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A Comparative Study on Metalorganic Vapor Phase Epitaxial InGaN with Intermediate In Compositions Grown on GaN/Sapphire Template and AlN/Si(111) Substrate

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The growth of InGaN with intermediate In compositions on GaN/sapphire template and AlN/Si(111) substrate has been comparatively studied. By using an metalorganic vapor phase epitaxy (MOVPE) system with a horizontal reactor, InGaN films are grown at a temperature of 600–800 °C in the pressure of 150 Torr. By optimizing growth temperature and trimethylindium/(trimethylindium + triethylgallium) molar ratio, single crystalline $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$ with $x = 0$–1 are successfully grown on both substrates. The films grown at a relatively high temperature (≥700 °C) with In compositions of 0.3 or less show phase separation when their thickness exceeds a critical value (0.25–0.4 µm), while the samples grown at 600 °C with In compositions of 0.35–0.5 show no phase separation even if the thickness is increased to 0.7 µm. To evaluate the crystalline quality of grown films, FWHM of X-ray rocking curve (XRC) for InGaN(0002), tilt, is measured. There is no marked difference in tilt data between films grown on GaN/α-$\mathrm{Al_2O_3}$(0001) and AlN/Si(111). For the samples grown at 600 °C with In contents of 0.35–0.5, tilt data are drastically increased and widely scattered suggesting the existence of important unknown parameters that govern crystalline quality of InGaN grown at a relatively low temperature. © 2013 The Japan Society of Applied Physics

1. Introduction

Since the band-gap of InN was found to be around 0.7 eV,[1)] InN-based nitride semiconductor alloys have had much attention as materials for a variety of optical and electronic devices. This is because a wide range of band-gaps, for example from 0.7 to 3.4 eV for InGaN, can be realized by changing only composition of the alloys. Among the III–nitrides, GaN is the most extensively studied material and comparatively has matured, while the lower band-gap InGaN alloys, that are more useful for device application, are still a topic of fundamental research. The difficulties in growing high-quality InGaN materials can be attributed to a number of problems: for instance, the large difference in interatomic spacing between InN and GaN results in a solid phase miscibility gap[2,3)] and the relatively high vapor pressure of InN as compared to the vapor pressure of GaN leading to low indium incorporation in these alloys.[4)] In addition, the difference in the formation enthalpies for InN and GaN causes a strong indium surface segregation on the growth front.[5)] Nevertheless, single crystalline InGaN films with full composition range have been successfully grown by molecular beam epitaxy (MBE).[6)]

The use of conductive Si substrates in InGaN growth, instead of insulating sapphire substrates, is also a subject to be studied. The use of Si substrate will expand the freedom of device design, improve device performance mainly due to the high thermal conductivity of Si, and reduce device costs. For example, the growth of InGaN with an energy gap $E_\mathrm{g} \sim 1.8$ eV on Si is expected to provide a high efficiency two-junction tandem solar cell, because photocurrents generated in the InGaN top cell and the Si bottom cell coincide each other (current matching). Such current matching will result in a power conversion efficiency higher than 30%.[7)] Furthermore, the combination of n-$\mathrm{In_{0.45}Ga_{0.55}N}$ and p-Si has another advantage that a low resistance ohmic contact is formed at their interface.[8)] This means that no additional tunnel junction is necessary to connect the InGaN top cell with the Si bottom cell. Although GaN and InN layers have been grown on Si substrate, the growth of $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$ with $x > 0.1$ on Si remains a challenging task. Recently, we have successfully grown InGaN films with intermediate In compositions without phase separation on AlN/Si(111) substrates,[9,10)] as well as on GaN/$\mathrm{Al_2O_3}$(0001) templates.[11)]

Although InGaN films with intermediate In compositions have been prepared by MBE and metalorganic vapor phase epitaxy (MOVPE) as described above, their crystalline quality is considerably poor. Effects of growth parameters, such as substrate material, lattice mismatch, or growth temperature, on the quality of grown films have not yet been well-understood. Therefore, fundamental research on the growth behavior of InGaN is highly required to get high quality crystals.

In this paper, MOVPE InGaN films with intermediate In compositions are grown on GaN/sapphire template and AlN/Si(111) substrate and their growth behavior and crystalline quality are comparatively studied.

2. Experimental Procedure

The growth of InGaN is carried out using an MOVPE system with a horizontal reactor in the temperature range of 600–800 °C at the pressure of 150 Torr. As sources, trimethylindium (TMI), triethylgallium (TEG), and $\mathrm{NH_3}$ are used. By changing flow rates of TMI and TEG and their molar ratio TMI/(TMI + TEG), InGaN films with full composition range are grown with a growth rate of 0.2–0.25 µm/h. As substrates, α-$\mathrm{Al_2O_3}$(0001), GaN/α-$\mathrm{Al_2O_3}$(0001), and Si(111) are used. Two kinds of Si substrate are prepared; one is p-type Si(111) and the other is n-type Si(111) with a p layer on the surface. The p layer is formed by the B ion implantation [50–10 keV, $(7\text{–}1) \times 10^{12}/\mathrm{cm}^2$] into n-type Si(111) substrate followed by the RTA at 1000 °C. A 100 nm thick AlN layer grown at 1050 °C is used as an interlayer for the growth on Si(111). The composition of grown films is determined by using X-ray diffraction ($2\theta/\omega$) patterns with an assumption that InGaN films are fully relaxed. Full width at half maximum (FWHM) of (0002) X-ray rocking curve (XRC), tilt fluctuation, is also measured to evaluate crystalline quality of grown InGaN.

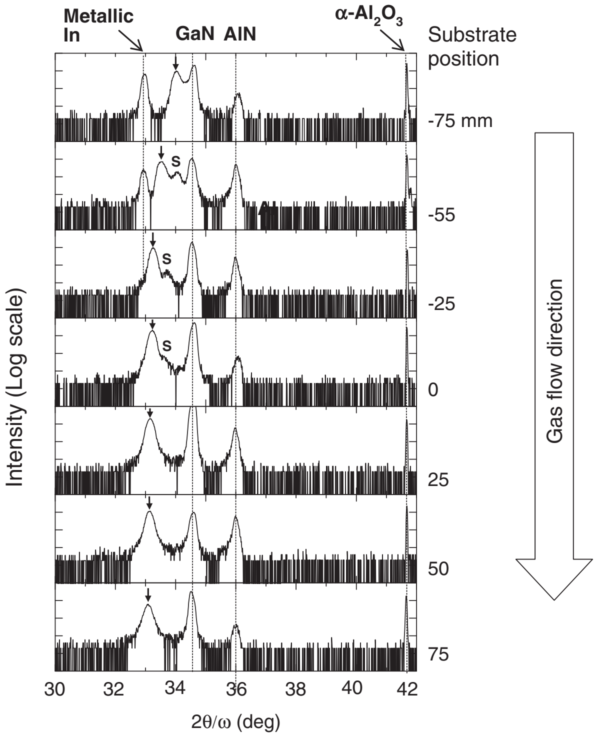

Fig. 1. X-ray diffraction $2\theta/\omega$ profiles for InGaN grown at 700 °C at a different substrate position on the 150-mm-long susceptor (along the gas flow direction) in the horizontal reactor.

3. Results and Discussion

Figure 1 shows the X-ray diffraction $2\theta/\omega$ profiles for films grown at 700 °C at a different substrate position on the 150-mm-long (along the gas flow direction) susceptor in the horizontal reactor. The substrate used here is a GaN/α-Al_2O_3(0001) template with an AlN buffer. As can be seen in Fig. 1, metallic In segregation is fund in films grown near the upstream end of the susceptor. In addition to the main InGaN peak marked by an arrow, a sub-peak denoted by "S" is observed in films grown near the upstream end of the susceptor, indicating the presence of phase separation. The occurrence of the metallic In segregation and the phase separation near the upstream end seems to show that such phenomena are related to unstable gas flow near the upstream end, which is close to the gas mixing zone. From the results shown in Fig. 1, one can see that both phase separation and metallic In segregation can be avoided by choosing the substrate positions near the downstream end of the susceptor. Thus, single-phase InGaN films with full range of composition are successfully grown. The composition is changed by varying growth temperature and TMI/(TMI + TEG) molar ratio. Figure 2 shows the result of composition control. In this study, In composition less than 0.4 is obtained by changing growth temperature with a constant TMI/(TMI + TEG) molar ratio 0.46. The incorporation of In into a grown film is reduced with increasing growth temperature. This seems to be due to the surface segregation and the subsequent evaporation of In from the growing surface. The InGaN films with an In composition more than 0.4 are grown at 600 °C by changing TMI/(TMI + TEG) molar ratio. Thus, InGaN films with full composition range are grown by the MOVPE with a horizontal reactor.

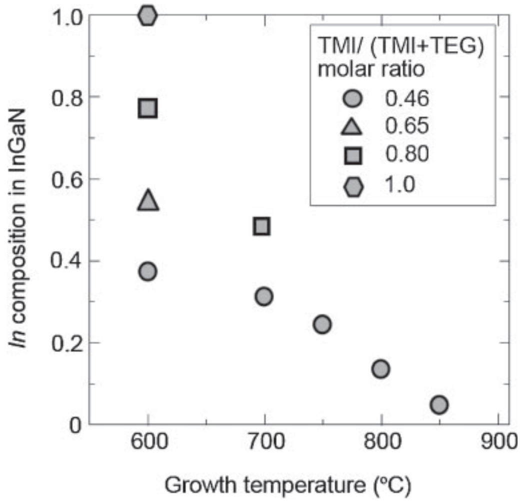

Fig. 2. Composition control of grown InGaN by TMI/(TMI + TEG) molar ratio and growth temperature.

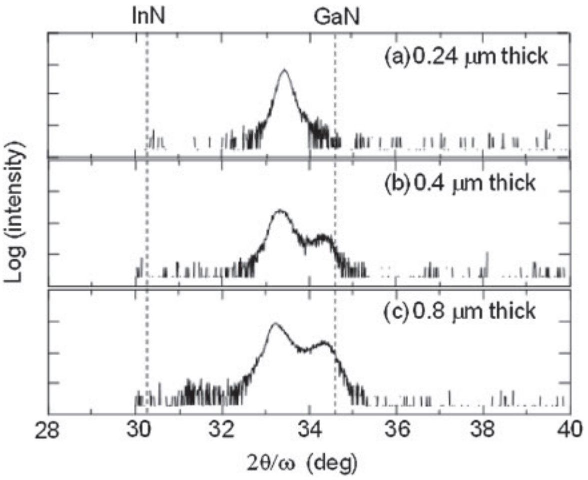

Fig. 3. X-ray diffraction $2\theta/\omega$ profiles for InGaN films grown at 700 °C with a different thickness.

Even for InGaN films grown near the downstream end of the susceptor (see Fig. 1), phase separation is found when their thickness is increased. Figure 3 shows the X-ray diffraction $2\theta/\omega$ profiles for InGaN films grown at 700 °C with a different thickness. The films are grown on α-Al_2O_3(0001) substrates without buffer layer. As can be seen in this figure, a 0.24-μm-thick film has no phase separation. When thickness becomes 0.4 μm or more, on the other hand, phase separation is clearly observed as shown in (b) and (c) in Fig. 3. Figure 4 shows the mapping of phase separation on the plane of thickness vs growth temperature of InGaN. The films grown at a relatively high temperature (700–750 °C) show phase separation when their thickness exceeds a critical value. As can be seen in Fig. 4, critical thickness is smaller for a film grown at a higher temperature with a lower In content. The samples grown at 600 °C show no phase separation even if the thickness is increased to about 0.8 μm. In Fig. 4, results for InGaN films grown on GaN/α-Al_2O_3(0001) template and AlN/Si(111) substrates are also shown. One can see that critical thickness for phase separa-

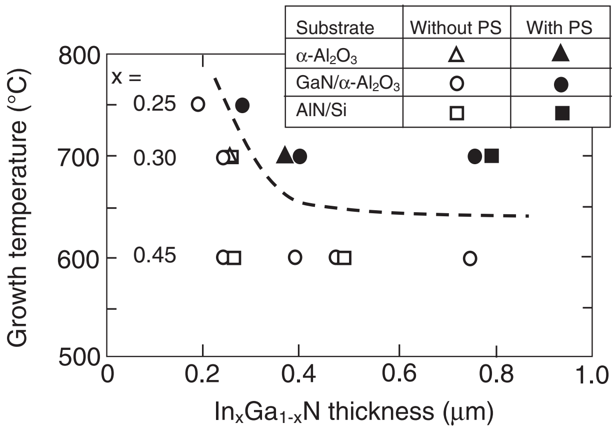

Fig. 4. A mapping of phase separation (PR) on the plane of InGaN thickness vs growth temperature.

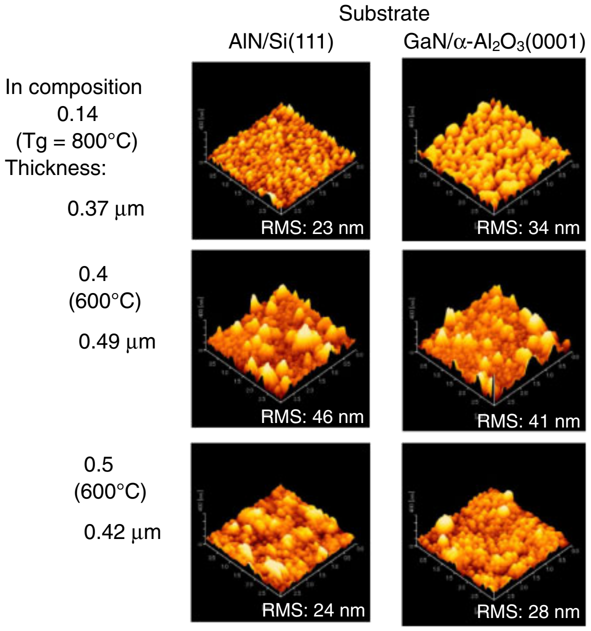

Fig. 5. (Color online) AFM images of InGaN films with a different In composition grown on AlN/Si(111) and GaN/α-Al$_2$O$_3$(0001) substrates.

tion is not dependent on substrate material. Some groups[12,13] have reported that stress in InGaN films can suppress phase separation. Since critical thickness for misfit dislocation generation is estimated to be 5–3 nm for InGaN films with an In content of 0.25–0.45 grown on GaN,[14] all the films with a thickness of 0.2–0.8 µm (shown in Fig. 4) are believed to be fully relaxed. Since Si has a much smaller thermal expansion coefficient compared with GaN and sapphire, residual stress induced in InGaN on Si during the cooling stage after the growth is expected to be different from those in InGaN films grown on GaN template or sapphire. However, no difference is found in critical thickness for phase separation among the three different substrates. In order to understand the results shown in Fig. 4, further investigations will be needed.

Figure 5 shows atomic force microscope (AFM) images for InGaN films grown on AlN/Si(111) and GaN/α-Al$_2$O$_3$(0001) substrates with a different In composition. There is no marked difference in the morphology of the films grown on both substrates. The films with higher In compositions have a rougher surface.

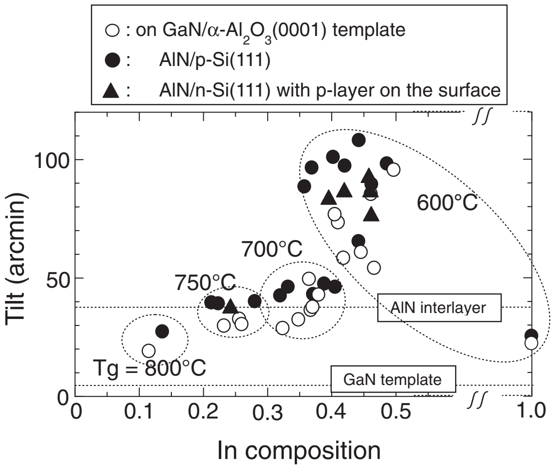

Fig. 6. FWHM of XRC, tilt, for InGaN(0002) diffraction for samples with a different In composition grown on three different substrates at a different temperature (T_g). Data for the underlying GaN template and AlN interlayer are also shown for comparison.

Figure 6 shows the FWHM of XRC, tilt, for InGaN(0002) diffraction for samples with a different In composition. The figure includes the data for InGaN grown on three different substrates at 600–800 °C. Also shown are tilt data for the underlying GaN template and AlN interlayer for comparison. In spite of the relatively large difference in tilt between GaN and AlN underlying layers, no marked difference in tilt between the InGaN films grown on them is observed. It is noted that, for a sample grown at 800 °C, a tilt value better than that of the AlN interlayer is obtained. One can see that better results are obtained for samples grown higher temperature. This is due to the lower In content in such samples, in addition to the higher growth temperature. When the samples with In contents around 0.4 are grown at 600 °C, tilt data are drastically increased and widely scattered. The larger lattice mismatch between the epilayer and the substrate is not responsible for the large and widely-scattered tilt values, because InN grown at 600 °C shows a small tilt value comparable to InGaN films with In content around 0.1. Therefore, the largely scattered data seems to be a characteristic growth behavior of the alloy material. The results in Fig. 6 indicate the existence of important unknown parameters that govern crystalline quality of InGaN grown at a relatively low temperature. One of them may be surface condition of the substrates just before the growth. Some surface preparation of substrate, including the use of a buffer layer, will be able to solve this problem. It is also confirmed that there is no significant difference in tilt data between InGaN films grown on AlN/p-Si(111) and AlN/n-Si(111) with a B-implanted p-layer on the surface. This result suggests a possibility of the realization of an InGaN/Si 2-junction solar cell.

4. Summary

MOVPE InGaN films with intermediate In compositions are grown on GaN/sapphire template and AlN/Si(111) substrate and their growth behavior and crystalline quality are comparatively studied. The films grown at a relatively high temperature (700–750 °C) with In compositions of 0.25–0.3 show phase separation when their thickness exceeds a critical value (0.25–0.4 µm). The critical thickness for phase separation is smaller for a higher growth temperature sample with a lower In content, and is independent on substrate material: α-Al_2O_3(0001), GaN/α-Al_2O_3(0001) and AlN/Si(111). The samples grown at 600 °C having In compositions of 0.4–0.5 show no phase separation even if the thickness is increased to about 0.8 µm. There is no marked difference in tilt data between the films grown on GaN/α-Al_2O_3(0001) and AlN/Si(111). No significant difference in tilt data are also found between InGaN films grown on AlN/p-Si(111) and AlN/n-Si(111) with a B-implanted p-layer on the surface. For the samples grown at 600 °C with In contents around 0.4, tilt data are drastically increased and widely scattered suggesting the existence of important unknown parameters that govern crystalline quality of InGaN grown at a relatively low temperature.

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