On the mechanisms affecting aluminum transport and incorporation efficiency during AlGaN MOVPE

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Introduction

Elevated temperatures typically used to grow III−nitrides result in "switching on" some physical−chemical mechanisms that are not so important for conventional III−V compounds. Such phenomena as the production of adducts via reactions between metalorganic precursors (TMGa, TMAl and the products of their decomposition) and ammonia, gas−phase clustering, and formation of particles in the reactor hot zones are generally recognized to be the source of the material losses and, therefore, to limit the growth rate and govern largely the layer composition. In addition, there is an interplay between these phenomena, their intensities may depend considerably on the operating conditions (temperature, pressure, precursor flow rates, and residence time), so that different mechanisms may play a key role in different reactor configurations.

The models of III−nitride MOVPE that can be found in the literature (see, for instance [1−3]) provide usually a reasonable fit to experimental observation for a particular growth system, but a general understanding of the mechanisms underlying the epitaxial process is not gained yet. Here, we analyze critical features to be taken into account in group−III nitride MOVPE modeling and suggest some explanations and models that can reproduce these effects.

Gas−phase chemistry and particle formation in GaN/AlGaN MOVPE

A comprehensive study of the growth rate and incorporation efficiency of GaN and AlN during GaN/AlGaN MOVPE in a vertical high−speed rotating−disk reactor has been presented in [4]. TMGa, TMAl, and both TMGa and TMAl were opened sequentially to measure separately the growth rates of GaN, AlN, and AlGaN at varied partial pressures of hydrogen and ammonia. It has been found that the GaN growth rate has a weak dependence on the NH_3 partial pressure at the H_2 pressure below 20 Torr, whereas the AlN growth efficiency decreases rapidly as the NH_3 flow rate is increased. A similar tendency has been reported in [5] for a close−spaced rotating−disk reactor, and the authors of both papers attribute this decrease in the AlN growth rate to the enhancement of the parasitic reaction between TMAl and ammonia. Han et al. [4] have also shown that the AlGaN growth rate is always lower than the sum of the growth rates of the binary constituents (GaN and AlN) and is close to this sum only at fairly low pressures, and it depends on the ammonia flow in a way similar to the AlN growth rate. Moreover, the authors of [4] and [6] note that the rate of Ga incorporation into AlGaN drops as the NH_3 or TMAl flow rate is raised, and they suggest two possible interpretations of this effect: the influence of Al−containing adducts or the products of their decomposition on Ga−containing species and surface kinetic processes, namely, a site blocking effect, when Ga− and Al−containing molecules adsorb on the same surface sites.

It is interesting to consider how the Al content in AlGaN varies with different operating conditions. From the analysis of the facts that the AlGaN growth rate decreases and Al molar fraction in the alloy grows with the substrate temperature in the range from 900 to 1100 °C, a conclusion is made in [6] that the incorporation rate of both Ga and Al decrease, with the incorporation rate of Ga decreasing faster. It is demonstrated in [5, 6] that the enhancement of the Al flow results in a nearly proportional increase of the Al concentration in the solid only at low Al gas−phase contents, and this dependence saturates at high Al gas compositions. At the same time, the Al content in the solid represents almost linear dependence on that in the gas, if the latter parameter is increased by decreasing the TMGa flow rate. Thus, it is pointed out in [5] that the parasitic reaction between TMAl and NH_3 is much more intensive than that between TMGa and NH_3.

There are a number of papers reporting on the formation of particles in the gas phase during the growth of III−nitrides. When GaN was deposited in an atmospheric pressure vertical MOCVD system [7], the choice of the process parameters providing the formation of a vortex above the susceptor and, therefore, a longer residence time, resulted in appearance of "smoke" in this region. Recently, images of light−scattering particles formed during GaN

MOVPE in an inverted stagnation point flow reactor have been published in [8, 9]. The authors also note that nearly identical particle layer is produced in the reactor under AlN MOVPE conditions. It has been observed that both AlN and GaN growth rate in the vertical reactor of the conventional configuration (non−inverted with rotating disk) decreases with the temperature, total pressure, and residence time (rotation rate). The GaN growth rate reaches the transport limit, predicted by computations with no loss mechanisms, only at the rotation rate of 1800 RPM, whereas the AlN growth rate is always significantly lower than such a limit. Speculating on the nature of parasitic reaction mechanisms, the authors suggest that in case of GaN growth the parasitic reaction is initiated by homogeneous decomposition of TMGa and further reactions involving radicals. A lower activation energy for AlN scattering appears to be consistent with the activation energy of the methane elimination from the $TMAl{:}NH_3$ adduct.

From the above information, we can formulate the most important and repeatedly indicated trends that should be captured by a model of GaN/AlGaN MOVPE: (a) the reduction of the growth efficiency (increasing loss mechanism intensity) with the increase in the ammonia flow rate; (b) the decrease in the GaN and AlN growth rate with the operating temperature, pressure, and residence time; (c) sublinear and even saturating dependence of the Al incorporation efficiency on the Al precursor molar fraction; (d) mutual influence of Al− and Ga−containing species during AlGaN growth, which results in the lowering of Ga incorporation rate compared to pure GaN deposition. On the other hand, the mechanisms involved seem to be different for GaN and AlN growth [4, 8, 9], so it looks reasonable to develop a model step−by−step, starting from AlN and GaN separately and then generalizing and extending the models for the case of AlGaN MOVPE. In this paper, we advance the basic postulates of a model of AlN growth and demonstrate how the model reproduces the experimental data from [8] and general tendencies reported in the literature.

To simulate the gas−phase chemistry, we rely on the most frequently cited work by Mihopoulos et al. [1] considering a set of reactions, including the formation of $TMAl{:}NH_3$ adduct, subsequent elimination of methane, the formation of oligomers, and the production of AlN particles from $(DMAl{-}NH_2)_2$ and $(DMAl{-}NH_2)_3$ species. We suggest to revise this kinetic mechanism in the part concerning the formation of particles, namely, to consider the condensation consisting of two stages. One is AlN nucleation, whose rate can be estimated from the bimolecular collision frequency between AlN molecules. The other is the subsequent growth of the solid particles due to mass exchange between AlN nuclei and those gaseous species that are considered in [1] to contribute to the growth of AlN on the substrate: TMAl, $TMAl{:}NH_3$, MMAl, $DMAl{-}NH_2$, and $(DMAl{-}NH_2)_2$. This allows us to extend the set of species that may be involved into the particle formation and to make the model more flexible in terms of predictability for a wider range of operating conditions. The computational implementation of the model consists in solving the evolution equations for the first three moments of the size distribution function of the clusters and the particle continuity equation, as described in detail by Vorob'ev et al. [10]. Due to steep temperature gradients near the hot susceptor in vertical reactors, the model additionally accounts for the thermophoretic force that brings the particles away from the susceptor in the direction of the temperature decrease [10]. The surface reaction mechanism includes the growth of AlN due to the contribution of $DMAl{-}NH_2$, $(DMAl{-}NH_2)_2$, and gaseous AlN.

To verify the model developed, we have performed a number of 2D computations of flow dynamics, heat transfer, and mass transport for the operating conditions reported in [8] for the growth of AlN. A typical distribution of the AlN particle density is demonstrated in Fig. 1. At the operating pressure of 40 Torr, temperature of 1050 °C, and the susceptor rotation rate of 1200 RPM, the maximum particle density is about 10^{-5} kg/m^3, and the layer is located about 7 mm above the susceptor. Fig.2 displays a comparison of the computed AlN growth rate dependence on the susceptor rotation rate to experimental data. As the spin rate is increased, the gas residence time becomes shorter, reducing the intensity of the parasitic chemical processes. The computational results are in a good quantitative agreement with this tendency. It should also be noted that, following [8], the hydrogen and ammonia flow rates were scaled as (rotation rate)$^{1/2}$ to maintain matched flow conditions, so that the AlN growth rate would be independent of the rotation rate, if no material losses took place. Figs. 3−5 show the variations in the AlN growth rate with different operating conditions. The decrease in the growth rate with temperature (Fig. 3) can be attributed to greater material losses in the gas phase through both an enhanced formation of $(DMAl{-}NH_2)_n$ ($n>2$) molecules that are assumed not to contribute to the growth [1] and intensification of the condensation process. It

can be seen from Fig. 4 that an increase in the operating pressure also leads to the lowering of the AlN growth efficiency. This is due to a higher frequency of the molecular collisions and, as a result, an enhanced gas−to−particle conversion. Fig. 5 demonstrates that the AlN growth rate dependence on the TMAl flow rate deviates considerably from the linear one to be expected in the absence of material losses.

Conclusions

From an analysis of experimental observations found in the literature, we have suggested and tested numerically various ways of material losses in AlGaN MOVPE. A detailed mechanism of gas−phase reactions of the precursor decomposition and formation of complex molecules that do not contribute to the growth is combined to a model of particle formation during AlN growth. The model application demonstrates a good quantitative agreement to the experimental data on the AlN growth rate dependence on the susceptor rotation rate, obtained in a vertical MOVPE reactor. In addition, the basic trends reported in the literature (the reduction of the AlN growth rate with the operating temperature, pressure, and TMAl flow rate) are also reproduced by our computations.

References

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Fig. 1. Layer of particles during AlN growth in a vertical reactor, predicted by the computations.

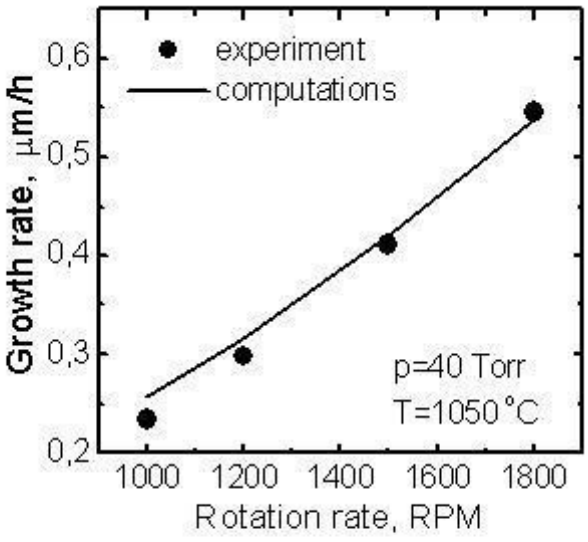

Fig. 2. AlN growth rate as a function of the susceptor rotation rate. Experimental data from [8].

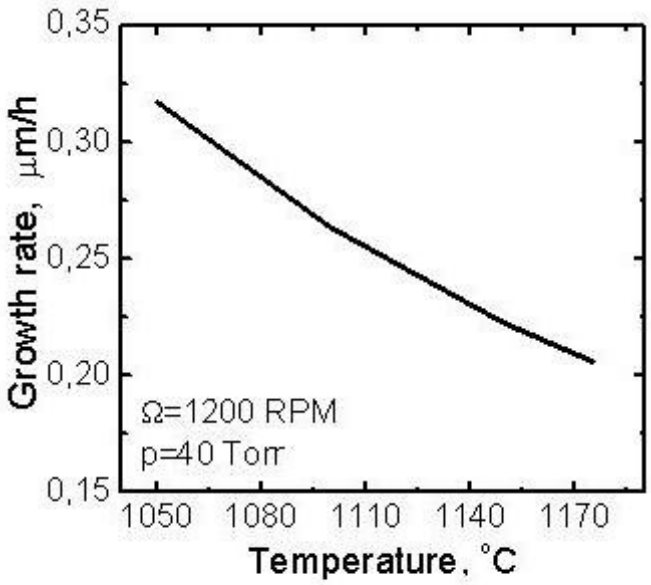

Fig. 3. AlN growth rate as a function of the deposition temperature.

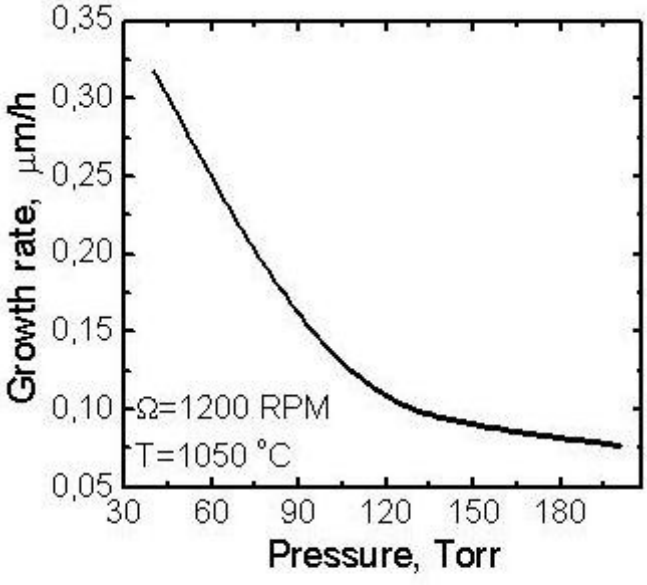

Fig. 4. AlN growth rate as a function of the operating pressure.

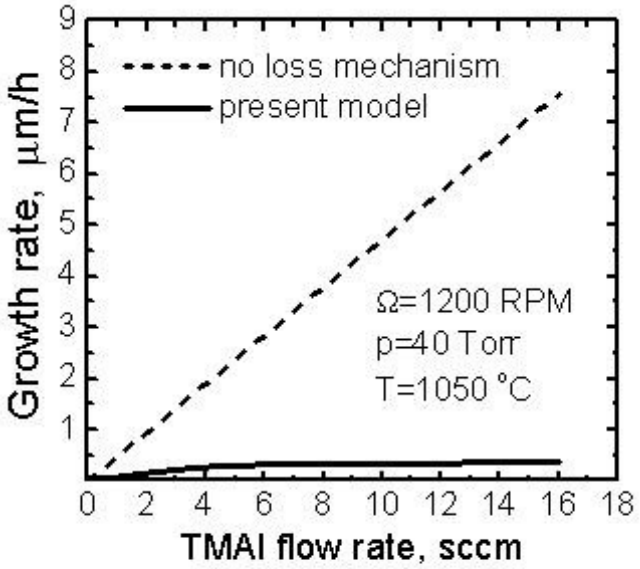

Fig. 5. AlN growth rate as a function of the TMAl flow rate.