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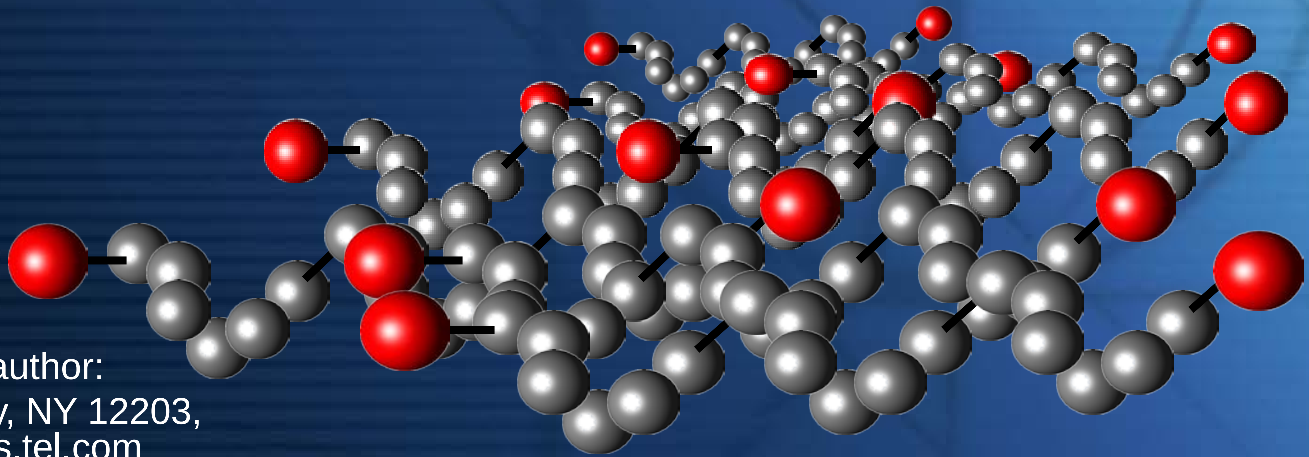
Model of a Filament Assisted CVD reactor

Jozef Brcka*

TEL US Holdings, Inc., Technology Development Center



*Corresponding author:
255 Fuller Rd., Albany, NY 12203,
jozef.brcka@us.tel.com

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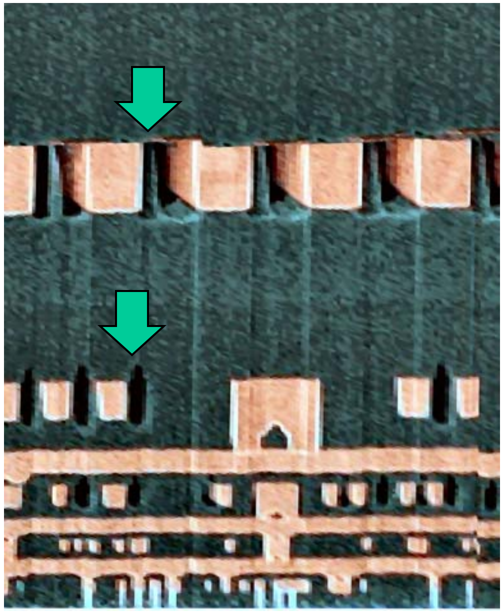
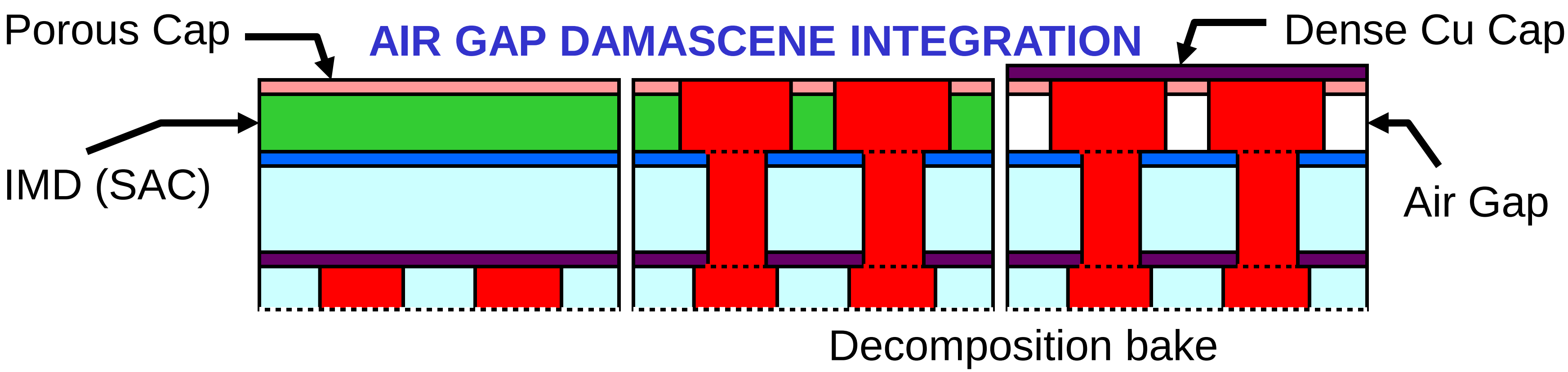
FACVD method …

- Deposition of polymer films – with original functionality without introduction of a damage
- FACVD , iCVD - dry process and non-plasma environment
- Suitable precursors are thermally activated into radical components which participate directly on the film growth or are initiating those processes
- Substrate at room temperature
- Thermal activation by very moderate temperatures ~ 200 °C - several hundreds
- Applications extending from semiconductor technology into nanotechnology

Motivation …



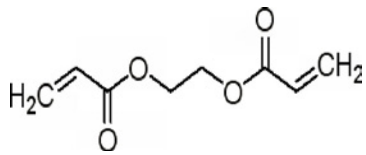
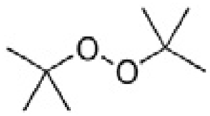
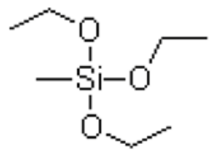
- Air-gap applications in semiconductor devices: The basic principle consists of dielectric material removal (from in-between the metal lines)
- Other applications: organic devices, bio-passivation, 3D interconnect, and energy
  - ✓ Transfer specific process from laboratory experimentation towards semiconductor processing tool
  - ✓ Match and optimize chemistry and process - enhanced flexibility of a process development



Sacrificial material (decomposable polymer) is selectively removed through a dielectric permeable cap

Precursors and chemistry

- Precursors w low decomposition T
- Compatibility with semiconductor processing
- More complex mixture and chemistry for an increased adhesion, film properties, …

EGDA ETHYLENE GLYCOL DIACRYLATE	TBPO TERT-BUTYL PEROXIDE	MTEOS METHYLTRIETHOXY-SILANE
$C_8H_{10}O_4$	$C_8H_{18}O_2$	$C_7H_{18}O_3Si$
		

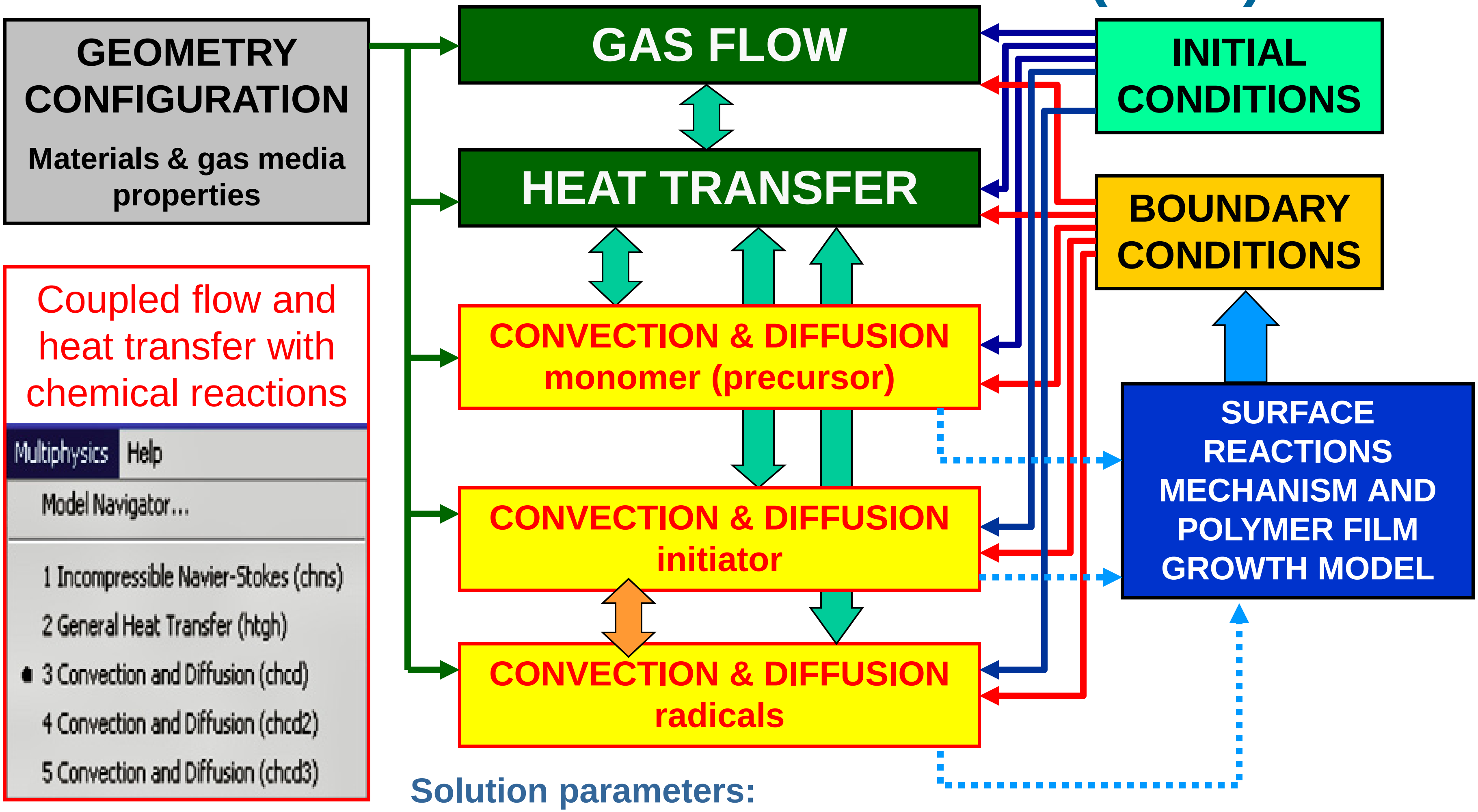
"LOGIC SWITCHES" implemented to use same model for different chemistry

Process selection

- **PROCESS "A"** → $[k_A = 1, k_B = 0]$
- **PROCESS "B"** → $[k_A = 0, k_B = 1]$
- **PROCESS "A+B"** → $[k_A = 1, k_B = 1]$

→ **RESULTANT PROCESS MODE**

FACVD model
Comsol-based scheme (v.3.5)

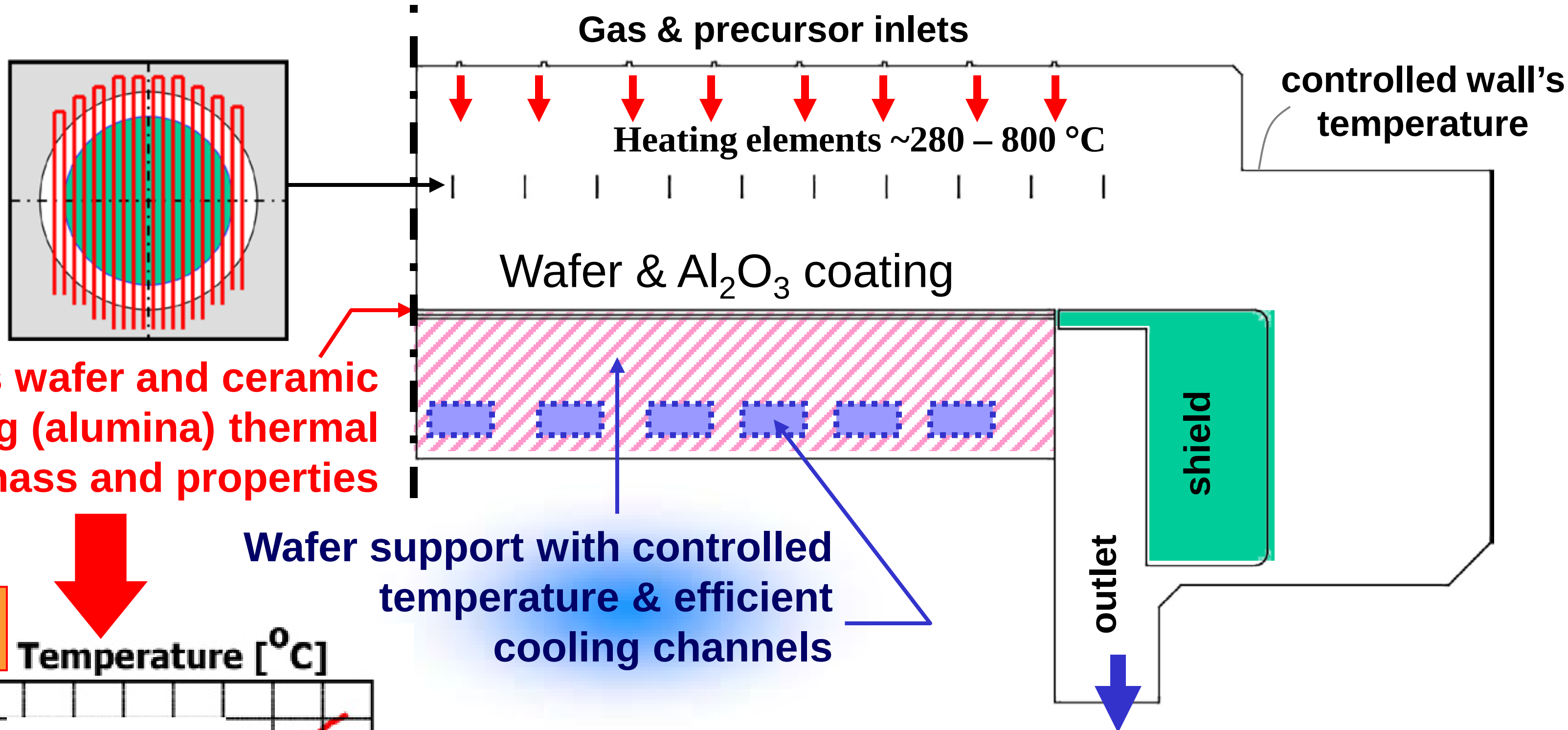


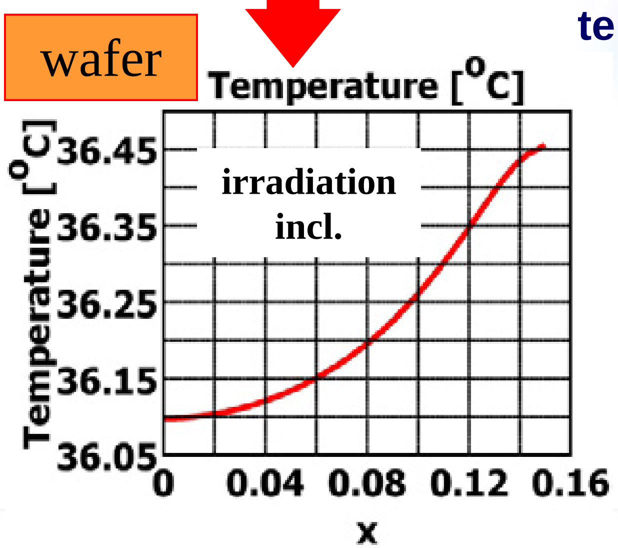
Solution parameters:

Stationary Analysis types

Direct (PARDISO) solver

Model geometry & features

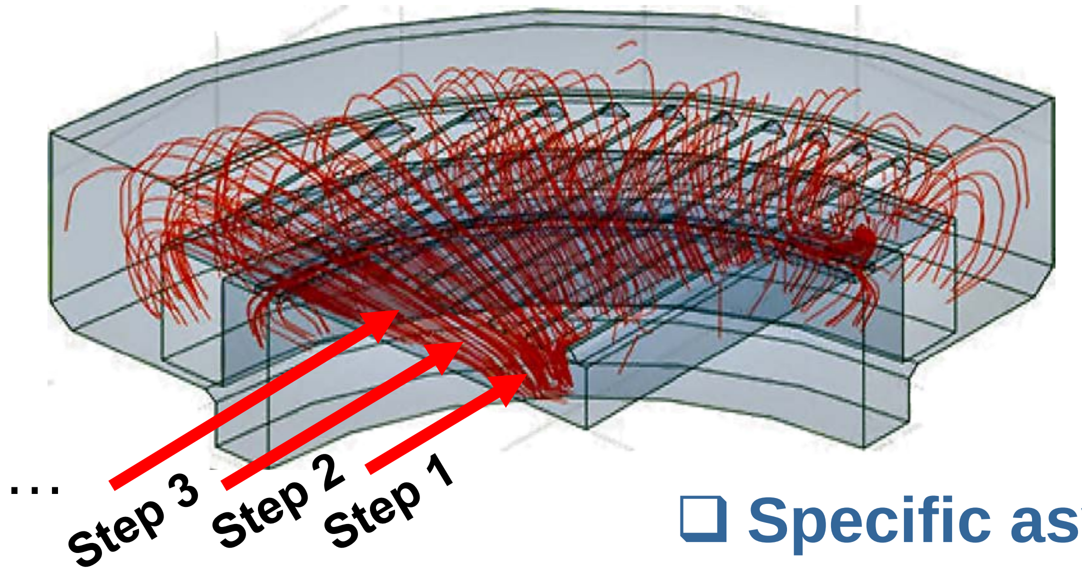




2D model in Cartesian coordinate system

- Detailed inlets geometry
- Radiation from heater elements to wafer (analytical approach - it consider a heater's element geometry)
- Variable coating thickness under wafer

3D model - gas flow computation



page file usage up to 18.5 GB

dual duo-core CPU usage at 100 %

To achieve converging solution in full geometry – ongoing recurrent simulations were performed

- Specific asymmetry due to multi-linear heater and quasi-axial symmetry of the flow
- Approach for 3D computations to validate 2D cartesian model
- ⇒ Significant time resources could be saved

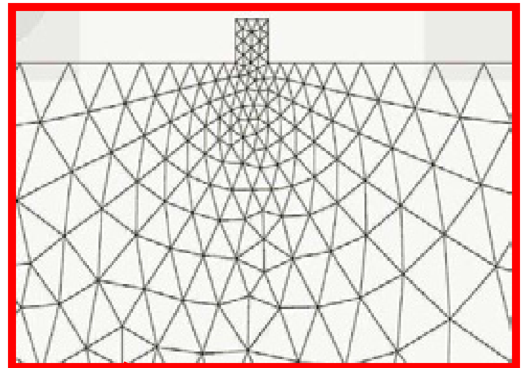
Meshing properties

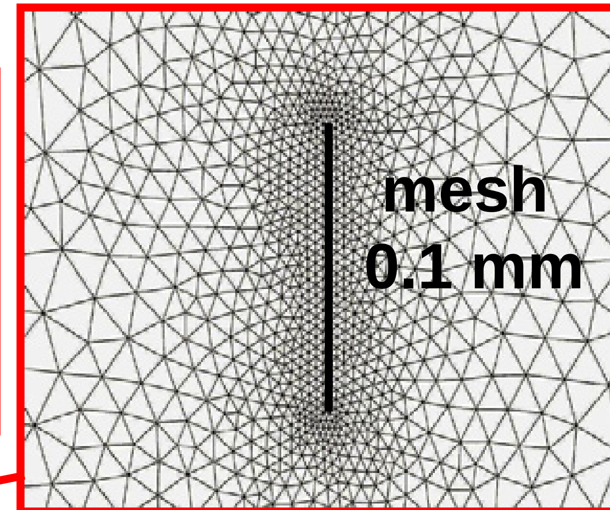
Mesh Statistics

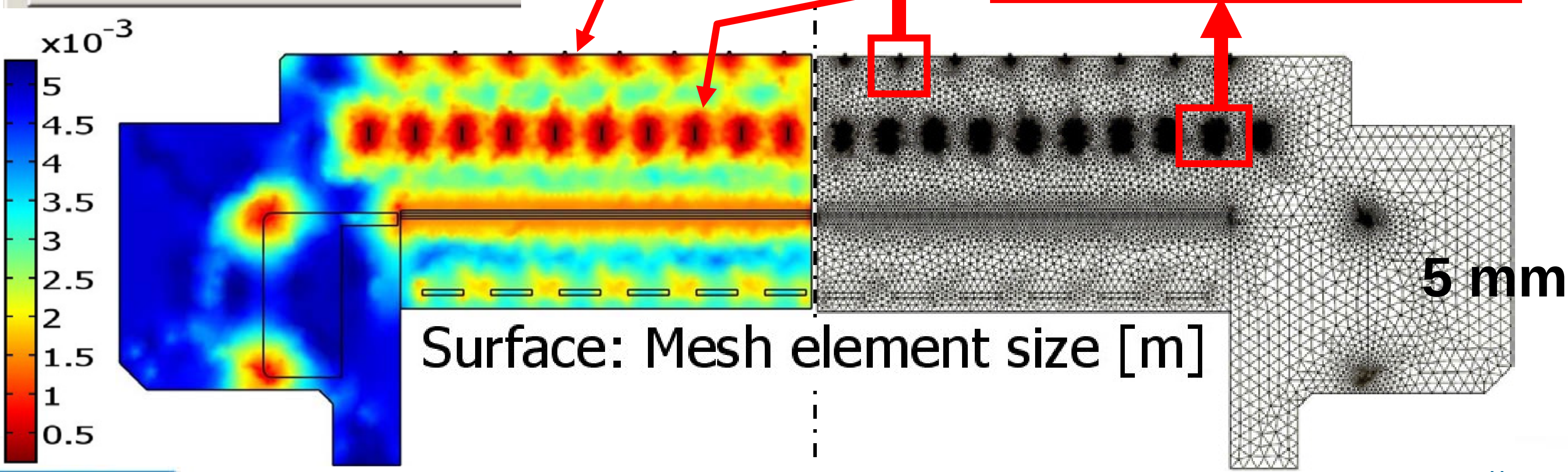
Global | Subdomain | Boundary | Point

Extended mesh:	
Number of degrees of freedom:	365681
Base mesh:	
Number of mesh points:	16284
Number of elements:	32151
Triangular:	32151
Quadrilateral:	0
Number of boundary elements:	1616
Number of vertex elements:	126
Minimum element quality:	0.7892
Element area ratio:	3.84E-4

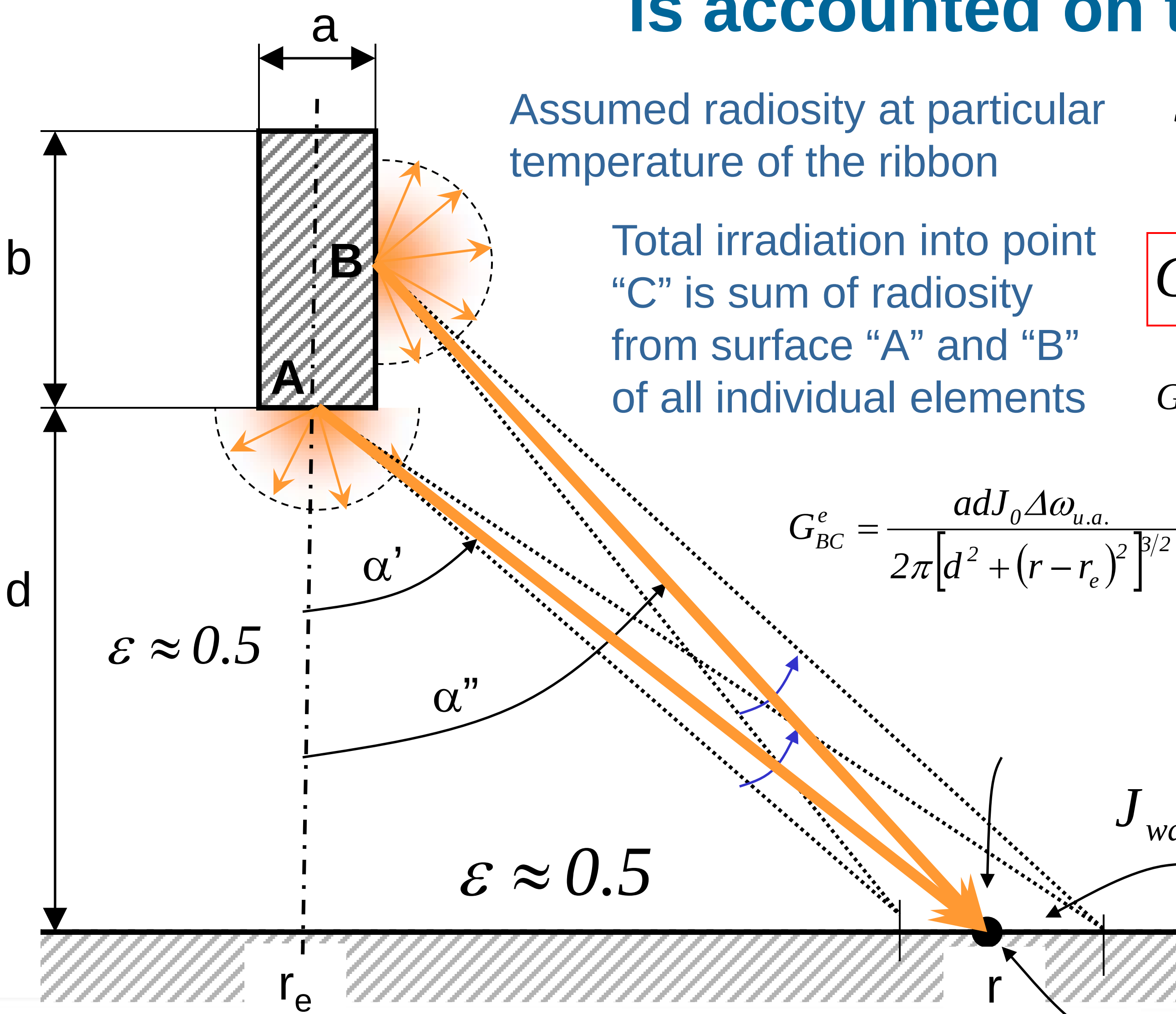
- **Mesh size ~0.1 mm – 5 mm**







Radiant power from heater is accounted on the wafer



Assumed radiosity at particular temperature of the ribbon

$$J_0\left[Wm^{-2}\right] = \varepsilon\sigma T^4_{heater}$$

$$\varepsilon \approx 0.03 - 0.75$$

Total irradiation into point "C" is sum of radiosity from surface "A" and "B" of all individual elements

$$G^e_C \approx G^e_{AC} + G^e_{BC}$$

$$G^e_{AC} = \frac{adJ_0\Delta\omega_{u.a.}}{2\pi\left[d^2 + (r - r_e)^2\right]^{3/2}}$$

$$G^e_{BC} = \frac{adJ_0\Delta\omega_{u.a.}}{2\pi\left[d^2 + (r - r_e)^2\right]^{3/2}} \times \frac{b(d + b/2)}{ad\left[\frac{(d + b/2)^2 + (r - r_e)^2}{d^2 + (r - r_e)^2}\right]^{3/2}}$$

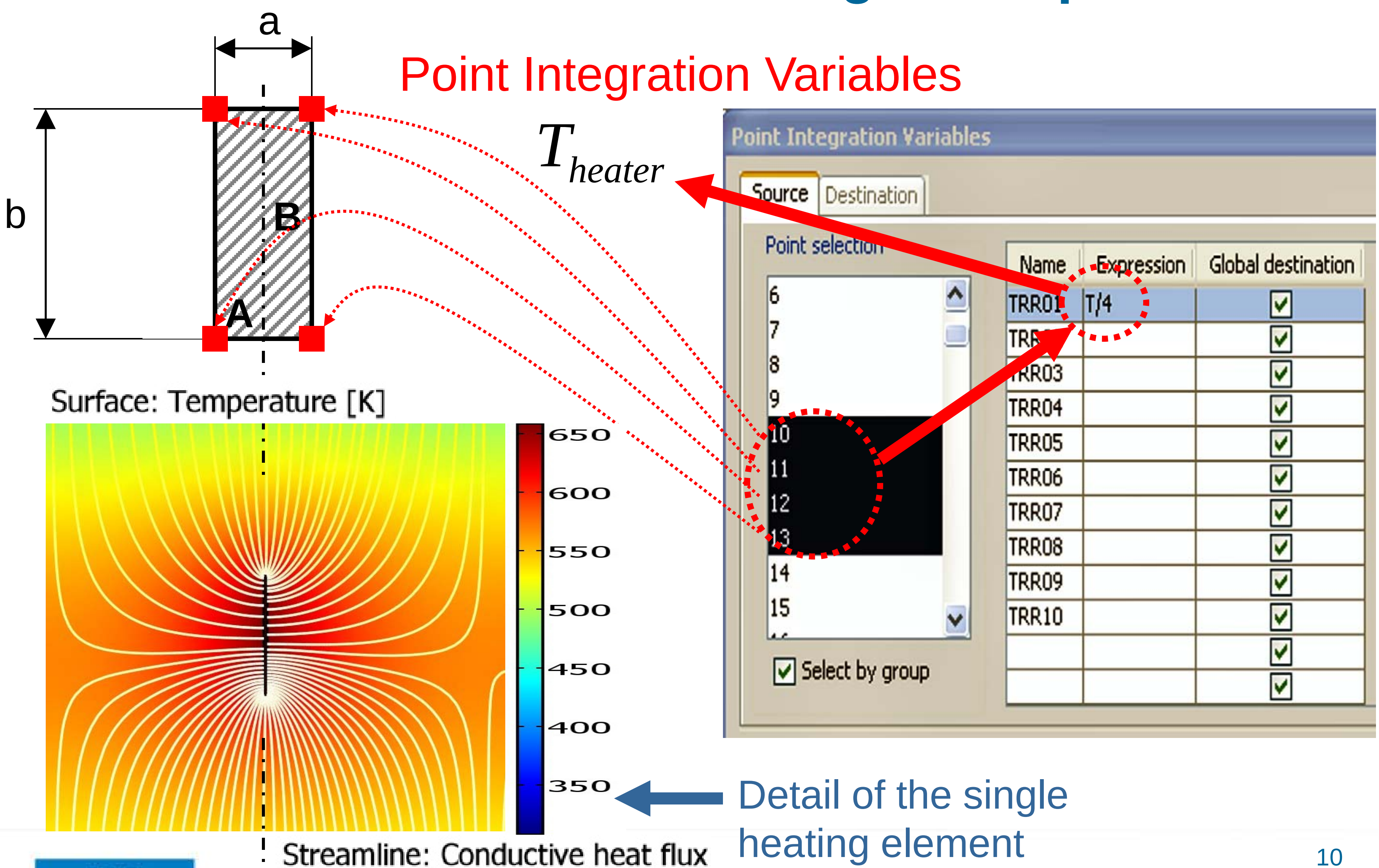
$$\Delta\omega_{u.a.} \sim \left[1 + (r - r_e)^2 / d^2\right]^{-1/2}$$

$$J_{wafer} = \varepsilon\sigma\left(T^4_{heater} - T^4_{wafer}\right)$$

unit area

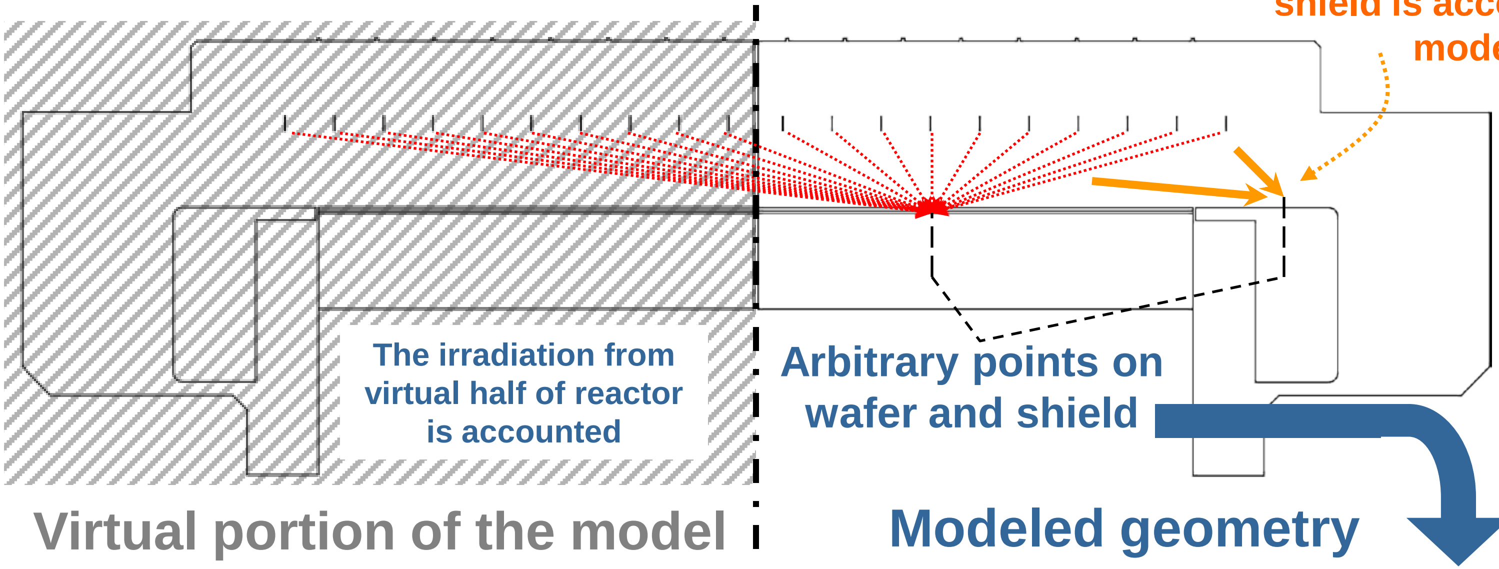
irradiation into the point "**C**" at the wafer surface

Heater averaged temperature



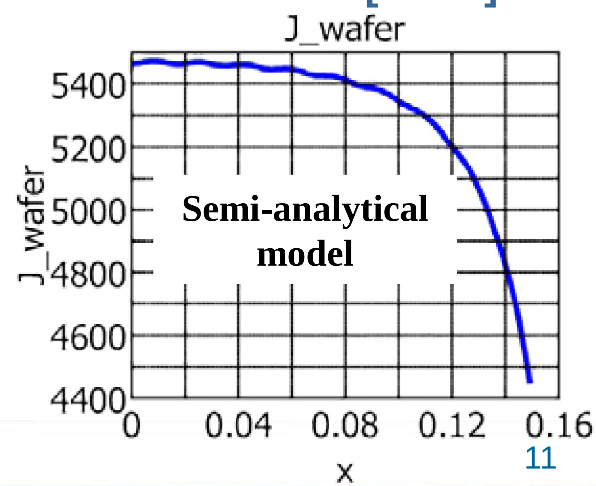
Detail of the single heating element

Irradiation geometry

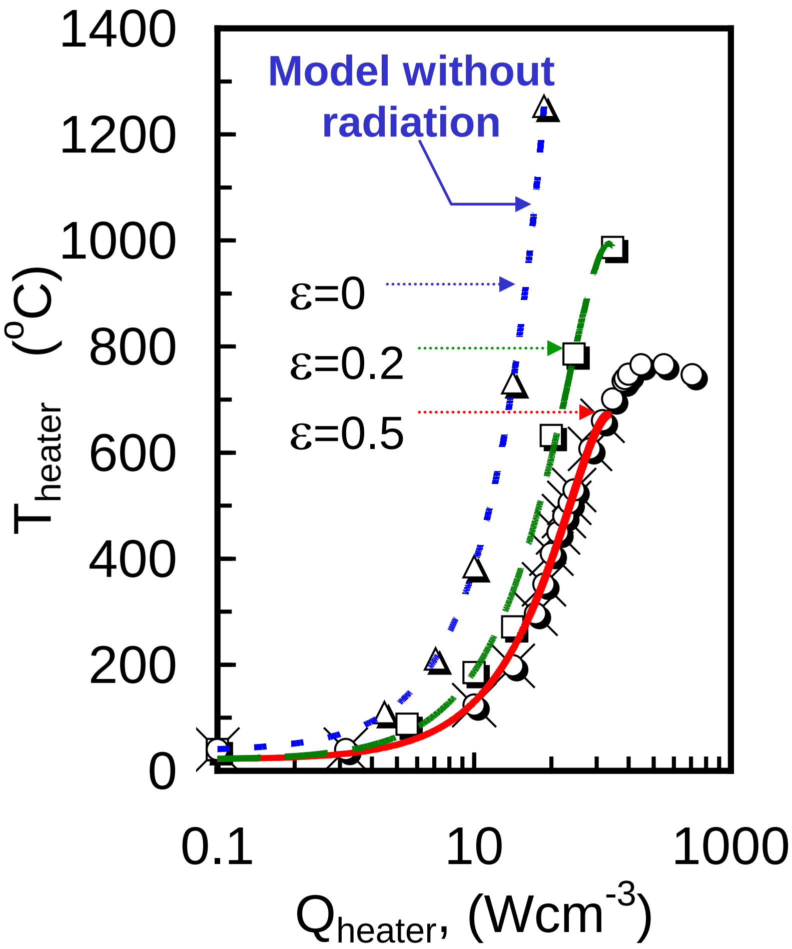


- radiation - loss at elements and increased T at wafer
- radiosity is uniform from planar heating assembly (planar source, no edge effect)
- No integration in normal direction to geometry
- Reflection on the wafer and ribbons is set to = 0
- Formally, the alumina coating is assumed to be 1 micron thick (actual geometry is 1 mm thick)

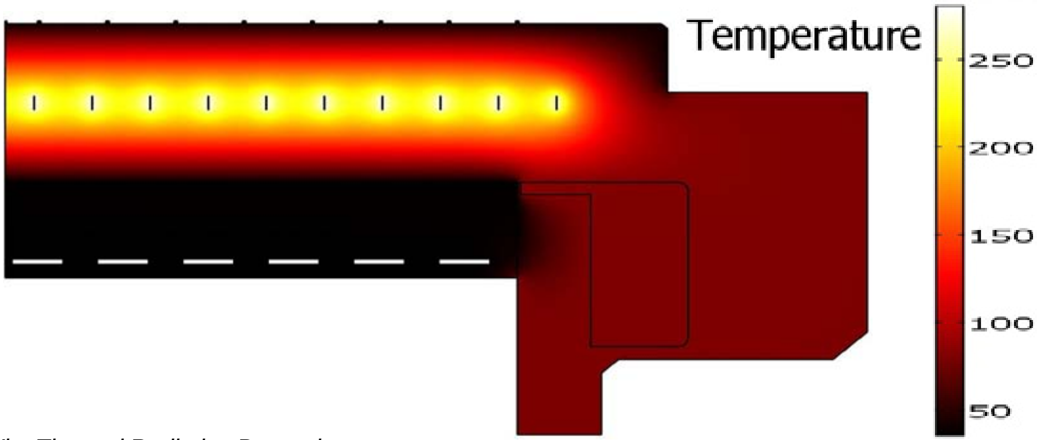
Irradiation [W/m²]



Impact of NiCr emissivity

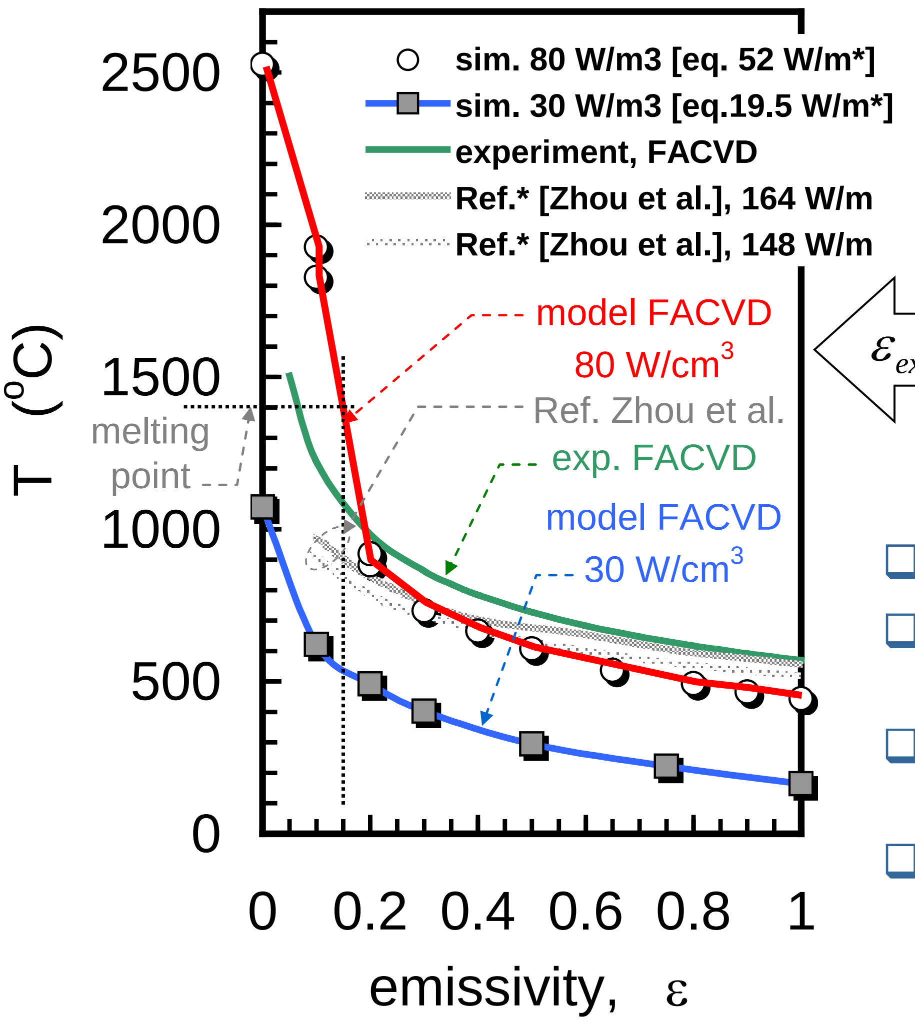


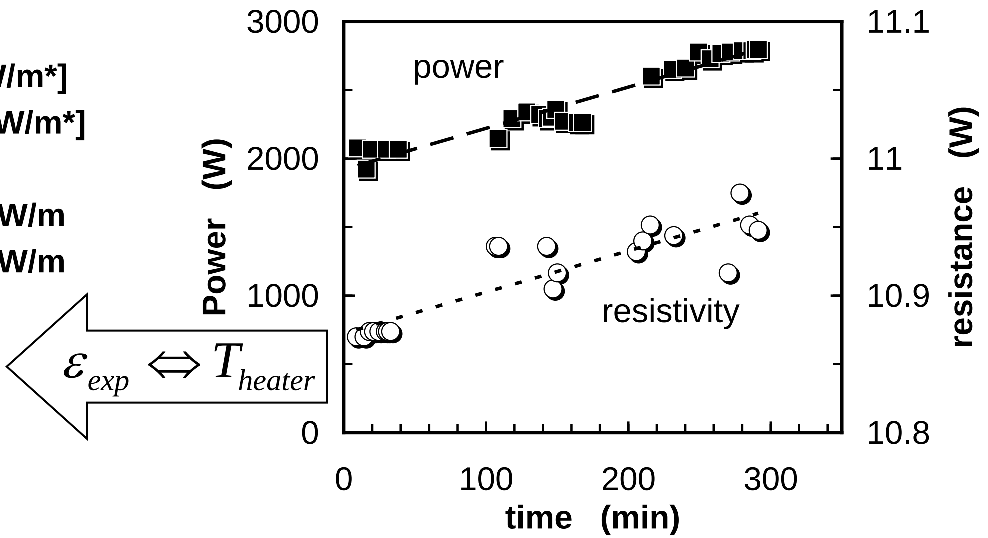
- Clean surface emissivity from 0.2 to 0.3 – aging over time
- Model provides
  - ✓ Identification of the operation window for particular HW geometry
  - ✓ Process sensitivity to heater aging
  - ✓ To address process control issues



Ref.: Y. S. Touloukian and D. P. DeWitt, Thermal Radiative Properties - Metallic Elements and Alloys, Thermophysical Properties of Matter (IFI/Plenum, New York, 1970).

NiCr emissivity performance

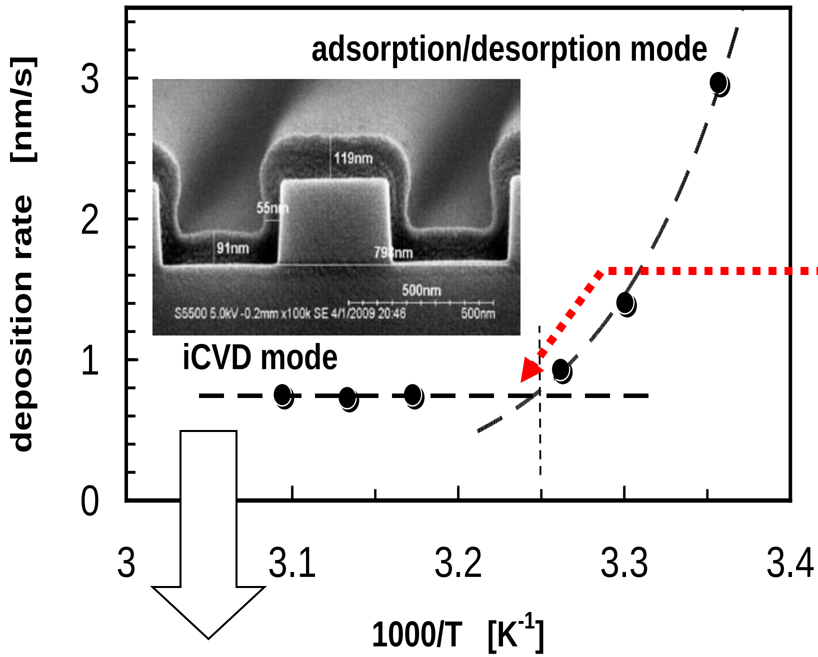


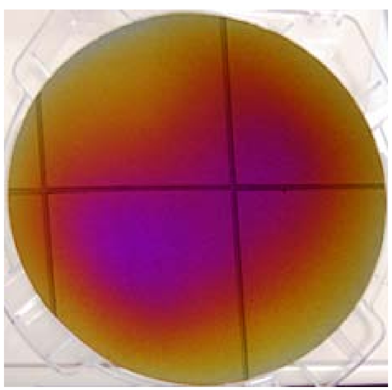


- Model correlates with published data
- Good validation with measurements in our FACVD reactor
- When ε<0.2 increased sensitivity of model⇒ consideration of 3D
- "clean" NiCr (ε~0.4) to "heavily oxidized" surface (ε~0.85) generates temperature change – important for process control

Ref.: J. Zhou, T.R. Ohno, and C.A. Wolden: The high temperature stability of nichrome in reactive environments. J. Vac. Sci. Technol. A 21(3), May/Jun 2003, 756-761

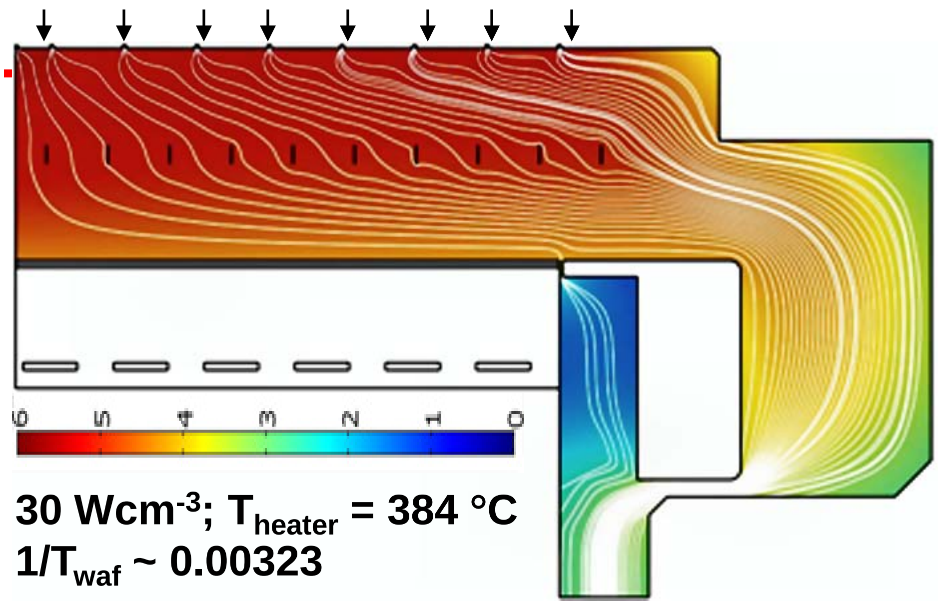
iCVD process development for SAC film





EGDA / TBPO deposition on wafer at substrate temperature T = 40 °C

Simulation was performed at process conditions and iterating for sticking coefficient to fit deposition rate



30 Wcm^{-3}; T_{heater} = 384 °C
$1/T_{waf}$ ~ 0.00323

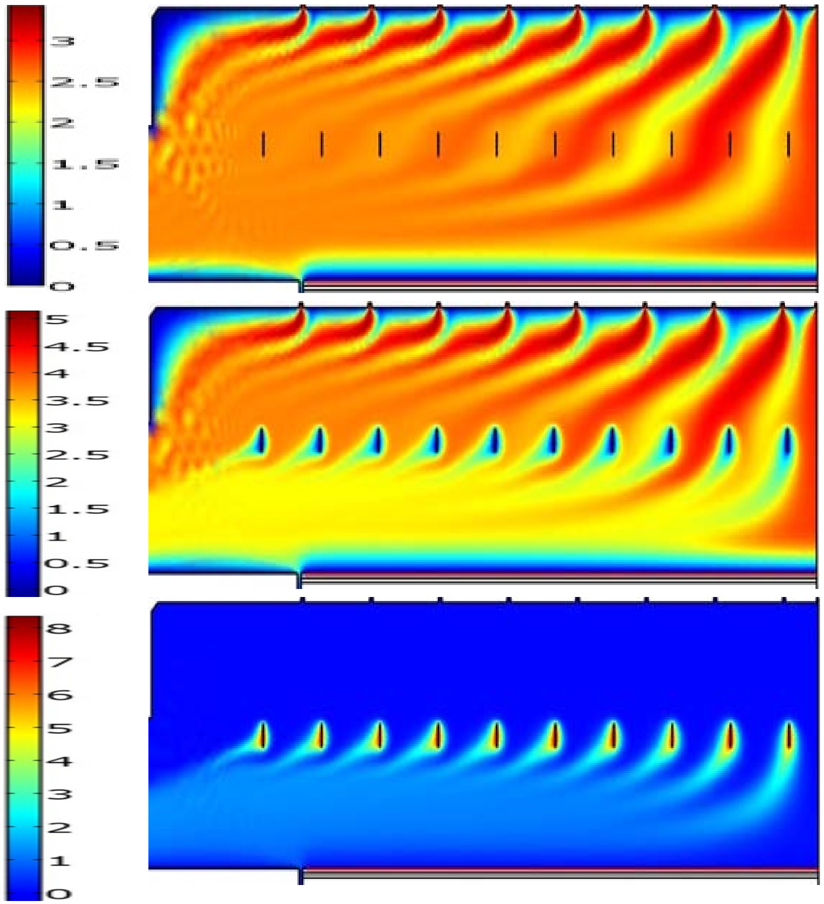
EGDA flux ~ 2×10^{15} molecules.cm^{-2}s^{-1}

$$\zeta_{EGDA} \approx 0.023\,exp(0.5945/T\,)$$

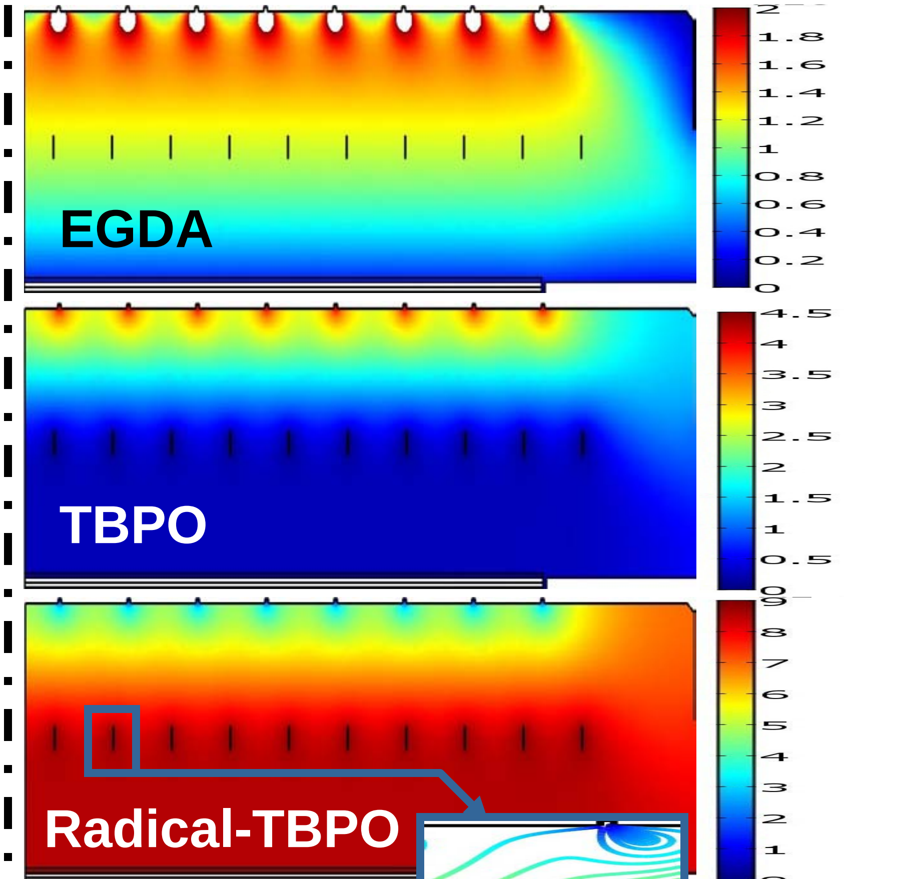
S.H. Baxamusa, K.K. Gleason, Initiated Chemical Vapor Deposition of Polymer Films on Nonplanar Substrates, Proc. 5th Int. Conf. on HWCVD, MIT, Cambridge (2008)

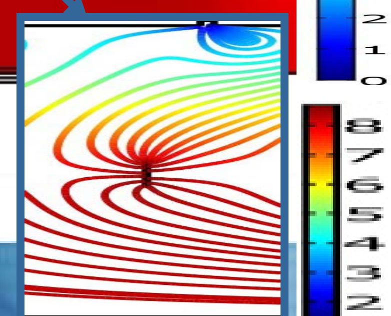
Precursor transport

Underestimated diffusivity



Correct diffusivity and empirical sticking coefficient





reactor scaling & performance simulation

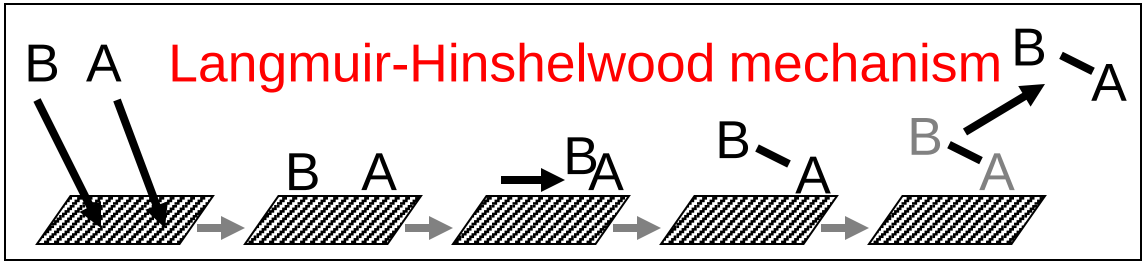
TBPO radicals flux

General mechanisms of surface reactions

$$A + B \rightarrow AB$$

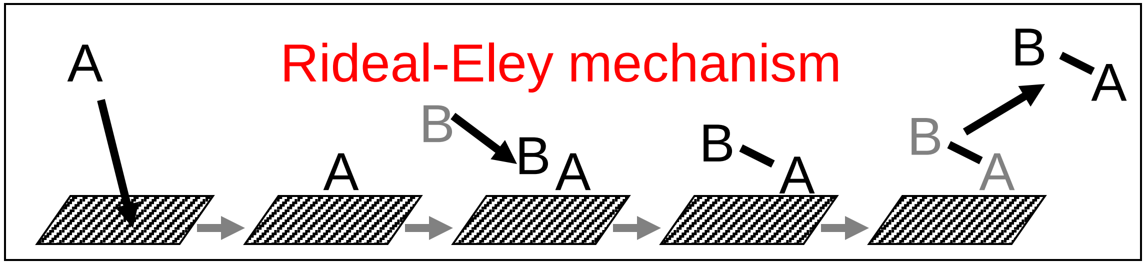
Langmuir-Hinshelwood mechanism

A and B first adsorb on the surface. Next, the adsorbed A and B react to form an adsorbed AB complex. Finally, the AB complex desorbs.



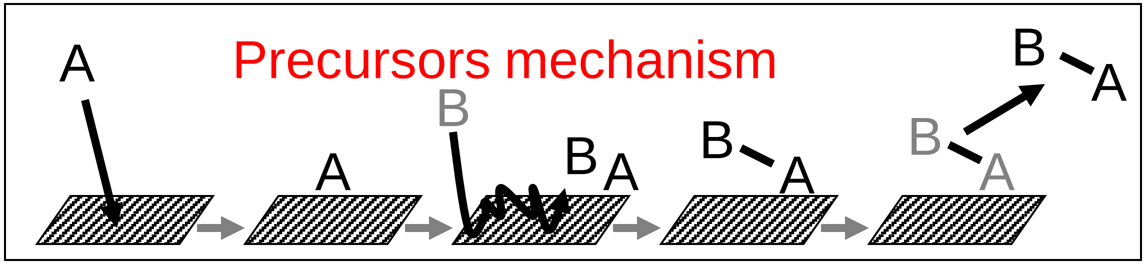
Rideal-Eley mechanism[2]

The reactant A chemisorbs. The A then reacts with an incoming B molecule to form an AB complex. The AB complex then desorbs.



Precursors mechanism

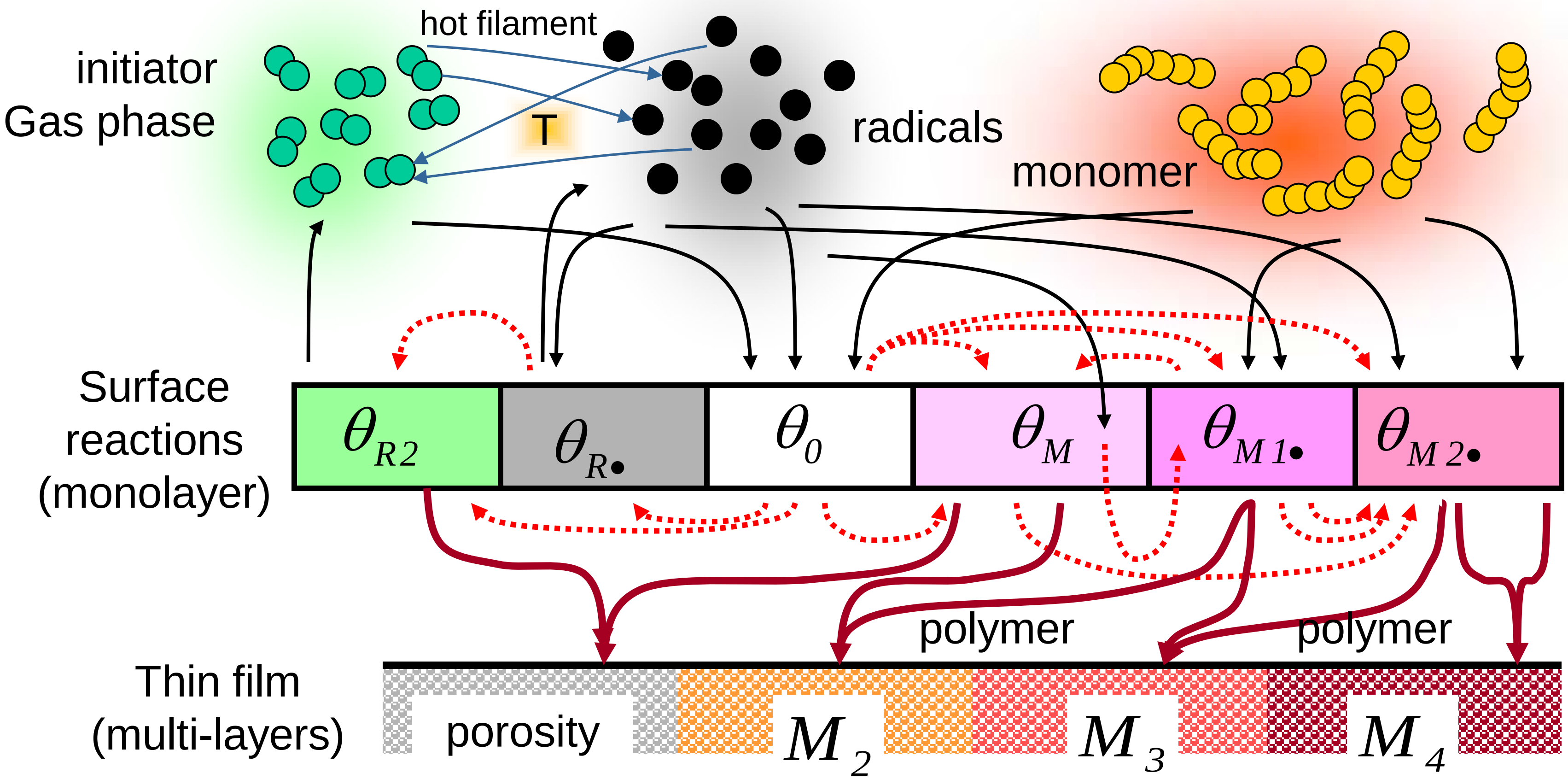
The reactant A adsorbs. Next, B collides with the surface and enters a mobile precursor state. The precursor rebounds along the surface until it encounters an adsorbed A molecule. The precursor then reacts with the A to form an AB complex, which desorbs.



[2] originally Rideal and Eley did not distinguish "precursor" mechanism within their definition of mechanism, however, more workers now make a distinction.

[1] Richard I. Masel, Principles of adsorption and reaction on solid surfaces. John Wiley & Sons, New York (1996) 444.

Mass transport and surface mechanism flow



- System can be analytically solved to compute surface fraction coverage and analyze polymer growth

$$\theta_0^{solved}, \theta_{R2}^{solved}, \theta_{R\bullet}^{solved}, \theta_M^{solved}, \theta_{M1\bullet}^{solved}, \theta_{M2\bullet}^{solved}$$

Deposition rate and polymer composition

$$DR(M_2) = \left[\begin{array}{l} \left(k_t^{a1} \theta_{M1\bullet}^{\;2} + k_t^{b2} \theta_{M1\bullet} \theta_{M2\bullet} + k_t^{b3} \theta_{M2\bullet}^{\;2} \right) \sigma_s^{\;2} + \\ + k_t^{c2} \theta_{M2\bullet} n_{R\bullet} \sigma_s \end{array} \right] V_{M2}$$

$$DR(M_3) = k_t^{a2} \theta_{M1\bullet} \theta_{M2\bullet} \sigma_s^{\;2} V_{M3}$$

$$DR(M_4) = k_t^{a3} \theta_{M2\bullet}^{\;2} \sigma_s^{\;2} V_{M4}$$

$$\sum_j DR(M_j)$$

$$(\ldots + porosity)$$

$$DR(M_{j_1 + j_2 + j_3})$$

Final film & structure of grown polymer is affected by many factors – post processing

Full surface chemistry models result in transcendent nonlinear equations - very complex solutions or unsolved cases

To avoid disambiguation within Comsol-based environment – substantially simplified versions of surface chemistry and solved analytically

Advantage – fast computation

- **model designated to verify various hypothesis on film growth mechanism and determine empirical rate constants vs input parameters – process engineering & development**

Deposition rate and polymer composition

$$DR(M_2) = \left[\left(k_t^{a1}\theta_{M1\bullet}^{\;2} + k_t^{b2}\theta_{M1\bullet}\theta_{M2\bullet} + k_t^{b3}\theta_{M2\bullet}^{\;2} \right)\sigma_s^{\;2} + k_t^{c2}\theta_{M2\bullet} n_{R\bullet}\sigma_s \right] V_{M2}$$

$$DR(M_3) = k_t^{a2}\theta_{M1\bullet}\theta_{M2\bullet}\sigma_s^{\;2} V_{M3}$$

$$DR(M_4) = k_t^{a3}\theta_{M2\bullet}^{\;2}\sigma_s^{\;2} V_{M4}$$

unknown

$$\sum_j DR(M_j)$$

$$(\ldots + porosity)$$

$$DR(M_{j_1+j_2+j_3})$$

Methods used in Modeling & Simulation in Materials Science & Engineering

Final film & structure of grown polymer is affected by many factors – post processing

- **model designated to verify various hypothesis on film growth mechanism and determine empirical rate constants vs input parameters – process engineering & development**

Conclusions

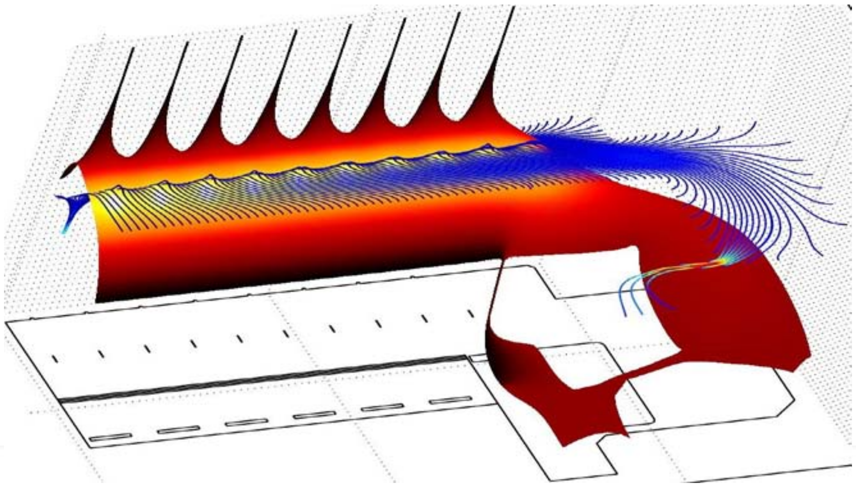
- Developed a pivotal model for FACVD / iCVD reactor. Baseline for investigation and virtual process development

- PROS / advantages
  - ✓ thermal performance was validated and it is in good agreement with experiments
  - ✓ Determined sticking coefficient of EGDA monomer ~ 0.023 and effective activation energy ~ 4.94 J/mol for EGDA “iCVD mode polymerization”
  - ✓ In virtual reactor, the film properties and complex processes can be adjusted simply by input parameters - computational DOE and hypothesis verification

- CONS / limitations
  - ✓ Too many adjusted and unknown parameters
  - ✓ Surface chemistry to be enhanced – it relies on a growing experimental database

Acknowledgement

to Jacques Faguet, Eric Lee, Dorel Toma and Akiyama Osayuki for technological and application insights on FACVD / iCVD processes and experimental data.



- **Continuing work on upgrading chemistry, enhancing film growth model, conversion to pulsed operation, …**