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High-quality GaN/Si(1 1 1) epitaxial layers grown with various $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattices as intermediate layer by MOCVD

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Abstract

We have grown and characterized GaN/Si(1 1 1) epitaxial layers having different total thicknesses and periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattices using metalorganic chemical vapor deposition. When the total thickness of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice is 60 nm, GaN/Si(1 1 1) epitaxy shows the best surface and crystal quality. Under the same total thickness of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice of 60 nm, as the number of periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattices increases, the quality of GaN/Si(1 1 1) epitaxy is also improved. GaN/Si(1 1 1) epitaxy grown with optimized $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice of total thickness of 60 nm and 20 periods, shows crack distance of about 120 nm between cracks, FWHM of double crystal X-ray diffractometry rocking curve for GaN(0002) of 690 arcsec and FWHM of photoluminescence at RT of 34.49 MeV, which is compared with the best results reported for GaN/Si(1 1 1), so far. Therefore, we obtained a high-quality and nearly crack-free GaN/Si(1 1 1) epitaxy by optimizing $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice, possibly for the applications of LED or other photon devices, and, we found that the optimized total thickness and periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice play a very important role in the improvement of quality and reducing cracks in the growth of GaN/Si(1 1 1) epitaxy.

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1. Introduction

III-nitride semiconductors are promising materials which have great potential for use in display, optical data storage, high-power and frequency

electronic devices and its related technologies. However, the lack of a suitable substrate has always hindered the growth of high-quality GaN films. Most of the GaN layers have been grown on sapphire (0001) substrates in spite of some serious limitations such as their insulating property, unavailability of large size and extreme hardness. Recently, there has been a considerable interest in

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the heteroepitaxial growth of GaN on Si substrate because of the potential applicability in integration of well-established Si electronics with GaN-based photonic devices such as light-emitting diodes [1], laser diodes and UV detectors [2]. Actually, Si has many advantages due to its high crystal quality, low cost, large-area size, good electrical and thermal conductivity as compared with sapphire and SiC. However, due to reasons such as large mismatch of the lattice constants (-16.9%) and thermal expansion coefficients (about 57%) between GaN and Si, difference of crystal structures (GaN: hexagonal, Si: cubic) and thermal diffusion of Si at high temperature, it is really difficult to grow high-quality GaN on Si substrate. One of the major problems which indeed prevents direct growth of GaN on Si surface is poor nucleation of GaN on Si, which leads to an island-like GaN structure [3].

Cracking is currently a main issue in the growth of GaN/Si(111) epitaxy, which results in low performance of devices, such as current-scattering centers for light propagation as well as poor crystal quality [4]. The cause of crack initiation is generally assumed to be caused by tensile stress due to a mismatch of thermal expansion coefficient between GaN and Si during cooling after growth, but there is no apparent reason for it [5]. The other unresolved issue for the growth of GaN/Si epitaxy is why cracking occurs to relieve the tensile stresses rather than dislocation flow as usually occurs during the growth of other semiconductors, especially in metalorganic chemical vapor deposition (MOCVD) growth. According to Etzkorn et al. [6], the simplest explanation is that typical MOCVD growth temperatures, about 1000 – 1100°C , are below the brittle to ductile transition so that appreciable stress relaxation cannot occur by dislocation plasticity within the time frame of growth.

Recently, several groups have reported on the removal of these cracks for the growth of GaN on Si substrate using various methods by MOCVD and MBE, such as laterally epitaxial overgrown technique by Zamir et al. [7], selective area growth method by Sawaki et al. [8], graded AlGaIn interlayer growth by Min-Ho Kim et al. [9], and AlGaIn/GaN superlattice by Nikishin et al. [10].

But, these methods have not yet achieved perfect crack-free GaN/Si(111) epitaxy compared with the growth of GaN on sapphire substrate.

Among the above-mentioned methods, GaN/Si(111) MBE growth with AlGaIn/GaN superlattice, between AlN nucleation layer and GaN epitaxy used by Nikishin et al. [10] for strain relief by reducing lattice and thermal mismatches was performed successfully. While MBE growth has advantages of relatively low growth temperature and pressure compared with MOCVD growth, it is unsuitable for commercial application due to very low growth rates. Although MOCVD growth has a higher probability for crack generation than MBE growth due to relatively high growth temperature, it has the advantage of rapid growth rates. So, it is essential to use MOCVD growth to enlarge commercial productivity by using the advantages of Si substrates such as low cost and large-area size for the growth of GaN on Si.

In this paper, we demonstrate the high-quality and nearly crack-free GaN/Si(111) epitaxy with different thicknesses and periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}$ /GaN superlattice using the MOCVD system.

2. Experimental procedure

The growth was brought about in MOCVD system with a horizontal quartz reactor. Phosphorous-doped n-type Si(111) wafers having a cut-off angle of 4° were used as substrates. Si(111) plane is chosen because of its trigonal symmetry favoring epitaxial growth of the GaN(0001) plane. Trimethylaluminum (TMA), Trimethylgallium (TMG), and ammonia were used as Al, Ga, and N sources, respectively. H_2 was used as a carrier gas. The substrates were degreased by $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2\text{:H}_2\text{O}$ (3:1:1) solutions for 5 min, and etched with HF (2%) for 5 min to remove the surface oxide layer. After preparations, Si(111) substrates were heated under H_2 ambient at 1000°C for 5 min to etch its surface thermally prior to growth. Pre-deposition of Al for 3 s was used just before introducing NH_3 into the reactor to prevent the formation of SiN_x . AlN nucleation layer of about 80 nm thickness was grown at 1080°C for 25 min by feeding TMA and NH_3 with

the flow rates of 14.7 $\mu\text{mol/min}$ and 1.6 SLM, respectively. Then, $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice with different total thicknesses and periods on AlN nucleation layer was grown at 1080°C. Total thickness of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice was changed from 30 to 120 nm, and periods of it varied from 5 to 20 as set with total thickness is 60 nm. Introduction of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice as an intermediate layer between AlN nucleation layer and GaN epitaxy is a method for improving the quality and reducing the cracks by releasing the stress due to lattice and thermal mismatch between GaN and Si. Finally, GaN epilayer of about 1.0 μm thickness was grown at 1090°C for 20 min by feeding TMG and NH_3 with the flow rates of 70.0 $\mu\text{mol/min}$ and 1.6 SLM, respectively. The reactor pressure was 150, 150, and 300 Torr for AlN, $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice and GaN, respectively. Fig. 1 shows the schematic diagram of layer structure for GaN/Si(111) epitaxy, and Table 1 indicates specifica-

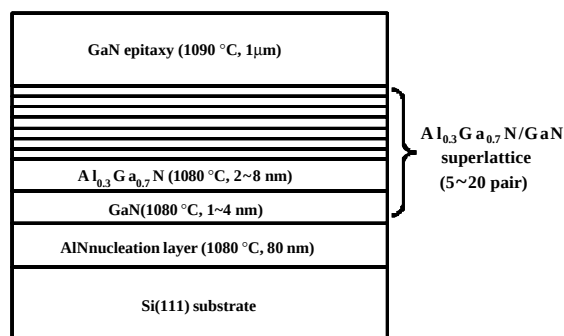


Fig. 1. Layer structure of GaN/Si(111) epitaxy grown with different total thicknesses and periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice.

tions of used samples for $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice with different total thicknesses and periods.

Scanning electron microscopy (SEM), atomic force microscopy, double crystal X-ray diffractometry (DCXRD) and photoluminescence (PL) were used to characterize the surface morphology, crystallinity, and optical properties of GaN/Si(111) epitaxial layers grown using $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice with different total thicknesses and periods.

3. Experimental results

Fig. 2 shows surface images of low magnification observed by SEM for the GaN/Si(111) epitaxy grown using $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice with different total thicknesses ranging in 30–120 nm. Total thickness of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice is 30 nm for S1, 60 nm for S2 and 120 nm for S3. Some cracks with cross-hatched patterns in all the samples are seen. For S1 and S5 samples, some pits generally generated by poor coalescence seen on the surface, reduced the quality of GaN epitaxy. But, S3 sample without any pits shows that the distance between cracks is longer than in others. It is indicated that S3 sample has the lowest crack density and the best surface morphology among them, which means total thickness of 60 nm in $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice is more suited than other total thicknesses of 30 or 120 nm for the growth of high-quality GaN/Si(111) epitaxy.

Even if $\text{Al}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$ superlattice as an intermediate layer was used in growth of GaN/Si(111), GaN surface shows cracks. The reason why some of these cracks are generated on the

Table 1

Specification of GaN/Si(111) epitaxy grown with various total thickness and periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice

Sample no.	Spec no.	Growth thickness of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice	The number of periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice (total thickness)
S1	#SMP02-12	$\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}$ (2 nm)/GaN (1 nm)	10 period (30 nm)
S2	#SMP02-11	$\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}$ (2 nm)/GaN (1 nm)	20 period (60 nm)
S3	#SMP02-52	$\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}$ (4 nm)/GaN (2 nm)	10 period (60 nm)
S4	#SMP02-53	$\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}$ (8 nm)/GaN (4 nm)	5 period (60 nm)
S5	#SMP02-54	$\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}$ (8 nm)/GaN (4 nm)	10 period (120 nm)

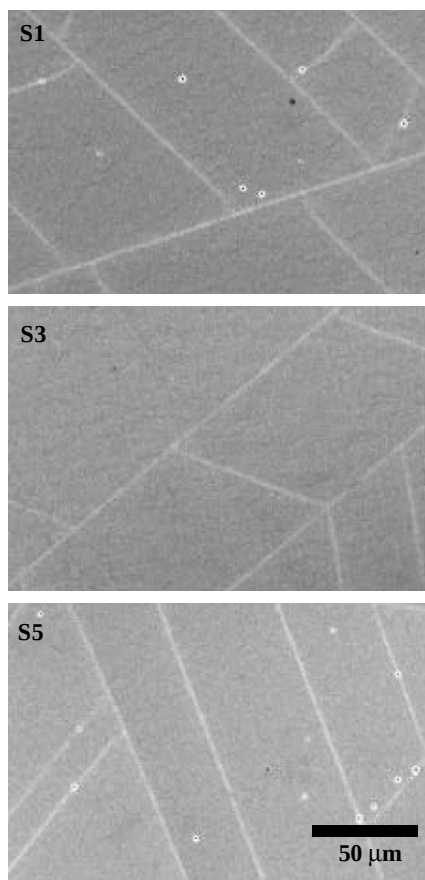


Fig. 2. SEM surface images of GaN/Si(111) epitaxy grown with different total thicknesses of 30 nm for S1, 60 nm for S3 and 120 nm for S5 in $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice.

surface of GaN epitaxy is the tensile stress which appears by mismatch of thermal expansion coefficient between GaN and Si during cooling of the samples after growth. However, we found that the crack density for GaN epitaxy grown with $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice is much lower than that of GaN grown using only AlN buffer [11]. In our experiment, although perfectly crack-free GaN is not grown, nearly crack-free GaN can be grown by using $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice. It is considered that $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice attributes the tensile stress to relief.

Fig. 3 exhibits DCXRD rocking curves for GaN(0002) and its FWHMs grown with different total thicknesses of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice.

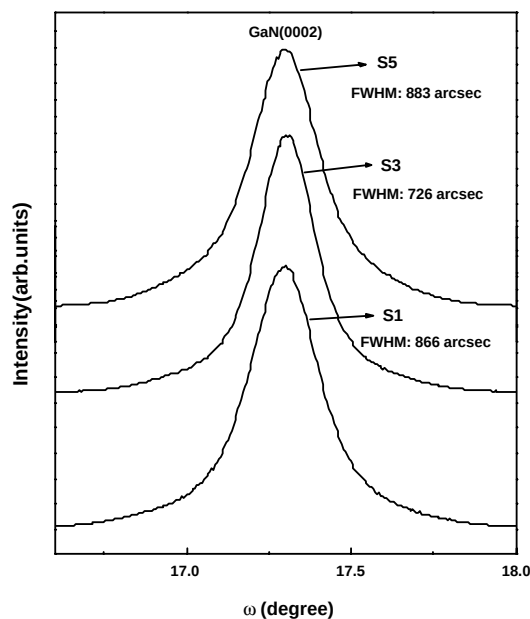


Fig. 3. DCXRD rocking curves for GaN(0002) and its FWHMs of GaN/Si(111) epitaxy grown with different total thicknesses of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice.

As shown in the figure, FWHMs of DCXRD rocking curves for GaN(0002) grown with different total thicknesses of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice for S1, S3 and S5 are 866, 726 and 883 arcsec, respectively. It means that GaN/Si(111) grown with $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice of 60 nm is of the highest crystal quality. This behavior of crystallinity is very similar to the changes of surface property shown in Fig. 2. It is thought that the reason for poorer crystal quality of S1 and S5 compared to S3 results from some pits. From these results of surface and crystal quality shown in Figs. 2 and 3, we found that total thickness of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice gives rise to a significant improvement in the quality of GaN/Si(111) epitaxy when it is 60 nm. Therefore, it suggests that $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice plays an important role in the improvement of quality in growing GaN/Si(111) epitaxy.

Now, we set the total thickness of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice as 60 nm and investigate the influence of the number of periods for $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice on the growth of GaN/Si(111) epitaxy. Fig. 4 shows surface images of

low magnification, observed by SEM, of the GaN/Si(111) epitaxy grown using $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice with various periods ranging in 5–20. The number of periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice is 20 for S2, 10 for S3 and 5 for S4.

Surfaces without any pits can be seen in the entire sample but some differences in crack density still exists. S2 sample grown with 20 periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice shows the best surface crack density with crack distance of about $120\text{ }\mu\text{m}$ between cracks, which indicates that crack density decreases with increase in periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice when the total thickness is constant. As the number of periods of superlattice increases, the number of interfaces between $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattices increases.

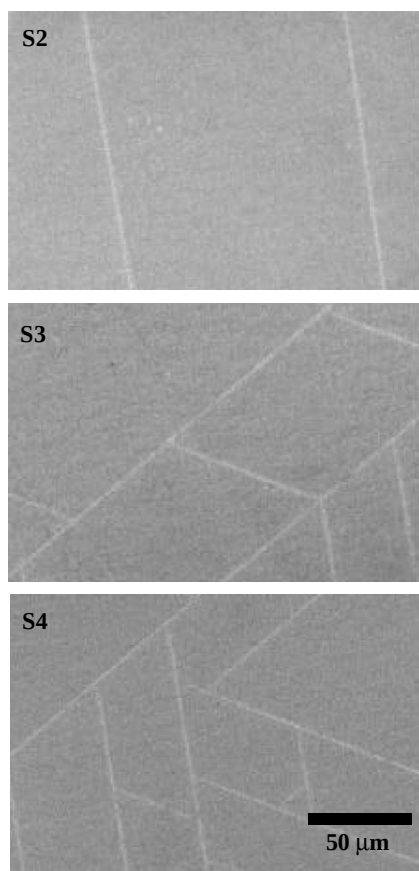


Fig. 4. SEM surface images of GaN/Si(111) epitaxy grown with various periods of 20 for S2, 10 for S3 and 5 for S4 in $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice.

It is considered that the reason for the lowest crack density of S2 sample under the properly constant total thickness is because these interfaces release the stress. Comparing S4 and S5, however, one sees that the number of periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice for S5 sample is more than that of the S4 sample. The reason why the quality of S5 is poorer than that of S4 in spite of more interfaces between $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattices is the total thickness. If total thickness is too large, its quality is poorer due to induced strain and excess of critical thickness. Therefore, optimizing total thickness and periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice is simultaneously very important for the growth of GaN/Si(111) epitaxy.

Crack distance of $120\text{ }\mu\text{m}$ for S2 sample is comparable with crack-free GaN/Si epitaxy grown by ELO techniques or patterned structures, because pattern size of those is usually about $100\text{--}200\text{ }\mu\text{m}$ in length. Also, it is possible to apply this LED or other photon device without serious current loss as current-scattering site has two or three cracks because fabrication size is about $200\text{--}300\text{ }\mu\text{m}$ in length.

Fig. 5 exhibits FWHMs of DCXRD rocking curves for GaN(0002) grown with different periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice. FWHM values for S2, S3 and S4 are 690, 726 and 804 arcsec, respectively. It means that GaN/

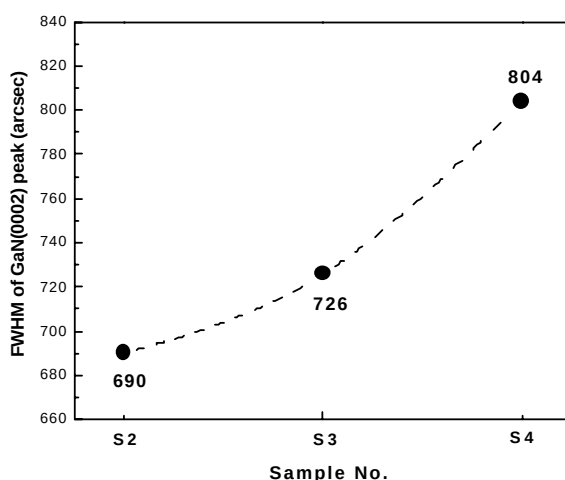


Fig. 5. FWHMs of DCXRD rocking curves for GaN(0002) of GaN/Si(111) epitaxy grown with various total periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice.

Si(111) epitaxy grown with 20 periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice is of the highest crystal quality, which is compared with the best results of approximately 600 arcsec reported by Armin dadgar et al. [12]. This behavior of crystallinity shows a tendency similar to that found with the changes of surface property shown in Fig. 4 related to the cracks.

From above-mentioned results, comparing S1 and S5, we see that optimized $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice with 60 nm total thickness and 20 periods lead to greatly improved quality of GaN/Si(111) epitaxy related to pits, crack density and FWHM of DCXRD for GaN(0002). Therefore, it suggests that $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice plays an important role in the growth of GaN/Si(111).

In Fig. 6, photoluminescence spectra at room temperature for GaN/Si(111) grown using $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice with various periods show a sharp band edge emission at 364 nm, which does not have yellow luminescence related to various defects such as vacancy and dislocations. In general, the typical band edge emission peak for GaN on sapphire is 362 nm at room temperature.

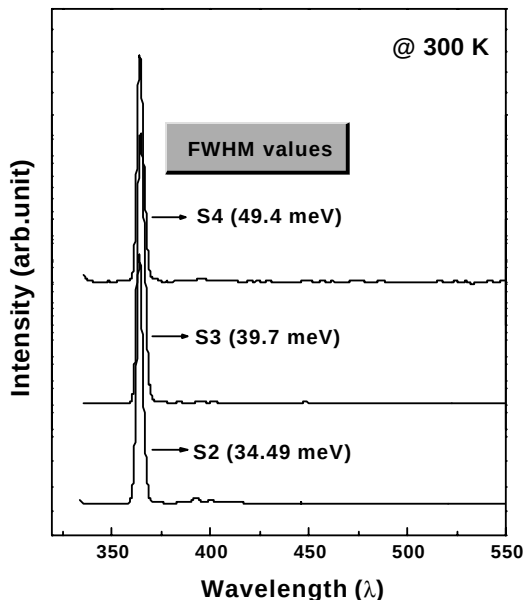


Fig. 6. PL spectra at RT and its FWHMs of GaN/Si(111) epitaxy grown with various total periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice.

The red-shifted peak of 2 nm in our case may be due to the lattice deformation resulting from the difference in the thermal expansion coefficients of GaN and Si [13]. The FWHMs of near-band edge emission peak are 34.49 for S2, 39.70 for S3 and 49.40 for S4. It is indicated that S2 sample grown with 20 periods of superlattice is the best optical property, which is compared with the best result achieved for GaN/Si, so far [14]. This reason is the effect that $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}$ layer of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice has as barrier in confining free carriers to the GaN-superlattice sublayer, which thereby may form a quasi-two-dimensional carrier gas if the wells are sufficiently small [15]. Also, this behavior of optical property shows a tendency similar to that of surface and crystal quality. Therefore, for applications of LED or other photonic device, it is primarily necessary to optimize the conditions of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice such as its total thickness and periods in the growth of GaN/Si(111) epitaxy.

4. Conclusions

In conclusion, we found that the optimized total thickness and periods of $\text{Al}_{0.3}\text{Ga}_{0.7}\text{N}/\text{GaN}$ superlattice play a very important role in the improvement of quality and reducing cracks for the growth of GaN/Si(111) epitaxy.

Acknowledgements

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