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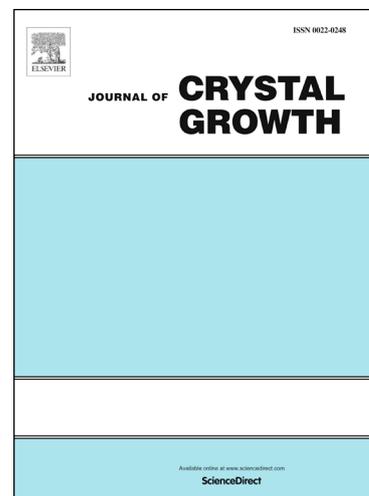
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Influence of polymerization among Al- and Ga-containing molecules on growth rate and Al content in AlGaN

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Abstract

AlGaN metalorganic vapor-phase epitaxial growth simulation in a TMAI/TMGa/NH₃/H₂ system was studied to explain its growth rate and Al content. We proposed three kinds of Al- and Ga-containing polymers in this system. By using those polymers, we got good agreements in pressure, TMAI/(TMAI+TMGa) inlet ratio, and temperature dependences of AlGaN growth rate and its Al content between simulations and experiments, even at pressures higher than 40 kPa. Our results showed that the formation of these polymers is enhanced under higher pressures. The simulation considering those polymers could explain the linearity in the TMAI/(TMAI+TMGa) inlet ratio dependences of growth rate and Al content at lower pressure and their non-linearity at higher pressure.

Keywords 6

A1. Computer simulation, A1. Growth models, A3. Metalorganic vapor phase epitaxy,
B1. Nitrides, B2. Semiconducting III-V materials, B3. Light emitting diodes

1. Introduction

The bandgap of the $\text{Al}_x\text{Ga}_{1-x}\text{N}$ system covers from 3.42 eV to 6.04 eV [1, 2] as a function of Al content from zero to unity. AlGaN materials are useful for ultraviolet (UV) LEDs and laser diodes as a host material [3-9], visible LEDs as AlGaN barriers in the active region [10-14], artificial photosynthesizers as photoanodes [15-17], and electronic devices [18-20]. Metalorganic vapor-phase epitaxial (MOVPE) growth of AlGaN is unique. AlN growth rate has a linear dependence on the flow rate of trimethyl aluminum (TMAI) [21]. However, the AlGaN growth rate decreases with the TMAI flow rate under the constant flow of trimethyl gallium (TMGa) [21-23]. That decline in AlGaN growth rate indicates that additional polymerizations among Al- and Ga-containing molecules occurs in the MOVPE process using a TMAI/TMGa/ NH_3/H_2 system, and those polymers prevent the AlGaN growth.

There are experimental and theoretical works to understand GaN, AlN, and AlGaN MOVPE [24-27]. Creighton et al., have observed the formation of gas-phase nanoparticles during AlN and GaN MOVPE [27]. The introduction of the polymer formation in AlN and GaN MOVPE simulations exhibits good agreements with the experimental results [28-30]. The growth of polymers would make them to have a nanoparticle size eventually. There are some successful simulations of AlGaN MOVPE using a low-pressure rotating-disk or showerhead reactor [31-33]. They considered Al- and Ga-containing particles to calculate the AlGaN growth rate and its composition. However, the possible polymers were not shown in those pieces of literature. Also, they simulated AlGaN MOVPE only at low pressures. AlGaN barrier and electron-blocking layers grown by atmospheric pressure MOVPE are used for blue, green, amber, and red InGaN-based LEDs [10-14]. Therefore, the understanding of AlGaN MOVPE at higher pressure is valuable to grow those device structures.

In this paper, we study additional polymers possibly included in AlGaN MOVPE. We will also examine the effectiveness of the proposed polymer formation from experimental and

numerical comparisons of AlGa_N MOVPE under various growth conditions of pressure, temperature, and TMAI / (TMAI + TMGa) inlet ratio.

2. Simulation and experiment

2.1 Experimental MOVPE growth of AlGa_N

We used a single-wafer horizontal MOVPE reactor as shown in Fig. 1. The flow-channel is made of quartz GE124 (GE Quartz, USA). Precursors were TMGa, TMAI, and ammonia (NH₃). The carrier gas was hydrogen. Substrates were 2-inch c-plane sapphire. The typical growth temperature was 1025°C. The growth temperature was calibrated by the melting point of gold on the substrate surface. The values of growth temperature and growth rate hereafter are those at the center of a substrate because in our machine the temperature decreases in the last 5 mm of the edge area of the substrate. The set of substrate/quartz tray/susceptor can rotate together, but we did not turn the substrate for the comparison with computational results since the substrate rotation is not included in our simulation model.

The gas-flow conditions of the experiments for pressure and temperature dependences were TMAI=47.3 μmol/min, TMGa=52.7 μmol/min, NH₃=4.5 slm, and H₂=4.6 slm. To study pressure dependence, we adjusted the conductance valve to control pressure from 10 kPa to 100 kPa. In the case of growth temperature dependence, the temperature was set among 1000–1150°C under 10 kPa. The value of 1150°C is the maximum temperature of our system to avoid the softening of quartz parts. To change the TMAI/(TMAI+TMGa) ratio from 0 to 1, we varied TMAI and TMGa from 0 μmol/min to 100 μmol/min under the constant total flow of TMAI+TMGa=100 μmol/min.

The sample structure was unintentionally-doped (uid) AlGa_N (ca. 500 nm)/uid-GaN (500 nm)/low-temperature (LT=525°C) GaN buffer/c-sapphire. Their Al contents and thicknesses

were evaluated at the center of wafers by x-ray reciprocal space mapping and a scanning electron microscope, respectively.

2.2 Simulation model

The computational fluid dynamics (CFD) code we used was CFD-ACE+ (ESI, France) [34] with the nitride-MOVPE database (Wave Front, Japan) [35]. This database is based on our previous works [28-30, 36]. The code cannot consider strain in nitride layers. We performed two-dimensional (2D) simulations at steady state. The geometry of the 2D reactor is the same as the experimental setup shown in Fig. 1. There was a small leakage of the precursors from the 2-mm spaces before and after the quartz tray both in experiment and simulation. We adopted the thermal radiation and absorption spectra from the quartz (GE124) parts measured experimentally at elevated temperatures [36]. Our simulation has considered the imperfect thermal contacts among the sapphire substrate, the quartz tray, and the susceptor by considering some spaces. We set 8.5 μm as the space between the substrate and the tray. Such spacing comes from the difference of the maximum and minimum surface heights in a 500- μm length of the finely grounded backside of a sapphire substrate measured by an alpha-step (KLA-Tencor, USA). The spacing was filled with hydrogen gas which was used as the carrier gas during growth. The hydrogen gas in the space acts as a thermal conductor. Also, thermal radiation and absorption in both sides were considered. Figure 1 shows the temperature distribution simulated under the growth conditions at 1025°C and 40 kPa with TMGa, TMAI, and NH_3 . The outside of the flow channel both in simulation and experiment was filled with nitrogen gas.

3. Results and discussion

We tried to find out the reactive molecules forming Al- and Ga-containing polymers in AlGaN MOVPE using a TMAI/TMGa/NH₃/H₂ system by simulation. We assumed no polymerization among Al- and Ga-containing molecules in this AlGaN MOVPE simulation. Such assumption means that the gas-phase reactions are the simple addition of the reactions occurring in the TMAI/NH₃/H₂ and TMGa/NH₃/H₂ systems. We studied the spatial distributions of reactive molecules under the growth conditions of temperature 1025°C, and pressure 40 kPa. Figure 2 shows the spatial distributions of the reactive molecules such as MMGaNH (monomethyl gallium-ammonia monohydride), MMAINH (monomethyl aluminum-ammonia monohydride), Ga-N, and Al-N. It should be noted that the spatial distributions of those species have similar shapes than part of the temperature distribution shown in Fig. 1. MMGaNH molecules exist only at a temperature around 350°C, then decomposes into Ga-N molecules with CH₄ emissions at around 450°C [28]. Ga-N molecules are reactive, and its distribution is spatially wide. In the case of the TMAI/NH₃/H₂ system, reactive molecules of MMAINH and Al-N are created at around 900°C and 1000°C, respectively. These molecules exist widely in the space above the substrate.

Polymerization happens when reactive molecules exist in the same space. Figure 2 shows that the spatial distributions of Ga-N, MMAINH, and Al-N overlap each other in some regions. Thus, these reactive species have a probability of forming Al- and Ga-containing polymers. MMGaNH molecules will not contribute significantly to the formation of Al- and Ga-containing polymers given their small spatial overlapping with the other reactive molecules. Therefore, the possible combinations of Al- and Ga-containing polymers will be mainly three kinds: [MMAINH]_i-[Ga-N]_n, [Al-N]_m-[Ga-N]_n, and [MMAINH]_i-[Al-N]_m-[Ga-N]_n. Figure 3 shows the schematic reaction pathways for AlGaN MOVPE. Temperature becomes higher close to the growth surface. AlGaN growth consists of two paths of AlN and GaN growth. On the way to the growth region, larger molecules are decomposed, and the reactive molecules are generated. At the same time, each

reactive molecule forms a different polymer by itself as shown in Fig. 3. Therefore, we considered the polymers of $[\text{DMAINH}_2]_n$, $[\text{MMAINH}]_n$, $[\text{Al-N}]_n$ and their Ga-related ones. The Al- and Ga-containing polymers formed $[\text{MMAINH}]_l\text{-}[\text{Ga-N}]_n$, $[\text{MMAINH}]_l\text{-}[\text{Al-N}]_m\text{-}[\text{Ga-N}]_n$, then $[\text{Al-N}]_m\text{-}[\text{Ga-N}]_n$ as they approach the substrate. The total number of $l+m+n$ was limited by seven in our calculation due to our computer processing limitation. We considered their reverse reactions (decompositions) until $l+m+n \leq 3$ and assumed that polymers would not decompose in the case of $l+m+n \geq 4$. Our simulation includes GaN crystal decomposition, but no AlN decomposition. More details of reactions in the $\text{TMGa}/\text{NH}_3/\text{H}_2$ and $\text{TMAI}/\text{NH}_3/\text{H}_2$ systems are shown in refs. 28 and 29.

Pressure dependences of growth rate and Al content in AlGaN are shown in Fig. 4. The experimental results exhibited strong pressure dependences of growth rate and Al content. The black line is the virtual simulation without the polymerization among Al- and Ga-containing molecules. In this case, the pressure dependence of Al content indicates good agreement with the experiments, and at around 10 kPa the calculated growth rate is not far from the experimental value. However, the calculated growth rate diverges from the experimental values as the pressure increases. Al-containing molecules easily form polymers with pressure [29]. Therefore, at higher pressure, the AlGaN growth rate approaches to the GaN growth rate, and the Al content approaches to zero. The previous studies on AlGaN MOVPE simulation were mainly at low pressures of 5-40 kPa [31-33]. Using our polymerization model in Fig. 3, the calculated AlGaN growth rate and its Al content show good agreement with the experiments up to 100 kPa, which supports the proposed formation of Al- and Ga-containing polymers.

It is useful to vary the $\text{TMAI}/(\text{TMAI}+\text{TMGa})$ inlet ratio to control the Al content in AlGaN. We compared the $\text{TMAI}/(\text{TMAI}+\text{TMGa})$ ratio dependences of AlGaN MOVPE simulations under 10 kPa and 40 kPa with experiments. As can be seen from Fig. 5, the simulated and experimental features are in good agreement qualitatively and quantitatively for both values of pressure.

These results also support the polymerization among Al- and Ga-containing molecules. The ratio dependences of growth rate and Al content at low-pressure show almost linear characteristics, which means that in this case, the polymer formation would be suppressed. A previous work reported a linear dependence of growth rate and Al content on the TMAI/(TMAI+TMGa) inlet ratio experimentally and numerically only at low pressure [32]. At a pressure of 40 kPa, the ratio dependence became non-linear. The good agreement between our simulated results and the experimental values in the non-linear region suggests that our polymerization model works even at high-pressure values. We think that the non-linearity arises from the enhanced polymerization at around a TMAI/(TMAI+TMGa) ratio of 0.5 because the loss of precursors of TMAI and TMGa is high at such ratio.

Figure 6 shows the experimental and numerical temperature-dependences of the AlGaN growth rate and Al content. In the experiment, the growth rate decreases with temperature, but Al content increases. We simulated AlGaN growth with and without GaN decomposition, and included our polymerization model for both cases. We assumed that GaN crystal re-evaporates as Ga atoms, MMGa, N₂, and NH₂ molecules. GaN decomposition is relevant at temperatures at 1100°C and more. We confirmed an excellent agreement between experiment and simulation considering the GaN decomposition, which supports the result of a previous work [33]. Although the maximum temperature of our MOVPE system is 1150°C, our simulation model presumably works even at higher temperatures as long as the AlN decomposition remains negligible.

4. Summary

We have developed the AlGaN MOVPE simulation in a TMAI/TMGa/NH₃/H₂ system by considering additional polymer formation among Al- and Ga-containing molecules. We also proposed that the Al- and Ga-containing polymers are [MMAINH]_l-[Ga-N]_n, [Al-N]_m-[Ga-N]_n, and

$[MMAINH]_i-[Al-N]_m-[Ga-N]_n$. By considering this polymer model, we got good agreements with the experiments in pressure dependences from 10 kPa to 100 kPa, the TMAI/(TMAI+TMGa) inlet ratio dependences from 0 to 1, and temperature dependences from 1000°C to 1150°C on AlGa_nN growth rate and Al content, qualitatively and quantitatively. Thus, we achieved a successful simulation of AlGa_nN MOVPE even at atmospheric pressure.

Acknowledgments

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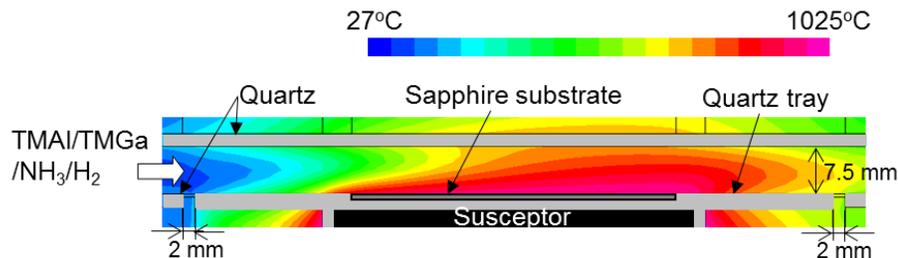


Fig. 1. The cross section of the experimental horizontal reactor at the center line of a substrate. The 2D simulation model has the same geometry in this area. The colors show a typical temperature distribution simulated at a substrate temperature of 1025°C and a pressure of 40 kPa. The substrate was not rotated in both simulation and experiment.

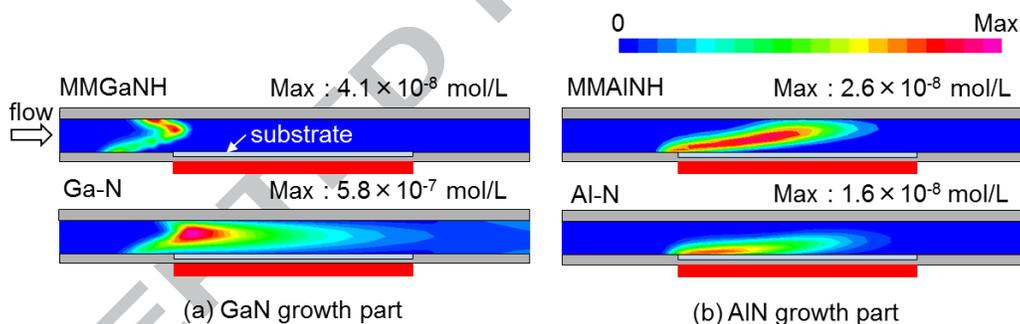


Fig. 2. Spatial distributions of reactive molecules during AlGaIn growth in a horizontal reactor. Any Al- and Ga-containing polymerization is not included. Therefore, the left side (a) is the GaN-related part, and the right side (b) is the AlN part. A simplified 2D reactor model was used. The substrate temperature was 1025°C, and the pressure was 40 kPa.

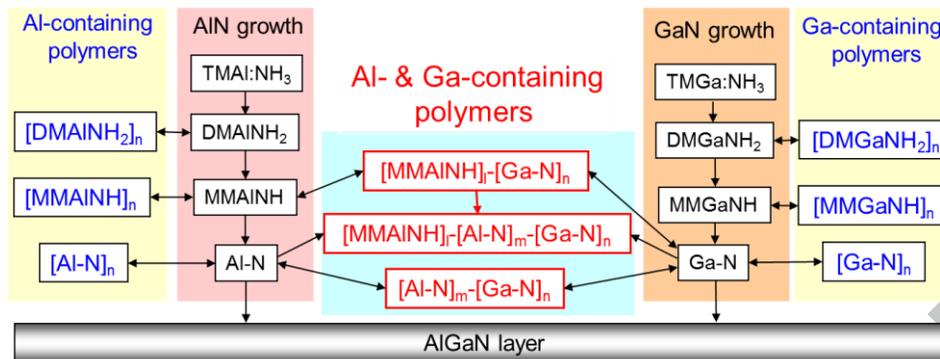


Fig. 3. Schematic reaction pathways in the TMAI/TMGa/NH₃/H₂ system. The simplified reactions for AlN growth and Al-containing polymers are shown at the left side. Those for GaN-related are on the right side. The middle part indicates our proposed polymers between Al- and Ga-containing molecules. The maximum number of $l+m+n$ was set at seven due to our computational processing limitations.

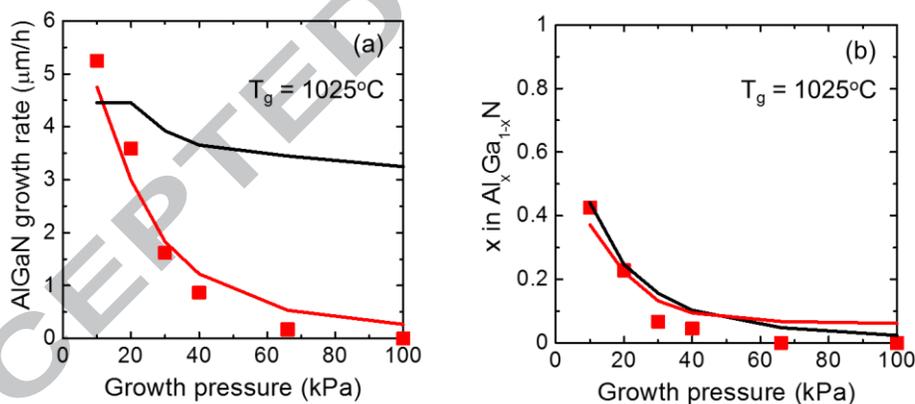


Fig. 4. Pressure dependences of AlGaIn growth rate and Al content. Red solid squares are experimental values. The black line is the simulation result without any Al- and Ga-containing polymer formation. The red line indicates the simulated results of the AlGaIn reaction model with Al- and Ga-containing polymerization.

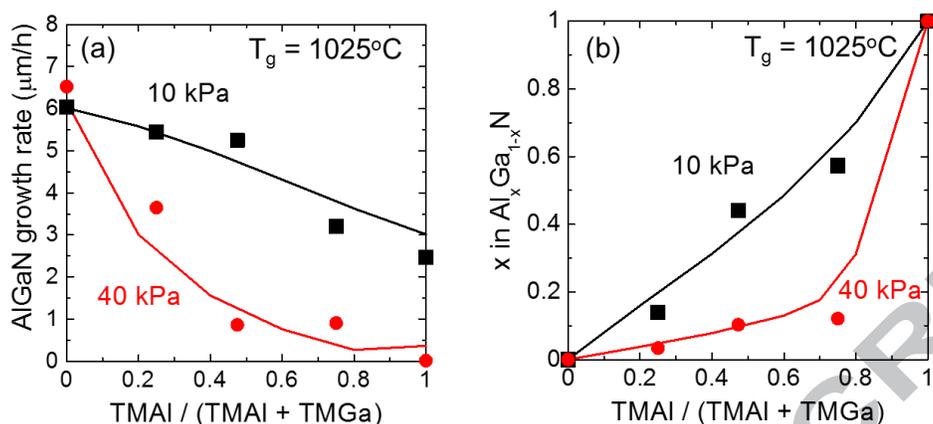


Fig. 5. Ratio [TMAI/(TMAI+TMGa)] dependences of AlGaN growth rate and Al content with two different growth pressures of 10 kPa and 40 kPa. Points and lines are experimental and calculated values, respectively.

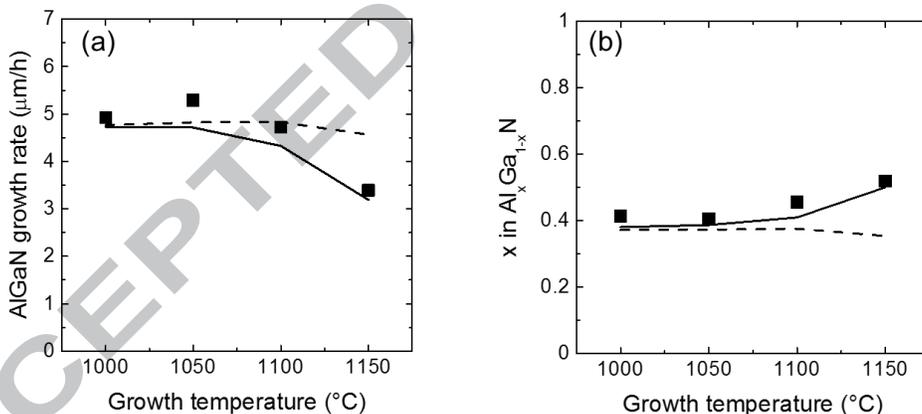


Fig. 6. Temperature dependences of AlGaN growth rate and Al content in the experiment (solid squares) and simulations with different models (lines). Solid and broken lines indicate the models with and without GaN decomposition, respectively. The growth pressure was 10 kPa.

Highlights of the manuscript “**Influence of polymerization among Al- and Ga-containing molecules on growth rate and Al content in AlGaN**” written by Kazuhiro Ohkawa^a, Kenichi Nakamura^b, Akira Hirako^b, Daisuke Iida^a

Highlights

1. The additional Al- and Ga-containing polymers in AlGaN MOVPE was proposed.
2. The AlGaN simulation explained the pressure dependence of growth up to 100 kPa.
3. The simulation clarified the linear and non-linear trends of growth in Al/(Al+Ga).