CHAPTER 2

EPITAXIAL GROWTH OF GaN/AlN MULTIPLE QUANTUM WELLS

2.1 Metalorganic Vapor Phase Epitaxy

Metal-organic vapor phase epitaxy (MOVPE) is currently the most widely used growth technology for III-V compound semiconductors. It has become a process for the production of semiconductor film for modern devices. Indeed, most of all commercially available optoelectronic devices such as light emitting diodes (LED) and laser-diodes are fabricated using MOVPE. In this technique organometallic compounds such as metal alkyls and hydrides as vapors are transported to the growth chamber using a carrier gas such as hydrogen. The substrate wafer is mounted on a graphite holder or susceptor that is uniformly heated to a growth temperature by radio-frequency (RF) heating. The basic reaction, for example, for the growth of GaN is:

$$Ga(CH_3)_3\,(l) + NH_3\,(g) + H_2\,(g) \rightarrow GaN\,(s) + 3\,CH_4\,(g) + H_2\,(g) \qquad (2.1)$$

In this study, the MOVPE growth was carried out by low-pressure MOVPE using AIX 200/4 RF-S system from AIXTRON. Figure 2.1 schematically shows the diagram of this MOVPE system. Similar to another MOVPE system, this system consists of four major parts as follows:

(1) Gas handling system
(2) Reactor chamber
(3) Heating system for pyrolysis temperatures
(4) Exhaust system

The gas handling system includes the sources of alkyls and hydrides, and all of the valves, pumps and instruments necessary to control the gas flows and mixtures. In this system, Trimethylgallium (TMGa), Trimethylaluminum (TMAl), Trimethylindium (TMIn) and Triethylgallium (TEGa) are used as group III sources, while pure ammonia (NH_3) is used for group V source. The other sources used in this system are Silane (SiH_4) and Bis-cyclopent Dienylmagnesium (Cp_2Mg), which are used as *n*-type and *p*-type dopants, respectively. Pure hydrogen (H_2) and nitrogen (N_2) are used as carrier gases during the growth. For pure H_2, the 99.999% pure hydrogen is used along with a Pd-cell purifier to obtain the ultra-pure hydrogen. All flow rates of these gases are controlled by electronic mass flow controllers (MFC).

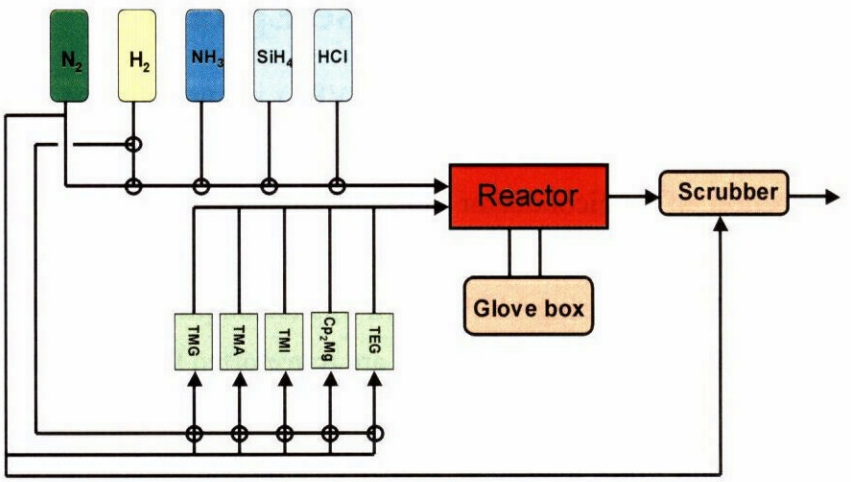

Figure 2.1 Schematic diagram of MOVPE system

The growth of epilayer by this system is performed inside the reactor chamber. The pressure inside the reactor chamber can be controlled in the pressure range of 50 mbar to atmospheric pressure. The substrate is placed on a silicon-carbide graphite susceptor, and during the growth it is rotated by flowing gas through the rotation disk, which is at the bottom of the susceptor. This rotation helps making the chemical reaction occurring at any position of the substrate with an equal possibility. The epilayer can thus be grown with a uniform thickness for the entire substrate.

The radio frequency (RF) induction heating is used as the heating system in this system. In RF heating, a silicon-carbide graphite susceptor is inductively coupled to the RF coil. By varying input power of the RF coil, the temperature of the substrate can be controlled from 100 ℃ to the highest temperature of about 1300 ℃.

The exhaust system is the most critical part of the MOVPE system in terms of safety. It serves two main functions: removing unreacted gases and byproducts from the reaction chamber and providing a path for reactants to bypass the reaction zone. In this MOVPE system, a scrubbing system is used as exhaust system. The toxic chemicals such as NH_3 and SiH_4 are diluted to a safe concentration level inside the scrubber by the reaction with sulfuric acid. In addition to the above systems, glovebox is also another important component for the MOVPE system. The exchange of the substrate before and after the growth is performed inside the glovebox. The glovebox can control the humidity and oxygen levels to be always less than 1 ppm. The reactor chamber is therefore not contaminated by the oxygen and other impurities existing in the air, especially when it is opened to the glovebox.

Apart from such main parts, "dummy line" is also an important part in the MOVPE system in order to obtain sharp hetero-interface. In the epitaxy process, the MFC regulation steps are kept to a minimum number of times, since the regulation requires a certain length of time which could result in a rough interface between different epitaxy layers. For the fast and stable switching, injection of source-containing gas into the reactor is not a simple open/close valve, but it is a switch value between "Run" and "Vent" line. Basically, when the source-containing gas is switched from "Vent" line to "Run" line, the same quantity pure H_2 dummy gas is switched through dummy lines. With this process, the flow of gas and pressure of growth chamber can be keep constant during the growth of quantum wells, possible to obtain sharp interfaces.

2.2 Growth and Characterization of GaN and Si-doped GaN

Several attempts were made to grow GaN crystals since 1930, but good quality crystals could not be grown. The first success in the growth of GaN epitaxial layers was reported in the late 1960s using hydride VPE (HVPE) [117]. However, good epilayers could not be obtained until the late 1980s because of the lack of lattice-matched substrate. Sapphire is the most extensively used substrate for growth of the III-nitrides because the good quality crystals of sapphire are easily available at low cost. However, there exists a lattice mismatch of 16.1% between GaN and (0001)-oriented sapphire in *a*-axis direction, and thermal expansion coefficient difference of 25.5% (a-axis) compared with GaN, making it difficult to grow high-quality GaN on the sapphire substrate [118].

Many growth techniques have been developed to grow GaN epilayer with high quality. The growth of high quality GaN epilayers on sapphire substrates by MOVPE was successful in early 1990s by first depositing a thin AlN buffer layer at low temperature before growing GaN at high temperature [119-123]. This two-step growth method was demonstrated that the GaN epilayers could be much improved in crystalline quality, electrical property and optical property [124]. In the early work, it was demonstrated that the growth of GaN buffer layer, instead of AlN layer, at low temperature in the first step of two-step growth method could get better crystalline quality of GaN [125-128]. Recently, the growth of high quality GaN epilayer was also achieved by molecular beam epitaxy (MBE) [129,130]. However, the GaN epilayer grown by MBE still contains high dislocation density, and the electrical and optical properties are still not good compared to ones grown by MOVPE. The high crystalline quality of GaN grown by MOVPE has led to many optical devices application such as blue-color light emitting diode (LED) [106] and blue-color laser diode (LD) [109-111]. In this section, the growth of GaN by MOVPE is discussed in details.

2.2.1 Growth of GaN using low-temperature buffer layer technique

Since a high-quality GaN substrate is still not commercially available at a low price. In this study, the GaN buffer layer is therefore grown on the c-plain sapphire substrate which is easily available at low cost with very high crystalline quality. The growth of

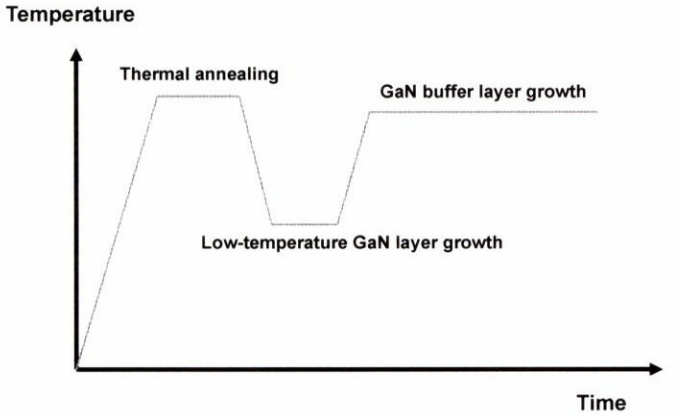

Figure 2.2 Temperature diagram during growth of GaN with low-temperature GaN buffer layer technique.

GaN on sapphire substrate was performed by the two step growth technique with a temperature diagram as shown in Fig. 2.2. Before the growth, the thermal cleaning is performed to remove any contamination attached on the substrate and inside the reactor. For thermal cleaning, the temperature was raised to 1200 °C and only H_2 is flew into the reactor. The flow rate of H_2 during this process is approximately 10 standard liters per minute (slm), and the thermal cleaning is performed for 10 minutes.

After the thermal cleaning, GaN buffer layer is grown using low-temperature GaN buffer layer technique. To deposit the low-temperature GaN buffer layer, substrate temperature is slowly decreased to 550 °C. Then, approximately 25-nm-thick low-temperature GaN layer is firstly grown at this temperature. Subsequently, the temperature is raised to 1150 °C to grow the high temperature GaN layer. The nucleation layer is annealed at this temperature for a few minutes before growing a GaN buffer layer. Then the GaN layer is deposited upon the low-temperature GaN layer with

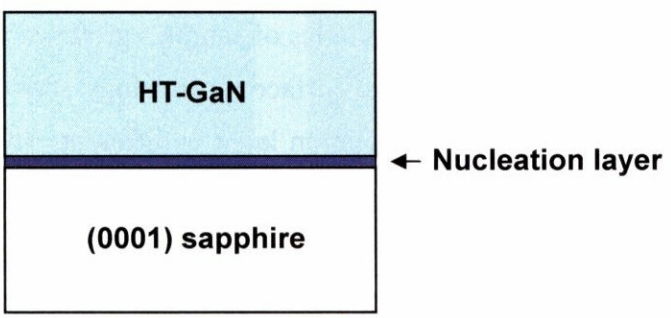

Figure 2.3 Schematic structure of GaN buffer layer grown on c-plane sapphire substrate

the thickness of approximately 1.5 μm. Figure 2.3 shows a schematic structure of GaN buffer layer grown on a sapphire substrate.

2.2.2 Dependence on low-temperature GaN buffer layer

The deposition of a low temperature buffer layer, or "*nucleation layer*" is a key discovery in improving surface morphology and crystalline quality of GaN. It was demonstrated that the surface morphology of the subsequent thick GaN layers could be markedly improved if thickness of the buffer layer is optimized [118]. In addition, the optimization of the nucleation layer could result in the reduction of dislocation density.

In order to find the optimum growth condition of the nucleation layer, the growth temperature and the thickness of nucleation layer were varied, while the growth condition of the high-temperature GaN buffer layer was kept constant at a growth temperature of 1150 °C, and a growth pressure of 200 mbar. The thickness of the high-temperature GaN buffer layer was approximately 1.5 μm in every sample. The crystalline quality and the surface morphology of the grown samples were investigated by means of X-ray diffraction (XRD) measurement and Nomarski microscope, respectively.

1) Dependence on thickness of nucleation layer

The dependence on thickness of nucleation layer is investigated by varying the thickness of nucleation layer from 10 nm to 60 nm, while the growth temperature of the nucleation layer is kept constant. At first, the optimum growth temperature for this system is still unknown; the growth temperature was therefore set to a value reported in the literatures, which is 550 °C.

Figure 2.4 shows surface morphologies of samples grown with different nucleation layer thickness. It can be seen that the surface morphology shows different patterns of roughness when the thickness of nucleation layer is different. The surface morphology shows very smooth surface in the sample that its nucleation layer thickness is 25 nm. For other nucleation layer thicknesses, they are observed that the surface contains some facet-like defects which suggest that three-dimensional growth is occurred in such samples. Indeed, the three-dimensional island growth-mode usually occurs at the first

step of the nucleation layer. However, after a while, the growth mode changes to two dimensional growth, and becomes three-dimensional growth again when the nucleation layer is even thicker [131]. This is the reason why the thickness of the nucleation layer had a major influence on the surface roughness of the GaN buffer layer. From this experiment, the optimum thickness of the nucleation layer was found at approximately 25 nm.

2) Dependence on growth temperature of nucleation layer

Besides the optimization of nucleation layer thickness, the effect on the growth temperature of nucleation layer was also investigated. Three samples grown with different nucleation-layer growth-temperature varied from 500 °C to 600 °C, while maintaining the optimum thickness of 25 nm, were characterized by X-ray diffraction measurements. The full-width at half-maximum (FWHM) of the rocking curve scan of the (0002) plane of GaN was used as a parameter to characterize the crystalline quality. It is found that in the range of 500-600 °C, there was no big difference in the crystalline quality in such samples, evaluated by the FWHM of rocking curve scan. The surface

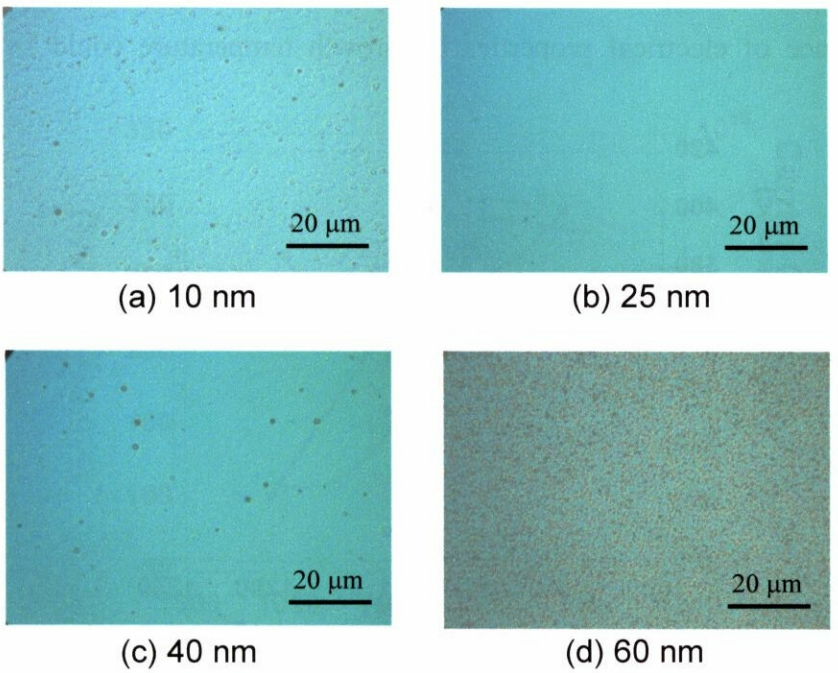

Figure 2.4 Surface morphology of GaN buffer layer grown with different nucleation layer thickness: a) 10 nm, b) 25 nm, c) 40 nm, d) 60 nm

morphologies taken by Nomarsky microscope also show smooth surfaces for all samples. It is therefore considered that the growth temperature of nucleation layer is not a sensitive parameter, compared to its thickness. However, the crystalline quality became the best for growth temperature of 550 °C. The optimum thickness and growth temperature of the nucleation layer are therefore 25 nm and 550 °C, respectively.

2.2.3 Dependence on growth temperature

In order to find the optimum growth temperature of GaN layer, five GaN samples were investigated; each of which differs in the growth temperature: i) 1050, ii) 1075, iii) 1100, iv) 1150, v) 1200 °C. The nucleation layer was grown at 550 °C with the thickness of approximately 25 nm in every sample. The crystalline quality of such samples was examined by X-ray diffraction (XRD) measurements. Figure 2.5 shows the dependence of full-width at half maximum (FWHM) of XRD rocking curve on the growth temperature. As can be seen, the FWHM decreases with increasing growth temperature, indicating improved crystalline quality. However, for the sample grown at 1200 °C, the surface morphology turns out to be rough with three dimensional growth observed. To further examine the crystalline quality, the electrical properties, including the carrier concentration and mobility of the samples, were investigated by the Hall measurements. The dependence of electrical properties on growth temperature could be plotted as

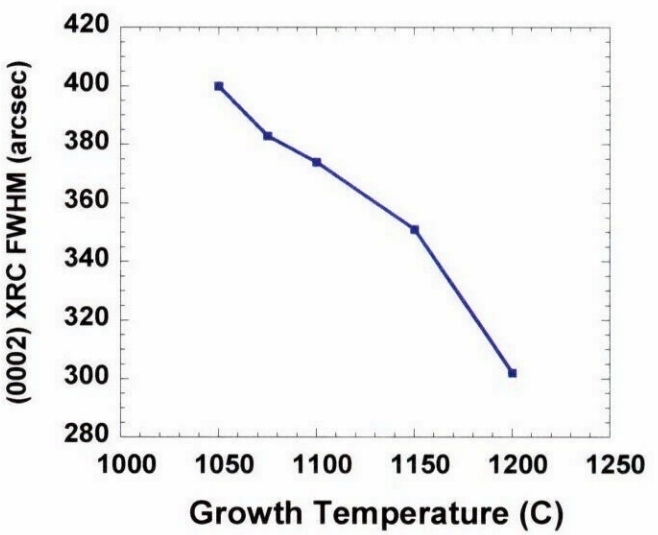

Figure 2.5 Full width at half maximum of XRD rocking curve scan of (0002) GaN as a function of growth temperature

shown in Fig 2.6. It can be seen that the sample grown at the growth temperature of 1150 °C has the best electrical properties: the highest carrier mobility of 293 cm^2/Vs and the least carrier concentration of $3.7x10^{16}$ cm^{-3}. The results from Hall measurements therefore give a good agreement with the result from XRD measurements. From these results, it can thus be concluded that the growth temperature of 1150 °C is the optimum temperature for the growth of GaN buffer layer. To investigate optical properties of the sample, photoluminescence (PL) measurement was also performed at room temperature, as shown in Fig. 2.7. The spectrum shows a sharp peak of GaN at 363 nm with the FWHM of 66 meV. The yellow emission in the wavelength range of 500-600 nm was also observed with relatively low intensity, indicating good quality of GaN layer.

Figure 2.8 shows a surface morphology of as-grown GaN taken by atomic force microscope (AFM). As seen in the figure, the step-flow growth mode was confirmed, suggesting that the GaN layer was psudomorphically grown with high quality. The surface of the GaN was very smooth as the roughness rms was as small as 0.2 nm. To investigate the threading dislocation density, a GaN sample was etched in HCl at 650 °C for 30 minutes. The threading dislocation density was then estimated from the numbers of pits which can be observed by AFM. It is found that the threading dislocation density

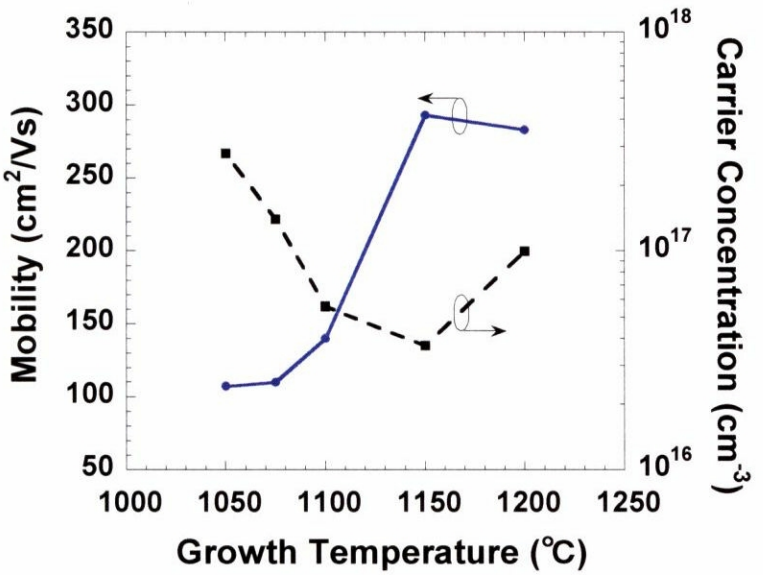

Figure 2.6 Electron mobility and carrier concentration of GaN as a function of growth temperature

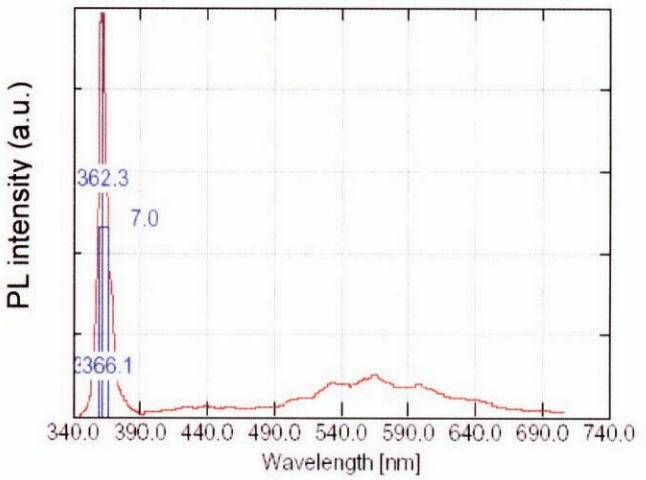

Figure 2.7 PL spectrum of GaN at room temperature

was $3x10^8$ cm^{-2}, showing relatively low defect density compared to GaN grown with the same two-step growth technique [132]. It can be seen that the growth condition of GaN was successfully optimized to obtain the high-quality GaN buffer layer with very good optical and electrical properties. This growth condition is therefore used as a base condition for the growth of GaN buffer layer in this study.

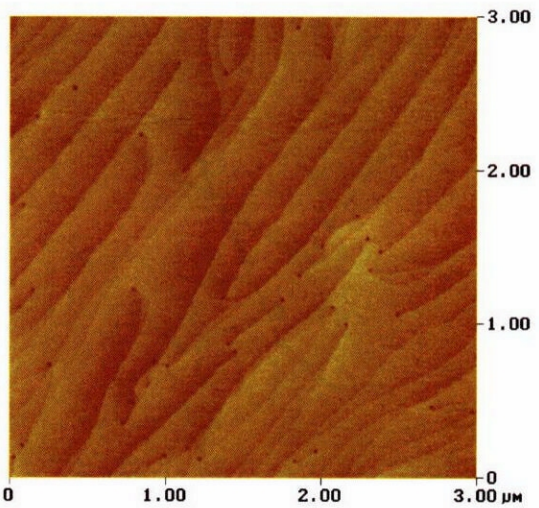

Figure 2.8 AFM surface morphology of GaN

2.2.4 Growth of Si-doped GaN

The intersubband absorption involves with the transition of electrons from the first conduction subband energy level to the higher one; therefore, the electron population in the first conduction subband must be very high to obtain strong absorption. It is thus necessary to dope the GaN wells in the MQWs structure to obtain a carrier concentration of about 10^{19} /cm^3 to fulfill the first conduction subband with electrons.

Typical n-type dopant for GaN is Si, since the Si doner lies just below the conduction band ($E_a \sim 25$ meV) [133]. Therefore well-controlled n-type doping can be easily accomplished using silicon as a doner. The typical precursors for n-type doping in MOVPE are silane (SiH_4) and disilane (Si_2H_6). In this study, 100 ppm of SiH_4 diluted with hydrogen is used as a precursor. The dependence of the carrier concentration on the flow rate of SiH_4 dopant was investigated, by varying the flow rate of SiH_4 : i) 3, ii) 5, iii) 10, iv) 22 nmol/min. In Fig. 2.9, the (0002) rocking curve FWHM and carrier concentration of the grown samples examined by XRD measurements and room-temperature Hall measurements, respectively, are plotted as a function of the SiH_4 flow rate. As can be seen in Fig. 2.9, the carrier concentration is linearly dependent on the SiH_4 flow rate, while the crystalline quality became worse when samples were

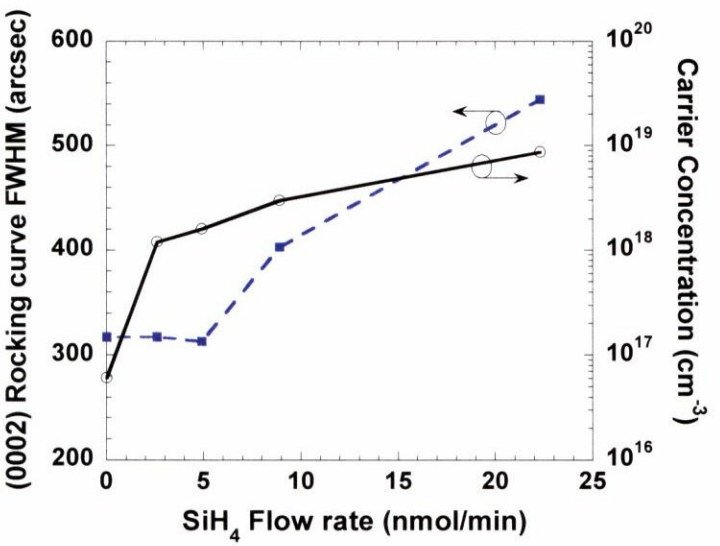

Figure 2.9 Carrier concentration and full width at half maximum of XRD rocking curve of (0002) as a function of SiH_4.

doped to the carrier concentration over 10^{18} cm^{-3}. With these results, it can be concluded that the Si-doped GaN can be successfully grown with the maximum carrier concentration of $9x10^{18}$ cm^{-3} using the SiH_4 flow rate of 22 nmol/min.

2.3 Growth and Characterization of GaN/AlN Multiple Quantum Wells

In the last section, high quality GaN and Si-doped GaN have been demonstrated with excellent electrical and optical properties. In order to observe the intersubband absorption, GaN quantum wells with AlN or AlGaN barriers are needed to be fabricated. This study pays attention mostly on the GaN quantum wells with AlN barriers, because the largest conduction band offset could be obtained in such quantum wells, which is needed for the realization of near-infrared intersubband transition.

As already mentioned, the intersubband absorption requires high density of carriers in quantum wells for the transition of electrons from the first conduction subband energy level to higher one. The electron population in the first conduction subband must therefore be very high for observation of the intersubband absorption. Besides the high concentration of Si doped in quantum wells, the absorption coefficient could be improved by increasing the number of quantum wells. Therefore, the growth of 100-period GaN/AlN MQW structure is investigated here to find out the optimal growth condition, especially the growth temperature, to achieve high-quality MQW. Moreover, effects of some parameters including barrier thickness and number of quantum wells are also studied in order to find the structure that can be grown with high quality.

2.3.1 Dependence on growth temperature

At the first step, the optimum growth temperature for the MQW structure is investigated. The GaN/AlN MQW structures with 100 quantum wells were grown on 0.6-μm-thick GaN buffer layers, which were fabricated with the optimum condition found in Section 2.2. The GaN quantum wells were doped with Si to get the carrier concentration at $9x10^{8}$ $/cm^{3}$. During the growth of the MQW structure, the reactor pressure was maintained at 60 mbar. The temperature dependence was investigated by growing the

samples at different growth temperature varied from 1050 °C to 1125 °C. The thickness of the quantum wells and the barriers in the every sample were set equally at 5 nm and 4 nm, respectively. The crystalline qualities and the abruptness of the interfaces were determined by the XRD measurements.

In Fig. 2.10, the 2θ/ω-scan XRD profiles for GaN/AlN MQW structures grown with different growth temperature are shown. As can be seen from the figures, the growth temperature has a great influence to quality of interfaces, which are evaluated by the order of satellite peaks that can be observed from the XRD profiles. The XRD profile with the MQW-related satellite peaks from -4th to +3rd was observed in the sample which was grown at the growth temperature equal to 1100 ℃, while the lower order number of satellite peaks are observed in the other samples. This result indicates that the optimum temperature for the growth of MQW structure that can give the best quality of interfaces is 1100 ℃. This growth temperature is used as a standard temperature for the growth of the MQW structures in latter sections.

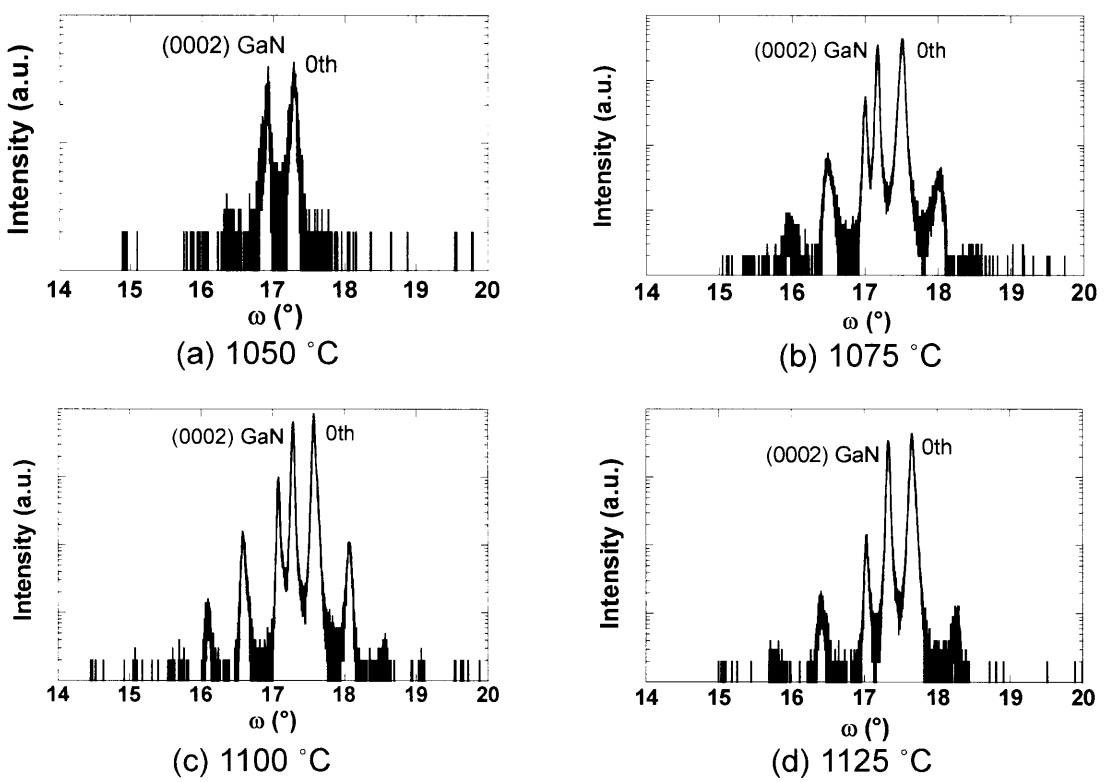

Figure 2.10 2θ/ω scan XRD profile of GaN/AlN MQW structure grown with different temperatures: a) 1050 °C, b) 1075 °C, c) 1100 °C, d) 1125 °C

2.3.2 Dependence on barrier thickness

In order to find the effect of the barrier thickness on the crystalline quality, the GaN/AlN MQW samples was investigated with 100 quantum wells grown on 1.5-μm -thick GaN buffer layer. The growth condition was maintained to be the same as that described prior. The thickness of Si-doped GaN quantum wells with the carrier concentration around $9x10^8$ /cm^3 was controlled to be constant at 9.5 nm in every sample, whereas the barrier thickness was varied: 1.2 nm, 2.5 nm and 5.5 nm. Figure 2.11 shows the surface morphology of these samples. It can be seen from the surface morphology that the barrier thickness has a big influence on the density of the cracks. The cracks could not be observed for 1.2-nm-thick barrier MQW, whereas the cracks were observed for MQW with barrier thicker than 2.5 nm. It should be noted here that the other important parameter to determine the strain in the MQW structure is the average Al-composition of the MQW structure. With increasing barrier thickness and a constant well thickness, the average Al-composition increases, inducing even higher stress in the MQW structure. In the samples with barrier thickness of 2.5 nm and 5.5 nm, the average Al-composition became too high; therefore, the stress in the MQW structure is relaxed through the formation of cracks.

2.3.3 Dependence of period number

Although the thickness of AlN barriers was reduced, cracking was still observed when the MQW was grown for 100 periods. It could be considered that the total thickness of the MQW structure has exceeded the critical thickness, the thickness that the structure

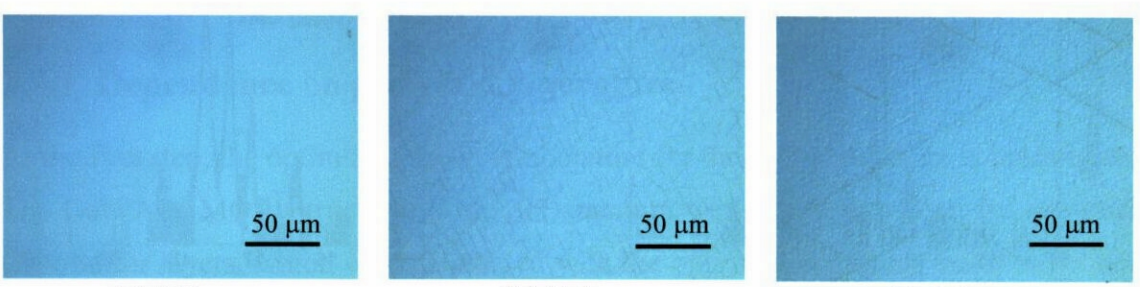

Figure 2.11 Surface morphology of 100-period GaN/AlN MQW structures grown with different barrier thickness: a) 2.0 nm, b) 2.5 nm, c) 5.5 nm

can be psudomorphically grown without lattice relaxation, of the GaN/AlN MQW on GaN buffer layer. Therefore, in this section, to study the effect of numbers of quantum wells, the number of quantum wells in GaN/AlN MQW structure was reduced from 100 periods to 15 periods, while the thickness of barriers and quantum wells were maintained at approximately 3.5 nm and 5.0 nm, respectively. Firstly, the surface morphologies observed by Nomarsky microscope revealed that the crack density reduced when the number of quantum wells was reduced. The structural quality and optical property are then further investigated by XRD measurements and PL measurements, respectively.

In Fig. 2.12, the XRD profiles of 2θ/ω scan of (0002) GaN are shown. It can be seen that the MQW-related satellite peaks in 100-MQW sample have the higher intensity than those of 15-MQW sample. For 100-MQW sample, the intensity of the MQW peak is higher than the peak of (0002) GaN. This is because the total thickness of MQW structure in this sample is nearly 0.85 μm, which is thicker than the 0.6 μm thick GaN buffer layer. However, the number of satellite peaks observed in both samples is almost the same, -3^{rd} to $+2^{nd}$, indicating that although the number of periods is increased, the structural quality of the MQW structure did not get improved, and might be worse than that of 15-MQW sample.

Figure 2.13 shows photoluminescence spectra measured at 77 K. As can be seen, the emission intensity is higher in 100-MQW sample than that of 15-MQW sample, while

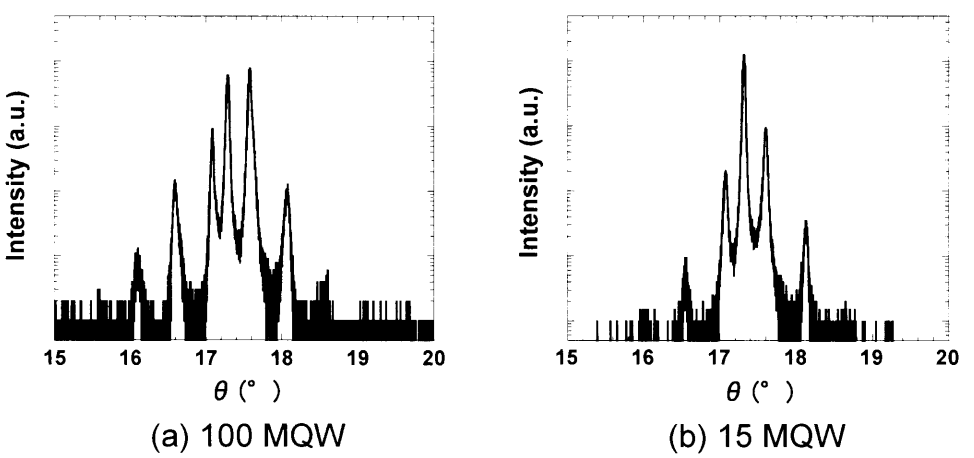

Figure 2.12 2θ/ω scan XRD profile of GaN/AlN MQW structure grown with different number of quantum well: a) 100 periods, b) 15 periods

the emission peak becomes much sharper in the 15-MQW sample than in 100-MQW sample. The full-width at half maximum (FWHM) of the emission peaks are estimated to be 150 meV and 400 meV, for 15-MQW sample and 100-MQW sample, respectively. It should be noted here that the peak of emission is at 3.13 eV for 15-MQW and at 3.30 eV for 100-MQW. Both of them obviously show the red-shift from the GaN peak, which is at 3.40 eV, showing that there exists the built-in electric field induced by the strain in the MQW structure [81,82]. A larger red-shift of the peak for 15-MQW sample is an indicator that the quantum wells is more strained, and there is no much lattice relaxation in 15-period MQW than in 100-period MQW. This can therefore be a good reason to explain that why 15-MQW has better structural and crystalline quality than 100-MQW. In conclusion, these results suggest that in 100-MQW, the structural quality of the MQW is deteriorated by the formation of cracks. It is therefore necessary to control the number of periods to be in a range that the structural quality is still maintained. However, the intersubband transition in the 15-MQW sample could not be observed by conventional measurements, because the absorption is too weak and is hidden by the optical interference which is described in Chapter 3. It is therefore needed to develop a growth method that can grow many periods of MQWs with high crystalline and structural quality.

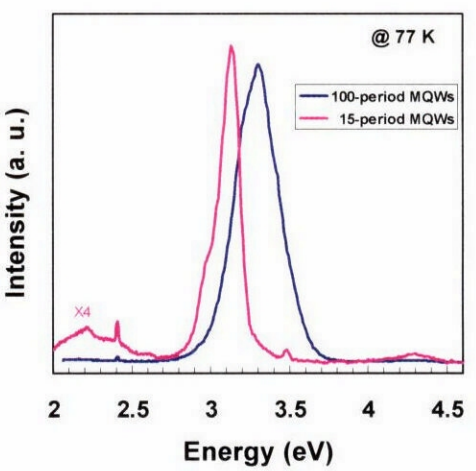

Figure 2.13 PL spectra of GaN/AlN MQW structures grown on 0.6-μm-thick GaN with different number of quantum well: a) 100 periods, b) 15 periods