growth pressure was maintained at 100 torr during the growth process. A wavelength-tunable CO$_2$ laser (PRC, wavelength range from 9.2 to 10.9 µm) was used to achieve resonant
vibrational excitation of the NH₃ molecules. The laser was tuned at a wavelength of 9.219 μm with a power of 80 W to resonantly excite the rotational-vibrational transition of the NH-wagging mode (ν₂, 1084.63 cm⁻¹) of NH₃ molecules and couple the laser energy into the molecules. The laser beam, with a diameter of around 6-9 mm, was irradiated in parallel to the substrate surface inside the chamber through a zinc selenide (ZnSe) window, as shown in Fig. 6.1. The distance between the laser beam and substrate surface was maintained at about 20 mm. The substrate temperature was maintained at a constant temperature of 150, 250, 350, 450, and 600 °C, respectively. The deposition time was kept at 1 hr. To understand the effects of laser-induced energy coupling, GaN films were also synthesized by the conventional MOCVD technique under the same growth conditions (deposition temperature, deposition time, gas flow rate, and growth pressure) without laser irradiation.

6.2.3 Characterization of GaN films

The crystallinity of the GaN films was examined using a powder X-ray diffractometer (Rigaku D/Max B diffractometer, Co Kα₁ λ= 1.788 Å). Surface morphologies and dimensions of the GaN films were studied using a field emission scanning electron microscope (FESEM, S4700). An energy dispersive X-ray spectrometer (EDX, Oxford X-max 20 mm²) was applied to analyze the composition of the GaN films. The optical properties of GaN films were studied using a photoluminescence spectrometer (iHR320 photoluminescence spectrometer with Si detector and indium gallium arsenide (InGaAs) detector).
6.3 Results and discussion

6.3.1 The roles of resonant vibrational excitation of NH$_3$ in GaN growth

NH$_3$ is a dominant nitrogen source in GaN synthesis. However, NH$_3$ has low decomposition efficiency due to a high NH bond energy (93-105 kcal/mol). A sufficient amount of active N species are required for GaN growth. The growth rate of GaN depends on the molecular flux of active N and Ga species that transport to substrates. The dissociation energies for dissociating TMGa into active gallium species has been reported to be much lower than that of NH$_3$. It is found that with the laser photons, the TMGa molecules undergo fragmentation with relative ease in analogy with their thermolytic instability. However, it is difficult to grow GaN films at temperatures lower than 500 °C using a conventional MOCVD method due to the low dissociation efficiency of NH$_3$. To increase the reactivity of NH$_3$ is, therefore, critical in low-temperature
growth of GaN. Through resonant vibrational excitation of the NH-wagging mode in NH$_3$ molecules, the reactivity of NH$_3$ is selectively enhanced; and the dissociation efficiency of NH$_3$ at low temperature is promoted$^{25-26}$.

![Absorption Spectra](image)

**Figure 6.2 Illustration of the experimental setup for the CO$_2$ laser-assisted MOCVD growth of GaN films at low temperatures.**

The absorption spectra of the CO$_2$ laser power by NH$_3$ gas at different gas pressures of 1, 10, and 100 torr are shown in Fig. 6.2. Three strong absorption peaks were observed at 9.219, 10.35, and 10.719 µm, respectively, at the NH$_3$ pressure of 10 and 100 torr. At a pressure of 100 torr, the laser energy at these three wavelengths was completely absorbed by NH$_3$ gas, while only one absorption peak at 9.219 µm was observed at a
pressure of 1 torr. The absorptions at these wavelengths were attributed to the resonant vibrational excitation of the NH-wagging mode ($v_2$) of the NH$_3$ molecules.$^{25-26}$ NH$_3$ has a pyramidal shape with three hydrogen atoms forming the base and a nitrogen atom at the top. The NH-wagging mode vibrates in an umbrella inversion way. There is a barrier to umbrella inversion that the nitrogen atom faces on its travels through the hydrogen plane.$^{25}$ The existence of the barrier results in a splitting of a fundamental vibrational level of the NH-wagging mode into two components at 932.51 ($v_2^+$) and 968.32 cm$^{-1}$ ($v_2^-$), giving rise to the observed absorption peaks at laser wavelengths of 10.719 (932.92 cm$^{-1}$) and 10.35 µm (966.18 cm$^{-1}$), respectively.$^{25-26}$ The strongest absorption peak at 9.219 µm is attributed to a rotational-vibrational transition ($J=5 \rightarrow J'=6$, $K=0$) of the $v_2$ mode at 1084.63 cm$^{-1}$. The perfect match between the CO$_2$ laser wavelength at 9.219 µm (1084.71 cm$^{-1}$) and the rotational-vibrational transition line of the NH$_3$ (1084.63 cm$^{-1}$) makes a stronger absorption at 9.219 µm than that at 10.35 and 10.719 µm. The rotational-vibrational excitation of NH$_3$ molecules at 9.219 µm contributes to dissociating of NH$_3$ molecules at low temperatures.

OES spectrum of the laser-irradiated NH$_3$ under laser irradiation at wavelength of 9.219 µm in open air are shown in Fig. 6.3. Emissions from OH, NH, N$^+$, H$\alpha$, N, and H$\beta$ are observed at 309, 336, 463, 486, 496, and 656 nm, respectively. Strong emissions from NH$_2$ radicals are observed at 525, 543, 569, 603, 629, and 663 nm in all OES spectrum from resonantly excited NH$_3$ flows, indicating effective dissociation of NH$_3$ molecules in room temperature. It worthy to note the N, NH, and NH$_2$ are active nitrogen species for growing GaN. Therefore, OES results indicate that the resonant vibrational excitation effectively dissociates NH$_3$ molecules.
6.3.2 Characterization of GaN films

X-ray diffraction (XRD) 2θ spectra of the GaN films grown at different temperatures (i.e., 150, 250, 350, 450, and 600 °C) are shown in Fig. 6.4. Figs. 6.4(a) and 6.4(b) compare the XRD 2θ patterns of the GaN films grown by LMOCDV and MOCVD, respectively. A XRD peak attributed to the (0002) plane of GaN is observed in the GaN samples grown by LMOCDV at temperatures from 250 to 600 °C. This peak is indexed to wurtzite GaN with a hexagonal structure, indicating the high c-plane orientation of the GaN films. Therefore, it can be confirmed that the synthesis of GaN...
films was achieved at a temperature as low as ~250 °C by the LMOCVD technique with the laser resonant vibrational excitation of NH₃. In contrast, the (0002) diffraction peak was only found for the sample grown by MOCVD at a temperature of 600 °C, suggesting that a much higher substrate temperature is required for the growth of GaN using conventional MOCVD (Fig. 6.4(b)). As shown in Fig. 6.4(a), the intensity of the (0002) peak increases as the substrate temperature increases from 250 to 600 °C. The intensity increase can be attributed to the improved crystalline quality of the GaN films due to the substrate temperature increase.²⁸ Additionally, a 2θ signal at 86° was observed for the GaN film grown at 600 °C with LMOCVD (Fig. 6.4(a)). This (0004) GaN peak also refers to c-axis-oriented GaN films.

![Figure 6.4 X-ray diffraction spectra of the GaN films grown on sapphire substrates at different temperatures (250-600 °C) by (a) LMOCVD and (b) MOCVD.](image)

The XRD φ-scan determined the degree of in-plane alignment of GaN films grown at different temperatures (250-600 °C) by LMOCVD relative to the sapphire substrate, as shown in Fig. 6.5. The scanning planes used for φ-scan were (11-20) for sapphire and hexagonal (10–11) and cubic (200) for GaN films. The diffraction peaks from (10–11) plane of GaN film were observed at intervals of 60° for all samples grown...
at temperatures from 250 to 600 °C, which confirmed the hexagonal structure of the epitaxial GaN films. It is also observed that there is a ~30° rotation of the GaN unit cell with respect to sapphire substrate due to the large lattice mismatch between GaN and sapphire substrate (Fig. 6.5). However, no diffraction peaks from the (200) plane of cubic GaN film were observed for all samples grown at different temperatures (250-600 °C) by LMOCVD (Fig. 6.6).

Figure 6.5 XRD φ-scan of (11-20) plane of sapphire substrate and (10–11) plane of GaN films grown on sapphire at different temperatures (250-600 °C) by LMOCVD.
115

Figure 6.6 XRD phi-scan of (200) plane of GaN films grown by LMOCVD.

The 2θ position and full width at half maximum (FWHM) of (0002) diffraction peaks obtained from XRD are shown in Table 6.1. The FWHM of the (0002) plane reflects lattice distortion from screw dislocations and mixed dislocations.\(^{28}\) As shown in Table 6.1, a small FWHM value of 0.18° was obtained for the GaN sample grown by LMOCVD at 600 °C. For the GaN film grown by MOCVD at 600 °C, the FWHM of (0002) was 0.20°. The distinctive reduction in the FWHM of GaN films deposited by LMOCVD indicates that the laser resonant vibrational excitation of NH\(_3\) leads to a decrease in lattice distortion and improvement in the quality of the GaN films. For the GaN films grown by LMOCVD, the FWHM of the (0002) plane decreased monotonically with the increase in the substrate temperature from 250 to 600 °C (Table 6.1). This means that the crystalline quality of GaN films improves continuously with the increase in the growth temperature, which is explained by the reduction in diffusion
barriers and increase in diffusion rates of Ga and N species as the substrate temperature increases.\textsuperscript{28}

Table 6.1 The GaN (0002) diffraction peak position, FWHM of GaN (0002) peak, GaN growth rates, and the grain size of GaN films grown at different temperatures (250-600 °C).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate temperature (°C)</th>
<th>2θ (°)</th>
<th>FWHM of (0002) (°)</th>
<th>Growth rate (µm/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMOCVD</td>
<td>250</td>
<td>40.55</td>
<td>0.27</td>
<td>0.15</td>
</tr>
<tr>
<td>LMOCVD</td>
<td>350</td>
<td>40.60</td>
<td>0.25</td>
<td>0.60</td>
</tr>
<tr>
<td>LMOCVD</td>
<td>450</td>
<td>40.42</td>
<td>0.21</td>
<td>1.60</td>
</tr>
<tr>
<td>LMOCVD</td>
<td>600</td>
<td>40.40</td>
<td>0.18</td>
<td>12</td>
</tr>
<tr>
<td>MOCVD</td>
<td>600</td>
<td>40.47</td>
<td>0.20</td>
<td>2.60</td>
</tr>
</tbody>
</table>

The effectiveness of laser resonant vibrational excitation of NH\textsubscript{3} on the uniformity and surface morphology of GaN films is clearly shown by the FESEM images shown in Fig 6.7. For the GaN film grown with LMOCVD at 250 °C (Fig. 6.7(a)), small domains of about \(~30 ± 5\) nm with hexagonal facets were obtained. The average domain sizes were \(~65 ± 10\) and \(~100 ± 10\) nm for the GaN films grown by LMOCVD at 350 and 450 °C, respectively (Figs. 6.7(b) and 6.7(c)). With a further increase in the substrate temperature to 600 °C, the lateral size of the islands with hexagonal facets increased. With a coalescence of crystallite islands, GaN structures with flat facets were obtained by LMOCVD at 600 °C, as shown in Fig. 6.7(d). In contrast, the surface of the GaN sample grown at 600 °C by MOCVD was rough with obvious hexagonal hillocks (Fig. 6.7(f)). Additionally, the threshold temperature to grow GaN films by MOCVD is 600 °C. Below this temperature, no GaN deposition is observed on substrate surfaces (Fig. 6.7(e)) that agree with the XRD results.
Figure 6.7 SEM images of GaN films grown by LMOCVD at temperatures of (a) 250, (b) 350, (c) 450, and (d) 600 °C; and SEM images of GaN films grown by MOCVD at temperatures of (e) 450, and (f) 600 °C.

The cross-sectional SEM images of the GaN films were obtained to explore the effect of laser resonant vibrational excitation of NH$_3$ on the growth rate. Figs. 6.8(a) and 6.8(b) show the cross-sectional SEM images of the GaN films grown at 600 °C by LMOCVD and MOCVD, respectively. A growth rate of 12 µm/h was achieved by
LMOCVD, which is \(~4.6\) times faster than that of MOCVD (this work, \(~2.6\ \mu m/h\)). Moreover, compared with the growth rate of GaN synthesized by other studies (MBE: \(~1\ \mu m/h\); and MOCVD: \(~4\ \mu m/h\)),\(^{15-16}\) laser resonant vibrational excitation contributes to a drastic enhancement in the GaN growth rate. Table 6.1 shows the GaN growth rates by LMOCVD at different temperatures from 250 to 600 °C. As the substrate temperature increased, the thickness of the GaN films increased.

Figure 6.8 Cross-sectional SEM images of GaN films grown at 600 °C by (a) LMOCVD (b) MOCVD.

Figure 6.9 EDX spectra of GaN films grown at 600 °C by (a) LMOCVD (b) MOCVD.
The EDX results in Fig. 6.9 confirm the presence of Ga and N elements in the GaN films, as well as carbon (C), oxygen (O), and silicon (Si) as impurities. According to the EDX spectra obtained from GaN films grown at 600 °C by LMOCVD and MOCVD, obvious increases of 7.84% in N concentration and 1.7% in Ga concentration were observed in the sample grown with LMOCVD. The resonant vibrational excitation of the NH bond vibration in NH₃ molecules plays an important role in the dissociation of NH₃ and the increase of N species in the reaction. The increase in N content in the deposited films explains why the GaN growth rate was highly improved using LMOCVD, which is in agreement with other studies.²⁹ Furthermore, it is worthy to note that the impurity content (C, O, and Si) in the GaN film grown with LMOCVD decreased considerably (Fig. 6.9). In MOCVD growth, Ga reacts with impurity elements in the absence of sufficient active N atoms or N-related intermediates. However, laser resonant vibrational excitation of NH₃ in LMOCVD increased the production of active N-related intermediates, eliminating the impurity content incorporated into the film during GaN growth. With the reduction in impurities, the GaN crystal islands grow larger in size, leading to higher crystallinity, a full coalescence, and a smooth surface morphology of GaN films. It is also worthy to note that EDX measurements here just express a semi-quantitative analysis and the values do not reflect actual composition of the GaN films.³⁰ Large concentration of oxygen and carbon in the films is just an artifact resulting from the very low detection efficiency of EDX for light elements.
The PL spectra of GaN films have been acquired using a laser with a wavelength of 325 nm. As shown in Fig. 6.10, two peaks located at ~3.4 and ~3.2 eV are observed in the PL spectra of the samples grown at different temperatures from 250 to 600 °C by LMOCVD. The strong peak at ~3.4 eV is the near band edge (NBE) transition peak, while the weak peak at ~3.2 eV can be attributed to radiative recombination between a shallow donor and the valence band. Another possible reason for the peak at ~3.2 eV can be associated with the formation of small amount of cubic GaN at low temperatures growth. The PL spectra further confirmed the hexagonal structure of the GaN films grown on sapphire substrates at different temperatures from 250 to 600 °C by LMOCVD. The GaN film grown at 600 °C by LMOCVD showed a near-band-edge (NBE) emission at about ~3.398 eV which was closer to the NBE emission of bulk GaN (3.47 eV),
compared to that of MOCVD with ~3.394 eV. The NBE peaks of GaN films grown by LMOCVD at 250, 350, and 450 °C are ~3.388, ~3.391, and ~3.392 eV, respectively.

It is valuable to note that there are several studies of using the polycrystalline GaN films with columnar structures for photonic and electronic devices. In this study, the quality of the polycrystalline GaN films grown at low temperatures by LMOCVD are comparable to those reported values, suggesting a potential of heteroepitaxial GaN film grown by LMOCVD for electronic and photonic applications.

6.4 Conclusions

The LMOCVD technique was developed for low-temperature growth of GaN films on sapphire substrates through laser resonant vibrational excitation of NH₃ molecules. The highly c-oriented GaN films were successfully grown at temperatures as low as 250 °C. Low-temperature growth of GaN films is ascribed to the enhanced decomposition efficiency of NH₃ with resonant excitation of rotational-vibrational transition (1084.71 cm⁻¹) of the NH-wagging mode at the laser wavelength of 9.219 µm. The FWHM of (0002) diffraction peaks obtained from XRD for GaN films grown at 600 °C decreased from 0.20° (MOCVD) to 0.18° (LMOCVD), indicating an improvement in crystalline quality by LMOCVD. SEM images showed that the laser resonant vibrational excitation of NH₃ helped to grow GaN films with smooth and uniform surface morphology. A high GaN growth rate of up to 12 µm/h was achieved at 600 °C by LMOCVD, which is ~4.6 times faster than that of conventional MOCVD with 2.6 µm/h. This approach suggests that the laser resonant vibrational excitation of precursors is promising in increasing NH₃ reactivity and promoting GaN synthesis, which could be extended to synthesis of other nitride semiconductors.
6.5 References


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CHAPTER 7 LMOCVD GROWTH OF HIGH QUALITY GAN EPILAYER

7.1 Introduction

7.2 Methods

7.3 Results and Discussion

7.4 Conclusions

7.5 References
7.1 Introduction

Gallium nitride (GaN) with excellent physical properties, such as wide direct bandgap, high electron mobility and high thermal stability, has been extensively studied and attracted attentions for applications in light-emitting diodes (LEDs), high-power electronic devices and short wavelength optoelectronics.\textsuperscript{1-3} Current commercial GaN-based devices are fabricated by epitaxy onto foreign substrates because the GaN bulk and freestanding substrate technology is still immature.\textsuperscript{4} High-quality GaN are routinely grown by hydride vapor phase epitaxy (HVPE), ammonothermal, molecular beam epitaxy (MBE), and metal-organic chemical vapor deposition (MOCVD).\textsuperscript{5-11} Although HVPE and ammonothermal methods with the advantage of high growth rates have emerged to obtain bulk GaN,\textsuperscript{5-7} they lack the precise control and heterojunction layer growth required for device structures. The overwhelming majority of GaN epilayers and GaN-based devices are grown by MOCVD and MBE.\textsuperscript{8-12} The MOCVD growth rate of GaN epilayers commonly exceeds 1–3 µm/h, while MBE is typically performed with a growth rate up to 1 µm/h.\textsuperscript{8-12} The relatively slow growth rates limit these traditional methods for many device structures that require thick GaN layers. Therefore, synthetic techniques with high growth rates are highly in demand for the scalable production of high-quality GaN epilayers to satisfy the steadily increasing requirement, since it can help reducing the cycle time in device fabrication.

Laser-assisted MOCVD (LMOCVD) is an ideal method for various material growth with advantages of low growth temperature, fast growth rate, and the capability to deposit patterned materials.\textsuperscript{13-17} Several semiconductor materials, including silicon, gallium arsenide, indium phosphide, and aluminum nitride, have been successfully grown
using the LMOCVD.\textsuperscript{13-17} For instance, Zhou \textit{et al.}\textsuperscript{18} reported ultraviolet laser LMOCVD growth of GaN at low temperatures, leading to films having (0002) preferential orientation with a broad XRD peak. However, the photolysis of the precursors with UV laser resulted in the low density of the reactive radicals and a low GaN growth rate. On the other hand, CO\textsubscript{2} laser LMOCVD has been successfully used to prepare various kinds of thin films at high growth rates.\textsuperscript{16,19-25} For example, Iwanaga \textit{et al.}\textsuperscript{19} reported the deposition of large-area amorphous silicon films using CO\textsubscript{2} laser LMOCVD with a high growth rate of > 60 µm/h in a relatively low laser power and low substrate temperatures. In chapter 6, we have demonstrated the fast growth of GaN films with (0002) preferential orientation using CO\textsubscript{2} laser LMOCVD with a growth rate up to 84 µm/h at low temperatures,\textsuperscript{23} where the experiments were designed to elucidate the GaN growth mechanism via CO\textsubscript{2} laser LMOCVD rather than to optimize the material crystalline quality. The high GaN growth rate is due to the mixed photolysis/pyrolysis reactions of the precursors and the photo-induced effects, as has been evidenced by wavelength dependence of GaN growth rates.\textsuperscript{22-24} However, the low-temperature deposition resulted in films with broad XRD peaks and low crystalline quality.\textsuperscript{19,22} It has been reported that the deposition of high-quality GaN films, which is preferred for device applications, requires high growth temperatures.\textsuperscript{26-29}

In this chapter, we successfully demonstrated the fast growth of high-quality GaN epilayers on sapphire substrates with a high growth rate of 25.8 µm/h using an optimized CO\textsubscript{2} laser LMOCVD method. The growth of GaN epilayers followed previously documented two-step growth steps,\textsuperscript{30} including a thin three dimensional (3D) GaN layer growth, lateral growth and coalescence of the 3D layer and, finally, quasi-two
dimensional (2D) growth at high temperatures. The growth rate of 25.8 µm/h is 8.6 times higher than that has been used in GaN epilayers by traditional MOCVD.\textsuperscript{11,12} This work provides a simple and cost-effective way to realize fast and high-quality GaN epilayer growth with high potential in GaN-based optoelectronic applications.

![Figure 7.1 Schematic of the experimental setup of CO\textsubscript{2} laser LMOCVD system.](image)

### 7.2 Methods

#### 7.2.1 Growth of GaN layers

The growth of GaN layers on c-plane (0001) orientation sapphire substrates was performed in a home-made vertical LMOCVD system. The schematic experimental setup of the LMOCVD system is shown in Fig. 7.1. Trimethylgallium (TMGa) and ammonia (NH\textsubscript{3}) were used as the Ga and N precursors, respectively. Prior to the GaN growth, a thin Si layer was coated on sapphire as thermal conductive layer to absorb laser energy. Then, 1 × 1 cm\textsuperscript{2} sapphire substrates were successively cleaned in piranha and 15% HCl solution, and then loaded into the LMOCVD reactor. A continuous-wave (CW) and wavelength-tunable CO\textsubscript{2} laser (PRC Inc., λ = 9.201 µm) was used for substrate heating. A
flat-top laser beam shaper (Edmund Optics) was used to generate a beam with a uniform power distribution (output beam diameter ~ 20 mm) from a Gaussian CO$_2$ laser beam (Fig. 1a), in order to realize a uniform substrate temperature for material growth with controlled crystal orientations. The chamber pressure during the growth process was kept at ~ 10 Torr. A two-step growth process was used for growing high-quality and smooth GaN layers without using AlN buffer layers. NH$_3$ (26 mmol/min) and TMGa (20 μmol/min) were introduced simultaneously into the reactor chamber after the substrate temperature was stable under laser irradiation. The growth process started with deposition of a very thin 3D GaN layer for 10 second at 700 °C (laser power ~ 95 W). The growth was then interrupted and the 3D GaN layer was annealed at 990 °C for 5 min (laser power ~ 160 W) under NH$_3$ with a flow rate of 26 mmol/min. The subsequent growth of unintentionally doped GaN epilayer was carried out for 10 min at substrate temperatures ranging from 930 to 990 °C by adjusting the laser power. The substrate temperature during the growth was monitored using a pyrometer (Omega, OS3752).

7.2.2 Characterization

The morphology of GaN layers was examined by scanning electron microscopy (SEM, S4700) and atomic force microscopy (AFM, Bruker Dimension ICON SPM). The structural properties of GaN layers were investigated using transmission electron microscopy (TEM, FEI Tecnai OsirisTM), high-resolution X-Ray diffraction (HR-XRD), and Raman spectroscopy. High-resolution TEM (HRTEM) was performed in a FEI Tecnai OsirisTM instrument operated at 200 kV. Cross-sectional TEM samples were prepared using a FEI Helios NanoLab 660 FIB/SEM. To minimize ion beam damage to the surface of the top layer (GaN), a 20 nm-thick Ti coating was deposited on the GaN
surface prior to FIB processing. Bulk milling of the sample was performed using a 30 keV Ga+ beam and polishing step was done using a 10 keV Ga+ beam. The approximate thickness of the final lamellae, mounted on Cu grids, was 60-100 nm. HR-XRD measurements were performed using Rigaku Smart Lab Diffractometer with Cu Ka1 radiation (λ = 1.5406 Å). Raman spectra were recorded using a Raman microscopy (Renishaw inVia H 18415, Argon ion laser, λ = 514.5 nm). Hall effect measurements were carried out via the Van der Pauw method at room temperature. Optical transmission data were collected using a Perkin-Elmer LAMBDA 1050 UV/Vis/NIR spectrophotometer.

Figure 7.2 (a) Cross-sectional SEM image of the ~ 4.3 μm thick GaN epilayer grown on a sapphire (0001) substrate at 990 °C for 10 min. (b) A comparison of growth rate between different techniques used for growth of high-quality GaN.

7.3 Results and discussion

The cross-sectional SEM image in Fig. 7.2 is a typical LMOCVD GaN sample grown at 990 °C for 10 min, which shows a very sharp interface between GaN and sapphire substrate. The thickness of GaN epilayers was measured to be ~ 4.3 μm, corresponding to a growth rate of ~ 25.8 μm/h which was much higher compared to the
conventional MBE (~ 1 μm/h) and MOCVD (~ 3 μm/h) techniques for GaN epilayer growth (Fig. 1c). In addition, the overall processing time for LMOCVD was less than 20 min, but not several hours as required for the HVPE, ammonothermal, MOCVD, and MBE techniques.

Morphological evolution of GaN during the growth process was investigated, as shown in Fig. 7.3. In step 1, very thin GaN 3D islands were grown at 700 °C. With annealing at 990 °C for 5 min under NH₃ flow, the GaN islands grew up laterally, and started to coalesce gradually. In step 2, with increasing of growth time at high temperature (HT), the GaN islands increased in sizes and grew into a continuous and smooth film followed by a rapid coalescence. Figs. 7.3a and 7.3b show the top view of GaN islands after 30 and 90 s HT growth, respectively. It is notable that the size and height distribution of the GaN islands are rather uniform after 90 s. The coalescence of GaN islands with a smooth surface was completed after ~ 120 s HT growth, and inverted hexagonal pyramid pits were formed, diminishing and disappearing eventually (not shown here). Fig. 7.3c shows the SEM image of the GaN epilayers after 10 min HT growth. It is clear that very smooth GaN surface is obtained and 2D step growth mode is dominant over the entire substrate.
Figure 7.3 Morphological characterization of GaN epilayers grown on sapphire substrates. SEM plan views of GaN during growth process: (a) GaN islands after 30 s HT growth, (b) GaN islands after 90 s HT growth, and (c) GaN epilayers after 10 min HT growth.

The AFM images of 2×2 µm² surface area of fully coalesced GaN epilayers in Fig. 7.4 shows excellent dislocation-mediated step-flow morphology with spiral hillocks, which is similar to that of high-quality GaN grown by MOCVD and MBE methods at much lower growth rates. AFM measurement further reveals that the surface root-mean square (RMS) roughness for GaN layers grown at 990 °C is as small as 1.892 nm, slightly higher than that of reported works with much lower growth rates. This flat GaN surface is of paramount importance for the fabrication of high-performance GaN-based optical and optoelectronic devices. The RMS roughness for GaN layers grown at
930 and 960 °C with identical growth conditions was calculated to be 1.103 and 1.253 nm (Figs. 7.4a and 7.4b), respectively, revealing a smoother GaN growth at relatively lower temperatures in this work.

![AFM images of GaN epilayers grown on sapphire substrates at different temperatures](image)

**Figure 7.4** AFM images of GaN epilayers grown on sapphire substrates at (a) 930 °C, (b) 960 °C and (c) 990 °C for 10 min.

The cross-sectional TEM image of the GaN layers grown at 990 °C, sapphire substrate and GaN/sapphire hetero-interface are shown in Fig. 7.5a to c, respectively. It is observed that the as-grown GaN layer has a single-crystalline structure with an epitaxial layer even at the GaN/sapphire hetero-interfaces. The lattice fringes with a spacing of ~ 0.517 nm correspond to the GaN c-plane interplanar distance, indicating that the epitaxial layer is c-plane oriented. All the (0002) lattice fringes appear parallel to the substrate.
surface. Fig. 7.5d shows the selected-area electron diffraction (SAED) pattern for GaN epitaxial layer, further revealing the single crystal array of spots indexed to the (0002) of wurtzite GaN. The regularity of the atomic arrangement and the absence of a diffuse streak from the SAED pattern indicate the high quality of the crystalline phase.34

Figure 7.5 Structural characterization of GaN epilayers grown on sapphire substrates at 990 °C. High-resolution cross-sectional TEM image of (a) GaN epilayer, (b) sapphire substrate and (c) the GaN/sapphire hetero-interface. (d) Selected-area diffraction pattern for the GaN epilayer.
Figure 7.6. Crystallographic characterization of GaN epilayers grown on sapphire with respect to growth temperatures ranging from 930 to 990 °C. (a) X-ray 2θ scan. (b) X-ray φ scan. (c) XRC curves of the GaN (0002) peak. (d) Temperature dependence of the dislocation density (■) and XRC (0002) FWHM (●) for the GaN epilayers grown on sapphire.

XRD was performed to study the structural properties of the GaN epilayers grown on sapphire. Fig. 7.6a is a typical XRD 2θ scan for the GaN films on sapphire grown at different temperatures. Two peaks at around 34.51 and 72.64 were observed in each spectrum, which correspond to the wurtzite GaN (0002) and (0004) reflections, respectively. Therefore, the out-of-plane epitaxial relationship of GaN (0001)/sapphire can be determined for these samples. Furthermore, it can be seen that the intensity of GaN (0002) and (0004) is gradually increased and the peaks become sharper as the GaN
growth temperature increases from 930 to 990 °C, revealing the improved crystalline quality of the GaN films at higher temperatures.

To evaluate the in-plane epitaxial relationship between the GaN films and the sapphire substrates, XRD $\phi$ scan was conducted while 2$\theta$ was kept constant at the peak position and the sample was rotated 360° around the surface normal. Fig. 7.6b shows the normalized $\phi$ scans of GaN (10-12), where six-fold rotational peaks with an interval of 60° can be clearly identified for all samples. The variation in the peak intensity versus $\phi$ is obvious for each diffraction due to the noncoplanarity of the beam vector and the surface normal, which is very common in practice. A quantitative comparison of the peak intensity among samples grown at different temperatures was not undertaken, because in thin films with strong preferential orientation, the diffraction intensity of the planes parallel to the surface is extremely sensitive to the sample orientation. Both the XRD 2$\theta$ and $\phi$ scan results clearly confirm that single-crystalline hexagonal GaN epilayers have been grown on the sapphire substrates at temperatures ranging from 930 to 990 °C.

X-ray rocking curve (XRC) is a valid method to determine the crystalline quality of GaN films. The full-width at half-maximum (FWHM) of XRC for the (0002) peak is usually used to evaluate the screw treading dislocations density (TDD), while the FWHM of XRC for (10-12) peak corresponds to the lattice distortion from all components of the TDDs, including edge and screw dislocations. Fig. 7.6c compares the GaN (0002) XRCs for the GaN epilayers grown on the sapphire substrates at different temperatures. The FWHM values of the GaN (0002) and (10-12) planes were summarized in Table 7.1. For the sample grown at 930 °C, the FWHMs of the GaN (0002) and (10-12) planes were
measured to be 396 and 471 arcsec, respectively. Both values monotonously decreased to 324 and 443 arcsec for the sample grown at 960 °C, and further decreased to 313 and 390 arcsec for the sample grown at 990 °C, indicating that the GaN layers grown at higher temperature correspond to higher purity and crystalline quality. Note that the low FWHM values obtained at 990 °C are also comparable to those of GaN layers grown on sapphire using the conventional MOCVD and MBE technique.\textsuperscript{37} We have estimated the dislocation density existing in the GaN layers grown on sapphire at various growth temperatures using the following equation:\textsuperscript{36}

\begin{equation}
D_{\text{screw}} = \frac{\beta(0002)^2}{9b_{\text{screw}}^2}, \tag{7.1}
\end{equation}

\begin{equation}
D_{\text{edge}} = \frac{\beta(10-12)^2}{9b_{\text{edge}}^2}, \tag{7.2}
\end{equation}

\begin{equation}
D_{\text{Total}} = D_{\text{screw}} + D_{\text{edge}}, \tag{7.3}
\end{equation}

where $D_{\text{screw}}$ and $D_{\text{edge}}$ are the screw dislocation and edge dislocation density, respectively. $\beta$ is the FWHM value measured from XRC (0002) and (10-12) planes in degrees and $b$ is the Burgers vector length ($b_{\text{screw}} = 0.5185$ nm, $b_{\text{edge}} = 0.3189$ nm) for GaN. Fig. 7.6d shows the temperature dependence of dislocation density in the as-grown GaN epilayers. The estimated total dislocation densities $D_{\text{Total}}$ for the samples grown at 930, 960 and 990 °C are $8.1\times10^8$, $6.6\times10^8$ and $5.9\times10^8$ cm$^{-2}$, respectively. These findings further indicate that the LMOCVD GaN layers grown at higher temperatures have relatively lower crystalline defects.

Raman spectroscopy has been widely used to evaluate the quality and residual stress of nitride films.\textsuperscript{35} Fig. 7.7a shows the room-temperature Raman spectra of GaN films grown at different temperatures. Two prominent phonon modes which are Raman
active, $E_2$ (high) and $A1$ (LO) modes, are observed in each spectrum, where $E_2$ (high) phonon is used to characterize the in-plane stress state of the GaN films. The stress can be calculated by

$$\sigma = \frac{\Delta \omega}{4.3 \text{ (cm}^{-1} \text{ GPa}^{-1})}$$

(7.4)

where $\sigma$ is the biaxial stress and $\Delta \omega$ is the $E_2$ (high) phonon peak shift. The $E_2$ (high) phonon of stress-free GaN is around 567.6 cm$^{-1}$. The $E_2$ (high) phonon modes obtained from GaN films grown at 930, 960 and 990 °C are located at 568.7, 571.5 and 570 cm$^{-1}$, respectively. The $E_2$ (high) mode peaks for all the samples blue-shift compared to that of stress-free GaN, which indicates that all the GaN films are under compressive stress, as predicted for the GaN grown on sapphire substrates. It is known most of the film stresses arise during sample cooling-down after growth.

Fig. 7.7b compares the measured compressive stresses in the GaN films grown at different temperatures. The GaN sample grown at 930 °C shows less in-plane compressive stress compared with the samples grown at higher temperatures of 960 and 990 °C. Additionally, the FWHM values of the $E_2$ (high) peak for GaN epilayers decreased with the increase in the growth temperature, further indicating of high crystalline quality of GaN epilayers obtained at higher growth temperatures.
Electrical and optoelectronic properties of the GaN epilayers were also investigated (Fig. 7.8). Room-temperature Hall effect measurements were performed to study the electrical property of the GaN epilayers, as shown in Fig. 7.8a and Table I. We found that as the growth temperature increases from 930 to 960 and 990 °C, the mobility increases from 226 to 293 and 369 cm² V⁻¹ s⁻¹ and the carrier concentration decreases from $8.4 \times 10^{16}$ to $5.3 \times 10^{16}$ and $3.1 \times 10^{16}$ cm⁻³, respectively. The mobility measured in our study is comparable to those reported in several studies for high-quality GaN films deposited using MOCVD and MBE at high temperatures. The observed mobility increase with the increased temperature was also reported in the MOCVD GaN films. This can be attributed to the increased film thickness and the improved crystallinity, namely, the crystal defects in the GaN films affect their mobility by scattering the charge carriers.
The optical transmission and absorption spectra of GaN epilayers grown at 990 °C are shown in Fig. 7.8b. The absorption coefficient was derived from spectrophotometry in transmission mode (Fig. 7.8c). The band gap, $E_g$, of semiconductors with direct band gaps can be estimated using the following equation:\footnote{46}

$$\alpha^2 \sim (h\nu - E_g),$$

(3)

where $\alpha$ is the absorption coefficient, $h$ is the Plank’s constant, $\nu$ is the frequency, and $E_g$ is the semiconductor band gap.\footnote{46} The value of optical band gap can be
approximated from a linear extrapolation of square absorption, $a^2$, to the point of interception with the photon energy axis (Fig. 5c). As shown in the inset of Fig. 5c, the extracted band gaps, $E_g$, for GaN epilayers grown at 930, 960 and 990 °C are 3.36, 3.39 and 3.38 eV, respectively. These values are slightly smaller than that of bulk GaN.

Although high crystalline quality GaN epilayers have been realized based on CO$_2$ LMOCVD, there are still some issues to address for the industrialization of GaN epilayer growth via LMOCVD technique. For instance, when compared with MOCVD and MBE techniques, the size of GaN samples grown by LMOCVD are relatively small due to the relatively small beam size (20 mm in diameter). By adding a beam expander, laser beams could be extended to cover the whole wafers as well as maintain the required laser fluence for GaN growth, based on which LMOCVD technique is feasible for wafer-scale GaN growth. However, further optimization and design improvement are still required to achieve GaN epi-structures with a homogeneous thickness and quality over the whole wafers. Overall, the CO$_2$ LMOCVD proposed in this work is a simple and low-cost method for fast and high-quality GaN epilayer growth, and might bring up a broad application in future electronics and optoelectronics.

Table 7.1 Summary of characteristics of the LMOCVD GaN epilayers grown on sapphire at different temperatures

<table>
<thead>
<tr>
<th>No.</th>
<th>Temp. (°C)</th>
<th>RMS (nm)</th>
<th>Bandgap (eV)</th>
<th>$E_{2H}$ (cm$^3$)</th>
<th>$\sigma$ (Gpa)</th>
<th>(0002) FWHM (arcsec)</th>
<th>(10-12) FWHM (arcsec)</th>
<th>Dislocation density (cm$^2$)</th>
<th>Mobility (cm$^2$/Vs)</th>
<th>Carrier concentration (cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>930</td>
<td>1.103</td>
<td>3.36</td>
<td>568.7</td>
<td>0.26</td>
<td>396</td>
<td>471</td>
<td>8.1E8</td>
<td>226</td>
<td>8.4×10$^{16}$</td>
</tr>
<tr>
<td>II</td>
<td>960</td>
<td>1.253</td>
<td>3.39</td>
<td>571.5</td>
<td>0.82</td>
<td>324</td>
<td>443</td>
<td>6.6E8</td>
<td>293</td>
<td>5.3×10$^{16}$</td>
</tr>
<tr>
<td>III</td>
<td>990</td>
<td>1.892</td>
<td>3.38</td>
<td>570</td>
<td>0.47</td>
<td>313</td>
<td>390</td>
<td>5.9E8</td>
<td>369</td>
<td>3.1×10$^{16}$</td>
</tr>
</tbody>
</table>
7.4 Conclusions

In conclusion, we have demonstrated the rapid growth of high-quality GaN epilayers with an extremely high growth rate of ~25.8 µm/h via a CO₂ laser-assisted MOCVD method. It is found that the substrate temperature plays an important role in different aspects of GaN film growth, including morphology, structural evolution, electrical and optical properties. The surface morphology of LMOCVD GaN films demonstrates no degradation of the growth mode, maintaining a dislocation-mediated step-flow growth with RMS roughness of ~1.9 nm. For the GaN sample grown at 990 °C with high growth rates, the FWHM in rocking curve ω-scan for GaN (0002) line and (10-12) line are, 313 and 390 arcsec, respectively, suggesting its high purity and high crystalline quality. Raman measurement shows the presence of biaxial compressive stress in the as-grown GaN layers. These results demonstrate that LMOCVD technique can produce high-quality GaN epilayers with fast growth rates, opening a new pathway for nitride related materials fabrication used for next-generation electronics and optoelectronics.
7.5 References


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CHAPTER 8 BACK-TO-BACK SCHOTTKY METAL-SEMICONDUCTOR-METAL (MSM) PHOTODETECTOR ON LMOCVD-GROWN GAN FILMS

8.1 Introduction

8.2 Experimental Details

8.3 Results and Discussion

8.4 Conclusions

8.5 References
8.1 Introduction

In this chapter, the optical quality of as-grown GaN layers by CO\textsubscript{2} laser LMOCVD in chapter 7 are further evaluated by fabricating ultraviolet (UV) photodetector. The performance of GaN-based UV detectors is highly dependent on the crystallinity of GaN films.\textsuperscript{1-4} It has been reported that threading dislocation has an adverse effect on the performance of GaN photodetectors, including dark current and responsivity.\textsuperscript{1-4}

The GaN-based material system is appropriate for photodetection applications operated in the 200–365 nm wavelength range because of its tunable wide direct bandgap. In addition, nitride-based photodetectors also have the advantages of being solid-state and small in size, with good chemical and thermal stability, and having long lifetimes. GaN UV photodetectors have obtained increasing interest with various applications, such as flame monitoring, biomedicine, and UV astronomy.\textsuperscript{5-7} These photodetectors are suitable for harsh environments with chemically inert properties.

GaN-based detectors with a variety of device structures, including Schottky-type\textsuperscript{8-10}, metal-semiconductor-metal (MSM)-type\textsuperscript{1,2,11-13}, and p--i--n type.\textsuperscript{14-16} With a high response speed and low dark current characteristics, GaN MSM photodetector has attracted more attentions for UV photodetection applications as compared to GaN photodetectors with other device structures. Additionally, with no n- and p-type doped layers, GaN MSM device has simple fabrication processes (inset in Fig. 8.1).\textsuperscript{17,18} Normally, MSM structures can use either back-to-back Schottky contacts or back-to-back ohmic contacts during photoconductive operation and cannot operate under 0 V bias.\textsuperscript{1-3} Schottky contact photodetector is appropriate for applications with fast response speeds
and low dark current, while the ohmic contact photoconductor is suitable for high photosensitivity applications. Our devices in this chapter are Schottky-contact MSM-type detectors.

Figure 8.1. Schematic device structure of GaN MSM detector with Ni/Au contacts.

8.2 Experimental details: device fabrication and characterization

The undoped GaN epilayer used in our devices was grown on c-plane sapphire substrates at different temperatures 930, 960 and 990 °C by CO₂ laser MOCVD. The details of the crystal growth process have been reported in chapter 7. The sample was prepared before processing by first using standard solvent clean, then dipping in boiling aqua regia (3HCl : 1HCl) then buffered oxide etch (BOE) to remove any native oxide. GaN devices were fabricated using a standard photolithography: 1) patterning of photoresist, 2) deposition of Ni/Au (100 nm/20 nm) Schottky contact via magnetron sputtering, and 3) liftoff to form Schottky contacts (50 μm long, 10 μm wide with a spacing of 10 μm) on the GaN. Before electrical measurement, annealing treatment of GaN MSM devices was performed at 500 °C for 5 min in rapid thermal processing (RTP) furnace. The current-voltage (I-V) measurements of the GaN UV photodetectors were carried out using a Keithley 237 electrometer. Photoresponse measurements were
realized by using a Xe arc lamp with power of 150 W as UV light source. External quantum efficiency (EQE) measurement was performed by using an incident monochromatic light beam directed onto the photodetector and the data was collected via a Newport QE measurement kit. Transient response measurements were taken using a 337 nm, 4 ns pulsed laser as light source, and voltage variations were collected using an oscilloscope (LeCroy WaveRunner). All measurements were conducted at room temperature.

![I-V curves of GaN MSM photodetectors](image)

Figure 8.2. I-V curves of GaN MSM photodetectors fabricated on CO₂ laser LMOCVD GaN epilayers grown at (a) 930 (b) 960 and (c) 990 °C under light intensity of 0.1 mW cm⁻² (red) and in dark (black). (d) Dark I-V characteristics of GaN detectors fabricated on GaN epilayers grown at different temperatures of 930 (device A), 960 (device B) and 990 °C (device C).
8.3 Results and discussion

Fig. 8.2 compares the current-voltage (I-V) characteristics of the MSM photodetector fabricated on CO\textsubscript{2} laser LMOCVD GaN epilayers grown at different substrate temperatures under light and in dark (light intensity \( \sim 0.1 \text{ mW cm}^{-2} \)). The device dark currents were \( 1.96 \times 10^{-6}, 1.3 \times 10^{-6}, \) and \( 2 \times 10^{-7} \) A at a bias voltage of -5 V and increased to \( 7.7 \times 10^{-6}, 1.05 \times 10^{-5}, \) and \( 1.2 \times 10^{-5} \) A under light irradiation for GaN samples grown at 930, 960 and 990 °C, respectively, indicating a highly UV-sensitive photoconduction. The dark currents of devices are quite low like that of best GaN UV detectors reported previously with the same device structures.\textsuperscript{1-4}

The dark current of MSM photodetectors was investigated, where they showing nearly symmetrical characteristics and for forward biases the dark current was almost the same, indicating that a good Schottky contact have been formed between the GaN epilayer and Ni/Au metal contact. However, the dark current values of the MSM photodetectors were different from one to another at given reverse biases. Fig. 8.2d displays the dark current of the three typical GaN-based MSM UV photodetector samples, A, B and C fabricated on LMOCVD GaN epilayers grown at different temperatures of 930, 960 and 990 °C, respectively. The dark current values of the three samples follows a sequence of \( C < B < A, \) which the lowest one is for the GaN sample grown at higher temperatures. Comparing the main parameters of the three samples as listed in Table 8.1, they have almost the same carrier concentrations but different dislocation densities, and both screw and edge dislocation densities of the samples are consistent with \( C < B < A. \) These results suggest that the lower dislocation densities are, then the lower the dark current is in the GaN MSM photodetectors. It has been reported that the dislocations are the paths of carrier
transportation and has a strong influence on the dark current of the GaN detectors.\textsuperscript{3,4}

Figure 8.3. EQE spectra of GaN MSM photodetectors fabricated on CO\textsubscript{2} laser LMOCVD GaN epilayers grown at (a) 930 (b) 960 and (c) 990 °C under reverse bias from -5 to 0 V. (d) A comparison between peak EQE and responsivity of the detectors fabricated on GaN epilayers grown at different temperatures.

Fig. 8.3 shows the EQE of UV detectors measured at different reverse biases. The devices show a high sensitivity and high responsivity in the UV range that is near the band edge of GaN. However, EQE is quickly reduced with either decreasing or increasing wavelength, which is attributed to the increased electron-hole recombination and the reduced photo-penetration depth.\textsuperscript{1-4} The EQEs are lower than 5 % at zero bias, and increase sharply with the increase in reverse bias and reach to 36, 38 and 40 % at a bias voltage of -5 V for photodetectors fabricated on LMOCVD GaN epilayers grown at 930,
960 and 990 °C, respectively. The sharp increase of EQE versus reverse bias voltage corresponds to the rapid increase in photocurrent. The responsivity ($R$) of the device can be measured according to the following equation:\cite{19}

$$R = \frac{EQE}{hc/\lambda}, \quad (8.1)$$

where $h$ is the Planck’s constant, $c$ is the speed of light, and $\lambda$ is the wavelength of light. The responsivity peak values of 0.108, 0.115, and 0.12 AW$^{-1}$ were obtained at reverse bias voltage of 5 V for photodetectors fabricated on LMOCD GaN epilayers grown at 930, 960 and 990 °C, respectively. These values are comparable to that of commercial GaN UV photodetectors with value in the range of 0.1 to 0.2 AW$^{-1}$.\cite{20,21} It is found the responsivity of the photodetectors decreases with increasing dislocation densities. The maximum responsivity is for the device fabricated on GaN epilayers grown at 990 °C with lowest dislocation densities and highest crystalline quality.

According to the results in Table 8.1, the electron mobility of the three GaN samples grown at different temperatures are very different. The electron mobility of the undoped GaN epilayer decreases with the increase of the dislocation densities. Among the three undoped samples, the dislocation densities of sample C is the lowest and correspondingly the electron mobility is the highest. This phenomenon can be interpreted that the dislocation acts as charge defect traps in the GaN and these charge defect traps can increase the recombination probability of photogenerated electron-hole pairs and thus reduce the responsivity of GaN-based MSM photodetectors.\cite{4} Additionally, since the photocurrent in these MSM photodetectors primarily comes from the drift current, the negatively charged scattering center may have a strong influence on the photogenerated
holes. This may be another reason why the responsivity of the GaN-based MSM photodetectors becomes lower as dislocation density increases.

![Figure 8.4 Typical transient photocurrent curve of GaN MSM photodetectors fabricated on CO₂ laser LMOCVD GaN epilayers grown at (a) 930 (b) 960 and (c) 990 °C under reverse bias of -5 V measured with a 337 nm 4 ns-pulse laser as the light source. (d) A comparison between response time and cut-off frequency of the detectors fabricated on GaN epilayers grown at different temperatures.](image)

Table 8.1 Summary of characteristics of MSM photodetectors fabricated on the LMOCVD GaN epilayers grown on sapphire at different temperatures.

<table>
<thead>
<tr>
<th>Sample No</th>
<th>GaN Grown Temp. (°C)</th>
<th>Bandgap (eV)</th>
<th>Dislocation density (cm²)</th>
<th>Mobility (cm²/vs)</th>
<th>Carrier concentration (cm²)</th>
<th>Resistivity (mΩ-cm)</th>
<th>Dark Current (A)</th>
<th>Peak Responsivity (AW⁻¹)</th>
<th>Response Time (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>930</td>
<td>3.36</td>
<td>8.1E8</td>
<td>220</td>
<td>8.4×10¹⁵</td>
<td>19</td>
<td>1.96E-6</td>
<td>0.108</td>
<td>168</td>
</tr>
<tr>
<td>B</td>
<td>960</td>
<td>3.39</td>
<td>6.6E8</td>
<td>299</td>
<td>5.3×10¹⁵</td>
<td>11</td>
<td>1.30E-6</td>
<td>0.115</td>
<td>147</td>
</tr>
<tr>
<td>C</td>
<td>990</td>
<td>3.38</td>
<td>5.9E8</td>
<td>365</td>
<td>3.1×10¹⁵</td>
<td>9</td>
<td>0.20E-6</td>
<td>0.12</td>
<td>125</td>
</tr>
</tbody>
</table>
Finally, the response speed of the GaN UV photodetectors was measured by transient photocurrent method using a 337 nm pulsed laser with the pulse width less than 4 ns as the light source. Fig. 8.4 shows the response curves of the GaN photodetectors under a reverse bias voltage of -5 V. By fitting the photocurrent decay curve with the single exponential decay function, the response time of the devices was derived to be 168, 147 and 125 ns for photodetectors fabricated on LMOCVD GaN epilayers grown at 930, 960 and 990 °C, respectively, revealing a fast response speeds. It has been reported that the response time of the device should be limited by the resistor-capacitor time constant but not the GaN crystallinity or carrier mobility. Therefore, the theoretical charge transit time of the UV photodetector was evaluated using the equation below:\textsuperscript{22,23}

\begin{equation}
t_e = \frac{L^2}{2 \mu_e V}
\end{equation}

where \( \mu_e \) is the carrier mobility, \( t_e \) is the charge transit time, \( L \) is the electrode gap spacing, and \( V \) is the applied bias. Based on the above equation, an increase in \( V \) leads to reduction of \( t_e \), and thus the gain subsequently increases linearly. Using electron mobility measured for the GaN epilayers, \( L = 10 \mu m \), and the applied voltage 5 V, the \( t_e \) was calculated to be 0.183, 0.134 and 0.11 ns, which was much lower than the measured response times of 168, 147 and 125 ns, respectively. The fastest response speed is for device fabricated on LMOCVD GaN epilayers grown 990 °C with highest crystalline quality and carrier mobility. Based on the measured response time of 125 ns, its 3-dB cut-off frequency \( (f_{3\text{dB}}) \) can be calculated by

\begin{equation}
f_{3\text{dB}} = \frac{0.35}{t_e}, \text{ }^{22,23}
\end{equation}
where $t_r$ is the response time of the device. The 3-dB cut-off frequency of the UV GaN detectors were calculated to be 2.1, 2.4 and 2.8 MHz. Overall, the responsivity of 0.12 AW$^{-1}$, fast response time of 125 ns and 3-dB cut-off frequency of 2.8 MHz for the GaN UV detector are comparable to those of previously reported,$^{1-4}$ indicating the excellent optical properties of LMOCVD GaN layers grown with high growth rates.

### 8.4 Conclusions

In conclusion, we have reported the growth and characterization of back-to-back Schottky MSM UV photodetectors on LMOCVD-grown GaN films. The dark current, responsivity and, response speed of GaN UV detectors are comparable to those of commercial devices, indicating the excellent optical properties of LMOCVD GaN layers. We have also investigated the effect of GaN crystallinity and TDs on the property of GaN-based MSM photodetectors. It is found that the dark current of the GaN photodetectors increases with increasing TDs and the responsivity of the photodetectors decreases with increasing TDs. The best performance was obtained for device fabricated on LMOCVD GaN epilayers grown at 990 °C with highest crystalline quality and carrier mobility. Low dark current as low as $2 \times 10^{-7}$ A and peak quantum efficiency as high as 40% was achieved at -5 V bias. The quantum efficiency showed a bias dependence, which are postulated to be due to the bias dependence of the depletion region width and corresponding electric field inside the space gap. Initial time-domain pulse response measurements show a 3-dB cut-off frequency of 2.8 MHz. These results demonstrate that LMOCVD technique can produce high-quality GaN epilayers with fast growth rates, opening a new pathway for nitride related materials fabrication used for next-generation electronics and optoelectronics.
8.5 References


CHAPTER 9 SUMMARY AND FUTURE DIRECTIONS

9.1 Summary

9.2 Future Directions

9.3 References
9.1 Summary

This dissertation mainly focused on laser incorporation in metal organic chemical vapor deposition of gallium nitride films, which led to: 1) rapid growth of m-plane gallium nitride nanoplates 2) promotion of energy coupling efficiency and enhancement of gallium nitride deposition; 3) low-temperature growth of gallium nitride films; 4) fast growth of gallium nitride epilayers; and 5) realization of ultraviolet photodetectors based on the as-grown gallium nitride layers. Infrared-laser excitations of precursor molecules were used to assist the conventional MOCVD for promoting the GaN growth. In this dissertation, the different irradiation geometries were employed in LMOCVD growth of GaN. With a perpendicular laser-beam irradiation, the gas was excited and the substrate surface was heated up. While, with a parallel incidence related to the substrate surface, lasers permit pure gas-phase excitations, leaving the substrate cold.

The interlinked m-plane-oriented GaN nanoplates were rapidly grown on Si substrates using the LMOCVD method in perpendicular irradiation geometries. The FESEM and HRTEM images confirmed the formation of m-plane GaN nanoplates. The growth direction of GaN nanoplates was found to be the direction <10-10>. The A1 (TO) mode of Raman further confirmed the m-plane orientation of the GaN nanoplates. The high deposition rate, low-growth temperature, and repeated growth on the different facets of the nanoplates resulted in the formation of m-plane-oriented interlinked GaN nanoplates. Therefore, the L-MOCVD is a suitable technique for the rapid growth of m-plane-oriented GaN nanoplates on Si substrate at low-growth temperatures.

Vibrational excitations of NH3 molecules were studied using a tunable CO2 laser in growing crystalline GaN films on Si (100) substrates. The resonant vibrational
excitation at 9.219, 10.350, and 10.719 µm were more efficient than nonresonant excitation in dissociating NH$_3$ molecules and enhancing the GaN deposition rate and quality. The OES results showed the resonant excitation of the NH-wagging modes modifies the synthesis process in a way that increases the supplies of NH, NH$_2$, N, N$^+$, and H. This leads to the enhancement in GaN deposition rates and improvement in crystalline quality. The extremely high GaN growth rate of ~ 84 µm/h with an improved crystalline quality was achieved under the resonant excitation at 9.219 µm. The red-shift in the position of E$_{2H}$ of Raman spectra indicated that the GaN films grown on Si suffered from tensile stress and the films grown at laser wavelengths of 9.219 µm exhibited the lowest stress. The FWHM value of the XRD rocking curves of GaN (0002) and GaN (10-12) diffraction peaks decreased at resonant depositions and reached its minimum values at 9.219 µm, indicating reduced TDs density.

The LMOCVD technique was developed for low-temperature growth of GaN films on sapphire substrates through laser resonant vibrational excitation of NH$_3$ molecules. With a parallel incidence related to the substrate surface, lasers permit gas-phase excitations and precursor disassociations, leaving the substrate temperature very low. The highly c-oriented GaN films were successfully grown at temperatures as low as 250 ºC. Low-temperature growth of GaN films is ascribed to the enhanced decomposition efficiency of NH$_3$ with resonant excitation of rotational-vibrational transition (1084.71 cm$^{-1}$) of the NH-wagging mode at the laser wavelength of 9.219 µm. The FWHM of (0002) diffraction peaks obtained from XRD for GaN films grown at 600 ºC decreased from 0.20° (MOCVD) to 0.18° (LMOCVD), indicating an improvement in crystalline quality by LMOCVD. SEM images showed that the laser resonant vibrational excitation
of NH$_3$ helped to grow GaN films with smooth and uniform surface morphology. A high GaN growth rate of up to 12 µm/h was achieved at 600 °C by LMOCVD, which is ~4.6 times faster than that of conventional MOCVD with 2.6 µm/h.

We have demonstrated the fast growth of high-quality GaN epilayers with an extremely high growth rate of ~ 25.8 µm/h using the CO$_2$ laser LMOCVD method in a perpendicular irradiation geometry. It is found that the substrate temperature plays an important role in different aspects of GaN film growth, including morphology, structural evolution, electrical and optical properties. The surface morphology of LMOCVD GaN films demonstrates no degradation of the growth mode, maintaining a dislocation-mediated step-flow growth with RMS roughness of ~ 1.9 nm. For the GaN samples grown at 990 °C with high growth rates, the FWHM in rocking curve ω-scan for the GaN (0002) line and (10-12) lines are 313 and 390 arcsec, respectively, suggesting the high purity and high crystalline quality. Raman measurement shows the presence of biaxial compressive stress in the as-grown GaN layers. We have also fabricated UV photodetectors based on the as-grown GaN layers, which exhibit a high responsivity of 0.12 AW$^{-1}$ and a fast response time of 125 ns, indicating the excellent optical properties of GaN layers. These results demonstrate that LMOCVD technique can produce high-quality GaN epilayers with fast growth rates, opening a new pathway for nitride related material fabrication used for next-generation electronics and optoelectronics.
9.2 Future directions

9.2.1 Investigation of the unexplored photocatalytic mechanism in 2D/3D graphene-MoS₂ (MoSe₂)-GaN heterostructure photocatalysts for stable water splitting and hydrogen (H₂) generation

H₂ is a major energy carrier in future, which can provide high combustion heat. The industrial production of H₂ is achieved by steam reforming of methane and water, in which the byproduct is carbon dioxide as greenhouse gas.¹⁻⁴ Since, sunlight and water as clean and renewable are most abundant energy source and natural resource, respectively, the production of H₂ via photocatalytic water splitting has been considered as one of the key sustainable energy technologies to enable storable and affordable energy for future generations and an ideal solution to counter the depletion and environmental problems of fossil fuels.¹⁻⁴

Photocatalytic water splitting and H₂ production system involves three fundamental processes: photon absorption of photocatalytic semiconductor with bandgap higher than 1.23 eV to generate electron-hole pairs, charge separation and migration of photogenerated carriers to surface, and surface reduction and oxidation of water by photoelectrons and holes, respectively. Considering the requirements for efficient light absorption and photogenerated carrier separation and transfer, photocatalytic semiconductors preferably should have high surface area, good crystallinity and stability, and a suitable band structure.⁵,⁶

Currently, photocatalytic semiconductors are metal oxides, nitrides, or sulfides, such as titanium oxide (TiO₂), carbon nitride (C₃N₄) and cadmium sulfide (CdS).⁷⁻⁹ Most of photocatalysts require the loading of a high-cost co-catalyst such as Pt, Rh, and RuO₂ to
obtain a good activity.\textsuperscript{10} On the other hand, various photocatalysts including inorganic
sulfide same as CdS and (oxy) nitride-based photocatalysts are less stable and more
susceptible to oxidation than water and show poor stability.\textsuperscript{11} Wide band-gap materials
including TiO\textsubscript{2} is the most commonly used photocatalyst due to its exceptional stability
to exposure to sunlight and electrolyte. However, indirect and large band gap of 3.2 eV
severely limit absorption of most solar spectrum and generation of electron-hole pairs and
catalysts suffer from low quantum efficiency (QE) in the visible range with low solar to
hydrogen (STH) efficiencies. Moreover, despite progress in the past decade,
photocatalytic semiconductors that can harvest visible light typically do not exhibit good
activity.\textsuperscript{12,13} The STH efficiency of photocatalytic water-splitting devices is still low
around 1\% and far from 10\% STH, which allows achievement of the DOE price target for
H\textsubscript{2} production.\textsuperscript{14,15}

Recently, the emerging two-dimensional (2D) nanosheets and layered materials hold a
high potential to address the existing challenges in the photocatalysts. Due to their unique
physicochemical properties, 2D material as photocatalysts and co-catalysts are expected
to offer fascinating features such as high specific surface areas, high stability, better
charge carrier separation, and abundant surface active sites. Moreover, graphene is an
excellent sunlight absorber, achieving 2.3\% visible light absorbance in just 3.3 Å
thickness and TMD monolayers including MoS\textsubscript{2} and MoSe\textsubscript{2} can absorb up to 10\%
incident sunlight in a thickness of less than 1 nm.\textsuperscript{16,17} Graphene could function as an
efficient and cost-effective cocatalyst to promote electron separation and transfer from
semiconductor catalysts and catalyze the proton reduction on its surface. Molybdenum
disulfide (MoS\textsubscript{2}) with a layered structure and band gap of 1.9 eV has been investigated as
a promising potocatalyst for $H_2$ evolution under visible light irradiation. Moreover, the significant enhancement of the photocatalytic $H_2$ production activity of CdS and TiO$_2$ by loading MoS$_2$ layers as cocatalyst were recently reported opening new insights into high-performance cost-effective photocatalyst based on 2D materials.

On the other hand, Gallium nitride (GaN) has received much interest for use in the photocatalyst as it offers several advantages. It is resistive to chemical corrosion during an electrochemical process and its direct band structure straddles with water redox potentials. The photocatalytic activity of p-type GaN photocatalyst has been reported and can reach to 1525.0 µmol h$^{-1}$ $H_2$ evolution rate, with a 1.8% STH efficiency under light incident in the UV wavelength range which is much higher than that of previously reported photocatalyst materials even in visible light range. However, with a large band gap of 3.4 eV, GaN only absorbs UV light which is about 4% of the solar spectrum. The integration of GaN and 2D semiconductors including MoS$_2$ and (molybdenum selenide) MoSe$_2$ is anticipated to extend the light absorption in visible range and significantly enhance charge separation, photocatalytic efficiency and long-term stability. Thus, it is strategically important to explore the water splitting mechanism in unexplored MoS$_2$ (MoSe$_2$)/GaN heterostructures and develop 2D/3D photocatalysts suitable for stable $H_2$ production.

9.2.1.1 Growth of large-scale MoS$_2$ (MoSe$_2$)/GaN heterostructures

The growth of 2D materials on semiconductor substrates and formation of large-scale MoS$_2$ (MoSe$_2$)/GaN heterostructures is still limited. In this task, a scalable, cost-effective synthesis method will be investigated to grow MoS$_2$ (MoSe$_2$)/GaN 2D/3D heterostructures through RTP process. Our previous studies demonstrated fast growth of
high-quality c-plane GaN films on various substrates by LMOCVD, as discussed in chapter 8. In this subtask, the objective is to form 2D/3D heterostructures based on the epitaxially grown MoS\textsubscript{2} (MoSe\textsubscript{2}) on GaN films. The MoS\textsubscript{2} (MoSe\textsubscript{2})/GaN heterostructures are a lattice matched system, unlike most reported epitaxial 2D/2D and 2D/3D heterostructures to date. The Mo film of particular thickness will be deposited on cleaned GaN films for the controlled MoS\textsubscript{2} (MoSe\textsubscript{2}) synthesis in a single-step RTP process. Then, Mo films will be directly sulfurized (selenidized) in the RTP furnace in an Ar/S atmosphere. The critical parameters, including heating time, temperature, heating rate, and cooling rate, will be systemically studied to achieve large-scale MoS\textsubscript{2} (MoSe\textsubscript{2}) synthesis with controlled layer numbers. Compared with the mechanical transferring method, the direct synthesis of 2D MoS\textsubscript{2} (MoSe\textsubscript{2}) on GaN via the RTP method will be much more cost-effective. Moreover, by tuning the deposition thickness of Mo films prior to the RTP step, the final layer numbers of MoS\textsubscript{2} (MoSe\textsubscript{2}) films will be precisely controlled. Due to a very small lattice mismatch of 0.8\% (3\%) the lattice parameter of GaN and layer MoS\textsubscript{2} (MoSe\textsubscript{2}), an intimate contact will be formed between MoS\textsubscript{2} (MoSe\textsubscript{2}) and GaN.

9.2.1.2 Investigation of photocatalytic water-splitting and H\textsubscript{2} production mechanism in 2D/3D heterostructures

In this task, heterostructure interfaces between the GaN films and layers MoS\textsubscript{2} (MoSe\textsubscript{2}) are studied using ab-initio calculations. By comparing the lattice mismatch along crystallographic orientations, it is found that the mismatch is quite small between layer MoS\textsubscript{2} (MoSe\textsubscript{2}) and GaN and an intimate contact with excellent charge transport in vertical direction is predicted. The effects of junction on the charge separation properties
of MoS$_2$ (MoSe$_2$)/GaN semiconductor heterostructures will be theoretically determined. Several physical mechanisms that need to be modelled in order to understand and predict the behaviour of such heterostructures for photocatalysis;\textsuperscript{14} the relative positions of the band edges of materials, which determine the band offsets; the electronic structure of materials (density of states), which provide information on the charge separation properties of photocatalysts such as electron and hole mobility and information on the alignment of bands and the magnitude and effects of any interface dipoles.

To accurately determine the band offsets of semiconductor heterojunctions, the calculations will be directly done by modelling of periodic heterojunctions and construction of a supercell MoS$_2$ (MoSe$_2$)/GaN heterostructure. The ab-initio calculations will be performed based on the density functional theory (DFT) with the generalized gradient approximation (GGA, in the PBE version\textsuperscript{20}) in the plane-wave basis code Quantum ESPRESSO Simulation Package.\textsuperscript{21}

Additionally, a systematic experimental investigation will be conducted to unveil the photocatalytic mechanism in a MoS$_2$ (MoSe$_2$)/GaN heterostructures. Similar to the proposed mechanism for photocatalytic H$_2$ production from conventional photocatalysts, under the excitation of light, photo-induced electrons and holes were produced in the conduction band and valance band of both GaN, and MoS$_2$ (MoSe$_2$) semiconductors. GaN absorbs only UV light because of its wide band gap. Due to its direct band gap, photo electron-hole pairs generate easily. There are three ways to consume photo-induced electrons: (a) recombine with holes inside the material (b) recombine with spices on particle surface (surface recombination); (c) react with protons to produce H$_2$. The
recombination of the photo-induced electrons and holes resulted in low photocatalytic water-splitting and H₂ production activity.

When MoS₂ (MoSe₂) layers are synthesized on the surface of GaN with RTP process, vertical heterojunction with an intimate contact with high charge transfer properties between MoS₂ (MoSe₂) and GaN semiconductors are formed.²² The band positions of the p-type GaN and MoS₂ (MoSe₂) are appropriate as shown in Fig. 9.3, photo-induced electrons produced in GaN conduction band transferred to MoS₂ conduction band. Therefore, recombination possibility of electron-hole pairs will decrease and more electrons can be used to produce H₂. Moreover, single layer MoS₂ serves as an ideal candidate for an efficient photocatalyst powering the visible sunlight-driven photocatalytic water splitting reaction. While, the absorption edge of GaN falls in the UV region, with small band gap of MoS₂ (MoSe₂) (E_{g(MoS₂)} ≈ 1.89 eV, E_{g(MoSe₂)} ≈ 1.4 eV), the MoS₂(MoSe₂) can absorb more than 10% of solar light and MoS₂ (MoSe₂)/GaN heterostuctures can absorb most of solar light including UV and visible lights. A broader absorption of the solar energy spectrum will highly improve photocatalytic activity.
Figure 9.1. Proposed mechanism for photocatalytic water splitting in MoS$_2$ (MoSe$_2$)/GaN 2D/3D heterostructures with graphene layers as cocatalyst.

Previous computational and experimental results confirmed the high activity of adsorbed H$^+$ ions of unsaturated active S atoms on exposed edge of MoS$_2$ (MoSe$_2$). Therefore, the photogenerated electrons could directly react with H$^+$ ions to form H$_2$. However, active catalytic sites of layered MoS$_2$ (MoSe$_2$) crystals are located at the sulfur edge (Fig. 9.1), while basal planes are catalytically inert. The electrical conductivity and activity for photocatalytic H$_2$ production can be improved through decreasing the MoS$_2$ (MoSe$_2$) layers and adding other conducting materials.

The advantageous material properties of graphene, including large exposed area (2630 m$^2$ g$^{-1}$, calculated value), high charge mobility (200,000 cm$^2$ V$^{-1}$ s$^{-1}$), and high mechanical
and chemical strength, make graphene a promising candidate not only to replace traditional co-catalysts but also to improve the stability of catalyst underlayers. It is a widely held belief that graphene can quickly separate and transfer photo-generated electrons from the conduction band of photocatalysts. Under UV-visible light, the photogenerated electrons of GaN are excited and transferred to the MoS$_2$ surface. Some of the electrons approaching the edge of MoS$_2$ (MoSe$_2$) are directly reacted with adsorbed H$^+$ in H$_2$O to produce H$_2$ under the catalytic activities of unsaturated active S atoms, which can accept electrons and act as active sites for H$_2$ production. Other electrons on the MoS$_2$ (MoSe$_2$) basal planes, which have no catalytic activity, can be transferred to the edge of MoS$_2$ (MoSe$_2$) through the graphene sheets and then react with adsorbed H$^+$ at the edges or graphene surface to form H$_2$ (see Fig. 9.1). Therefore, in this task, graphene will be chosen as co-catalyst to further enhance the catalytic efficiency and stability of MoS$_2$ (MoSe$_2$)/GaN for H$_2$ reduction.

9.2.1.3 Characterization of the performance of photocatalytic water splitting and H$_2$ production of proposed heterostructures

Micro Raman spectroscopy in aqueous environment will be applied to microscopically investigate the stability of MoS$_2$ (MoSe$_2$)/GaN under photocatalytic conditions, respectively. The photodegradation process can be monitored in situ by real-time Raman (Renishaw InVia Reflection) utilizing the irradiation laser. The diffuse reflectance spectra of the GaN and MoS$_2$ (MoSe$_2$)/GaN samples will be recorded on a UV-visible spectrophotometer (UV-2500PC; Shimadzu Corp., Japan) and the absorption spectra will be obtained from the reflectance spectra. The range of light absorption plays a very important role in photocatalysis. To understand the interaction between GaN and MoS$_2$
(MoSe₂), X-ray photoelectron spectroscopy (XPS) measurement (XPS, Thermo Scientific, ESCALAB 250Xi) will be also carried out to investigate the surface composition and the electronic states of the catalysts (GaN, MoS₂ (MoSe₂), MoS₂ (MoSe₂)/GaN, and Graphene/MoS₂/GaN). Photoelectrochemical activity measurements including cyclic voltammetry and stability will be carried out using a three electrodes configuration on a CHI 760D (Shanghai Chenhua, China) electrochemical workstation. Therefore, both high-resolution AFM (Bruker Dimension ICON SPM) and cross-sectional TEM (Hitachi H7500 transmission electron microscope) will be used to observe the morphological and interfacial contact of the photocatalyst structures under photocatalytic conditions, with an aim to verify the proposed interfacial photocatalytic water splitting mechanism.

The H₂ evolution of photocatalytic heterostructure devices will be separately carried out with samples suspended in an appropriate amount of different aqueous solutions in a Pyrex glass reaction cell and the reaction cell will be connected to a gas-closed system with a gas-circulated pump. A 300 W xenon (Xe) lamp is used as light source to generate visible (λ > 420 nm) and UV lights with different long-pass filters. The evolved H₂ was analyzed using an online gas chromatograph (GC-8A, Shimadzu Co., Japan) equipped with a thermal conductivity detector. The apparent quantum yield (AQY) and STH conversion efficiency i.e ECE (energy conversion efficiency) will be measured by applying a Xe lamp (300 W). The number of incident photons was measured using a radiant power energy meter (Ushio spectroradiometer, USR-40). The AQY and STH will be calculated using the following equations:
\[ AQY (\%) = \frac{4 \times \text{Number of evolved } H_2 \text{ molecules}}{\text{Number of incident photons}} \times 100, \]  
\[ STH (\%) = \frac{R(H_2) \times \Delta G_r}{P \times S} \times 10, \]

Where \( R(H_2) \), \( \Delta G_r \), \( P \) and \( S \) denote the rate of \( H_2 \) evolution during the water splitting reaction, the reaction Gibbs energy of the water splitting reaction, the energy intensity of the AM1.5G solar irradiation and the irradiated sample area, respectively.
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LIST OF PUBLICATIONS

1. Patent and patent applications (1)


2. Journal papers (10)


Qiming Zou; Leimin Deng; Dawei Li; Yunshen Zhou; **Hossein Rabiee Golgir**; Kamran Keramatnejad; Lan Jiang; Jean-Francois Silvain, "Thermally stable and electrically conductive, vertically aligned carbon nanotube/silicon infiltrated composite structures for high-temperature electrodes. “ Carbon, (2017).


3. Conference papers (5)


4. Presentation (2)

H. Rabiee, Golgir “Synthesis of m-plane gallium nitride nanoplates using laser-assisted metal organic chemical vapour deposition” ICALEO, 2013, Miami, FL, USA.
Note: The content of this dissertation has been gathered from my below publications.

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