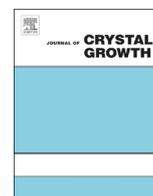




ELSEVIER

Contents lists available at ScienceDirect

## Journal of Crystal Growth

journal homepage: [www.elsevier.com/locate/jcrysgro](http://www.elsevier.com/locate/jcrysgro)

# Growth temperature dependent critical thickness for phase separation in thick ( $\sim 1 \mu\text{m}$ ) $\text{In}_x\text{Ga}_{1-x}\text{N}$ ( $x=0.2-0.4$ )



A. Yamamoto<sup>a,b,\*</sup>, Tanvir Md Hasan<sup>a,b</sup>, K. Kodama<sup>a</sup>, N. Shigekawa<sup>c</sup>, M. Kuzuhara<sup>a</sup>

<sup>a</sup> University of Fukui, 3-9-1 Bunkyo, Fukui, Fukui 910-8507, Japan

<sup>b</sup> JST-CREST, 7 Goban-Cho, Chiyoda, Tokyo 102-0076, Japan

<sup>c</sup> Osaka City University, 3-3-138 Sugimoto, Abeno, Osaka 558-8585, Japan

## ARTICLE INFO

## Article history:

Received 11 September 2014

Received in revised form

16 January 2015

Accepted 27 February 2015

Communicated by A. Bhattacharya

Available online 10 March 2015

## Keywords:

A1. Phase separation

A3. Metalorganic vapor phase epitaxy

B2. Nitrides

## ABSTRACT

This paper reports phase separation in thick ( $\sim 1 \mu\text{m}$ ) MOVPE  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $x=0.2-0.4$ ) films grown by MOVPE at 570–750 °C on  $\text{AlN}/\text{Si}(111)$ ,  $\alpha\text{-Al}_2\text{O}_3(0001)$  and  $\text{GaN}/\alpha\text{-Al}_2\text{O}_3(0001)$  substrates. Phase separation occurs when  $\text{InGaN}$  thickness exceeds a critical value. Critical thickness for phase separation is markedly increased with decreasing growth temperature. It is around  $0.2 \mu\text{m}$  for a film grown at 750 °C, while it is more than  $1 \mu\text{m}$  for that grown at 570 °C. No substrate dependencies are found in critical thickness. The cross-sectional SEM views of phase-separated films grown at 650 °C show that phase separation is initiated at parts far more than  $0.2 \mu\text{m}$  from the substrate and extended to the area near the substrate. SIMS analysis shows a possibility that phase separation is initiated at a part with relatively large  $\text{In}/\text{Ga}$  ratio fluctuations in  $\text{InGaN}$  films.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

Direct-band-gap  $\text{InGaN}$  alloys have proven to be important materials because of their unique property of wide spectral tunability, which can be adjusted continuously from the ultraviolet to infrared region. This tunability offers many possibilities in a variety of device applications, including high-brightness visible light emitting diodes, lasers, and full-spectrum multi-junction solar cells. In the growth of  $\text{InGaN}$  alloys, phase separation is the most serious problem. For the development of a variety of  $\text{InGaN}$ -based device technologies, this phenomenon should be thoroughly understood and, then, growth conditions should be optimized to avoid this problem if possible. For bulk  $\text{InGaN}$  and thin  $\text{InGaN}$  well layer in  $\text{InGaN}/\text{GaN}$  quantum structures, there have been many reports on phase separation and/or thermal decomposition of  $\text{InGaN}$  during growth and subsequent thermal processes. Ho and Stringfellow [1] have theoretically showed that the large difference in interatomic spacing between  $\text{GaN}$  and  $\text{InN}$  gives rise to a solid phase miscibility gap. They also predicted that spinodal decomposition should result in the simultaneous formation of  $\text{InN}$ -rich  $\text{InGaN}$  and  $\text{GaN}$ -rich  $\text{InGaN}$ . However, such simultaneous formation of the two phases has not been so clearly observed. Very recently, by employing  $\text{AlN}/\text{Si}$  substrate and appropriate growth conditions of epitaxial  $\text{InGaN}$ , such as growth temperature and  $\text{InN}$  composition, we have clearly observed the simultaneous emergence of  $\text{InN}$ -rich  $\text{In}_{1-y}\text{Ga}_y\text{N}$  ( $y \sim 0.03$ ) and  $\text{GaN}$ -rich  $\text{In}_z\text{Ga}_{1-z}\text{N}$

( $z \sim 0.03$ ) as a result of phase separation of bulk  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $x \sim 0.3$ ) at 650 °C [2]. Such an emergence of the both phases was found to occur when  $\text{InGaN}$  thickness exceeded a critical value. This fact suggests that the development of bulk  $\text{InGaN}$  devices is seriously influenced by this problem because the growth of thick  $\text{InGaN}$  films is a key step to the bulk  $\text{InGaN}$  device fabrication. For example, we need a thick  $\text{InGaN}$  to make a p-i-n structure in the fabrication of homojunction  $\text{InGaN}$  solar cell [3]. Also, the growth of thick  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $x \sim 0.45$ ) on  $\text{AlN}/\text{Si}$  substrate is the first step to the fabrication of an  $\text{InGaN}/\text{Si}$  2-junction tandem solar cell [4]. In this paper, we have studied phase separation in MOVPE  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $x=0.2-0.4$ ) grown at 550–750 °C. It is found that critical thickness for phase separation is markedly dependent on growth temperature and, by reducing growth temperature to around 570 °C, an  $\text{InGaN}$  film with a thickness more than  $1 \mu\text{m}$  can be grown without phase separation. Based on the characterization with cross-sectional SEM, RSM and SIMS, initiation mechanism of phase separation is also discussed in this paper.

## 2. Experimental

The growth of  $\text{InGaN}$  alloys was made using a MOVPE system with a horizontal reactor.  $\text{Si}(111)$  wafers with a layer of separately MOVPE-grown  $\text{AlN}$  (100 nm thick) were used as substrates.  $\alpha\text{-Al}_2\text{O}_3(0001)$  and  $\text{GaN}/\alpha\text{-Al}_2\text{O}_3(0001)$  were also used as substrates for comparison.  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloys ( $x=0.2-0.4$ ) were grown directly on the substrates. Triethylgallium (TEG), trimethylindium (TMI), and ammonia ( $\text{NH}_3$ ) were used for Ga, In, and N sources,

\* Corresponding author.

respectively, and TMI/(TMI+TEG) molar ratio in the vapor was kept at 0.4 in this study. Growth temperature was varied from 550 to 750 °C, while growth pressure was fixed at 150 Torr. Growth rate of InGaN was about 0.2–0.7 μm/h depending on growth temperature, and InGaN films with a thickness of 0.2–2 μm were prepared. The structures of the films were characterized by high resolution X-ray diffraction (HRXRD), and field emission scanning electron microscopy (FESEM). By using the HRXRD, composition and reciprocal space mapping (RSM) for InGaN were also obtained. Depth profiles of In and Ga atoms in InGaN films were measured with the secondary ion-mass spectrometer (SIMS) (outsourced to Toray Research Center, Inc., Japan).

### 3. Results and discussion

Fig. 1 shows the X-ray diffraction  $2\theta/\omega$  profiles for epitaxial  $\text{In}_x\text{Ga}_{1-x}\text{N}$  films grown on AlN/Si substrates at a temperature between 570 and 700 °C. All films were prepared with a growth time of 90 min and with a constant TMI/(TMI+TEG) molar ratio of 0.4. With increasing growth temperature, both growth rate and InN composition for the grown films were decreased. The reduction of InN composition is mainly due to the evaporation of In from the growing surface. On the other hand, the reduction of growth rate with increasing growth temperature seems to be brought by the increased consumption of the source materials (TMI and TEG) at the upstream side of the susceptor. This is because the substrates were placed at the center of the 20 cm-long susceptor in the horizontal reactor. All the films shown in Fig. 1, except for that grown at 570 °C, are judged to be phase separated due to the following reason. As reported previously [2], InN-rich  $\text{In}_{1-y}\text{Ga}_y\text{N}$  ( $y \sim 0.03$ ) and GaN-rich  $\text{In}_z\text{Ga}_{1-z}\text{N}$  ( $z \sim 0.03$ ) emerges as a result of phase separation of epitaxial  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $x \sim 0.30$ ). However, phase-separated samples usually show a metallic  $\text{In}_{1-y}\text{Ga}_y$  ( $y \sim 0.03$ ) and GaN-rich  $\text{In}_z\text{Ga}_{1-z}\text{N}$  ( $z \sim 0.03$ ) peaks. This is because the InN-rich  $\text{In}_{1-y}\text{Ga}_y\text{N}$  ( $y \sim 0.03$ ) is unstable and easily decomposed into metallic In containing about 3 at% of Ga

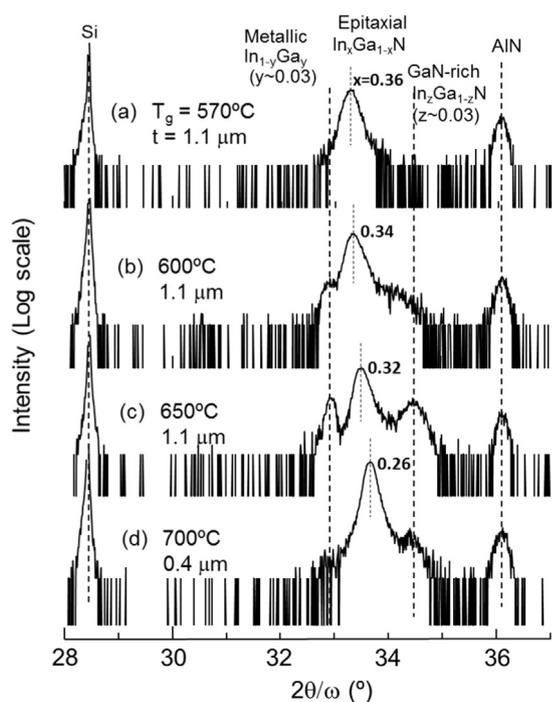


Fig. 1. X-ray diffraction  $2\theta/\omega$  profiles for epitaxial  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $x=0.26\text{--}0.35$ ) films grown on AlN/Si substrates with a constant TMI/(TMI+TEG) molar ratio 0.4. Growth time is 90 min for all samples.

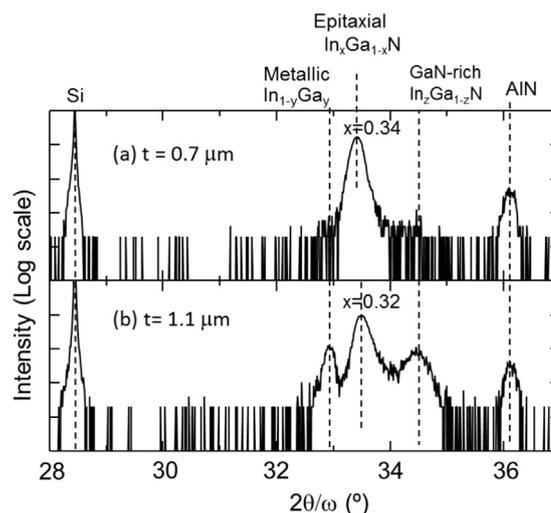


Fig. 2. X-ray diffraction  $2\theta/\omega$  profiles for epitaxial  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $x \sim 0.35$ ) films with a different thickness grown at 650 °C.

( $\text{In}_{1-y}\text{Ga}_y$ ,  $y \sim 0.03$ ). Occasionally, a weak peak of the InN-rich  $\text{In}_{1-y}\text{Ga}_y\text{N}$  ( $y \sim 0.03$ ) is observed in grown samples [2], although it is not found in Fig. 1. For the film grown at 700 °C, the peak of the metallic  $\text{In}_{1-y}\text{Ga}_y$  ( $y \sim 0.03$ ) is scarcely seen, while the peak of GaN-rich  $\text{In}_z\text{Ga}_{1-z}\text{N}$  ( $z \sim 0.03$ ) is clearly observed. This is due to the evaporation of metallic In from the growing surface due to the high growth temperature (700 °C). The results in Fig. 1 show that the film grown at 650 °C has the most severely phase-separated situation since the intensity of the GaN-rich  $\text{In}_z\text{Ga}_{1-z}\text{N}$  is the highest. As described above, we can define a phase separated sample to have the GaN-rich  $\text{In}_z\text{Ga}_{1-z}\text{N}$  peak, at least, in addition to the epitaxial  $\text{In}_x\text{Ga}_{1-x}\text{N}$  peak. One should pay attention to that the detection of phase separation by X-ray diffraction  $2\theta/\omega$  profile is difficult for samples grown on GaN templates or GaN substrates at relatively high temperatures ( $\geq 700$  °C), because the GaN-rich  $\text{In}_z\text{Ga}_{1-z}\text{N}$  peak is very close to that for GaN. Fig. 2 shows the X-ray diffraction  $2\theta/\omega$  profiles for epitaxial  $\text{In}_x\text{Ga}_{1-x}\text{N}$  films with a different thickness grown at 650 °C on AlN/Si substrates. The film with a thickness of 0.7 μm (Fig. 2(a)) shows no phase separation, while that with a thickness of 1.1 μm (Fig. 2(b)) shows phase separation. In spite of the same growth conditions for both samples in Fig. 2, except for growth time, the epitaxial  $\text{In}_x\text{Ga}_{1-x}\text{N}$  in the sample (b) has a lower InN content compared with the sample (a) with a shorter growth time. This indicates that parts with a higher InN composition in the epitaxial  $\text{In}_x\text{Ga}_{1-x}\text{N}$  are preferentially consumed to form the metallic  $\text{In}_{1-y}\text{Ga}_y$  ( $y \sim 0.03$ ) and the GaN-rich  $\text{In}_z\text{Ga}_{1-z}\text{N}$  ( $z \sim 0.03$ ), as reported previously [2]. Fig. 3 shows X-ray diffraction  $2\theta/\omega$  profiles for epitaxial  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $x \sim 0.30$ ) films grown at 700 °C on  $\alpha\text{-Al}_2\text{O}_3$  and AlN/Si substrates. In this case, a film with a thickness as small as 0.4 μm shows phase separation. As pointed out above, the peak of  $\text{In}_{1-y}\text{Ga}_y$  ( $y \sim 0.03$ ) is scarcely observed in this case. Note that no marked differences are found in the emergence of phase separation between AlN/Si and  $\alpha\text{-Al}_2\text{O}_3$  substrates.

In order to know the general trend of the emergence of phase separation, InGaN films with and without phase separation are plotted in Fig. 4 on the plane of film thickness and growth temperature. The dotted line in Fig. 4, which is drawn between samples with and without phase separation, shows critical thicknesses for phase separation at different growth temperatures. One can see that critical thickness is markedly decreased with increasing growth temperature. No marked differences are found in critical thicknesses between AlN/Si(111) and  $\alpha\text{-Al}_2\text{O}_3(0001)$ , GaN/ $\alpha\text{-Al}_2\text{O}_3(0001)$  substrates. Thus, phase separation is effectively

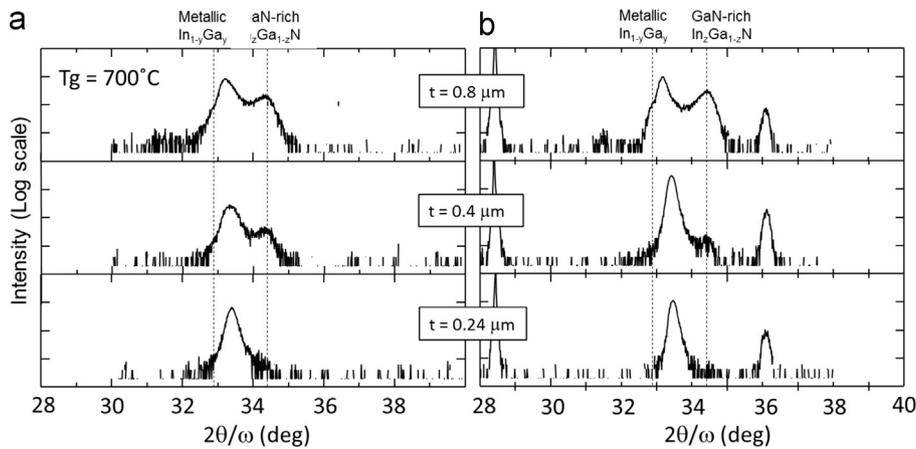


Fig. 3. X-ray diffraction  $2\theta/\omega$  profiles for epitaxial  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $x \sim 0.3$ ) films with a different thickness grown on  $\alpha\text{-Al}_2\text{O}_3$  and AlN/Si substrates at  $700^\circ\text{C}$ . (a) Sub:  $\alpha\text{-Al}_2\text{O}_3(0001)$  and (b) Sub: AlN/Si(111).

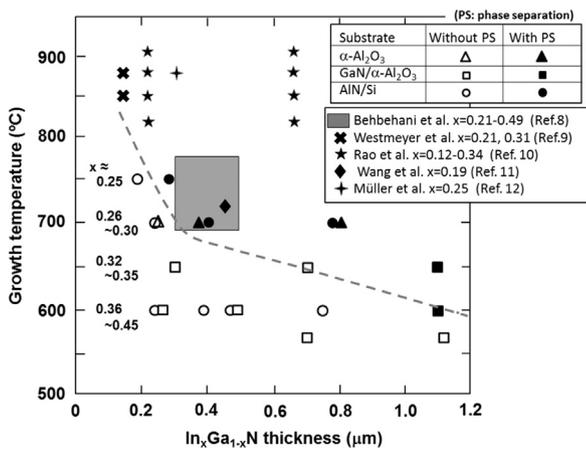


Fig. 4. Mapping of InGaN films with and without phase separation, displayed on the plane of film thickness and growth temperature. The dotted line is drawn between samples with and without phase separation, shows critical thicknesses for phase separation at different growth temperatures. Also plotted are growth temperatures and thicknesses for InGaN samples reported in the literatures [8–12].

suppressed by reducing growth temperature. However, the crystalline quality of InGaN is deteriorated with reducing growth temperature, as reported previously [5]. Therefore, further investigations are needed to improve the quality of such low temperature-grown InGaN in order to realize high-performance devices. Generally, an epitaxial film grown under conditions far from thermal equilibrium is known to be a “frozen” solid [6]. Such a solid can be decomposed into two phases through the solid-state diffusion of constitutional atoms, in order to minimize the free energy of mixing for the system [1]. Because rate of the decomposition is governed by diffusion mobility of constitutional atoms, it should be increased as growth and/or annealing temperature increases. Therefore, the reduced critical thickness for higher temperature-grown samples, shown in Fig. 4, is explained by the increased diffusion mobility of constitutional atoms. The existence of a maximum thickness (critical thickness) that can be grown without phase separation was reported for  $\text{In}_{0.65}\text{Ga}_{0.35}\text{N}$  films by Pantha et al. [7] for the first time. They found that critical thickness was markedly increased with increasing growth rate, and interpreted such an increase in critical thickness to be due to the shift of the thermodynamic condition toward more nonequilibrium-like. This means that an InGaN grown with a high growth rate is less affected by the decomposition reaction during growth. A shorter growth duration may be more effective to suppress phase separation, because the annealing time for the initially grown

InGaN near the substrate is reduced. We have checked which is more dominant against the emergence of phase separation between growth temperature and growth rate. Two epitaxial  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $x \sim 0.30$ ) films with  $0.5\ \mu\text{m}$  thickness were grown at  $600^\circ\text{C}$  with a different growth rate, 0.2 and  $0.7\ \mu\text{m}/\text{h}$ . No phase separation was generated in both cases. As seen in Fig. 4, critical thickness for phase separation in InGaN grown at  $600^\circ\text{C}$  is  $\sim 1\ \mu\text{m}$ . Thus, growth temperature is found to be more dominant than growth rate under the conditions employed in the present study.

Also plotted in Fig. 4 are growth temperatures and thicknesses for InGaN samples reported in the literatures [8–12]. These samples were grown to contain InN compositions (0.1–0.4) similar to those for InGaN samples studied in this study. Due to growth temperatures higher than  $700^\circ\text{C}$  and film thicknesses larger than  $0.15\ \mu\text{m}$ , it is obvious that those samples were grown under the conditions where phase separation occurred. For the sample reported by Müller et al. [12], for example, critical thickness is estimated to be  $\leq 0.1\ \mu\text{m}$ . In all the samples reported [8–12], a two-layer structure was found. Such a two-layer structure is a “result” of phase separation.

Fig. 5 shows cross-sectional SEM images for InGaN samples at a different stage of phase separation at  $650^\circ\text{C}$ . As reported previously [2], phase separation of InGaN grown at around  $650^\circ\text{C}$  is accompanied with the formation of porous regions in the films. The formation of such porous regions is a characteristic feature of phase separated samples with the metallic  $\text{In}_{1-y}\text{Ga}_y$ . Therefore, the observation of porous regions gives us useful information about phase separation. Note that the porous region shown in Fig. 5(b) is formed at around the middle part of the film and is about  $200\ \text{nm}$ , at least, far from the InGaN/AlN interface. It should be also pointed out that such a part has no signs of phase separation when thickness is around  $0.7\ \mu\text{m}$  (Fig. 5(a)) or less. As phase separation proceeds further, the porous region is extended to the InGaN/AlN interface as shown Fig. 5(c). In this process, the non-stoichiometric metallic  $\text{In}_{1-y}\text{Ga}_y$  ( $y \sim 0.03$ ) enhances the decomposition by solving parts with a higher InN composition in the epitaxial  $\text{In}_x\text{Ga}_{1-x}\text{N}$ . Once metallic In-Ga is formed by the thermal decomposition of InN-rich  $\text{In}_{1-y}\text{Ga}_y\text{N}$ , it enhances the decomposition reaction by solving InN-rich parts preferentially. This means that the thermal decomposition of InN-rich  $\text{In}_{1-y}\text{Ga}_y\text{N}$  can initiate the decomposition reaction of epitaxial InGaN. This is similar to the case of the thermal degradation of InGaN/GaN quantum wells, where the degradation is initiated at InN-rich clusters [14]. Once metallic In-Ga is formed, it is difficult to suppress the decomposition reaction of InGaN because metallic In is not converted into InN even if it is annealed in the  $\text{NH}_3$

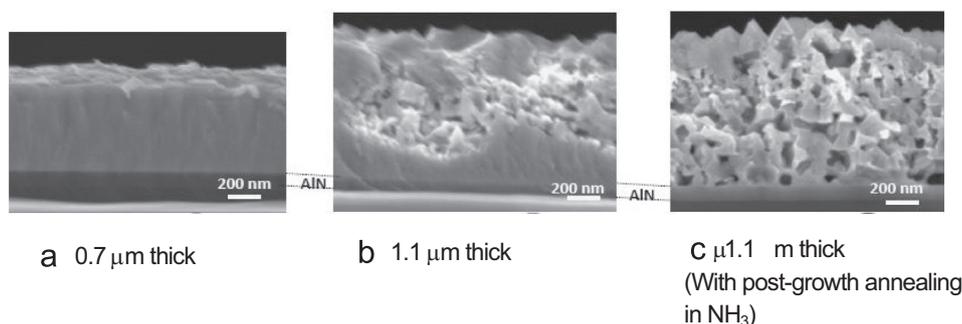


Fig. 5. Cross-sectional SEM images for epitaxial  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $x \sim 0.35$ ) films with a different stage of phase separation.

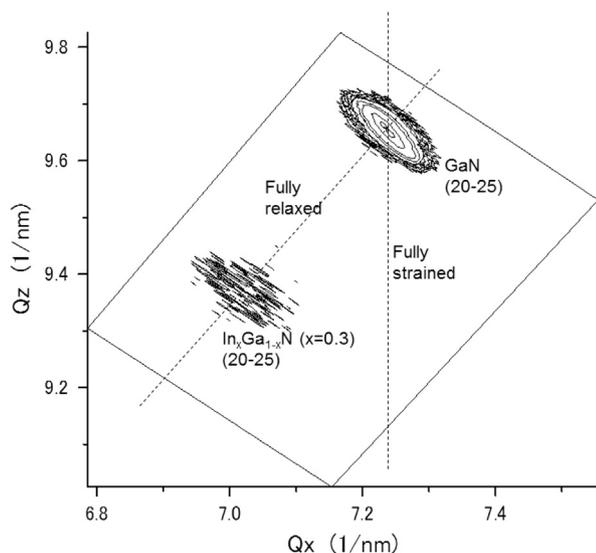


Fig. 6. Reciprocal space mapping (RSM) of the (20–25) reflections by HRXRD for a 0.3  $\mu\text{m}$ -thick  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $x=0.3$ ) grown on a  $\text{GaN}/\alpha\text{-Al}_2\text{O}_3$  template.

atmosphere at around 600 °C [15]. The situation of phase separation in InGaN grown at  $\geq 700$  °C should be different from that for samples grown at  $< 700$  °C. That is, phase separation in high temperature-grown InGaN does not proceed so fast because the metallic In as a result of phase separation is evaporated so swiftly. In such a case, a two-layer structure, a combination of a layer near the substrate with a homogeneous InN content and a phase-separated layer with large compositional fluctuations [12,13], seems to be formed.

From the viewpoint of thermal annealing of a grown film, a part just contacted with the AlN/Si substrate should suffer the most severe annealing with the longest time during growth. Such an idea is supported by the results for high temperature (650 °C)-grown InN on sapphire [16]. In that case, the thermal decomposition of InN was started just near the  $\alpha\text{-Al}_2\text{O}_3$  substrate and cavities with some facet planes were formed there. As growth time increases, the thermally deteriorated region was expanded to the film surface. Although the cavity formation in the porous region in the phase-separated InGaN (Fig. 5(c)) is very similar to the case for the thermally deteriorated InN films; the direction of the expansion of the deteriorated region is reverse each other. The results shown in Fig. 5(b) show that the parts just contacted with the AlN/Si substrate is not a starting point of phase separation. This fact suggests a possibility either that there are some causes to suppress phase separation near the substrate interface, such as strain and/or compositional change in the InGaN, or that there are some causes to initiate phase separation in the middle or surface part of the film. To confirm it, the measurement of reciprocal space mapping

(RSM) and the secondary ion-mass spectrometer (SIMS) analysis of the samples were conducted. Fig. 6 shows the RSM of the (20–25) reflections by HRXRD for a 0.3  $\mu\text{m}$ -thick  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $x=0.3$ ) grown on a  $\text{GaN}/\alpha\text{-Al}_2\text{O}_3$  template. The results in Fig. 6 clearly show that the InGa film is grown under the fully-relaxed condition even on a  $\text{GaN}/\alpha\text{-Al}_2\text{O}_3$  template. Therefore, strain in the film is ruled out as a major reason for the stability of the film. Of course, the  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $x=0.3$ ) grown on  $\text{GaN}/\alpha\text{-Al}_2\text{O}_3$  template has a layer affected by the composition pulling effect, as shown later with SIMS data. However, the effect is limited to a very thin ( $\leq 50$  nm) region from the substrate interface. Fig. 7 shows the SIMS profiles of Ga and In atoms in  $\text{In}_x\text{Ga}_{1-x}\text{N}$  ( $x=0.3$ ) films without phase separation grown on  $\text{GaN}/\alpha\text{-Al}_2\text{O}_3$  and AlN/Si substrates at 650 °C. An intensity In/Ga ratio normalized by a value at the middle part of the film is also plotted in the figures. The results for the film grown on  $\text{GaN}/\alpha\text{-Al}_2\text{O}_3$  (Fig. 7(a)) show that the layer affected by the composition pulling effect is limited to approximately 50 nm thick and, except of this layer, the fluctuation of In/Ga ratio is within  $\pm 10\%$  over the entire region of the 0.3  $\mu\text{m}$  thick sample. Even in the case for the film grown on AlN/Si (Fig. 7(b)), In/Ga ratio is constant over the range of 0.3  $\mu\text{m}$  thick from the substrate interface. It is reasonable to consider that the film on AlN/Si is also grown under the fully-relaxed conditions. Without introducing strain, thus, a thick ( $\geq 0.3$   $\mu\text{m}$ ) InGa film with a constant composition can be grown. This is in contrast with the results reported by Müller et al. [12]. In their study, it apparently seems to show that the relaxed layer was phase separated and only the  $\sim 40$  nm thick layer strained by the composition pulling effect was free from phase separation. This was due to that strain was known to suppress phase separation [17]. As seen in Fig. 4, their sample is expected to have a critical thickness for phase separation of  $\leq 0.1$   $\mu\text{m}$ . In such a situation, only the strained layer seems to be able to escape from phase separation. However, this does not mean that strain is inevitable to suppress phase separation and relaxed layers are always phase separated. As described above, thick ( $\geq 0.3$   $\mu\text{m}$ ) InGa films without strain can be grown without phase separation.

It is noted that, in Fig. 7(b), the fluctuation of intensity In/Ga ratio is considerably increased at a thickness of 0–0.2  $\mu\text{m}$  from the film surface. Since this region is in agreement with the parts where porous regions are formed at a relatively early stage of phase separation (Fig. 5(b)), there is a possibility that the phase separation initiation is closely related to such a large In/Ga ratio fluctuation. It was reported that InN-rich clusters initiated the phase separation in InGaN/GaN quantum well structures [14] and dislocation sites in InGaN well layers contained higher In compositions [18]. Also, the surface segregation of In and composition fluctuations were found in MOVPE InGaN [19]. Such unstable growth of InGaN and inhomogeneities in grown InGaN seems to be closely correlated with the initiation of phase separation. Regarding phase separation in InGaN films with InN contents

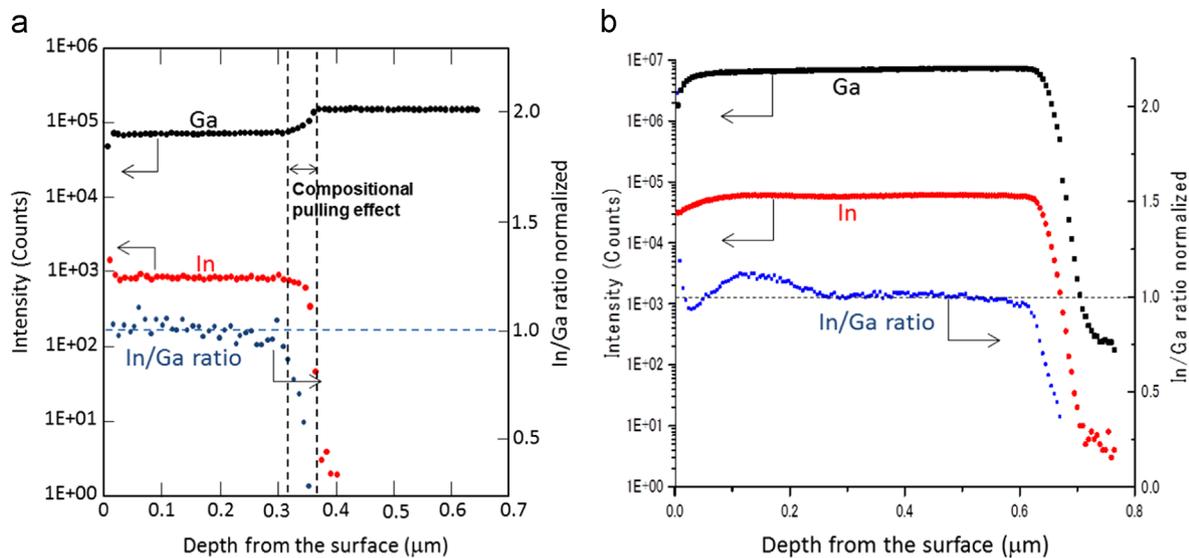


Fig. 7. SIMS depth profiles of In and Ga in InGaN films without phase separation grown on GaN/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and AlN/Si substrates at 650 °C. Intensity In/Ga ratio normalized by a value at the middle of the film is also shown. (a) GaN/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrate and (ii) (b) AlN/Si substrate.

more than 0.4, we do not have enough data to discuss it at present. The followings are our speculation based on the experiences. The MOVPE growth of InGaN with a full composition range has been performed previously [20]. As reported there, a film with a higher InN content shows a larger FWHM value of X-ray diffraction  $2\theta/\omega$  profile (except for the binary compound InN). This fact indicates that such a film has a larger fluctuation of composition. As discussed above, a film with a higher compositional inhomogeneity or fluctuation seems to have more serious phase separation.

This work was done using only one type of reactor. Therefore, it is difficult for us to discuss any effects of reactor design on phase separation. On the other hand, we can say that reactor design should be fixed to one type when we study effects of growth temperature and film thickness. Since phase separation is a phenomenon occurring in a deposited InGaN, reactor design is believed not to be directly correlated to phase separation. Because of the following reason, however, there is a possibility that reactor design has an effect on phase separation. As discussed in this paper, phase separation seems to be initiated at parts containing a higher InN content. Degree of such inhomogeneity in a film can be dependent on reactor design. For example, a reactor containing turbulent flows of source gasses in the growth zone may result in a serious compositional inhomogeneity in a grown film. A film grown using such a reactor will have severer phase separation due to the serious compositional inhomogeneity.

Further investigations are needed to confirm above hypotheses and speculation, and to improve the quality of low temperature ( $\leq 600$  °C)-grown InGaN in order to realize high-performance devices.

#### 4. Conclusions

We have studied phase separation in thick ( $\sim 1$   $\mu$ m) In<sub>x</sub>Ga<sub>1-x</sub>N ( $x=0.2$ – $0.4$ ) grown at 570–750 °C on AlN/Si(111),  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) and GaN/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) substrates. Critical thickness of phase separation of In<sub>x</sub>Ga<sub>1-x</sub>N is found to be markedly increased with decreasing growth temperature. No difference in critical thickness are found between AlN/Si(111) and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001), GaN/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) substrates. The cross-sectional SEM views of phase-separated films grown at 650 °C show that phase separation is initiated at parts farer more than 0.2  $\mu$ m from the substrate and extended to the area near the substrate. RSM and SIMS measurements show that an InGaN film grown on a GaN/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> template are relaxed, although it contains a

thin ( $\sim 50$  nm) strained layer at the InGaN/GaN interface. It is shown that thick ( $\geq 0.3$   $\mu$ m) InGaN films without strain can be grown without phase separation. FESEM and SIMS analysis show a possibility that phase separation is initiated at parts with large In/Ga ratio fluctuations in the film.

#### Acknowledgments

This work was supported in part by “Creative research for clean energy generation using solar energy” project in CREST programs of JST, Japan.

#### References

- [1] I-hsiu Ho, G.B. Stringfellow, *Appl. Phys. Lett.* 69 (1996) 2701.
- [2] A. Yamamoto, M.d.T. Hasan, A. Mihara, N. Narita, N. Shigekawa, M. Kuzuhara, *Appl. Phys. Express* 7 (2014) 035502.
- [3] A.G. Bhuiyan, K. Sugita, A. Hashimoto, A. Yamamoto, *IEEE J. Photovolt.* 2 (2012) 276.
- [4] A. Yamamoto, A. Mihara, D. Hironaga, K. Sugita, A.G. Bhuiyan, A. Hashimoto, N. Shigekawa, N. Watanabe, *Phys. Status Solidi C* 10 (2013) 437.
- [5] A. Yamamoto, A. Mihara, Y. Zheng, N. Shigekawa, *Jpn. J. Appl. Phys.* 52 (2013) 08JB19.
- [6] Y. Qiu, S.A. Nikishin, H. Temkin, V.A. Elyukhin, Yu.A. Kudriavtsev, *Appl. Phys. Lett.* 70 (1997) 2831.
- [7] B.N. Pantha, J. Li, J.Y. Lin, H.X. Jiang, *Appl. Phys. Lett.* 96 (2010) 232105.
- [8] M.K. Behbehani, E.L. Piner, S.X. Liu, N.A. El-Masry, *Appl. Phys. Lett.* 75 (1999) 2202.
- [9] A.N. Westmeyer, S. Mahajan, *Appl. Phys. Lett.* 79 (2001) 2710.
- [10] M. Rao, D. Kim, S. Mahajan, *Appl. Phys. Lett.* 85 (2004) 1961.
- [11] H. Wang, D.S. Jiang, U. Jahn, J.J. Zhu, D.G. Zhao, Z.S. Liu, S.M. Zhang, Y.X. Qiu, H. Yang, *Physica B* 405 (2010) 4668.
- [12] M. Müller, G.D.W. Smith, B. Gault, C.R.M. Grovenor, *Acta Mater.* 60 (2012) 4277.
- [13] Y. Kawaguchi, M. Shimizu, M. Yamaguchi, K. Hiramatsu, N. Sawaki, W. Taki, H. Tsuda, N. Kuwano, K. Oki, T. Zheleva, R.F. Davis, *J. Cryst. Growth* 189/190 (1998) 24.
- [14] Z. Li, J. Liu, M. Feng, K. Zhou, S. Zhang, H. Wang, D. Li, L. Zheng, D. Zhao, D. Jiang, H. Wang, H. Yang, *Appl. Phys. Lett.* 103 (2013) 152109.
- [15] A. Yamamoto, T. Shin-ya, T. Sugiura, M. Ohkubo, A. Hashimoto, *J. Cryst. Growth* 189/190 (1998) 476.
- [16] K. Sugita, A. Hashimoto, A. Yamamoto, *Phys. Status Solidi C* 6 (2009) S393.
- [17] S.Y.u. Karpov, *MRS Internet J. Nitride Semicond. Res.* 3 (1998) 16.
- [18] T. Sugahara, M. Hao, T. Wang, D. Nakagawa, Y. Naoi, K. Nishino, S. Sakai, *Jpn. J. Appl. Phys.* 37 (1998) L1195.
- [19] S.Y. Karpov, R.A. Talalaev, E.V. Yakolev, Y.N. Makarov, *Mater. Res. Soc. Symp. Proc.* 639 (2001) G3.18.
- [20] A. Yamamoto, K. Sugita, A.G. Bhuiyan, A. Hashimoto, N. Narita, *Mater. Renew. Sustain. Energy* 2 (2013) 10.