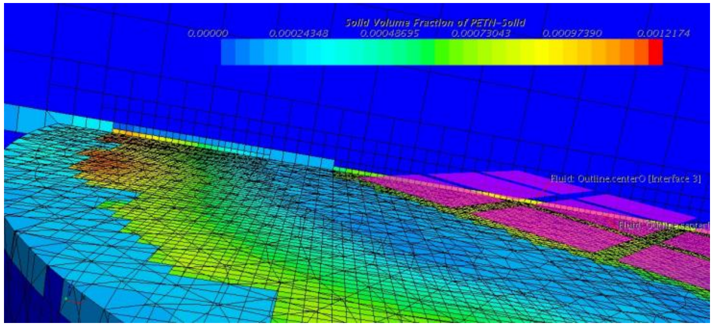
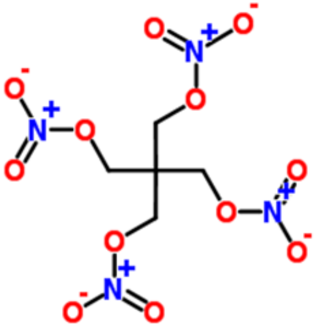
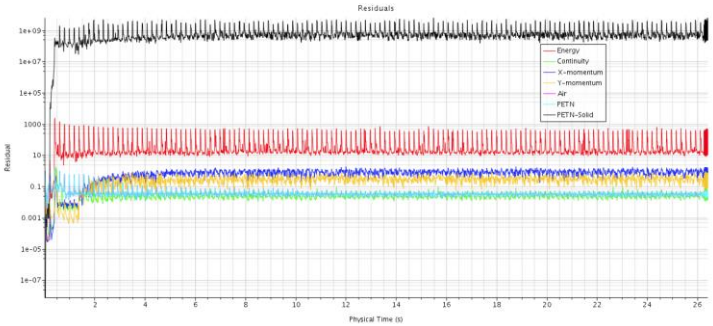
SAND2017-11025C

Modeling Physical Vapor Deposition of Energetic Materials







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Massachusetts Institute of Technology

**AVS 64th International Symposium & Exhibition,
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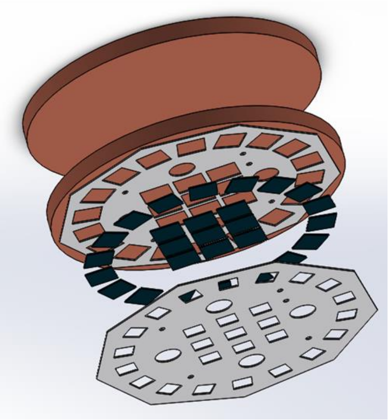
Background and Objective

- Morphology and microstructure of organic explosive films formed using physical vapor deposition (PVD) processes strongly depend on local surface temperature during deposition.
  - Homologous temperature at point of deposition, along with cooling rate, key in determining film growth mode.
- Currently, there is no accurate means of quantifying local surface temperature during vapor-deposition of PETN or other energetic materials.
  - Goal has been to maintain consistent deposition temperature, though this becomes challenging for thicker films.
- The Center for Advanced Nuclear Energy Systems (CANES) at MIT is supporting SNL to significantly improve the prediction of local deposition surface temperature.

Problem Definition

- Deposition takes place against gravity
- The deposition plate rotates at 50 rpm



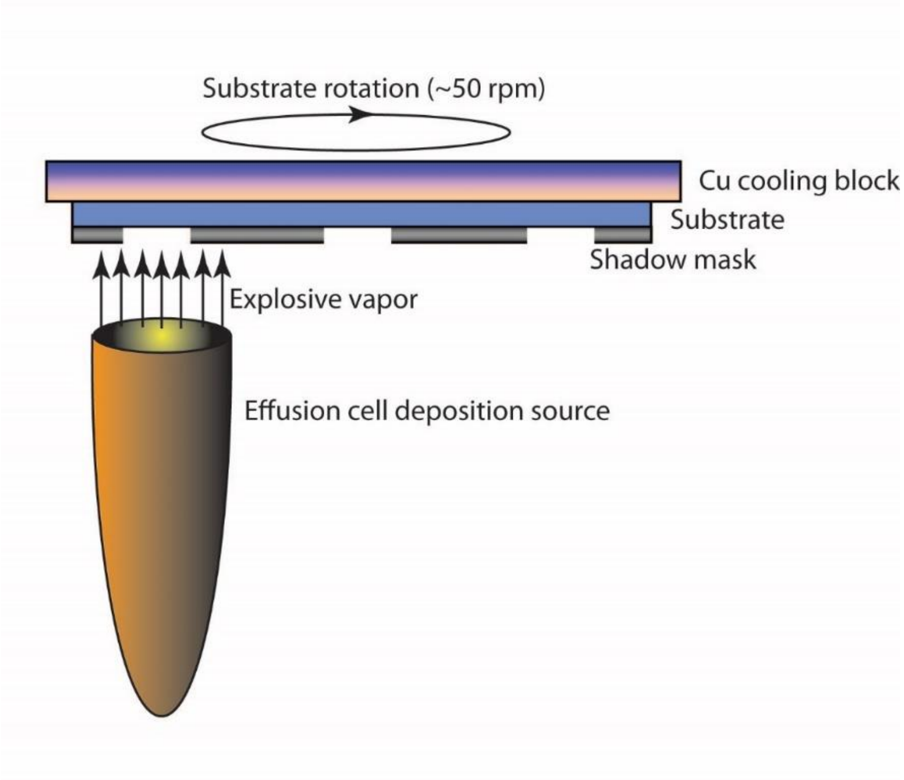
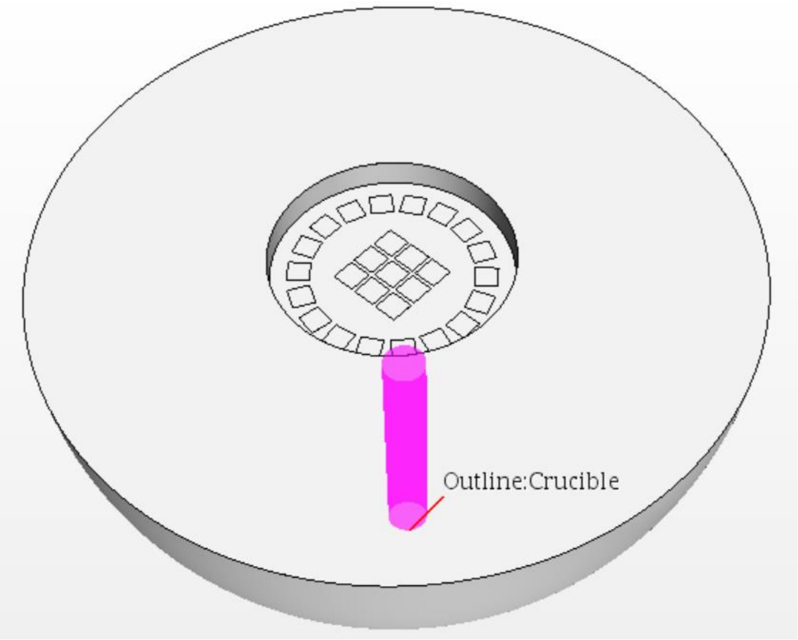
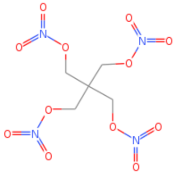


Image from SNL



CFD Simulation Geometry
(Copper plates not shown)

Thermophysical Properties of PETN

			Temperature Dependent Relation
Chemical Formula	$C_5H_8N_4O_{12}$		
Molecular Weight, M.W.	316.1366 g/mol		
Melting Point at 1 atm	142.9 ºC		N/A
Density, *ρ*	1.778 g/cm^3 (22 °C)		N/A
Thermal Conductivity, *k*	0.251 W/m-K		N/A
Specific Heat Capacity, c_s	1088 J/kg-K (20 °C)		[1075.288 + 2.1799·T] J/kg-°C, T in °C
Linear Coefficient of Thermal Expansion, *α*	76.5 μm/m-K (20 °C)	89.9 μm/m-K (90 °C)	N/A
Latent Heat of Deposition, h_{dep}	-480.8 ± 6.3 kJ/kg (standard conditions)	-496.3 ± 2.5 kJ/kg (83 °C to 109 °C) -480.5 ± 6.4 kJ/kg (97 °C to 138 °C)	N/A
Static Tensile Strength (all failures by brittle fracture)	Strain Rate (s^{-1}) 10^{-3} 10^{-2} 10^{-1} 1000 1120 1300 2600	Ult. Stress (MPa) 1.10 1.48 1.48 4.96 4.83 5.41 5.79	N/A

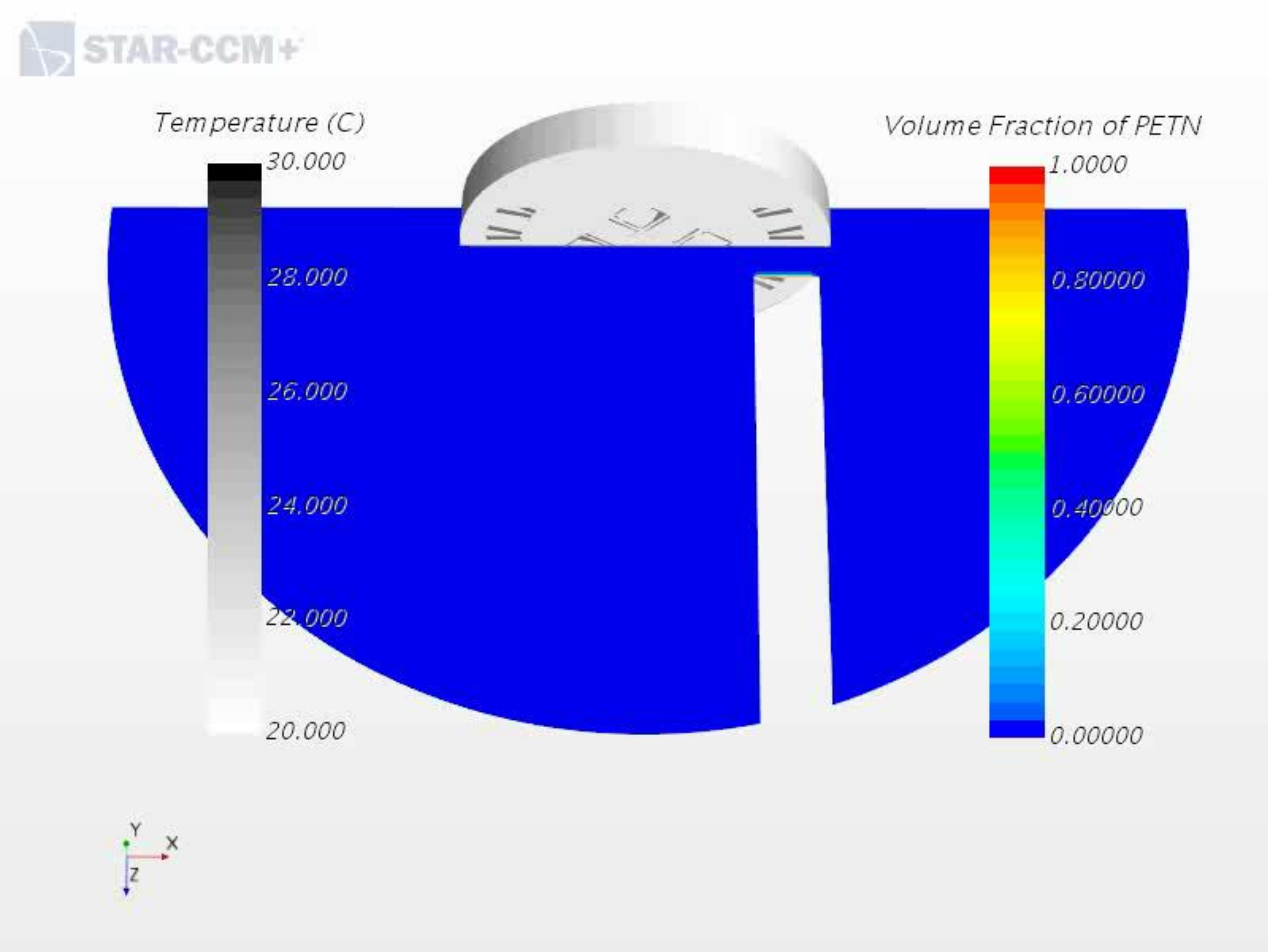
Methodology

- Computational Fluid Dynamics (CFD) Framework
  - STAR-CCM+ 11.04.08 (CD-Adapco)
- Considered Mediums:
  - Vacuum Chamber (Gas)
  - PETN Vapor Phase (Gas)
  - PETN Solid Phase (Solid)
  - Cooling Copper Blocks/Wafers (Solid)
- PETN was treated with Volume of Fluid Method as Eulerian Phases.
  - The mediums were thermally coupled to the copper block
  - PETN Sublimation and Evaporation were modeled
- Implicit time-dependent scheme was utilized to model the PVD process.
  - 3D Fluid/Solid Model: Investigate PVD coverage with respect to the Vacuum chamber
  - 2D Fluid/Solid Model: Investigate heat and mass transfer at deposition blocks.
  - 3D Solid Model: Investigate the bounds of the solid PETN formation temperature

Model Inputs/Assumptions

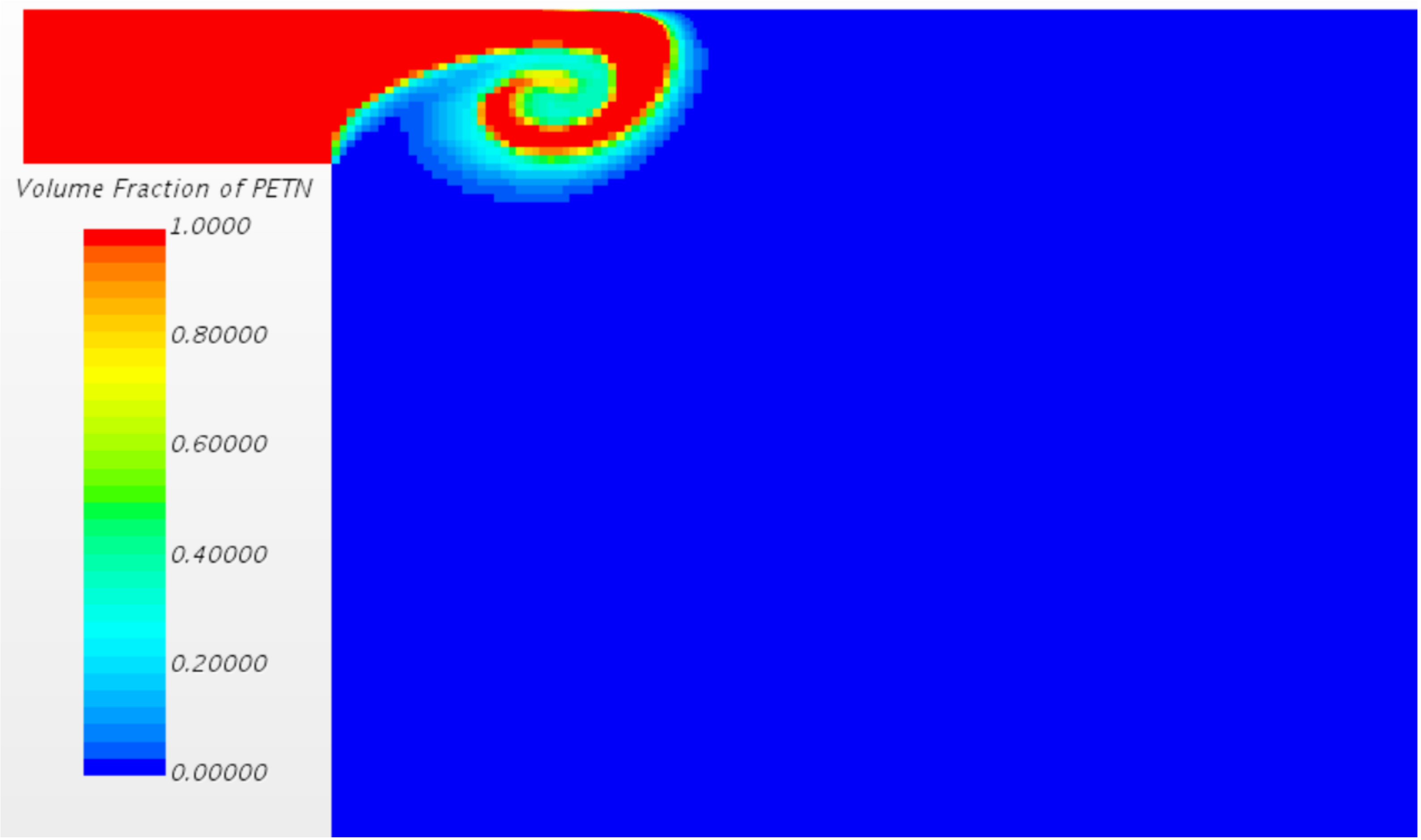
- PETN is deposited at 142.9 ^{o}C on a wafer with initial temperature of 22^{o}C
  - The rate of deposition is 1.4E-8 m/s.
- Chiller: Flow in 5 mm ID pipe of length 3 m with gauge pressure of 80.6 kPa leads to mass flux of ~3000 kg/m^2-sec
  - The heat transfer coefficient (HTC) is ~5000 W/m^2-K.
  - Using heat balance with $\Delta T = 1$ ^{o}C and cooler heat capacity of 3140 J/kg-K, we arrive at power of ~200 W.
  - Given the wafer plate has radius of 5.4 cm, then the heat flux removed by the cooler is 21 kW/m^2.
- 3D Solid Calculation Inputs: Sublimation of PETN on the wafers occurs with calculated HTC of ~400 W/m^2-K
  - Once the initial layer is formed then the HTC at the wafer-PETN interface increases to 4500 W/m^2-K (calculated).

3D Flow Geometry



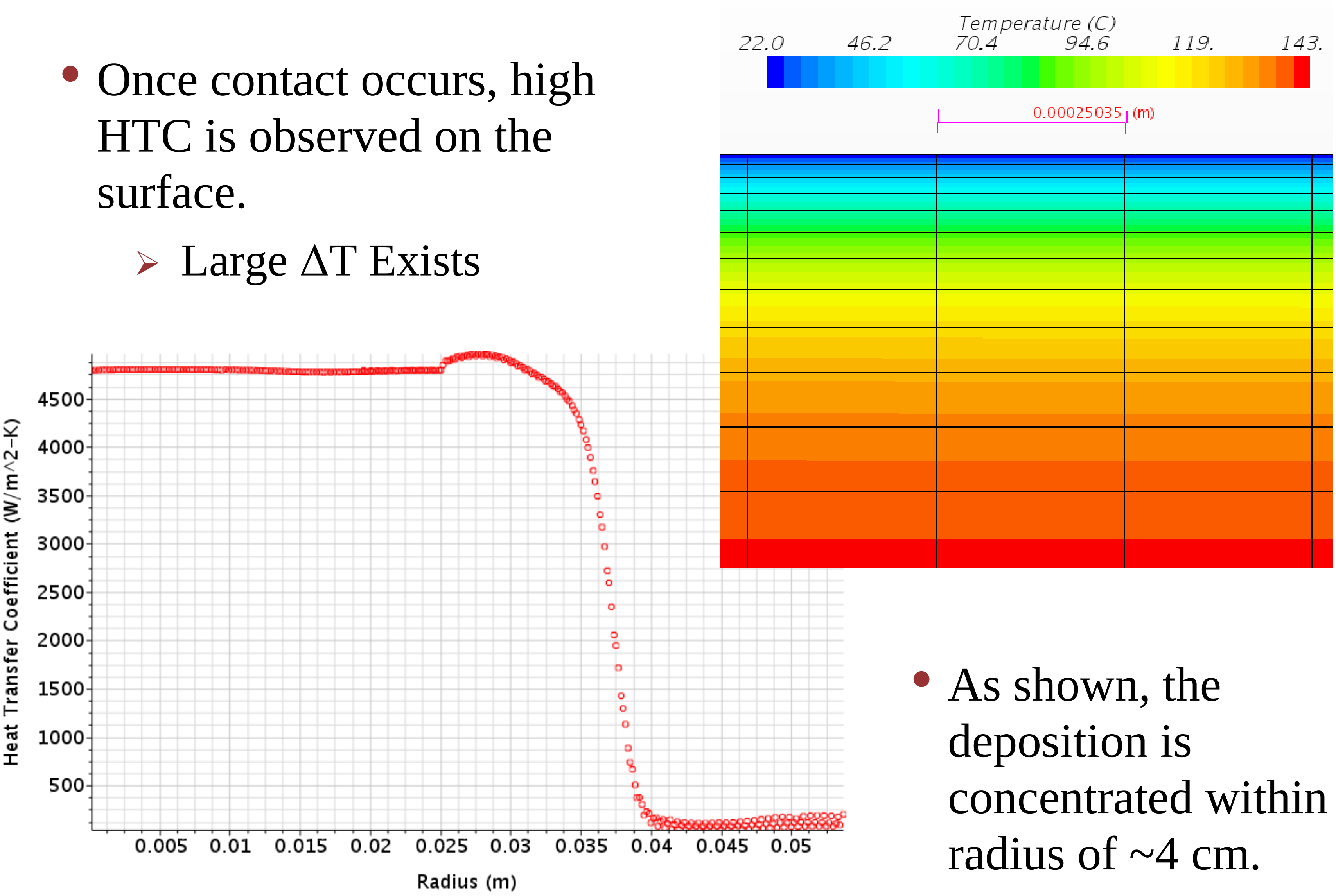
2D Flow Geometry

- PETN vapor deposition at center of a circular plate.



2D Flow Interface

- Once contact occurs, high HTC is observed on the surface.
  - Large ΔT Exists



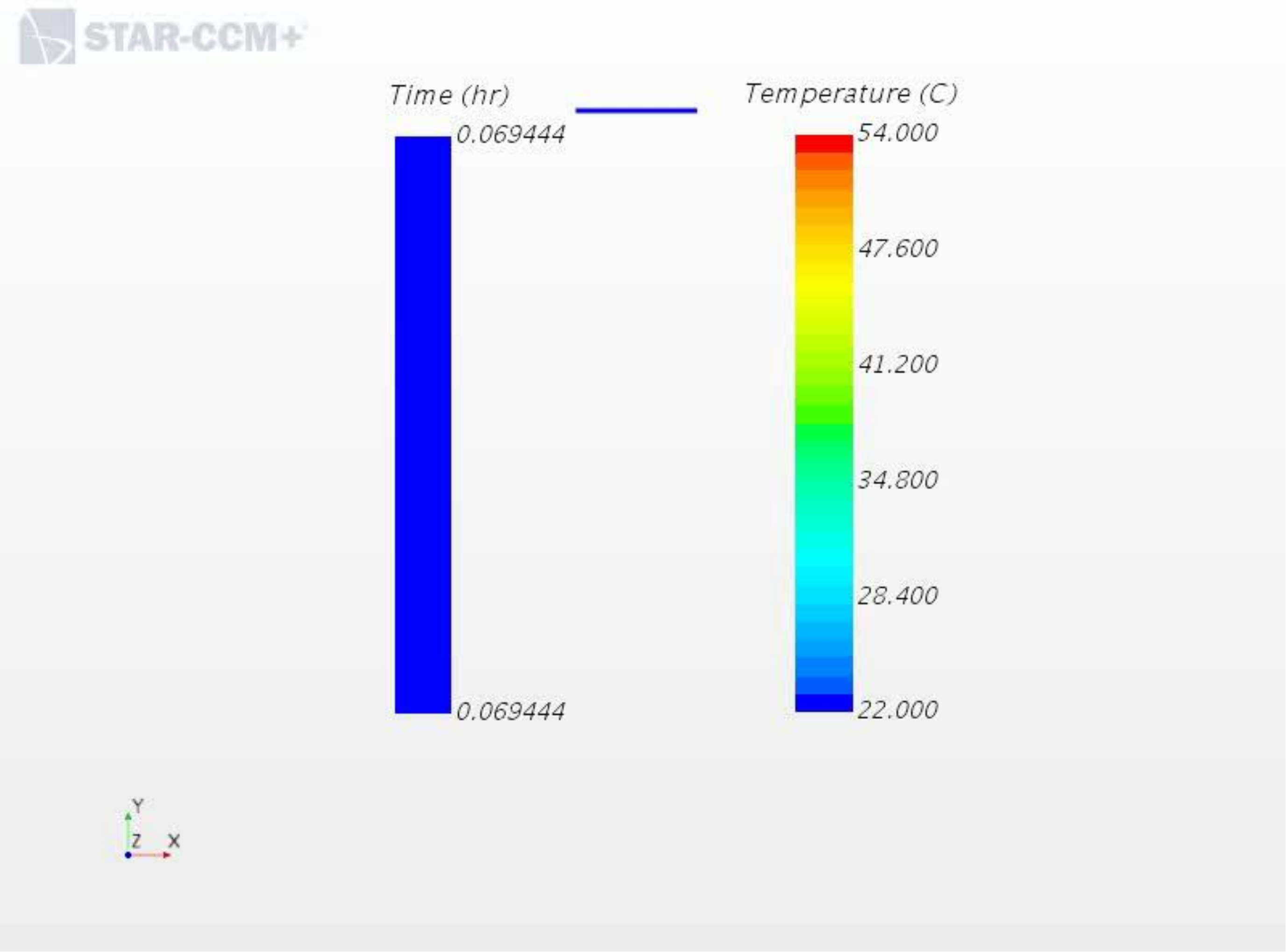
- As shown, the deposition is concentrated within a radius of ~4 cm.

2D Transient Temperature Profile with Film Growth

- Results show temperature evolution with time as PETN film grows on wafer from 0 µm to 500 µm
- The copper plate has a very large heat capacity and thermal conductivity → Results insensitive to HTC of the Water-Glycol fluid
  - Consistent with full 3D geometry
- 10 hr per 500 µm
  - 30 °C gradient is observed in PETN film.

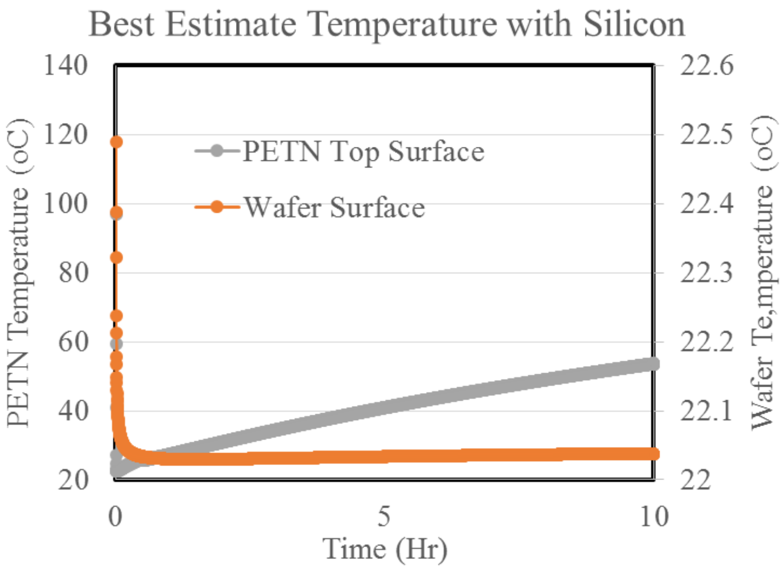
2D Transient Temperature Profile Evolution with Film Growth

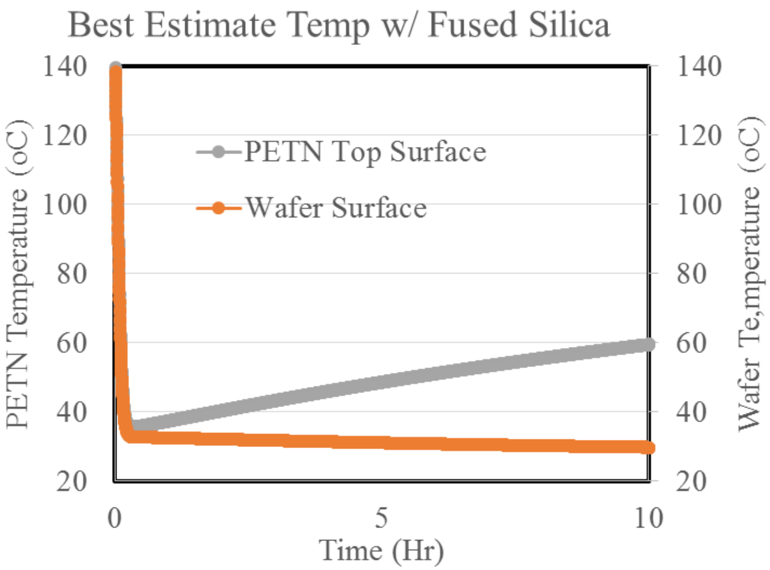
0→500 μm



Impact of Fused Silica Substrate

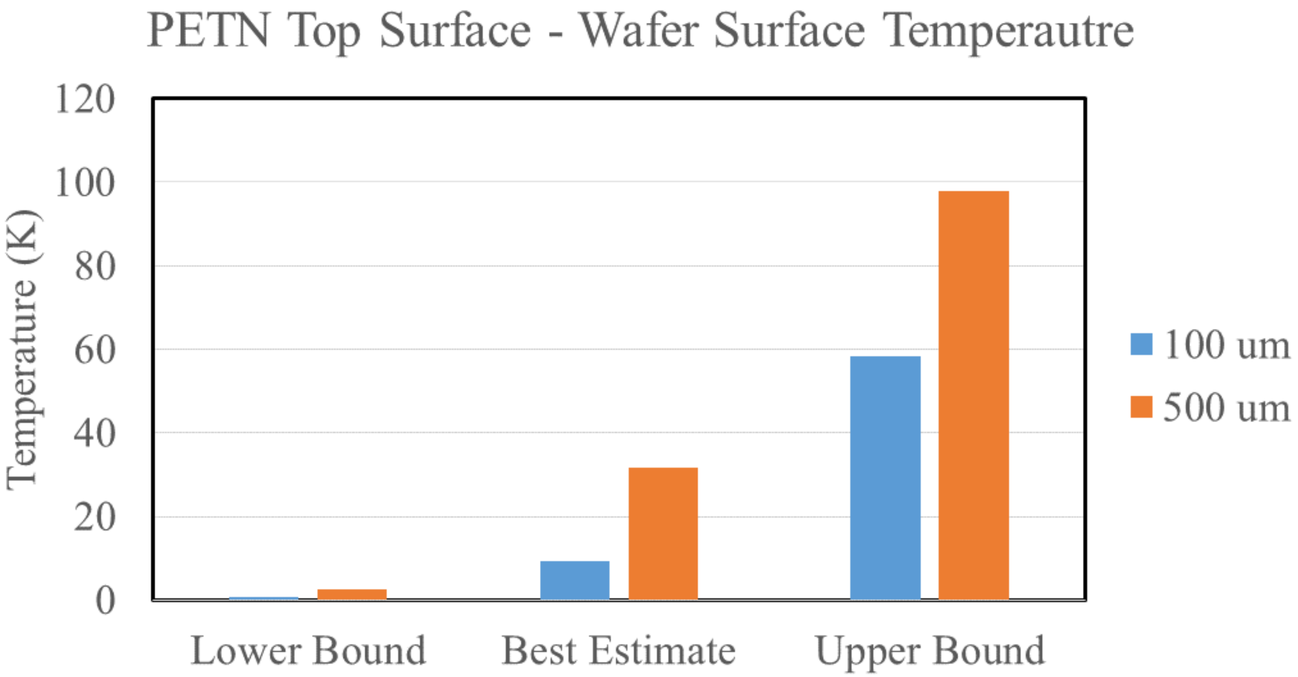
- Given 0.5 mm fused silica substrate with *k*=2 W/m-K
  - **~8 to10 ºC** increase in temperature during 10 hr (500 µm) deposition.
- Fused silica slows initial substrate cooling.
  - Substrate temperature reaches 32ºC after 15 min for fused silica vs. constant ~22ºC for silicon





Sensitivity Study

- PETN Sublimation HTC (Nominal 400 W/m^2-K):
  - Lower Bound → Condensation at room temperature (25 W/m^2-K).
  - Upper Bound → Solid PETN particle deposition (4500 W/m^2-K).
  - Results imply need for validation.



Conclusion & Future Work

- Best estimate multi-phase simulations show that 500 μm deposition of PETN takes place in presence of ~30 °C temperature gradient.
- Use of fused silica substrates results in PETN temperature increase of at least 8 to 10 °C (excludes interface resistance).
- In order to validate simulations:
  - The copper blocks, and wafer surface need to be instrumented with thermistors or RTD's for both Silicon and Fused Silica cases
    - Note it is expected the Silicon case will not give meaningful results for model validation.
  - Thermophysical properties of PETN vapor need more thorough characterization.
- **Future work should focus on modeling induced residual thermal stress in PETN film and microstructure evolution.**

Backup Slides

- Multiphase Formulation (Assumed Segregated Flow)

Continuity

$$\frac{\partial}{\partial t}\int_V \alpha_i \rho_i \chi dV + \oint_A \alpha_i \rho_i \chi (\mathbf{v}_i - \mathbf{v}_g) \cdot d\mathbf{a} = \int_V \sum_{j \neq i} (m_{ij} - m_{ji}) \chi dV + \int_V S_i^\alpha dV$$

- Where i is a phase, α is volume fraction, χ is void fraction, m is mass transfer rate between phases and S$^\alpha$ is phase mass source term,

Momentum

$$\frac{\partial}{\partial t}\int_V \alpha_i \rho_i \chi \mathbf{v}_i \, dV + \oint_A \alpha_i \rho_i \chi \mathbf{v}_i \otimes \left(\mathbf{v}_i - \mathbf{v}_g \right) \cdot d\mathbf{a} = -\int_V \alpha_i \chi \nabla p \; dV$$

$$+ \int_V \alpha_i \rho_i \chi \, \mathbf{g} \; dV + \oint_A \left[\alpha_i (\tau_i + \tau^t{}_i) \right] \chi \;\; \cdot d\mathbf{a} + \int_V \mathbf{M}_i \chi \, dV$$

$$+ \int_V \left(\mathbf{F}_{int} \right)_i \chi \, dV + \int_V \mathbf{S}_i^v dV + \int_V \sum \left(m_{ij} \mathbf{v}_j - m_{ji} \mathbf{v}_i \right) \chi \, dV$$

Backup Slides

- Multiphase Formulation (Assumed Segregated Flow)

Momentum

$$\frac{\partial}{\partial t}\int_V \alpha_i \rho_i \chi \mathbf{v}_i \, dV + \oint_A \alpha_i \rho_i \chi \mathbf{v}_i \otimes \left(\mathbf{v}_i - \mathbf{v}_g\right) \cdot d\mathbf{a} = -\int_V \alpha_i \chi \nabla p \; dV$$
$$+ \int_V \alpha_i \rho_i \chi \, \mathbf{g} \; dV + \oint_A \left[\alpha_i\left(\tau_i + \tau^t{}_i\right)\right] \chi \; \cdot d\mathbf{a} + \int_V \mathbf{M}_i \chi \, dV$$
$$+ \int_V \left(\mathbf{F}_{int}\right)_i \chi \, dV + \int_V \mathbf{S}_i^v dV + \int_V \sum \left(m_{ij}\mathbf{v}_j - m_{ji}\mathbf{v}_i\right) \chi \, dV$$

- Where M is interphase momentum transfer, F is internal forces between solids, τ is molecular stress and τ^t is turbulent stress which are neglected for the problem.

Backup Slides

- VOF Formulation for a given control volume uses single set of properties.

$$\rho = \sum_i \rho_i \alpha_i$$

$$\mu = \sum_i \mu_i \alpha_i$$

$$c_p = \sum_i \frac{(c_p)_i \rho_i}{\rho} \alpha_i$$

- The transport of volume fractions, α, is performed using:

$$\frac{d}{dt} \int_V \alpha_i dV + \int_S \alpha_i (\mathbf{v} - \mathbf{v}_g) \cdot d\mathbf{a} = \int_V \left(s_{\alpha_i} - \frac{\alpha_i}{\rho_i} \frac{D\rho_i}{Dt} \right) dV$$

- Where $s_{\alpha i}$ is the source or sink of the I th phase and $D\rho_i/Dt$ is the material derivative of the phase densities.

Backup Slides

- Solidification only impacts the energy equation.

$$h_{\mathrm{ls}}^* = h_{\mathrm{ls}} + \left(1 - \alpha^*{}_s\right) h_{fusion}$$

- Linear relationship with temperature was assumed for solidification volume fraction.
- Slurry viscosity model is used to account for the flow resistance by the solid formation:

$$\mu^* = \mu_l \left[1 - \left(\frac{\alpha^* \cdot F_\mu\left(\alpha^*{}_s\right)}{A}\right)\right]^{-2}$$

- Where F is a switching function. It was assumed that beyond 80% solid fraction in a control volume, flow stops.