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AlInN MOVPE: growth chemistry and analysis of trends

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ABSTRACT

Comprehensive model of AlInN Metal-Organic Vapor Phase Epitaxy (MOVPE) accounting for the gas-phase and surface chemistry including parasitic reactions/particle formation is developed. Experimental data and modeling results suggest that as V/III ratio increases from several tens (growth of pure AlN) to several thousands (growth of AlInN), the partial AlN growth rate decreases even in the absence of strong particle formation. This effect is associated with the formation of heavy molecular weight/low diffusivity gas-phase dimer species at high ammonia concentration. At elevated pressures growth rate decreases with pressure at a weakly changing composition, which is related to the gas-phase losses of In- and Al-containing species due to reaction with AlN particles. Model allows the prediction of both the AlInN growth rate and composition versus group-III flow rates, temperature, and pressure.

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1. Introduction

AlInN is an attractive material for various electronic and optoelectronic devices [1]. However, development and optimization of AlInN MOVPE is a challenging problem because of the difference in the growth conditions for binary AlN and InN constituents and large AlN–InN lattice mismatch. Problems of gas-phase parasitic chemistry and, in particular, generation of particles, stress relaxation, phase separation, etc, make the growth of high-quality AlInN a fairly complex problem.

Experimental studies reveal some trends in the process behavior. So, rather sharp decrease of In content in the alloy with temperature at a weakly changing growth rate is reported in [2–4]. Dependencies of the alloy growth rate and composition on temperature and precursors flow rates are studied in the recent papers [5–7]. It is emphasized there that the data are obtained under low-pressure conditions (~50 Torr) corresponding to weak parasitic reactions between TMAl and ammonia. Enhancement of the parasitic chemistry at a higher pressure was demonstrated in [8–10]. The effect seems to be related to the fact that high ammonia flows normally used for InN and InGaN growth may initiate parasitic reactions as applied to AlN growth. For AlN MOVPE, strong parasitic chemistry was shown to play an important role at both high temperatures up to 1600 °C [11–14] and low temperatures within 500–1000 °C [15]. Reduction of the AlN growth rate with the ammonia flow is commonly observed. Decrease of the AlN growth rate by about 40% as V/III ratio increases from several tens (growth of AlN) to several thousands (growth of AlInN) was shown in [13]. The AlN growth rate as high as 6 μm/h was achieved at V/III=116 while it was fairly low at V/III=2338 [14]. Strong reduction of the AlN growth rate with ammonia at high pressure and temperature as low as 500 °C was reported in [15]. Thus, since AlInN is typically grown at high V/III ratio and low temperature (700–800 °C), the Al-related parasitic chemistry seems to be the major source of the material loss.

Despite the reported results, there is still lack of systematic data on the process behavior and little interpretation of the observed effects. Here, we present a modeling study of AlInN MOVPE with varying process parameters that is aimed at systematization and interpretation of the experimental results. The major focus is made on the model of Al-related gas-phase chemistry, especially with varying ammonia flow. Besides, the model of particles formation has been modified to account for the loss of both In and Al via deposition of In- and Al-containing species on the initially nucleated AlN particles. Good agreement of the results of computations with the model and various experimental data on AlInN MOVPE available in the literature is demonstrated.

2. Model description

The model of AlInN MOVPE accounts for the conductive, convective, and radiant heat exchange, dynamics of gas mixture, multicomponent species diffusion, thermal diffusion, gas-phase and surface chemistry, and formation of particles. As previously [4,13], we use the quasi-thermodynamic model of surface chemistry that accounts for the strain effects and a simple model of In-related gas-phase chemistry including two-stage TMIn decomposition

$$TMIn \rightarrow MMIn + 2CH_3 \quad (R1)$$

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$$MMIn \rightarrow In + CH_3 \quad (R2)$$

The model of Al-related gas-phase chemistry is generally based on that developed by Mihopoulos et al. [16] and the kinetic mechanism of AlN particle nucleation and growth suggested in [17]. The mechanism starts with the fast reversible reaction of the adduct formation

$$TMAl + NH_3 \leftrightarrow TMAl \cdot NH_3 \quad (R3)$$

The stable species TMAl is assumed to reach the growth surface without further conversion and gives direct contribution to the AlN growth. In contrast, the adduct decomposes in the gas giving rise to the reaction chain as follows:

$$TMAl \cdot NH_3 \rightarrow DMAl \cdot NH_2 + CH_4 \quad (R4)$$

$$TMAl \cdot NH_3 + NH_3 \rightarrow DMAl \cdot NH_2 + CH_4 + NH_3 \quad (R5)$$

$$2DMAl \cdot NH_2 \rightarrow (DMAl \cdot NH_2)_2 \quad (R6)$$

$$(DMAl \cdot NH_2)_2 + DMAl \cdot NH_2 \rightarrow (DMAl \cdot NH_2)_3 \quad (R7)$$

$$(DMAl \cdot NH_2)_2 \rightarrow 2AlN + 4CH_3 \quad (R8)$$

$$(DMAl \cdot NH_2)_3 \rightarrow 3AlN + 6CH_3 \quad (R9)$$

In the refined model, both the direct and backward reactions (R3) are considered as rather fast, so that TMAl and adduct prove to coexist near the equilibrium line in the reactor. At low V/III ratio, the equilibrium is shifted towards TMAl, in which case the growth proceeds without significant material loss. Note that the idea of low material loss at low V/III ratio is in agreement with high AlN growth rate ($\sim$6 μ/h) obtained at V/III=116 by Imura et al. [14]. Lundin et al. have recently demonstrated AlN epitaxy in an AIX2000HT $6 \times 2''$ MOVPE planetary reactor with the growth rate exceeding 8 μm/h at V/III ratios as low as 1.5–2 [18].

As V/III ratio increases, the equilibrium shifts to adduct, which then decomposes to produce heavy (low-diffusivity) oligomers $(DMAl \cdot NH_2)_2$, $(DMAl \cdot NH_2)_3$, and maybe AlN particles. Considerable role of reactions (R4) and (R5) at high V/III ratio, resulting in generation of monomer $DMAl \cdot NH_2$, correlates with the data of Nakamura et al. [19] who have proved theoretically that the barrier for the methane elimination is reduced considerably in excess ammonia. Contribution of reaction (R6) is in line with the data of Creighton and Wang [20] who have studied TMAl decomposition in a gas cell under conditions similar to those for MOCVD growth but at low temperature and concluded that "majority of Al product exist in $(DMAl \cdot NH_2)_2$ dimer form at 473–523 K when ammonia is in excess". Excessive ammonia also makes more intensive production of low-diffusivity trimer in reaction (R7), and maybe heavier oligomers in similar reactions, which serve as certain sources of material loss as they give little contribution to the growth.

At high temperature and residence time, dimers can considerably convert into gaseous AlN, following reactions (R8) and (R9), that in turn can nucleate into AlN particles.

The developed model also accounts for possible deposition of both the Al- and In-containing species on the initially nucleated AlN particles. The mechanism is similar to that considered in [21] for AlGaN MOVPE, where Ga-containing species could stick to the initially nucleated AlN particles. The latter mechanism was found to be responsible for the effect of a lower AlGaN growth rate as compared to the sum of the AlN and GaN growth rates measured under similar conditions [11,22,23]. We expect that similar mechanism may take place in AlInN MOVPE. So, Kim-Chaveau et al. considered AlInN MOVPE with In content less than 20% at 800 °C [8] and observed saturation of In content at $P \geq 300$ mbar, which indicates probable correlated loss of Al and In in their system. Simultaneously, growth of AlInN alloys with In content more than 60% at 730 Torr and 600–700 °C was demonstrated in [9,10]. Here, In content rises under the conditions providing dominant Al-related gas-phase parasitic chemistry.

Since the growth of AlInN is normally performed at high V/III ratios, the AlN model is expected to predict accurately partial contribution of the AlN constituent into the AlInN growth rate, which is also important to fit the experimental data on the alloy composition. The model accounts for loss of material due to the formation of heavy Al-containing oligomers and deposition of Al- and In-containing species on the AlN particles. The resulting AlInN growth rate and composition is determined by the interplay of these effects and eventually depend on the particular process parameters.

3. Results and discussion

The developed model was first verified in the part concerning growth of the AlN constituent using experimental data of [13] on AlN MOVPE. Experimental data of [13] show that the AlN growth rate can decrease by about 40% as V/III varies in the range of 266–8430. Computations with the model allow associating this result with the formation of heavy (low-diffusivity) dimer $(DMAlNH_2)_2$ at high ammonia flow, which can be followed by the formation of AlN particles at high V/III ratio.

The verified model has been applied to the analysis of experimental data obtained by Sadler et al. [5,6] on the AlInN growth rate and composition as functions of group-III flow rates and temperature obtained in a $6 \times 2''$ CCS reactor. The CCS concept represents a vertical-type reactor with the showerhead injector located close to the susceptor. It is reasonable to utilize two-dimensional axi-symmetric model of the reactor with uniform velocity and gaseous mixture composition at the inlet. Here, *c*-plane AlInN epilayers of about 100 nm thickness were grown on GaN/Al_2O_3 substrates in a nitrogen atmosphere at 50 Torr. TMIn and TMAl were used as the group-III precursors. Details of the experiments can be found in the original papers. Conditions close to lattice-matching allowed us to treat the layers as fully-strained in the model.

Computations with the developed model reproduce well increasing dependencies of the AlInN growth rate and In content in the alloy on the TMIn flow rate (Fig. 1, data of [6]). Here, the TMGa and ammonia flow rates are also raised to keep the same V/III ratio. At such a low pressure, particles are not intensively generated in the gas and the process features are largely determined by the interaction of species transport and gas-phase and

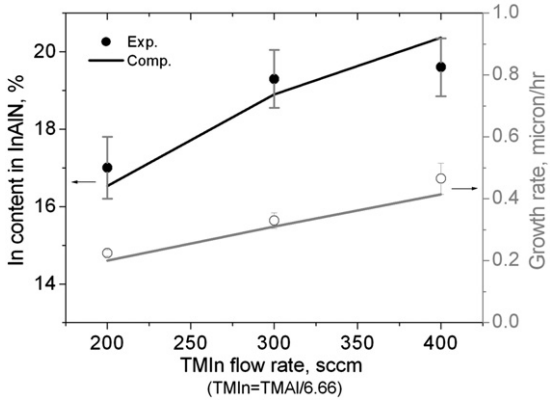

Fig. 1. Indium content and AlInN growth rate vs. group-III precursors flow rates—comparison of the results of computations with the experimental data of [6] (T=790 °C, P=50 Torr, Q_{NH3}=4–8 slm, Q_{N2}=16–12 slm, V/III=5600).

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