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Effects of growth pressure on AlGaN and Mg-doped GaN grown using multiwafer metal organic vapor phase epitaxy system

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Abstract

We investigated the effects of growth pressure on AlGaN growth and material properties of GaN:Mg using a multiwafer metal organic vapor phase epitaxy (MOVPE) reactor. We developed a three-layer laminar flow gas injection reactor to control the pre-reaction between adducts in GaN MOVPE. Using this reactor, we could grow $Al_{0.09}Ga_{0.91}N$ at a growth rate of 0.8 μm/h, and GaN:Mg with a carrier concentration of $1.4\times10^{18}\,cm^{-3}$ at a growth rate of 3.5 μm/h at atmospheric pressure. While we grew $Al_{0.24}Ga_{0.76}N$ at a growth rate of 0.8 μm/h at 300 Torr, we found that the hole carrier concentration of GaN:Mg grown at 300 Torr is more than one order of magnitude lower than that of GaN:Mg grown at atmospheric pressure.

Keywords: A1. Parasitic reaction; A1. Mg doping; A2. Atmospheric pressure growth; A3. Metalorganic vapor phase epitaxy; B1. AlGaN; B1. GaN

1. Introduction

Growth pressure equal to or higher than atmospheric pressure is important in obtaining high-quality GaN and related alloys. The impact of high growth pressure on GaN metal organic vapor phase epitaxy (MOVPE) can be summarized as smaller threading dislocation density (TDD) in the film on a sapphire substrate [1], higher Mg activation efficiency [2], and better InGaN

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quantum well (QW) with a more coherent interface [3] compared with those in the case of low-pressure growth. However, parasitic reaction between trimethylaluminum (TMA) and ammonia (NH_3) impedes a uniform and high aluminum content AlGaN growth at high growth pressures. To date, the design of a large-scale atmospheric pressure MOVPE (AP-MOVPE) reactor has been very difficult. Therefore, from a practical viewpoint, it is important to understand the effects of growth pressure on material properties and the parasitic reaction on the growth in light of the tradeoff between the two. Thus far, the favorable growth condition of AlGaN is not compatible with that of Mg-doped GaN. Our challenge is to realize larger scale MOVPE reactors to grow nitride compounds at atmospheric pressure. To this end, we have been studying vapor phase reaction of organometallics and NH_3 experimentally and by quantum chemical analysis [4,5]. To the best of our knowledge, there are no reports on the effects of growth pressure on both AlGaN and Mg-doped GaN in a pressure range from 300 to 760 Torr in the same reactor, at which pressure, significant parasitic reactions between organometals and NH_3 begin to occur. In this study, we investigated the effects of growth pressure on AlGaN and Mg-doped GaN using a horizontal reactor with a 180-mm-diameter platen having a three-layer gas injection in a pressure range from 300 to 760 Torr.

2. Experimental procedure

Fig. 1 shows a schematic drawing of our horizontal reactor. We employed a three-layer laminar flow gas injection [6,7]. As shown in Fig. 1, organometallics and NH_3 are separately injected and mixed together to form an adduct $(CH_3)_3M:NH_3$ by molecular diffusion. Under a typical flow condition, the spacing between the gas separators and their position are designed so that organometallics would diffuse laterally to the flow direction and would reach the substrate surface at the inlet of the growth region. Thereby, the adduct $(CH_3)_3M:NH_3$ would be transported to the growth region by keeping the main adduct flow isolated from the heated reactor wall. A flow liner made of quartz was installed in the stainless steel chamber. A 180-mm-diameter carbon susceptor coated with SiC can be rotated on one axis and is heated radiatively using a resistance heater.

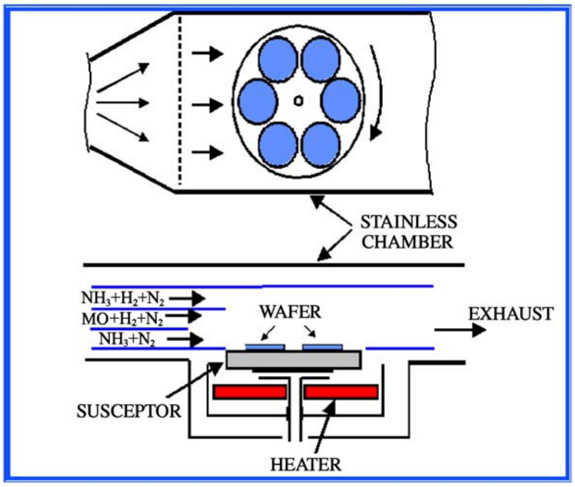

Fig. 1. The reactor with the three-layered laminar flow gas injection is shown.

NH_3, trimethylgallium (TMG), trimethylaluminum (TMA) and bis-cyclopenta-dienyl-magnesium (Cp_2Mg) were used as precursors, and hydrogen and nitrogen were used as carrier gas. Sapphire with (0 0 0 1) orientation was used as a substrate. Substrates were thermally treated in H_2 at 1100 °C, followed by a low-temperature GaN buffer layer growth of 25 nm thickness at 500 °C. Then, 3.0 μm thick undoped GaN was grown at atmospheric pressure for all samples. On top of the thick GaN films, Mg-doped GaN films or AlGaN films were grown at various growth pressures. The growth pressure for these films was varied in the range from 76 to 760 Torr with a constant flow rate for the carrier gas, organometallics and NH_3. The Cp_2Mg/TMG input ratio was varied in the range from 3×10^{-4} to 3×10^{-3} for Mg-doped GaN, and that of TMA/(TMG + TMA) was varied between 0.091 and 0.3 for AlGaN. The total input flow rate of organometallics for AlGaN was ~110 μmol/min.

Post-growth thermal annealing was performed at 800 °C for 10 min to activate p-type GaN. The Mg concentration in the solid was measured by secondary-ion mass spectroscopy (SIMS) and Hall measurements were performed by the van der Pauw method at room temperature. The aluminum composition of the AlGaN film was evaluated by X-ray diffractometry (XRD). The lattice relaxation in the AlGaN film was estimated to be within two to three percent by a reciprocal lattice mapping measurement. Thus, the Al composition incorporated in the solid phase was determined by assuming a complete coherent growth through these experiments.

3. Results and discussion

Fig. 2 shows Hall carrier concentration and Mg concentration in the solid as a function of input Cp_2Mg/TMG ratio. The highest Hall carrier concentration of $1.5 \times 10^{18}\,cm^{-3}$ with a hole mobility of $3.0\,cm^2/V\,s$ was obtained at an input Cp_2Mg/TMG ratio of 1.5×10^{-3} while the Mg concentration in the solid continuously increased with Cp_2Mg supply. This result indicates that Mg is not incorporated in the exact acceptor site under a heavy doping condition. Fig. 3 shows the growth pressure dependence of hole carrier concentration with a constant Cp_2Mg/TMG ratio of 1.5×10^{-3}. With decreasing growth pressure, the hole carrier concentration decreased, and eventually, the electronic conductivity changed to n-type at 76 Torr even after post-growth annealing, while the incorporated Mg concentration was constant under all growth pressure conditions. In the low-temperature photoluminescence measurements, the neutral donor exciton lines for the samples grown at 300 Torr were several times larger than those for the samples grown at 760 Torr, indicating that the compensation ratio increased with decreasing growth pressure. The origin of the donor is considered a nitrogen vacancy [8,9]. However, it is not very clear whether n-type defect is responsible for the smaller hole concentration. Under the present growth condition, the growth rate of GaN:Mg of 3.5 μm/h was approximately one order of magnitude higher than those shown in other reports. By optimizing the growth condition, the hole carrier concentration at low-pressure growth could be improved. Nevertheless, it is apparent that a higher growth pressure is preferable for

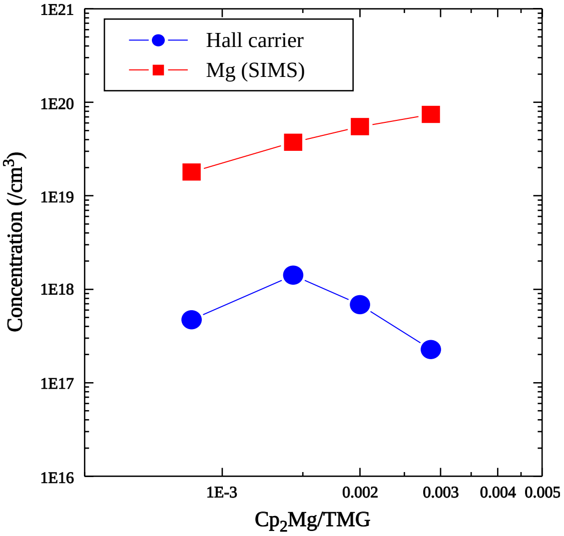

Fig. 2. Hole carrier concentration and the atomic Mg concentration in the solid for Mg-doped GaN are plotted as a function of input Cp_2Mg/TMG ratio.

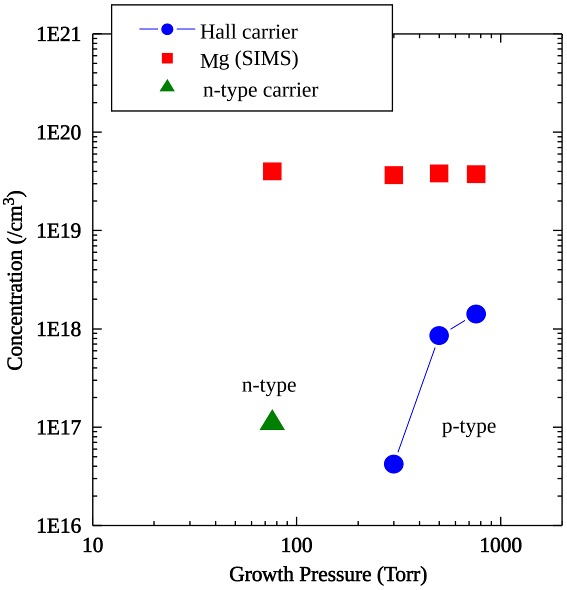

Fig. 3. Hole carrier concentration and the atomic Mg concentration in the solid for Mg-doped GaN are shown as a function of growth pressure.

GaN:Mg growth, if you consider the requirement of a smaller thermal budget on InGaN multi-quantum well (MQW) when a p-type cladding layer is grown on top of the MQW. A promising pressure range for p-type GaN may exist at more than 500 Torr.

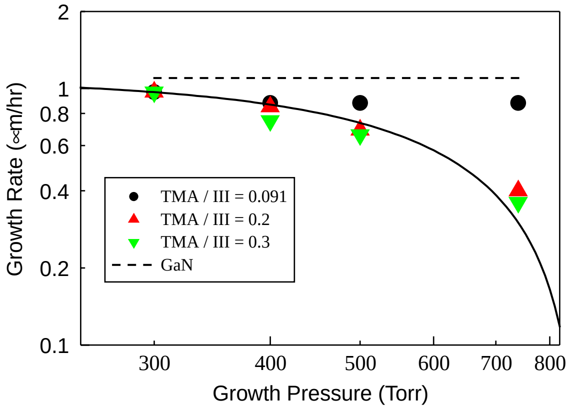

Fig. 4. AlGaN growth rate is shown as a function of growth pressure for various input TMA/(TMA + TMG) ratios.

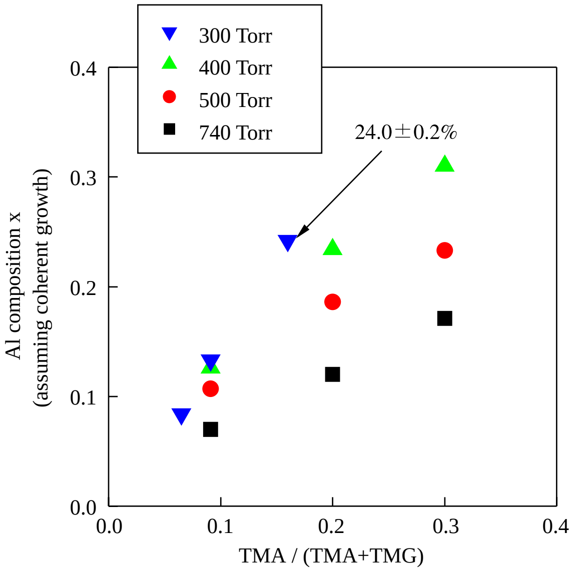

Fig. 5. Al composition in the solid is shown as a function of input TMA/(TMA + TMG) ratio for various growth pressures. Each data point corresponds to the one in Fig. 4.

Fig. 4 shows the dependence of the AlGaN growth rate on the growth pressure. The growth rate of GaN is also shown as a broken line. The total mole flow rate of (TMA + TMG) was kept constant for all the samples, and only the Al partial pressure was changed between zero and 0.3. The growth rate was nearly constant as a function of growth pressure at an input TMA/(TMA + TMG) = 0.091, at which Al composition incorporated into the solid was 0.08. The growth rate of 0.88 μm/h was obtained under this TMA flow condition. It seems that the effect of a parasitic reaction is small for this TMA supply rate. This is the result of the suppression of parasitic reaction using a three-layer laminar flow gas injection. However, the growth rate of AlGaN of an input TMA/(TMA + TMG) of 0.2 and 0.3 showed a steep decrease of growth rate at the growth pressure more than 500 Torr. This comes from a parasitic reaction of TMA and NH_3. When there is a parasitic reaction, aluminum composition of AlGaN decreases as well as a growth rate. The aluminum composition for each growth pressure is shown in Fig. 5. Each data point in Fig. 5 corresponds to that of Fig. 4, which has a same input TMA/(TMA + TMG) ratio. In Fig. 5, aluminum composition increases proportionally with the TMA partial pressure at each growth pressure. Thereby, the Al incorporation efficiency increased as the growth pressure decreased. At the growth pressure below 400 Torr, the Al composition in the solid phase is larger than the input ratio in the vapor phase, while the Al incorporation efficiency is less than one for AlGaN grown at 740 Torr. The result at 740 Torr can be explained by the vapor phase reaction of TMA and NH_3. However, a result at low pressure is not apparent. One possible reason for this would be the insufficient reaction time for TMG to decompose at low pressure. Quantum chemical study suggests that elimination of methane from TMA is much easier than that from TMG [4]. Therefore, if the parasitic reaction to form oligomer is suppressed, Al is more easily incorporated than Ga at a high-speed flow condition of more than 3 m/s. Following this explanation, the GaN growth rate should decrease as the growth pressure decreases. However, the GaN growth rate was almost constant for the growth pressure studied here. This can be

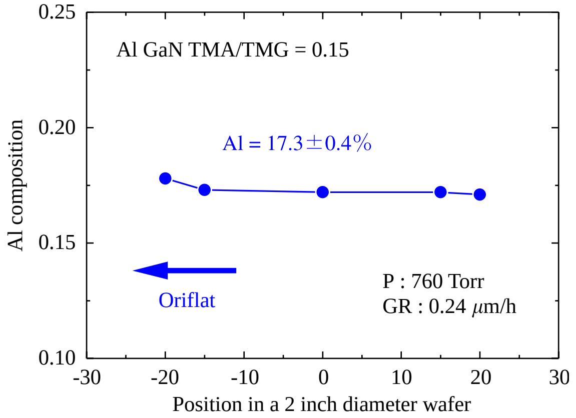

Fig. 6. Al composition uniformity of $Al_{0.17}Ga_{0.83}N$ grown at atmospheric pressure is shown. The film was grown at 0.24 μm/h.

explained by the difference in the growth conditions of GaN and AlGaN. For GaN, the carrier gas flow rate was 70% that for AlGaN and the growth temperature was 1150 °C, which is higher than 1050 °C used for AlGaN. A higher Al concentration can also be obtained by reducing the growth rate. Fig. 6 shows the result of Al composition uniformity of $Al_{0.17}Ga_{0.83}N$ grown at a growth rate of 0.24 μm/h at atmospheric pressure. The uniformity of Al composition was 17.3 ± 0.4% over a 2-in-diameter wafer placed at one of the six identical pockets on a 180-mm-diameter susceptor. The Al composition uniformity of $Al_{0.24}Ga_{0.76}N$ grown at 300 Torr was 24 ± 0.2% over a 2-in-diameter wafer.

4. Conclusion

The effects of growth pressure on AlGaN and Mg-doped GaN grown using the multiwafer MOVPE system with a 180-mm-diameter platen were investigated. GaN:Mg with a carrier concentration of $1.4 \times 10^{18}\,cm^{-3}$ was grown at 3.5 μm/h at atmospheric pressure. The hole carrier concentration decreased as the growth pressure decreased. A reasonable activation of Mg was realized at a growth pressure higher than 500 Torr under the growth conditions used here. $Al_{0.08}Ga_{0.92}N$ with a composition variation of 8 ± 0.5% was grown at 0.8 μm/h at atmospheric pressure by improving the design of the reactor. $Al_{0.17}Ga_{0.83}N$ with Al-incorporated uniformity of 17 ± 0.4% was also obtained by reducing the AlGaN growth rate to 0.24 μm/h at atmospheric pressure. Judging from the present results, entire LED and laser structures with wavelength from near UV to visible region could be grown at atmospheric pressure using a 180-mm-diameter susceptor horizontal reactor. On the other hand, electron devices or DUV optical devices, which require AlGaN having more than 30% Al, may need a low-pressure growth at 300 Torr or less. Further studies on the relationship between the quality of materials and growth condition are required for the optimal design of a large-scale GaN MOVPE reactor.

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