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GROWTH OF III-V NITRIDES AND BUFFER LAYER INVESTIGATION BY PULSED LASER DEPOSITION

A DISSERTATION
SUBMITTED TO THE DEPARTMENT OF MATERIAL SCIENCE AND ENGINEERING
AND THE COMMITTEE ON GRADUATE STUDIES
OF STANFORD UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

By
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July 1999
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I certify that I have read this dissertation and that in my opinion it is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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Abstract

III-V nitrides have been investigated intensively due to the enormous interest in opto-electronic device applications in the green, blue, violet, and near-ultraviolet regions. Advances in III-V nitride materials for short wavelength light sources will lead to both a revolution in optical disk storage, as higher densities can be achieved with shorter wavelengths, and a major impact on imaging and graphic technology as high quality red, green, and blue light-emitting diodes (LED) and lasers become available. High quality GaN films have mostly been prepared by metal-organic vapor phase epitaxy (MOCVD), molecular beam epitaxy (MBE) and vapor phase epitaxy (VPE). Compared to the MOCVD and MBE techniques, pulsed laser deposition (PLD) is a relatively new growth technique used widely for the growth of oxide thin films. However, several advantages of PLD make it worthy of study as a method of growing nitrides. The congruent ablation achieved with short UV-laser pulses allows the deposition of a multicomponent material by employing a single target and the ability for depositing a wide variety of materials. This advantage makes PLD very suitable for growing multilayer structures sequentially in the same chamber and investigating the effect of buffer layers. Moreover, the strong nonequilibrium growth conditions of PLD may lead to different nucleation and growth processes.

In this work, GaN and (Al,Ga)N films have been epitaxially grown on (0001) sapphire substrates by PLD, which has been successfully applied to controlling the lattice constant and bandgap of (Al,Ga)N. Results from optical and structural characterizations are presented, along with the studies on the nucleation and growth processes. In addition, epitaxial ZnO buffer layers with better crystalline structure and surface flatness have been developed by PLD for GaN epitaxy. The effects of ZnO buffer on
GaN grown by both PLD and VPE are discussed.
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Chapter 1

Introduction

The recent surge of activity in III-V wide bandgap semiconductors has arisen from the need for optoelectronic devices in the blue and ultraviolet wavelength region, and for electronic devices capable of operation at high power levels, high temperatures and hostile environments. The most recognizable applications of optoelectronics are light emitting diodes (LEDs) for displays, and semiconductor lasers for use in such areas as optical storage, reprographics and communication. Prior to the introduction of GaN-based blue light emitting diodes and laser diodes, III-V materials were limited to the GaAs-based and InP-based semiconductor devices which only emit from infra-red (IR) to orange wavelengths, as shown in Figure 1.1. With III-V nitrides, the spectrum can be extended to green, blue and violet wavelengths. The III-V nitride semiconductor family, AlN, GaN and InN, crystallize in both stable wurtize and non-equilibrium zinc-blende polytypes. Wurtize AlN, GaN and InN have direct room temperature bandgaps of 6.2, 3.4 and 1.9eV, respectively. In cubic form, GaN and InN have direct bandgaps, while AlN is indirect. With proper bandgap engineering, a continuous range of direct bandgap energies throughout of the visible spectrum well into the ultraviolet (UV) wavelengths can be formed. Thus, three primary colors (red, green and blue) of the visible spectrum could be emitted by semiconductor components. This will have a major impact on full color displays, imaging and graphics applications and allow the reliable, compactness, low cost and other desirable attributes of semiconductors to be applied to these important markets.
Figure 1.1: Bandgaps and in-plane lattice constants of III-V materials and commonly used substrates

Furthermore, optical data storage can especially benefit from short wavelength coherent light sources from III-V nitrides. One of the important figures of merit for optical based technologies is the optical storage areal density, which scales as $1/\lambda^2$, where $\lambda$ is the wavelength used to read and write data. The optical storage density increases dramatically as the probe laser wavelength is reduced. Therefore, more data can be stored in a smaller disc. The ever-increasing need for denser optical storage media and full color display technologies are driving the development of short-wavelength semiconductor devices.

Electronics based on the existing semiconductor devices of Si and GaAs cannot tolerate extremely high temperatures or chemically hostile environments due to the uncontrolled generation of intrinsic carriers and their low resistance to caustic chemicals. The wide bandgap nitride semiconductors, with their excellent thermal conductivities, large breakdown fields and resistance to chemical attack, will be the choice for many of these applications.

In spite of the promising potential of III-V nitrides in optoelectronic and electronic
applications, early studies pinpointed a number of problems which hindered their advance. They were lack of suitable substrate materials, large n-type background carrier concentrations, and an inability to dope p-type.

Unlike GaAs, bulk GaN crystals can not be produced in size and quantity needed by conventional crystal growth methods at this moment, causing the growth efforts to utilize heteroepitaxy on a variety of substrates, such as sapphire, 6H-SiC, Si, GaAs, MgO and others. Figure 1.1 shows the in-plane lattice constants of III-V materials and other commonly used substrates. None of the commonly available substrates has a good lattice or thermal expansion match to the nitrides, giving rise to rough and highly defected heteroepitaxial films. By low temperature deposition of AlN [1] or GaN [2] buffer layers, the crystal quality of the GaN epilayers can be considerably improved, and this will be discussed in more detail in Chapter 2. Among the above substrates, sapphire is the most common substrate and generally yields the best films.

In addition, films grown invariably showed n-type conduction without any intentional doping and p-type GaN was unavailable. The equilibrium partial pressure of nitrogen over the nitrides is extremely high at typical growth temperatures, rendering difficult the incorporation of sufficient nitrogen into the growing film. In addition, various types of acceptor atoms were tried but led only to compensated high resistivity material. In 1989, Amano et al. [3] demonstrated that compensated Mg-doped GaN could be converted into conductive p-type material by low energy electron beam irradiation (LEEPB). Nakamura [2] later achieved p-GaN with hole concentrations as high as $3 \times 10^{18} \text{cm}^{-3}$ after annealing at 700°C under N$_2$ ambient, which served the same purpose as LEEPB process. This breakthrough has permitted the realization of blue LEDs [2] as well as pulsed [5] and recently continuous wave laser devices [6] grown on sapphire.

Because of successful demonstrations of blue LEDs and lasers on GaN-based epitaxial films on sapphire substrates, the properties of III-V nitride compounds have attracted a lot of attention. Defect structures of the films have been widely studied by TEM, primarily for threading dislocations in the GaN films on sapphire substrates. It has been previously reported by Lester et al. [7] that the GaN-based light emitting diode has dislocation densities on the order of $10^{10} \text{cm}^{-2}$ despite its high efficiency.
They also claimed that the dislocations do not act as efficient nonradiative recombination sites, which is in marked contrast to the recognition that in other III-V semiconductor materials, such as GaAs and InP-based compounds, dislocations do act as efficient nonradiative recombination sites. On the other hand, several efforts have been made for controlling and minimizing the dislocation densities from $10^{10}$ to $10^8 \text{cm}^{-2}$ resulting in improved optical and electrical properties. Consequently, reducing dislocation density is one of the key issues in obtaining better performance from GaN-based devices. Intensive research has been devoted to the reduction of defects which are closely tied to buffer layers and substrates.

High quality GaN films have mostly been prepared by metal-organic vapor phase epitaxy (MOCVD) [8] [9], molecular beam epitaxy (MBE) [10] and vapor phase epitaxy (VPE) [11]. Compared to these techniques, pulsed laser deposition (PLD) [12] is a relatively new growth technique used widely for the growth of oxide thin films. PLD is typically accomplished with a high power pulsed laser beam irradiating a bulk stoichiometric target. Through the interaction of the laser beam with the target, a forward-directed flux of material is ejected, a plasma formed which is then transported toward a heated substrate placed directly in the line of the plume. PLD is an extremely versatile technique for depositing epitaxial films of a wide variety of materials; however, only a few studies have been done on semiconductor III-V nitrides. There are several advantages of PLD, which will be discussed in Chapter 3, for depositing high quality thin films and make it worthy of study as a method of growing nitrides.

One of the focuses of this work is to study the growth kinetics and the properties of the GaN films grown by PLD. The results of different characterization techniques provide not only essential feedback for the growth studies but also knowledge of material properties. Furthermore, we would like to investigate the potential to grow ternary alloys and achieve bandgap engineering by PLD, which will widen the application of PLD. While MOCVD has been the dominant epitaxial growth technique for III-V nitrides, it is easier to explore the growth and effects of buffer layers by PLD because of its simplicity, versatility and greater range of non-equilibrium low temperature growth. Buffer layer nucleation and growth are also better studied due to the
availability of *in-situ* Reflective High Energy Electron Diffraction (RHEED) in our PLD system. The efforts have been aimed at growing buffer layers with low threading dislocation density and studying the effects of the buffer layer on GaN epitaxy.

This thesis addresses the study and development of III-V nitrides and the buffer layer investigation by PLD. Chapter 2 provides a brief background of thin film epitaxy and the III-V nitride research. Chapter 3 reviews the PLD process and Chapter 4 describes the PLD system used to grow films studied in this work. Chapter 5 details the growth and properties of III-V nitrides. The investigation of the growth and the effects of ZnO buffer layer on PLD-GaN and VPE-GaN epitaxy are discussed in Chapter 6. Finally, conclusions and suggestions for future research are offered in Chapter 7.
Chapter 2

Background

The goal of this chapter is to provide a brief overview on the fundamental issues of epitaxial growth. The structure and the defects in films in a given deposition process are usually strongly influenced by what happens during film nucleation and subsequent growth. We will first review topics on nucleation, growth, strain and defects in Section 2.1. Section 2.2 will focus on GaN in particular, summarizing previous developments of nucleation and growth processes in GaN as well as defects generated in the process.

2.1 Epitaxy

Epitaxial growth means a deposited film which replicates the crystalline order of the single-crystalline substrate on which it is deposited. There are a number of conditions required for epitaxy to occur. One is that the arriving atoms need to have sufficient energy to be able to diffuse on the substrate surface until a correct lattice position is found. Otherwise, amorphous or polycrystalline materials will be grown instead. Another requirement is that the film and the substrate have similar symmetry or sets of lattice planes which can line up with each other. Epitaxy can be divided into two categories: homoepitaxy, where the film and the substrate are the same materials, and heteroepitaxy, where the film and substrate are two different materials. Growth of GaN on sapphire is an example of heteroepitaxy.
2.1.1 Nucleation

During deposition, the arriving atoms or molecules first adsorb on the surface, then diffuse some distance before reacting with each other and the substrate surface to form the bonds. The initial aggregation of the materials is called nucleation. When atoms or molecules arrive within a few atomic distances of the substrate surface, they begin to feel an attractive force due to interaction with the surface molecules. This interaction is known as the van der Waals force. The atoms or molecules are trapped in a weakly-adsorbed state known as physical adsorption or physisorption. The physisorbed species are mobile on the surface and can diffuse between surface atomic sites. They may desorb after a while by gaining enough energy or they may undergo the formation of chemical bonds with the surface atoms; that is, chemisorption. Chemisorption involves the sharing of electrons in new molecular orbitals and is much stronger than physisorption, which involves only dipole interaction.

Nucleation can occur either at random sites or at active surface sites, such as atomic steps, crystal defects, or impurities. First, we are going to discuss the case where nuclei form at random surface locations by accumulating atoms until the size exceeds a "critical" size which is big enough to be stable. In the equilibrium process of vapor-solid transformation, the chemical free energies of two phases are equal \( (\mu_v = \mu_s) \) and the vapor is at its saturation vapor pressure, \( P_v \). If the vapor pressure of arriving atoms, \( P \), is increased above \( P_v \), \( \mu_v \) increases.

\[
\Delta \mu = \mu_v - \mu_s = \frac{kT}{\Omega} \ln \frac{P}{P_v} = \frac{kT}{\Omega} \ln \frac{J}{J_e} = \frac{kT}{\Omega} \ln \xi
\]

(2.1)

where \( \Omega \) is the atomic volume, and the ratio of pressures or the ratio of fluxes is known as the supersaturation ratio, \( \xi \) [15]. When nuclei form on the substrate, new surfaces and interfaces form, resulting in a change in the surface free energy of the system. Consider the simplest case of forming a nucleus with a height of "s" atoms and a square base of "n" atoms on the edge, as shown in Figure 2.1. \( W, W_p, W_s \) and \( W_i \) are the surface energy of film top surface, film periphery, substrate, and film/substrate interface, respectively. the nuclei forms at the surface. The total free energy change
CHAPTER 2. BACKGROUND

![Diagram of a nucleus with height "s" and base "n" atoms on a substrate.]

Figure 2.1: A nucleus with a height of "s" atoms and a square base of "n" atoms on the edge formed on a foreign substrate.

The energy of formation associated with the formation of a nucleus is

\[ \Delta G = -a^3 sn^2 \Delta \mu + a^2 n^2 \Delta W + 4nsa^2 W_p \]  \hspace{1cm} (2.2)

where \[ \Delta W = (W + W_l - W_s) \] and "a" is the atomic diameter. The energy of formation will have a peak value at \( n = n_c \) and \( s = s_c \) satisfying

\[
\frac{(d\Delta G/dn)}{n_c} s_c = \left( \frac{d\Delta G/ds}{s_c} \right) n_c, s_c = 0 \\
n_c = \frac{4W_p}{a\Delta \mu} \\
s_c = \frac{2\Delta W}{a\Delta \mu} \\
\Delta G_c = \frac{16\Delta W W_p^2}{\Delta \mu^2} \hspace{1cm} (2.3)
\]

which gives the size of the critical nucleus and the corresponding free energy as a function of the supersaturation. The free energy change versus the size of the nucleus is shown in Figure 2.2. Nuclei with sizes less than the critical size are unstable and will spontaneously shrink since that is the direction of decreasing free energy. Nuclei larger than the critical size will grow since this lowers the free energy. The concentration of critical nuclei will be proportional to \( \exp(-\Delta G_c/kT) \).

When the process objective is to produce a smooth, uniform film, a small critical nucleus size and high nucleation density are preferred. Either a decrease in the net surface/interface free energy or an increase in the magnitude of the (negative)
Figure 2.2: Total free energy change as a function of cluster size

volume free energy will produce a decrease in the critical size, a decrease in the nucleation barrier for nucleation, and an increase in the nucleation rate. For a given film substrate combination, we typically have little control over the surface and interface energy terms. Therefore, we modify the free energy change, $\Delta \mu$, in the deposition process. In practice, the free energy change can become more negative by using a very high vapor arrival rate (i.e. high supersaturation), at least until the nucleation phase is over and the film is continuous. At sufficient supersaturation, the number of atoms in the critical nucleus approaches unity and $\Delta G_c$ becomes negligible. Mobility allows the nuclei to migrate and coalesce with each other, becoming larger and fewer with time.

In addition to nucleating homogeneously at random locations on the substrate surface, nucleation and growth can take place by attachment of atoms to active surface sites, such as atomic steps, point defects, and dislocation intersections, which are more energetically favorable. Attachment of atoms to random sites on a smooth surface involves an increase in total surface energy because it increases the surface area, while attachment to the kink sites makes no change in the surface area [16]. As shown in Figure 2.3, this attachment can result in motion of the kinks along the face of the step. This motion in turn results in motion of steps along the surface and this step
motion results in addition of a layer of atoms, which gives a deposition rate. During the deposition, if the surface diffusion rate is high enough (i.e. surface diffusion length is greater than the distance between terraces), atoms are more likely to attach to an edge than to form a critical nucleus. Then the edge attachment becomes the dominant process, which results in the step-flow growth.

2.1.2 Growth

Once nuclei have formed, the transformation proceeds with the process of growth. There are three types of growth modes which follow [17]. The selection of which of the growth modes depends on the thermodynamics related to the surface energies of the film and substrate, the film substrate interface energy, and the accumulated strain energy.

(i) Frank-van der Merwe (FM) growth mode. Material initially forms a complete monolayer on the substrate. Subsequently, it grows in sequential monolayers of coverage upon itself.

(ii) Volmer-Weber (VW) growth mode. Stable nuclei grow three-dimensionally. They may later coalesce and form a continuous film, with or without orientation coherence between individual islands.
(iii) Stanski-Krastinov (SK) growth mode. First, one or a few monolayers completely cover the surface, followed by nucleation and growth of three-dimensional islands.

When the substrate surface energy ($W_s$) exceeds the sum of the surface energy of the film ($W, W_p$) and the interfacial energy ($W_i$), the film grows in the FM mode. Otherwise, the VW mode will occur. In order to describe the SK growth mode, we need to consider the accumulated strain energy, which increases with film thickness due to mismatched lattice spacing. In the initial stages of growth, the film grows two-dimensionally. As the strain builds up with film thickness, island formation becomes energetically favorable. The strain energy due to misfit can be reduced by forming three-dimensional islands and the surface energy can be minimized because of the low surface to volume ratio.

2.1.3 Strain and Defects

One of the major concerns of heteroepitaxial growth is a suitable substrate. In addition to epitaxial strains resulting from lattice mismatch between film and substrate, there are other types of strains such as thermal strains which arise from differential thermal expansion coefficients of film and substrate as well as growth strains which develop if the density of the film changes after it has been bonded to the substrate. When the film and substrate are bonded, they are constrained to the same lateral dimension. $F_f = F_s; \sigma_f h_f = \sigma_s h_s$. Since the thickness of the film, $h_f$, is typically much smaller than that of the substrate, $h_s$, essentially all of the strain appears in the film and the lateral dimensions of the films are determined by those of the substrate.

As the epilayer thickens, the stored elastic energy increases, making the system unstable. At this point, the situation is energetically favorable for generation of new misfit dislocations by multiplication and nucleation to allow further strain relaxation. The thickness of the film at this stage is the critical thickness, $h_c$. It can be calculated by comparing the strain energy of the biaxial strained film and the energy associated
with creating a misfit dislocation, which can be obtained from the formula [18]

$$\frac{h_c}{\ln(\beta h_c/b)} = \frac{\mu b}{4\pi(1-\nu)M\epsilon}$$  \hspace{1cm} (2.4)

where $\mu$ is the shear modulus of the thin film, $\nu$ is Poisson’s ratio, $M$ is the biaxial elastic modulus of the film, $\epsilon$ is the biaxial elastic strain imposed on the film, $b$ is the Burgers vector of the dislocation and $\beta$ is a numerical constant of the order of unity. Detailed review of the derivation of critical thickness and the mechanical testing techniques are illustrated in [18]. As describe earlier, films tend to generate dislocations when the film thickness exceeds the critical thickness. There are two basic types of dislocations: edge and screw dislocations. For edge dislocations, the Burgers vector, $b$, lies in the slip plane and is perpendicular to the dislocation line. For screw dislocations, $b$ also lies along the slip plane but is parallel to the dislocation line. If a screw dislocation were to lie in the interface, it does not contribute to the release of misfit strain since there is no extra plane of atoms involved. Only the edge type dislocation at the interface can efficiently release misfit strain energy. A dislocation can change from screw to edge type by changing direction as it threads its way through a crystal. In doing so, $b$ remains unchanged.

In addition to geometrical misfit dislocations, another way that dislocations can be generated is due to growth errors. During the initial stages of film growth and island coalescence, dislocations can develop when there are misalignments between nuclei, which will be discussed more in the next section.

2.2 III-Nitrides Growth

One of the major problems hindering the growth of high quality III-V Nitrides is the lack of an ideal substrate material that is well lattice and thermally matched to GaN. Due to the high dissociation pressure of nitrogen over GaN, GaN single crystalline substrates are extremely hard to produce. Efforts are ongoing to grow bulk GaN crystals for substrates, but at present, the size obtained are only a few millimeters, which is not very convenient for device applications. Therefore, other
alternative substrates have been investigated over the years, such as Si, GaAs, SiC, ZnO, MgO, and Al₂O₃. Sapphire, with a lattice mismatch of 16% with respect to GaN, is the most common substrate material for wurtzite III-V Nitrides. Other, more closely matched substrate options, such as SiC with a 4% mismatch and ZnO with a 2% mismatch with respect to GaN, are still expensive at present. The preference of sapphire substrates can be attributed to their wide availability, ease of handling, and stability at the elevated temperatures and in chemically aggressive reactants, like ammonia. However, the huge lattice and thermal mismatches between sapphire and GaN result in a very high dislocation density and considerable strain after postgrowth cooling.

Early efforts to grow GaN directly on sapphire without substrate treatments and/or buffer layers usually result in a high density of macroscopic defects, such as cracks and pits in GaN films. Akasaki et al. [1] have reported a substantial improvement by employing low temperature AlN buffer layers for the growth of GaN by MOCVD and studied in detail the role of low temperature buffer layers as illustrated in Figure 2.4. For a crystal to orient itself successfully, the energies of the material impinging on the substrate must be sufficient for atoms or ions to move and relocate at the correct lattice sites. Therefore, there is a critical substrate temperature below which the atoms do not have sufficient mobility so that epitaxy can not take place. For GaN grown by MOCVD, high quality epitaxial growth occurs only at a temperature higher than 1000°C. When GaN is grown directly on sapphire at high temperature, the resulting film is epitaxial but is very rough and highly defected with a lot of cracks and pits. At high temperature, atoms tend to accumulate rapidly and form big nuclei with poor uniformity in both size and distribution across the substrate. These islands grow and coalescence, as shown in Figure 2.4, producing a highly defected film. On the other hand, high supersaturation achieved at low temperature will result in uniform and high density nucleation. The low temperature (~500°C) buffer layer is typically amorphous. Upon heating to the normal growth temperature (> 1000°C), the low temperature buffer crystallizes and forms columnar fine crystals, providing an excellent template for GaN epitaxy. The initial growth of GaN is also columnar on top of the fine crystals in the buffer. During further growth, some fine crystals
Figure 2.4: Schematic diagram showing the nucleation and growth process of GaN on sapphire with and without low temperature buffer layer [1]
then become larger size islands as the result of geometric selection. With a thin low
temperature buffer layer prior to high temperature growth of GaN, the resulting film
is smooth and the quality is greatly improved. The GaN films grown on top showed
narrower x-ray diffraction peaks, more intense photoluminescence, lower background
carrier concentration and higher carrier mobility.

grown by MOCVD, employing a low temperature GaN buffer layer. Electron diffraction patterns confirm that an amorphous buffer layer crystallized when growth conditions were simulated by a 1000°C anneal. GaN film quality was observed to be
a strong function of buffer layer thickness, with an optimum thickness between 25
and 50nm. Today, low temperature buffer layers are standard in growing GaN on
sapphire.

Although the crystal quality of GaN can be considerably improved by employing low temperature buffer layers, the films still have a very high density of structural defects. Structural defects observed in GaN are vacancies, dislocations, and planar boundaries. The vacancy is known as one of the origins of n-type conductivity. Planar defects and dislocations (both misfit and threading types) play significant roles in determining optical performance of the compound semiconductor devices. The structural defects of GaN have been extensively studied using TEM. Qian et al. [19] and Ning et al. [20] have shown that the defects in GaN on sapphire were predominately edge dislocations with Burgers vectors of $\frac{1}{3} < 11 - 20 >$ type, lying along [0001] direction. Ponce et al. [21] investigated the threading dislocations formed in GaN films on SiC with AlN buffers and found that threading dislocations originated at substrate imperfections producing low angle domain boundaries in the AlN buffer layer along the growth direction. Threading dislocations then developed during the subsequent growth of the GaN film. Chien et al. [22] found that the predominant dislocations in GaN on 6H-SiC were of the edge type with $b = \frac{1}{3} < 11 - 20 >$ and a small fraction of $b= [0001]$ dislocation half-loops.

The majority of these structural defects are believed to form during coalescence of islands at the initial stages of GaN growth. Since these islands are more likely to preserve a hexagonal shape, and often have a small misorientation with their neighbors,
dislocation arrays are created during the coalescence of these islands. There are two components of the misorientation. One is tilt of the c axis with respect to the growth direction and the other is twist of the column orientation about the c axis [23]. Small tilt will be accommodated by edge dislocations lying at the film/substrate interface and screw dislocations parallel to [0001]. The twist induces edge dislocations parallel to [0001]. The misoriented grains, bounded by arrays of dislocations, once formed, are not likely to expand.
Chapter 3

Pulsed Laser Deposition

3.1 Introduction

Pulsed laser deposition (PLD) is an extremely versatile technique for depositing epitaxial films of a wide variety of materials including metals, insulators, semiconductors and superconductors [12]. It expands the range of materials that can be deposited in thin film form. PLD is typically accomplished with a high power pulsed laser beam irradiating a bulk stoichiometric target. Through the interaction of the laser beam with the target, a forward-directed flux of material is ejected, a plasma is formed and subsequently transported toward a heated substrate placed directly in the line of the plume, as shown in Figure 3.1.

The advantages of the PLD approach for depositing high quality thin films begin with the simplicity and versatility of the experiment. An intrinsic advantage of the PLD method for synthesis of multicomponent thin films is its ability to transfer the target stoichiometry to the film. The congruent ablation achieved with short UV-laser pulses allows deposition of multicomponent materials by employing a single target. This feature makes PLD the best initial investigation tool for complex materials because the stoichiometry control is vastly easier. A useful feature of the PLD method is that multiple targets can be loaded inside the chamber on a rotating holder, which can be used to sequentially expose different targets to the laser beam, thereby enabling the in-situ growth of heterostructures and superlattices with relatively clean interfaces.
Therefore, PLD is suitable for rapid exploration of new materials-integration strategies to develop heterostructures and to perform basic studies at the laboratory scale. Virtually any material can be laser evaporated, leading the possibility of multilayers of a variety of materials. The growth rate achieved by PLD can easily be varied from sub-angstrom per second to a few microns per hour through adjusting the repetition rate and fluence of the laser, which is useful for both atomic level investigations and thick layer growth. Moreover, the strong nonequilibrium growth conditions of PLD may allow exploration of a much broader range of metastable materials growth, including the introduction of higher dopant concentrations and alloy compositions that in equilibrium phase segregate.

In this chapter, a brief overview of the history of PLD is given in Section 3.2 which followed by discussion on the basic mechanisms of PLD in Section 3.3. Section 3.4 will illustrate some limitations of the PLD process.
3.2 Historical Review

The development of the PLD technique can be divided into several stages by considering the progress of new laser technology, and by examining the successful application of new laser technology to deposit thin films of a new class of materials. The first experiment was reported in 1965 by Smith and Turner, and they used a ruby laser to deposit thin films of various materials [24]. Their work was followed by other researchers using different types of lasers, such as CO\textsubscript{2} lasers and Nd:YAG lasers. However, due to the limitations of laser wavelength and power density, the materials which could be deposited was limited and film qualities were inferior to those grown by other conventional techniques [25]. During the 1970s, the material selection of PLD was expanded because of the availability of high-energy Q-switch lasers, generating very short optical pulses with peak power densities exceeding 10\textsuperscript{8} W/cm\textsuperscript{2}. By generating high peak power density, congruent evaporation, which is the most important advantage of PLD, was observed in many systems from ternary compounds to superconductors with very complex stoichiometries. During the early 1980s, PLD was used for the first time to deposit high quality epitaxial CdTe and other Cd-based II-VI semiconductor compounds [26]. Quantum Hall effect due to two-dimensional carriers in a II-VI semiconductors was first observed in a HgTe/CdTe superlattice grown by PLD [27].

A wide variety of materials have been investigated by PLD in the 80s and the number of research groups has increased. However, PLD was not widely used until 1987 when Dijkkamp \textit{et al.} from Bellcore successfully grow high T\textsubscript{c} superconductors \textit{in-situ} [28]. This initiated rapid acceleration in growth by PLD. Due to its capability to stoichiometrically transfer the composition from target to film, complex multicomponent materials can be grown by simply employing a single target. Therefore, there is no need to adjust the fluxes of individual sources to obtain the correct composition, which is especially useful for studying superconductors since there is commonly more than 4 elements in the compound, often with widely varying vapor pressures at a given temperature. With the success achieved in the growth of superconductors, a lot of studies have been devoted to understanding the ablation process, which will be
discussed in Section 3.3. Various analytical techniques, such as optical spectroscopy, ion probe, time-of-flight analysis and high speed CCD camera, are used to probe the plume characteristics and their relationship to laser conditions and their impact on film properties [29].

3.3 Basic Mechanisms

The deposition characteristics of the pulsed laser deposition technique for thin film growth have been found to be significantly different from other vaporization techniques. For PLD operated under high vacuum, two features that separate PLD from other techniques are (i) pulses of high instantaneous vapor flux \(10^{18} - 10^{22} \text{ cm}^{-2}\text{s}^{-1}\) separated by periods of no vapor flux (ii) relatively high energies of ablated species (several eV to keV) arriving at the substrate and high degree of ionization (up to 50%) [31]. When PLD is applied to the deposition of oxide films, a background oxygen pressure in the range of a few hundreds to a few tens of mtorr are sustained inside the chamber. The velocity and density of ions of PLD vapor decrease in the presence of the background gas pressure. Figure 3.2 illustrates the difference between PLD and other techniques, such as MBE and MOCVD, by showing the range of deposition rate and the average energy per deposited atom under common operating conditions [32].

For MOCVD and MBE, atoms in the deposition flux typically have thermal energies of a few tenths of an eV. Due to the intense excimer laser interaction with the target, the energies of the species arriving on the substrate in the PLD process are approximately an order of magnitude higher and the process is highly non-equilibrium [33]. It may reduce temperatures for epitaxial growth and allow the growth of materials that may be hard to synthesize during equilibrium processes. The average deposition rate of PLD can be easily controlled by laser repetition rate and laser fluence. One of the features which sets PLD apart from all other methods is high instantaneous deposition rates that can exceed 10,000 Å/s, which could affect the film nucleation and growth.

Conceptually and experimentally, PLD is simple compared with other techniques,
Figure 3.2: The range of deposition rate versus the average energy per deposited atom for PLD, MOCVD, and MBE
such as MOCVD and MBE. However, the interactions of laser-target, laser-plume, and plume-ambient gas are extremely complex processes and it is difficult to formulate a complete and consistent model to interpret all observations. Many researchers have simulated the PLD process and proposed various models [33] [34]. Due to the complex physical phenomenon and lack of suitable models, a great deal of empirical studies have been done to understand the underlying mechanisms associated with the process. Several references provides detail reviews on the theoretical modeling and experimental studies of the PLD process [12] [33] [35] [36] . In this section, we will briefly illustrate three main regimes of the PLD process involved in the interaction of laser with targets resulting in evaporation, plasma formation/expansion, and subsequent deposition of thin films on the substrate.

3.3.1 Laser-Target Interaction

The interaction of a short-pulse high-power laser with a target is illustrated in Figure 3.3 [25]. In the beginning of the laser pulse, the optical energy is largely absorbed by the surface of the target. Since the laser energy is supplied to a small volume (10^{-13} m^3) in a short time (typically 30ns), the local temperature of the target, frequently on the order of 10^4K, can easily exceed the melting temperatures of most materials. Thus, all the species of the target evaporate simultaneously, i.e. congruent evaporation. This condition ensures that the ejected materials have the same stoichiometry as the target which makes the PLD process particularly suitable for exploring binary, ternary and more complicated systems without having to adjust fluxes from multiple sources.

The evaporation of the materials from targets by laser irradiation depends on the laser parameters (such as laser fluence, pulse duration, shape, and wavelength) and material properties (such as reflectivity, absorption coefficient, heat capacity, thermal conductivity). At wavelengths of 250nm and below and the power range of 10^8 W/cm^2, virtually all materials absorb the laser emission either via linear or nonlinear processes whereby coupling of the energy is possible to most surfaces. Therefore, virtually any material can be laser evaporated leading to the possibility of multilayers
Figure 3.3: Schematic representation of the laser-target interactions. Interactions occurring are (a) absorption and surface melting (b) vaporization, multiphoton ionization, and plasma production (c) plasma emission, inverse bremsstrahlung, and self-regulation [25]

of a variety of materials. Many studies have shown that there is a threshold energy density for the removal of target material by ablation [37]. In excimer laser irradiation, the energy threshold value varies from 0.1–0.4 J/cm² for YBCO targets to 3.5–4.0 J/cm² for silicon. If the laser fluence is less than the threshold value, the material is removed by thermal evaporation instead of laser ablation. Above the threshold, material removal varies linearly with laser fluence until a plateau is reached.

For efficient material removal and congruent evaporation of multicomponent targets, short wavelengths (UV) and short pulse width (30ns) yield superior film quality. While long optical pulses (μs) and/or IR radiation result in a more thermal-like heating of the target material. A number of different types of lasers as e.g. CO₂ and Nd:YAG lasers have been used to induce the ablation process; however, currently most work has shifted over to using pulsed excimer lasers. These lasers utilize a gas mixture containing a small quantity of halogen (Cl, F) and rare gas (Ar, Kr, Xe) in a
buffer of helium or neon. Upon excitation, the halogen and rare gas atoms combine to form a rare gas halide molecule which emits at a well defined wavelength in the ultraviolet. There are three commonly used gas mixtures: XeCl(308nm), KrF(248nm), ArF(193nm). All excimer lasers operate in pulsed mode only, with a pulse duration of tens of nanoseconds. The output power of the excimer laser degrades with operation and time, requiring refilling of the gases in the laser cavity.

3.3.2 Laser-Plume Interaction

One of the results of laser-plume interactions is vapor breakdown, i.e. plasma ignition, during which electron and ion densities increase rapidly and at the same time the neutral density in the plume decreases dramatically. Once a plasma is generated, it will expand during transport towards the substrate, either freely or adiabatically in vacuum or through frontal shock wave propagating in the ambient gas [38]. It is crucial to understand the phenomenon of laser-plume and ambient gas-plume interactions since it sets up the final state of the plume, which has a dominant effect on the energies of the species in the plume and therefore on the growth of thin films.

High temperatures generated at the target surface cause emission of many species from the target, emission of ions and electrons as well as neutral atoms, molecules and clusters. Continued interaction of the laser beam with the plume results in the photodissociation and photoionization of the evaporated material. Photodissociation breaks molecular species and clusters and photoionization of the evaporated material by nonresonant multiphoton processes and leads to the formation of an expanding plasma above the surface, as shown in Figure 3.3(b). The plasma absorbs the laser radiation by inelastic free electron scattering (or inverse bremsstrahlung), which results in further heating of the plasma and regulates further interaction of the radiation field with the target (Figure 3.3(c)).

The ablated plume is highly cone-shaped and characterized by a forward peaked distribution, \( \cos^n \theta \) with \( 8 < \theta < 12 \), where \( \theta \) is measured with respect to target normal [33]. In addition to the highly forward peaked distribution, a weaker angular dependence distribution, \( \cos \theta \), is observed which is due to thermal evaporation [39].
CHAPTER 3. PULSED LASER DEPOSITION

The sharply forward peaked distribution has the same stoichiometry as the target while the broad distribution is nonstoichiometric. The relative ratio of the materials emitted in the two different components depends upon the laser density. At laser densities lower than the threshold energy densities of the materials, thermal evaporation dominates so that the compositions of the deposited films deviate from the proper stoichiometry, whereas the ablation process dominates at the laser densities above threshold. Therefore, it is important to deposit films with a laser fluence larger than the ablation threshold to ensure stoichiometric composition transfer between target and film.

As mentioned before, the evaporated species in a forward ejected plume include neutrals, electronically excited species, ions, electrons, molecules and macroscopic particles. Their numbers and distributions depend on the excitation condition, gaseous ambient and the material. A great deal of research has been performed to analyze the plume constituents of materials with various techniques, such as optical and mass spectroscopy, time of flight analysis, atomic absorption measurements. Otis et al. has utilized laser induced fluorescence to show the evidence for metal-atom/ambient reactions [40]. Formation of CuO has been observed in the vaporization of YBCO as a function of oxygen pressure. While little or no CuO is present in the vacuum vaporization of a stoichiometric target, an increase in CuO is observed as O₂ introduced into the chamber, with a maximum CuO observed at 100 mtorr O₂. It indicates that CuO is mainly produced by aggregation process with the background oxygen gas rather than by direct ablation.

3.3.3 Film Growth

In order to optimize film properties, good control of growth parameters is essential. There are a number of parameters which affect film properties, such as laser wavelength, laser fluence, substrate temperature, reactive gas partial pressure, laser pulse repetition rate, and target-substrate distance. Table 3.1 summarizes the relationships between major processing parameters and film properties.

Among these variables, the substrate temperature, reactive gas pressure, and laser


<table>
<thead>
<tr>
<th>Parameters</th>
<th>Effect on Process</th>
<th>Main effects on film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser wavelength</td>
<td>thermal or non-thermal evaporation ratio of neutral to ion species in plasma kinetic energy of the ejected species</td>
<td>retention of target stoichiometry epitaxy particulates</td>
</tr>
<tr>
<td>Laser fluence</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>surface mobility of ablated species adsorption/desorption</td>
<td>microstructure, epitaxy, stoichiometry</td>
</tr>
<tr>
<td>Reactive gas partial</td>
<td>energy of arriving species on substrate constitutes of arriving species</td>
<td>microstructure, epitaxy, stoichiometry</td>
</tr>
<tr>
<td>pressure</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1: Effects of the process parameters on the properties of the resulting films deposited by PLD [41]

fluence are the most important. For a crystal to orient itself successfully, the energies of the material impinging on the substrate must be sufficient for atoms or ions to move and relocate at the correct lattice sites. These energies can come from the thermal energy of the substrate supplied by the heater on the kinetic energy of the plume. PLD deposition is typically performed in a chamber with a background gas. The ejected vapor, whose energy is affected by laser fluence, then involves a large number of gas phase collisions with the ambient gas, reducing the energy of the vapor flux before reaching the substrate. In addition to crystallinity, chemical composition is dependent on these parameters. The laser fluence has to exceed the threshold for congruent ablation so that the composition of the target can be transferred to the film. The background gas modulates the species and composition arriving at the surface while the substrate temperature controls the adsorption and desorption of species on the substrate.

The deposition rate can be easily varied over a wide range, both the instantaneous and average deposition rate. The laser fluence affects the instantaneous deposition rate and the degree of supersaturation of the vapor. The average deposition rate can be controlled by the laser repetition rate and the target-substrate distance.

When the film is deposited in vacuum, the effect of target-substrate distance is mainly reflected in the angular spread of the ejected flux. The angular distribution of a laser- ablated plume is described in the previous section. The specific effects of target-substrate distance and ambient pressure are interrelated. Due to the increase in
collisions between laser-ablated plume and the background gas, the plume dimension decreases as the background pressure increases. It has been shown that $E/P_0$ is the scaling parameter of the plume range, where $E$ is the laser energy and $P_0$ is the background gas pressure [42]. The length of the plume, $L$, is proportional to $(E/P_0)^{1/3\gamma}$, where $\gamma$ is the ratio of specific heats of elements in the plume. For an ambient pressure of 35 mtorr and a laser fluence of 4 J/cm$^2$, the plume range, $L$, corresponds to approximately 5.5cm [43]. In addition to the control of growth parameters, the preparation of the substrates and targets contributes to the film quality. Substrates have to be free of grease or surface layers to ensure the film quality and reproducibility. Powders used for targets must be of high purity to avoid accidental doping and well mixed to insure stoichiometry. Low-density targets can result in a high density of particulates on films.

### 3.4 Limitation

PLD is a very promising technique for thin film deposition; however, there are still several inherent drawbacks of PLD that need to be overcome in order to develop it into a manufacturing process.

(i) Scalability to cover large-area substrates. Because the stoichiometric plume produced by laser ablation is highly peaked in the forward direction, good uniformity of thickness and composition can therefore only obtained within 10-15° to the target normal, i.e. within the forward peaked cone. By scanning or rotating substrates, large area deposition may be possible. Recent work has shown the feasibility of producing YBCO thin films with uniform composition and good properties over 6” wafers [44] though uniform coating of large-area wafers has still not been routinely achieved for many materials systems. This requires not only the deposition of material with uniform thickness, composition and microstructure over the whole surface but also the uniform heating of large-area wafers.
(ii) Production of macroscopic particles. One of the major factors that impeded the more widespread applications of the PLD process is the presence of particulates in the deposited films. The particulates ejected from the target are deposited on the substrate, which are especially detrimental to multilayer structures and for high-performance optical and electronic applications where stringent constraints exist for surface smoothness. There are several mechanisms proposed for particulate generation [45]: (1) protruding surface features or pits that exist in the fresh target surface or are progressively formed after laser ablation and, are mechanically dislodged from the target due to laser induced thermal or mechanical shock; (2) during the laser-target interaction, the rapid heating and surface evaporation causes superheating of a subsurface layer that leads to explosive evaporation (3) condensation from vapor species, mostly likely observed when a ambient high gas pressure is used. The size of particulates formed from the vapor state tends to be in the nanometer range, while the size from the other two are in the micron and submicron range. The number density and the size depend on the nature and preparation of the target, the laser beam characteristics and ablation parameters. The particulate density and size distribution has been reduced considerably through several modifications, such as the use of mechanical velocity filters [46], off-axis deposition [47], dual laser-ablation techniques [48], or an oscillating target scanning technique.

(iii) Target texturing. It has been found that a cone morphology gradually develops on the surface of the target as the laser ablation process continues. The cone formation leads to several problems: a drop in the deposition rate with time, an increase in the incidence of particle formation on the films, and a change in plume direction that is tilted away from the target surface normal by as much as $20^\circ$. Since the composition and thickness is optimum at the peak of the emitted plume, a shift of the plume direction is a problem in producing high quality films. By scanning the laser beam
across the target, it is possible to prevent these formation of the cone features.
Chapter 4

Experimental Setup and \textit{In-situ} Characterization

A schematic diagram of the setup used in this research is shown in Figure 4.1. A KrF excimer laser operating at a wavelength of 248 nm, a pulse duration of 20ns, and pulse energies ranging from 210 to 260mJ are used to ablate materials from the targets. The beam area on the target is $1.5 \times 5 \text{mm}^2$. The laser is incident at 45° from the target normal and the substrate is centered along the target normal. The system is capable of holding six targets for multilayer growth. Each target is rotated about its axis to ensure uniform wear on the targets, and individual targets can be successively cycled into position for the ablation of multi-targets. A load lock chamber with a magnetically coupled transfer rod is equipped to facilitate the transfer of both targets and substrates without breaking the vacuum of main chamber. The base pressure on the order of $10^{-8}$ torr is achieved by pumping the chamber with turbo and mechanical pumps.

The target to substrate distance can be varied over 15cm to operate in different pressure regions. The substrate is rotated to enhance the temperature and thickness uniformity during deposition. The substrate heater is made of Inconel metal wires capable of reaching 800 °C in either an oxygen ambient for oxide growth or a nitrogen ambient for nitride growth. The substrate temperature is kept constant by a temperature controller responding to a thermocouple signal. In order to enhance
the accuracy of the temperature readings, the thermocouple is calibrated using a pyrometer. In addition, the system is equipped with Reflective High Energy Electron Diffraction (RHEED) setup to monitor the initial stages of nucleation and growth and an oscillating quartz crystal thickness monitor is used to measure the deposition rate.

An attractive feature of our PLD apparatus is the capability of in-situ monitoring of the growth process by RHEED. RHEED not only offers abundant information on the crystal structure and the quality of the growing film, but also provides means to study surface structure and growth kinetics. For the application of RHEED for PLD, only few studies have been published so far. This is partly due to the fact that standard laser ablation is done in a pressure range in which conventional RHEED guns can not operate. We employ a differential pumping line which is connected to the RHEED to ensure the pressure inside the RHEED gun is less than $10^{-5}$ torr while the pressure inside the chamber during growth is $10^{-2}$ torr.

As shown in Figure 4.1, a high-energy (5-40keV) beam of electrons from RHEED gun is directed at the surface of a film. It hits the film at a glancing angle (1°
CHAPTER 4. EXPERIMENTAL SETUP AND IN-SITU CHARACTERIZATION

Figure 4.2: Correlation between the surface roughness and the RHEED pattern

- 3°) and is diffracted by the atoms in the top few atomic layers. The scattered electron beam strikes a phosphor screen on the opposite side of the PLD chamber, showing a pattern. The RHEED patterns come from the intersection of the Ewalds sphere, whose diameter is proportional to $1/\lambda$, with the reciprocal lattice of the film. Since electrons are only diffracted by atoms in the top few layers, arrays of reciprocal lattice points are elongated into rods, tangential to the Ewalds sphere. In addition, the high electron energies lead to a very large Ewalds sphere. Therefore, the RHEED pattern from a very smooth surface will consist of streaks on the phosphor screen, as shown in Figure 4.2(a). If the surface roughness of the film increases, the glancing incident electron beam can be transmitted through small islands, and this adds a third dimension to the diffraction geometry. Islanded or roughened surfaces produce spotty RHEED patterns (Figure 4.2(b) and (c)). Therefore, RHEED can provide information on the smoothness of growth with atomic layer sensitivity.

Furthermore, RHEED reveals the crystallinity of the film. The arrangement of spots or streaks has a symmetry which is characteristic of the symmetry of the atoms on the surface. For example, GaN can exist in two crystal structures, wurtzite and zincblende, giving rise to different epitaxial RHEED patterns when the electron beam
is incident at \([-110]_{\text{cubic}}\) or \([2\text{I}-1\text{0}]_{\text{hex}}\), as shown in Figure 4.3 [9]. From the pattern, one can determine the phase being grown and the epitaxial relationship to the substrate. In addition, atoms sometimes rearrange themselves on the surface in order to take up dangling bonds. From these surface reconstructions, one can deduce the chemical composition of the surface and the mechanism by which adatoms are incorporated into the growing film.

RHEED can also provide a valuable epitaxial monitoring process which involves oscillation in spot intensity as film growth proceeds. The quantitative analysis of RHEED oscillation behavior is much more complex [49]. As new layers are added to the film, the surface becomes alternately rough and smooth. This causes the intensity of the RHEED features to vary periodically. Each period corresponds to the addition of one atomic layer. Measuring the intensity of the specular reflection over time is the standard way of calibrating growth rates in MBE machines. RHEED oscillations do not occur if film growth takes place at step edges, since the surface stays equally smooth the entire time.

The crystal thickness monitor is used to calibrate the deposition rate. This information can be used to grow a sequence of different layers with predefined thickness
and determine when to switch the targets in multilayer growth. In addition, it reveals some characteristics of the PLD process. For example, threshold energies of targets can be determined from the characteristics of the deposition rate versus laser fluence. The thickness monitor also can measure the effect of ambient gas on deposition rate and angular distribution of the fluxes. The thickness variations of the PLD process show cosine distributions \((\cos \theta)^n\) where \(n\) is usually larger compared to other techniques [36]. In the presence of an ambient gas, the plume angular distribution is broadened by the plume particle collisions with the background gas, resulting in more uniform thickness and composition over a larger substrate area. The cosine distribution is slightly asymmetric and directed slightly toward the incoming laser.
Chapter 5

III-V Nitrides Growth and Characterization

5.1 Introduction

As mentioned in Chapter 2, group III nitrides have been investigated intensively because of the enormous interest in optoelectronic device applications in the green, blue, violet and near-ultraviolet regions. High efficient light-emitting diodes based on InGaN/AlGaN heterostructures are commercially available and electrically pumped III-V nitride lasers have succeeded in continuous-wave operation [13]. High quality GaN films have mostly been prepared by metal-organic vapor phase epitaxy (MOCVD) [8] [9], molecular beam epitaxy (MBE) [10] and vapor phase epitaxy (VPE) [11]. A great deal of research has been done in understanding the growth kinetics and the properties of the GaN films grown by these techniques. Compared to the MOCVD and MBE techniques, pulsed laser deposition (PLD) [12] is a relatively new growth technique used widely for the growth of oxide thin films, such as ferroelectrics and superconductors. There are, however, several advantages of PLD, as mentioned in Chapter 3, for depositing high quality thin films and make it worthy of study as a method of growing nitrides. The congruent ablation achieved by PLD and the capability of holding six targets inside our chamber enable the in-situ growth
of heterostructures and the rapid investigation of the effects of buffer layers on nitride growth. Due to the availability of in-situ RHEED, buffer layer nucleation and growth kinetics can be studied in the PLD environment. The growth rate achieved by PLD can be varied through adjusting the power and the repetition rate of the laser, which is useful for both atomic level investigations and thick layer growth. Moreover, the strong nonequilibrium growth conditions of PLD allow a much broader range of metastable materials to be grown. Because of these attractive features of the PLD technique, there has been a growing interest in the deposition of GaN by PLD [51] [52] [53] [54]. In this chapter, we discuss the influence of the deposition parameters, the substrate temperature and the nitrogen pressure during growth, on the optical and the structural properties of GaN films. Furthermore, we report studies of PLD growth of GaN on sapphire, with particular emphasis on its initial nucleation and its relationship to the resulting microstructure. The types and the distribution of extended defects observed in TEM were correlated with the film growth modes and the layer nucleation mechanism which was characterized by RHEED and AFM. Finally, the studies of the growth of AlGaN ternary alloy by PLD will be discussed in Section 5.3.

5.2 GaN

GaN films were deposited on (0001) sapphire using a pulsed laser deposition (PLD) apparatus described in Chapter 4. A pressed pellet of dark gray GaN powder (99.9% purity) was used as a target. The substrate temperature was varied from 300 to 800°C and the nitrogen partial pressure was varied from 0.1 to 450 mtorr. No low temperature buffer layer or substrate pretreatment was employed prior to the deposition of GaN films. After deposition, the substrates were cooled slowly to room temperature at a rate of 5°C/min. under 1 torr nitrogen.
Figure 5.1: $2\theta$ scans of GaN grown at various temperatures 400°C – 700°C

Figure 5.2: $\phi$ scan of GaN grown at 750°C
5.2.1 Effect on crystallinity

As shown in Figure 5.1, GaN films deposited below 400°C are amorphous. As the growth temperature increases, the films become crystalline and c-axis oriented. GaN films grown above 750°C are epitaxial from x-ray ϕ scans and the epitaxial relationships are GaN[0001] || Al₂O₃[0001] and GaN[10–10] || Al₂O₃[11–20] (Figure 5.2). The 30° rotation about [0001] axis of GaN film leads to a 14.6% lattice mismatch for the basal plane growth. The substrate temperature and nitrogen partial pressure during growth play important roles in the deposition of GaN by PLD. Figure 5.3 shows the dependence of (0002) rocking curve widths on growth temperature and nitrogen pressure during growth. As shown in Figure 5.3(a), the crystallinity of the films can be greatly improved at higher growth temperatures. Figure 5.3(b) shows that the better quality films lie in the range of 10–50 mtorr. For films grown at higher and lower pressures, the crystal quality degrades. This phenomenon can be related to the kinetic energy of the arriving species at the substrate. At low N₂ pressure, the ablated species go through few collisions before they arrive at the surface of the substrate.
With sufficient kinetic energy, arriving species can produce lattice displacement damage in the growing film. Such damage can be reduced by increasing the nitrogen pressure in the chamber to promote collisions between ablated species and ambient gas. However, increasing the nitrogen pressure beyond 100 mtorr degrades the film properties. Significant collisions occurring at high pressure can reduce the energy of the ablated species below what is necessary to grow epitaxial films. The films grown beyond 400 mtorr become amorphous and no x-ray diffraction peaks are detected. The optimum nitrogen pressure for PLD-GaN growth is in the range of 10–50 mtorr. A similar optimal pressure range was found for the growth of ZnTe films in a N₂ ambient and it has been suggested that the optimum kinetic energies for film growth by PLD are in the range of a few eV [55].

5.2.2 Effect on optical property

In addition to the film crystallinity, the optical properties of PLD-GaN films are greatly dependent on the growth temperature and nitrogen partial pressure. Figure 5.4(a) and (b) show the effects of substrate temperature and nitrogen partial pressure on the optical transmission below the bandgap of GaN films, respectively. At low growth temperatures, the color of the films is gray, indicating insufficient nitrogen incorporation. As the growth temperature increases, the films become more transparent.

When the film is grown at 0.1 mtorr, the transmission drops below 60% and the color of the film is gray. Ga-rich films could form under low nitrogen pressure growth conditions, resulting in the reduction of transmission due to absorption. More nitrogen could be incorporated into the films by increasing the nitrogen pressure during growth. As the nitrogen pressure during growth increases to the range of 10 mtorr, the films become transparent. However, as the nitrogen pressure increases beyond 100 mtorr, the surfaces of the films are rough and the particle size increases, which reduces the transmission due to surface scattering. From these studies, we conclude that the substrate temperature and the nitrogen pressure during growth are very important, not only for the film structure, but also for the preservation of the
Figure 5.4: The effect of (a) growth temperature on maximum transmission below bandgap of GaN grown at 10 mtorr. (b) nitrogen pressure during growth on maximum transmission below bandgap of GaN grown at 775°C.

stoichiometry of GaN films grown by PLD.

5.2.3 Photoluminescence

The photoluminescence (PL) spectra were excited with the 325nm line of a 12mW He-Cd laser. Holographic notch filters were used to reject the scattered and reflected light at the laser wavelength. The signal was then diffracted by a grating and collected by a CCD camera. For low temperature PL measurements, the sample was mounted in a cryostat and cooled by liquid He. Figure 5.5 shows the PL spectrum at 25K and room temperature for the GaN films grown at 800°C and 50 mtorr nitrogen. At 25K, the near band edge (NBE) emission at 3.467eV with FWHM of 18 meV is the I₂ line which results from the annihilation of excitons bound to neutral shallow donor sites (BX). Another distinct peak occurs at 3.413eV with FWHM of 10 meV, accompanied by a pair of LO phonon replicas at 3.329eV and 3.236eV, which may be attributed to the appearance of oxygen impurities [56]. Oxygen is suspected of being either a shallow or deep level donor, or possibly both thus causing the material to be
Figure 5.5: The photoluminescence spectrum of GaN measured at (a) 25K (b) room temperature
n-type without doping and creating difficulty to achieve p-doping. In addition, a zero phonon line is observed at 3.28eV along with its LO phonon replicas which are due to the donor-acceptor pair (DAP) transitions. The LO phonon energy is 90meV. As the temperature increases, the donors and acceptors ionize. The free exciton (FX) line at 3.4eV with FWHM of 98meV becomes the dominant feature in the PL spectrum at room temperature, as shown in Figure 5.4(b). The oscillations of the spectrum observed at low energy are caused by the system response of the PL setup.

5.2.4 TEM

As discussed in Chapter 2, the majority of defects in GaN are directly related to the growth errors occurring at the initial 3-D growth. Slight tilting or twisting of nuclei on a sapphire substrate could be an origin of the threading dislocations at the island edge. Epitaxial GaN on sapphire typically consists of subgrains/domains slightly misoriented with respect to each other and the underlying substrate. There are two components of the misorientations [23]. One is twist of the columns orientation about the c axis (Figure 5.6(a)) and the other is tilt of the c axis with respect to the growth direction (Figure 5.6(b)). The twist generates edge dislocations on the prismatic planes parallel to the growth direction. The tilt induces edge type dislocations parallel to the basal plane and screw dislocations on the prismatic planes parallel to the growth direction. For GaN films grown by MOCVD, MBE and VPE, the threading dislocations are predominantly edge dislocations lying along c-axis with 1/3 < 11-20 > Burgers vectors, forming low angle twist boundaries. Cross-section TEM studies were performed on PLD-GaN film grown on c-cut sapphire at 800°C and 30 mtorr. Figure 5.7 shows a series of TEM images taken from the same area under different two beam diffracting conditions with diffraction vectors g= 0002, 11-20, and 10-10. TEM results showed that the major defects in PLD-GaN film are threading dislocations perpendicular to the interface (Figure 5.7(a)) and stacking faults parallel to the interface (Figure 5.7(c)). Comparing the TEM images with g=0002 (Figure 5.7(a)) and g=11-20 (Figure 5.7(b)), the majority of the dislocations are in contrast with g=0002 and out of contrast with g=11-20, indicating that the Burgers
Figure 5.6: Two types of misorientations of domains in GaN. (a) Twist of the column orientation about the c-axis (b) Tilt of c-axis with respect to the growth
Figure 5.7: Cross-section TEM images of GaN taken with different diffraction vectors, g (a) 0002 (b) 11-20 (c) 10-10
vector is parallel to the c-axis. Since the line direction of the dislocations is mostly parallel to the c-axis, the threading dislocations are mostly screw dislocations. A high density of dislocations near the GaN/sapphire interface region is observed and the dislocation density decreases with increasing distance from the interface. One of the origins of these screw dislocations is that they are created at the domain boundary to accommodate the tilt of misaligned island nuclei with respect to the growth direction. This is illustrated in Figure 5.8, a high resolution cross-section TEM image taken at the domain boundary. The c-axis of one domain is found to tilt with respect to that of the neighboring domain. Stacking faults are another type of defect which is observed in PLD-GaN. A high density of horizontal defects are evident in Figure 5.7(c), which is imaged using g=10-10. These defects did not produce contrast under g=0002 and 11-20 imaging conditions and therefore corresponding to stacking faults with displacement vector $\frac{1}{3} < 10-10 >$. As shown in Figure 5.9, the high resolution TEM image of the stacking faults reveals lattice images consisting of an error in the stacking sequence of the (0002) planes. The high density of stacking faults observed may also be related to low surface adatom mobility. If an adatom does not have sufficient mobility to jump to the proper wurzite position, a stacking faults with displacement vector $\frac{1}{3} < 10-10 >$ will form. The threading dislocations in GaN grown by PLD are predominantly screw dislocations, while edge dislocations are the dominant defects.
in GaN grown by MBE [59], MOCVD [19] [20] and VPE [60]. This indicates that the misorientation of nuclei in the initial stages of PLD growth is mainly the tilt of the c-axis of domains with respect to the growth direction, instead of the twist of domain orientation about the c axis. The variation in misorientation of nuclei observed in GaN grown by PLD and other techniques is related to the initial stages of nucleation and growth kinetics, which will be discussed in the next section.

5.3 Kinetics of PLD

It is generally agreed that the initial stages of nucleation and growth play a crucial role in determining the quality of the final GaN film. Because of the intense plasma that is generated in the ablation process, nucleation of PLD could be somewhat different from MBE and MOCVD, thus providing another approach to addressing the important issue of nucleation. In this section, RHEED and AFM are used to study film nucleation, growth modes and surface roughness of GaN. Such information is essential for understanding the fundamental nucleation and growth kinetics of GaN. The difference between PLD and other techniques can be understood from the difference in vapor-generation/vapor transport mechanism involved in PLD and the influence of the sudden arrival of a plume of supersaturated vapor on the growth mode of a depositing film. The high instantaneous vapor arrival rate from each laser pulse
in the PLD process would cause rapid nucleation of very small nuclei, compared to steady-state deposition at the same average deposition rate. At the high deposition rates in PLD, the instantaneous flux supersaturation reaches a value of $10^8$ J/mol, which is many orders of magnitude higher than conventional steady-state deposition techniques \[15\].

With the capability of in-situ monitoring of the growth in the PLD system by RHEED, we are able to study the crystallinity, roughness and kinetics of growth of freshly grown surfaces. Figure 5.10 shows the evolution of the RHEED patterns of GaN at initial stages of nucleation and growth as well as the corresponding AFM images of the surface morphology. GaN films grown at 800°C and 30 mtorr N$_2$ with the electron beam parallel to the [10–10] direction of the c-cut sapphire substrate. RHEED pattern of sapphire substrate at 800°C is shown in Figure 5.10(a). After one-minute GaN deposition, a streak RHEED pattern occurs, indicating 2-D nucleation (Figure 5.10(b)). The high degree of supersaturation in PLD leads to small size of nuclei, which results in two-dimensional nuclei of atomic height. When growth continues after seven minutes, the RHEED pattern consists of truncated streaks (Figure 5.10(c)). This type of pattern is consistent with a surface which is locally smooth on an atomic scale, but has macroscopic steps. As the growth continues, the truncated streaks are replaced by spots, corresponding to 3-D diffraction from a surface that is rough on an atomic scale (Figure 5.10(d)(e)). AFM studies are consistent with the RHEED observations and reveal the changes in the film growth modes. The surface morphology of the sapphire substrate prior to GaN deposition was quite smooth (r.m.s: 0.2 nm) with a few steps/scratches, possibly from polishing (Figure 5.10(f)). After one-minute GaN growth, AFM images clearly show 2-D nucleation with r.m.s. of 0.11 nm (Figure 5.10(g)). Apparent island formation can be seen on the surface after seven minutes of deposition. The diameters of the islands range from 10 to 20 nm, with a height between 1 and 2 nm (Figure 5.10(h)). As the growth continues, islands grow laterally with little change in height (Figure 5.10(i)). Gradually these islands coalesce. After a sixty-minute deposition, the layer exhibits a grain-like structure with a surface roughness of 1.1 nm, and the island size ranges from 70 to 80 nm with heights between 3 and 5 nm (Figure 5.10(j)).
Figure 5.10: Evolution of RHEED patterns during GaN growth with the electron beam parallel to [10–10] sapphire and the corresponding AFM.
The results from RHEED and AFM indicate that 2-D epitaxial nuclei form homogeneously on substrates in the PLD process because of the high instantaneous flux supersaturation. For MOCVD conducted at high temperature, low supersaturation condition could result in big nuclei with poor uniformity in size and possibly preferential nucleation at low energy sites, such as point defects and dislocation intersections. Therefore, the initial buffer layer is deposited at low temperature to increase supersaturation and achieve uniform nucleation, as discussed in Section 2.2. Low temperature GaN or AlN buffer layers are amorphous and become crystalline as the growth temperature ramps up prior to high-temperature GaN growth. Through geometric selection, epitaxial GaN can grow on top of the low temperature buffer sequentially. However, the in-plane misorientations of the buffer layer are likely to cause “twist boundary” to form during coalescence of islands at the initial stages of GaN growth. The twist induces edge dislocations parallel to [0001]. PLD-GaN, on the other hand, has fewer edge threading dislocations along the c-axis, i.e. less in-plane twist of the column orientations about the c axis. The 2-D homogeneous epitaxial nuclei achieved by PLD in the initial stages may contribute to the reduction of in-plane misorientation, therefore the reduction of edge threading dislocations. As growth continues, the growth mode become 3-D, which may be due to insufficient mobility or time to rearrange atoms on the surface before the next incoming atoms arrive and to grow laterally. 3-D growth reduces the planarity and introduces various dislocations and planar defects, such as stacking faults, to develop.

It has been suggested that a step-flow growth mode can reduce defect density. If adatoms have a large surface diffusion length, they move relatively freely across a terrace until incorporated at a step edge. Then growth proceeds by the continuous flow of step edges across the surface rather than by cycles of nucleation and monolayer completion. Control of nucleation in this manner can reduce the crystallographic defect density. For example, the bonding configuration at the step edge may help ensure that the “proper” (wurtzite) out-of-plane stacking sequence is preserved in GaN, thereby reducing the probability of stacking disorder.
5.4 AlGaN

In order to fabricate optoelectronic and electronic devices, it is important to be able to control the energy bandgap and lattice constant by varying alloy composition. \( \text{Al}_x\text{Ga}_{1-x} \text{N} \) films with \( x \) less than 0.3 are commonly used for carrier confinement in quantum well light emitting diodes (LED) and laser diodes. There is also a great potential to develop optoelectronic devices in the UV region using \( \text{Al}_x\text{Ga}_{1-x} \text{N} \) with higher Al content. In addition, \( \text{Al}_x\text{Ga}_{1-x} \text{N} \) can be used as the electron supply layer and confining layer for high electron mobility transistors (HEMTs). In this section, we demonstrate the capability of PLD for growth of \( \text{Al}_x\text{Ga}_{1-x} \text{N} \) films. The properties of \( \text{Al}_x\text{Ga}_{1-x} \text{N} \) films are characterized by X-ray diffraction scans, RHEED, optical transmission, and Hall measurement. The dependence of the lattice constant and the absorption edge on the composition is discussed.

\( \text{Al}_x\text{Ga}_{1-x} \text{N} \) films were deposited on (0001) sapphire at a substrate temperature of 800°C and nitrogen pressure of 30 mtorr. The deposition parameters of \( \text{Al}_x\text{Ga}_{1-x} \text{N} \) are similar to those of GaN growth except the target-substrate distance. The epitaxial growth of \( \text{Al}_x\text{Ga}_{1-x} \text{N} \) is found to be very sensitive to the target-substrate distance, which is not a strong factor on the epitaxial growth of GaN. The optimum distance is 2–3 cm and the films will become amorphous if the distance is greater than 6 cm. The targets with compositions from \( x = 0 \) to 0.6 are obtained by mixing various ratios of GaN powder (99.9% purity) and AlN powder (99.995% purity).

5.4.1 Composition

The alloy composition of the \( \text{Al}_x\text{Ga}_{1-x} \text{N} \) films was determined by electron probe microanalyses (EPMA). The composition, \( x \), was calculated from the measured intensity ratio of Al and Ga, taking into account atomic number, absorption and fluorescence corrections. Figure 5.11 shows the Al mole fraction of films obtained from EMPA versus Al mole fraction of targets defined by \( n_{\text{AlN}}/(n_{\text{AlN}} + n_{\text{GaN}}) \), \( n_{\text{AlN}} \) is the amount of AlN powder in moles. The solid line shows the expected composition of the film if it is identical to that of the target. We observe a small deviation, less than 2%, between the composition of the films and the targets. The accuracy of EPMA in
determining elemental composition is about 2% to 3%, thus the above deviation may be largely experimental measurement error. This result indicates excellent stoichiometric transfer between films and targets by pulsed laser deposition, even when the target is a mixture of powders from two different compounds. This enables growth of films with different alloy compositions by simply mixing powders which are commercially available. In addition, we may be able to introduce dopants by the same method.

5.4.2 X-ray diffraction and RHEED

RHEED and x-ray diffraction are used to examine the crystalline structure of the films. Figure 5.12 shows the RHEED pattern observed for an Al_{x}Ga_{1-x}N (x=0.6) film on (0001) sapphire with the electron beam parallel to the [10-10] direction of sapphire. The films throughout the composition range we investigated (0 ≤ x ≤ 0.6) show epitaxial RHEED patterns. No detectable change in RHEED pattern is observed while scanning the electron beam over the film surface, indicating uniform crystallinity across the film. From x-ray 2θ scans, we observe only peaks corresponding
to (000c) planes of $\text{Al}_x\text{Ga}_{1-x}\text{N}$. As shown in Figure 5.13(a), the peak shifts towards higher angles with increasing $x$, indicating that the lattice constant decreases with Al composition. From x-ray diffraction results, the c-axis lattice constants of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ films can be calculated using Bragg's equation $d_{hkl} = \frac{n\lambda}{2\sin\theta}$, as a function of $x$. The solid line in Figure 5.13(b) is the relationship between lattice constant, $c_0$, and Al mole fraction, $x$, assuming the lattice constants of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ films follow Vegard's law. According to Vegard's law, the lattice constants $c_0(x)$ of stress-free $\text{Al}_x\text{Ga}_{1-x}\text{N}$ films depend linearly on the composition; i.e. $c_0(x) = x \ast c_0^{\text{GaN}} + (1 - x) \ast c_0^{\text{AlN}}$. Figure 5.13(b) shows that the lattice constants, $c$, obtained from x-ray diffraction vary linearly with composition, but deviate to a higher value from the relaxed lattice constants, $c_0$. From x-ray $\phi$ scans, all the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ films grow epitaxially with the an epitaxial relationship of $\text{Al}_x\text{Ga}_{1-x}\text{N}[10\text{-}10] \parallel \text{Al}_2\text{O}_3[11\text{-}20]$. Figure 5.14 is the $\phi$ scan of $\text{Al}_{0.6}\text{Ga}_{0.4}\text{N}$ film. From the x-ray rocking curve scan, the full widths at half-maximum (FWHM) of (0002) $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys are between 0.45° and 0.55°, higher than the value for GaN. Note that all the films have been grown at a substrate temperature of 800°C, and the optimum growth temperature for AlGaN alloy is known to be higher than GaN [61], which may contribute to the larger FWHM in the rocking curve scans. We have previously found that the crystalline quality of GaN films can be greatly improved at higher growth temperature [51]. Vispute et al. [53] recently
Figure 5.13: (a) X-ray 2θ scans of Al$_x$Ga$_{1-x}$N films, $x = 0, 0.1, 0.3$ and 0.6. (b) The variation of lattice constant $c$ with Al mole fraction $x$ of Al$_x$Ga$_{1-x}$N films.
Figure 5.14: X-ray \( \phi \) scan of Al\(_{0.6}\)Ga\(_{0.4}\)N \(\{11-22\}\) peaks. The dash line is the \( \phi \) scan of Al\(_2\)O\(_3\) \(\{11-23\}\) peaks.

reported a great reduction in the FWHM of GaN \(0002\) peaks from 0.85° to 0.12° when the growth temperature was raised from 850 to 950°C. With increased growth temperature, we expect that the crystalline quality of Al\(_x\)Ga\(_{1-x}\)N films might be further improved.

5.4.3 Bandgap

Figure 5.15 shows the optical transmission spectra of Al\(_x\)Ga\(_{1-x}\)N films. The absorption edge shifts to a shorter wavelength, corresponding to a larger bandgap with increasing \( x \), indicating the bandgap can be controlled by PLD. The squared absorption coefficient, \( \alpha^2 \), of the films calculated from transmission spectra versus photon energy is shown in Figure 5.16(a). For direct bandgap transitions, the absorption coefficient near the absorption edge has the form \( (h\lambda - E_g)^{\frac{1}{2}} \), where \( h\lambda \) is the photon energy and \( E_g \) is the bandgap energy. \( E_g \) can thus be obtained by extrapolation of the linear fit to the axis of photon energy in Figure 5.16(a). The composition dependence of the direct bandgaps of Al\(_x\)Ga\(_{1-x}\)N films is shown in Figure 5.16(b). The graph of bandgap versus composition deviates from linearity and bows downwards, with the
bowing parameter of 1.8eV. In addition to lattice constants, bandgaps of $\text{Al}_x\text{Ga}_{1-x}\text{N}$ films can be controlled by varying the ratios of AlN and GaN powders of the targets.

### 5.4.4 Electrical Characterization

Hall measurements show that the GaN films are heavily n-type with electron concentrations on the order of $10^{19}$cm$^{-3}$ and mobilities around 30cm$^2$/Vs. For $\text{Al}_x\text{Ga}_{1-x}\text{N}$ alloys, accurate results from Hall measurements are difficult to obtain because of the high resistivity or low mobility of the films. There are several factors that cause high carrier concentration and low mobility of GaN films grown by PLD. One of the major factors is that high purity source materials, such as GaN powder, are not available. With GaN powder of 99.9% purity, it is predictable that the resulting films can easily have an impurity level on the order of $10^{19}$cm$^{-3}$ even though the deposition system is clean. PLD may be an attractive technique for III-V nitride growth, but source materials with higher purity are essential to further improve the electrical and optical properties of the films.
Figure 5.16: (a) The squared absorption coefficient $\alpha^2$ of Al$_x$Ga$_{1-x}$N films versus photon energy $h\nu$. (b) The dependence of the energy bandgaps $E_g$ on Al mole fraction $x$ of Al$_x$Ga$_{1-x}$N films.
5.5 Conclusion

Epitaxial GaN films were grown on (0001) sapphire substrates by pulsed laser deposition without employing any low temperature buffer layer. The structural and optical properties of the films are greatly improved at higher growth temperatures and at a nitrogen pressure of 10 mtorr during growth. Room temperature PL exhibits strong band edge emission. Transmission electron microscopy studies reveal that the defects observed in PLD-GaN layers consist of stacking faults and threading dislocations parallel to the c-axis. The threading dislocations of GaN are predominantly screw dislocations while edge dislocations are the dominant ones in GaN grown by MBE, MOCVD and VPE. This variation observed in defect characteristics may come from the differences in nucleation and growth kinetics of the PLD process compared with other techniques due to the intense plasma that is generated in the ablation process. The first compositionally controlled growth of epitaxial Al$_x$Ga$_{1-x}$N films on c-cut sapphire substrates has been demonstrated at 800°C and 10 mtorr N$_2$ by PLD from $x = 0$ to 0.6. Excellent stoichiometric transfer between targets and films by PLD has been demonstrated, even when the target is a mixture of powders from AlN and GaN. Furthermore, the energy bandgap and lattice constant of Al$_x$Ga$_{1-x}$N films can be engineered by alloy composition. The lattice constants, c, of Al$_x$Ga$_{1-x}$N films vary linearly with chemical composition and the composition dependence of the bandgaps of the films is found to deviate from linearity and bows downward.
Chapter 6

Growth and Effect of ZnO on GaN Epitaxy

6.1 Introduction

As mentioned in Chapter 2, one of the major problems inhibiting the growth of high quality III-nitrides is the lack of either a bulk GaN substrate for homoepitaxy or a well lattice and thermal expansion matched substrate for heteroepitaxy. Sapphire, with a lattice mismatch of 16% with respect to GaN, is the most common substrate material for wurtzite III-nitrides. However, huge lattice (~16%) and thermal mismatches between sapphire and GaN result in a very high dislocation density and considerable strain after postgrowth cooling. For epitaxial growth, 16% mismatch is almost the largest misfit that can be tolerated while still getting a well-aligned film. Island growth is typical for high temperature (~1000°C) growth of GaN directly on sapphire, resulting in a high density of macroscopic defects, such as cracks and pits in GaN films. Use of low temperature (~500°C) buffer layers such as AlN [1] and GaN [2] at the initial stage of the growth substantially improve the surface morphology and the crystalline quality of GaN on sapphire. The essence of a low temperature buffer layer is to provide a uniform and high density nucleus for the GaN growth and to insert a slightly “softer” material in order to reduce the interfacial energy between the epitaxial layer and the highly mismatched substrates.
ZnO is another buffer layer material of interest for GaN growth because the physical properties of ZnO are similar to those of GaN. The lattice mismatch between ZnO and GaN is 1.7%, which leads to a range of critical thickness between 80 to 120 Å, estimated using different elastic models [62]. GaN grown on ZnO buffer layers is expected to have better surface morphology and lower dislocation densities than GaN grown directly on sapphire substrates. Another advantage of a ZnO buffer layer is the possibility of releasing thick GaN from ZnO and sapphire by etching ZnO since ZnO can be selectively etched by any acid. Because bulk GaN is nearly impossible to produce, thick epitaxial layers can be used as substrates have fabricated thick GaN films by vapor phase epitaxy (VPE) on a sapphire substrate with a sputtered ZnO buffer layer [11] [63]. However, the sputtered ZnO layer was polycrystalline and the effects of the growth condition and thickness of ZnO buffer layers on the growth of GaN were not fully examined.

In addition to being a good candidate for a GaN buffer layer, ZnO is attractive for a number of other applications, including surface acoustic waves (SAW) [64], opto-electronic and piezoelectric devices [65], because of its high electromechanical coupling factor and large piezo-optic and piezo-electric properties. Due to its optical transparency throughout the visible region of the spectrum and good electrical conductivity, ZnO is also a good transparent conducting material [66]. In addition to ZnSe and GaN, ZnO has recently been reported to be another candidate for short wavelength lasers [67].

As discussed in Chapter 3, PLD is very suitable to investigate multilayer growth in the same chamber due to its simplicity and versatility. There are very few limitations on material selection. In addition, buffer layer nucleation and growth kinetics are also better studied in the PLD environment due to the availability of in-situ RHEED. In this chapter, the growth of single-crystalline ZnO films on c-cut sapphire substrates by PLD and their crystal structure, optical properties and surface morphology will be discussed in Section 6.2. The effect of PLD-ZnO on the properties of PLD-GaN and VPE-GaN will be discussed in Section 6.3 and Section 6.4.
6.2 ZnO buffer layer

ZnO films were deposited on c-cut sapphire substrates using the PLD apparatus described in Chapter 4. ZnO films were grown under an oxygen partial pressure of 10 mtorr controlled by an automatic pneumatic valve, at a flow rate of 5 sccm. Targets were prepared by pressing ZnO powder of 99.999% purity under 10,000 lb/cm² and sintering at 1100°C for three hours. After deposition, the substrates were cooled slowly to room temperature at a rate of 5°C/min. under 1 Torr oxygen.

6.2.1 Structural Characterization

RHEED and X-ray diffraction studies were used to investigate the nature of the epitaxial growth and crystalline quality of the films. At growth temperatures of 350–650°C and 10 mtorr O₂, ZnO films grown on (0001) sapphire substrates show (000c) peaks from x-ray 2θ scans (Figure 6.1(a)). There are only six peaks observed in the x-ray φ scan of ZnO {10-12} with 60° spacing (Figure 6.1(b)), indicating single crystalline growth despite high lattice mismatch between ZnO and sapphire. The epitaxial relationships are ZnO[0001]||Al₂O₃[0001] and ZnO[10–10]||Al₂O₃[11–20]. The optimum growth temperature is 550°C with a FWHM of 0.35° of ZnO (0002) peak from x-ray rocking curve ω scans.

*In-situ* RHEED patterns are taken along < 2110 > azimuth of ZnO films grown at 10 mtorr O₂ and various substrate temperatures. The RHEED gun operates at 14KV and 1.6amp. At the growth temperature of 350°C, a streaky pattern with a regular array of elongated spots indicates that the transmission pattern appears superimposed on the reflection pattern, as shown in Figure 6.2(a). The transmission pattern shown by RHEED is due to the surface roughness of the film, which may occur if the film is grown in a Stranski-Krastanov or Volmer-Weber mode. Another reason for surface roughness may be particulates on the films which are produced by ablating targets during growth. If the surface roughness increases, the RHEED becomes a regular array of spots from transmission through the peaked regions. For ZnO films grown at temperatures lower than 350°C, extra spots gradually develop, indicating the film is polycrystalline. As the growth temperature increases to 550°C, a
Figure 6.1: (a) 2θ scan (b) φ scan of ZnO grown at 550°C and 10 mtorr
Figure 6.2: (a) and (b) are *in-situ* RHEED patterns taken along $<2110>$ azimuth of ZnO films grown on c-cut sapphire substrates at 0.01 torr O$_2$. (c) and (d) are AFM images of the same films. (a), (c) at $T_s = 350^\circ$C (b), (d) at $T_s = 550^\circ$C
sharp and streaky ZnO RHEED pattern is observed, indicating good crystallinity and
atomically smooth surface (Figure 6.2(b)). The quality of the pattern is comparable
with that of MBE-grown ZnO films [68] and is much better than those grown by other
techniques [11] [66] [69].

6.2.2 Surface Morphology

Surface roughness of ZnO films was examined by scanning electron microscopy (SEM)
and atomic force microscopy (AFM). From SEM, the topography of ZnO films is
featureless with very few particulates. By contact-mode AFM, the films are very
smooth with only several monolayers of roughness (c=5.2065Å for ZnO). ZnO films
grown at 350°C (Figure 6.2(c)) have a r.m.s. roughness of 7.1Å, two times higher than
films grown at 550°C. ZnO films grown at 550°C show a r.m.s. roughness of 3.5Å,
one of the smoothest ZnO film reported by any growth technique (Figure 6.2(d)).
This result agrees with the RHEED observation. At low growth temperature, atoms
arriving at the substrate surface may not have enough kinetic energy to move around
before the next atoms arrive. Thus, island growth dominates, which results in a
rougher surface of the film. This is the main reason that the RHEED pattern for low
temperature grown ZnO shows a regular array of elongated spots.

6.2.3 Optical Properties

Figure 6.3 shows the photoluminescence (PL) spectrum of ZnO grown at 550°C. The
film is excited by He-Cd laser (λ= 325nm) at 77K. A strong near band edge peak at
3.34eV is observed. This has been previously attributed to the annihilation of bound
excitons in ZnO [70]. Deep level emission, which usually originates from crystal
defects or impurities, is not detectable. Transmission measurements show over 85%
transmission in the visible region with a steep fall-off at 380 nm, characteristic of
high quality ZnO films. A bandgap energy of 3.26eV is estimated, which is identical
to the value reported for single crystal ZnO.
6.3 Effect of a ZnO buffer on PLD-GaN

With the development of a ZnO buffer with good crystallinity, optical properties and smooth morphology, we initiated a study on the effect of ZnO buffer layers on GaN epitaxy. Figure 6.4 is the evolution of RHEED pattern during the initial growth of GaN on ZnO buffer/sapphire. A ZnO buffer with a thickness of 100nm was prepared at 550°C and 10 mtorr. A sharp and streaky ZnO RHEED pattern was observed before the growth of GaN at 800°C and 30 mtorr, as shown in Figure 6.4(a). The pattern remains streaky after 1-minute growth of GaN (Figure 6.4(b)) and gradually develops regular spots as GaN growth continues, similar to the situation we observed previously in the growth of GaN on sapphire. Figure 6.4(c) is the RHEED pattern of GaN after three hours of growth on ZnO buffer layer. PLD- GaN grown epitaxially on ZnO buffer with the relationships:

GaN[0001] || ZnO[0001] || Al₂O₃[0001] and

As discussed in Chapter 5, PLD-GaN tends to have 3-D growth at 800°C because
Figure 6.4: RHEED pattern evolution during GaN growth on a sapphire substrate with a ZnO buffer layer. (a) ZnO only (b) after 1 min. GaN growth (c) after 3 hrs GaN growth
of insufficient mobility or time to rearrange atoms on the surface before the next incoming atoms arrive. With a ZnO buffer layer, the growth mode of GaN remains the same since the reason for 3-D growth of PLD-GaN is mainly due to kinetic limitation.

Two TEM images of ZnO/sapphire were taken under two beam conditions using \( g = 11-20 \) and 0002 of ZnO, as shown in Figure 6.5. The defects observed in ZnO are mostly lying in the basal plane (parallel to the interface), whereas the majority of the dislocation lines of III-nitrides are along \(< 0001 >\) direction and constitute low angle tilt and twist boundaries. ZnO films were found to have layered growth morphology, contrary to columnar morphology observed in III-nitrides. Consequently, the threading dislocation density in ZnO is lower. It is believed that low threading dislocation density in buffer layer is desirable since the threading dislocations generated in the buffer layer could be a potential source of threading dislocations for subsequent GaN film growth.

High resolution TEM images of the PLD-GaN on ZnO buffer/sapphire are shown in Figure 6.6(a). PLD-GaN with ZnO buffer showed similar columnar structure to the PLD-GaN without ZnO buffer, but the lateral dimension of the domain structure is larger and more regular. Most threading dislocations in GaN originate from GaN/ZnO interface due to the growth errors produced by 3-D island growth of GaN and not from the defects of ZnO.

There is an interfacial layer of 10–15 nm at the interface of GaN and ZnO. From the EDS measurement at the interface layer, peaks of Ga, Zn, N, and O were observed and the layer appears to be the intermixing of GaN and ZnO. Figure 6.6(b) showed that the atomic arrangement of the interfacial layer was different from ZnO and GaN. The GaN film did not deteriorate due to the interfacial layer and GaN maintained its epitaxial relationship with ZnO. This suggests that the interfacial layer most likely forms after GaN has already grown to a certain thickness, instead of right at the initial stages of GaN nucleation and growth. RHEED studies also support this argument because only the epitaxial RHEED pattern of GaN was observed immediately after starting growth on a ZnO buffer layer.
Figure 6.5: TEM of ZnO (a) g=11−20 (b) g=0002
Figure 6.6: (a) TEM of GaN on ZnO buffer (b) HRTEM at the GaN/ZnO interface
CHAPTER 6. GROWTH AND EFFECT OF ZNO ON GaN EPITAXY

6.4 Effect of a ZnO buffer on VPE-GaN

As mentioned in Chapter 1, room temperature cw laser operation by current injection has been achieved in GaN-based structures [13]. These structures are fabricated on a highly lattice mismatched sapphire substrate by MOCVD with a dislocation density of $10^8 \text{cm}^{-2}$. Moreover, because of the insulating substrate, a substantial series resistance between the active region and the n-type contact results in high operation voltage, causing heating and a high threshold current density. Among various growth techniques, VPE is very promising to obtain thick GaN films because of its high growth rate. Laser structures grown on a thick VPE-GaN "substrate" would have better crystallinity and lower series resistance than heteroepitaxial growth on sapphire.

In Section 6.2, ZnO buffer layers of high quality, in terms of crystalline structure, optical properties, and surface flatness have been grown by PLD. Moreover, the characteristic feature of ZnO 2-D growth, a low density of threading dislocations in ZnO as well as low lattice mismatch with GaN and AlN can be quite beneficial for subsequent III-nitride growth. By introducing a PLD-ZnO buffer layer, substantial improvement of VPE-GaN can be obtained and these results will be discussed in this section.

6.4.1 Vapor Phase Epitaxy

A chloride VPE system was employed to grow thick GaN layers using GaCl$_3$ and NH$_3$ as source materials and nitrogen as a carrier gas, as shown in Figure 6.7. A notable feature of the system was that the gallium supply was precisely controlled by the temperature of the GaCl$_3$ cell and the nitrogen flow rate for the cell. The system was simpler than a conventional hydride VPE system in which GaCl (prepared by reaction of liquid Ga and HCl) is used as the Ga source. The growth was carried out at 1000°C with a (NH$_3$/GaCl$_3$) ratio of 500 in an open-tube flow-through system operated at atmosphere pressure. The growth rate was approximately 6μm/hr. To prevent thermal desorption of the ZnO buffer layer, the growth was immediately started after the substrate temperature reached the growth temperature.
6.4.2 Effect of Buffer Layer Thickness

Different thickness of buffer layers on c-cut sapphire substrates were deposited at 550°C and 10 mtorr, the optimum growth conditions as described above. Single crystalline VPE-GaN films were grown on ZnO buffer layers. The epitaxial relationships are the same as the PLD-GaN on ZnO buffer layer, which were verified by x-ray (2θ, φ) scans. The thickness of GaN is around 1.5μm. Two dimensional lateral growth of GaN is greatly enhanced on a single crystalline ZnO buffer layer (Figure 6.8). With a ZnO buffer layer thickness around 25nm, the surface of the GaN films is relatively flat and featureless by scanning electron microscope. However, a GaN film grown on a 200-nm thick buffer layer exhibits cracks and peeling. In addition to better surface smoothness, the crystallinity of GaN is greatly improved by employing a ZnO buffer layer of around 25 nm. The FWHM of x-ray rocking curve of GaN (0002) is reduced to 0.35° while the peak width of GaN film without ZnO buffer layer is four times greater, as shown in Figure 6.9.
Figure 6.8: Surface morphology of VPE-grown GaN films (a) directly on a sapphire substrate, on (b) 25nm (c) 75nm (d) 200nm ZnO buffer layer. Images are taken by SEM.
Figure 6.9: Thickness effect of ZnO buffer on FWHM of x-ray rocking curve scans of GaN (0002)

6.4.3 Growth mode

It is clear that the crystalline quality and the surface morphology can be remarkably improved by employing ZnO buffer layers. In order to investigate the role of ZnO layer, initial stages of GaN growth were studied by SEM. Figure 6.10 shows the changes in surface morphology during the early stages of the GaN growth on a ZnO buffer layer of 25 nm. Single crystalline ZnO films grown at low temperature on sapphire substrates can act as nucleation sites for further high temperature GaN growth. As shown in Figure 6.10(a), many hexagonal mesas are formed and grow laterally after 15-minute deposition of GaN. After 25-minute growth (Figure 6.10(b)), GaN mesas coalescence and there are still a few hexagonal-shaped voids at this stage. Finally, the GaN film covered the entire substrate with a specular surface, as shown in Figure 6.10(c). Direct high temperature growth of GaN on sapphire without ZnO buffer layer leads to a low nucleation density. GaN columns with different heights and sizes are formed and grow three-dimensionally, resulting in pits and a rough surface. One concern about the presence of ZnO buffer at the early stages of VPE growth is whether they remain because of the reactivity of ZnO with NH₃ under high temperature. A clear difference in the surface morphology and crystallinity of GaN films when a ZnO buffer is used.
suggests that the ZnO exists at least in the early stages of GaN growth. Reducing the exposure of ZnO under NH₃ and 1000°C is the key to successful application of ZnO buffer layers to improve VPE-GaN growth.

### 6.4.4 Raman

Raman spectra were collected on a Renishaw Raman imaging microscope system 2000. A 25mW, 514.5nm argon ion laser was used as the light source for Raman. A 40x objective was employed, giving a lateral resolution of 1–1.5μm. Notch filters were used to reject the scattered and reflected light at the laser wavelength and as the microscope beam splitter. The scattered light was analyzed with a spectrometer grating and CCD detector.

Raman spectroscopy has been used to investigate the phonons in GaN in order to obtain information on the crystalline quality of the layers. The spectrum is more sensitive to the lengths, strengths and arrangement of bonds in materials rather than to chemical composition. Therefore, Raman spectra reveal more details of defects and disorder rather than trace impurities and related chemical imperfections. For hexagonal GaN, the Raman active modes predicted by group theory are two non-polar E₂ phonons and the polar A₁(z) and E₁(x,y) modes. The polar A₁(z) modes are polarized along the z axis and the polar E₁(x,y) are polarized in xy plane. A₁(z)
Table 6.1: Selection rules of q=0 Raman modes in GaN for various polarization configurations.

phonons propagating along the z axis are purely longitudinal (LO) while propagating in xy plane are purely transverse. Table 6.1 summarises the allowed Raman modes under various polarization conditions.

Figure 6.11 shows the Raman spectra of VPE-GaN with and without a ZnO buffer layer. These are measured in the backscattering geometry with incident and scattered light propagating along the z axis. Two E₂ modes at 144cm⁻¹ and 568 cm⁻¹ were observed in both spectra, suggesting the growth of hexagonal GaN. With 25nm ZnO buffer layer, the linewidths of phonon lines are narrower than the ones without buffer layers, indicating higher crystalline quality and less phonon scattering by defects. In the spectrum of GaN without a ZnO buffer, the A₁(LO) mode at 734cm⁻¹ disappeared due to screening by free carriers. However, other peaks showed up at 530 and 660cm⁻¹. The line at 530cm⁻¹ is close in frequency to A₁(TO) which is forbidden by selection rules under this geometry. The line at 530cm⁻¹ may be attributed to the coupled plasmon-phonon modes of the lower energy branch and leaking of forbidden A₁(TO) phonon line. The origin of 660cm⁻¹ is not clear. Defects correlated to 3D growth and to non-radiative recombination processes are the possible origins of heavy n-doping and of the wave-vector non-conservation. On the other hand, the spectrum of GaN with ZnO buffer presents A₁(LO) mode, indicating high crystalline quality and low unintentional doping.

6.4.5 TEM

As discussed in Chapter 5, slight tilting or twisting of nuclei on sapphire substrate could be an origin of the threading dislocations at the island edge. Smoother surface
morphology and lower threading dislocation density of PLD-ZnO buffer layers could act as a better nucleation template for VPE-GaN growth. Figure 6.12 shows cross-section TEM images of VPE-GaN on a 25nm PLD-ZnO with reflection vectors g=11-20 and 0002. With PLD-ZnO, the dislocation density of VPE-GaN is significantly reduced, especially in the vicinity of the GaN/sapphire interface. Though no ZnO could be detected at the interface by HRTEM images or chemical x-ray analysis, a clear difference in the surface morphology and crystallinity of GaN films is apparent when a ZnO buffer is applied, suggesting that the ZnO exists at least in the early stages of the GaN nucleation and growth.

6.5 Conclusion

Single-crystalline ZnO films have been grown on c-cut sapphire substrates by PLD using a KrF laser. The optimum growth conditions are 550°C and 10 mtorr O₂. We observe a sharp and streaked RHEED pattern and atomically smooth surface with
Figure 6.12: TEM of VPE-GaN with (a) $g=11\text{−}20$ (b) $g=0002$
a r.m.s. roughness of only 3.5 Å measured by atomic force microscope. Photoluminescence at 77K shows a strong near-band-edge peak at 3.34eV with no deep level emission. Contrary to the columnar morphology observed in III-nitrides grown on sapphire, ZnO films were found to have layered growth morphology with most defects lying parallel to the interface and low threading dislocations density.

With good crystalline structure, optical properties and surface flatness of the PLD- ZnO buffer layer, two dimensional growth of VPE-GaN is greatly enhanced. The properties of the VPE-GaN are strongly dependent on ZnO layer thickness. The optimum thickness of ZnO buffer layer is around 25nm. From Raman studies, narrow linewidth and the appearance of A₁(LO) peak in the spectrum of GaN with ZnO buffer indicates high crystalline quality and low unintentional doping. Furthermore, the defect density of VPE-GaN is greatly reduced by employing a ZnO buffer layer.
Chapter 7

Conclusion and Future Work

7.1 Conclusion

This thesis has demonstrated new research in the application of PLD to produce III-V nitrides. Several studies have been conducted to understand the growth and properties of III-V nitrides as well as the properties and the effects of ZnO buffer on GaN epitaxy. Here is a summary of the results.

Epitaxial GaN and Al$_x$Ga$_{1-x}$N films have been grown on c-cut sapphire substrates by PLD without employing any low temperature buffer layer. The structural and optical properties of the films can be greatly improved at higher growth temperature and at a nitrogen pressure of 10 mtorr during growth. Below 400°C, the films are amorphous. With increasing substrate temperature, single crystalline GaN films are obtained above 700°C, which is lower than the epitaxial growth temperature for MOCVD. Room-temperature photoluminescence of PLD-GaN exhibits strong band edge emission at 3.4eV. Transmission electron microscopy studies reveal that the dominant type of defects observed in PLD-GaN layers are stacking faults parallel to the interface and threading dislocations along the c-axis. The threading dislocations of GaN are predominantly screw dislocations with Burgers vector of $<0001>$ while edge dislocations with Burgers vector of $\frac{1}{3}<11-20>$ are the dominant ones in GaN grown by MBE, MOCVD and VPE. This variation observed in defect characteristics may come from the difference in nucleation and growth kinetics between PLD and
other deposition techniques. The surface morphology and crystalline quality in the initial stages of the film growth of PLD are first investigated in this work. High flux supersaturation in the PLD process is found to result in small size nuclei.

In addition, we have demonstrated the effectiveness of PLD in engineering bandgap and lattice constant for the formation of Al$_x$Ga$_{1-x}$N ternary alloys. Throughout the composition range from $x = 0$ to 0.6, the films show epitaxial RHEED patterns, in agreement with the results from x-ray diffraction. The lattice constants of the films vary linearly with $x$ and the composition dependence of the band gaps of the films deviates from linearity and bows downward. This represents the first time that PLD has been successfully applied to controlling the lattice constant and bandgap by varying the proportion of AlN and GaN in the target mixture. By analyzing the alloy composition of Al$_x$Ga$_{1-x}$N films and comparing with the composition of the targets, we found excellent stoichiometric transfer between films and targets by pulsed laser deposition, even when the target is a mixture of powders from two different compounds. This may enable the deposition of films with different alloy compositions by simply mixing powders which are commercially available. In addition, dopants may be introduced by the same method.

Furthermore, atomically smooth epitaxial ZnO buffer layers have been developed for GaN epitaxy. With a lattice mismatch of less than 2% between ZnO and GaN, GaN with a ZnO buffer layer should, therefore, have better surface morphology and lower dislocation densities than GaN grown directly on sapphire substrates. Single-crystalline ZnO films have been grown on c-cut sapphire substrates by PLD. The optimum growth conditions are 550°C and 10 mtorr O$_2$. We observe a sharp and streaked RHEED pattern and atomically smooth surface with a r.m.s. roughness of only 3.5Å measured by atomic force microscope. Photoluminescence at 77K shows a strong near-band-edge peak at 3.34eV with no deep level emission. Contrary to the columnar morphology observed in III-nitrides grown on sapphire, ZnO films grow two-dimensionally with most defects lying parallel to the interface and low threading dislocations density. We further employ ZnO film as a buffer layer for GaN growth by vapor phase epitaxy (VPE). Two dimensional growth of GaN by VPE is greatly enhanced, compared to earlier results using RF-sputtered ZnO buffer layers. The
properties of the VPE-GaN are strongly dependent on ZnO layer thickness. The optimum thickness of ZnO buffer layer is around 25–50nm. From Raman studies, narrow line-width and the appearance of A\textsubscript{1}(LO) peak observed in the spectrum of GaN with ZnO buffer indicate high crystalline quality and low unintentional doping. Furthermore, the defect density of VPE-GaN is greatly reduced by employing a ZnO buffer layer.

7.2 Future Work

There are several interesting avenues for continuing research. The focus in the future should be on those aspects of GaN growth in which PLD has either unique possibilities or is easier to explore than via MOCVD. The specific research topics are listed below and each is then briefly described.

1. Investigation of alternative p-type doping sources.

2. Investigation of engineered pseudo-substrates and excimer laser crystallization.

7.2.1 Alternative P-Type Doping Sources

A major limit to nitride device development is the difficulty in obtaining highly p-type doped material. Mg, which is the currently available acceptor, has a very large ionization energy and thus only a small fraction is electrically active. Systematic investigation of alternative p-type dopants is important to improve the performance of the devices. This is hard to study by MOCVD because of the difficult synthesis, limited availability, high cost and large quantities of dopants required for MOCVD. While MOCVD has been the dominant epitaxial growth technique for GaN, PLD may be more suitable for investigating various p-type dopants.

It has been demonstrated in the deposition of oxides by PLD that dopants can be incorporated directly in the ablation targets and transferred to the films. For example, low resistivity ZnO films doped with Al can be achieved by ablating targets which consist of ZnO powers mixed with either Al or Al\textsubscript{2}O\textsubscript{3} powders [75]. Doping of epitaxial compound semiconductors, such as p-type ZnTe films has also been previously
obtained by PLD [76] [77]. PLD allows for a quicker and far easier change of sources than is possible with a standard MBE or MOCVD reactor, enabling one to investigate several different sources in a relatively short time. Due to this intrinsic advantage of PLD, it makes PLD suitable for rapid exploration of alternative p-type dopants which may be expensive or of limited availability for both MOCVD and MBE.

7.2.2 Substrates

Another interesting research topic in PLD is to make an engineered substrate for subsequent growth of MOCVD or MBE by applying the concepts of compliant substrate [78] [79] and excimer laser crystallization [80] [81] [82]. Because of the difficulty on growing single crystal bulk GaN, the growth of GaN epitaxial layers on a lattice mismatched substrate is almost a certainty for a variety of heterojunction devices. In view of potential applications, Si is an interesting substrate to consider for group III-nitride growth. PLD-ZnO studied in this work could be a good buffer layer for the growth of III-nitrides on Si.

If thin deposited ZnO films can expand and contract laterally without being constrained by Si substrates, they can serve as a template for thick GaN growth on Si. From the previous studies of the growth of SiGe alloys on SOI (silicon-on-insulator) substrates [78], amorphous oxides are found to be suitable candidates for this purpose. The vertical bonding between the oxides and the first thin film provides the required mechanical support, while the amorphous nature of the oxide still allows slippage at thin film and oxide interface, without much contribution to the strain parallel to the film plane. Utilizing this intrinsic property of SiO$_2$, thin layers of ZnO could be deposited on Si substrates with SiO$_2$ as an intermediate layer (see in Figure 7.1), in hope to provide a sliding interface that does not constrain ZnO at the growth temperature. Misfit strain between ZnO and GaN during growth may be accommodated predominantly by formation of defect structures in the thin ZnO layer rather than in the III-nitride layer.

Since the SiO$_2$ is amorphous, ZnO deposited on top will be either amorphous or
Figure 7.1: Excimer laser crystallization of a thin layer of ZnO or GaN deposited on Si substrate with SiO₂ as an intermediate layer

polycrystalline. To further improve the quality of ZnO films, excimer laser crystallization may be employed to convert amorphous/polycrystalline ZnO to single crystalline islands. As shown in Figure 7.1, SiO₂ patterned capping oxides are fabricated on top of the ZnO film to induce selective melting of the ZnO film. The selective melting of ZnO thin films can induce substantial lateral crystal growth from the incompletely melted portion of the film into the completely melted portion. Large single crystal grains are likely to form when the experimental conditions are carefully controlled. For example, the laser energy density must be sufficient to induce selective melting of the ZnO film. A proper combination of the film thickness, substrate temperature, and width of patterned oxide distance is necessary to prevent the onset of nucleation of solid in the supercooled liquid ZnO. When these conditions are satisfied, lateral directional growth could convert the entire, completely molten area into elongated parallel grains with one perpendicular grain boundary in the middle. The induced super-lateral growth of ZnO may greatly reduce the defect density while the SiO₂ intermediate layer between thin ZnO layer and Si substrate may release the constrain of Si on ZnO. This could be an interesting topic and may have the potential to create an engineered substrate for subsequent growth of MOCVD or MBE epitaxial layers.
Bibliography


BIBLIOGRAPHY


