# Chapter 1

# Introduction

## 1.1 Research Background of the Group III-Nitrides

Group III-nitrides have received significant research attention and have been widely used in optoelectronics and high-power/high-frequency/high-temperature applications. As members of the III-nitride system shown in Fig. 1-1, wurtzite GaN, AlN and InN have direct room temperature bandgap energy (Eg) of 3.4, 6.2 and 0.7 eV.

Group III-nitrides applications in the optoelectronics field include solar blind and visible detectors, light emitting diodes (LEDs) and lasers diodes (LDs) operating in the blue/ultraviolet (UV) part of the spectrum, and optical data storage [1]. Efficient red, yellow and less efficient green light emitting diodes existed for some years before GaN light emitters were developed. However, with these previous LEDs full color displays were not possible because previous blue and green LEDs were much too weak, and also did not cover the necessary color spectrum. The newly developed GaN LEDs fill this gap. Now, it is possible that the high brightness light emitter can be used in full color displays indicators, and as lamps with high efficiency, high reliability, and high speed.

Group III-nitrides are also applied to high power,/high frequency,/high temperature field effect transistors (FETs) for cellular, personal communications services, and broad-band access are expanding and thirdgeneration (3G) mobile systems coming closer to reality, radio frequency (RF) and microwave power amplifier. The GaN has excellent electron transport, including good mobility and high saturated drift velocity as shown in Fig. 1-2 [2], thus making this material suitable for high frequency device application such as microwave rectifiers. The wide bandgap makes GaN promising for high temperature application, because

GaN has less intrinsic carriers at much higher temperature than Ge, Si and GaAs. The critical electric field for the breakdown scales roughly with the square of the energy bandgap of the material, and is estimated to be be >4 MV/cm for GaN [3] , as compared to 0.2 and 0.4 MV/cm for Si and GaAs, respectively.

There are many techniques to grow III-nitrides such as metalorganic chemical vapor deposition (MOCVD), hydride vapor phase epitaxy (HVPE) and radio frequency plasma-assisted molecular beam epitaxy (RF-MBE). In this study, we grew group III-nitrides by MBE system, the nitrogen source is supplied by RF plasma. The MBE has attracted a much attention due to such distinctive features as low impurity environment, excellent abrupt interface controllability, low temperature growth for incorporation of In in (Ga,In)N QWs [4], in-situ monitor growth process by using reflection high-energy electron diffraction (RHEED). On the other hand, it has been demonstrated that the ability to control the transition from a two- to a three-dimensional (2D → 3D) growth mode [Stranski-Krastanov (SK) growth mode] of nitrides leads to the growth of quantum dots, opening the way towards the realization of low threshold lasers [5]. However, III-nitride films grown by MBE always show poor surface morphology, high TD density, normally N-polarity compared with films grown by MOCVD.

The major challenge of growing high quality GaN epitaxy layer is the lacking of suitable substrate. For III-nitrides, low cost, easily available, transparent, stable at high temperature sapphire ($Al_2O_3$) is mostly to be used as substrate. But the 16.1% mismatch and large difference in the thermal expansion coefficients between sapphire and GaN are the disadvantages. To overcome large lattice mismatch for GaN epitaxy layer on sapphire, buffer layer is induced to decrease the mismatch between GaN and sapphire. The original idea by H. Amano et al. [6] was that AlN having less lattice mismatch (13.2%) than GaN (16.1%). Instead of using AlN as buffer, S. Nakamura [7] used low temperature GaN as buffer layer also achieve good quality GaN epilayer.

GaN epitaxy layer grown on vicinal sapphire substrates shows better crystal quality due

to that vicinal plane has micro-step. Since strain field situation at the macro-step position is different from that at the flat region due to the structural irregularity. The TDs at the macro-step position were bended and terminated on the surface [8]. Consequently, using vicinal sapphire substrates is another method to obtain high quality GaN epitaxy layer.

Recently, silicon as a substrate has attracted much attention for the epitaxial growth of group-III-nitride semiconductors because of its low cost, well-conducting, large size in large diameters up to 12 inches and potential in the integration of microelectronic and optoelectronic devices. However, large difference in in-plane thermal expansion coefficient (56%) [9,10] between GaN and Si, which causes a large tensile stress in the GaN epilayers during cooling down process resulting in cracked layers especially in MOVPE system [11]. In MBE grown GaN epitaxy layer the critical thickness of the crack is higher than in MOVPE grown because of the lower growth temperature.

Other substrates such as 6H-SiC, ZnO, GaAs, GaP, MgO, $MgAl_2O_4$, LiGaO2, and $LiAlO_2$ are also to be used to grow GaN. Table 1-1 [12] shows some important properties of III-nitrides and substrates including the lattice mismatch between GaN and the commonly used substrates.

The GaN epitaxy layer has two kinds of the lattice polarities, which are Ga-polarity and N-polarity, as shown in Fig. 1-3 [13]. It is found that the surface morphology, luminescence property and polarization effect of the films are strongly dependent on the polarity of substrate [14]. The polarization effect is important for the AlGaN/GaN heterostructures, which can induce high sheet carrier density at AlGaN/GaN interface. The polarization effect can be divided to spontaneous ($P_{SP}$) and piezoelectric ($P_{PE}$) polarization. The direction of spontaneous polarization in Ga-polarity GaN points towards the substrate, but in N-polarity, it points to the surface. The piezoelectric polarization is due to strain in AlGaN layer. In the AlGaN/GaN heterostructures, the AlGaN layer contains the tensile strain, which makes the direction of piezoelectric polarization points to the substrate. In the Ga-polarity AlGaN/GaN

heterostructures, the overall polarization points towards the substrate. The two dimension electron gas (2DEG) accumulates at the interface between AlGaN and GaN layer. However, in the N-polarity, the 2DEG does not accumulate in the interface due to inverse the direction of overall polarization, which is shown in Fig. 1-4 [14]. It is well recognized that the GaN grown on sapphire with MOCVD mostly behaviors Ga-polarity [38, 39]. It was known that the MBE grown GaN film on sapphire with low temperature (LT) GaN, high temperature (HT) GaN and LT AlN as buffer layer all present N-polarity. Only the GaN grown on HT AlN buffer layer exhibits Ga-polarity [40 ,41].

## 1.2 Organization of this thesis

The thesis is divided into five chapters. In Chapter 1, we introduce the application of group III-nitrides, and some issue of GaN epilayer growth.

In Chapter 2, we will describe the experimental techniques to grow and characterize the GaN epilayer on sapphire (0 0 0 1) and Si (1 1 1) substrates. They include growth method and material characteristic analysis method.

In Chapter 3, we will investigate the crystal quality of GaN epitaxy layer with different nitridation temperatures which from 200 to 800℃ and characteristics of GaN on nitrided or non-nitrided sapphire. Then, we use AlN-IL to reduce TDs and optimize the deposition time of AlN-IL to obtain high quality of GaN epitaxy layer. Final, we study the influence of GaN epitaxy layer on vicinal sapphire substrate.

In Chapter 4, we will investigate the effect of Al pre-seeding layer deposition time on the quality of the GaN epitaxial layer. After Al pre-seeding layer deposition, we also find the crystal $\alpha$-Si$_3$N$_4$ layer was accompanied with AlN growth process. Crack free GaN layers were demonstrated by using simultaneous AlN/$\alpha$-Si$_3$N$_4$ buffer structure. In addition, we also investigated the formation of high-quality, hexagonal and vertical GaN nanorods buffer grown

by a self-assembled mechanism on Si (1 1 1) substrates at different molecular beam epitaxy condition. We use the novel substrate engineering (nanorods buffer) technique to develop strain-free GaN by MBE and MOCVD-overgrown GaN.

In Chapter 5, important conclusions are drawn.

**Table 1-1** Parameters of III-nitrides and some substrates

| Material | Structure | Mismatch to GaN (%) | Lattice constant (Å) | | Melting point (K) | Thermal conductivity (W/cm K) (300 K) | Thermal expansion ($\times 10^{-6}$ K$^{-1}$) | |
|---|---|---|---|---|---|---|---|---|
| | | | $a$ | $c$ | | | //$a$-axis | //$c$-axis |
| GaN | Wurtzite | 0 | 3.1885 | 5.185 | > 2573 | 2.0–2.1 | 3.17 | 5.59 |
| AlN | Wurtzite | ~2 | 3.1106 | 4.9795 | 3273 | 2.85 | 5.27 | 4.15 |
| InN | Wurtzite | ~10 | 3.5365 | 5.7039 | 1373 | 0.45 | 3.8 | 2.9 |
| Al$_2$O$_3$ | Rhombohedral | ~16 | 4.765 | 12.982 | 2303 | 0.23 | 5.0 | 9.03 |
| SiC (6H) | Wurtzite | ~3.5 | 3.0806 | 15.1173 | 3103 ± 40 | 4.9 | 4.3 | 4.7 |
| Si | Diamond | ~21 | 5.431 | | 1687 | 1.56 | | 2.616 |
| GaAs | Zincblende | ~20 | 5.6536 | | 1513 | 0.45 | | 6.03 |
| ZnO | Wurtzite | ~1.8 | 3.2495 | 5.2069 | 2248 | 0.6 | 6.5 | 3.0 |
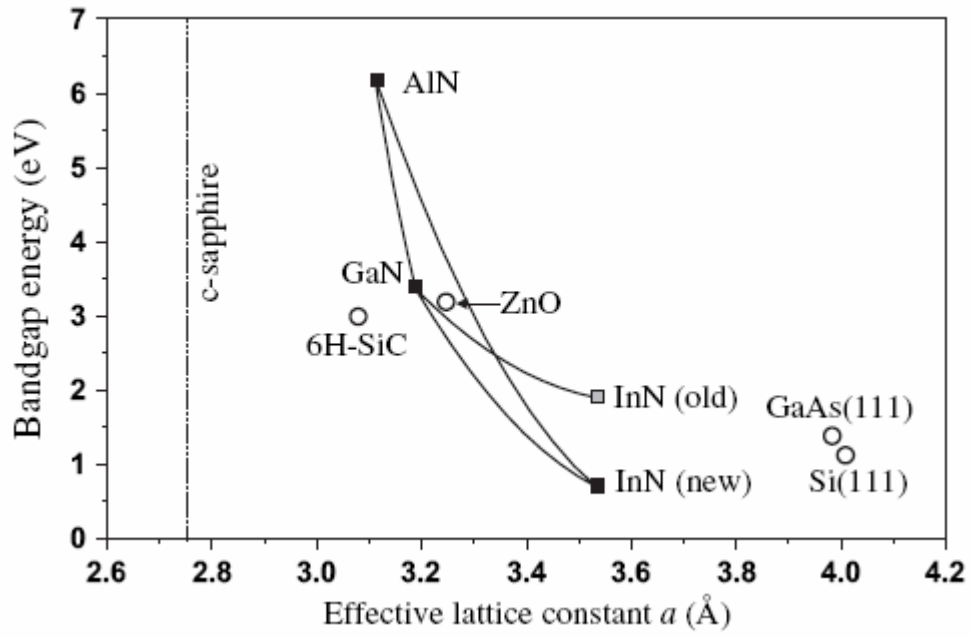
**Fig. 1-1** Bandgap and lattice constants of III-nitrides (solid rectangles). Effective lattice constants considered as substrates for hetero-epitaxy of III-nitrides are also shown (hollow circles).
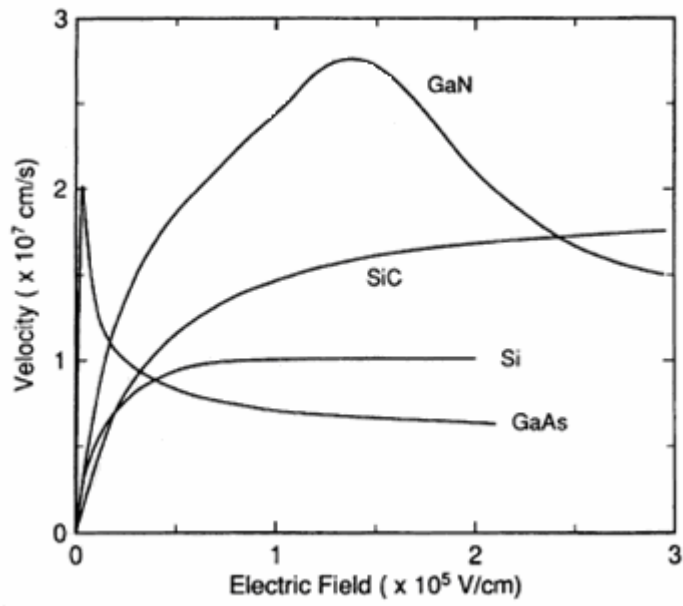
**Fig. 1-2** Electron drift velocity at 300 K in GaN, SiC, Si and GaAs computed using the Monte
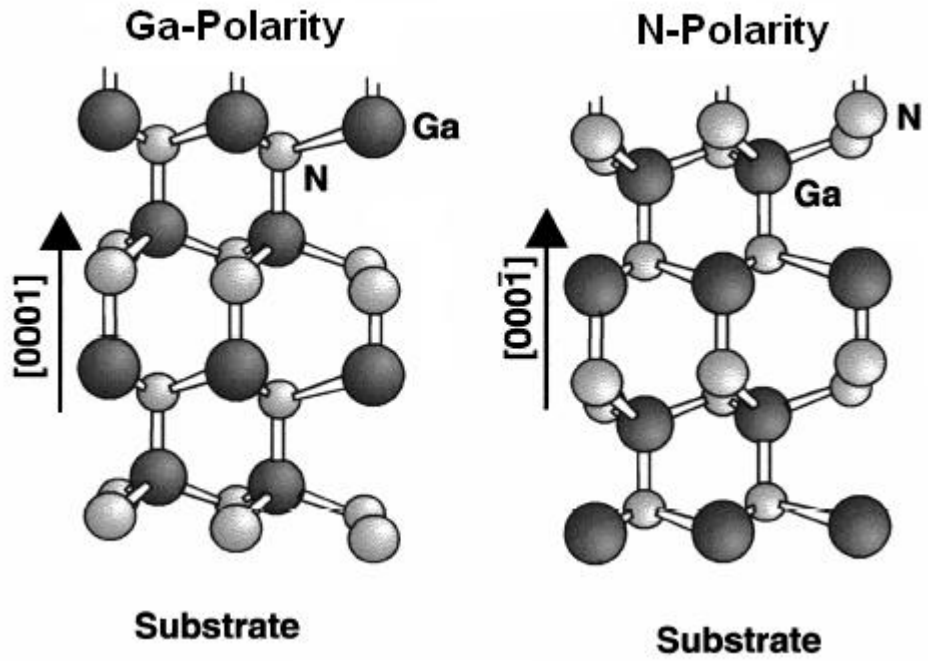
Carlo technique.

**Fig. 1-3** Schematic drawing of the crystal structure of wurtzite Ga-polarity and N-polarity GaN.

Ga-polarity                                      N-polarity

AlGaN
tensile strain

GaN relaxed

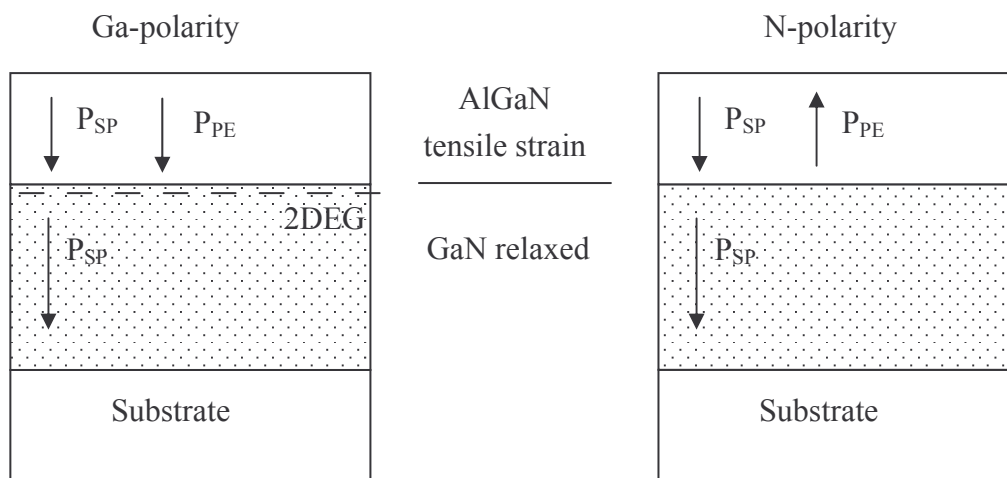Substrate                                        Substrate

**Fig. 1-4** Polarization effect of Ga-polarity and N-polarity in the AlGaN/GaN hetrostructures.