

Metal-organic vapor-phase epitaxial growth of InGaN and InAlN for multi-junction tandem solar cells

A. Yamamoto¹, K. Sugita², A. G. Bhuiyan³, A. Hashimoto¹, and N. Narita⁴

¹Graduate School of Engineering, University of Fukui, 3-9-1 Bunkyo, Fukui 910-8507, Japan

²HISAC, University of Fukui, 3-9-1 Bunkyo, Fukui 910-8507, Japan

³Khulna University of Engineering and Technology, Khulna-9203, Bangladesh

⁴Energy Use R&D Centre, The Kansai Electric Power Co., Inc., 3-11-20 Wakoji, Amagasaki, Hyogo 661-0974, Japan

ABSTRACT

MOVPE growth of InGaN and InAlN has been studied to prepare a wanted band gap from 0.65 to 2.5 eV for multi-junction tandem solar cells. The main subjects in the growth of InGaN are the suppression of phase separation and metallic *In* incorporation and the control of composition in grown films. Both phase separation and metallic *In* segregation can be avoided by choosing the appropriate substrate position on the susceptor. By optimizing growth temperature and TMI/(TMI+TEG) molar ratio, InGaN films with full composition range are successfully grown. The Mg-doping behavior of MOVPE InGaN (*In* composition 0.1~0.4) is also studied using Cp₂Mg as a Mg source. The growth behavior of InAlN is studied with the dominant parameters such as growth pressure, TMI/(TMI+TMA) molar ratio and substrate position on the susceptor. The major difficulty in the InAlN growth is found to be the adduct formation by the parasitic reaction of TMA and NH₃. By employing the atmospheric-pressure growth, adduct-free InAlN films are grown with a reasonable growth rate (~ 1 μm/h). This enables us to grow InAlN films with an *In* content from 0.3 to 1, corresponding to band gaps from 3.6 to 0.65 eV. In order to demonstrate an ability to prepare these different alloys sequentially, InAlN/InGaN hetero-structures are prepared and the photo-response is observed for the first time for an n-InAlN/p-InGaN hetero-junction.

1. Introduction

Photovoltaic power generation is expected to be one of the key technologies for the realization of a low-carbon society. For this purpose, we need to develop low cost and high conversion efficiency solar cells. The most effective way to realize a high conversion efficiency is to fabricate a multi-junction tandem solar cell, where many sub-cells composed of a different band-gap material are stacked perpendicularly and electrically connected in series. Figure 1 shows the relationships between band-gap energy and lattice parameter for typical semiconductor materials applicable to solar cell. In order to realize a high-efficiency multi-junction cell, semiconductor materials with band-gap energies from 0.6 to 2.5 eV are required [1]. Since the band-gap of InN was found to be about 0.7 eV [2], InN-based nitride semiconductor alloys, such as InGaN and InAlN, have had much attention as materials for multi-junction solar cells [1,3]. This is mainly because a wide range of band-gaps can be realized by changing only their composition; from 0.65 to 3.4eV with InGaN and from 0.65 to 6.2eV with InAlN. Figure 1 shows that there is no such a material except for the InN-based materials. The authors have shown that, using InGaN or InAlN films with a band gap energy from 0.7 to 2.5 eV, a multi-junction tandem solar cell with a conversion efficiency more than 50% is expected to be realized [1]. Thus, the InN-based alloys are ones of a few of the promising materials for multi-junction solar cells.

Since 2003, the studies on InN-based solar cells, especially InGaN cells, have been started using Ga-rich materials [1,3]. Single-junction cells composed of GaN/InGaN heterojunction and InGaN homojunction have been extensively studied. However, their efficiencies and performances are still poor, mainly due to theoretical limits or transparency loss for high bandgap energy InGaN cells as a result of low *In* composition and poor crystalline quality of the grown InGaN cells. Although various efforts have been carried out toward the goal of high efficiency solar cells from different viewpoints, however, still there are lots of challenges to achieve a high efficiency cell.

The most important challenging task for tandem cell fabrication is to grow high quality InGaN or InAlN materials with wide range of *In* content. Among the III-nitrides, GaN is the most extensively studied material and comparatively has matured, while the lower band-gap InGaN or InAlN alloys, that are more useful for device application, are still a topic of fundamental research. The difficulties in growing high-quality InGaN and InAlN materials can be attributed to a number of problems: for instance, the large difference in interatomic spacing between InN and GaN or AlN results in a solid phase

miscibility gap [4, 5] and the relatively high vapor pressure of InN as compared to the vapor pressure of GaN or AlN leading to low indium incorporation in these alloys [6]. In addition, the difference in formation enthalpies for InN and GaN or AlN causes a strong indium surface segregation on the growth front [7]. Nevertheless, single crystalline InGaN films with full composition range have been successfully grown by MBE [8]. The growth of high-quality InAlN seems to be more difficult compared with InGaN growth because the optimum growth temperatures for InN and AlN are largely different. The growth of the InAlN film in all composition regions has been realized with MBE [9], while In-rich InAlN with an In content >32% grown by MOVPE was reported to show phase separation [10]. It is also expected that the MOVPE growth of InAlN is hindered by the parasitic reaction of TMA and NH₃, which was observed in the MOVPE growth of AlN [11].

In this work, the metal-organic vapor phase epitaxial (MOVPE) growth of InGaN and InAlN is studied to grow high quality InGaN or InAlN materials with wider range of *In* content. It is shown that InGaN films with a full range of *In* compositions can be grown using MOVPE by optimizing growth temperature and TMI/(TMI+TEG) molar ratio. The Mg-doping behavior and p-type conduction of MOVPE InGaN are also studied using Cp₂Mg as a Mg source. As a result of detailed investigation of the growth behavior of MOVPE InAlN including the adduct formation, a single-crystalline InAlN film with an *In* content of 0.3-1 are successfully grown by using the atmospheric-pressure MOVPE. Based on these achievements, an n-InAlN/p-InGaN hetero-structure is successfully prepared and its photo-response is confirmed for the first time.

2 Experimental procedures

The growth of InGaN and InAlN is performed using a metal-organic vapor phase epitaxy (MOVPE) system with a horizontal reactor. As sources, trimethyl-indium (TMI), triethyl-gallium (TEG), trimethyl-aluminium (TMA) and ammonia (NH₃) are used. As substrates, α -Al₂O₃(0001) and GaN/ α -Al₂O₃(0001) templates are used. A 20 nm thick GaN layer grown at 550°C is used as a buffer for the growth on α -Al₂O₃(0001). In the growth of InGaN, growth pressure is fixed at 150 Torr and growth temperature is varied from 600 to 900°C. In the growth of InAlN, growth temperature is fixed at 600°C and growth pressure is varied from 76 to 730 Torr. TMI/(TMI+TEG) molar ratio is varied from 0 to 1 for the InGaN growth, while TMI/(TMI+TMA) molar ratio is varied from 0.3 to 1 for the InAlN growth.

The substrates are placed at different positions on the 150 mm-long carbon susceptor. The composition of grown films is determined by using X-ray diffraction ($2\theta/\omega$) patterns. Full width at half maximum (FWHM) of (0002) X-ray rocking curve, tilt fluctuation, is also measured for grown InGaN and InAlN. The Mg-doping of MOVPE InGaN is performed using bis-cyclopentadienyl magnesium (Cp_2Mg) as a Mg source. Carrier concentration is measured using the Hall effects with the Van der Pauw method. As an ohmic contact to p-InGaN, Ni/Au is used. The Mg concentration in InGaN is measured with the secondary ion-mass spectrometer (SIMS) (outsourced to Toray Research Center, Inc., Japan).

3 MOVPE growth of InGaN with full composition range

3.1 Growth behavior and composition control of InGaN

Non-doped InGaN films are grown at a growth temperature from 600 to 900°C with a different TMI/(TMI+TEG) molar ratio. Figure 2 shows the X-ray diffraction $2\theta/\omega$ profiles for films grown at 700 °C at a different substrate position on the 150mm-long (along the gas flow direction) susceptor in the horizontal reactor. The substrate used here is a GaN/ $\alpha\text{-Al}_2\text{O}_3$ (0001) template with an AlN buffer. Metallic *In* segregation is found for the films grown near the upstream end of the susceptor. In addition to the main peak marked by an arrow, a sub-peak denoted by “S” is found for the films grown near the upstream end of the susceptor, indicating phase separation. It is noted that that both phase separation and metallic *In* segregation can be suppressed by choosing the substrate position near the downstream end of the susceptor, as shown in Fig. 2. As reported in literatures, there are many parameters that affect phase separation in InGaN, such as growth temperature [12], strain in growing films [12,13], film thickness [14], growth rate [14] or Impurity incorporation [15]. We believe that, through such parameters, the gas flow near the upstream side indirectly affects the phase separation. Further investigation will be needed to clarify the thermodynamics for phase separation and metallic *In* segregation near the upstream side.

The *In* composition in single-phase InGaN is changed by varying growth temperature and TMI/(TMI+TEG) molar ratio. Figure 3 shows the X-ray diffraction $2\theta/\omega$ profiles for InGaN with a different *In* composition. The films are grown on $\alpha\text{-Al}_2\text{O}_3$ (0001) with a GaN buffer. As can be seen in this result, all samples show a distinct single peak of InGaN (0002), indicating that they have no phase separation

and no metallic *In* segregation. Even for the InGaN with *In* content of 0.7, no obvious phase separation is observed, although its diffraction peak is relatively broad. The films with *In* contents up to 0.4 were grown by changing growth temperature with a constant TMI/(TMI+TEG) molar ratio 0.45. Those with an *In* content from 0.4 to 1.0, on the other hand, were grown by changing TMI/(TMI+TEG) molar ratio at the same temperature 600°C. Figure 4 shows the growth temperature dependence of *In* composition with a parameter of TMI/(TMI+TEG) molar ratio. At 600°C, the *In* composition in solid InGaN is very close to that in the gas phase (TMI/(TMI+TEG) molar ratio), showing that the *In* composition in solid is controlled by *In*/(*In*+*Ga*) ratio in gas phase. At a growth temperature higher than 700°C, on the other hand, *In* composition in solid is almost independent on TMI/(TMI+TEG) molar ratio and is gradually decreased with increasing growth temperature. For example, the InGaN grown at 700°C has *In* composition of about 0.45 even though the TMI/(TMI+TEG) molar ratio is high (0.8). In this growth temperature range ($\geq 700^\circ\text{C}$), thus, *In* composition in InGaN is almost governed by growth temperature. This is due to the decomposition of InN component and the consequent evaporation of metallic *In* from the growing surface. Thus, growth temperature, as well as TMI/(TMI+TEG) ratio, should be carefully managed in the growth of In-rich InGaN.

In order to evaluate crystalline quality of InGaN films, tilt fluctuation is measured using X-ray diffraction method. The results are shown in Fig. 5. The samples with *In* composition up to 0.4 show relatively good results; tilt fluctuations less than 50 arcmin. On the other hand, the samples with *In* composition from 0.55 to 0.75 show large tilt fluctuations. In Fig. 5 also shown are the data for InN and InGaN with *In* content of 0.83. They were grown under the typical growth conditions for InN; at a pressure of 760 Torr and at a growth temperature of 600°C [14]. Such data are largely deviated from the results for the InGaN with *In* composition from 0.55 to 0.75. The major difference between the present growth conditions and the typical growth conditions for InN is growth pressure. The result shown in Fig. 5 seems to suggest that InGaN with *In* composition more than 0.5 should be grown under the growth conditions similar to those for InN.

3.2 Mg doping and p-type conductivity of InGaN

The Mg-doping for InGaN with *In* contents 0.1-0.4 has been performed using Cp_2Mg as a Mg precursor. The films are grown on $\text{GaN}/\alpha\text{-Al}_2\text{O}_3(0001)$ templates. Figure 6 shows the carrier

concentration in Mg-doped InGaN as a function of $\text{Cp}_2\text{Mg}/(\text{TMI}+\text{TEG})$ molar ratio. When $\text{Cp}_2\text{Mg}/(\text{TMI}+\text{TEG})$ molar ratio is 2-5 %, p-type conduction is achieved for InGaN films with In content of 0.25-0.4. These samples are grown at 700-750°C. Their hole concentrations are in the order of 10^{18} cm^{-3} . In the previous study [15], $\text{Cp}_2\text{Mg}/(\text{TMI}+\text{TEG})$ molar ratio of 4 % or more was needed to get p-type conduction for InGaN with In content of 0.2. In the present case, on the other hand, p-type conduction is achieved for InGaN with In content of 0.24 when $\text{Cp}_2\text{Mg}/(\text{TMI}+\text{TEG})$ molar ratio is only 2 %. Such an effective Mg-doping in this case is believed to be owing to the improved crystalline quality of the present samples. The samples with In content of 0.24-0.38 show n-type conduction again when $\text{Cp}_2\text{Mg}/(\text{TMI}+\text{TEG})$ molar ratio is around 7 % or more. Similar behavior has been observed for Mg-doped GaN [16], indicating that the excess Mg doping leads the formation of donor-type defects in the crystals. In this study, p-type conduction has not been obtained for the sample with an In content 0.15, which is grown at 800°C. One of the possible reasons for this may be the larger activation energy for Mg in a sample with a lower In content [17]. The SIMS analysis has been made for Mg-doped InGaN samples. Figure 7 shows the relationship between $\text{Cp}_2\text{Mg}/(\text{TMI}+\text{TEG})$ molar ratio in the gas phase and Mg concentration in the grown InGaN (measured with SIMS). From this result, one can see that Mg concentration in grown InGaN is decreased as growth temperature increases, even when a constant $\text{Cp}_2\text{Mg}/(\text{TMI}+\text{TEG})$ molar ratio is supplied. From the results in Fig. 7, a very low Mg concentration is expected for a sample grown at 800°C. This may be also one of the reasons for the unsuccessful p-type conduction of the sample grown at 800°C with an In content 0.15. In Fig. 7, one can also find that the data lines do not pass the origin. For the samples grown at 750 °C, a $\text{Cp}_2\text{Mg}/(\text{TMI}+\text{TEG})$ molar ratio less than 0.25% gives no detectable Mg concentration in the grown InGaN. Further investigation will be needed to clarify the Mg-doping behavior in InGaN.

4. MOVPE growth of InAlN with intermediate In compositions

4.1 Growth behavior of InAlN and suppression of adduct formation

It is found that the MOVPE growth behavior of InAlN is more complicated compared with the growth of InGaN. Here, the effects of growth pressure, substrate position and TMA/(TMA+TMI) molar ratio on

the growth of InAlN are shown and discussed. Figure 8 shows the growth pressure dependence of the thickness of the material deposited on the substrate. Also shown in this figure is XRD intensity of InAlN peak detected from the deposits. The intensity is normalized by that of the sapphire substrate. As can be seen in Fig. 8, the XRD intensity ratio is the highest at a pressure 730 Torr, while it is very small at a pressure around 300-600 Torr in spite of the large thickness of the deposits. Figure 9 shows the typical surface morphologies (SEM images) of the deposits formed at a different pressure. The surface feature is markedly different depending on pressure. The deposits consist of small grains are obtained at 730Torr. The thick deposits with micrometer-size grains are obtained at a pressure in the range 380-530Torr. When the growth pressure is further reduced to 76Torr, thin deposits with flat surface are obtained. Accordingly, it is concluded that the deposits with micrometer-size grains formed at a pressure around 380-530 Torr, shown in Fig. 9 (b) and (c), scarcely contain InAlN component, indicating that these deposits are composed of adducts through the parasitic reaction between TMA and NH_3 [11].

Figure 10 shows the substrate position dependence of the thickness of the deposited material formed at a different pressure. One can see that the position where the largest thickness is obtained is moved from the upstream side to downstream side as growth pressure is reduced. The amount of the deposits is also decreased with reducing growth pressure. These results are caused by the increase in the gas flow speed and the consequent decrease of parasitic reaction, since the reduction of growth pressure results in increase in gas flow speed under the constant gas supply condition. In the case of the growth at 730 Torr, adducts formation mainly occurs at the upstream side of the susceptor, as shown in Fig. 10. This is due to the considerably low gas flow speed. When we grow InAlN at the downstream side (substrate position +25 mm), therefore, a single crystalline InAlN can be obtained without obstruction of adducts formation, although the Al content in the grown film is much reduced in this case. The low Al content is due to the TMA consumption by the adduct formation at the upstream side. This is the reason why we couldn't find adducts formation in the previous study on the InAlN growth at 730 Torr [18]. Figure 11 shows the growth pressure dependence of Al composition in the grown InAlN. At a growth pressure in the range of 300-600Torr, single-crystalline InAlN films are not obtained due to the adduct formation at the substrate position +25 mm. The Al composition increases with decreasing growth pressure, as seen in the figure. This is due to that the TMA consumption by the

adduct formation is reduced with decreasing growth pressure. Figure 12 shows the substrate position dependence of Al composition in InAlN films. At a pressure around 730 Torr and at the substrate position +25 mm, an InAlN with a relatively low Al content is obtained. With decreasing growth pressure Al composition increases and the gradient of Al composition decreases. This is also due to the reduced TMA consumption in the parasitic reaction with decreasing growth pressure. That is, with decreasing growth pressure, more TMA can be delivered to the downstream side. In order to avoid the problems of the adduct formation, we need to select growth pressure less than 300 Torr or at around 730 Torr or more, as shown in Fig. 11. In the case of a pressure less than 300 Torr, however, growth rate of InAlN is very low (less than 0.05 $\mu\text{m/h}$), as shown in Fig. 8. Therefore, the growth at 730 Torr is the most practical choice to get an InAlN film with a reasonable growth rate (0.5-1 $\mu\text{m/h}$). In this case, substrate positions on the downstream side should be selected because adduct formation occurs at the upstream side, as can be seen in Fig. 12.

4.2 Composition control of MOVPE InAlN

In this study, InAlN films with a thickness 0.5-0.8 μm have been grown on nitrided (0001) sapphire substrates at 600 °C. Due to the reasons described above, a growth pressure of 730 Torr and the substrate position +25 mm are selected. Figure 13 shows the XRD patterns around (0002)-plane of InAlN. By changing TMA/(TMA+TMI) molar ratio, InAlN films with a different In composition are obtained. It is noted that all films prepared here do not show phase separation, although the intensity of XRD peak for the InAlN is decreased and the FWHM of the peaks is increased with increasing Al content. Figure 14 shows the relationship between TMI/(TMA+TMI) molar ratio in the gas phase and Al content in InAlN. InAlN films with Al content from 0 to 0.7 are obtained as seen in Fig. 14. The experimental data are markedly deviated from the line of slope 1. This deviation is due to the TMA consumption by the adduct formation at the upstream side, as discussed above. The carrier concentration of InAlN films grown at 600°C at the pressure of 730 Torr is in the range of $2\text{-}5 \times 10^{19} \text{ cm}^{-3}$ and does not show a marked dependency on Al composition. On the other hand, the mobility decreases with increasing Al composition; from 200 cm^2/Vs for InN to 10 cm^2/Vs for InAlN with Al content 0.43. The InAlN films with an Al content of 0-0.3 show a PL spectrum even at room temperature [16]. Although the PL intensity is decreased with increasing Al content, the intensity

difference between InN and InAlN is less than one order of magnitude even for the film with Al content 0.3.

5. Preparation and characterization of p-InGaN/n-InAlN hetero-structures

As described above, we have successfully grown both InGaN films with full composition range and InAlN films with In content from 0.3 to 1. In order to demonstrate an ability to prepare these different alloys sequentially, the formation of InAlN/InGaN hetero-structures has been studied. At the substrate position +25 mm, InGaN and InAlN films have been grown sequentially at 150 Torr and 730 Torr, respectively. Figure 15 shows the X-ray diffraction $2\theta/\omega$ profiles for “ $\text{In}_{0.57}\text{Al}_{0.43}\text{N}$ on $\text{In}_{0.4}\text{Ga}_{0.6}\text{N}$ ” structure and “ $\text{In}_{0.4}\text{Ga}_{0.6}\text{N}$ on $\text{In}_{0.57}\text{Al}_{0.43}\text{N}$ ” structure. The insets in the figure show the surface morphologies (SEM images) for such samples. When an $\text{In}_{0.57}\text{Al}_{0.43}\text{N}$ film is grown on an $\text{In}_{0.4}\text{Ga}_{0.6}\text{N}$ film prepared beforehand, the hetero-structure is successfully prepared. On the other hand, an $\text{In}_{0.4}\text{Ga}_{0.6}\text{N}$ film is grown on an $\text{In}_{0.57}\text{Al}_{0.43}\text{N}$ film prepared beforehand, the $\text{In}_{0.57}\text{Al}_{0.43}\text{N}$ film is found to be decomposed during the $\text{In}_{0.4}\text{Ga}_{0.6}\text{N}$ growth. This means that the $\text{In}_{0.57}\text{Al}_{0.43}\text{N}$ is more unstable compared with the $\text{In}_{0.4}\text{Ga}_{0.6}\text{N}$, even though the growth temperature is same for both materials. By using an n- $\text{In}_{0.3}\text{Al}_{0.7}\text{N}$ and p- $\text{In}_{0.2}\text{Ga}_{0.8}\text{N}$ films, a heterojunction has been fabricated on a GaN template for the first time. Figure 16 shows (a) the structure of the fabricated device and (b) the current density-voltage characteristics of the device in the dark and under AM1.5, 100 mW/cm^2 illumination. The thicknesses of the Mg-doped p-InGaN and non-doped n-InAlN layers are 1.2 μm and 0.1 μm , respectively. The device clearly shows photo-response to the AM1.5. As can be seen in Fig. 5, $V_{oc} = 0.25$ V and $J_{sc} = 0.01$ mA/cm^2 are obtained. Such a low J_{sc} seems to be due to the large bandgap and the low quality of the films. The low quality of the InAlN films seems to be also mainly responsible for the low V_{oc} .

6. Summary

The InN-based nitride semiconductor alloys such as InGaN and InAlN are one of a few of the promising materials for multi-junction solar cell, because a band-gap energy from 0.7 to 2.5 eV can be realized by changing only the composition of these alloys. In order to prepare such alloys, MOVPE growth using a horizontal reactor has been applied in this work. It is shown that InGaN films without phase separation and metallic *In* segregation can be grown by optimizing gas flow conditions and substrate position on the susceptor. The *In* composition in InGaN is controlled by growth temperature

and TMI/(TMI+TEG) molar ratio and InGaN films with full composition range are successfully obtained. The Mg-doping behavior and p-type conduction of MOVPE InGaN are also studied using Cp₂Mg as a Mg source. P-type conduction is achieved for InGaN films with In content up to 0.4. A detailed investigation has been also made of the growth behavior of MOVPE InAlN. The InAlN growth using NH₃ and TMA is found to be seriously hindered by the adduct formation based on the parasitic reaction of NH₃ and TMA. By choosing the atmospheric-pressure MOVPE and by optimizing substrate position on the susceptor, a single-crystalline InAlN film with an *In* content from 0.3 to 1 are successfully grown. Based on these achievements, an n-InAlN/p-InGaN hetero-structure is successfully prepared and its photo-response is confirmed for the first time.

REFERENCES

- [1] A. Yamamoto, Md. R. Islam, T.-T. Kang, and A. Hashimoto, *phys. stat. sol. (c)*, **7**, 1309 (2010).
- [2] V. Yu. Davydov, A. A. Klochikhin, V. V. Emtsev, S. V. Ivanov, V. V. Vekshin, F. Bechstedt, J. Furthmuller, H. Harima, A. V. Mudryi, A. Hashimoto, A. Yamamoto, J. Aderhold, J. Graul, and E. E. Haller, *phys. stat. sol. (b)*, **230**, R4 (2002).
- [3] A. G. Bhuiyan, K. Sugita, A. Hashimoto, and A. Yamamoto, *IEEE J. Photovoltaics*, **2**, 276 (2012).
- [4] G. Popovici and H. Morkoc, in: S.J. Pearton (Ed.), "GaN and Related Materials II," Gordon and Breach Science, Netherlands, 2000, pp. 93.
- [5] I. Ho and G.B. Stringfellow, *Appl. Phys. Lett.*, **69**, 2701 (1996).
- [6] T. Nagatomo, T. Kuboyama, H. Minamino, and O. Omoto, *Jpn. J. Appl. Phys.*, **28**, L1334 (1989).
- [7] N. Yoshimoto, T. Matsuoka, T. Sasaki, and A. Katsu, *Appl. Phys. Lett.*, **59**, 2251 (1991).
- [8] E. Iliopoulos, A. Georgakilas, E. Dimakis, A. Adikimenakis, K. Tsagaraki, M. Androulidaki, and N. T. Pelekanos, *phys. stat. sol. (a)*, **203**, 102 (2006).
- [9] W. Terashima, S. B. Che, Y. Ishitani, and A. Yoshikawa, *Jpn. J. Appl. Phys.* **45**, L539 (2006).
- [10] C. Hums, J. Blasing, A. Dadgar, A. Diez, T. Hempel, J. Christen, and A. Krost, *Appl. Phys. Lett.* **90**, 022105 (2007).
- [11] D. G. Zhao, J. J. Zhu, D. S. Jiang, H. Yang, J. W. Liang, X. Y. Li, and H. M. Gong, *J. Cryst. Growth*, **289**, 72 (2006).
- [12] C. Tessarek, S. Figge, T. Aschenbrenner, S. Bley, A. Rosenauer, M. Seyfried, J. Kalden, K. Sebal, J. Gutowski, and D. Hommel, *Phys. Rev. B* **83**, 115316 (2011).
- [13] A. Tabata, L. K. Teles, L. M. R. Scolfaro, J. R. Leite, A. Kharchenko, T. Frey, D. J. As, D. Schikora, K. Lischka, J. Furthmüller, and F. Bechstedt, *Appl. Phys. Lett.*, **80**, 769 (2002).
- [14] B. N. Pantha, J. Li, J. Y. Lin, and H. X. Jiang, *Appl. Phys. Lett.*, **96**, 232105 (2010).
- [15] Nola Li, Shen-jie Wang, Eun-Hyun Park, Zhe Chuan Feng, Hung-Li Tsai, Jer-Ren Yang, and Ian Ferguson, *J. Cryst. Growth*, **311**, 4628 (2009).
- [16] A. Yamamoto, K. Sugita, and A. Hashimoto, *J. Cryst. Growth*, **311**, 4636 (2009).
- [17] M. Horie, K. Sugita, A. Hashimoto, and A. Yamamoto, *Sol. Energy Mater. Sol. Cells*, **93**, 1013 (2009).
- [18] H. Tokunaga, I Waki, A. Yamaguchi, N. Akutsu, and K. Matsumoto, *J. Cryst. Growth*, **189/190** 519 (1998).
- [19] C. Chang, T. Tang, P. Chang, N. Chen, and C. Liang, *Jpn. J. Appl. Phys.* **46**, 2840 (2007).
- [20] Y. Houchin, A. Hashimoto, and A. Yamamoto, *phys. stat. sol. (c)*, **5**, 1571 (2008).

Figure captions

Fig. 1. Relationship between band-gap energy and lattice parameter for typical semiconductor materials. a_z is lattice parameter for diamond-structure or zincblende materials and a_w is a-lattice parameter for wurtzite materials. For nitrides, $\sqrt{2}a_w$ is used for the horizontal axis for the convenience of the combination of nitrides and diamond-structure or zincblende materials.

Fig. 2. X-ray diffraction $2\theta/\omega$ profiles for InGaN grown at a different substrate position on the 150mm-long susceptor (along the gas flow direction) in the horizontal reactor.

Fig. 3. X-ray diffraction $2\theta/\omega$ profiles for $\text{In}_x\text{Ga}_{1-x}\text{N}$ with a different In content x .

Fig. 4. In composition in InGaN grown at a different temperature with a different TMI/(TMI+TEG) molar ratio.

Fig. 5. Tilt fluctuations of InGaN with a different In composition.

Fig. 6. Electron or hole concentration in Mg-doped InGaN as a function of $\text{Cp}_2\text{Mg}/(\text{TEG}+\text{TMI})$ molar ratio.

Fig. 7. Relationship between $\text{Cp}_2\text{Mg}/(\text{TMI}+\text{TEG})$ molar ratio and Mg concentration (measured with SIMS) in grown InGaN.

Fig. 8. Growth pressure dependence of the thickness of deposits and XRD intensity of InAlN peak normalized by that of sapphire substrate.

Fig. 9. Surface morphologies (SEM images) of the deposited materials on sapphire substrate at a different pressure (substrate position on the susceptor: +25mm).

Fig. 10. Substrate position dependence of the thickness of the deposit formed at a different pressure.

Fig. 11. Growth pressure dependence of Al composition in InAlN.

Fig. 12. Substrate position dependence of Al composition in InAlN.

Fig. 13. XRD patterns around (0002)-plane of $\text{In}_x\text{Al}_{1-x}\text{N}$. The samples are grown at a different TMA/(TMA+TMI) molar ratio at the substrate position +25 mm.

Fig. 14. Relationship between TMA/(TMA+TMI) molar ratio in the gas phase and Al content in grown InAlN. Substrate position +25 mm.

Fig. 15. X-ray diffraction spectra for " $\text{In}_{0.57}\text{Al}_{0.43}\text{N}$ on $\text{In}_{0.4}\text{Ga}_{0.6}\text{N}$ " and " $\text{In}_{0.4}\text{Ga}_{0.6}\text{N}$ on $\text{In}_{0.57}\text{Al}_{0.43}\text{N}$ " structures. The insets show the surface morphologies (SEM images) for such samples.

Fig. 16. Schematic drawing of InAlN/InGaN hetero-structure device (a) and current density-voltage characteristics of the device in the dark and under AM1.5 illumination (b).