Development of a gas-phase chemistry model for numerical prediction of MOVPE of GaN in industrial scale reactors

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A mathematical model has been developed to describe gas-phase chemical transformations during MOVPE of GaN. Attention was paid primarily to the processes of formation and decomposition of the stable adduct compounds as a salient feature of CVD of group III-nitrides. The model relies upon estimation of the thermochemical properties of the feasible adducts, and detection of the predominant gas-phase species and reaction paths. No fitted parameters are necessary for a complete mathematical formulation due to the assumption of the partial equilibrium character of chemical behaviour of the considered gas mixture flows. The chemical model developed has been incorporated into a general numerical model of the MOCVD reactor. The last one is based on the complete Navier-Stokes equations for fluid dynamics simulation and takes into account all important physical processes such as conjugated heat transfer, radiation, multi-component diffusion as well as stiff gas-phase chemical reactions. Numerical simulation of commercial AIXTRON® reactors (a horizontal tube reactor AIX 200 and a multiwafer Planetary Reactor® AIX 2000) have been performed to obtain better understanding and optimization of nitride growth. Experimental growth conditions have been used as input parameters for calculations. Satisfactory agreement with the measured growth rate indicates a quantitatively appropriate prediction.

A selected approach for the modelling of chemical behaviour of gas mixture flows in epitaxial reactors for group III-nitrides employs the partial equilibrium description of multi-scale chemistry. The well-studied pyrolysis of the most popular initial precursor $Ga(CH_3)_3$ (or Me_3Ga)

$$Me_3Ga \Rightarrow MeGa + 2\ CH_3\ , \qquad MeGa \Rightarrow Ga + CH_3$$

are treated as non-equilibrium finite-rate reversible reactions. In addition, additional fast chemical reactions take place in the gas mixture between the metalorganic molecules and ammonia (a nitrogen precursor). Available data of mass-spectroscopy measurements makes it reasonable to admit the following effective path of the reactions, resulting in formation of the stable cyclic compound molecule $[Me_2Ga{:}NH_2]_3$:

$$Me_3Ga + NH_3 \Rightarrow Me_3Ga{:}NH_3\ , \quad 3\ Me_3Ga{:}NH_3 \Rightarrow [Me_2Ga{:}NH2]_3 + 3\ CH_4$$

The estimated thermodynamic properties of reactants and products of the reactions above seem to agree well with the experimentally observed stable behaviour of the cyclic adduct up to a temperature value of 500°C. Regarding adduct decomposition at higher temperatures, it is generally accepted that it goes through issuing CH_4 molecules and the formation of intermediate molecules of a smaller size. Estimation of thermodynamic properties of several possible intermediate compounds pointed to gas-phase GaN as a dominating product in the temperature range up to 1000°C with corresponding effective brutto-reaction

$$[Me_2Ga{:}NH_2]_3 \Rightarrow 3\ GaN(gas) + 6\ CH_4$$

All the reactions of formation and decomposition of adducts are assumed as very fast.

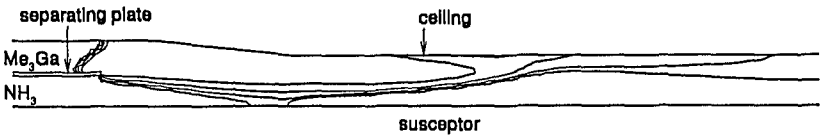

Figure 1: Contours of molar fraction of $[Me_2Ga{:}NH_2]_3$ in the horizontal AIX 200 reactor

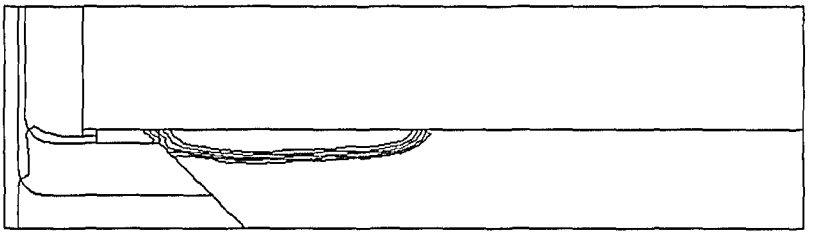

Figure 2: Contours of molar fraction of $[Me_2Ga{:}NH_2]_3$ in the planetary reactor for the growth temperature of 1050°C. Contour levels are arranged between 10^{-7} and 10^{-5}. Superfluous lines are interface boundaries of the grid blocks.

Results of the implementation of the developed model to numerical simulation of MOVPE of GaN in AIXTRON reactors are depicted in Figs.1-2. They confirm the advantageous design of the Planetary Reactor® with respect to the undesired formation of stable adducts during MOVPE of the group III-nitrides. A parametric study of influence of the growth conditions on the adduct formation and deposition rate will be discussed. Also, an extension of the model for application to AlN and AlGaN MOVPE growth will be discussed at the conference.