Complex Flow and Gas Phase Chemical Reactions in GaN MOVPE Reactor

K. Harafuji, Y. Hasegawa, A. Ishibashi, A. Tsujimura, N. Otsuka,

I. Kidoguchi and Y. Ban

Advanced Technology Research Laboratories, Matsushita Electric Ind. Co., Ltd.
3-1-1 Yagumo-Nakamachi, Moriguchi, Osaka 570－8501, Japan

While violet laser diodes and blue/green light emitting diodes using gallium nitride (GaN) materials are commercially available, the crystal quality has not yet been satisfactory and strongly depends on the method of metalorganic vapor phase epitaxy (MOVPE). Horizontal MOVPE reactors have been commonly used in a single crystalline growth of III-V GaAs and InP materials, and are reported for GaN related materials in recent years. In this paper, three-dimensional (3D) simulations of thermohydrodynamics and chemistry are presented in a horizontal reactor for GaN epitaxy.

The model reactor geometry made of quartz is shown in Fig.1. This is a two-split-flow reactor with a linear expansion entrance region of 10.7 ° tapering angle. The length, the width and the height of the reactor are 0.6m, 0.1m, and 0.014m, respectively. Flow channel heights of upper, lower expansion regions and the reaction space are 4mm, 4mm, and 10mm, respectively. Bottom planes of the lower channel and the reaction space correspond to z=2mm. From the upper inlet, trimethylgallium(TMG) diluted by mixed H_2-N_2 carrier gas is fed. On the other hand, NH_3 is fed from the lower inlet. Both the molar ratios of H_2:N_2 and H_2-N_2:NH_3 are 1:1. The V/III ratio is fixed at 10000. The rectangular heater with 1300K is placed on the bottom in the reaction space. The cold wall temperature is 310K.

The formulation for a steady state problem consists of following conservation equations of mass, momentum, energy and individual species in a laminar and compressive fluid model:

$$\frac{\partial r u_i}{\partial x_i} = 0 \quad (1) \qquad \frac{\partial u_j r u_i}{\partial x_j} = \frac{\partial s_{ij}}{\partial x_j} + r g_i \quad (2)$$

$$\frac{\partial u_j r H}{\partial x_j} = \frac{\partial u_j p}{\partial x_j} + s_{ij}\frac{\partial u_i}{\partial x_j} + \frac{\partial}{\partial x_j} l \frac{\partial T}{\partial x_j} + q \quad (3) \qquad \frac{\partial u_j r C_k}{\partial x_j} = \frac{\partial}{\partial x_j} r D_m \frac{\partial C_k}{\partial x_j} + r d \quad (4)$$

where σ_{ij} is the stress tensor, H the specific enthalpy, g_i the gravity, λ the thermal conductivity, q the heat generation, d the source term due to chemical reaction, C_k the mass fraction of k-th species. The other notations are standard ones. Here, Einstein's summation rule is used. These equations are approximated by a control volume method with a collocated mesh, and resultant asymmetric-matrix equations are solved iteratively by conjugate gradient squared method. The thermal diffusion is neglected here. A kinetic mechanism of MOVPE gas-phase reactions are based on the work by Mihopoulos [1]. The mechanism consists of six reactions and ten species, which are shown in Fig.2. Reaction rates obey Arrhenius behavior. Gas mixture properties of H_2-N_2-NH_3 on temperature are modeled as follows [2]. The viscosity and the thermal conductivity for each gas are, respectively, based on the Chapman-Enskog theory and the modified Euken relation, and those are extended to multicomponent gas mixture by the Wilke method and the Wassiljewa equation with the Mason/Saxena modification, respectively. Diffusion coefficients for binary gas system are based on the Fuller *et al.* method, and are extended to multicomponent gas mixture by the Blanc's law. The specific heat at constant pressure for the mixed gas is made 5037.5(J/(Kg・K)) according to molar ratios of H_2, N_2 and NH_3.

Simulation conditions are as follows: gas flow velocity at inlets is 5m/s, and gas pressure is 40000Pa (300Torr). Average flow velocity near the heater and the total gas flow rate for this condition are 0.167m/s and 9.6slm, respectively. Figure 3 shows the cross-sectional view of various quantity distributions at the symmetric plane (y=0m) around the heater: (a) temperature, (b)flow velocity vector, (c)$Ga(CH_3)_3$:NH_3 mass fraction, (d) $[Ga(CH_3)_2NH_2]_3$ mass fraction, (e) Ga-N mass fraction. Physical quantities are the larger, as densities are the darker. As is shown in Fig.3(b), developed Poiseuille flow pattern is achieved above the heater, with the velocity peak shifting to upward due to buoyancy. The mass fraction of adduct $Ga(CH_3)_3$:NH_3 as a precursor of $[Ga(CH_3)_2NH_2]_3$ is peaked near the mixing plane of upper and lower flow channels (see Fig.3(c)). It is clearly understood from Figs.3(c), (d) and (e) that the adduct $Ga(CH_3)_3$:NH_3 is changed to $[Ga(CH_3)_2NH_2]_3$ by the chemical reaction near the front of the heater portion, and that the adduct $[Ga(CH_3)_2NH_2]_3$ itself is further changed to adduct Ga-N above the heater portion. The spatial distribution of adducts $[Ga(CH_3)_2NH_2]_3$ and Ga-N have a direct influence on that of GaN film thickness [1]. The peak portion of $[Ga(CH_3)_2NH_2]_3$ shifts to cold top wall by the buoyancy as we go downstream. The temperature profile of Fig.3(a) supports the spatial variations of the velocity peak and the $[Ga(CH_3)_2NH_2]_3$ fraction as is described. This buoyancy effect can also be seen from Fig.4(a). Figure 4(b) is the cross-sectional view of flow velocity at x=0.24m (mid-plane of the heater).

Longitudinal vortices are seen near both side corners, that is, near the edge between heater portion and cold wall. Figure 5 shows the plan view of the distribution of several quantities. Due to high viscosity of NH_3 compared with H_2-N_2 mixture, flow-separation or return-flow near the gas entrance of expansion region in the lower flow channel is larger than that in the upper flow channel. As a result, in the lower channel, the effective flow channel width near the gas entrance becomes narrow, and the flow velocity near the symmetric plane (y=0m) is high (see Fig.3(b)). This velocity peaking causes the non-uniformity of temperature, mass fractions of $Ga(CH_3)_3$:NH_3, $[Ga(CH_3)_2NH_2]_3$, and Ga-N above the heater portion. Note that the mass fraction of $[Ga(CH_3)_2NH_2]_3$ is very small just above the rectangular heater portion due to buoyancy.

In conclusion, 3D simulations of complex flow and chemical reactions in horizontal MOVPE reactors for GaN epitaxy are studied. Spatial transitions of adducts are well described. Improvements of reactor geometry, especially gas inlet geometry, are necessary to achieve uniform physical quantities. Pressing flow to the substrate may be desirable above the heater portion to promote CVD surface reactions.

References

[1]T.Mihopoulos: Ph.D.Thesis, Massachusetts Institute of Technology, 1999.

[2]R.C.Reid, J.M.Prausnitz and B.E.Poling : The Properties of Gases & Liquids, 4th ed., McGraw Hill.

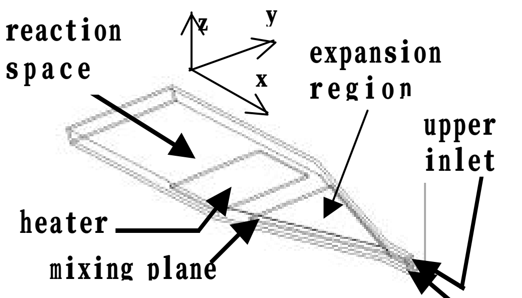

Fig.1 Model reactor geometry.

$Ga(CH_3)_3 \rightarrow GaCH_3 + 2CH_3$

$Ga(CH_3)_3 + NH_3 \rightarrow Ga(CH_3)_3{:}NH_3$

$Ga(CH_3)_3{:}NH_3 \rightarrow Ga(CH_3)_3 + NH_3$

$Ga(CH_3)_3{:}NH_3 \rightarrow (1/3)[Ga(CH_3)_2NH_2]_3 + CH_4$

$Ga(CH_3)_3{:}NH_3 + NH_3 \rightarrow (1/3)[Ga(CH_3)_2NH_2]_3 + CH_4 + NH_3$

$[Ga(CH_3)_2NH_2]_3 \rightarrow 3$"Ga-N"$ + 6CH_4$

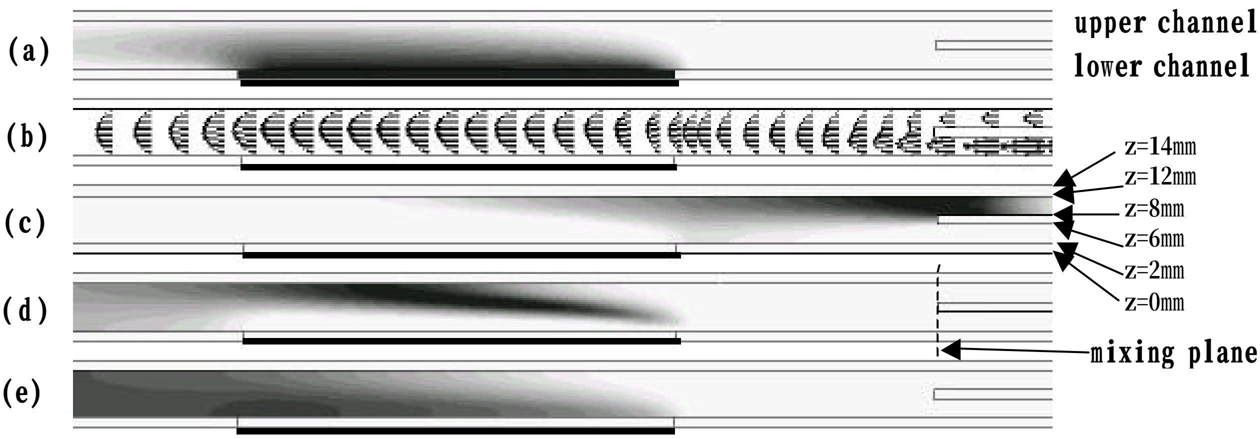

Fig.3 Cross-sectional view of various quantity distributions at the symmetric plane (y=0m) around the heater: (a) temperature, (b) flow velocity vector, (c) $Ga(CH_3)_3$:NH_3 mass fraction, (d) $[Ga(CH_3)_2NH_2]_3$ mass fraction, (e) Ga-N mass fraction. Physical quantities are the larger, as densities are the darker. The z-coordinate is shown in Fig.(c). Bold line denotes the heater.

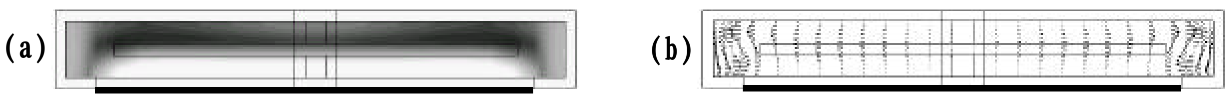

Fig.4 (a) Cross-sectional view of $[Ga(CH_3)_2NH_2]_3$ mass fraction distribution at x=0.24m (mid-plane of heater). Physical quantities are the larger, as densities are the darker. (b) Cross-sectional view of flow velocity at at x=0.24m. Bold line denotes the heater.

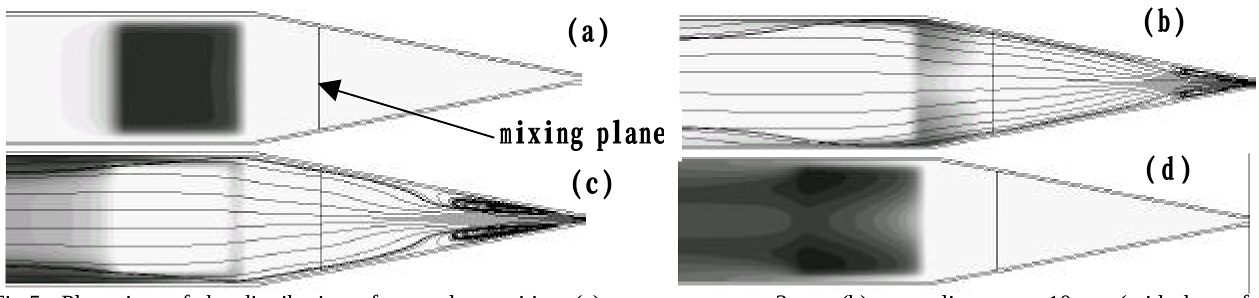

Fig.5 Plan view of the distribution of several quantities: (a)temperature at z=3mm, (b)stream lines at z=10mm (mid-plane of upper inlet) & $Ga(CH_3)_3$:NH_3 mass fraction at z=3mm, (c)stream lines at z=4mm (mid-plane of lower inlet) & $[Ga(CH_3)_2NH_2]_3$ mass fraction at z=3mm, (d)Ga-N mass fraction at z=3mm. Physical quantities are the larger, as densities are the darker.