Reaction Kinetics and Transport Model for Gallium Nitride MOVPE Reactor Showerhead Design

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MOTIVATION

Gallium Nitride (GaN) is a compound semiconductor material with tremendous potential in the electronics industry. Metalorganic vapor phase epitaxy (MOVPE) is the principal method used to grow thin films of this material. Therefore, fundamental understanding of complex gas phase and surface reactions combined with flow, heat transfer, and mass transfer processes is critical for the production of high quality deposited layers.

Applications of GaN based Materials

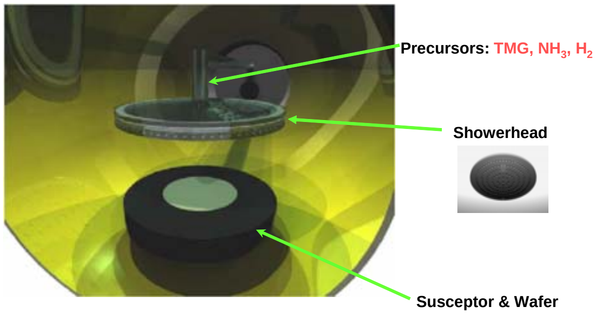
[1]Aerospace devices that can function over a wide temperature range and remain unaffected by radiation.

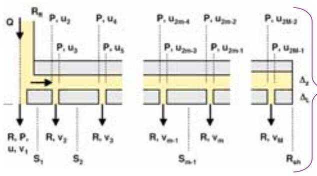
[2]Powerful new radar technology which will detect smaller and faster targets.

[3]A blue laser that will increase the storage capacity of a compact disc.

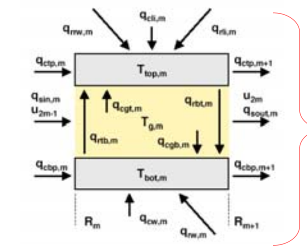
[1,2,3] Pictures taken from www.northropgrumman.com

MOVPE REACTOR SYSTEM





Cross-section of showerhead configuration
hole ring radii : $R_1,\ldots,R_M$
gas radial velocity inside showerhead : $u_1,\ldots,u_{2M-1}$
reactant gas velocity through holes : $v_1,\ldots,v_M$
showerhead gas pressure : $P_1,\ldots,P_{2M-1}$



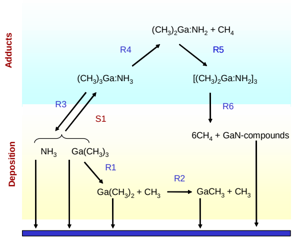
Showerhead internal heat transfer
conduction thru plates : q_{ctp} , q_{cbp}
plate/reactant gas : q_{cgt} , q_{cgb}
gas sensible heat : q_{sin} , q_{sout}

Wafer / showerhead heat transfer
radiation : q_{rrw} , q_{rw}
conduction : q_{cw}

Wafer / liner heat transfer
radiation : q_{rli}
conduction : q_{cli}

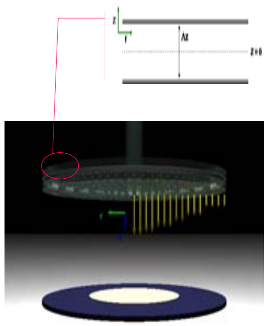
CHEMICAL KINETICS

The growth of quality GaN thin films is complicated by complex gas phase reactions between the common precursors: trimethylgallium (TMG) and ammonia (NH$_3$). Two competing reaction pathways exist which lead to either adduct formation or pyrolysis of TMG.



Problem: Adduct formation and deposition within the showerhead can contribute to poor growth rate and film quality.

Goal: Develop a model that captures mass transfer and kinetic effects (gas phase and surface reaction) inside showerhead



1D Modeling Equations:

Consider the gas phase thermal decomposition of TMG

TMG -> DMG -> MMG

Continuity Equation:

$$\frac{d}{dr}(v\rho r) = 0$$

Thermal Energy Balance:

$$\frac{1}{r}\frac{d}{dr}(vr) = h(T_s - T)$$

Species Balance Equations:

$$\frac{1}{r}\frac{d}{dr}\left(\frac{1}{T} r v x_{TMG}\right) = -\frac{1}{T}k_1(T)x_{TMG} - k_{dep}x_{TMG}$$

$$\frac{1}{r}\frac{d}{dr}\left(\frac{1}{T} r v x_{DMG}\right) = -\frac{1}{T}k_2(T)x_{DMG} + \frac{1}{T}k_1(T)x_{TMG}$$

$$\frac{1}{r}\frac{d}{dr}\left(\frac{1}{T} r v x_{MMG}\right) = \frac{1}{T}k_2(T)x_{DMG}$$

2D Modeling Equations:

$$\frac{\partial C_i}{\partial t} + \nabla\cdot(v C_i) = D_i\nabla^2 C_i + R_G^i \quad \text{(eq .1)}$$

General form of the species conservation equation for a pseudobinary mixture

$$v_r\frac{\partial C_i}{\partial r} = D_i\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_i}{\partial r}\right) + \frac{\partial^2 C_i}{\partial z^2}\right] + R_G^i \quad \text{(eq .2)}$$

Neglecting v_z and v_θ and Assuming $C_i(r,z)$

Boundary Conditions:

r – direction:

$$C_i(r_{in}, z) = C_{i0}$$

$$\frac{\partial C_i(r_{out}, z)}{\partial r} = 0$$

z – direction:

$$-D_i\frac{\partial C_i(r, -\Delta z/2)}{\partial z} = R^i_{S,bot}$$

$$D_i\frac{\partial C_i(r, \Delta z/2)}{\partial z} = R^i_{S,top}$$

Rate of Adsorption (R_S)

- Controlled by the rate of arrival of molecules to the surface, F, and the fraction of incident molecules which are adsorbed, S

$$R_S = S\cdot F \quad \text{(eq. 3)} \longrightarrow F = \frac{P}{(2\pi mkT)^{1/2}}\frac{1}{N_A} \quad \text{(eq. 4)}$$

Assumptions:

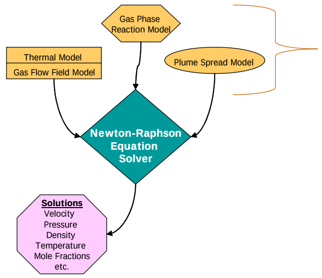
1) Surface reactions are controlled by arrival rate of gas phase species to top and bottom showerhead plates. (Arrival rate is approximated by kinetic theory)

2) Diffusional interaction among minor species can be neglected.

Ultimate Goal: Compute the amount of deposited material inside the showerhead. This will give a better indication of the intrinsic chemistry responsible for GaN growth.

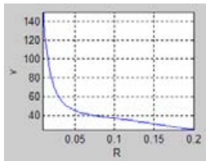
MODEL DEVELOPMENT

The simulator was developed using an object-oriented approach. Modeling equations for the showerhead thermal and gas flow field model, the plume spread model, and gas phase reaction model were decoupled from each other and placed in different model classes (modules).

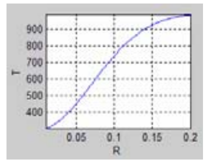


1. Model Development
2. Set up Quadrature Grid
   SG_1 = QuadGrid(' cyln ', nrFirst, ' r ', [Rft, ringLoc(2)]);
3. Create LinearOperator Object
   Dr = LinearOperator(SG_1, ' d ' ,' r ');
4. Construct ScalarField object for variables
   X_1 = ScalarField(SG_1, Xin(1,1));
   X_2 = ScalarField(SG_1, Xin(2,1));

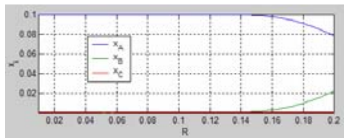
1D Simulation Results: Thermal model, Gas Flow Field, Kinetics



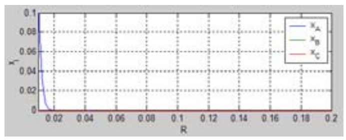
Velocity Profile



Temperature Profile



Species Profile for Gas Phase Reactions
A(g) -> B(g) -> C(g)



Species Profile for Gas Phase and Deposition Reactions
A(g) -> B(g) -> C(g)
Surface

SUMMARY & FUTURE WORK

- **Summary**
  - Object oriented techniques create an efficient approach to assembling models of this form, and allow the addition of more model components without much difficulty.
  - Developed a model that describes mass transport and kinetic effects within the showerhead
- **Future Work**
  - Examine kinetic theory of gases: bimolecular collision rate vs. impingement rate of molecules on a surface.