COMSOL CONFERENCE 2019

Impact of Operating Parameters on Precursor Separation in "Air Hockey" Spatial Atomic Layer Deposition Reactor

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Introduction: Atomic Layer Deposition (ALD)

What is ALD?

- Thin film deposition technique praised for high quality, conformal, dense films with atomic level thickness control

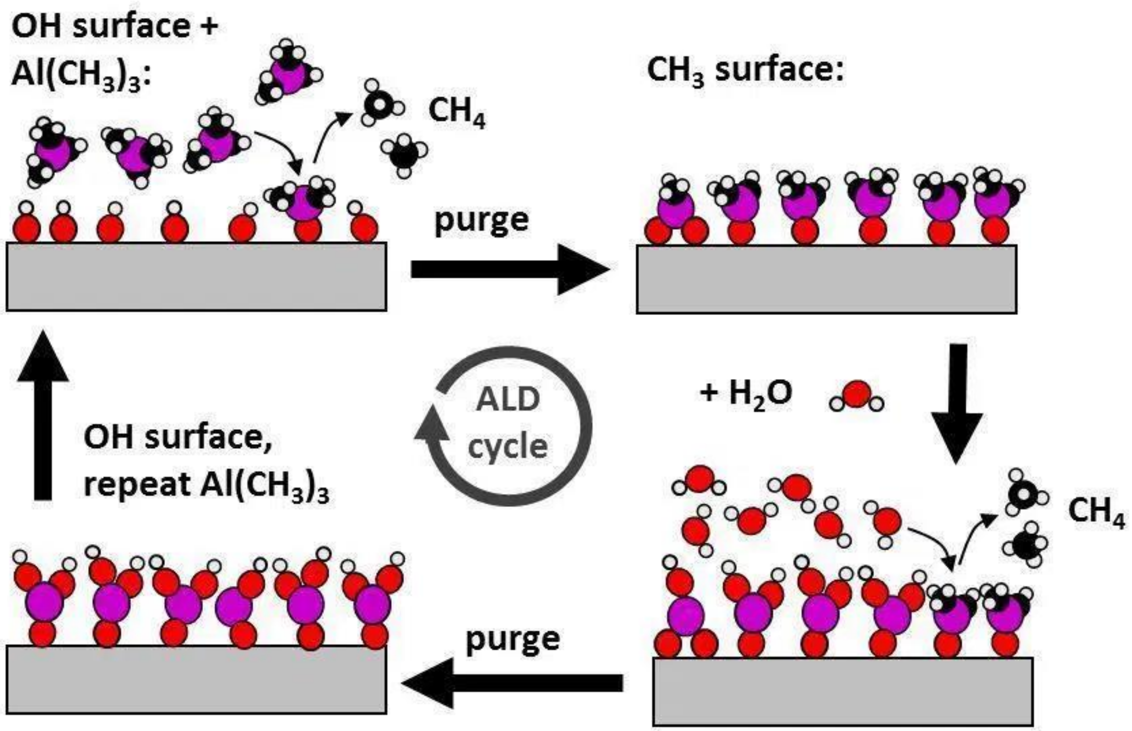
Critical Features:

- Sequential exposure of surface to saturating precursors
- Low growth rates (0.1 nm/s)
- Vacuum process

Applications:

- Semiconductors
- Solar Cells
- Optical Filters

Temporal ALD



N. Parsons, Gregory & George, S.M. & Knez, Mato. (2011). Progress and future directions for atomic layer deposition and ALD-based chemistry. MRS bulletin / Materials Research Society. 36. 865.10.1557/mrs.2011.238

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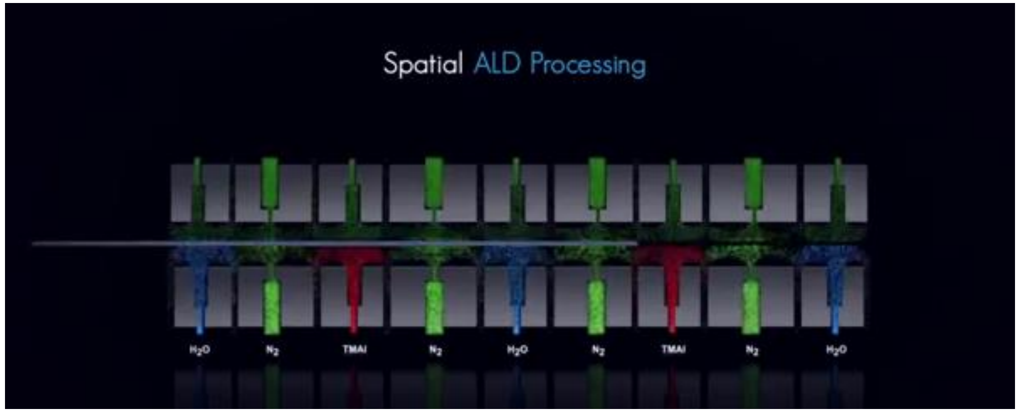
Introduction: Spatial ALD



Why Spatial ALD?

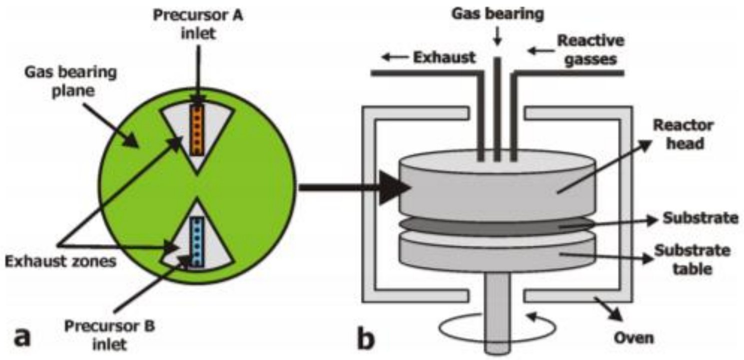
- Ultra-fast, uniform thin films deposited at low temperatures
- Industrially viable, high-throughput processing

Critical Feature of Spatial ALD Reactors:

- Successful spatial separation of the precursors

Types of Spatial ALD Reactors:

- Roll-to-Roll (Flexible Substrates)
- In-line deposition head (Sheet-to-Sheet)
- Rotary stage (Batch Processing)

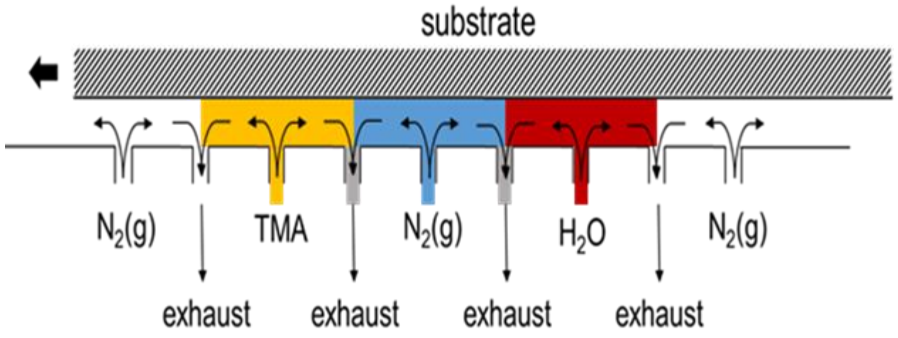


Poodt et al. (2012) *J. Vac. Sci. Technol.*
http://www.solaytec.com/

Overview: Air Hockey Reactor

Operation:

- The vents in the deposition region suspend the substrate on a bed of fluid
- Precursor separation is achieved through a barrier gas stream placed between the precursor vents
- Atmospheric pressure operation



Challenges:

- The deposition gap is a function of the flow parameters
- Deposition gap is critical to prevent precursor mixing

$$Mg = \int_0^R 2\pi r(\boldsymbol{p} - p_a)dr$$

Motivation and Approach:

- Develop a model to predict the flotation height
- Investigate how different operating conditions affect precursor separation and utilization

Part I: Flotation Height

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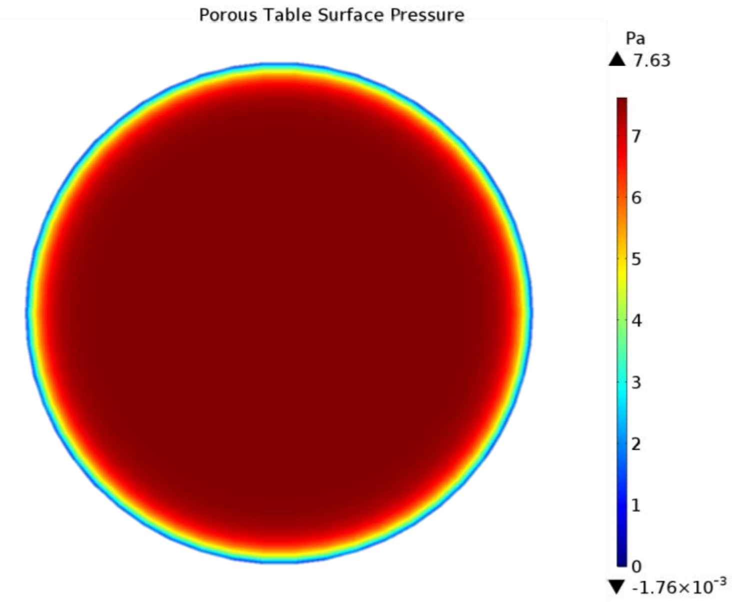
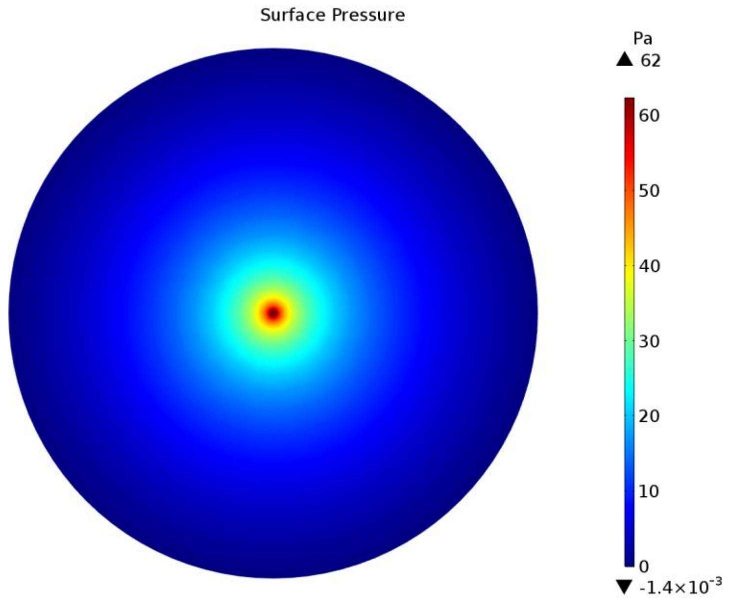
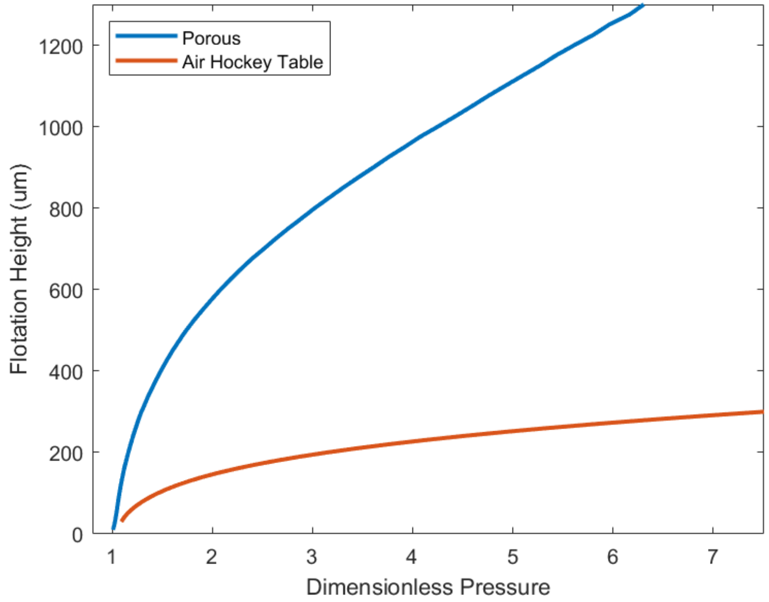
Summary – Poster Session







Hypothesis: The air hockey table will behave according to the porous table model at the limit of an infinitely sized array with infinitely small vertical jets

Visit my Poster – Thursday 6:00-7:00PM for more detailed information

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Part II: Diffusion Model

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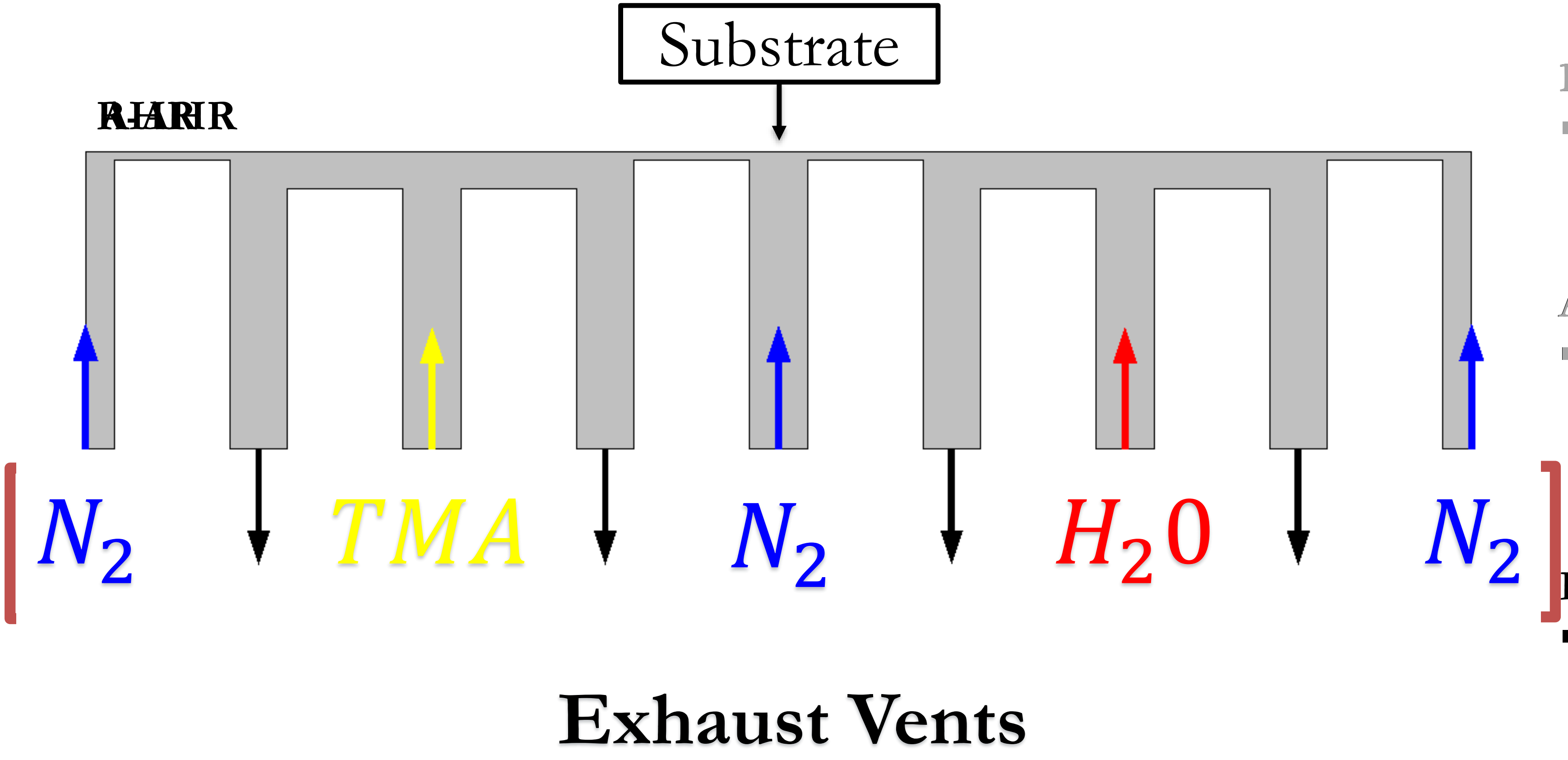
Diffusion Model Definition



Deposition Head Reactor:

- All parameters are set

Air Hockey Reactor:

- Force balance determines N_2 flow rate

Recessed - Air Hockey Reactor:

- Different geometry; identical operation

Regimes of Operation

(1) CVD Regime:

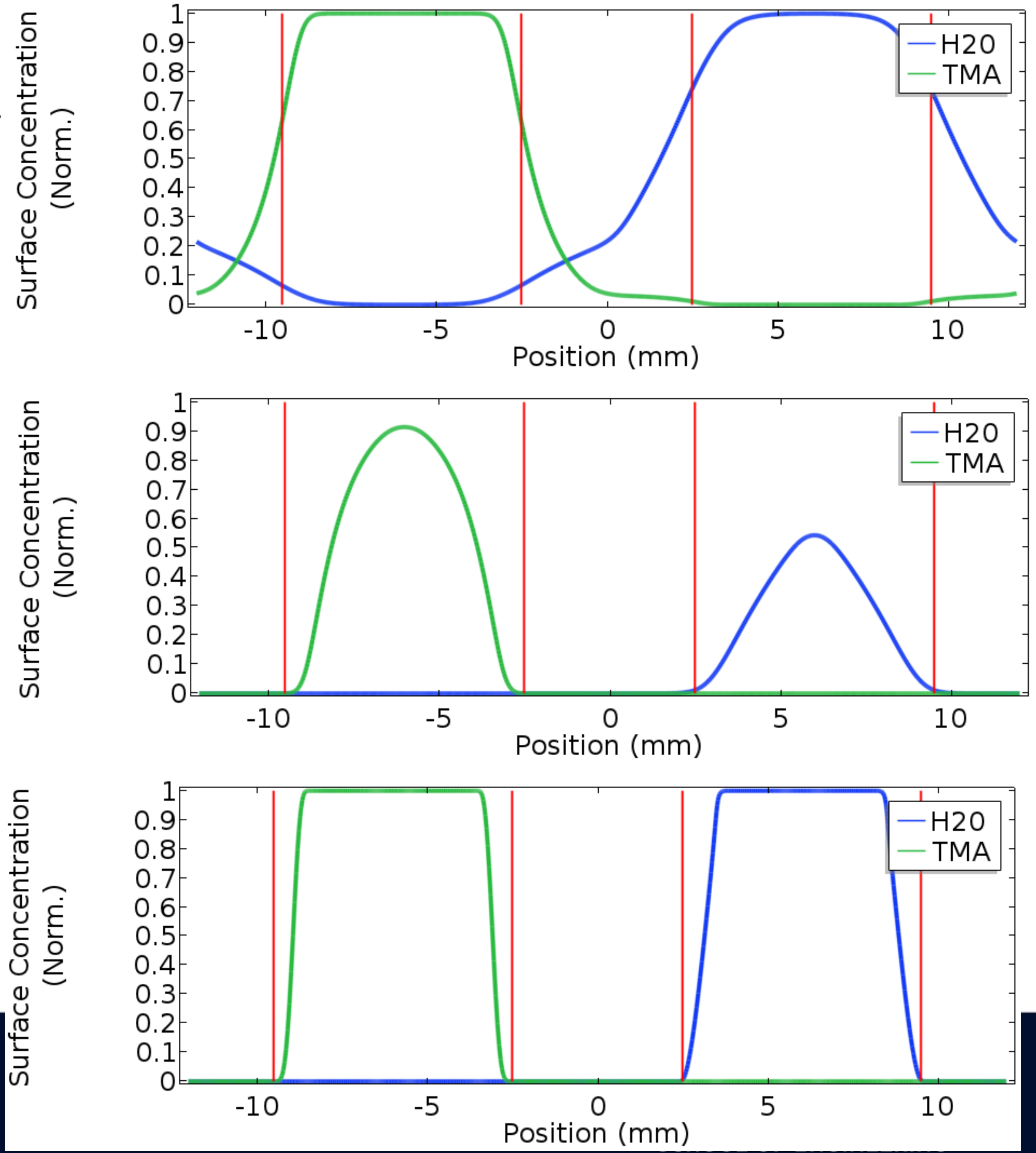
- Precursor mixing occurs in overlap region

(2) Precursor Deficient Regime

- Nonuniform surface concentration
- Insufficient precursor utilization

(3) ALD Regime:

- Effective precursor separation
- High surface concetration

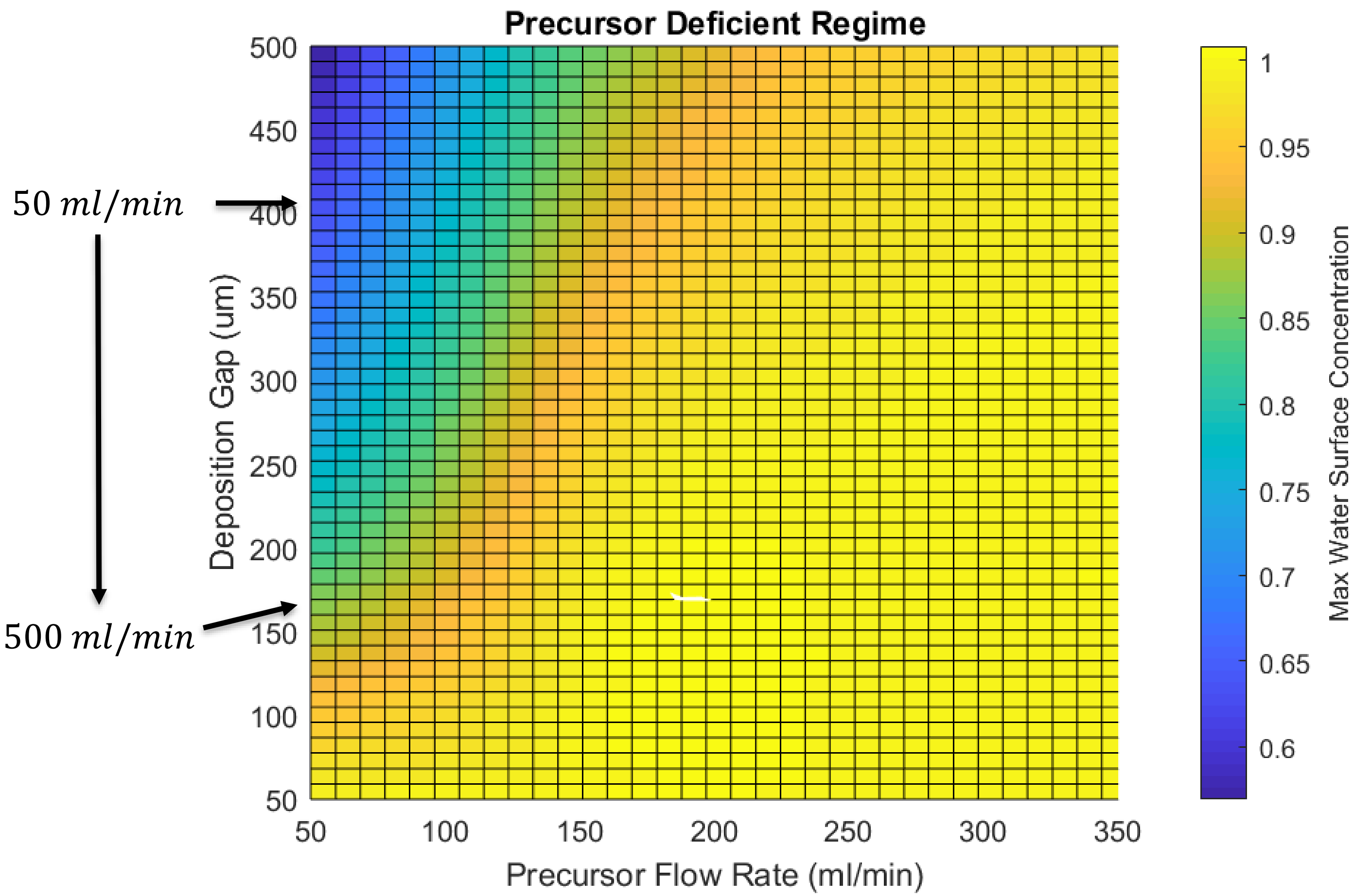


(1)

(2)

(3)

Deposition Head Reactor (DHR)



CVD Regime:

- Large deposition gaps
- Low barrier gas flow

ALD Regime:

- Small deposition gaps < 200 um
- Barrier gas flow > 250 ml/min

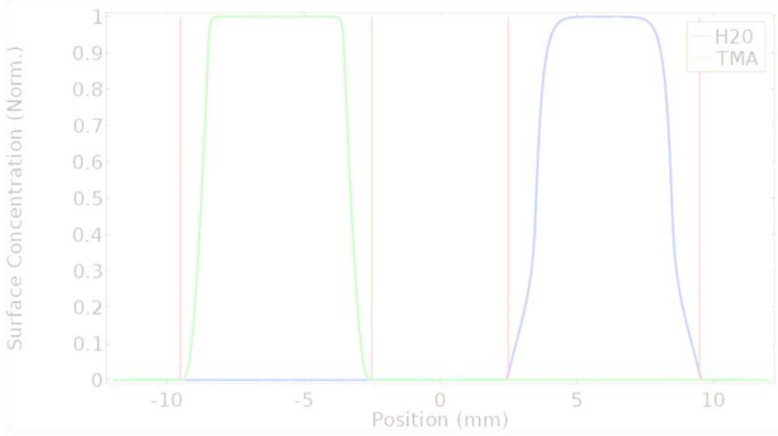
Precursor Deficient:

- Low precursor flow
- Large deposition gaps

Air Hockey Reactor (AHR)

Small Deposition Gaps (50 um):

- Effective precursor separation at all conditions except small deposition gaps
- $Q_{Precursor} > Q_{Barrier}$
- Pumping the exhaust vents can allow for effective separation

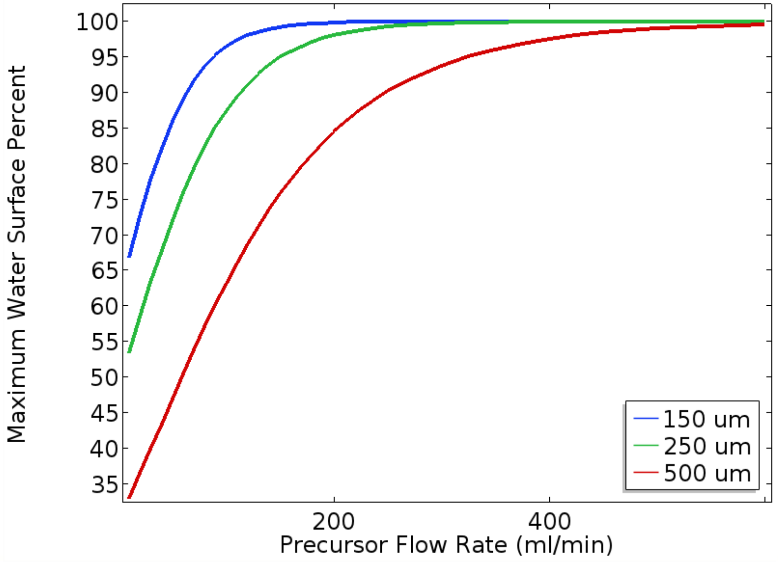


$d = 50\ um$

$Q_{Pre} = 100\ ml/min$

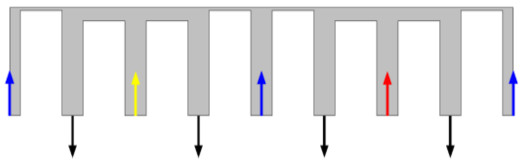
Precursor Deficiency:

- Sensitive to deposition height and precursor flow rate

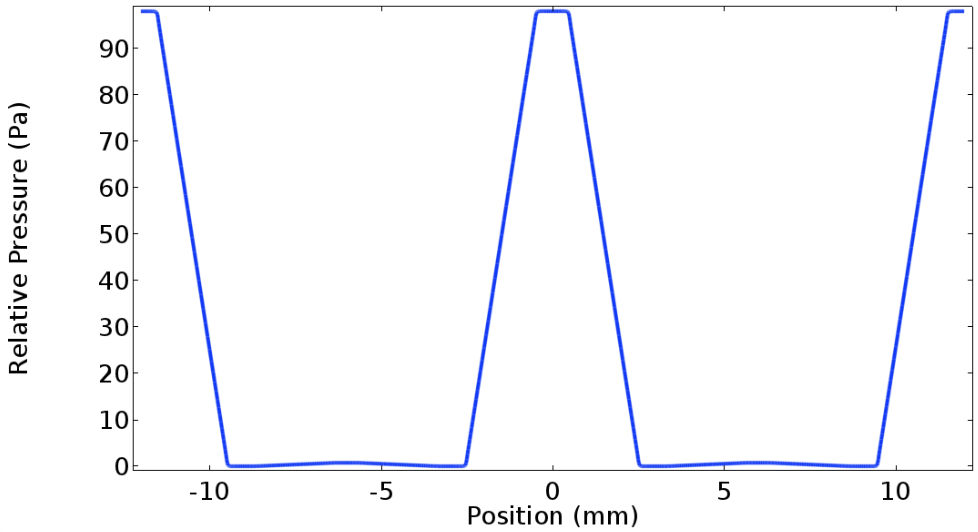


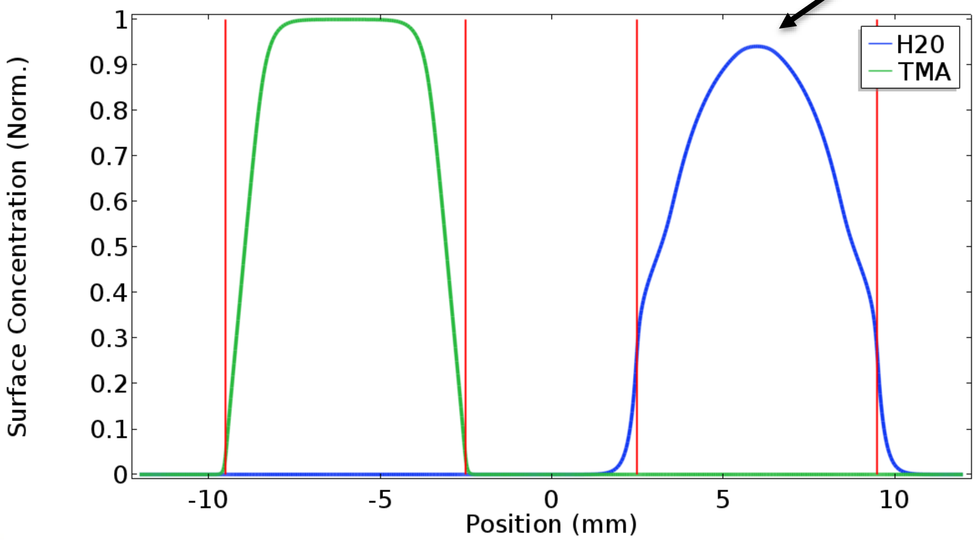
Recessed – Air Hockey Reactor (R-AHR)

- **Identical Operation** to AHR with improved ALD regime in small deposition gap
- The recessed region diminishes the force contribution from the precursor flow
  - Effect increases with increasing depth
- Tradeoff is low precursor surface concentration, greater barrier gas flow



$H_2 0$ Surface Loss





$$d = 50\ um$$
$$Q_{Pre} = 100\ ml/min$$

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Part III: Precursor Utilization

Defining Precursor Utilization

- Diffusion model alone does not adequately quantify precursor efficiency
- The surface reaction consumes precursor during operation

$$F_{IN} = F_{OUT} + F_{rxn}$$

- Define precursor utilization based on unreacted precursor

$$\eta_A = \left(1 - \frac{F_{OUT}}{F_{IN}}\right) x100$$

Is it possible to define a stationary model to quantify precursor utilization?

What is it missing?

1. Precursor adsorption surface reaction
   - Surface limited reaction
2. Substrate translational motion
   - Introduction of unreacted surface
3. Time dependency

$$R_A(t,x) = k_{ads} s_0 \big(1 - \theta_A(t,x)\big) C_A$$

$R_A \equiv Surface\ Reaction\ Rate$
$k_{ads} \equiv Adsorption\ Rate\ Constant$
$s_0 \equiv Sticking\ Coefficient$
$\theta_A \equiv Surface\ Coverage\ of\ A$
$C_A \equiv Bulk\ Concentration\ of\ A$

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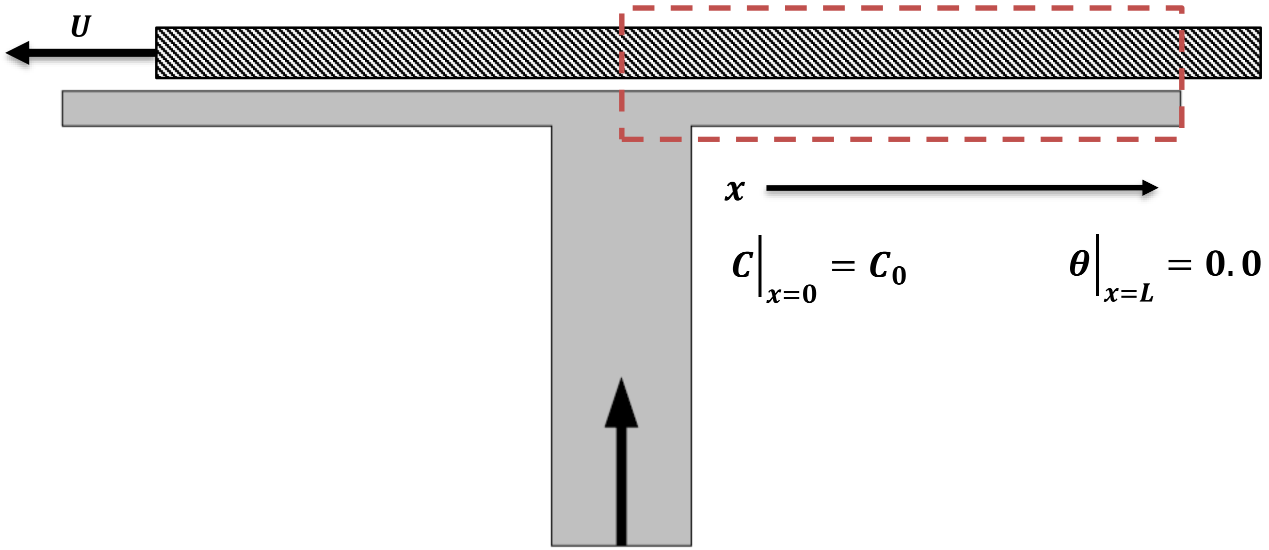
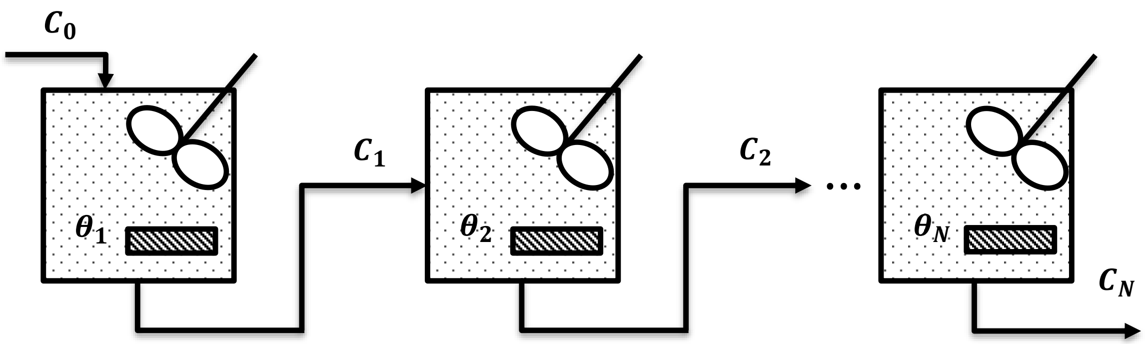
Proposed Stationary Method





CSTR in Series

Method:

- Simulate space-dependent model with global model of large N CSTR in series
- Map time domain to space domain for surface coverage

$$\theta_{ads}(t,x) \Rightarrow \theta_{ads}(x)$$
$$R_A(t,x) \Rightarrow R_A(x)$$

- Solve space-dependent transport of species and laminar flow interfaces
- Calculate precursor efficiency

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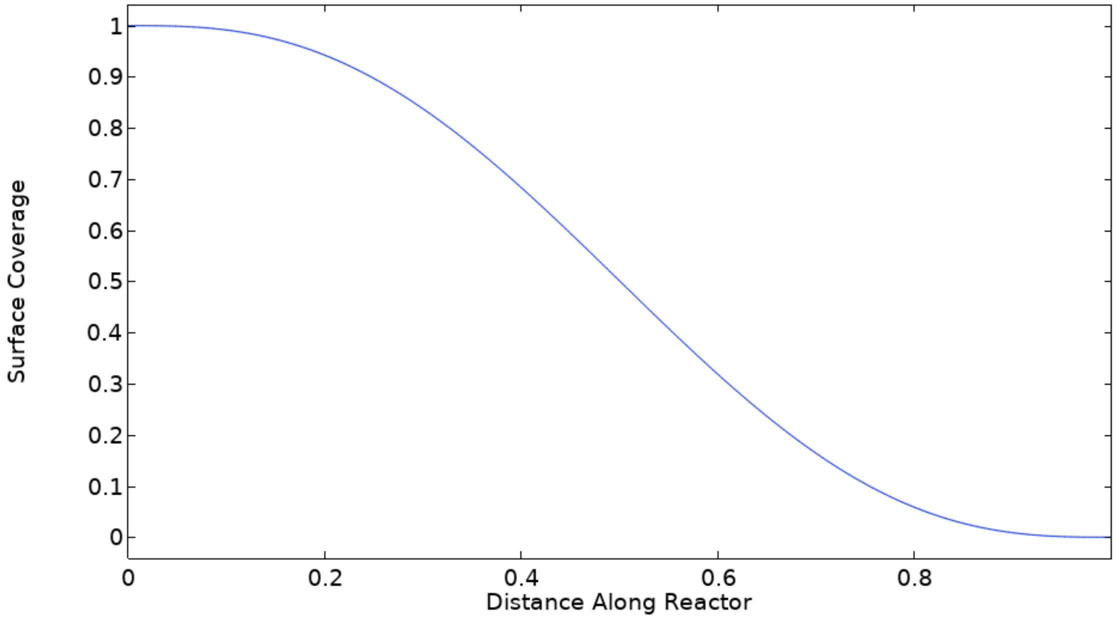
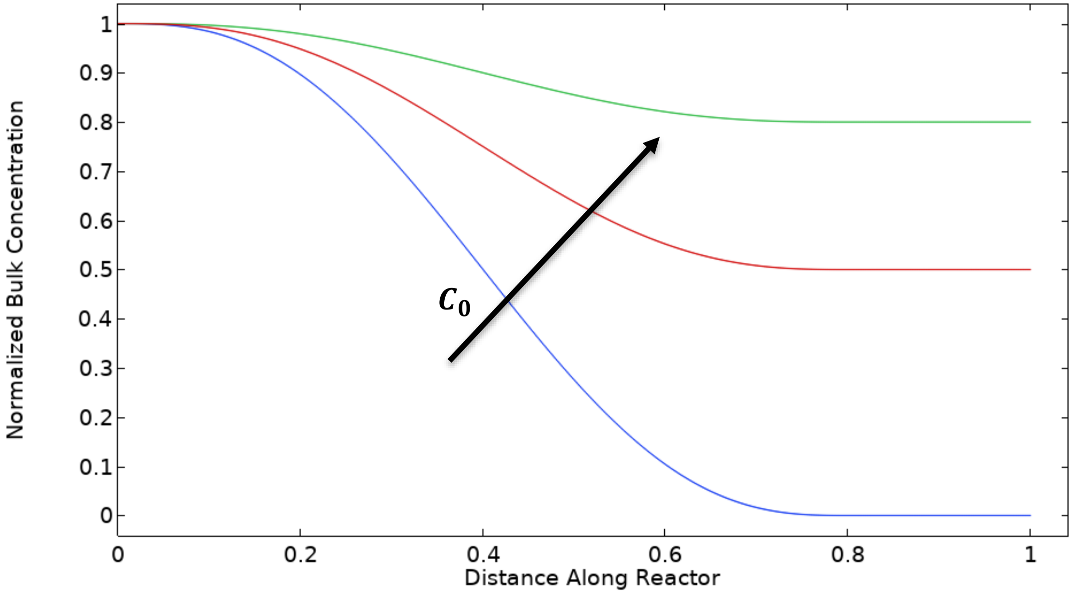
Hypothesis



- Each set of initial conditions will result in a different expression for $\theta(x)$
- This will adjust the reaction rate and solve for concentration



- If the initial concentration is too high, all unreacted precursor will leave through the outlet
  - Lowers precursor utilization
- Increasing deposition gap

Conclusions/Future Work

Conclusions:

- DHR: Both CVD and ALD Regimes
- AHR: Sensitive to process parameters at low deposition gaps
- R-AHR: Diminishes precursor force contribution, tradeoff with surface concentration
- Without surface reactions, precursor utilization can not be determined
- Current focus is on improvement of precursor efficiency

Future Work:

- Experimentally validate operating regimes through stationary deposition
- Quantitatively compare reactor type efficiency
- Use computational study as baseline for scaling air hockey table spatial ALD reactor

Acknowledgements

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