Encapsulix

Process Equipment for Large Scale Nano-technology

# Parallel Precursor Wave ALD :

## Minimizing the purge times of temporal ALD

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TU Eindhoven 9 6 2022

# Outline

- Introduction

- Analysis
  - Recirculation
  - Ideal Wave Propagation

- Implementation
  - The Parallel Precursor Wave (PPW) Reactor Architecture
  - Real World Experience

- Take Away Points and Outlook

# Intro :
# Why Worry About Purge Times in Temporal ALD?

- Temporal ALD is well established as a method capable of depositing coatings of exceptional quality

- Temporal ALD has the reputation of being slow, and thus expensive
  - Justified for a lot of traditional reactors and processes
  - This has motivated a lot of recent work on Spatial ALD

- But still, temporal ALD has many advantages/complementaries
  - Simplicity & robustness, flexible in materials and substrates, established body of know how , ..etc

- **Why can’t we make a temporal ALD process run faster ?**

  - What limits cycle time reduction to the 100 ms range in temporal ALD ?
  - Answer : The purge times

  - Is there a fundamental question why purge times are traditionally so high ?
  - Answer : No, it is just suboptimal design

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# Analysis :

## Effect of Recirculation

The flow behavior depends on the geometry, gas speed and pressure :
Reynolds Number

$$Re = \rho V L / \mu$$

If Re > 20, significant recirculation starts appearing

**Recirculation makes efficient purging nearly impossible**
- Precursor gets trapped in a vortex
- Will require a very long time to clear
- Counterintuitive : increasing purge gas flow only makes things worse

**Process and Equipment Design Considerations :**

1) For a given geometry, increasing pressure and speed increases recirculation effects

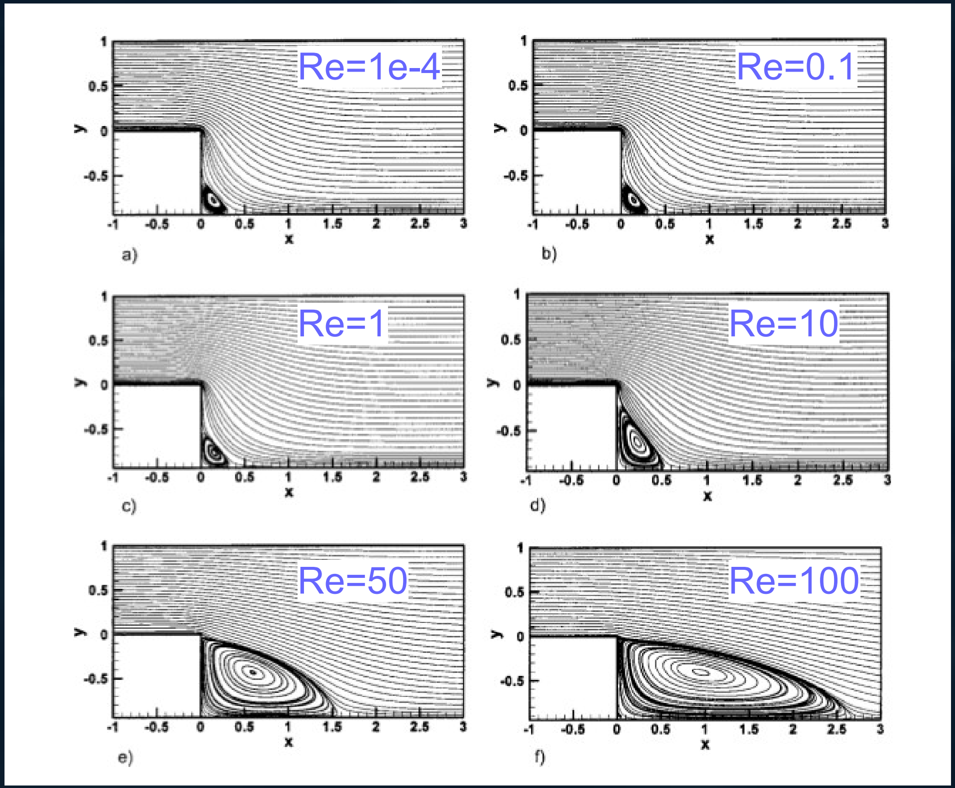
2) For a given set of operating conditions, smooth geometries will perform better

The conditions of onset of recirculation ( in Torr x m/s) is a good performance metric

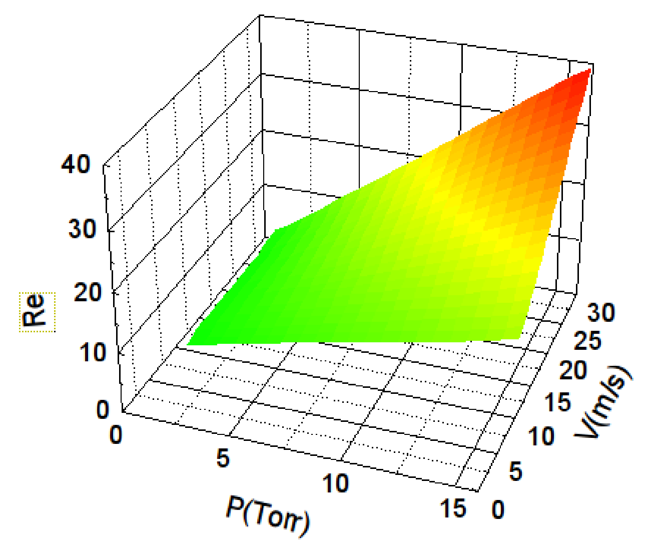
# When can we expect recirculation in ALD reactors ?

## Effect of flow speed and pressure on a backward facing step

Flow pattern vs Reynolds number for backwards facing step



Reynolds Number for $N_2$ flow over a 1mm step



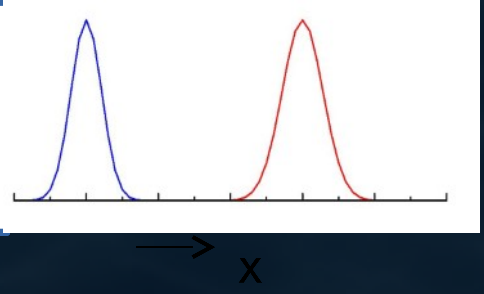
G. Biswas, M. Breuer, F. Durst
Transactions of the ASME p362  Vol. 126 (2004)

# Ideal One Dimensional Pulse Propagation

Ignoring the consumption at the walls, assume a composition wavefront c(x,t) with Gaussian Concentration profile propagating through the reactor with constant velocity V

Where C is the initial concentration.

$$c(x,t)=\frac{C}{\sigma\sqrt{2\pi}}e^{-\frac{(x-tV)^2}{2\sigma^2}}$$



The pulse width $\sigma$ varies over time :

- The pulse is created with a finite width $\tau$ at the ALD valve
- It broadens due to diffusion (D is the diffusion constant) , and t the time since the pulse entered the reactor
- The time needed to traverse the upstream volumes between the valves and the entrance of the reactor (injector and lines) can be written as $\lambda/v_r$, whereby $\lambda_\iota$ is an equivalent length for the injector and the lines )

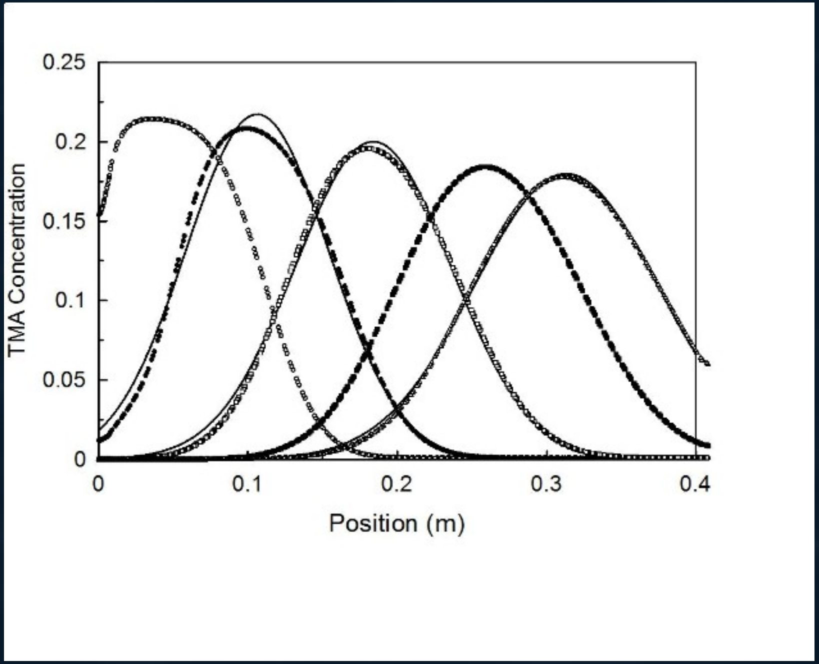
$$\sigma(t)^2=2D\left(\frac{\lambda}{V}+t+\tau\right)$$

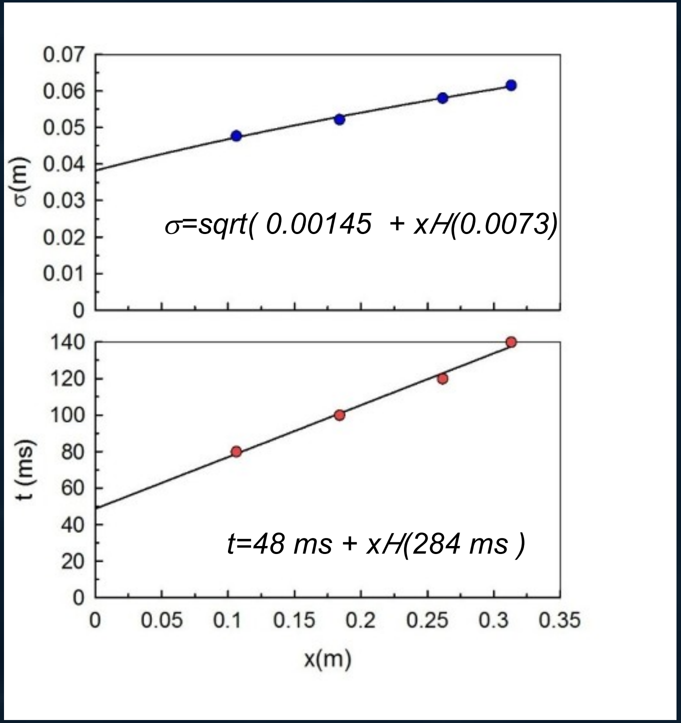
If the duration of the purge step is $t_p$ , the distance between two pulses = $t_p\ v_r$

The pulses overlap criterion can then be formulated as $t_p v_r < n\ \sigma$ where n~2-3

$$t_p < (n/v_r)\ \mathrm{sqrt}[2D(l_i)/v_r+t+\tau]$$

# Comparison simple 1D model with Computational Flow Dynamics Simulation





Initial concentration pulse profile is square
created by valve open/close

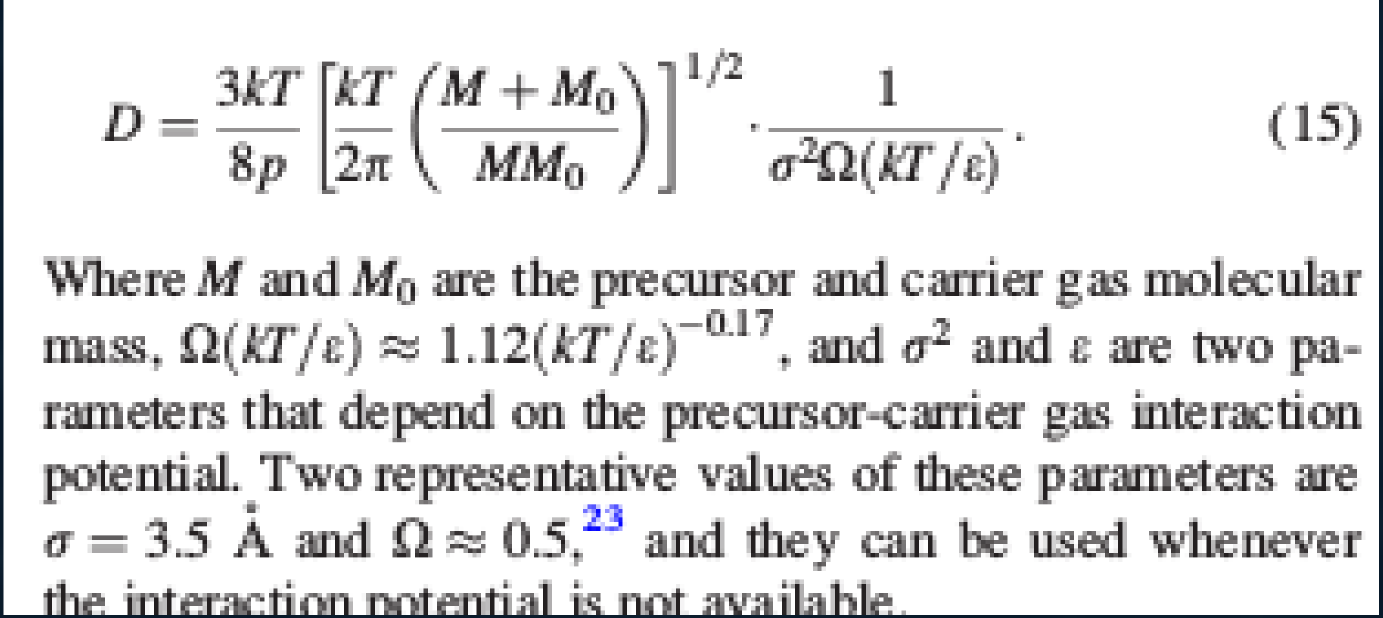
Morphs into Gaussian profile as it propagates through the reactor

Peak position moves with constant speed
Peak broadens with square root of time

$v_r$=3.52 m/s
$\tau$=17ms
$l_i$=0.139 m for injector + 0.023 m for lines = 0.162
D=0.0128 $m^2/s$ @ 7 Torr

# Diffusion Coefficient

Chapman Enskog Expression for binary diffusion coefficient :



$$D = \frac{3kT}{8p}\left[\frac{kT}{2\pi}\left(\frac{M+M_0}{MM_0}\right)\right]^{1/2} \cdot \frac{1}{\sigma^2\Omega(kT/\varepsilon)}. \qquad (15)$$

Where $M$ and $M_0$ are the precursor and carrier gas molecular mass, $\Omega(kT/\varepsilon) \approx 1.12(kT/\varepsilon)^{-0.17}$, and $\sigma^2$ and $\varepsilon$ are two parameters that depend on the precursor-carrier gas interaction potential. Two representative values of these parameters are $\sigma = 3.5$ Å and $\Omega \approx 0.5$,[23] and they can be used whenever the interaction potential is not available.

Depends on:

- Pressure : 1/p dependence
- Absolute Temperature $T^{1.67}$
- Mass and size of precursor and carrier gas

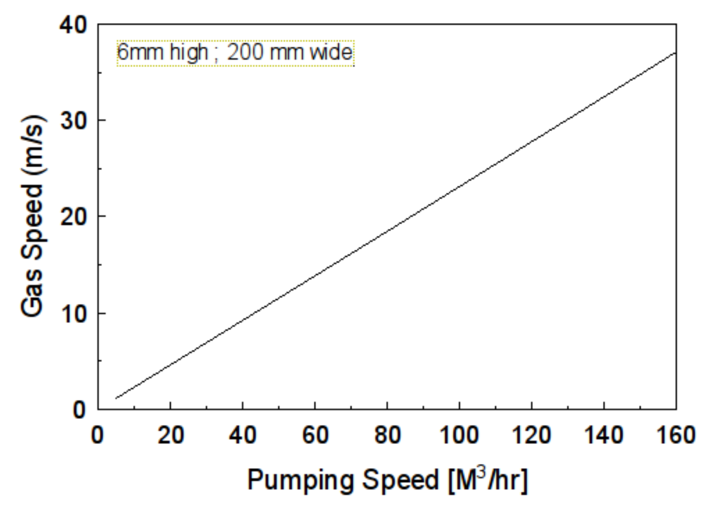
# Average Gas Velocity

For a given reactor with width w and height h , setting the value of the pumping speed S ( in liter/s)
and the gas flow $\Phi$ ,
determines the pressure P and the velocity V

$\Phi$(stcc/sec) =V . (p/1 atm).w.h= S. (p/1 atm)

And thus :

$$V = S/(w.h)$$



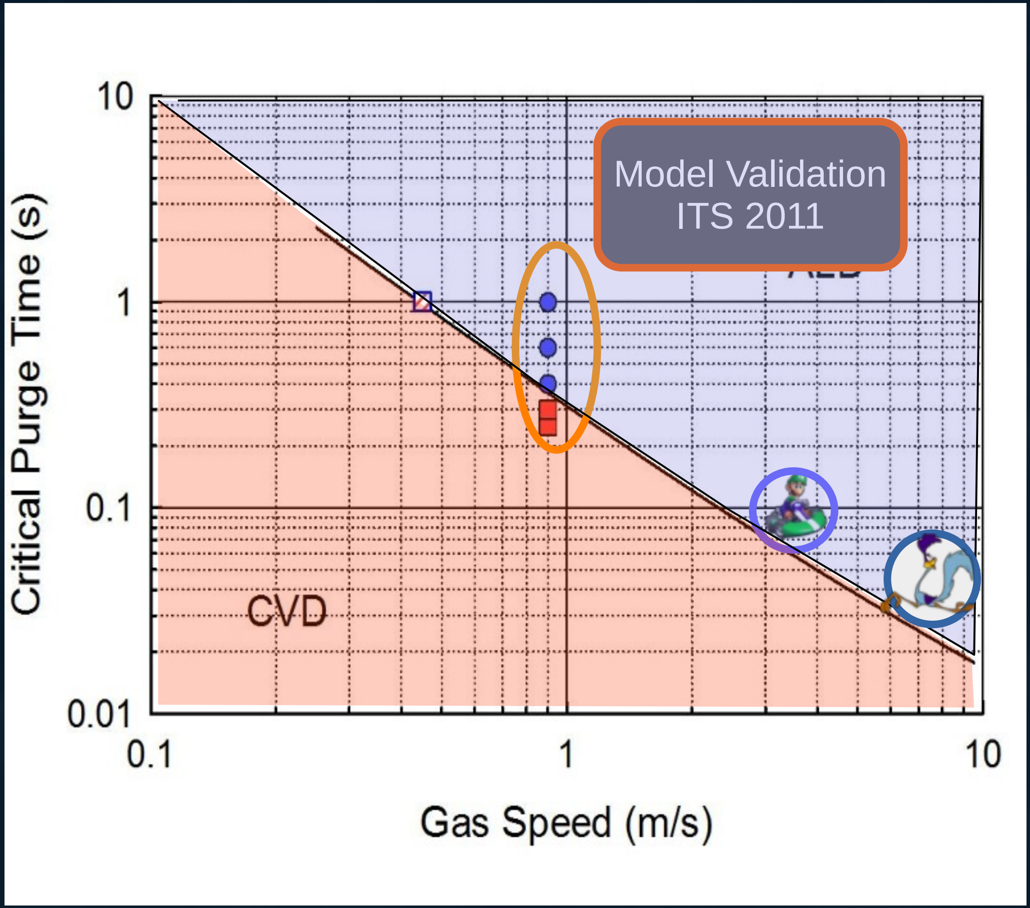
Important quantity is pumping speed, not gas flow

But pumping speed at lower pressure can be reduced by finite tube size

Thus same pump results in slightly higher gas speed at higher gas flow

# Phase Diagram

Transition between CVD growth and ALD growth depends critically on gas speed and purge time



Model Validation
ITS 2011

Infinity Product Recipes

« Luigi »,
« Mario » ,
« Roadrunner »

# Sweet Spot Parameters

**Pressure : [0.5 Torr, 3 Torr]**

If pressure too high, increased Reynolds number => recirculation
If pressure too low , diffusion coefficient is too high => peak smearing

**Gas speed : [1 m/s, 10 m/s]**

If gas speed too high , increased Reynolds number => recirculation
If gas speed too low , increased residence time => peak smearing

**Gas speed dispersion < 5 %**

**Reactor Height : [4mm, 25 mm]**

If reactor too high , replenishing precursor consumed at walls is too slow
If reactor too low , mechanical tolerances become critical

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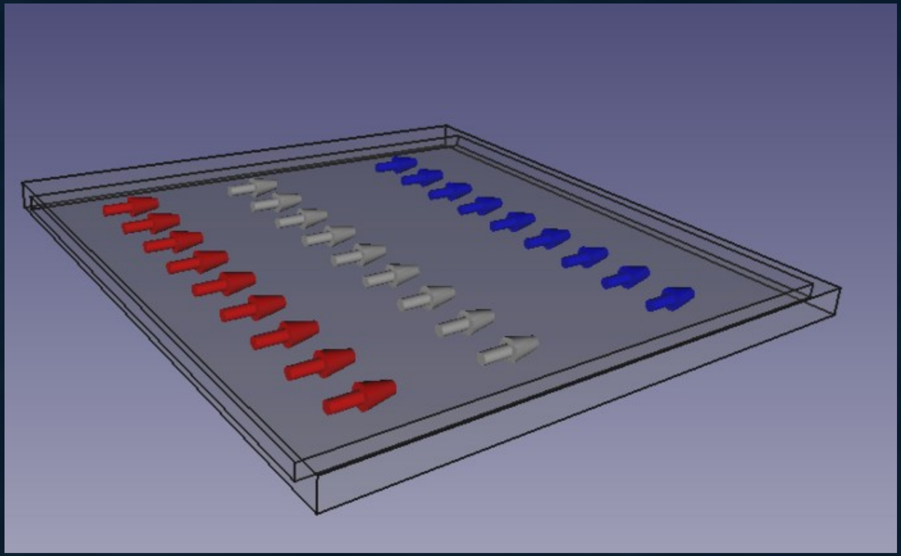
# Principle of Parallel Precursor Wave

Reactor is a shallow rectangular conduit
Pulse= Parallel wavefront of precursor vapor
Purge= Parallel wavefront of precursor vapor

Pulse and purge run through the reactor
Precursor absorbs on the reactor walls



Uniform, high speed gas front is generated by injector

Pulses are much closer to each other than a classical cross flow reactor

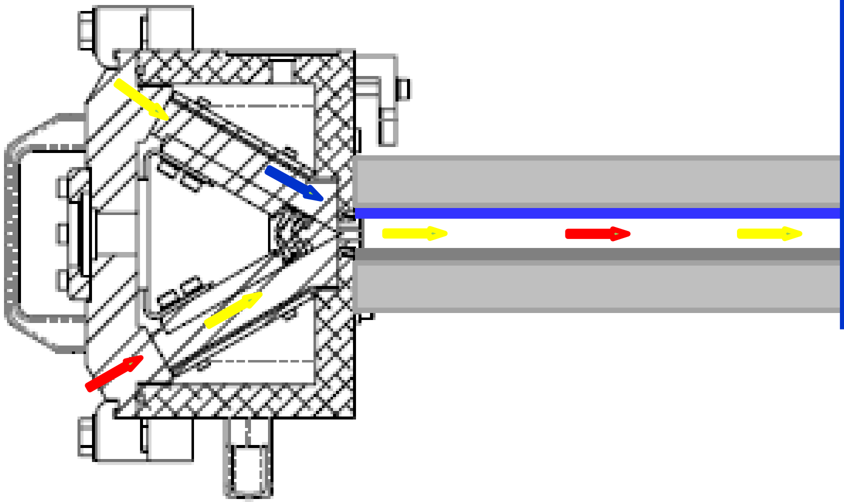
e.g. Suntola and Lindfors US patent 7404984 flow at least 2 x the reactor volume in between two pulses ;

We flow less than 0.5 x the reactor volume in between pulses

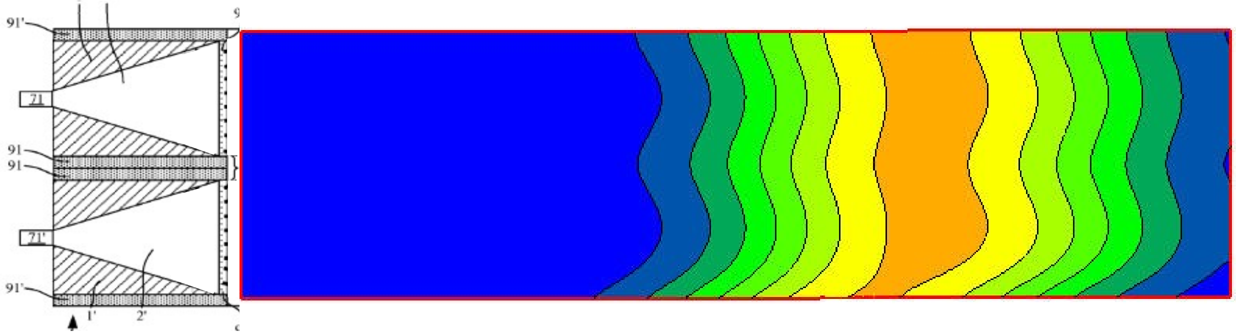
# Encapsulix Innovation

## Parallel Precursor Wave ( PPW) Gas Injection for Fast, Low Temperature Atomic Layer Deposition

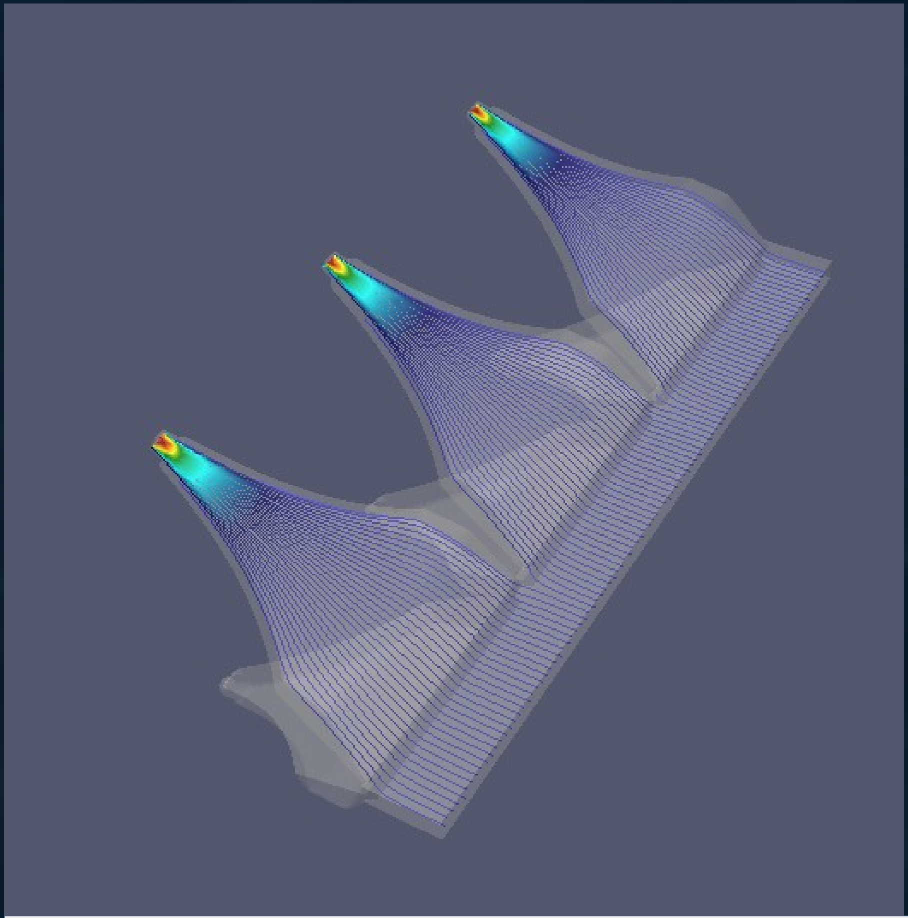
Patented Injector

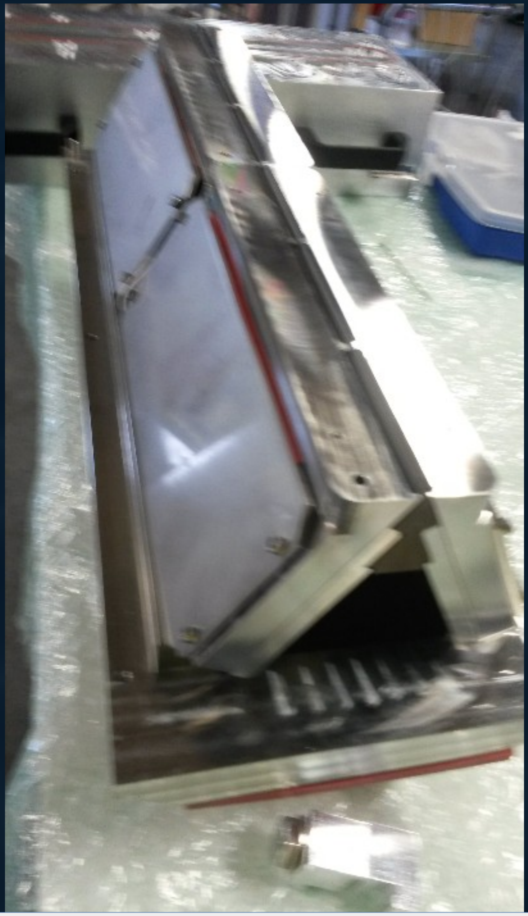


- Precise management of gas injection
- Rapid  precursor delivery and purge
- Scalable
- Throughput enhancement by factor  30-100 !



# Injector Module





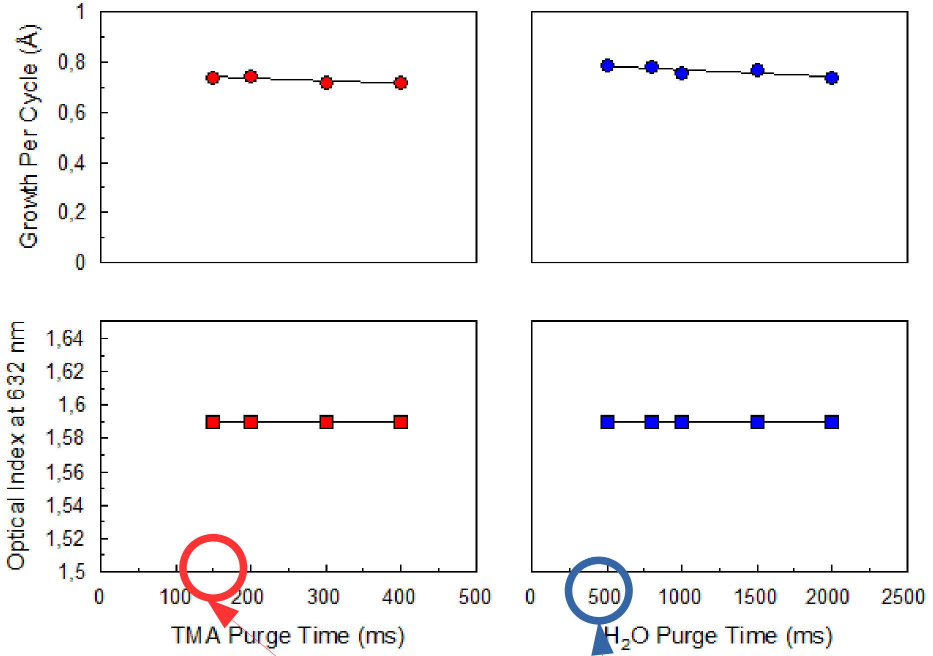
- Modular set of injectors provide smooth, laminar, uniform flow
  - Recirculation onset point higher than 100 Torr x m/s in reactor
  - See US Patent 8721835B2 and application 2013/0014698 for details
- Separate sets of injectors for oxidants and metal precursors
  - Confluence occurs at reactor entrance

# TMA + $H_2O$ @80 °C

Typical cycle times : 500-1000 ms a

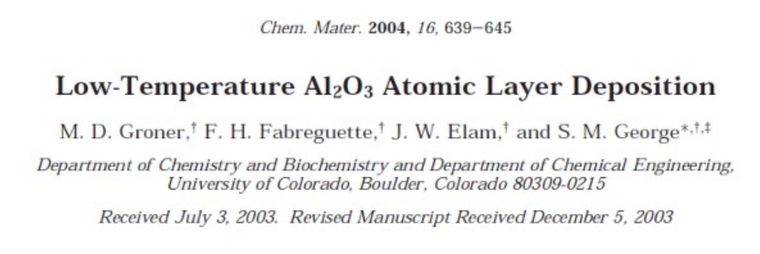
Typical GPC: 0.65-0.85 Å

**Dep Rate : 5-7 nm/min**



Factor 30

Factor 40



*Chem. Mater.* **2004,** *16,* 639–645

## Low-Temperature $Al_2O_3$ Atomic Layer Deposition

M. D. Groner,[†] F. H. Fabreguette,[†] J. W. Elam,[†] and S. M. George*[,†,‡]

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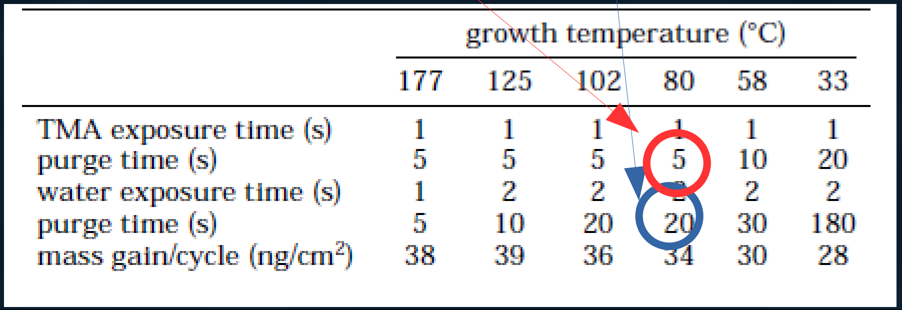
*Received July 3, 2003. Revised Manuscript Received December 5, 2003*



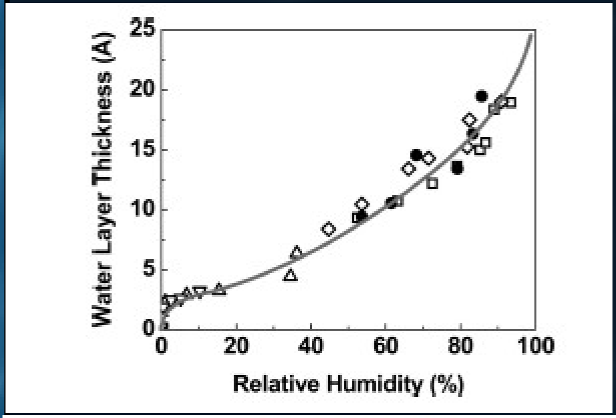
| | growth temperature (°C) | | | | | |
|---|---|---|---|---|---|---|
| | 177 | 125 | 102 | 80 | 58 | 33 |
| TMA exposure time (s) | 1 | 1 | 1 | 1 | 1 | 1 |
| purge time (s) | 5 | 5 | 5 | 5 | 10 | 20 |
| water exposure time (s) | 1 | 2 | 2 | 2 | 2 | 2 |
| purge time (s) | 5 | 10 | 20 | 20 | 30 | 180 |
| mass gain/cycle (ng/cm$^2$) | 38 | 39 | 36 | 34 | 30 | 28 |

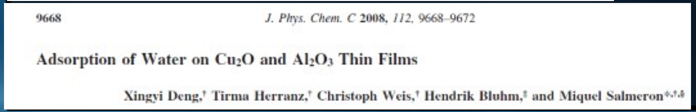
# Pulse smearing of water vapor pulse

## Physisorption at higher relative humidity

- Water vapor has both dissociative chemisorption and physisorption
  - Strongly bound OH and weakly bound $H_2O$
- Thickness of physisorbed layer increases with relative humidity
  - Typical residence time 10 μs

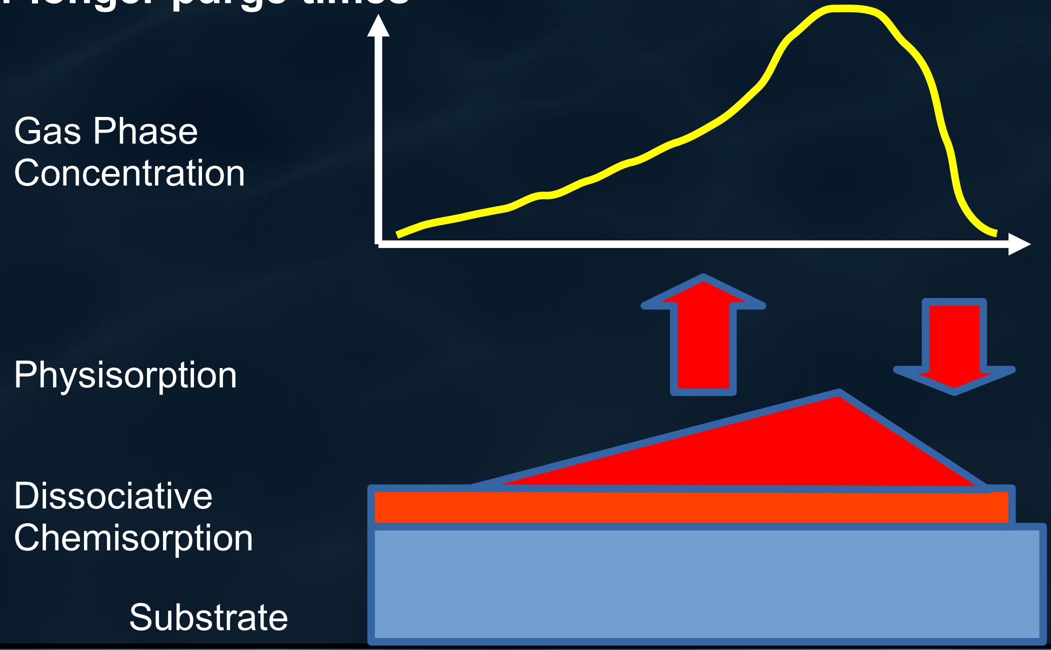
- During concentration peak, the physisorbed layer increases in thickness
- After the peak, water vapor is released
- **Leads to pulse smearing, need for longer purge times**




9668 J. Phys. Chem. C 2008, 112, 9668–9672

**Adsorption of Water on $Cu_2O$ and $Al_2O_3$ Thin Films**

Xingyi Deng,[†] Tirma Herranz,[†] Christoph Weis,[†] Hendrik Bluhm,[‡] and Miquel Salmeron[*,†,§]


Gas Phase Concentration

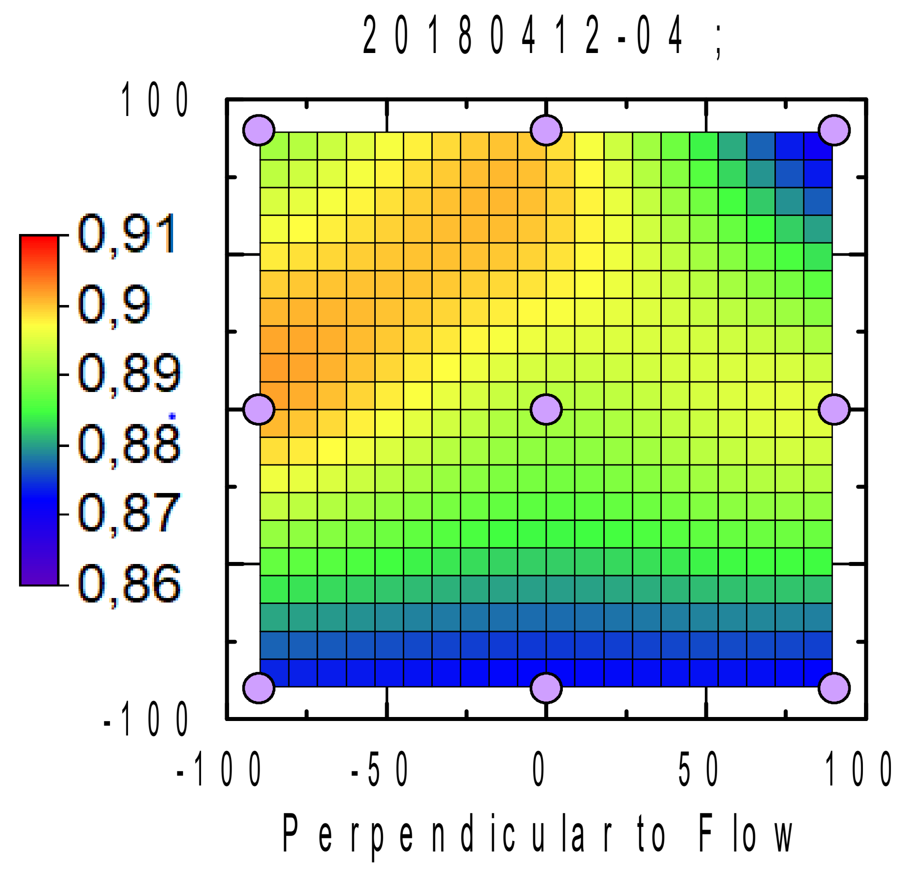
Physisorption

Dissociative Chemisorption

Substrate

# TMA&$O_3$

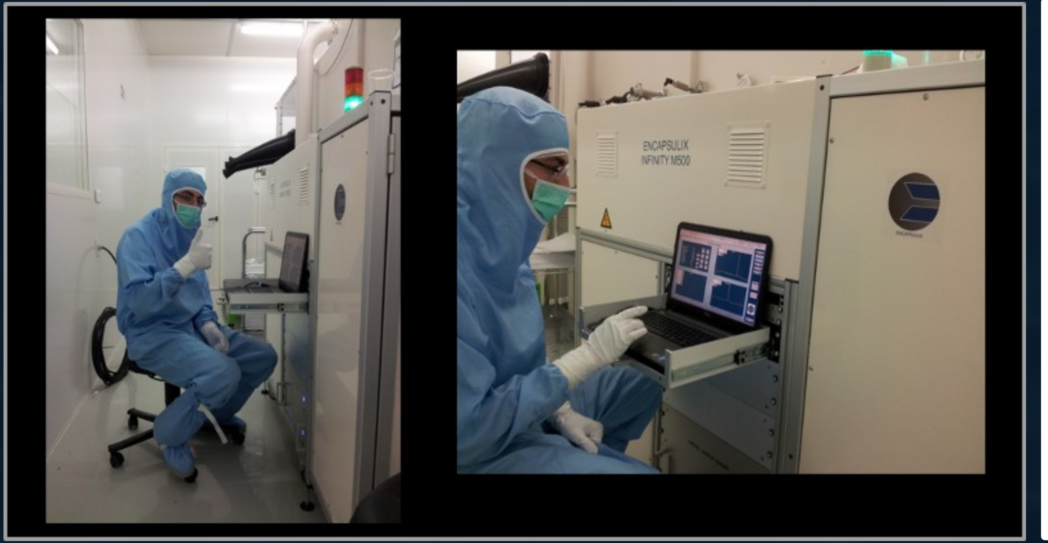
**Ozone does not stick to walls**
**Dep Rate : 7-10 nm/min**



| | 20180412-04 |
|---|---|
| Temperature | 90°C |
| GPC avg (A/cycle) | 0,88 |
| RI avg (@633) | 1,561 |
| **Dep rate** | **7,64** |
| **Unif (%)**<br>(Max-Min)/(Max+Min) | **1,92** |

# Real World Experience

## OLED Lighting Encapsulation



Gen 2.5 glass ( 370 mm x 470 mm)
TMA/$H_2O$ at 85°C
V~ 3 m/s ; P~ 1.5 Torr
80 ms TMA purge times
500 ms H2O purge times

Stable operation in pure ALD regime
Years of operation / thousands of runs
GPC constant at 0.85 A/cycle
Index constant at 1.595

| Date | GPC (Å) | Index |
|---|---|---|
| 31 03 | 0,891 | 1,592 |
| 24 04 | 0,846 | 1,598 |
| 1 7 | 0,846 | 1,599 |
| 4 8 | 0,864 | 1,593 |

# Take Away Points and Outlook

- Purge times in the sub 100 ms range are feasible in temporal ALD
  - Demonstrated in production in  PPW architecture
  - intermediate between classical temporal and spatial ALD

- Often the process requires more time

  - Precursor diffusion inside high aspect ratio structures
  - Reaction Kinetics limitation at low temperature
  - « Sticky Water »

  - These microscopic mechanisms are relevant for all reactor architectures