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High aluminium content and high growth rates of AlGaN in a close-coupled showerhead MOVPE reactor

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ABSTRACT

The growth rates and aluminium contents of $Al_xGa_{1-x}N$ layers grown in a close-coupled showerhead reactor were investigated as a function of growth pressure and chamber height during metal-organic vapour phase epitaxy. The data show strong non-linear dependencies due to nanoparticle formation in the gas-phase. Good agreement between the experimental data and modeling results is obtained when the contribution of both Ga- and Al-containing species to the gas-phase particle formation is considered.

1. Introduction

For ultraviolet light emitters AlGaN layers with high aluminium content are needed. However, the growth of AlGaN is quite challenging due to gas-phase pre-reactions and the formation of nanoparticles. For AlN growth rates are rarely exceeding 1 μm/h. Nevertheless, thick AlGaN layers are required in order to obtain low dislocation densities and low resistance current spreading layers.

It is well known that the growth rates and composition of Al(Ga)N layers depend strongly on temperature and reactor pressure due to particle formation in the gas-phase during metal-organic vapour phase epitaxy (MOVPE) [1–5]. In case of a close-coupled showerhead (CSS) MOVPE reactor the chamber height provides an additional growth variable to control these gas phase reactions. To optimize the growth process, modeling of all those effects on AlGaN composition and growth rate can be a powerful tool. For the CCS reactor, we introduce a 2D axisymmetric coupled transport and reaction model including both gallium and aluminium losses due to the growth of AlGaN particles in the reactor volume.

2. Experimental and modeling approach

The growth experiments were performed in an Aixtron 3 × 2 in CSS-MOVPE reactor, which has an adjustable chamber height between 6 and 21 mm. The samples were grown on GaN/sapphire templates. The growth time for AlGaN layer was fixed at 600 s, resulting in layer thicknesses between 100 and 700 nm. Growth rate and aluminium content were measured in situ by spectral reflectance using a LayTec EpiR-TT-DA-UV system and ex situ by X-ray diffraction. Additional characterization was performed by room temperature photoluminescence using a 266 nm Nd:YAG Laser excitation.

The modeling approach consists of a 2D calculation of flow, heat transfer and multi-component mass transport in the reactor, gas-phase and surface chemistry. Particle nucleation, growth and transport in the gas phase were modeled to determine the material loss. The basic features of the model and its application for GaN growth in a CSS-MOVPE reactor can be found in [6]. The computations have been performed using the CVDSim software [7].

3. Results and discussion

3.1. Simulations

A schematic overview of the gas-phase chemistry considered is shown in Fig. 1. We consider that the gas-phase reaction mechanism represents a multi-step pathway [8]. Reaction between TMAl and ammonia gives rise to TMAl:NH3 adduct that produces $DMAl:NH_2$ via methane elimination reaction and interactions with ammonia. Subsequently formed $(DMAl:NH_2)_2$ and $(DMAl:NH_2)_3$ species may produce AlN in the gas phase, initiating AlN particle nucleation. Further growth of the solid particles takes place at the expense of interactions between the AlN nuclei and Al-containing species such as AlN, $DMAlNH_2$, and $[DMAlNH_2]_2$. Another way of aluminium losses is the formation of oligomers ($(DMAl:NH_2)_n$, $n \geq 3$) that do not contribute to the layer

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deposition. For pure AlN this model describes well the growth rates in a CSS reactor [9].

Generally AlN particles are formed much more easily than GaN ones. Therefore, often AlGaN growth rates and aluminium content can be predicted without considering GaN particle formation. However, under certain operating conditions (high growth rates, high temperatures, large residence times, etc.) with a high density of AlN particles, the AlGaN growth rate GR_{AlGaN} appears to be lower than the sum of growth rates of binary compounds GR_{GaN} and GR_{AlN}, i.e. the growth efficiency is reduced [10]. We assume that there is an additional mechanism of Ga losses, becoming active in the presence of AlN particles due to consumption of gallium by the particles. The results of AlGaN growth presented in [5] agree well with the assumption. The experiments have been obtained in a vertical rotating disk reactor using TMAl, TMGa and NH3 as precursors and hydrogen as a carrier gas. Note that the GaN layers grow under these conditions without any losses. An increase of the AlGaN growth rate is expected with increasing the TMAl flow rate, however, it drops to the values even lower than the GaN growth rate. The drop can be explained assuming additional material losses due to passing of gallium into particles [11]. Hence, a higher TMAl flow rate and a higher deposition temperature decrease the AlGaN growth rate. The thermophoretic force drives the particles away from the growth surface to a region of lower temperature. We assume that the growth of particles at the expense of Ga-containing species (TMGa and its pyrolysis products) is kinetically limited by the desorption of the methyl groups from the particle's surface, as suggested in [11]. For the present study, the gas-phase chemistry model was extended to include this loss of gallium species by the kinetically limited growth of the AlGaN particles. In the following the influence of chamber height and reactor pressure on growth rates and aluminium incorporation will be discussed in detail.

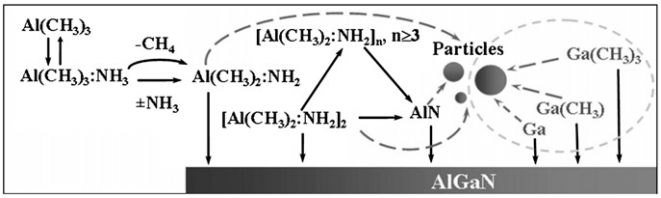

Fig. 1. Schematic overview over the loss mechanism during AlGaN growth. After nucleation of AlN particles, their subsequent growth proceeds at the expense of both Al- and Ga-containing species.

Fig. 2 shows that the influence of the additional gallium losses is most severe at reactor pressures exceeding 150 hPa. Neglecting gallium uptake results in overestimated growth rates and underestimates the aluminium content of AlGaN. The additional loss of gallium is best seen in the mono-methyl gallium (MMGa) concentration in the gas phase (Fig. 3). Without gallium losses (left column) the MMGa concentration distributions as well as its absolute values are very similar for different chamber heights. When the consumption of gallium by particles is considered (right column) the MMGa concentration is reduced by 20% for 15 mm chamber height and by 50% for 21 mm. As a consequence the concentration of group III elements at the surface is lower and the growth is slower compared to the expected value without this loss mechanism. For 400 hPa the calculated growth rate changes from 1.1 μm/h (neglecting the losses of gallium) to 0.3 μm/h (with losses), i.e. by more than a factor of three.

The calculated growth rates for different chamber heights are less affected by the uptake of gallium by particles (Fig. 5). Nevertheless, with gallium losses the growth rates are somewhat closer to the experimental values. More importantly, only the simulation considering AlGaN particles reproduced the observed saturation and even slight increase of the aluminium content at larger chamber heights. The relatively small influence of the additional gallium loss mechanism for smaller chamber heights (below 12 mm) is probably due to the position of the particle layer. For smaller chamber height the particles are located in a

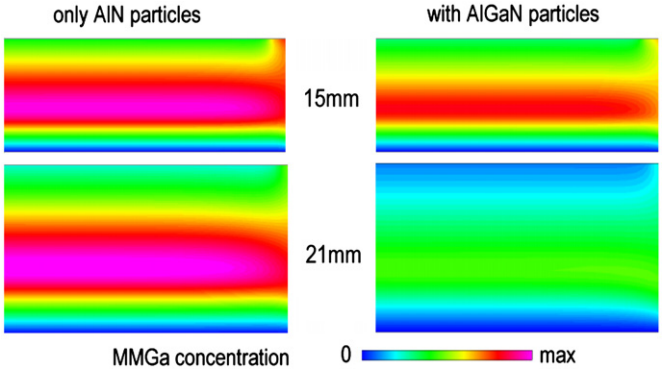

Fig. 3. Computed concentration of mono-methyl gallium (MMGa) for 15 and 21 mm chamber height at 150 hPa (similar conditions as in Fig. 2). Left side was calculated without uptake of gallium by the particles, while this process was included on the right side. Maximum concentration was 650 ppm at 15 mm chamber height and 800 ppm at 21 mm.

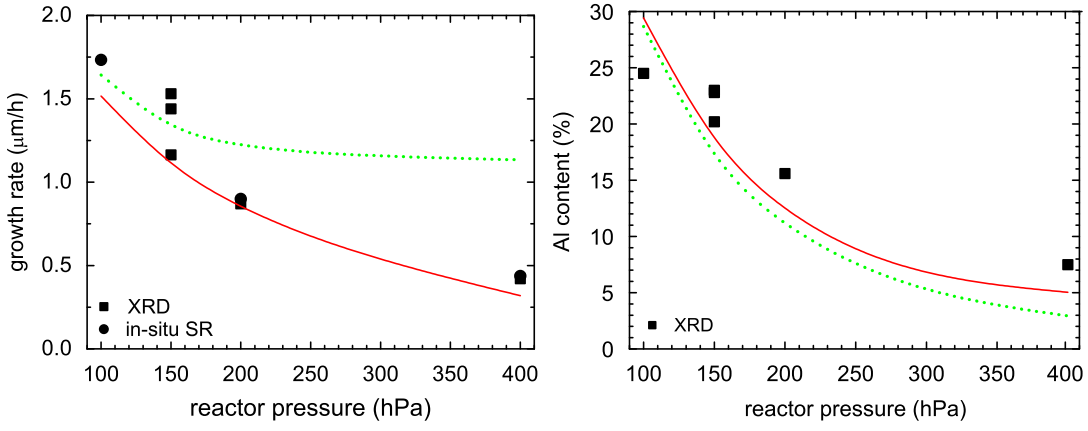

Fig. 2. AlGaN growth rate and aluminium content as function of the reactor pressure. The growth parameters were 15 mm chamber height, growth temperature: 1317 K, V/III=510 and TMAl/TMGa=1.2 (accounting for TMAl dimers). The dotted lines represent simulations without gallium losses, the solid lines include uptake of gallium by the particles.

thin layer near the showerhead (Fig. 4). The temperatures in this region are still relatively low. Since the model assumes that the adsorption of gallium species is kinetically limited, at such temperatures methyl radicals block free sites for III-group species adsorption. This mechanism is similar to that suggested in [12] for GaN growth below 600 °C. For larger chamber heights the particle layers float in the hotter middle of the chamber (Fig. 4), and thus the consumption of gallium by the particles is no longer limited by methyl desorption. Hence, the uptake of gallium becomes intensive and alters the predicted growth rates and aluminium contents.

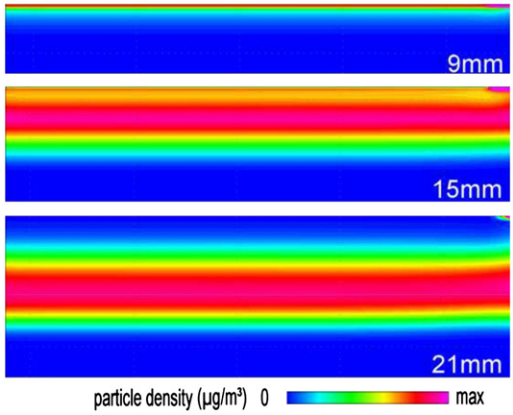

Fig. 4. Computed density of particles for 9, 15, and 21 mm chamber height at 150 hPa. Maximum density was 150 µg/m³ at 9 mm chamber height, 35 µg/m³ at 15 mm, and 42 µg/m³ at 21 mm.

3.2. Growth of AlGaN at reduced chamber height

Thick AlGaN layers are needed to significantly reduce dislocations. Therefore, we focused in the following on growth at 6 mm chamber height to realize high growth rates by a strong suppression of AlN particle formation and thus also gallium losses.

For 6 mm chamber height the losses are strongly suppressed and the growth rate is almost proportional to the total amount of group III species. The strong suppression of losses results in growth rates of more than 3 µm/h over the entire concentration range of AlGaN with reasonable fluxes through the bubblers (Fig. 6 left). In this series of experiments, we kept the TMGa partial pressure constant up to 70% TMAl in the gas phase, and obtained a noticeable increase of the growth rate vs. group-III flow rate (Fig. 6 left), contrary to the 15 mm chamber height when material losses are significant.

To obtain higher aluminium concentrations the TMGa partial pressure was reduced (Fig. 6, shaded area). Nevertheless, even for AlN, growth rates of 3 µm/h and higher are possible. The solid aluminium content dependence on the TMAl/(TMGa+TMAl) ratio is close to linear (Fig. 6 right), but some losses of aluminium still take place. In particular, at 70% TMAl in the gas phase the solid aluminium content is about 60%. The systematic deviation of the spectral reflectance data (SR in Fig. 6

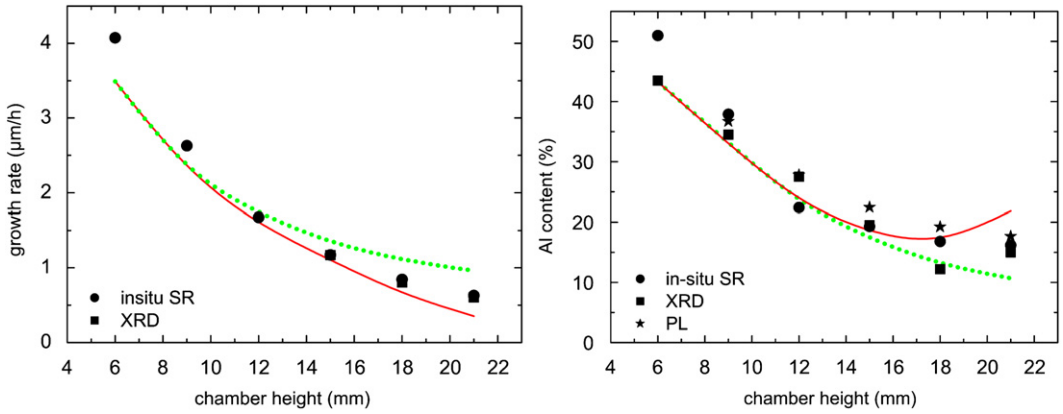

Fig. 5. AlGaN growth rate and aluminium content as a function of the chamber height. The growth parameters were 150 hPa at 1317 K (at 15 mm chamber height), V/III=510 and TMAl/TMGa=1.2 (accounting for TMAl dimers). The dotted lines are simulations without gallium losses, the solid lines include take up of gallium by the particles.

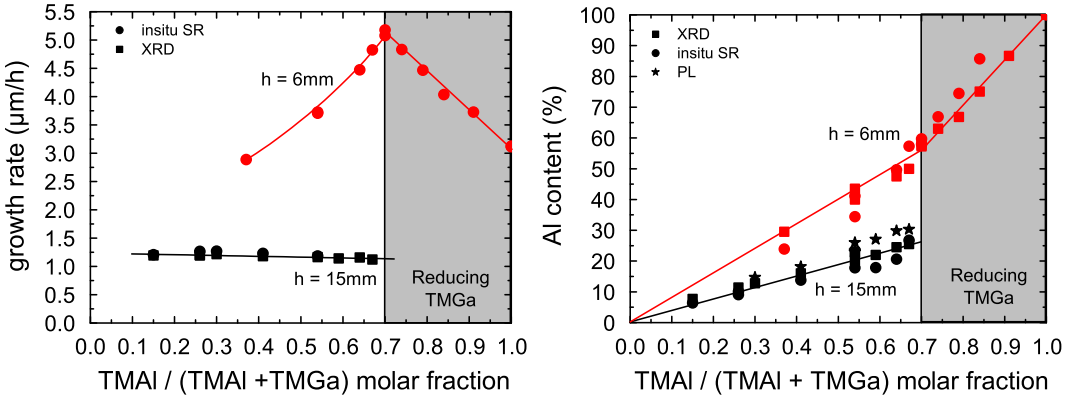

Fig. 6. Growth rates and aluminium content at 6 and 15 mm chamber height and 150 hPa total pressure at 1313 K. Up to 70% TMGa in the gas phase the TMAl partial pressure was increased, for higher aluminium contents the TMGa partial pressure lowered. Consequently the growth rate is maximum at 70% TMAl in the gas phase.

right) might be due to the lack of good reference data in this region.

Further studies on the effect of growth rate on surface morphology and layer properties are under way.

4. Conclusion

The growth rates and composition of AlGaN layers in a CSS-MOVPE reactor can be modeled accurately if a kinetically limited uptake of gallium species by particles is taken into account. The effect is most prominent for large chamber heights and high pressures, since under these conditions the nanoparticle formation will occur in the hot middle zone of the chamber. For small chamber heights the particle formation occurs almost exclusively near the cold showerhead and the loss is kinetically suppressed. Using a chamber height of 6 mm, AlGaN in the entire composition range was grown reproducibly with the growth rates exceeding 3 μm/h.

Acknowledgments

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