実験番号：2504053

低次元窒化物系半導体ヘテロ構造の原子レベル急峻性評価

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1. 測定実施日

25 年 11 月 21 日 9 時 – 18 時 00 分（2 シフト），BL8S1
25 年 11 月 29 日 9 時 – 18 時 00 分（2 シフト），BL8S1
25 年 12 月 11 日 9 時 – 18 時 00 分（2 シフト），BL8S1
26 年 02 月 25 日 9 時 – 18 時 00 分（2 シフト），BL8S1
26 年 02 月 26 日 9 時 – 18 時 00 分（2 シフト），BL8S1
26 年 03 月 11 日 9 時 – 18 時 00 分（2 シフト），BL8S1

2. 概要

Atomic-level control is becoming increasingly important for the realization of ultimate-performance and highest efficiency InGaN-based light emitting diodes (LEDs). An *in situ* atomic level surface monitoring tool such as reflection high-energy electron diffraction (RHEED) is effective for observing the atomic arrangement of a surface during growth. Unfortunately, however, RHEED cannot be applied to the *in situ* monitoring of the metalorganic vapor phase epitaxy (MOVPE) process because a high-vacuum condition is necessary. There are several *in situ* monitoring tools suitable for use during the MOVPE process using light such as interference monitoring and spectroscopic ellipsometry. In the case of interference monitoring, although we can estimate the surface thickness, roughness by monitoring the oscillation and its amplitude, the resolution is limited to close to the wavelength of the light used. In the case of spectroscopic ellipsometry, *real-time* monitoring is difficult because of the limited speed of the measurement. Furthermore, the interface and any changes underneath the surface are not traceable by these techniques. Therefore, *in situ* X-ray measurement techniques are expected to be applied for further analyzing and understanding the growth processes of the heterostructures, such as surface and interface roughness, strain relaxation, defects, and indium distributions and fluctuations and so on.

3. 背景と研究目的

We have conducted an atomic scale investigation on semiconductor interface structures using X-ray CTR scattering measurement. Demonstration of X-ray CTR scattering measurement and analysis at room temperature was from the sample measured using synchrotron radiation at the Photon Factory in the High Energy Accelerator Research Organization at Tsukuba, Japan. Information on the grown layers can be deduced from the curve fitting to the X-ray CTR scattering spectra. The fitting results were almost the same as the designed values. In a word, the X-ray CTR scattering measurement can reveal interface roughness, compositional distributions, and layer thicknesses, quantitatively and non-destructively. In order to realize *in-situ* X-ray CTR measurements, an MOVPE growth system for GaN and related semiconductors was installed in the

laboratory level X-ray measurement system. A more detailed description of the system can be found in references [1-3]. XRR is also a non-destructive technique used for evaluation of film thickness, density, and surface and interface roughness of thin film layer structures. This technique is also important for *in-situ* X-ray measurements at growth temperatures since it can be used for amorphous, crystalline, and liquid samples. We used XRR to investigate the wetting layer of liquid indium on GaN substrate [4]. Until now, we have demonstrated that it was possible to conduct *in-situ* XRD measurement, *in-situ* X-ray CTR scattering measurement, and *in-situ* XRR measurement under the growth ambient at the growth temperatures [5].

We propose new tools for *in situ* monitoring of the MOVPE growth process at the atomic level. The tool is grazing angle X-ray reflectivity measurement, for which atomic-level resolution is obtained because of the short wavelength of X-rays [6]. In addition, X-ray reflectivity is also sensitive to the density of valence electrons in each atom; therefore we can *in situ* measure the atomic-level surface roughness and heterostructure interface in real time. We observed two critical points at which the X-ray intensity corresponds to the roughness change. The first critical point shows the roughening without lattice relaxation, and the second point indicates the lattice relaxation caused by the generation of defects. Therefore, the purpose of this research is to demonstrate which point is the critical thickness of the strain relaxation. Since the thickness of InGaN is very thin (about 10 nm) on the GaN template, the lab-based X-ray is difficult to get the good spectra of the in-plane measurement due to the strange background noise. The synchrotron radiation is a powerful tool to know the strain relaxation of our samples.

4. 実験内容

InGaN epilayers were grown on c-plane GaN templates using the *in situ* MOVPE system at 150 Torr. The templates were MOVPE-grown (0001) hexagonal GaN (2 μm thick) epilayers on sapphire (0001). The full width at half maximum of the rocking curve of these templates was about 285 acrsec at the 0002 Bragg peak. The MOVPE precursors used were trimethylindium (TMIn), trimethylgallium (TMGa), and ammonia (NH_3) with nitrogen carrier gases. For InGaN growth at 830 ^{o}C, the fluxes of TMIn and TMGa were 0.043 and 0.19 μmol/min, respectively. The total V/III ratio was about 800,000.

Synchrotron Radiation (SR) at the beam line BL8S1 was used to *ex situ* confirm the strain relaxation of the thick $In_{0.11}Ga_{0.89}N$ grown on GaN template in the **Aichi Synchrotron Radiation Center, Aichi Pref. Japan.** The wavelength of the X-ray was set at 1.35326 Å. NaI scintillator detector whose ability is over 700,000 cps was used to collect the X-ray data. Symmetric and asymmetric 2theta-omega scans were along [0001] and [10-15] crystal direction around the GaN (10-15) diffraction peak. The angular resolution is 0.0021. The incident slit was 0.4mm×0.8 mm. Since there were two receiving slits 0.5 mm in height and two solar slits 0.541° between detector and sample, the intensity of the background diffuse scattering was effectively removed. The indium composition of the obtained InGaN epilayers was determined by X-ray CTR scattering measurements for the fully strained single quantum well (SQW) structure.

5. 結果および考察

a. The indium composition of the obtained InGaN epilayers was determined by X-ray CTR scattering measurements for the fully strained single quantum well (SQW) structure using *ex situ* synchrotron radiation. The CTR simulation results are shown in Fig. 1. The detailed description is shown in Ref. 7

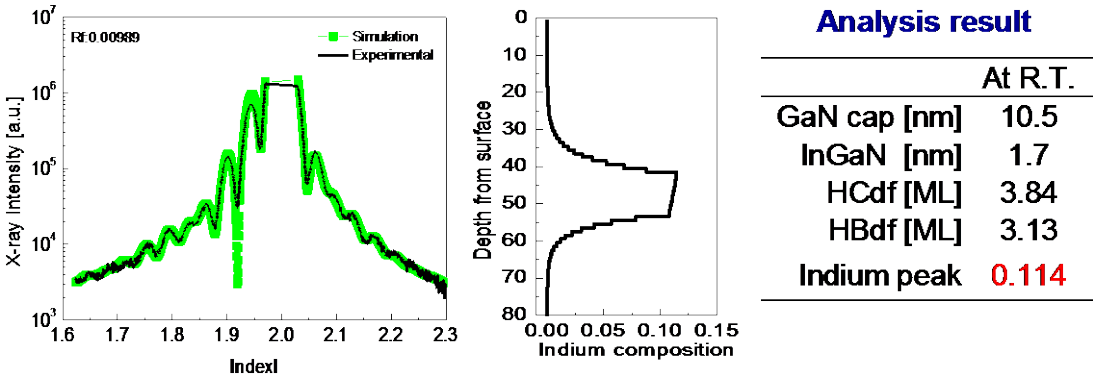

Fig. 1 The results of X-ray CTR scattering spectra measured using SR with well fitted curves and the indium composition profiles with analysis results.

b. Using *in situ* MOVPE system located in Akasaki Researcher Center, the reflected X-ray intensity was measured as a function of the growth time shown in Fig. 2. The total growth time changes in the film thickness d_2 and surface roughness of the InGaN layer calculated by the Parratt32 program, assuming the strained InGaN epilayer, is shown by the solid line. Because the experimental curve is well fitted by the calculated one, the surface roughening as a function of the growth time can be obtained from the calculation, as shown in Fig. 2 using the narrower solid line.

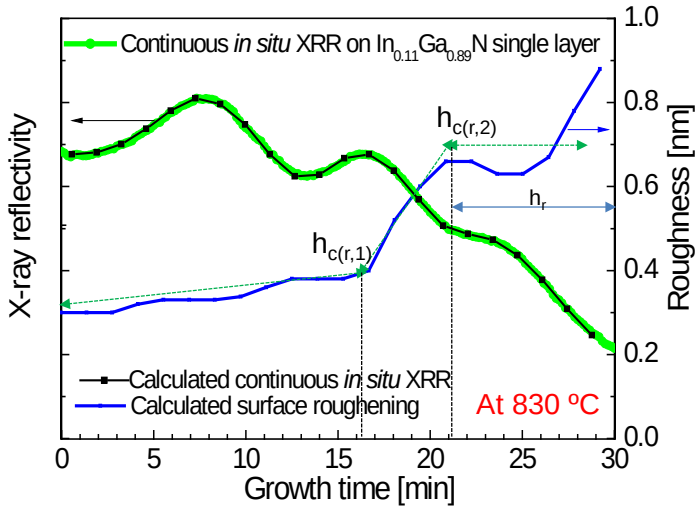

Fig. 2. Surface roughening of the thick $In_{0.11}Ga_{0.89}N$ grown on GaN template as a function of the growth time, as derived from the fitted experimental *in situ* XRR curve, assuming a strained $In_{0.11}Ga_{0.89}N$ epilayer.

This curve clearly shows two inflection points, which are the $In_{0.11}Ga_{0.89}N$ epilayer thickness (the growth time multiplied by the growth rate) $h_c(r,1)$ and $h_c(r,2)$. In order to figure out the growth process of $In_{0.11}Ga_{0.89}N$ epilayer shown in Fig. 2, the grown sample was *ex situ* measured by the BL8S1 of synchrotron radiation center around GaN (10-15) reflection along [0001] and [10-15] directions for symmetric and asymmetric 2theta-omega scans, respectively, as shown in Fig. 3. The conventional reciprocal space mapping by schematic diagrams is shown in the right side of Fig. 3. Fig. 3(a) shows the symmetric $2\theta/\omega$ scan along [0001] direction. The observed peaks are GaN (10-15) and fully strained InGaN. As expected, the fully relaxed InGaN peak is also observed in the asymmetric $2\theta/\omega$ scan along [10-15] direction, as shown in Fig. 3(b). It demonstrates that the strain relaxation occurred as the InGaN thickness increased. In another word, the thickness of InGaN epilayer exceeded the critical thickness. Moreover, the result also shows that the region closer to the GaN/InGaN interface is nearly pseudomorphic to the GaN template, whereas the surface region is

fully relaxed. Based on Vegard's law and Hooke's law in detail, and interplanar crystal spacing equation, the indium composition of the fully strained InGaN is 0.114, and the fully relaxed InGaN is 0.135. For the fully strained $In_{0.114}Ga_{0.886}N$ epilayer, the indium content is in very good agreement with X-ray CTR scattering measurement results for the fully strained SQW structure with the same growth condition. However, for the surface region, the indium fraction *x* increases as the film relaxed. This point has been reported by S. Pereira et al. [8]. Since the X-ray intensities of InGaN diffraction peaks may vary strongly with their thicknesses. The fully strained InGaN peak intensity is 2.3 times higher than the fully relaxed InGaN peak intensity based on Fig. 3(a) and (b). Assuming the constant growth rate, the thickness $h_c(r,2)$ of the $In_{0.11}Ga_{0.89}N$ epilayer in Fig. 2 was 14.8 ± 0.4 nm, calculated by multiplying the growth time of 21.2 ± 0.3 min b the growth rate of 0.70 ± 0.02 nm/min. The thickness h_r is about 6.3 nm, which is from $h_c(r,2)$ to the top surface of InGaN epilayer. So the thickness $h_c(r,2)$ is about 2.34 times thicker than the thickness h_r. The thickness ratio is in good agreement with the above-mentioned X-ray peak intensity ratio. Therefore, the thickness $h_c(r,2)$ seems to be the critical thickness of $In_{0.11}Ga_{0.89}N$ epilayer. In Fig. 2, when the thickness of the $In_{0.11}Ga_{0.89}N$ epilayer was below the thickness $h_c(r,1)$, the surface roughness changed very slowly. As the thickness of the growing epilayer increased and neared the critical thickness $h_c(r,2)$, slightly increased surface roughening took place at its surface. The roughening rate was about 0.07 nm/min. After the inflection point of $h_c(r,2)$, the roughness was firstly decreased and then largely increased. It might be impossible. So the roughness curve might not reflect the true changing of roughness, since the fully strained InGaN on GaN model was used to analyze the experimental in situ XRR curve. This phenomenon also demonstrates that the inflection point at $h_c(r,2)$ was caused by strain relaxation.

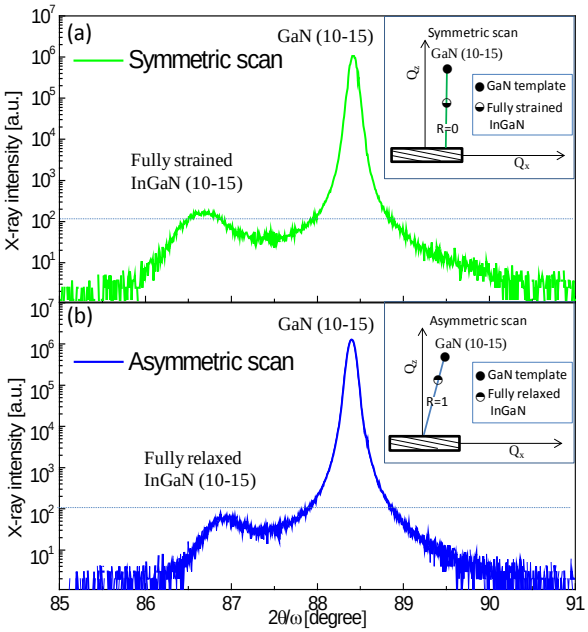

Fig. 3 2θ/ω scans around the GaN (10-15) diffraction peaks for the thick $In_{0.11}Ga_{0.89}N$ grown on GaN template. (a) Symmetric scan along [0001] direction for the fully strained InGaN. (b) Asymmetric scan along [10-15] direction for the fully relaxed InGaN. Schematic diagrams in the right of figures illustrating the effect of strain in the symmetric and asymmetric scan of InGaN.

6. 今後の課題

The investigation of AlGaN grown on GaN using *real-time* X-ray reflectivity is conducted during growth for strain relaxation, Al distribution at the interface, and so

on.

7. 参考文献

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