CVDSim™ – Nitride Edition

Chemical Vapor Deposition Simulator

Add-on for ESI CFD-ACE+

Simulation Tool for Modeling of CVD Processes
in Industrial Reactors

Release Notes

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1 AlN Model Revisions

The AlN model is revised to describe more accurately the gas-phase reaction mechanism between TMAl and NH_3. The key issue of the model is interplay between two different reaction pathways at high and low V/III ratios. At low V/III ratio, equilibrium for the reaction $TMAl+NH_3$<->$TMAlNH_3$ can be shifted toward TMAl. In this case AlN may grow without significant material losses due to AlN particles. At high V/III ratios, the $TMAlNH_3$ adduct is expected to decompose to $DMAlNH_2$ monomer with CH_4 elimination. Nakamura et al. [1] have proved that potential energy barrier of the methane elimination formation is reduced considerably in the excess of ammonia. Bimolecular coordination of $TMAlNH_3$ with NH_3 can accelerate formation of monomer at high ammonia flows. Authors of paper [2] studied TMAl decomposition pathways in a gas cell under conditions similar to that for MOCVD growth, but at low temperature. They concluded that “majority of Al product exist in $[DMAlNH_2]_2$ dimer form at 473-523 K when ammonia is in excess“. It can be suggested that reaction of dimer formation from monomer is failrly fast and dimer is main growth species even at low temperature. At high temperature, residence time etc., dimer can form AlN by the following reaction pathway $[DMAlNH_2]_2$->$2AlN+4CH_4$. So, at high V/III ratio main growth species are expected to be $[DMAlNH_2]_2$ and AlN. Excessive ammonia makes also more intensive production of low-volatile oligomers (trimer etc.). These species can be formed from monomer and dimer and serve a source of material losses, because they do not contribute to the growth. Besides, revised model assumes less intensive reaction for AlN vapor formation, but more intensive nucleation of AlN particles to fit better the available data.

The model was verified, using the data obtained in vertical research reactor [3] and CCS 3x2” [4] reactor. Growth rate variation with susceptor rotation rate given in [3] is shown in Fig. 1. The difference between data and transport limit is explained by formation of AlN particles in the high temperature region close to the wafer. Here, parasitic chemistry is so pronounced because of both high ammonia and TMAl flow rates at the reactor inlet. Paper [4] considers the V/III ratio effect (V/III=266-8430) at two different TMAl flow rates and variation of growth rate at high TMAl flow rate and low V/III ratio (Fig. 2). As V/III ratio increases, the AlN growth rate decreases due to the formation of heavy-molar-mass / low-diffusivity dimer $(DMAlNH_2)_2$ followed by possible formation of AlN particles.

The revised mechanism of gas-phase reactions is named ***AlN_revised***, the corresponding model of particle formation is available via section

CONDENSATION

2

in the ***model_name.SET file***. The previous model of condensation can be activated via the index 1 in the ***model_name.SET file***, as before. Similar changes have been introduced into the AlGaN model, so the revised mechanism of gas-phase reactions is named ***AlGaN_revised***, and the corrected condensation model has index 2.

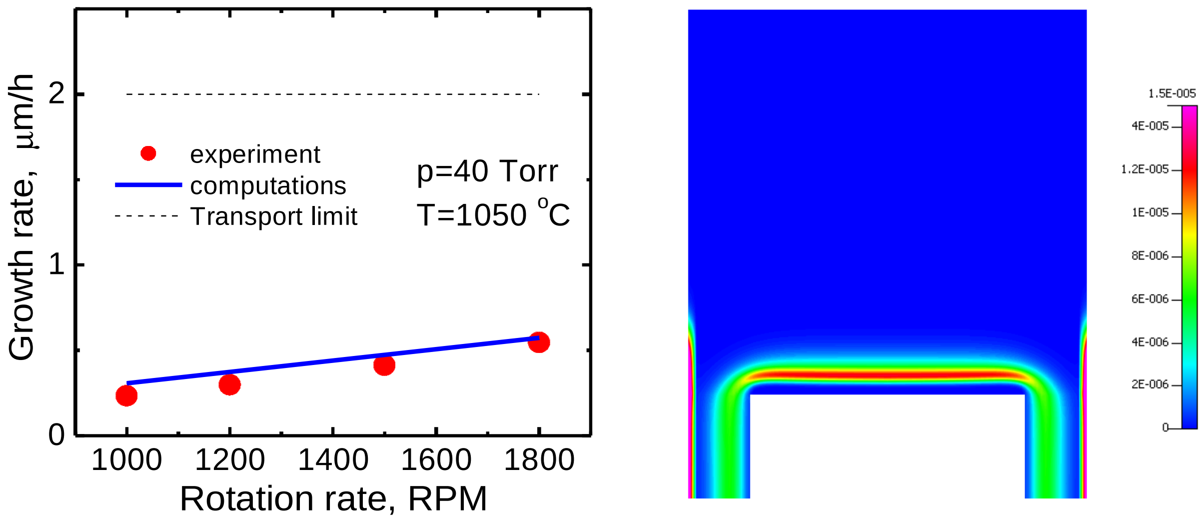


Fig 1. Variation of AlN growth rate with susceptor rotation rate for vertical research reactor: experiment and refined model (left); particle density distribution in kg/m^3 (right).

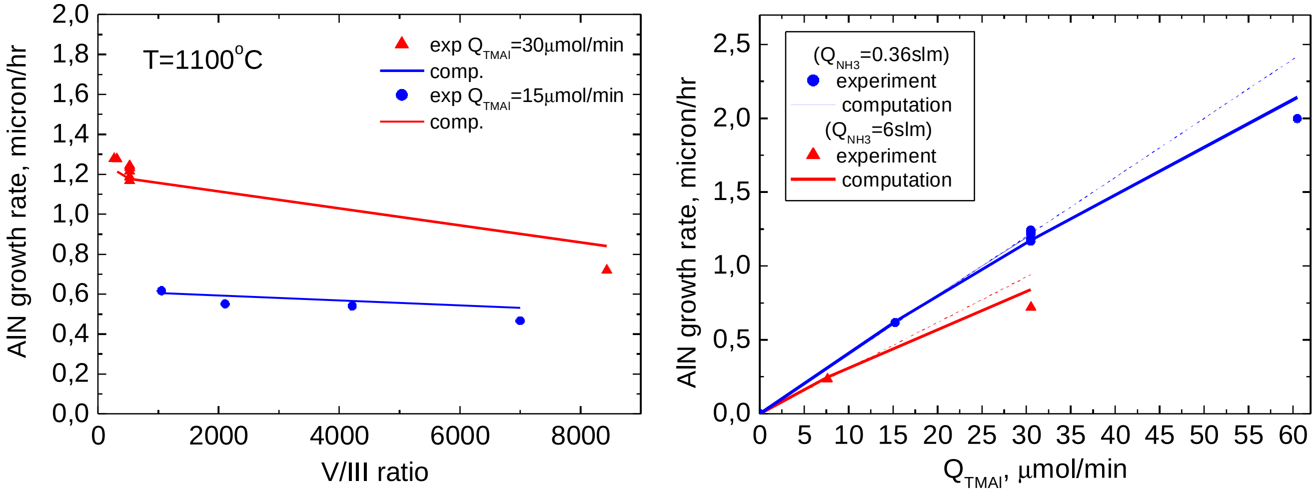


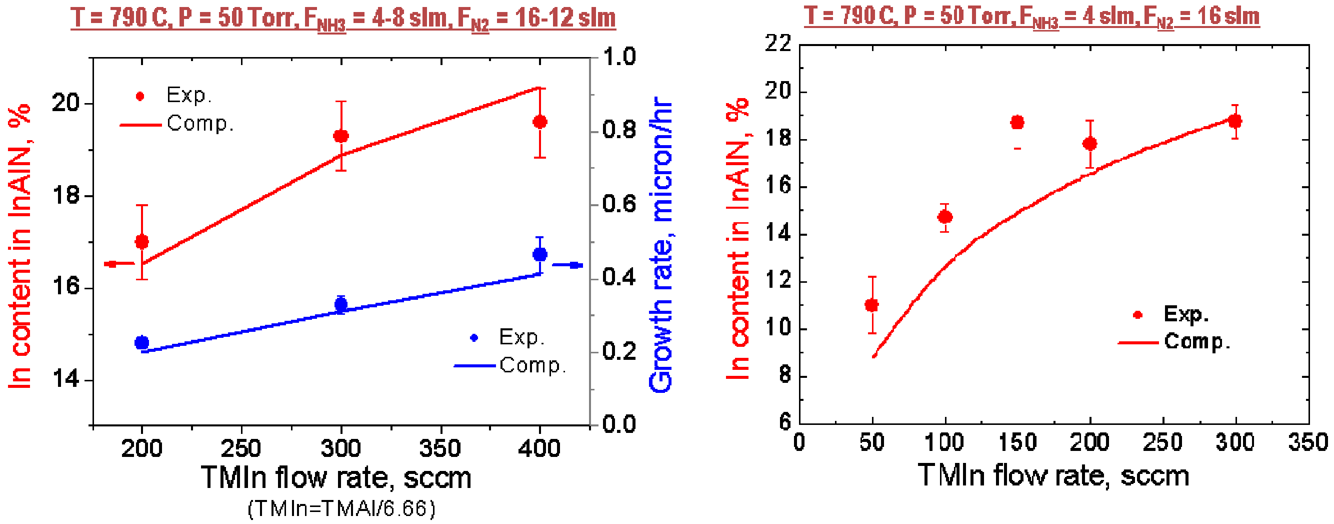
Fig 2. AlN growth rate variation with V/III ratio and TMAl flow rate: experiment and refined model.

2 AlInN Model is Released

Since the growth of AlInN is normally performed at high V/III ratios, the revised AlN model is expected to predict more accurately partial contribution of the AlN constituent into the AlInN growth rate, which is also important to fit experimental data on the alloy composition. We use the quasi-thermodynamic model of surface chemistry that accounts for the interface mass exchange and strain effects within a single approach. Gas-phase chemistry includes the decomposition of TMIn and more complex reaction pathways in the TMAl/NH_3 precursor system, adjusted using the data on the AlN growth rate. The first attempt to model AlInN MOVPE was made in [5] with reference to a single wafer horizontal Aix 200/4 RF-S reactor. Now, additional verification has been made, and the model is included into the CVDSim™ Nitride Edition.

Below we present AlInN model verification in CCS 6x2" reactor at a low pressure [6, 7]. In this case, the process behavior is largely determined by the interaction of species transport and surface kinetics. The model reproduces well the sublinear dependence of the AlInN growth rate and indium content in the layer on the group-III flow rate at high ammonia flows (Fig. 3). The good agreement is, in particular, due to the improvements of the AlN reaction mechanism.

As shown in Fig. 4, the indium content in AlInN rather sharply decreases with temperature due to a higher In desorption flux from the growth surface, and this effect is treated reasonably well by the model.


T = 790 C, P = 50 Torr, F_{NH3} = 4-8 slm, F_{N2} = 16-12 slm

T = 790 C, P = 50 Torr, F_{NH3} = 4 slm, F_{N2} = 16 slm

Fig. 3. AlInN growth rate and composition vs the group-III precursor flow rate (left) and TMIn flow rate (right).

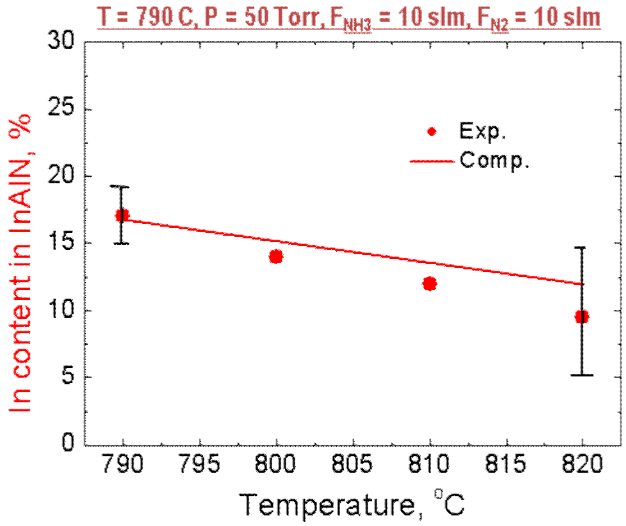


Fig. 4. In content in AlInN vs the temperature.

At elevated pressures (or other conditions favoring particle generation), the above effects are overcome by the gas-phase losses of indium and aluminum due to particle formation. The model accounts for the material losses due to both low-volatile Al-containing oligomers and AlInN particles. Mechanism presented in Fig. 5 illustrates nucleation of AlN particles with the subsequent condensation at the expense of both Al- and In-containing species. Note that there are several examples of AlGaN growth, where AlGaN growth rate was lower than sum of AlN and GaN growth rates measured under similar conditions [8-10]. The effect was explained by AlN particle formation with subsequent sticking of Ga-containing species [11]. We expect that similar mechanism may take place during AlnlN growth. As the pressure is raised, the decrease of the AlInN growth rate at a weakly changing layer composition (Fig. 6, solid lines) is predicted for the growth conditions from [6]. The account of the losses due to AlN particles only would give an increase of the In content with reactor pressure (Fig. 6, dashed lines).

For the results presented here, the model of mixed AlInN particle was used as the basic one, however, within the AlInN MOVPE model, the users of the CVDSim are allowed to consider different models of particle formation. As usually, the account of particle formation is controlled by the two lines:

1. Text string: CONDENSATION
2. Index of the condensation model: **0, 1, 2, 3**.

0 means that particle formation is ignored;

1 means that indium particles (the same model as in case of InGaN) are considered;

2 means that AlN particles (the same revised model as in case of AlN) are considered;

3 means that AlInN particles are considered.

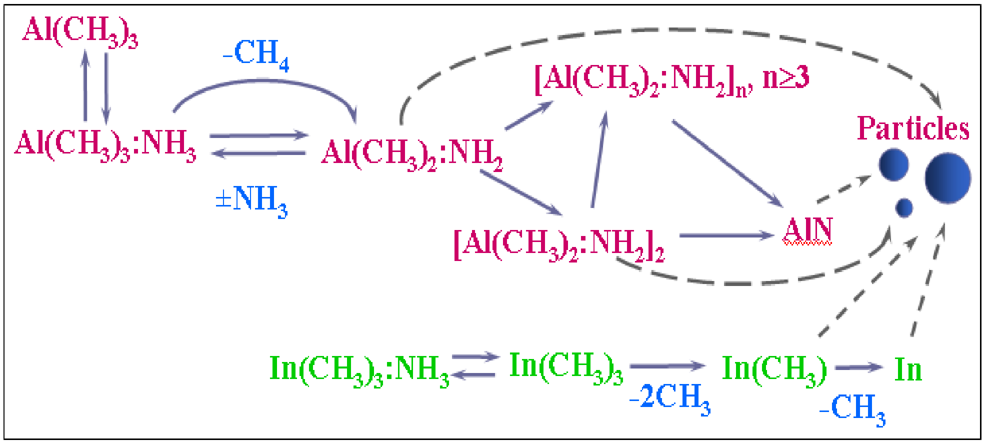


Fig. 5. AlInN gas-phase reaction mechanism.

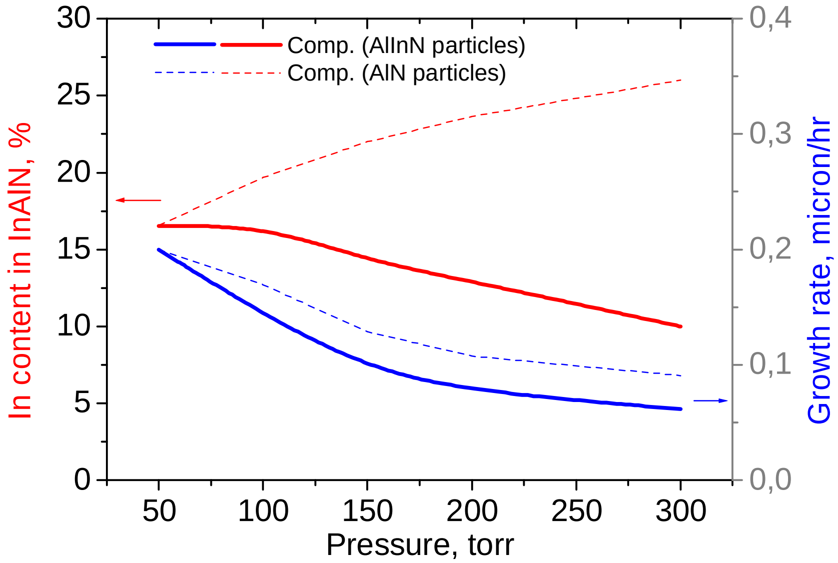


Fig. 6. Growth rate and In content as a function of reactor pressure with the account of AlInN particles (solid lines) and AlN particles (dashed lines).

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