

Process simulation of *p*-doping in GaN and related group III nitrides

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In this work we use the PROCOM software to model Mg doped GaN film growth by MOCVD. The 2/3D conservation equations of mass, energy, momentum and species are solved by the nonsymmetric conjugate gradient method with block preconditioning (H. C. Elman, Preconditioned conjugate gradient methods for nonsymmetric systems of linear equations (Yale University Research Report, 1981) [5]). A kinetics model with gas/surface adduct formation has been incorporated with detailed Mg dopant reaction mechanism. We reproduced broad doping profiles caused by memory effects and verified that the formation of $(\text{NH}_3)_2\text{-MgCp}_2$ and $\text{NH}_3\text{-MgCp}_2$ adducts play an important role in *p*-doping of GaN and related Group III nitrides.

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1 Introduction The group III nitrides, including GaN and its alloys with AlN and InN, have a number of properties, including a direct, wide band gap, high thermal conductivity, and high thermal stability, that makes them important for green-to-UV optoelectronics and high-power electronic devices. For the *p*-type doping of GaN and its alloys, the dominant species employed is magnesium, which is typically delivered during metal organic chemical vapour deposition (MOCVD) via the organo-metallic precursor magnesocene (MgCp_2) (Cp = cyclopentadienyl group). However, the performance of many of these devices is presently limited by the various difficulties associated with Mg doping, such as its deep acceptor nature, the formation of Mg-H complexes, and the memory effect commonly present in metal-organic chemical vapour deposition (MOCVD). Tight control of doping profiles is required for optimal device performance. Therefore, understanding Mg incorporation and its redistribution behaviour in MOCVD is very important.

In this work we use PROCOM [4] to model Mg doped GaN film growth by MOCVD. The process involves complex gas-phase and surface reactions combined with flow, heat transfer, and mass transfer processes. The results of these physical and chemical rate processes determine the quality of the deposited layers in terms of film thickness, composition uniformity as well as impurity incorporation.

2 Reactor model The reaction-transport model is based on numerical solution of the nonlinear, coupled partial differential equations representing the conservation of momentum, energy, total mass and individual species using the finite element method (FEM). The FEM transport model solves for flow and heat transfer (including conduction in the walls and convection) for realistic reactor configurations. The conservation of total mass and individual species equations are then solved on the same mesh to obtain the concentration profiles.

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Since ammonia and hydrogen are used at comparable flow-rates, mixture rules were used to compute the transport parameters and multicomponent diffusion was accounted for in the species conservation. The diffusion coefficients were estimated based on Leonard-Jones parameters for the gas phase species.

3 Kinetics model The kinetic mechanism for GaN deposition has been developed by Mihopoulos [1] which revolves around the formation and decomposition of TMGa:NH₃ adduct, the decomposition of TMGa, along with surface adsorption of various gas species, formation and decomposition of GaN bulk species. The decomposition of TMGa and NH₃ are well known, and the parasitic adduct formation of TMGa and NH₃ has also been studied extensively. The gas phase reaction rates for the GaN growth are based on those studies. The development of surface reaction mechanisms for GaN growth is complicated by the fact that there are a large number of possible gaseous species that can be adsorbed on the surface and the lack of experimental results. The proposed surface reaction model captures the most important pathways for the formation of GaN with limited number of fitting parameters. We have successfully modeled bulk GaN growth [6] by this mechanism.

The chemical mechanism of Mg incorporation during GaN growth is more complicated and not well understood. Wang and Creighton [2] proposed that magnesocene and ammonia (NH₃) can form condensable Lewis acid-base complexes with magnesocene in both 1:1 and 2:1 ratios (i.e., NH₃-MgCp₂ and (NH₃)₂-MgCp₂) via nucleophilic attack of NH₃ at the positively charged Mg centre of MgCp₂. Adduct formation is reversible, and the 1:1 and 2:1 products can be converted to one another by controlling the NH₃ partial pressure. The formation and condensation of NH₃-MgCp₂ and (NH₃)₂-MgCp₂ at room temperature is the probable parasitic source that leads to the observed broad concentration profiles of Mg during the *p*-type doping of group III nitride materials. The broad profiles of Mg corresponding to a slow response in the doping turn-on and turn-off sequence, is sometimes addressed as “memory effect”. This mechanism is considered in the simulation to reproduce the Mg doping profile and is listed in Table 1.

In the simulation, the dopant is in the form of MgNH and MgH₂, as Reboredo and Pantelides [3] suggested, accounting for MgGa-N-H and interstitial Mg (Mg_i) correspondingly. The detailed kinetic mechanism relating to the dopant is listed in Table 1. Since the doping procedure is carried out in a H-ambient environment the conservation of H atoms is not considered in the related reactions and will not affect the simulation results.

Table 1 Kinetic mechanism for Mg incorporation during the MOCVD growth of GaN

Reaction	K	E _a	ΔG
Gas phase reactions			
MgCp ₂ + NH ₃ = NH ₃ -MgCp ₂	1.e+07	1.0	-5.4 kcal/mol
NH ₃ -MgCp ₂ + NH ₃ = (NH ₃) ₂ -MgCp ₂	1.e+07	0.0	-6.9 kcal/mol
Surface phase reactions			
MgCp ₂ + NH ₃ + Sv<s> ⇌ MgNH + 10CH ₄	6.e+18	7.	-2.0 eV
2MgCp ₂ + Sv<s> ⇌ 2MgH ₂ + 20CH ₄	6.e+18	7.	-5.3 eV
NH ₃ -MgCp ₂ = NH ₃ -MgCp ₂ 	coll (σ=1.0e-5)	0	-2.3 kcal/mol
(NH ₃) ₂ -MgCp ₂ = (NH ₃) ₂ -MgCp ₂ 	coll (σ=1.0e-5)	0	-2.3 kcal/mol

Note: The forward rate constants for the reaction are assumed to have the following Arrhenius temperature dependence: $k_f = K \cdot \exp(-E_a/RT)$, where the pre-exponential factor(K) and the activation energy (E_a) are specified. The reverse rate constants are related to the forward rate constants through the equilibrium constants by $k_r = k_f/K_e$. K_e is the equilibrium constant, which is a thermodynamic property in concentration units. Activation energies (E_a) are in kcal/mol and pre-exponentials (K) are in (cm³/mol)ⁿ⁻¹s⁻¹ (for gas-phase reactions) where n is the order of the reaction and in (cm²/mol) s⁻¹ for surface reactions. σ denotes the sticking coefficient for the collisional type surface reaction. Due to limited available thermochemistry data, free Gibbs energy (ΔG) is assumed to be a temperature independent constant and listed above mainly based on calculations from [1] and [2].

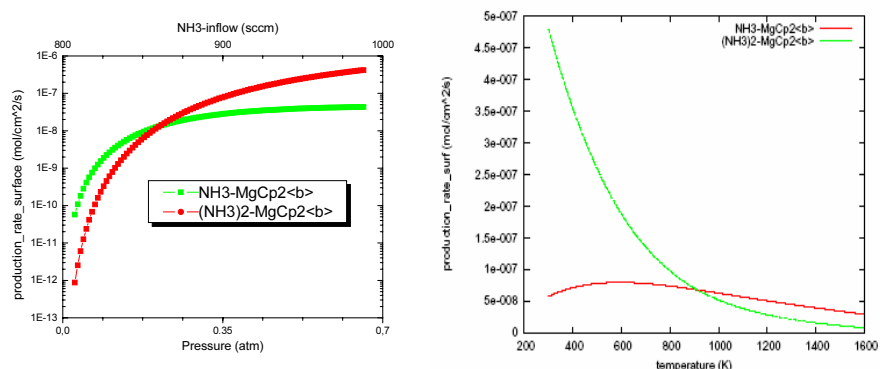


Fig. 1 (a) Production rate of condensed phase adduct of MgCp_2 and NH_3 as a function of pressure and NH_3 flow rate, and (b) production rate of $(\text{NH}_3)_2\text{-MgCp}_2$ and $\text{NH}_3\text{-MgCp}_2$ as a function of temperature.

4 Results, analyses and discussion We have carried out our study in two phases. The first phase of our research is to set up the kinetics using a well-stirred model where all gaseous species are assumed to be well mixed, requiring no diffusion time. The next phase is to transfer the kinetic model in the first phase to a full-scale 2/3-dimension simulation with detailed mass transport model and surface/bulk reactions.

Figures 1a and 1b are results of well-stirred simulation used to verify the experimental results reported in Ref. [1] regarding the condensed adduct behaviour. Figure 1a shows that an increase in pressure will have the effect of increasing NH_3 partial pressure, thus shifting the reaction from $\text{NH}_3\text{-MgCp}_2$ adduct to $(\text{NH}_3)_2\text{-MgCp}_2$ adduct. Consistent with Fig. 1a, Fig. 1b indicates that $(\text{NH}_3)_2\text{-MgCp}_2$ is favoured compared to $\text{NH}_3\text{-MgCp}_2$ at low temperature.

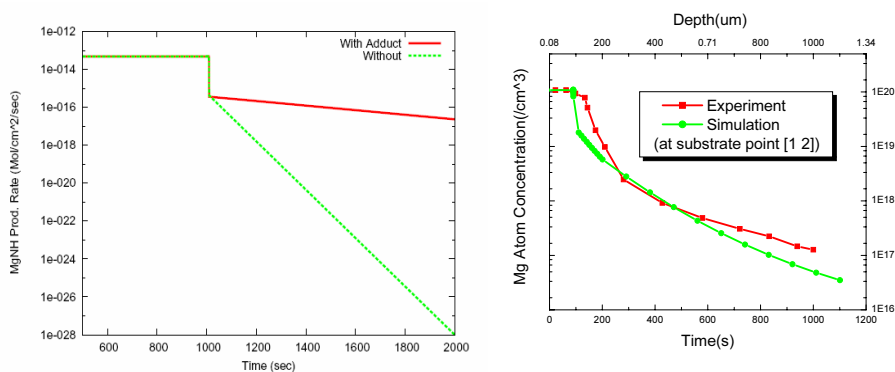


Fig. 2 a) Dopant bulk species production rate as a function of time in well-stirred model; b) Mg concentration as a function of time and depth as produced from 3D simulation of a vertical MOCVD reactor.

Figures 2a and 2b are our key results demonstrating the memory effects in producing the undesirable tail in the *p*-doping profile. The well stirred model in Fig. 2a shows the bulk production rate of Mg doping as a function of time as the inlet Mg source (MgCp_2) is turned off at 1000 seconds producing a sharp initial decrease followed by a longer tail if the adducts are present. The 3D vertical reactor model in Fig. 2b shows a reasonable agreement with experimental data as reported in Ref. [7]. We have obtained a

growth rate of $4.646 \mu\text{m/hr}$ from our simulations, which is used to convert time to thickness in Fig. 2b. As compared with Fig. 2a, Fig. 2b has a smoother profile due to diffusion mass transport absent in the former. In both Figures, we only consider dopant in the form of complex MgNH while all others are ignored since these are much smaller in concentration as the simulation indicated. Our interpretation of the longer tail in the well-stirred model is that adducts desorbed from the reactor wall contribute to the longer tail while the 3D model contains two effects due to the adducts. The first is due to desorption from the wall and the second is due to the heavier mass of the adducts during the diffusion/transport process.

Figures 3a and 3b show the distribution of $(\text{NH}_3)_2\text{-MgCp}_2$ before (10 sec before) and after (1000 sec after) the shutter is turned off. They indicate a 3 order of magnitude drop in gas phase $(\text{NH}_3)_2\text{-MgCp}_2$ adduct concentration near the substrate which corresponds to the tail in Fig. 2b at such a time interval. Figure 3b also shows that a substantial amount of the adduct remains near the centre of the vertical reactor while it is nearly depleted in all other locations.

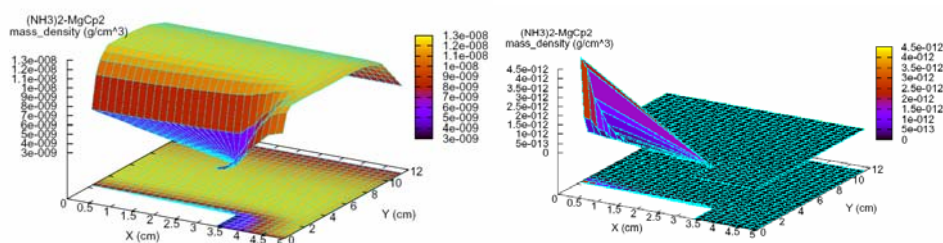


Fig. 3 a) Distribution of adduct within the reactor before turning off Mg source and b) 1000 seconds after. The x-coordinate is the radius of the reactor and the y-axis is the symmetry axis of the cylindrical vertical reactor. The substrate is located from $x = 0$ to 3.5 cm and at $y = 2 \text{ cm}$. The gas outlet is located from $x = 3.5$ to 4.98 cm at $y = 0$.

In summary, we have established a kinetic model to simulate doping of Mg in GaN and related group III nitrides based on adduct formation of $(\text{NH}_3)_2\text{-MgCp}_2$ and $\text{NH}_3\text{-MgCp}_2$. The transient simulation shows that the adducts of $(\text{NH}_3)_2\text{-MgCp}_2$ and $\text{NH}_3\text{-MgCp}_2$ remaining in the reactor after the Mg source (MgCp_2) is turned off are responsible for the long tail observed in experiments.

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