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Thick (~1 μm) p-type $In_xGa_{1-x}N$ ($x \sim 0.36$) grown by MOVPE at a low temperature (~570 °C)

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This paper reports the post-growth annealing effects of low-temperature grown Mg-doped InGaN. By using MOVPE, 1 μm-thick Mg-doped $In_xGa_{1-x}N$ ($x \sim 0.36$) films are grown at 570 °C. In order to activate the Mg acceptors, grown samples are treated by the conventional furnace annealing (FA) or the rapid thermal annealing (RTA). In the case of the FA at 650 °C for 20 min, the InGaN film is phase-separated. On the other hand, the RTA at a temperature higher than 700 °C enables us to get p-type samples. By using the RTA at 850 for 20 s, p-type samples with a hole concentration 10^{18}–10^{19} cm^{-3} are successfully obtained without phase separation.

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1 Introduction Direct-band-gap 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, especially, in full-spectrum multi-junction tandem solar cells [1, 2]. Achieving highly conductive p-type InGaN is one of the key issues in bulk InGaN solar cell technologies. As an acceptor impurity for GaN and related alloys, Mg has been widely used. Nakamura et al. [3] reported that Mg-doped MOVPE GaN should be annealed in hydrogen-free atmosphere at a temperature higher than 700 °C in order to remove H atoms from Mg atoms (Mg activation) and then, to achieve a low resistive p-type GaN. A similar annealing is necessary to get a low resistive p-InGaN. In almost all cases, temperatures of Mg activation (T_{act}) for InGaN are lower than those for their growth (T_g) [4–9]. However, it has been still unclear that the preparation of p-InGaN with intermediate In compositions needs T_{act} same as that for p-GaN preparation.

Recently, we have found that $In_xGa_{1-x}N$ ($x = 0.2$–0.4) films show phase separation when their thickness exceeds a critical value [10]. Critical thickness for phase separation is increased with decreasing growth temperature [11]. For example, a 1 μm-thick InGaN can be obtained at a growth temperature 600 °C or less, whereas a film as thin as 0.3 μm shows phase separation when it is grown at 750 °C. Therefore, we need to reduce growth temperature down to 600 °C or less in order to get a thick (~1 μm) InGaN. In such a case, a situation that $T_{act} > T_g$ will arise. This means that the Mg activation annealing has a possibility to bring about phase separation in grown films.

In this paper, we report the annealing effects of low-temperature grown Mg-doped InGaN. Mg-doped $In_{0.36}Ga_{0.64}N$ films are grown at 570 °C by MOVPE and treated by the furnace annealing (FA) or the rapid thermal annealing (RTA). It is found that, by using RTA at around 850 °C, low resistive p-type samples are successfully obtained without phase separation, while the furnace annealing at 650 °C brings about phase separation.

2 Experimental The growth of $In_{0.36}Ga_{0.63}N$ films was conducted using a MOVPE system. TEG, TMI, and NH_3 were used for Ga, In, and N sources, respectively. Cp_2Mg was used for Mg source. Growth temperature and pressure were fixed at 570 °C and 150 Torr, respectively. As substrates, AlN/Si(111) and α-Al_2O_3(0001) were employed. The latter was mainly used to prepare samples for electrical

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characterization. The growth rate of InGaN was about 0.7 μm h. Mg concentration in grown films was measured to be in the range of 10^{19}–10^{20} cm^{-3} by the secondary ion-mass spectrometer (SIMS) analysis. Grown films were annealed in N_2 atmosphere by means of FA or RTA. Electrical characterization was made by using Hall measurements at room temperature. Thermo-voltaic measurement was also employed to define conduction type of Mg-doped samples. The structures of the films were characterized by high resolution X-ray diffraction (HRXRD), and field emission scanning electron microscopy (FESEM). SIMS was also employed to measure impurity contamination levels in grown films.

3 Results and discussion Films of $In_{0.36}Ga_{0.63}N$ have been obtained by employing TMI/(TMI + TEG) molar ratio of 0.4 in the vapor. As reported previously [12], InN content in MOVPE InGaN is constant and is nearly equal to TMI/(TMI + TEG) molar ratio when growth temperature is $\gtrsim$700 °C. Figure 1 shows the X-ray diffraction $2\theta/\omega$ patterns for InGaN layers before and after the FA at 650 °C for 20 min. See Ref. [10] for detailed designation for each peak in Fig. 1. One can see that the annealed sample has new two peaks, metallic In-Ga and GaN-rich InGaN, in addition to the epitaxial InGaN. The emergence of these two new peaks is a typical result of phase separation of MOVPE InGaN. The metallic In-Ga is formed by the thermal decomposition of the InN-rich InGaN. Figure 2 shows the surface and cross-sectional FESEM views of InGaN layers before and after the FA at 650 °C for 20 min. Phase separation of MOVPE InGaN is accompanied with the formation of porous regions in the middle region of the film, and of metal In-Ga droplets on the surface [10]. Such typical features for phase separation are clearly seen in Fig. 2. On the contrary, phase separation can be suppressed for the RTA samples. As shown in Figs. 3 and 4, no additional peaks in the X-ray diffraction profiles and no porous regions in the cross-sectional view are found even for $T_{act} = 850$ °C.

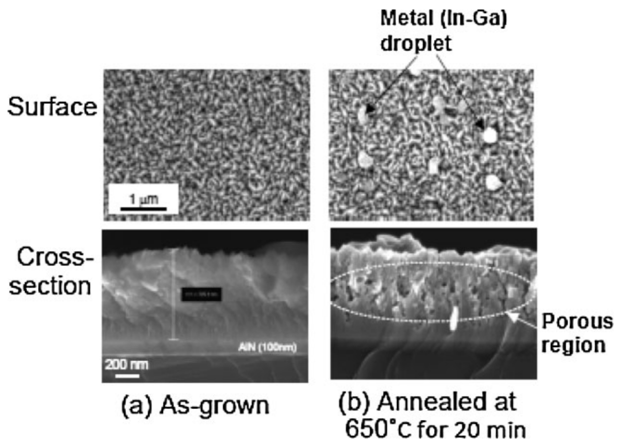

Figure 2 Surface and cross-sectional FESEM views of InGaN layers before and after the FA at 650 °C for 20 min.

Thus, it has been confirmed that the RTA even at 850 °C does not bring about phase separation in thick (~1 μm) InGaN. Then, electrical properties of Mg-doped InGaN after RTA are studied. All samples for this purpose were grown on α-Al_2O_3(0001) substrates. This is due to the fact that Hall measurement data for InGaN grown on AlN/p-Si substrates are somewhat affected by the presence of the conductive Si substrate, in spite of the presence of the AlN interlayer (100 nm thick). It has been also confirmed that no difference in the phase separation behavior of MOVPE InGaN is found between AlN/p-Si and α-Al_2O_3(0001) substrates [11]. Figure 5 shows the annealing temperature T_{act} dependence

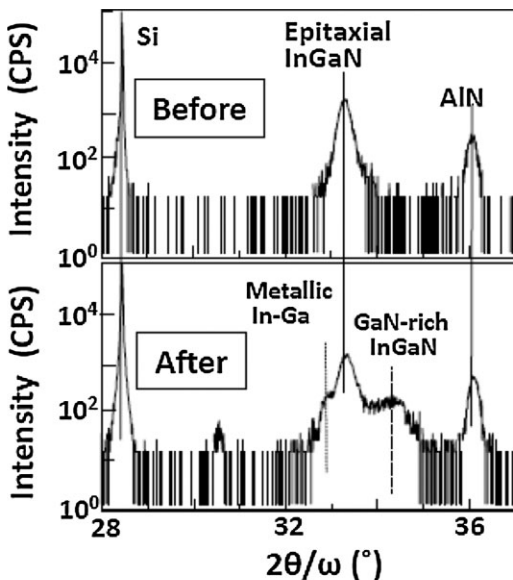

Figure 1 X-ray diffraction $2\theta/\omega$ patterns for InGaN layers before and after the FA at 650 °C for 20 min.

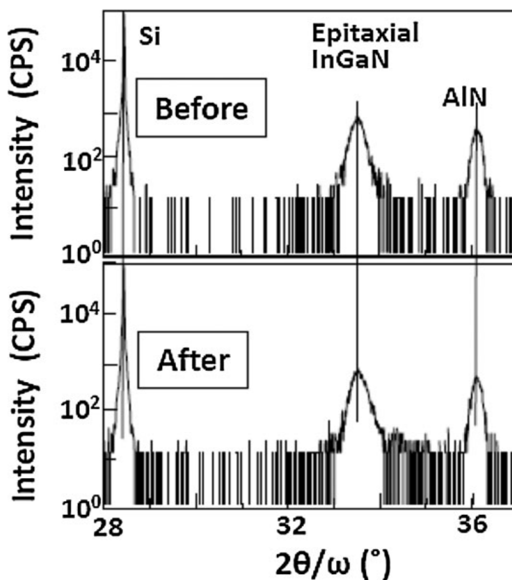

Figure 3 X-ray diffraction $2\theta/\omega$ patterns for InGaN layers before and after the RTA at 850 °C for 20 s.

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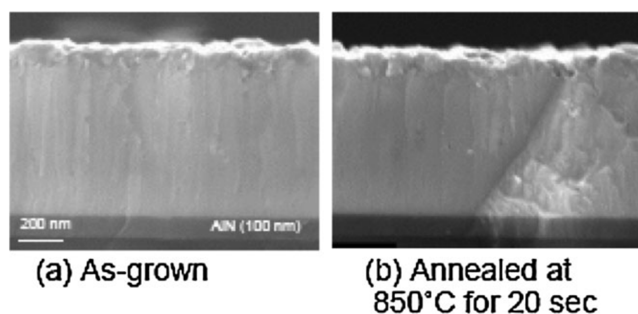

Figure 4 Cross-sectional FESEM views of InGaN layers before and after the RTA at 850 °C for 20 s.

of carrier concentration CC and Hall mobility μ for RTA samples. In this figure, t_{act} shows the duration for RTA. One can see that CC is markedly increased for $T_{act} > 700$ °C, and reached 10^{18}–10^{19} cm^{-3} at $T_{act} = 850$ °C. On the other hand, μ is markedly decreased for $T_{act} > 700$ °C, and reached 0.1–0.01 cm^2 Vs at $T_{act} = 850$ °C. Two methods are employed to judge conduction type of the annealed samples. One is Hall measurement and the other is thermo-voltaic effect. For samples with $T_{act} < 700$ °C, both methods are difficult to define their conduction type, due to very high resistivity of those samples. For samples with $T_{act} > 700$ °C, their conduction are proved to be p-type by the thermo-voltaic measurement. For samples with $T_{act} = 850$ °C, the Hall measurement also defines the conduction to be p-type. As can be seen in Fig. 5, the results for the relatively long (300 s) time annealing are not so different from those for the 30 s annealing. Therefore, the annealing time 10–300 s seems not to be so critical in the present case. Thus, p-type $In_{0.36}Ga_{0.63}N$ films with a hole concentration 10^{18}–10^{19} cm^{-3} are successfully obtained without phase separation by the RTA at around 850 °C. This is an important progress in realizing an InGaN/Si tandem solar cell. Chang et al. [6] studied the Mg doping of 550 °C-grown $In_xGa_{1-x}N$ ($x = 0.2$–1). However, those samples still showed n-type conduction after the activation annealing. The reason for this was not clarified.

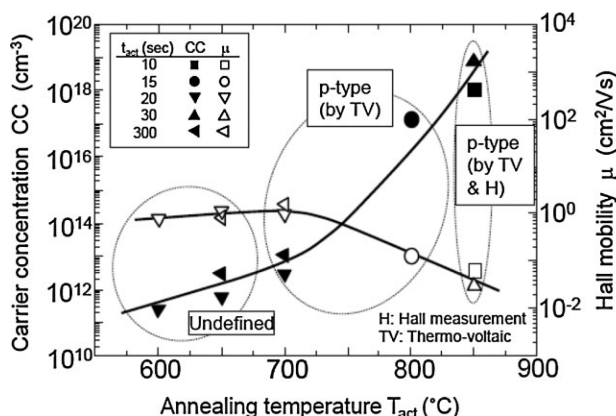

Figure 5 Annealing temperature T_{act} dependence of carrier concentration CC and Hall mobility μ for RTA samples. t_{act} in the figure is duration for RTA.

Compared with the electrical data previously reported for InGaN grown at a temperature higher than 700 °C with a similar InN content [8], Hall mobilities of 0.1–0.01 cm^2 Vs obtained in the present study (Fig. 5) are lower by more than one order of magnitude, although comparable hole concentrations are obtained. A high carbon contamination level of 10^{19}–10^{20} cm^{-3} (revealed by SIMS analysis) in the present samples seems to contribute to such a low mobility. It is reasonable to consider that defect density in the low-temperature grown samples is higher than that for a higher-temperature grown sample. Regarding the very low Hall mobilities, investigations from the viewpoint of hopping conduction or percolation path [13] may be also needed.

In order to realize an InGaN/Si tandem cell with a high performance, it is essential to improve electrical properties of low-temperature grown InGaN by improving their crystalline quality. Optimization of Mg doping level is also important to improve the crystalline quality of p-InGaN.

4 Summary The post-growth annealing effects of low-temperature grown Mg-doped InGaN has been studied. By using MOVPE, 1 μm-thick Mg-doped $In_xGa_{1-x}N$ ($x \sim 0.36$) films are grown at a low temperature (~570 °C). In order to activate Mg acceptors, grown samples are treated by the FA or the RTA. In the case of the FA at 650 °C for 20 min, the InGaN film is phase-separated. On the other hand, the RTA at a temperature higher than 700 °C enables us to get p-type samples. By using the RTA at 850 for 20 s, p-type samples with a hole concentration 10^{18}–10^{19} cm^{-3} are successfully obtained without phase separation. Hall mobility of 0.1–0.01 cm^2 Vs obtained in the present study is considerably low compared with that for InGaN grown at a temperature higher than 700 °C with a similar InN content. This may be due to the high carbon contamination and high defect density. The improvement of crystalline quality of low-temperature grown InGaN by reducing both carbon contamination level and defect density will be needed to fabricate an InGaN/Si tandem cell with a high performance.

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References

[1] A. Yamamoto, Md. R. Islam, T-T. Kang, and A. Hashimoto, Phys. Status Solidi C **7**, 1309 (2010).
[2] A. G. Bhuiyan, K. Sugita, A. Hashimoto, and A. Yamamoto, IEEE J. Photovolt. **2**, 276 (2012).
[3] S. Nakakumra, T. Mukai, M. Senoh, and N. Iwasa, Jpn. J. Appl. Phys. **31**, L139 (1992).
[4] T. Makimoto, K. Kumakura, and N. Kobayashi, Appl. Phys. Lett. **79**, 380 (2001).

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[5] K. Kumakura, T. Makimoto, and N. Kobayashi, J. Appl. Phys. **93**, 3370 (2003).
[6] C.-A. Chang, T.-Y. Tang, P.-H. Chang, N.-C. Chen, and C.-T. Liang, Jpn. J. Appl. Phys. **46**, 2840 (2007).
[7] H. Wang, J.-H. Zho, D.-S. Jiang, J.-J. Zhu, D.-G. Zhao, Z.-S. Liu, S.-M. Zhang, and H. Yang, Chin. Phys. Lett. **26**, 107302 (2009).
[8] B. N. Pantha, A. Sedhain, J. Ki, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **95**, 261904 (2009).
[9] Ö. Tuna, H. Hahn, H. Kalisch, C. Giesen, A. Vescan, M. V. Rzheutski, V. N. Pavlovski, E. V. Lutseko, G. P. Yablonski, and M. Heuken, J. Cryst. Growth **370**, 2 (2013).
[10] A. Yamamoto, T. M. Hasan, A. Mihara, N. Narita, N. Shigekawa, and M. Kuzuhara, Appl. Phys. Express **7**, 035502 (2014).
[11] A. Yamamoto, A. Mihara, T. M. Hasan, N. Narita, N. Shigekawa, and M. Kuzuhara, 14th International Workshop on Nitride Semiconductors, Aug. 25–29, 2014, Wrocław, Poland, WeGO3 (submitted to J. Cryst. Growth).
[12] A. Yamamoto, K. Sugita, A. G. Bhuiyan, A. Hashimoto, and N. Narita, Mater. Renew. Sustain. Energy **2**, 10 (2013).
[13] K. Billen, M. J. Kelly, R. M. Gwilliam, S. Hutchinson, L. Eaves, M. Henini, and T. J. Foster, Semicond. Sci. Technol. **12**, 1271 (1997).

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