2.4 Quality Improvement of Multiple Quantum Well Structures by Insertion of Intermediate layer

In the last section, it is shown that the growth of a large number of quantum wells with high quality could not be simply achieved by the conventional MQW structure because the structural quality gets worse when cracks are generated. In order to achieve a large number of quantum wells without cracking, a new structure or a new growth technique has to be developed. In this section, the growth of multiple quantum wells with high quality is demonstrated by means of strain-engineering using the structure shown in Fig. 2.14. The GaN/AlN MQW structures with 200 quantum wells were grown by inserting a 0.4-μm-thick intermediate GaN layers at each 10-40 periods of MQWs. This growth technique has been reported in the literature [71,134] with the improvement of quality of GaN/AlGaN quantum wells. For the sake of clarification, the structure could be depicted as the repetition of the MQWs structure which is capped with thick GaN cladding layers. Considering only a number of MQWs between two intermediate GaN layers, the MQW layer should be strained with no lattice relaxation. The lattice constant and the crystalline quality of the structure can thus be maintained with the 0.4-μm-thick

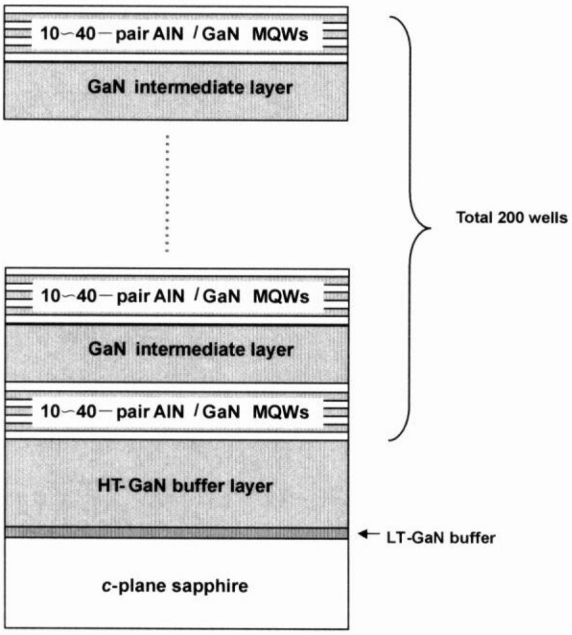
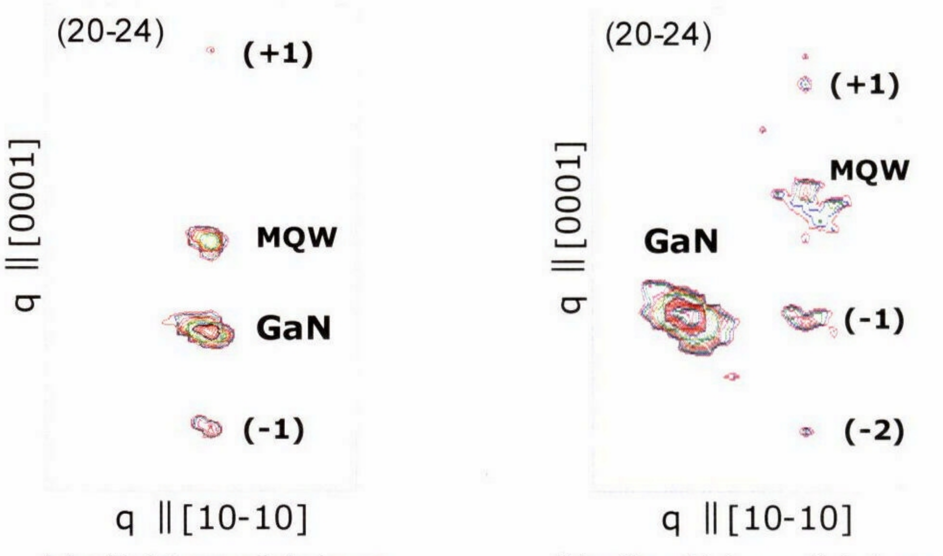


Figure 2.14 Schematic structure of 200-period GaN/AlN MQW structures grown on GaN with the insertion of GaN intermediate layer between 10-40 periods

GaN intermediate layer.

In order to investigate the structural quality of the MQW grown with this new structure, XRD reciprocal lattice mapping was taken, as shown in Fig. 2.15 (a) for (20-24) plain of 200-MQW with GaN and AlN thickness of 3.9 nm and 1.4 nm, respectively. It can be seen that the GaN peak and the MQW peak, including its satellite peaks, are aligned on the same plane that is parallel to [10-10] direction, indicating that the MQW layers are psudomorphically grown on GaN with the same lattice constant, or in other words, there is no lattice relaxation of MQW layer observed in this structure. In case of fully-lattice-relaxation, the MQW and its satellite peaks are aligned on a different plane of [10-10] direction, as shown in Fig. 2.15 for 200 periods of GaN(1nm)/AlN(11nm) MQW, indicating that both the MQW layer and GaN layers are grown independently with their lattice constants. It can be said that the insertion of GaN intermediate layers helps decreasing the stress in a thick MQW layer through the distribution of the stress to many MQW layers. This could therefore make the MQW being strained inside the structure without the lattice relaxation.

In order to investigate the crystalline quality of the MQW layers grown with this new structure, the photoluminescence measurements were performed for

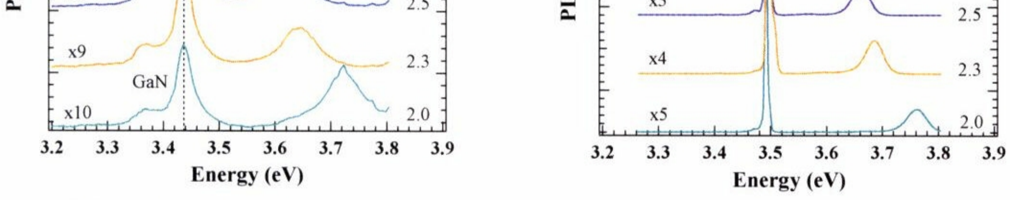


(a) with intermediate layer (b) without intermediate layer

Figure 2.15 XRD reciprocal lattice mapping in (20-24) plane of 200-period GaN/AlN MQW structures grown on GaN: a) with insertion of intermediate layer, b) without intermediate layer

GaN/$Al_{0.6}Ga_{0.4}N$ MQW and GaN/AlN MQW structures. The growth pressure and temperature for MQW layers were 60 mbar and 1100 °C, respectively, while the growth condition of the intermediate GaN layers was as same as that of GaN buffer layer. He-Cd laser was used as the excitation light source for the photoluminescence measurements, meaning that only emission energy lower than 3.82 eV (He-Cd laser energy) can be observed.

Figure 2.16 shows the PL spectra at room temperature and at 5.5 K of GaN/ $Al_{0.6}Ga_{0.4}N$ MQW structures with different well thickness: i) 4.0 nm, ii) 3.5 nm, iii) 3.0 nm, iv) 2.5 nm, v) 2.3 nm, vi) 2.0 nm, while using the same 1.7-nm-thick $Al_{0.6}Ga_{0.4}N$ barriers. The dashed line shows the PL peak energy of the bulk GaN. As can be seen in the figure, along with the peaks of GaN, the emissions from the MQW structures are observed at higher energy. The blue shift of the emission peaks with decreasing well width is the evidence of the formation of the first conduction subband in the MQW structures. The decrease of the intensity with decreasing well thickness is considered to be a result of the reduction of the active region thickness. At low temperature, the emission peaks of GaN are very sharp at 3.49 eV with a full width of half-maximum of less than 10 meV. These results indicate very good crystalline quality of the samples. The intensity of the MQW peaks increases a little bit with increasing temperature,



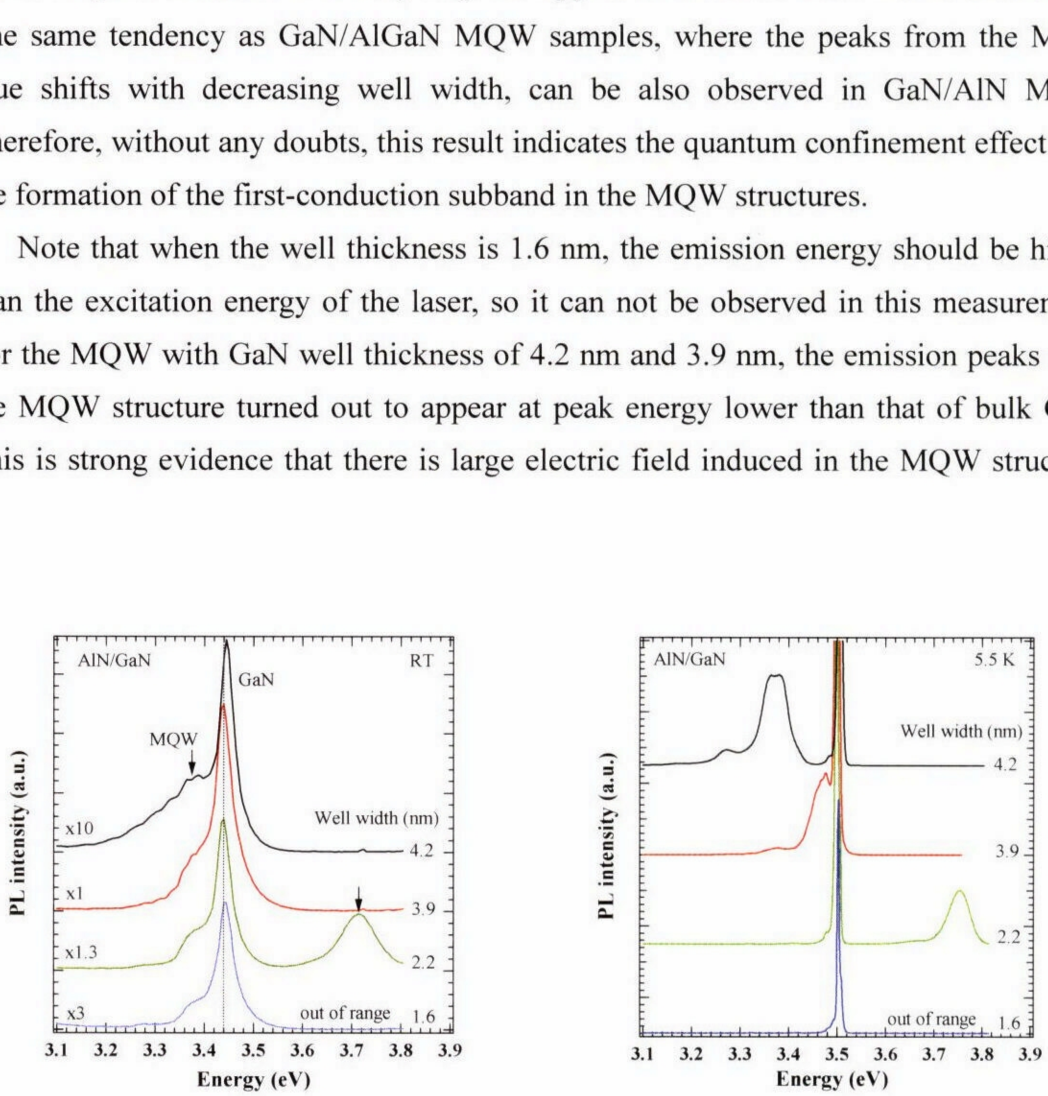
(a) at room temperature

(b) at 5.5 K

Figure 2.16 PL spectra of 200-period GaN/$Al_{0.6}Ga_{0.4}N$ MQW structures grown on GaN with the insertion of GaN intermediate layer. The well thickness is varied from 2.0 nm to 4.0 nm. (a) at room temperature (b) at 5.5 K showing small temperature dependence due to the carrier confinement effect of the quantum wells.

Figure 2.17 shows the PL spectra at room temperature and at 5.5 K of the GaN/AlN MQW structures with the same 1.5 nm AlN barriers and different well thickness: i) 4.2 nm, ii) 3.9 nm, iii) 2.2 nm, iv) 1.6 nm. At room temperature, the emission peaks from the MQW structure when the well thickness is 4.2 and 3.9 nm could not be clearly observed. The emissions from MQW are hidden by that of GaN due to the broad emission peak of GaN. However, all peaks appeared with narrower linewidth at 5.5 K. The same tendency as GaN/AlGaN MQW samples, where the peaks from the MQW blue shifts with decreasing well width, can be also observed in GaN/AlN MQW. Therefore, without any doubts, this result indicates the quantum confinement effect with the formation of the first-conduction subband in the MQW structures.

Note that when the well thickness is 1.6 nm, the emission energy should be higher than the excitation energy of the laser, so it can not be observed in this measurement. For the MQW with GaN well thickness of 4.2 nm and 3.9 nm, the emission peaks from the MQW structure turned out to appear at peak energy lower than that of bulk GaN. This is strong evidence that there is large electric field induced in the MQW structure,

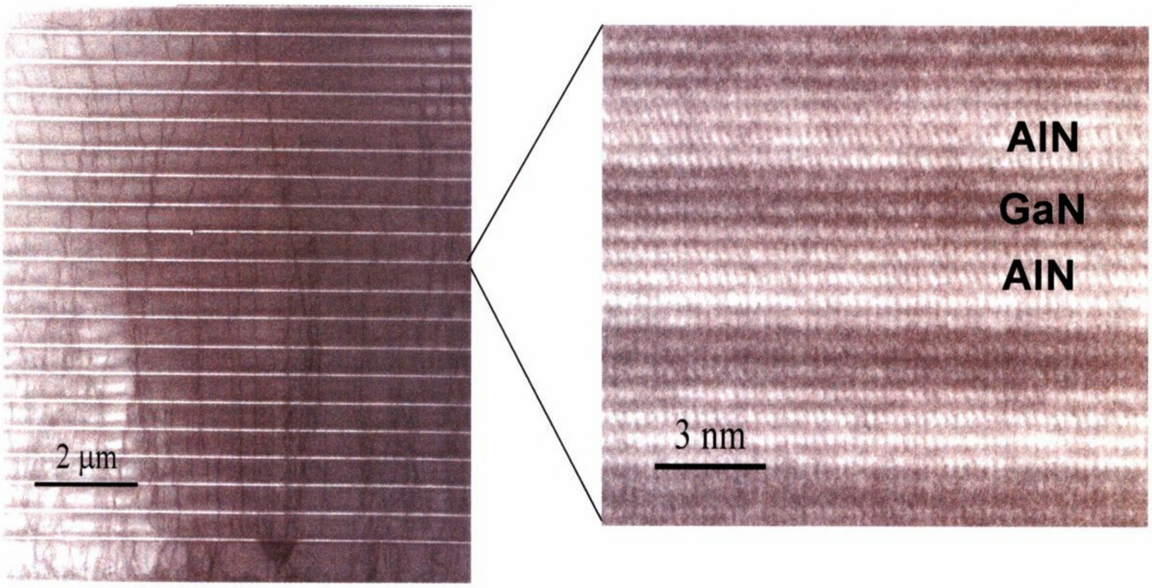


(a) at room temperature

(b) at 5.5 K

Figure 2.17 PL spectra of 200-period GaN/AlN MQW structures grown on GaN with the insertion of GaN intermediate layer. The well thickness is varied from 1.6 nm to 4.2 nm. (a) at room temperature (b) at 5.5 K causing the red shift of PL spectrum [82]. In the sample with a well thickness of 4.2 nm, the emission peak is broader than others. This could be due to the partial lattice relaxation in the sample as the cracking could be observed in the surface morphology. However, the emission peaks became sharper for thinner quantum wells, indicating that the quantum well is well strained without lattice relaxation in MQW with thin quantum wells. This suggests that the thickness of quantum wells and barriers must be carefully considered to obtain the high-quality MQW layer.

Figure 2.18 shows the cross-sectional transmission electron microscope (TEM) image of the 200-period GaN(1.6 nm)/AlN(1.7 nm) MQW grown on the GaN buffer layer. It can be seen that the threading dislocations in the GaN buffer layer are considerably reduced at the interface between the MQWs and the GaN buffer layer. It is believed that the MQWs possibly played a role to bend the dislocations which propagate from the underlying GaN buffer layer and combined with the nearby dislocations, finally resulting in the reduction of the dislocation density [135-138]. The magnified TEM image of the MQW layer is also shown in Fig. 2.18 (b). The bright parts and the dark parts in the image correspond to the AlN barriers and the GaN wells, respectively. It can be seen that the GaN/AlN MQW structures have sharp interfaces, but interfaces are not clear in some parts which could be a result of interface roughness and thickness



(a) TEM image of whole structure

(b) magnified TEM image of MQW

Figure 2.18 TEM image of MOVPE-grown MQW fluctuation. However, the interfaces observed in the TEM image of Fig. 2.18 (b) are relatively sharp compared to other MOVPE-grown MQW reported in literatures [139-143]. With these results, it can therefore be concluded that the GaN/AlN and GaN/AlGaN MQW up to 200 periods were successfully grown on GaN with the insertion of GaN intermediate layer. The crystalline and structural qualities of the MQW were improved by keeping the MQW well strained between two intermediate layers.

2.5 Molecular Beam Epitaxy

2.5.1 Introduction

In contrast with MOVPE growth of semiconductor crystals under quasi-equilibrium conditions, growth by molecular beam epitaxy is accomplished under nonequilibrium conditions and is principally governed by surface kinetic processes. Molecular beam epitaxy is a controlled thermal evaporation process under ultra high vacuum conditions. Ga vapor beam from an effusion cell and an activated nitrogen beam from a plasma source are directed toward a heated substate. Under suitable conditions, layer-by-layer deposition of Ga and N atomic planes is possible.

The process of crystalline growth by MBE involves the adsorption of the constituent atoms or molecules, their dissociation and surface migration, and finally incorporation, resulting in growth. An important point in the MBE growth of III-V compounds is that the cation incorporation rate is close to unity. Under these conditions, the growing crystal will retain a smooth and atomically abrupt surface only if the cation surface migration rate is very high. If the cations are given insufficient time or energy, then before a monolayer is completed, a new island will form on top of the former. Thus, the surface roughens and begins to resemble an assembly of three-dimensional islands. At high temperatures, the decomposition rate becomes faster than the deposition rate, setting an upper limit on MBE substrate temperature. However, low substrate temperature reduces surface atom mobility, leading to increased defect densities in the GaN epilayer.

The MBE systems are mostly equipped with *in-situ* monitoring, namely reflection high-energy electron diffraction (RHEED) system, which gives insight to the growth mechanism and surface reconstruction. The RHEED pattern is formed by the elastic scattering of electrons from the periodic crystal lattice. The distance between the streaks is an indication of the surface lattice unit cell size. The grazing incidence angle of the electron beam is set to be shallow, ensuring that it penetrates only the uppermost layers of the crystal. If a surface is atomically flat, then sharp RHEED patterns are seen. If the surface has a rougher surface, the RHEED pattern is more diffuse. This therefore gives very important information for the layer-by-layer growth of a very thin layer to achieve abrupt interfaces of the multiple quantum wells.

2.5.2 Growth and characterization of GaN/AlN multiple quantum well

In this study, apart from MOVPE growth, the growth of GaN/AlN MQW structures was also performed by MBE technique in order to study its advantages in fabricating the MQW structures and to compare with the MOVPE technique. The 40 periods of GaN/AlN MQW were grown on 1.5-μm-thick MOVPE-grown GaN at a growth temperature of 720 °C, while the substrate was kept rotating during the growth. This growth temperature was optimized to achieve the best interface quality. The quantum well and barrier thickness were set to be 1.7 nm and 2.5 nm, respectively. The surface morphology was observed by the nomarski microscope, revealing that the cracking also occurs in the as-grown sample. Since the MQW layer contains as many as 40 quantum

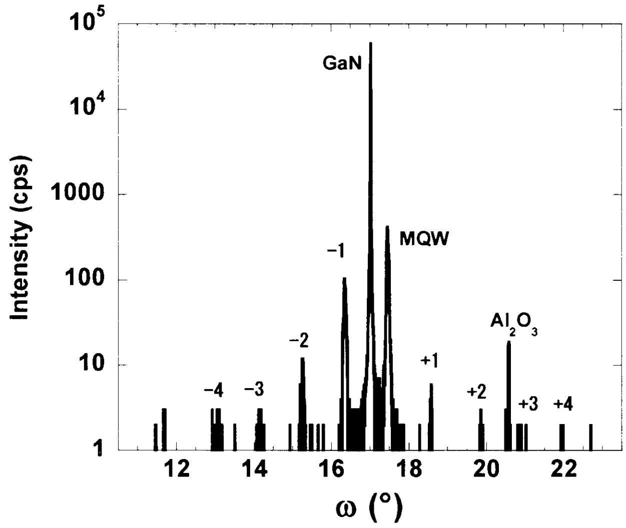


Figure 2.19 XRD profile of ω/2θ scan for (0002) GaN/AlN MQW grown by MBE on MOVPE-grown GaN

wells, which results in thick MQW layer with high Al composition, the cracking is considered to be unavoidable for such sample.

Figure 2.19 shows the XRD ω/2θ scan for the 40-period GaN/AlN MQW grown by MBE. It can be clearly seen that the MQW peak with its satellite peaks have shown up with high intensity. The higher order satellite peaks from -5th to +4th could be clearly seen, indicating that the MQW structure has very high structural quality and sharp GaN/AlN interfaces. To confirm this result, the cross-section TEM image was also taken to observe the quality of interfaces, as shown in Fig. 2.20. It can be seen that the AlN (white part) and GaN (black part) show very high contrast in the figure, suggesting that the interface is abrupt. The GaN and AlN thickness estimated in the TEM image are 1.7 and 2.5 nm, respectively, showing a good agreement with those estimated by the XRD measurements. Although the thickness fluctuation is observed in some areas of Fig. 2.20, most of areas show very sharp interfaces with no thickness fluctuation. The thickness fluctuation was estimated to be 2 monolayers at the maximum. These results are in good agreement with the XRD measurement result, showing that the GaN/AlN MQW can be grown with very high structural quality and sharp interfaces, suitable for the realization of near-infrared intersubband absorption.

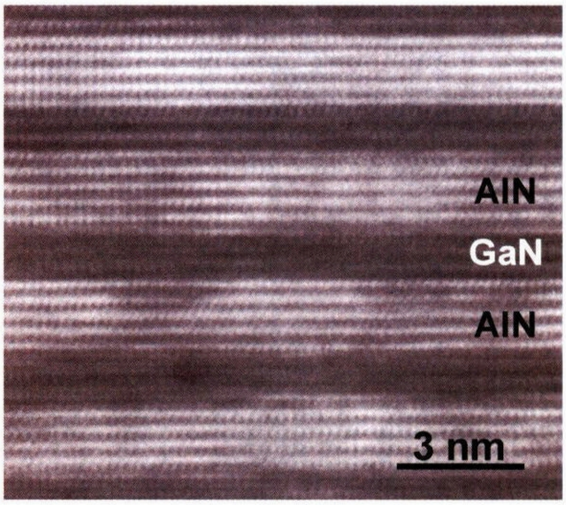


Figure 2.20 TEM image of MBE-grown MQW

2.6 Discussions

To compare the crystalline and structural quality of the MBE-grown MQW with the MOVPE-grown MQW, the MOVPE growth was performed to grow 1.5-μm-thick GaN on sapphire substrate, followed by a growth of 40 periods of GaN(1.7 nm)/AlN(2.5 nm) MQW. This could give the same structure as that of MBE-grown MQW which was described in the previous section. The growth condition used to grow such sample was the condition that is optimized for both GaN and MQW as previously described. Firstly, one can compare the interface quality of GaN/AlN MQW by observing the TEM image previously shown in Fig. 2.18 and 2.20 which were taken for MOVPE-grown MQW and MBE-grown MQW, respectively. It can be clearly seen that the MBE-grown MQW gives very good contrast between GaN layer and AlN layer, showing that the interfaces are excellent. For MOVPE-grown MQW, however, such contrast could not be achieved even though the brightness and contrast was well adjusted during the TEM observation. This difference could therefore be good evidence that the MBE-grown MQW has better

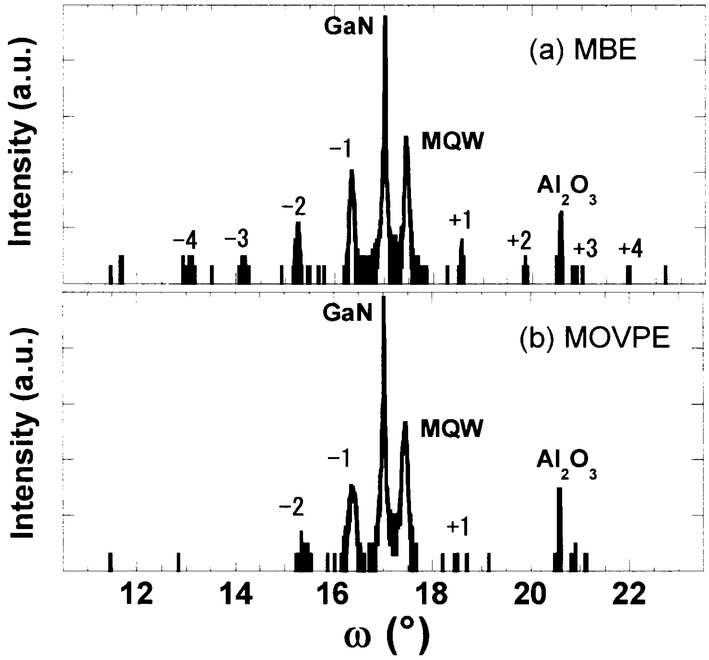


Figure 2.21 XRD profile of ω/2θ scan for (0002) GaN/AlN MQW
(a) MBE-grown MQW (b) MOVPE-grown MQW

interface quality than the MOVPE-grown MQW. This result could be confirmed by the XRD measurements, as shown in Fig 2.21. The results of XRD $\omega/2\theta$ scan are plotted in log scale on the same graph, comparing the MOVPE-grown MQW and MBE-grown MQW. As can be seen in the figure, although both MQW structures give the same intensity of MQW peak, the MBE-grown MQW gives much stronger and sharper satellite peaks. Moreover, the MBE-grown MQW shows many high-order satellite peaks (-4th to +3rd), while the MOVPE-grown MQW shows much fewer satellite peaks (-2nd to +1st). These are another evidence to show that the MBE-grown MQW has sharper interfaces than the MOVPE-grown MQW.

The reason that the MOVPE technique could not achieve the abrupt interfaces like those achieved with the MBE technique is considered to be the parasitic gas phase reaction during the growth. It is widely known that the parasitic gas phase reaction occurs during the MOVPE growth of nitride semiconductors owing to the fast reaction of NH_3 and alkali materials [143-145]. This reaction is very fast during the growth of AlN; therefore, it could deteriorate both the interface and crystalline quality. The parasitic gas phase reaction can be suppressed by reducing the source flow rate ratio of group V to group III (V/III ratio), which is discussed in Chapter 3.

The next reason that MBE technique can give better interface quality than the MOVPE technique is considered to be the growth temperature. As mentioned earlier, the growth temperature was 720 °C for MBE technique and 1100 °C for MOVPE technique. The difference of growth temperature is as large as 380 °C which is large enough to give difference in the fabricated quantum wells. Firstly, high growth temperature could cause diffusion of molecules especially at the interfaces of different materials such as GaN/AlN interface, which can deteriorate the interface quality. Since the MBE technique can successfully grow the MQW at low growth temperature, such interdiffusion is suppressed and therefore the ideal shape of interfaces is still maintained. In order to investigate the existence of interdiffusion, the MBE-grown sample was annealed at a pressure of 60 mbar and a temperature of 1100 °C for 45 minutes while flowing H_2 and NH_3, which is the same condition as the growth condition for MOVPE-grown MQW. Then the interface quality was characterized by XRD measurements and found that the satellite peaks was observed only from -2nd to +1st, reduced from up to the 4th order observed before annealing. It can thus be thought that the interdiffusion occurs at a high growth temperature of 1100 °C, causing the intermixing between GaN and AlN, and deteriorating the interface quality of the MQW.

The next results of growing the GaN/AlN MQW at high temperature is the generation of cracks and threading dislocations. As the GaN and AlN has different thermal expansion coefficient, the cracks and threading dislocations can be generated when reducing temperature from the normal growth temperature to room temperature after finishing the growth. It can be said that the higher the growth temperature is raised, the larger the amount of cracks and threading dislocations is generated. The cracking and threading dislocations generally deteriorate the crystalline quality and could cause the thickness fluctuation and rough interfaces. As a result, the interface quality could become worse when growing at high temperature. Considering the surface morphology of MOVPE-grown MQW compared with that of MBE-grown MQW as shown in Fig. 2.22, the MOVPE-grown MQW clearly shows that large amount of threading dislocations and cracks are generated, while the MBE-grown MQW shows much lower amount of cracks. Since both samples was grown on the same MOVPE-grown 1.5-μm-thick GaN buffer layer, the threading dislocation density is relatively low on the order of 10^8 cm^{-2}, thus the dislocation observed in MOVPE-grown MQW is considered to be generated in the MQW layer. These results clearly indicate that the growth temperature is a very important parameter that should be taken into consideration in order to control the sharpness of the interface.

Nevertheless, though MBE technique could be used to grow the MQW with sharp interfaces, the growth of GaN buffer layer on sapphire substrate still could not be

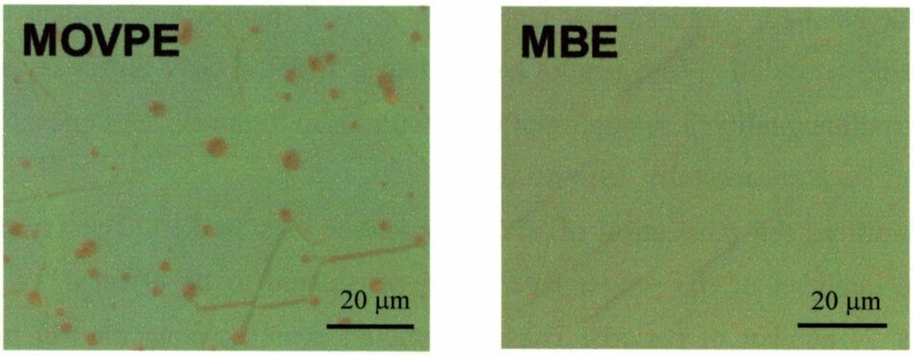


Figure 2.22 Surface morphology of GaN/AlN MQW by Nomarsky microscope
(a) MOVPE-grown MQW (b) MBE-grown MQW

achieved by the MBE technique. This could be because of the lack of growth technique that can use to grow large-lattice-mismatch materials for MBE growth, whereas the two-step growth is widely known as a growth technique for the MOVPE growth of high-quality GaN layer on sapphire substrate. The other reason could be the low growth temperature, as the optimized growth temperature to obtain high-quality GaN layer should be around 1150 °C, which is not possible to be grown by the MBE technique. It is therefore a trade-off between the crystalline quality and the interface quality. In order to make the intersubband transition devices operating at optical communication wavelengths, both growth techniques should therefore be applied to obtain both the high crystalline quality buffer layer and sharp MQW interfaces.

2.7 Concluding Remarks

In this chapter, the growth and characterization of nitride semiconductors by metalorganic vapor phase epitaxy were described. The GaN buffer layers were successfully grown on sapphire substrates with GaN low-temperature nucleation layer technique. It was found that the optimum thickness of GaN low-temperature buffer layer was about 25 nm at 550 °C and the optimum growth temperature and pressure of the GaN buffer layer was 1150 °C and 200 mbar, respectively. By this condition, high-quality GaN buffer layers were successfully grown. The GaN buffer layer has excellent electrical properties, where the electron mobility is very high at 537 cm^2/Vs with a low carrier concentration of 6×10^{16} cm^{-3}. Furthermore, PL spectrum shows very sharp near band-edge emission of GaN even at room temperature with a very small yellow-band emission. These results are evidences that the GaN buffer layer has very good crystalline quality. The doping of GaN with Si up to the carrier concentration of 9×10^{18} cm^{-3} was successfully demonstrated.

In addition, the fabrication of MQW structures was studied. The crystalline and structural qualities of the grown layer were considered to be affected by 1) barrier thickness, 2) number of periods. These parameters must be concerned to prevent the lattice relaxation by the formation of cracks that destroys the quality of MQW structures.

Finally, the MQW structures were grown with careful control of above parameters by the insertion of GaN intermediate layers between a numbers of MQWs. By this method, the MQW structures with high-structural quality were achieved. PL spectra illustrate blue-shifts of the emission peaks with decreasing well width, indicating that emissions come from the MQW structures. These PL results confirmed that the first conduction subband is formed in the MQW structure. The intersubband transitions in these structures can therefore be expected.

In Section 2.5, the molecular beam epitaxy was performed to compare with the above results. The interface quality observed by TEM image was very excellent. There is almost no thickness fluctuation in the MBE-grown sample. The characterization by XRD measurements also shows good agreement with the observation of higher order satellite peaks from -5 to +4.

The comparison of the MOVPE and the MBE shows that MBE has much better interface quality compared to the MOVPE. This was considered to be a result of low growth temperature of 720 °C for MBE growth. For MOVPE growth, besides the high growth temperature of 1100 °C, the problem concerning parasitic gas phase reaction is a hindrance to achieve such sharp interfaces. However, with only MBE growth, the GaN buffer layer could not be grown with high quality owing to a lack of growth technique that can provide high quality buffer layer. It is therefore interesting to use MOVPE growth for high-crystalline-quality buffer layer, while using MBE growth for the high-structural-quality MQW layer.