
CONTRIBUTED PAPERS

CHARACTERIZATION OF GROUP-III NITRIDE SEMICONDUCTORS BY X-RAY CTR SCATTERING AND REFLECTIVITY MEASUREMENTS

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Low-temperature deposited AlN layers on sapphire substrates that were treated with and without nitridation process were investigated by X-ray CTR scattering and X-ray reflectivity measurements. The results showed that 1) amorphous-like layers were formed on the sapphire substrates when the substrates were heated at 1,150EC in H₂, 2) 50-100 D thick amorphous-like AlN layers were formed on the sapphire substrates that were exposed to NH₃ for 10 min at 1,150EC (nitridation process), 3) when the temperature was lower than 800EC, the amorphouslike AlN layers were not formed on the substrates even when exposed to NH₃. Effects of nitridation process and AlN buffer layer (the low-temperature deposited amorphous-like AlN layer) on the quality of GaN and GaInN overlayers were described.

1. Introduction

Nobody, except for the two research groups in Japan (Prof. Akasaki and his group at Nagoya University and Dr. Nakamura and his group at Nichia Chemical Industries), expected that reliable and high brightness blue LEDs and even cw injection lasers can be realized with the crystals that contain high density defects. The crystal layers of GaN and GaInN were grown on a sapphire that has a different crystal structure from and a large lattice mismatch with the nitrides.

To realize the cw operation of the GaAs injection lasers at RT, very close lattice-matching, elimination of dislocations in the substrates, and very careful fabrication processes of the diodes were elaborated. This experience led people to search for the combinations of materials that are "lattice-matched and with no dislocations." Thus, majority of the researchers pursued the ZnSe/GaAs lattice-matched combinations as the right materials for blue/green lasers. However, the success of the GaN/GaInN LEDs and lasers on sapphire substrates with a low-temperature buffer layer has broken all the "common senses" and its impact on epitaxial crystal growers and device researchers was so strong. The success of GaN/GaInN LEDs and lasers on sapphire substrates is

really a break-through. If the technique of the low-temperature buffer layer is a universal one, then epitaxy is relieved from the constrain of lattice-matching.

It has been widely known that the low-temperature AlN or GaN buffer layer greatly improves the crystal quality, the surface flatness, the electrical and optical properties of GaN overlayers [1-3]. It is also known that nitridation of the sapphire surface to form AlN is effective to improve the quality of GaN layers [4]. However, very little is known on the structural properties of the buffer layer and the nitrided surface, and thus nothing is known for the initial stage, even though it determines the structure of the buffer layer and the nitrided layer.

We have been developing a technique that can evaluate the crystal structure, the thickness and the composition of a crystal layer of one monolayer (IML), even sub-monolayer. The technique is the X-ray crystal truncation rod scattering (X-ray CTR scattering) measurement using the synchrotron radiation as the X-ray source and has been applied for the study on the structures and the growth processes of the heterostructures [5-11]. The X-ray diffraction from a bulk crystal has a sharp intensity distribution in 3-dimension in reciprocal space. The intensity

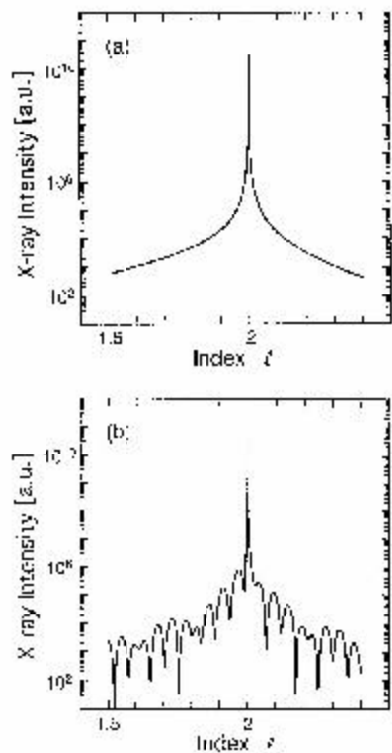


Fig. 1. Calculated spectra of X-ray CTR scattering from INP (002) (a) and from INP(10nm)/ Ga_{0.47}In_{0.53} As(10ML)/ InP (b). Due to heterostructure the tail portion of the spectrum (b) is largely modulated.

distribution of the diffraction from a crystal surface spreads, (looks like a rod in the reciprocal space), perpendicular to the surface due to the truncation of the periodicity of the crystal and is called as the X-ray CTR scattering [12-14]. Examples of the CTR scattering spectra are illustrated in Fig. 1 (a) and (b). Figure 1 (a) is the X-ray intensity distribution along (00x) of In P. It shows a sharp Bragg peak at $\chi=2$ and at the same time has widely spread tails on both sides. When the same measurement is done for the heterostructure of InP(10nm)/ Ga_{0.47}In_{0.53} As(10ML)/ InP substrate, the X-ray intensity distribution is largely modified in the tail part of the intensity distribution as illustrated in Fig. 1 (b). From the figure we can see that the spectrum is of information rich. Since the information rich part is 10^{-5} - 10^{-6} of the Bragg peak in intensity, a high intensity X-ray source such as the synchrotron radiation is necessary for the measurement.

The X-ray CTR scattering is useful for crystalline layer analysis since it is basically originated from the X-ray diffraction. The low-temperature AlN and GaN buffer layers are thought to be fine polycrystals or

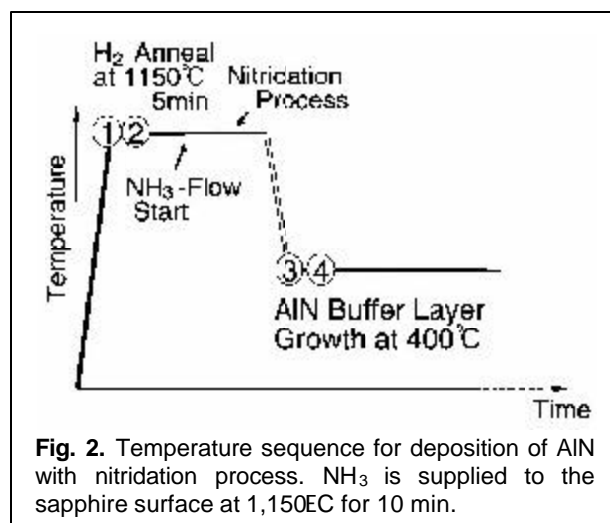


Fig. 2. Temperature sequence for deposition of AlN with nitridation process. NH₃ is supplied to the sapphire surface at 1,150EC for 10 min.

amorphous. To characterize them, the X-ray reflectivity measurement has been done. The reflectivity in the angle range from the total reflection to several degrees is modulated by the electron density and the layer thickness. The formula is established by Parratt *et al.* in 1950 and has been used as a non-destructive thickness measurements [15, 16]. Recently, by the X-ray reflectivity, the thickness of several nm is measured and the interface structure is evaluated [17-20].

In the present experiments, we prepared the sapphire substrates with and without the nitridation process and deposited the low-temperature AlN buffer layer, the GaN layer and the GaInN layer. The growth was stopped at each stage, samples were cooled down and used for the measurements. From the analysis of the X-ray CTR scattering spectra and the X-ray reflectivity spectra the structures, the thicknesses and the crystalline quality were evaluated and correlated with the growth processes.

2. Sample Preparation

The samples were grown by MOVPE (metal-organic vapor phase epitaxy). Figures 2 and 3 show the growth sequences. Figure 2 includes the nitridation process before deposition of the AlN buffer layer. Figure 3 skips the nitridation process by flowing NH₃ only after the substrate temperature is lower than 800EC. Those numbers 1, 2, 3, 4 ... on the temperature sequences are the stages where the process was stopped and the temperature was rapidly decreased.

The samples have the same numbers as in Figs. 2 and 3. The sample 1 was heated upto 1,150EC in H₂ and then quickly cooled down, and the sample 2 was kept for 5 min. The samples 3 and 4 go through the high temperature heat treatment in H₂ or NH₃,

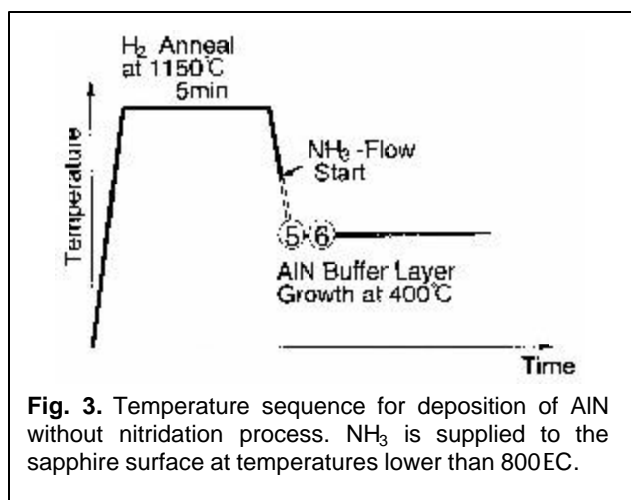


Fig. 3. Temperature sequence for deposition of AlN without nitridation process. NH_3 is supplied to the sapphire surface at temperatures lower than 800°C.

respectively and are cooled down just before the AlN deposition. The samples **N** and **O** have the low-temperature deposited AlN buffer layer with the thickness of 30 D (designed value).

GaN and GaInN layers were grown continuously after deposition of 300 D-thick AlN buffer layer.

3. Measurements

X-ray CTR scattering measurements were conducted at the beam line BL6A in the Photon Factory in Tsukuba using the Weissenberg camera (R-AXIS-RAPID, Rigaku) and the imaging plate (IP) as the 2-dimensional detector. The camera length was fixed at 286.5 mm and the wavelength of the X-ray at 1.600 D. The angle ω of the sample was scanned in the range between 2 E higher and 8 E lower than the (0006) Bragg point of sapphire.

The X-ray reflectivity measurements in the low glancing angle was conducted using the conventional X-ray generator and diffractometer (RUH-450, Rigaku). The target was Cu operated at 35 kV with 330 mA. The Cu $K_{\alpha 1}$ ($\lambda=1.54056$ D) line was chosen using Si(111) monochromator. The receiving slit was 0.05 mm.

4. Results and Analysis

The process for the analysis of the measured data is basically the same for the CTR scattering and for the reflectivity. 1) A model for the layer structure is constructed. 2) The X-ray CTR scattering spectrum or the reflectivity spectrum is generated by a computer simulation from the model. 3) By changing those parameters in the model structure the generated spectra and the measured data are compared. 4) At the best fit, the set of parameters are considered to give the most probable structure of the layer.

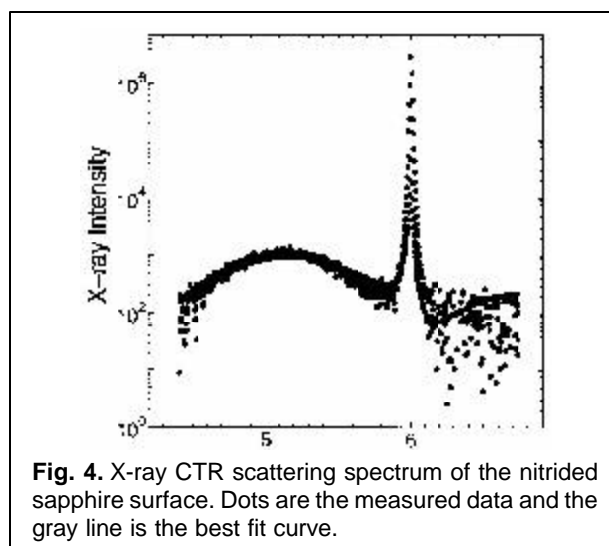


Fig. 4. X-ray CTR scattering spectrum of the nitrided sapphire surface. Dots are the measured data and the gray line is the best fit curve.

In the CTR scattering, the atom arrangements in each layer are the primary information to be obtained. In the reflectivity, the electron density in each layer is the primary information to be obtained. Therefore, good crystalline part of the layer is detected by the CTR scattering, and all of the crystalline, polycrystalline and amorphous part are detected by the reflectivity measurements.

4.1. X-ray CTR scattering

The samples **I** and **J** showed no specific features in the X-ray CTR scattering spectra, i.e., those were the same as the spectrum of the sapphire substrate.

On the other hand, the sample **D** had a clear bump in the lower angle side of the sapphire peak as shown in Fig. 4. In the figure dots are the measured data and the gray line is the best fit curve. Since the sample **D** was the nitrided sapphire in the NH_3 atmosphere, the surface of the sapphire (Al_2O_3) is considered to be converted to AlN. For the analysis by curve fitting, several possible model structures were assumed; Al in AlN is bonded to Al or O in sapphire, or N in AlN is bonded to Al or O in sapphire, the polarity of AlN is [0001]A or [0001]B, the top surface of AlN is covered by Al or N, the thickness of AlN, the roughness of AlN surface, the lattice distortion of AlN, and so on.

The results of the analysis are illustrated in Fig 5. The thickness of the AlN layer was 3ML (7.47 D), the polarity was [0001]A, and the top surface of AlN was mostly covered by N.

In the other samples **N-O**, the spectra were not clear and good fitting was not obtained. We considered that amorphous-like AlN containing fine

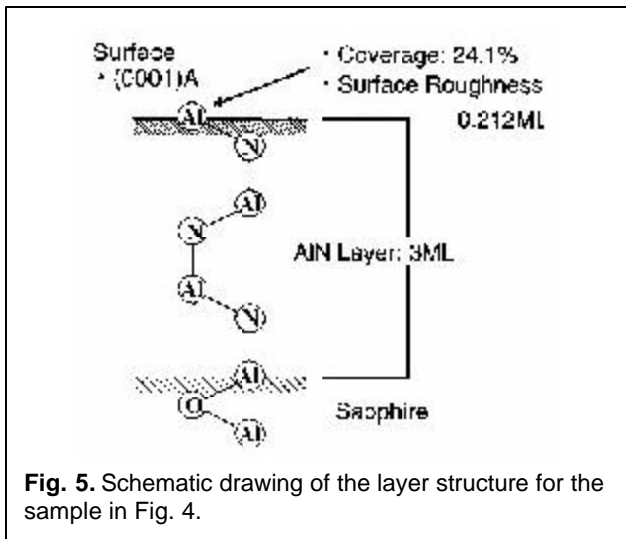


Fig. 5. Schematic drawing of the layer structure for the sample in Fig. 4.

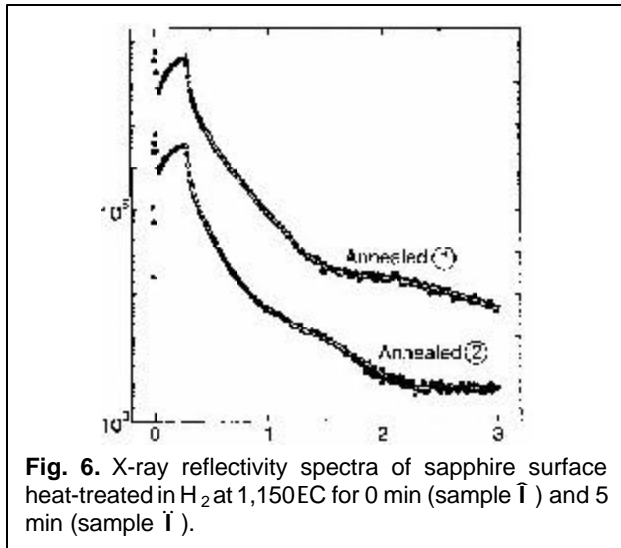


Fig. 6. X-ray reflectivity spectra of sapphire surface heat-treated in H_2 at 1,150EC for 0 min (sample \hat{I}) and 5 min (sample \check{I}).

polycrystals was deposited and it did not give a clear peak in the spectra.

4.2 X-ray Reflectivity

The measured data are shown in Figs. 6-8. The dots are the measured data and the gray lines are the best fit curves.

In the model layer structure, three different layers were assumed to exist on the sapphire substrate. The top surface layer is that formed by adsorption in the air. The bottom layer is that formed by the heat treatment in H_2 or in NH_3 (nitridation before deposition of the AlN buffer layer. Between them is the AlN layer deposited at the low temperature. The Fresnel equations were used for the X-ray reflectivity and calculated using the technique developed by Parratt *et al.* [15,16]. In Table 1 the results of

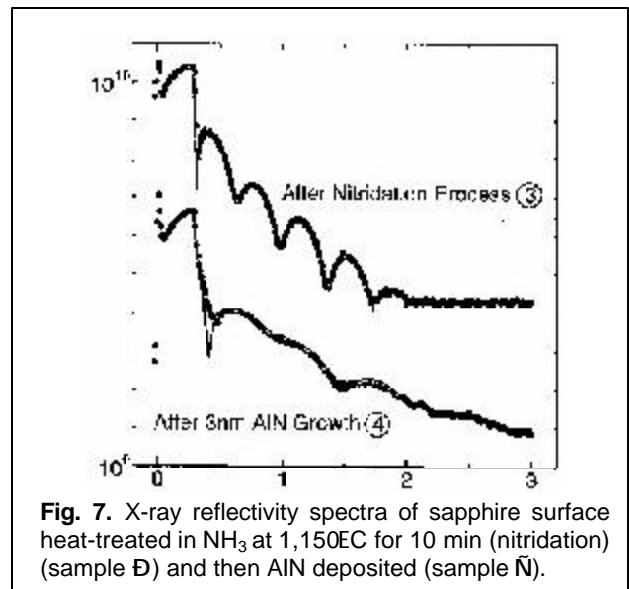


Fig. 7. X-ray reflectivity spectra of sapphire surface heat-treated in NH_3 at 1,150EC for 10 min (nitridation) (sample \hat{D}) and then AlN deposited (sample \check{N}).

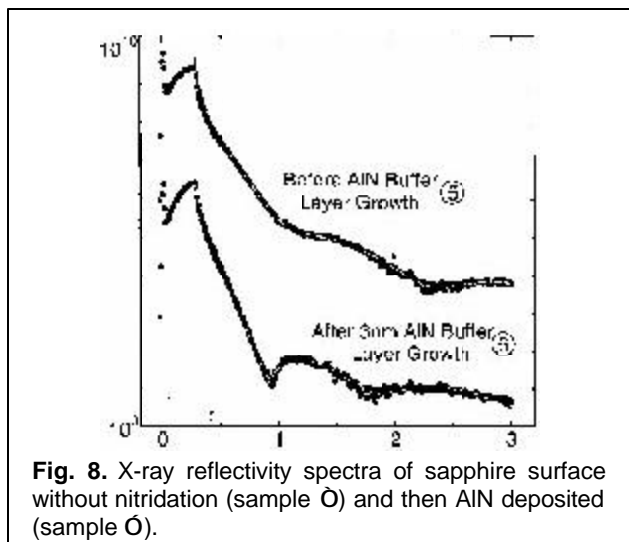


Fig. 8. X-ray reflectivity spectra of sapphire surface without nitridation (sample \hat{O}) and then AlN deposited (sample \check{O}).

parameters obtained from the best fit curves in Figs. 6-8 are listed.

The samples \hat{I} and \check{I} are the sapphire heat-treated in H_2 at 1,150EC for 0 min and 5 min, respectively. The slight modulation in the reflectivity spectra indicates that there is a layer (or layers) on top of the sapphire. From the Table 1, a very thin layer with the density about 3 gcm^{-3} is formed. Comparing the density with those of sapphire (4), crystal AlN (3.26) and metal Al (2.7), we considered that this layer is Al formed by the desorption of O from the sapphire surface and/or AlN (or AlO_xN_y) formed by reaction with residual NH_3 in the reaction chamber. The X-ray CTR scattering spectra of the samples \hat{I} and \check{I} were the same as that of sapphire substrate as supplied from a vender. It means that the layer found out in the samples \hat{I} and \check{I} are amorphous-like or fine poly-

Table 1. Parameters obtained by the analysis of X-ray reflectivity spectra.

Sample No.		1	2	3	4	5	6
1st layer (top surface)	Density (g/cm ³)	0.98	0.70	0.97	1.19	0.98	1.19
	Thickness	7.1	20.1	11.9	12.0	17.9	12.8
2nd layer	Density (g/cm ³)	-	-	-	2.95	-	3.06
	Thickness	-	-	-	4.5	-	6.4
3rd layer	Density (g/cm ³)	2.97	2.64	3.04	3.04	2.63	2.34
	Thickness	13.7	10.2	113.0	42.0	10.1	11.3

crystals. The top layers in all the samples are not discussed here, but though to be adsorbed water vapor in the air.

In Fig. 7, the number of oscillatory structure is more and clear. It indicates that a thicker layer is formed by the nitridation process and the deposition of AlN. In Fig. 8, the number of the oscillatory structure is less.

When the sample **D** (with nitridation process) and the sample **O** (without nitridation process) are compared, the largest difference is the thickness of the third layers. In the sample **D** it is as thick as about 100 D. From the preparation process and the density this layer is understood to be AlN formed by the nitridation process. As was shown in Fig. 4, the thickness of the crystalline AlN layer obtained by the X-ray CTR scattering was only 3 ML. Considering both results, a good crystalline thin (3 ML) AlN layer is generated at the beginning of the nitridation process and after that amorphous-like layer is formed. The layer structure of the sample **O** is almost the same as that of sample **I**. It means that the sapphire surface is not affected by the supply of NH₃ at temperatures lower than 800EC.

By the deposition of AlN at 400EC, very thin AlN layers of only several A are deposited, as shown in Table 1 (samples **N** and **O**), though the thickness was designed to be 30 D. The reason for this is not known, but we consider that for the initial short period of the AlN deposition process, the supply of source gases may not reach to the expected flow rates.

In the comparison of the samples **D** and **N** the difference of the AlN thickness formed by the nitridation process is large. This result may also indicate that the nitridation process is not very controllable, due to

fluctuation of the supply of NH₃ or due to surface conditions of sapphire.

5. Summary

By X-ray CTR scattering and X-ray reflectivity measurements, the layer structures, both crystalline and non-crystalline, after heat-treatment of sapphire surface in H₂ or in NH₃ (nitridation) at 1,150EC and after deposition of AlN layers at 400EC were analyzed.

From the X-ray CTR scattering, a good crystalline AlN thin layer (3 ML) with the polarity of [0001]A is formed by the nitridation process of the sapphire surface. In the other samples, good fitting to the spectra were not obtained. This may be due to fine polycrystalline layers or amorphous-like layers that do not contribute to the CTR signals.

Considering the results both of the X-ray CTR scattering and reflectivity, followings were revealed. 1) An amorphous-like layer is formed on the sapphire surface by the heat-treatment in H₂ at 1,150EC for several minutes. 2) An amorphous-like layer of the thickness of 50-100 D is formed on the sapphire surface by the heat treatment in NH₃ at 1,150EC for 10min. 3) The sapphire surface is not affected by NH₃ at temperatures lower than 800EC.

Though it was not described in the text, the effects of those different processes for the deposition of AlN buffer layers on the final structure of GaInN/GaN that are used for most device applications were examined. The X-ray CTR scattering spectra for GaInN(40 D)/GaN(2μm)/ AlN buffer/sapphire with (Fig. 9) and without (Fig. 10) the nitridation process. In Fig. 9, a clear AlN peak is observed. This means that more crystalline AlN is formed due to already existed crystalline AlN generated by the nitridation process, probably during the heating process before growth of GaN at 1,100EC. More crystalline AlN results in a simple shape of the X-ray CTR scattering spectrum of the GaInN/GaN layer. The difference is very clear when compared with the spectrum in Fig. 10. The modulation in the spectrum in Fig. 10 is due to the thickness fringe of the flat GaInN layer. The peak from AlN is not observed. Thus, without the nitridation process, the low-temperature deposited AlN layer remained as amorphous-like layer even after the heating process to start growth of and during growth of GaN, and this amorphous-like AlN caused growth of a flat GaN layer and then a flat GaInN layer.

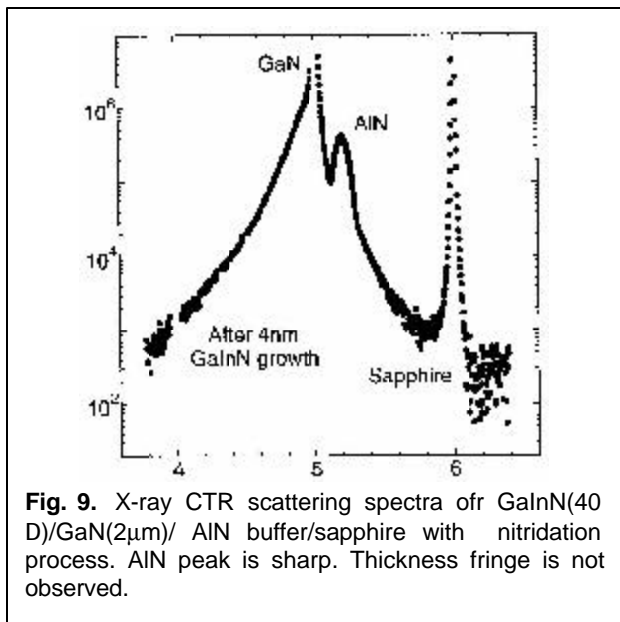


Fig. 9. X-ray CTR scattering spectra of GaInN(40 D)/GaN(2 μ m)/ AlN buffer/sapphire with nitridation process. AlN peak is sharp. Thickness fringe is not observed.

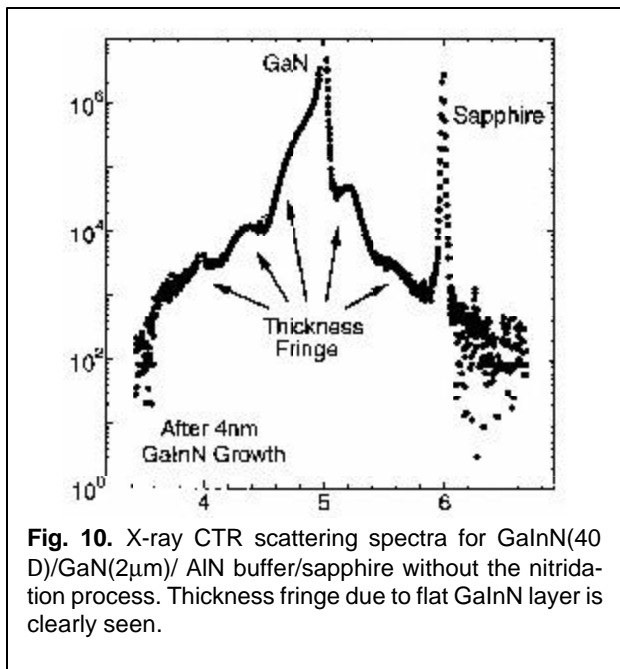


Fig. 10. X-ray CTR scattering spectra for GaInN(40 D)/GaN(2 μ m)/ AlN buffer/sapphire without the nitridation process. Thickness fringe due to flat GaInN layer is clearly seen.

Acknowledgments

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