3.2 Intersubband Absorption in MOVPE-Grown GaN/AlN Multiple Quantum Wells

The intersubband absorption in nitride-based multiple quantum wells grown by MOVPE has been reported mostly in the mid-infrared wavelength range with the shortest wavelength of 3 μm [81]. Most of such multiple quantum wells used AlGaN as barriers, while there are only a few reports on the growth of GaN/AlN MQW. However, in order to achieve the intersubband absorption in the near-infrared wavelength range, AlN should be used as barriers to obtain a large conduction-band offset. In this section, the intersubband absorption in MOVPE-grown GaN/AlN MQW is therefore described. The methods to tune the wavelength of intersubband absorption are also discussed. Finally, the achievement of the near-infrared intersubband absorption in MOVPE-grown GaN/AlN MQW is described.

3.2.1 Wavelength tuning by changing well width

The simplest way to change the wavelength of intersubband transition is to change the quantum well width. Changing the quantum well width can cause the shifting of each quantum energy levels, and can also induce the change of intersubband transition wavelength. It is known that an increase in quantum well width causes red shifting,

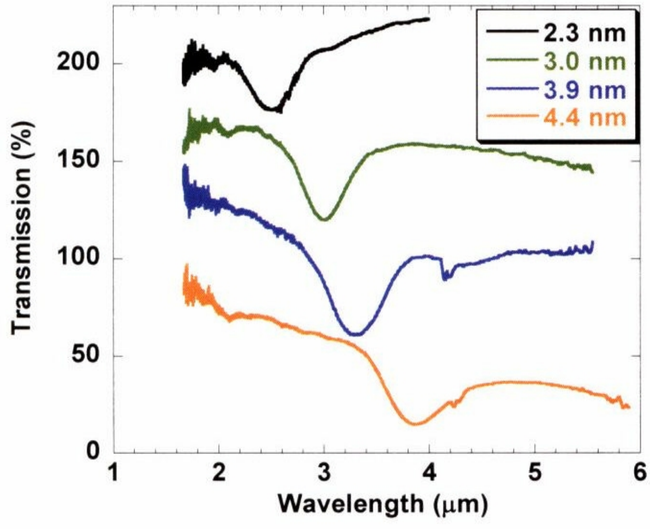

Figure 3.7 Transmission spectra of MOVPE-grown GaN/AlN MQW with different quantum well thickness measured by Multiple-reflection method

while a decrease in quantum well width causes blue shifting of intersubband transition wavelength. In order to obtain short wavelengths, the quantum well width should therefore be thin.

Figure 3.7 shows the transmission spectra measured by the multiple reflection method for the GaN/AlN MQW with quantum well thickness varied from 2.3 to 4.4 nm while the barrier thickness is kept constant at 1.5 nm. It can be obviously seen in the figure that the intersubband absorption wavelength shifts to shorter wavelength with decreasing well width. The wavelength shifted from 3.9 μm to 2.5 μm for a change of quantum well width from 4.4 nm to 2.3 nm. This result is a good evidence of the existence of intersubband transition. It also demonstrated the wavelength tunability of intersubband transition by means of changing the quantum well width.

3.2.2 Effect of built-in electric field

By plotting the intersubband absorption wavelength versus GaN quantum well width, as shown in Fig. 3.8, it was found that the relation between the wavelength and GaN quantum well width is different from the calculation value solved by Schrödinger equations. It can be seen that the absorption wavelength shifts to shorter wavelength compared to the calculated wavelength (solid line) in Fig. 3.8. This shifting is obviously

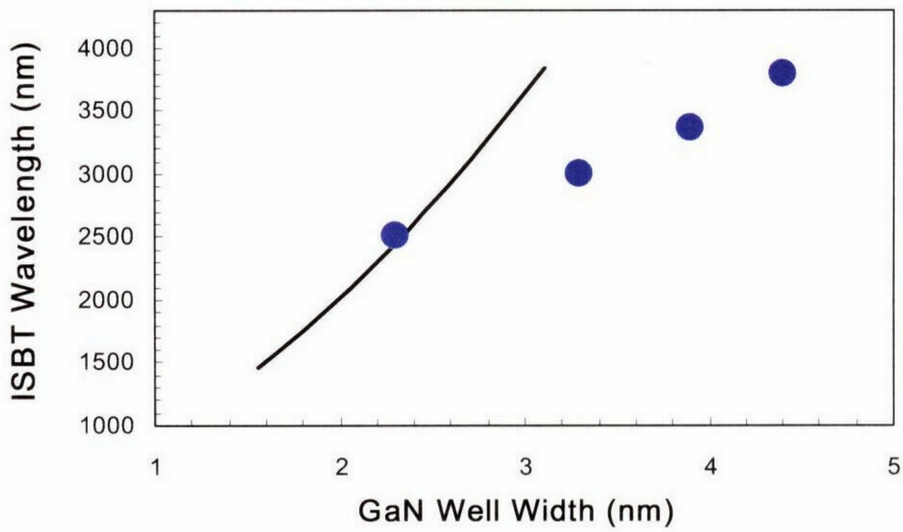

Figure 3.8 Relation between GaN well width and intersubband absorption wavelength
Solid line: calculation results, circle: experimental results

seen especially for the quantum wells thicker than 2.5 nm. For example, the peak wavelength is at 3 μm for the 3.2 nm thick GaN quantum wells, while the calculated peak wavelength is 3.75 μm. Such phenomenon is well known as an effect of built-in electric field [81,82], as schematically illustrated in Fig. 3.9. The conduction band and valence band of a symmetrical quantum well could be bent owing to the internal electric field induced in the quantum wells. This built-in electric field is considered to be a combination of many kinds of electric field, including spontaneous polarization field and piezoelectric field [156]. In GaN/AlN quantum wells, this internal electric field is very strong because of the large stress induced by lattice mismatch of more than 2% between GaN and AlN. To show the effect of this built-in electric field, the intersubband absorption wavelength is recalculated by taking into account the effect of built-in electric field as shown in Fig. 3.10 [157]. It is clearly seen that the wavelength shifts to shorter wavelength with increasing internal electric field. From these results, it can be considered that the thick quantum well tends to have large built-in electric field, while the effect of built-in electric field became almost negligible for the quantum well thinner than 2 nm. In this experiment, the wavelength of intersubband absorption is longer than the ideal value when the quantum well width is around 1.8 nm. This is considered to be the effect of interface roughness, as the quantum well is very thin, and the fluctuation of the quantum well thickness can make the quantum well different from the ideal condition, causing the longer wavelength of intersubband absorption.

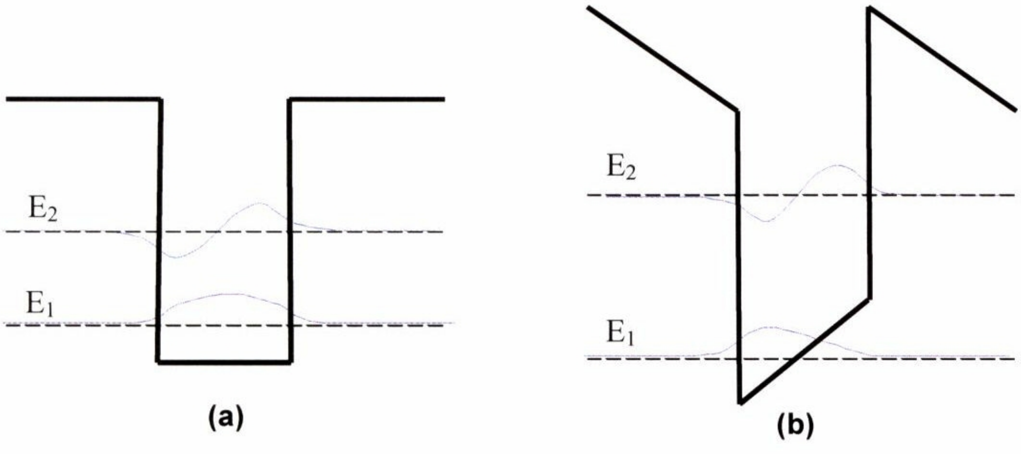

Figure 3.9 Effect of built-in electric field: (a) without built-in electric field (b) with built-in electric field

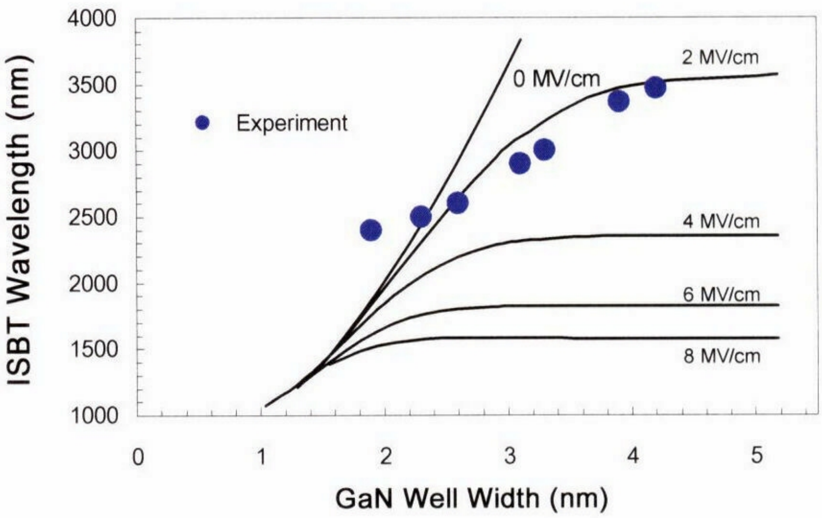

Figure 3.10 Calculation results of relation between GaN well width and intersubband absorption wavelength taken into account the effect of built-in electric field, compared with experimental results.

The built-in electric field, therefore, can be used as a parameter to change the wavelength of intersubband transition as illustrated in Fig. 3.11. For MQW with quantum well thickness of 3.1 nm, the intersubband absorption wavelength made a blue shift from 3 μm to 2.5 μm with an increase in AlN barrier thickness from 1.5 nm to 2.1 nm. In contrast, For MQW with quantum well thickness of 4.4 nm, the intersubband

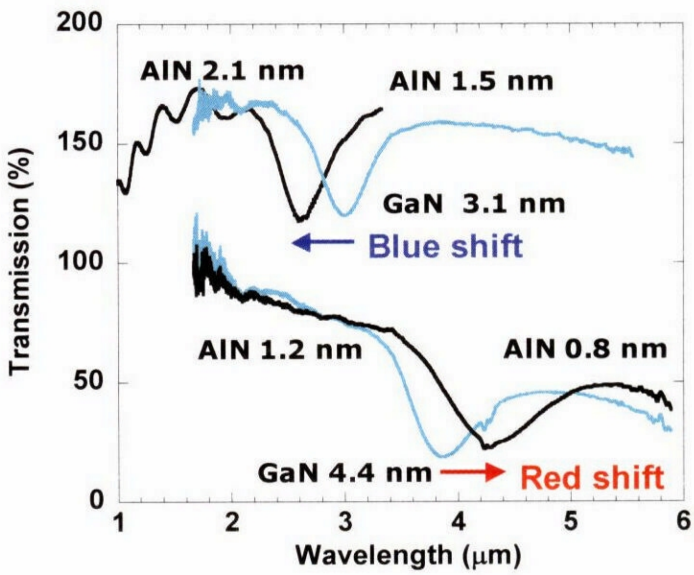

Figure 3.11 Demonstration of intersubband transition wavelength tuning by changing the barrier thickness

absorption wavelength makes a red-shift from 3.8 μm to 4.3 μm with a decrease in barrier thickness from 1.2 nm to 0.8 nm. These results clearly show that the built-in electric field can be tuned by changing the AlN barrier thickness, and can thus be used to change the wavelength of intersubband transition.

In general, growing thick AlN barrier can result in the large stress inside the quantum well structure, and therefore inducing large internal electric field. A decrease in the barrier thickness can cause a reduction of the strain in the quantum well structure, which can weaken the internal electric field, thus resulting in the shifts of intersubband transition wavelength to longer wavelength. In order to get the near-infrared wavelength intersubband transition, the thick barrier is therefore required to strengthen the built-in electric field. However, the thickness of AlN barrier has to be carefully concerned because too thick AlN layers deposited on GaN quantum wells could generate cracking and threading dislocations, making it not possible to obtain good crystalline quality for the observation of intersubband transition.

3.2.3 MQW quality improvement with low V/III ratio

As mentioned in Section 3.2.2, the shortening (blue-shifting) of the intersubband absorption wavelength requires thick AlN barriers in order to strengthen the internal electric field. Another reason that thick barriers are necessary is to prevent a leakage of carriers from a quantum well through a tunneling process, which could also result in a weak absorption. However, as a limitation of conventional growth technology, the growth of thick AlN barrier is much more difficult than the growth of thick GaN quantum wells because of following reasons:

1) *Parasitic gas phase reaction always occurs during the growth of AlN*
2) *Thick AlN layer grown on GaN generates threading dislocations and cracking*
3) *Optimal growth condition is different for GaN and AlN*

In above issues, the parasitic gas phase reaction is the issue that can be improved by optimization of growth condition. Typically, the parasitic gas phase reaction occurs from a fast reaction between NH_3 and Al. This reaction can therefore be reduced by decreasing the flow rate of NH_3, which also results in the reduction of V/III ratio. The NH_3 flow rate was thus optimized and found that the crystalline quality of AlN

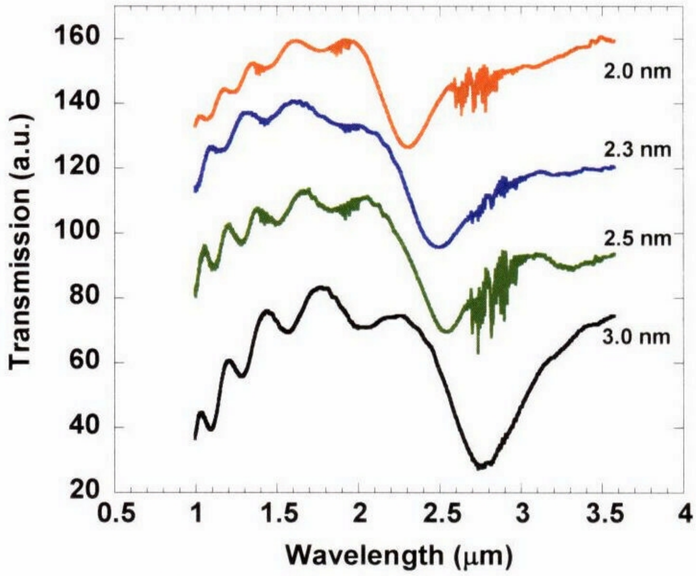

Figure 3.12 Well width dependence of intersubband absorption wavelength for GaN/AlN MQW grown with optimized V/III ratio

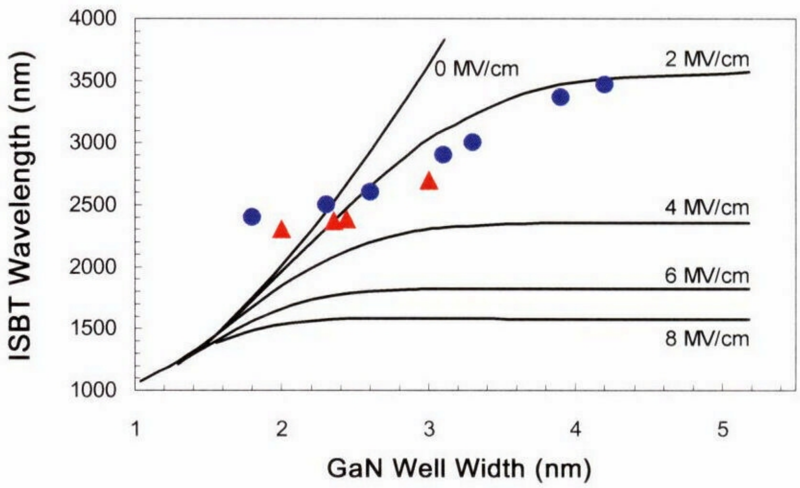

Figure 3.13 Relation between GaN well width and intersubband absorption wavelength for GaN/AlN MQW grown with optimized V/III ratio. Solid line: calculation results. Circle: experimental results.

improved with decreasing V/III ratio. Figure 3.12 shows the well width dependence of intersubband absorption after optimizing the V/III ratio during the growth of GaN/AlN MQW. The well width dependence is still observed, similar to that observed in Fig. 3.7. However, with this optimization, shorter intersubband absorption wavelength could be obtained for the same quantum well width. The shortest wavelength observed in this growth condition shifted to be 2.3 μm which is the shortest intersubband transition wavelength ever reported for the GaN/AlN MQW grown by MOVPE. The improvement of quality of MQW by means of optimizing growth condition provides a blue shift of intersubband absorption wavelength, as can be seen in Fig. 3.13, where the experimental results of intersubband absorption wavelength achieved by the new growth condition were compared to the previous result. It can be obviously seen that with this optimized growth condition, the intersubband absorption wavelengths make blue shifts for all GaN quantum well width. This shifting is considered to be due to improved interface quality as a result of suppression of parasitic gas phase reaction.

3.2.4 Shortest intersubband absorption wavelength achieved in MOVPE-grown GaN/AlN multiple quantum wells

Using the growth condition at low V/III ratio described in Section 3.2.3, the shortest intersubband absorption wavelength achieved in MOVPE-grown GaN/AlN MQW is demonstrated in this section. In order to obtain the near-infrared wavelength, the quantum well thickness should be reduced to be less than 2.0 nm, whereas the AlN barrier thickness should be thicker than 2.0 nm. The think barrier is necessary because it can prevent the coupling of energy levels between each adjacent quantum wells, and it can also strengthen the built-in electric field, resulting in a shift to short wavelength. The coupling of energy levels between each adjacent quantum wells typically generates

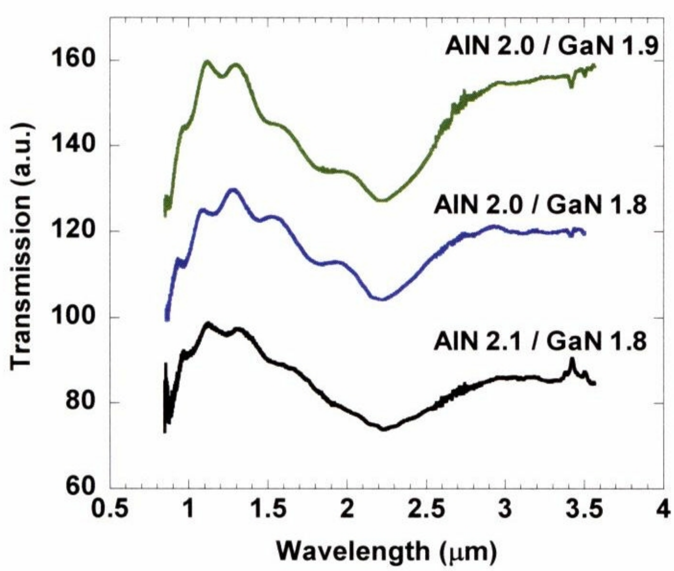

Figure 3.14 Shortest intersubband absorption wavelength for MOVPE-grown GaN/AlN MQW

a *miniband*, a broad band of energy containing many energy levels with small energy gap between each levels. The spectrum of intersubband transition between the minibands is always broader than that of a transition between energy levels. Hence, the formation of the miniband should not be allowed when the short intersubband absorption wavelength is required. To investigate the shortest intersubband transition wavelength that can be achieved by the MOVPE-grown GaN/AlN MQW, the GaN quantum well thickness was reduced to be around 1.8 nm, while the AlN barrier thickness was set to be around 2.0 nm. The intersubband absorption measurement results of three samples are shown in Fig. 3.14. Note that several samples with similar structures were fabricated to check the reproductivity since the production of narrow-width quantum wells is essentially difficult by the MOVPE growth. The reproductivity in fabricating such quantum wells was however confirmed in the MOVPE growth with the peak wavelength of around 2 μm as can be seen in Fig. 3.14. It can be also observed that the intersubband absorption peak is broader than those previously shown in Fig. 3.12, believed to be due to interface roughness [158,159].

To understand the cause of broadening of absorption wavelength, numerical simulation was performed with simulation model shown in Fig. 3.15. Three quantum wells with quantum well widths differ by +/- 1 monolayer are connected in parallel. Since the barrier width is thick enough to separate each quantum wells from the coupling of their energy levels, the intersubband transition from these three quantum wells can also be thought as the sum of three absorption peaks calculated from each quantum well. In this simulation, the effect of thickness fluctuation and interface roughness was also taken into consideration by adapting the shape of GaN/AlN quantum well to be a GaN/AlN quantum well with $Al_{0.5}Ga_{0.5}N$ ladder at each GaN/AlN

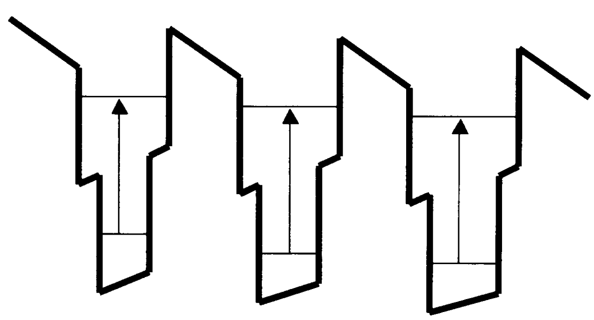

Figure 3.15 Simulation model of three quantum wells with interface roughness

interface as schematically shown in the figure. In addition, the thickness fluctuation was included by containing three different quantum wells with one-monolayer width difference. Figure 3.16 shows the simulation results using this simulation model with the quantum well thickness of 5, 6, and 7 monolayers which is correspondent to approximately 1.25, 1.50, and 1.75 nm, respectively. The $Al_{0.5}Ga_{0.5}N$ ladder was set to be 2 monolayers or approximately 0.5 nm. With this model, the average quantum well width can be approximated to be about 1.9 nm which is close to the value obtained from the XRD measurements at 1.8 nm. It also can be seen from the Fig. 3.12 that the intersubband absorption from this three quantum wells is quite broad and contains some shoulder peaks at the short wavelength side. This simulation result is very similar to the experimental result taken in Fig. 3.10, supporting the assumption that interfaces of quantum wells grown by MOVPE are not perfectly sharp, but contains thickness fluctuation. From this simulation, the interface roughness is estimated to be around 2 monolayers for each interface, showing that the near-infrared intersubband absorption wavelength is very sensitive to interface roughness. With only +/- 1 monolayer of thickness fluctuation, the intersubband absorption could not be achieved at the wavelength shorten than 2 μm. The shortening of intersubband absorption wavelength in the MOVPE-grown GaN/AlN MQW in this study is thus ended up with the achievement of the shortest intersubband absorption wavelength at around 2 μm. This is the shortest wavelength ever reported in GaN/AlN MQW grown by MOVPE.

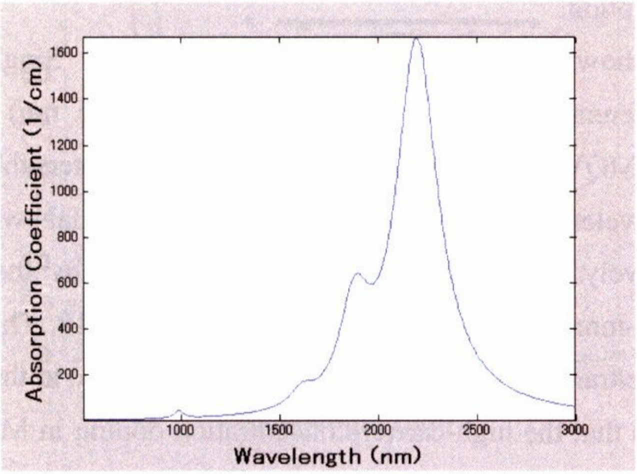

Figure 3.16 Simulation result of intersubband absorption spectrum for three quantum wells with 2-ML interface roughness

3.3 Intersubband Absorption in MBE-Grown GaN/AlN Multiple Quantum Wells

In contrast to MOVPE, the MBE provides very good interfaces of GaN/AlN multiple quantum wells. As already described in Chapter 2, the quantum well interfaces grown by MBE are nearly perfect. Indeed, there are many reports in the literatures on the growth of GaN/AlN MQW by MBE technique [88-90]. All of those reports show very good results in achieving the near-infrared intersubband absorption wavelength. The shortest intersubband absorption wavelength achieved in MBE-grown GaN/AlN is 1.08 μm [88]. In this section, the experiments on the measurements of intersubband absorption in MBE-grown MQW are therefore investigated in order to find out the problems of MOVPE growth and to obtain a good feedback for the MOVPE growth.

3.3.1 Intersubband absorption at 1.55 μm

The samples used for discussion in this section were grown by MBE for the MQW layer, while the buffer layer was grown by MOVPE to obtain good crystalline quality for intersubband absorption. The MQW was grown by MBE using the same structure as the samples grown for measurements in Section 3.2, composing of 40 periods of GaN/AlN MQW on 1.5-μm-thick MOVPE-grown GaN buffer layer. The quantum wells in the MQW layer were doped with Si to obtain a nominal carrier concentration of $2x10^{20}$ cm^{-3} to fulfill the first energy level in the quantum wells with electrons for the observation of intersubband absorption.

Figure 3.17 shows the transmission spectra taken by Single-pass transmission method for 2 different samples: i) GaN(1.35 nm)/AlN(2.5 nm) MQW, ii) GaN(1.8 nm)/AlN(2.4 nm) MQW. As can be seen in Fig. 3.12, the intersubband absorptions are observed at the wavelength of 1.45 μm and 1.55 μm for the GaN well width of 1.35 and 1.80 nm, respectively. The results were confirmed again by the Multiple-reflection method with the 6-mm-long specimens, as shown in Fig. 3.18. The absorption became very strong that the transmission intensity became almost zero at the peak of absorption. This clearly shows that the high-carrier-concentration doping in MBE was successfully achieved, while the structural quality was still maintained at high quality as the intersubband absorption at wavelength shorter than 2 μm could be easily observed. The observation of intersubband absorption at 1.55 μm could be achieved with the MBE growth technique by only a few times of experiment, suggesting that the MBE is a currently-available promising growth-technique for the fabrication of structures that require ultra-thin layer with sharp interfaces.

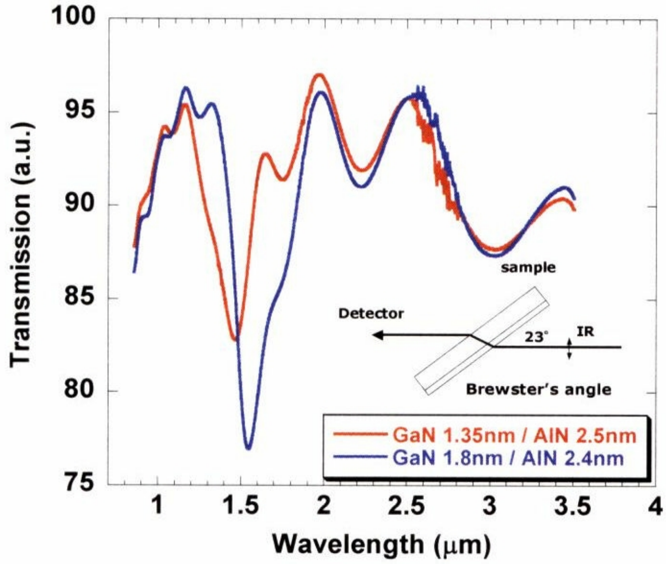

Figure 3.17 Transmission spectra of two MBE-grown GaN/AlN MQW samples measured by Single-pass transmission method

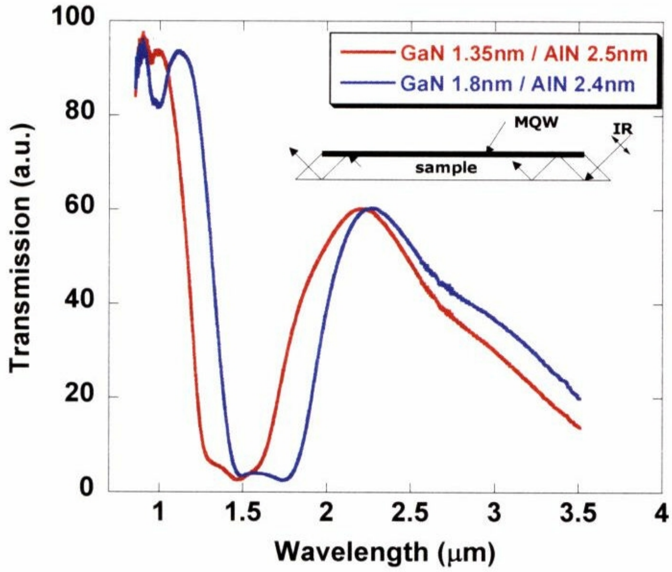

Figure 3.18 Transmission spectra of two MBE-grown GaN/AlN MQW samples measured by Multiple-reflection method

3.3.2 Intersubband absorption in low-carrier-concentration MBE-grown GaN/AlN multiple quantum wells

In order to compare the results with the samples grown by MOVPE, and to investigate the problems in achieving wavelength shorter than 2 μm for the MOVPE growth, the sample with 40 periods of MQW was fabricated with quantum wells doped with Si to a nominal carrier concentration of $1x10^{19}$ cm^{-3}. This carrier concentration is intended to be almost the same as that of samples grown by MOVPE ($9x10^{18}$ cm^{-3}). The intersubband absorption measurements were performed by both Single-pass transmission method and Multiple-reflection method as shown in Fig. 3.19 and Fig. 3.20, respectively. As can be seen in Fig. 3.19, the intersubband absorption could not be observed with the Single-pass-method for the 2-nm-thick quantum wells that are doped with a carrier concentration of $1x10^{19}$ cm^{-3}. In Fig. 3.20, it could be seen that the Multiple-reflection-method much better responsivity in detecting the intersubband absorption with a successful observation of clear intersubband absorption at a peak wavelength of 1.7 μm. These results suggest that for quantum wells with almost perfect interfaces, as achieved by the MBE growth, the carrier concentration of $1x10^{19}$ cm^{-3} is enough for the intersubband absorption measurements with Multiple-reflection method.

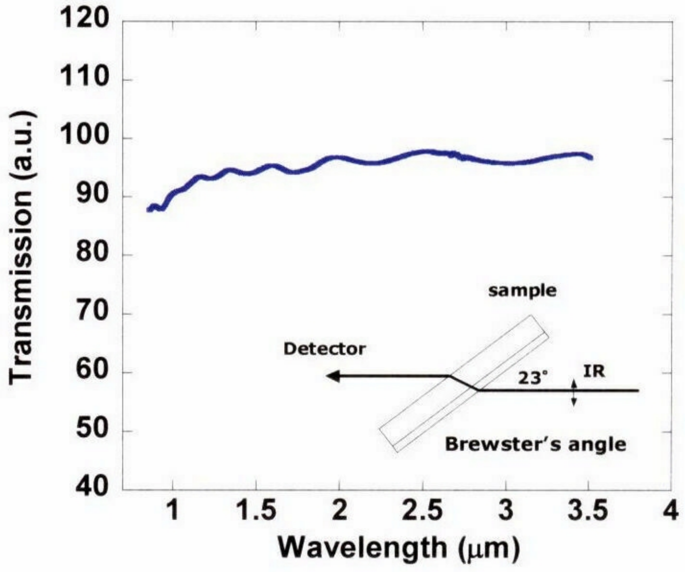

Figure 3.19 Transmission spectra of low-doping MBE-grown GaN/AlN MQW measured by Single-pass transmission

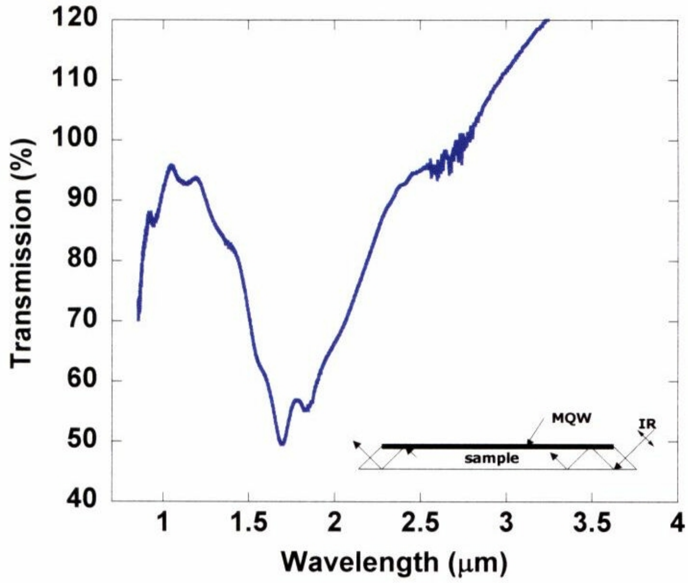

Figure 3.20 Transmission spectra of low-doping MBE-grown GaN/AlN MQW measured by Multiple-reflection method

3.4 Discussions

In previous sections, the experimental results have shown that the intersubband absorption at the wavelengths shorter than 2 μm could not be achieved in GaN/AlN MQW grown by MOVPE, while such wavelengths could be easily achieved in the GaN/AlN MQW grown by MBE. In this section, the intersubband absorption wavelengths achieved by both growth techniques are compared, and the problems of GaN/AlN MQW grown by MOVPE in achieving near-infrared wavelength are also discussed.

In order to compare the intersubband absorption wavelengths achieved by MOVPE to those by MBE, the experimental results of both techniques are plotted along with the calculation results, as shown in Fig. 3.21. The MOVPE results (circles) were obtained from this study, while the MBE results (triangles) were those reported in literatures [89-90]. The solid lines are calculation results obtained by taking into account the effect of built-in electric field, varied from 0 to 8 MV/cm. Obviously it can be seen that the intersubband absorption wavelengths obtained by the MOVPE are longer than those obtained by the MBE at any quantum well width. For MBE technique, the intersubband

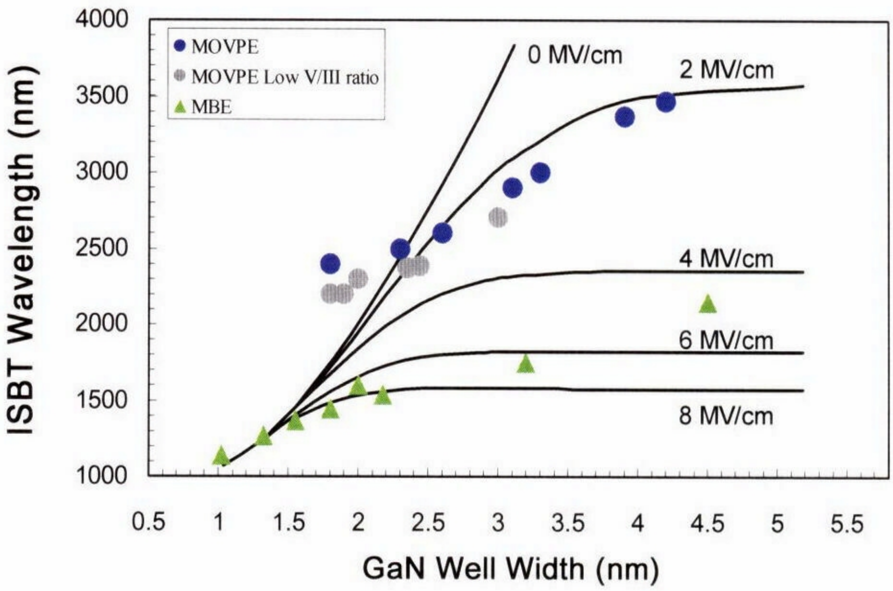

Figure 3.21 Relation between GaN well width and intersubband absorption wavelength for 3 types of GaN/AlN MQW; Blue circle: MOVPE-grown MQW, Gray circle: Low-V/III-ratio MOVPE-grown MQW, Triangle: MBE-grown MQW. Solid line: calculation results.

absorption was achieved from 1.08 μm to 2.2 μm with the estimated built-in electric field of 5-8 MV/cm. Note that with very thin quantum wells (< 1.5 nm), the effect of built-in electric field becomes very small and negligible, and this can be observed in the MBE-grown MQW as the wavelength of intersubband absorption clearly fits to the flat-band calculation results especially for thin quantum wells. Therefore, the results suggest that the quantum-well interfaces in the MBE-grown MQW must be very sharp with negligible thickness fluctuation.

On the other hand, the MOVPE-grown MQW provides longer wavelengths from 2.2 μm to 3.5 μm. For wide quantum wells (> 2.5 nm), the intersubband absorption wavelengths still fit to the calculation results with the built-in electric field of around 2 MV/cm, but for thin quantum wells (< 2.5 nm), the experimental results provide longer wavelengths than the calculation results. Note that there was no intersubband absorption observed for quantum wells thinner than 1.7 nm. As described in Section 3.2.4, one of the main problems in achieving the near-infrared intersubband absorption in the MOVPE-grown MQW is the roughness of quantum well interfaces. Indeed, many problems are generated by the interface roughness as follows:

1) Shifting of energy levels to higher energy

The energy level of each subband of GaN/AlN quantum wells can be calculated by solving the Schrödinger equation taken into account the effect of the built-in electric field. However, for quantum wells with rough interfaces, the energy levels changed from its calculated value: both 1^{st} and 2^{nd} subband energy level shifts to higher energy. The shift of the 2^{nd} subband energy level is usually smaller than that of 1^{st} subband energy level because it is limited by the conduction-band offset. As a result, the difference in energy between subband levels becomes smaller. In other words, this causes a red-shift of intersubband transition wavelength. This shifting is thought to be a main problem in achieving the intersubband transition at wavelength shorter than 2 μm.

Moreover, the interface roughness always occurs together with the thickness fluctuation. With thickness fluctuation, the MQW structure contains quantum wells with different thicknesses. In general, the 1^{st} subband energy level in a wide quantum well is at lower energy than that in a narrow quantum well. Thus, when there are quantum wells connecting in parallel like the one shown in Fig. 3.15, the carriers in the MQW structure tend to be confined in wide quantum wells than in thin quantum wells as demonstrated by simulation in Fig. 3.16. The wavelength of intersubband transition is thus dominated by wider quantum wells in the MQW with thickness fluctuation.

2) Effective carrier concentration in quantum wells

The nominal carrier concentration in the GaN quantum wells is typically determined from a hall-measurement of a 1-μm-thick Si-doped GaN layer grown at the same growth condition. However, the growth time of the doped layer is normally short on the order of a few seconds, which could possibly give different carrier concentration from the long-run growth (1 hour) that is used for calibration. Generally, there is no direct way to measure the carrier concentration in the very thin quantum wells; the carrier concentration is therefore calibrated by this method. However, the growth mode of the first few monolayers of GaN/AlN multiple quantum wells by MOVPE could possibly different from that of thick GaN layer, which might result in less carrier-concentration compared to the thick doped layer.

Considering the rough-interface quantum wells, the shift of 1^{st} subband energy level to higher energy always occurs, inducing a reduction in amount of effective carrier in the 1st subband energy level. Moreover, the rough interface normally means the incorporation of Al which is typically difficult to dope. It is thought that the carrier concentration in the ladder area of rough-interface quantum wells can be estimated as an undoped layer. The volume of quantum wells that is effective for the doping is therefore smaller than usual in case of rough-interface quantum wells. This make effective carrier concentration in quantum wells became very small, and could be too small for the detection of the intersubband absorption in case of quantum wells thinner than 2 nm.

3) Weakening of built-in electric-field

The built-in electric field is estimated to be 5-8 MV/cm for the MBE-grown MQW, while it is only 2 MV/cm for the MOVPE-grown MQW. The difference in strength of built-in electric field is considered to be the cause of crack generation. As shown in Chapter 2, the MOVPE-grown MQW contains higher density of cracks than the MBE-grown MQW. The cracks usually occur with the lattice relaxation. It can thus be said that the stress induced in the MQW is more relaxed by crack in MOVPE-grown MQW than in MBE-grown MQW, which is one of the main cause that the MOVPE-grown MQW has weaker built-in electric field.

Another parameter that involves with the strength of built-in electric field is considered to be the interface roughness. With the rough-interface quantum wells, the stress induced by lattice-mismatch between GaN and AlN is thought to be reduced, because the $Al_xGa_{1-x}N$ ladder formed at the rough interfaces can work as a buffer layer to form a GaN/$Al_xGa_{1-x}N$/AlN interface. The strength of the built-in electric field in rough-interface structure is therefore smaller than usual, making the MOVPE-grown MQW unable to utilize the effect of built-in electric field for blue-shifting.

These problems are considered to be the main causes that the intersubband absorption could not be observed for quantum well thinner than 2 nm. Improvement of interface is therefore considered to be a main solution to achieve intersubband absorption at wavelength shorter than 2 μm. The main solution to improve the interface quality is to find a growth technique that can grow the MQW with sharp interfaces such as Pulse atomic layer epitaxy method (PALE) [160-167]. With the PALE method, the effective V/III ratio during the growth is low, thus helps suppressing the parasitic reaction during the growth of the MQW. Moreover, the growth temperature can be reduced from normal growth temperature to be around 800 °C, reducing the effect of atomic diffusion which occurs at high temperature. Finally, with decreasing growth temperature, the problems concerning generation of cracks and dislocations induced by different thermal expansion coefficient could also be solved. The improvement of the interfaces with the PALE method is therefore very interesting to be studied.

3.5 Concluding Remarks

In this chapter, the intersubband absorption measurements were performed for GaN/AlN multiple quantum wells grown by MOVPE and MBE. Firstly, many measurement methods were introduced, including Single-pass transmission method, Attenuated total reflection method, Multiple reflection method and Waveguide coupling method.

It was found that the Multiple-reflection method can detect the intersubband absorption with high sensitivity, while a simple fabrication of a specimen with polished edges is required.

In Section 3.2, the intersubband absorption in GaN/AlN grown by MOVPE was investigated. The wavelength tuning was demonstrated by two methods: i) changing the quantum well width, ii) changing the barrier width. It was found that the effect of built-in electric field is very important for the study of intersubband absorption in GaN/AlN MQW. It was also shown that the improvement of the crystalline quality of the GaN/AlN MQW can help in blue-shifting of the intersubband absorption wavelength. Finally, the shortest intersubband absorption wavelength in MOVPE-grown GaN/AlN MQW was demonstrated and discussed with the simulation results. It was found that the interface roughness is the main problem in shortening the intersubband absorption wavelength.

In Section 3.3, the intersubband absorption in GaN/AlN grown by MBE was investigated. The intersubband absorption at 1.55 μm was easily obtained by adjusting the quantum well width to be around 2.0 nm with 2.5-nm-thick barriers. The intersubband absorption was also observed in the MBE-grown MQW with a carrier concentration of $1x10^{19}$ cm^{-3}, suggesting that such carrier concentration is enough for the observation of intersubband absorption if the sharp quantum well interfaces are obtained. The problem of MOVPE-grown MQW was therefore thought to be mainly due to the interface roughness, which induces a change of energy levels, resulting in a red shift of intersubband absorption with low effective carrier concentration. With these results, it can be concluded that the MBE technique is a promising technique to achieve the near-infrared intersubband absorption, while a further improvement in the growth technique is still required for the MOVPE.