Sources of the Parasitic Chemical Reactions during AlGaN OMVPE

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At normal operating conditions, most AlGaN OMVPE reactors exhibit non-ideal behavior with respect to the group-III precursor concentration. The deposition rate can be considerably less than the predicted transport-limited rate, and the solid AlGaN alloy composition is typically a nonlinear function of the gas-phase composition. It is generally thought that gas-phase "parasitic" reactions between trimethylgallium (TMGa), trimethylaluminum (TMAl), and ammonia are responsible for removing group-III material from the deposition process. One of the most basic questions deals with the thermal requirements of the parasitic chemistry. Does the parasitic pathway turn on at low temperatures (e.g. near the inlet), or does it only happen when the gases get very hot (e.g. near the wafer)? Much of the heuristic evidence regarding reactor design for AlGaN OMVPE revolves around this issue. We have explored many possible mechanisms for the parasitic pathways using a variety of experimental techniques and reactive flow simulations. Our experimental approaches include; (1) direct examination of metalorganic precursor reactions using FTIR and mass spectroscopy, (2) reactor-scale experiments in our research rotating disk reactor (RDR) to measure growth rates over a wide range of operating conditions, and (3) light scattering experiments to search for particle formation.

Results from our direct chemistry studies indicate that adducts form (as expected) between the metalorganic precursors and ammonia, e.g. TMAl + $NH_3 \rightarrow$ TMAl:NH_3. However, adduct formation alone cannot account for the parasitic losses (as long as the adduct vapor pressure is not exceeded). Methane elimination (e.g. TMAl:$NH_3 \rightarrow$ DMAl-NH_2 + CH_4) has often been proposed as a possible reaction that eventually creates the parasitic term, but at typical reactor concentrations and residence times these reactions require temperatures well above 100°C to become significant. These results imply that the parasitic chemistry requires high temperatures.

Results of the reactor-scale experiments also indicate that the parasitic term involves high-temperature chemistry. By examining simple kinetic models and the RDR scaling relationships we found that the two extreme scenarios (low temperature vs. high temperature) could be differentiated by varying the spin rate or the total reactor flow rate. This differentiation occurs because the reactor residence time and the boundary layer residence time respond differently to changes in spin rate or total flow rate. An extensive data set varying the spin rate for GaN deposition is shown in Fig. 1. At lower spin rates (e.g. 800 rpm) the growth rate is significantly below the transport limit, and it is sublinear with respect to TMGa flow. As the spin rate is raised to 1800 rpm the growth rate reaches the transport limit and becomes linear with respect to TMGa flow. The dominant reason for the increase in growth rate is the shorter residence time of the gases in the boundary layer. Our reactive flow simulations reproduce many of the trends we observe experimentally, but model refinement is still in progress.

Recent light scattering experiments in an inverted stagnation point flow reactor have produced the first direct observation of particle formation during AlGaN OMVPE (see Fig. 2). These particles are formed by chemical reactions that require the high temperatures encountered in the boundary layer. Thermophoresis keeps the particles from reaching the surface so they do not contribute to the deposition rate.

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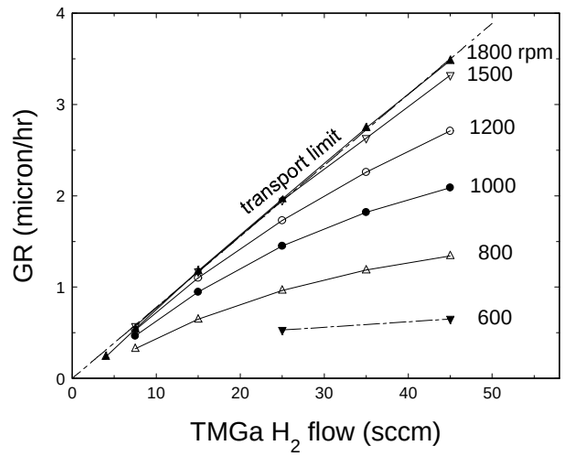

Fig. 1. GaN OMVPE growth rates (GR) as a function of TMGa flow rate and reactor spin rate under matched flow conditions, at 140 Torr and 1050°C.

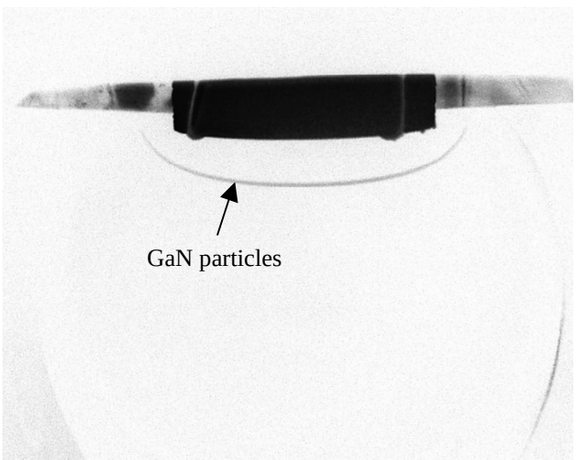

Fig. 2 Inverted stagnation point flow reactor growing GaN near standard OMVPE conditions; 140 Torr, 1050°C, flow velocity = 23 cm/sec. A layer of particles within 1 cm of the substrate is visible under laser irradiation (50 mW, 488 nm). The substrate diameter is 2.54 cm. A similar band of particles can be seen for AlN at 80 Torr.