Reducing the Thermal Effects during Coating of SRF Cavities: A Combined Numerical and Experimental Approach

Getnet Kacha Deyu *[1] , Trupen Parikh[2], Marc Wenskat[1,2], Isabel González Díaz-Palacio[1,3], Robert H. Blick[3], Robert Zierold[3], Wolfgang Hillert[1]

1. *Institute of Experimental Physics, Universität Hamburg, Luruper Chaussee 149, Hamburg D-22761, Germany*
2. *Deutsches Elektronen-Synchrotron, Notkestrasse 85, Hamburg D-22607, Germany*
3. *Institute of Nanostructure and Solid State Physics & Center for Hybrid Nanostructures, Universität Hamburg*, Germany

Deyu, Getnet Kacha, et al. Chemistry of Materials 36.6 (2024): 2846-2856.

*getnet.kacha.deyu@desy.de

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Universität Hamburg
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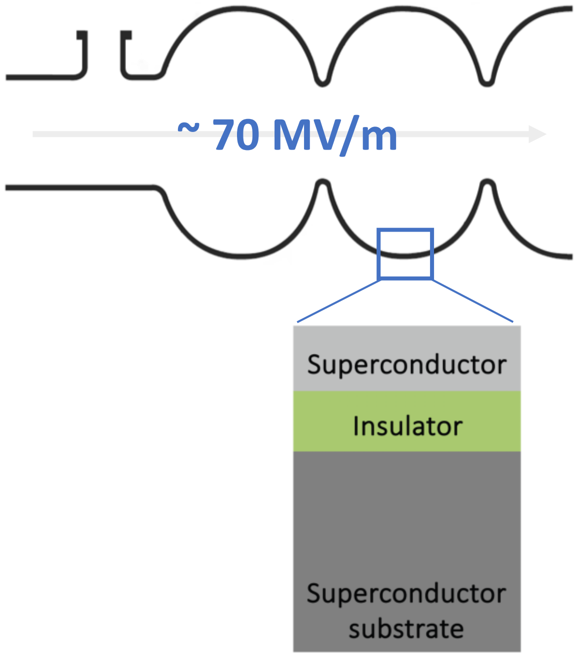
HELMHOLTZ
RESEARCH FOR GRAND CHALLENGES

DESY.

Insulator layer for SIS coating of SRF cavities

- SRF cavities approach thermodynamic limit of Nb
- SIS to enhance E_{acc} and achieve lower RF losses
- Superconductor (S) layer:
  - provide magnetic screening
- Insulator (I) layer:
  - stabilize coating
  - prevent global vortex penetration
  - candidates: Al_2O_3, AlN, Ta_2O_5, MgO…
  - need to have full coverage and uniform coating over the cavity volume



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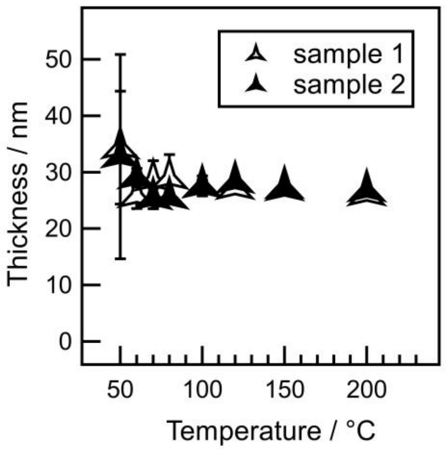
Atomic layer deposition (ALD)

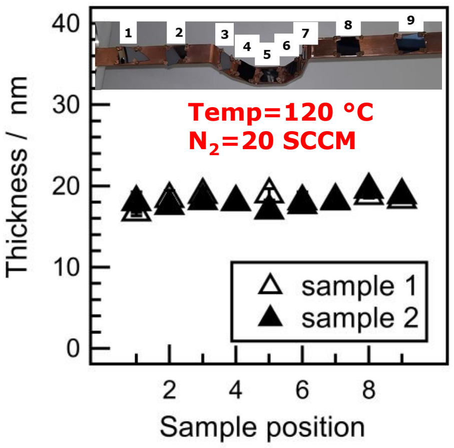
A. Gurevich, Appl. Phys. Lett. 88, 012511 (2006), A. Gurevich, AIP ADVANCES 5, 017112 (2015), T. Kubo, Appl. Phys. Lett. 104, 032603 (2014)

Successful ALD-Al_2O_3 coating on cavities

Recipe optimization

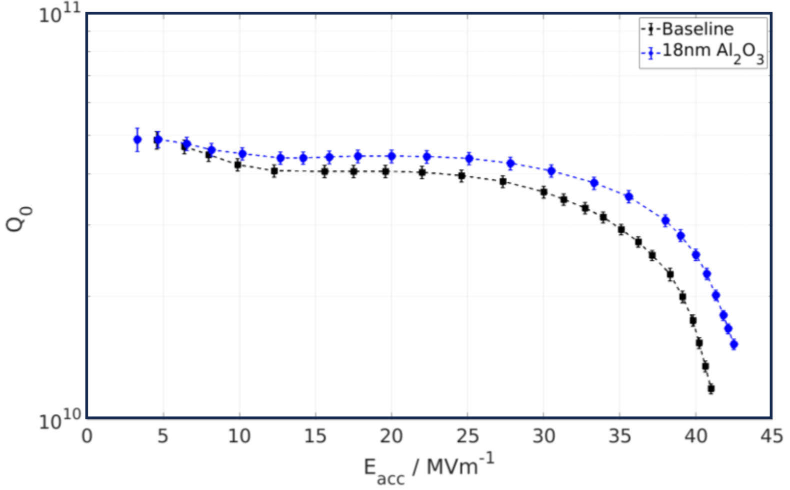


Small chamber



Cavity volume

1DE18, Q_o vs E_{acc} @ 2K



- Preserve extraordinary cavity performance after coating

Thermal effects in SRF cavities coating

- Deposition time for Al_2O_3 in cavity volume: ~3x longer than in small chamber
- PEALD: 60 nm of NbTiN/AlN deposition: ~5 days at 250°C*
- Time/temp. optimization can reduces parasitic temperature effects, crucial for maintaining cavity performance

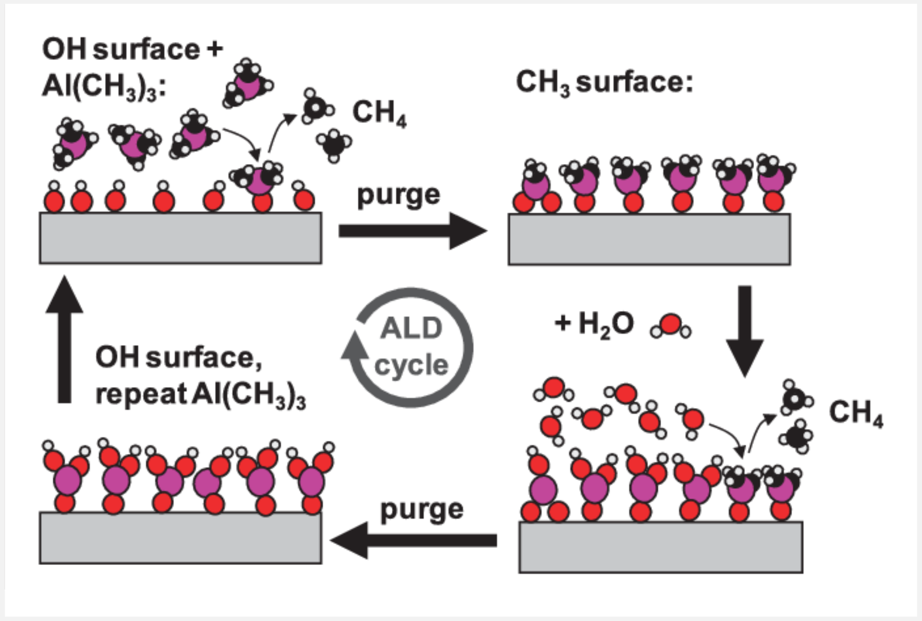
To explore the possibility of achieving shorter process times (reduced thermal exposure) while maintaining film quality, ALD-Al_2O_3 process modeling on an SRF cavity is carried out using ANSYS Fluent

Wenskat, Marc, Deyu, Getnet Kacha, et al. *Superconductor Science and Technology* 36.1 (2022): 01501

* González Díaz-Palacio, Isabel, et al. *Journal of Applied Physics* 134.3 (2023).

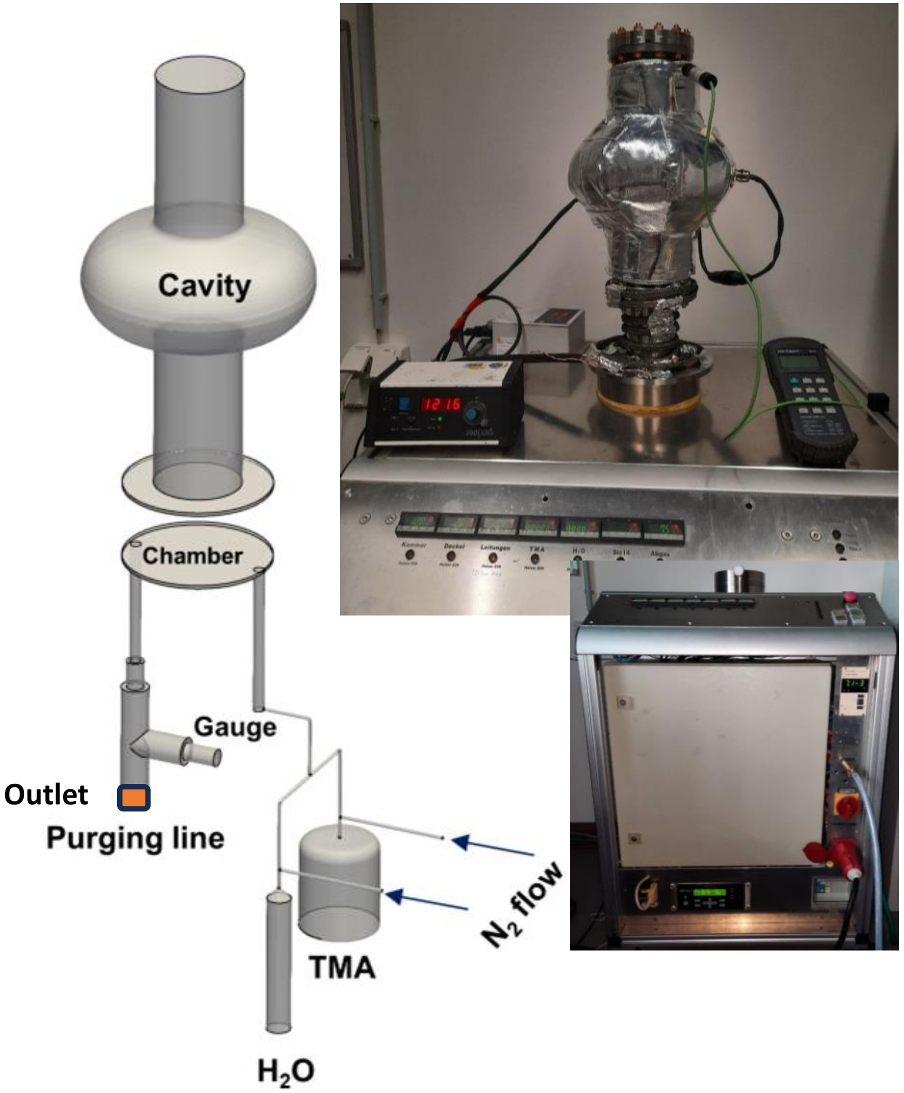
Atomic layer deposition - Al_2O_3

Working principles



- ❑ Atomic-scale precision
- ❑ Self limiting surface reactions
- ❑ Sub-nanometer thickness control
- ❑ A wide range of materials
- ❑ High conformality on complex, 3D structures

3D computational domain of ALD setup - thermal



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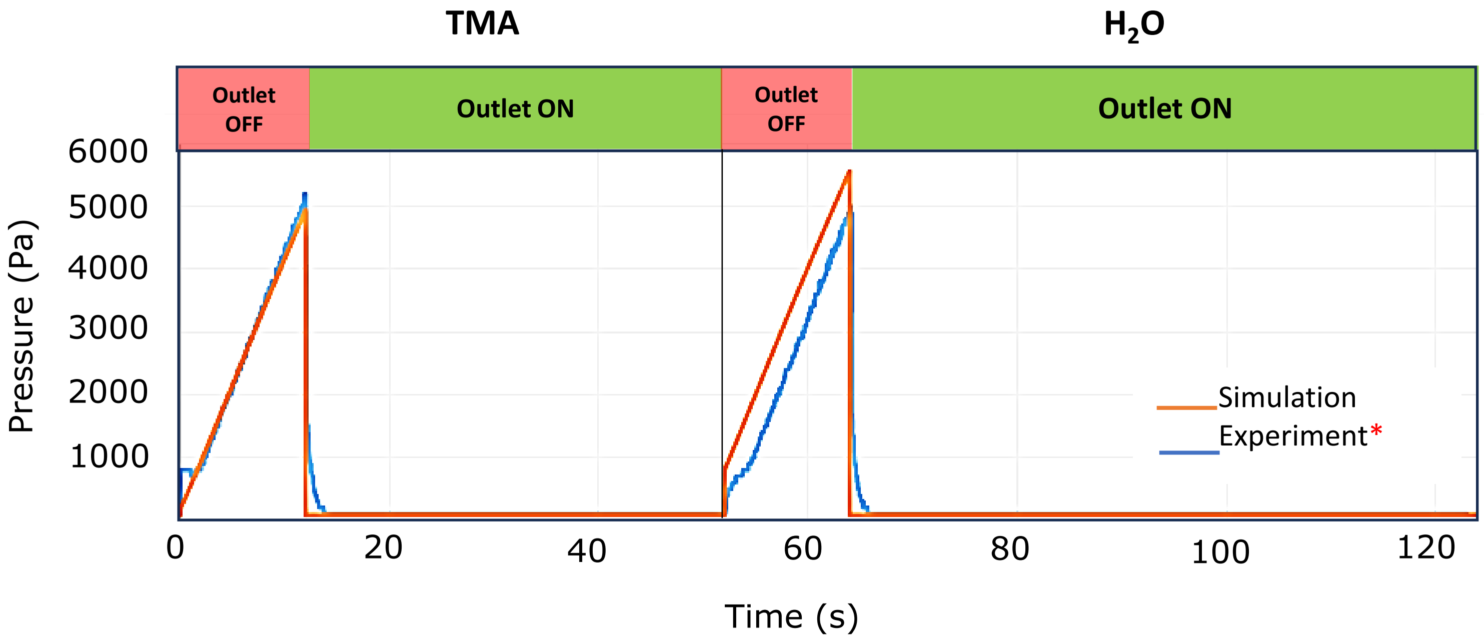
Simulated pressure profile agrees with experiment

Thin film chamber



Boundary conditions*

- ❑ Vapor pressures:
  - ❑ TMA: 1257.23 Pa
  - ❑ H_2O: 3157.07 Pa
- ❑ Base pressure:
  - ❑ ~80 Pa, by continuous N_2 flow at 20 sccm
- ❑ Precursor pulse/exposure/purge times:
  - ❑ **TMA: 50ms/12s/40s**
  - ❑ **H_2O: 50ms/12s/60s**

- ❑ **Only precursors distribution, no surface chemical reactions**
- ❑ Peak pressures during TMA and H_2O pulsing and exposure phases
- ❑ Overestimated purging time; **a short purge is sufficient to remove excess precursors**

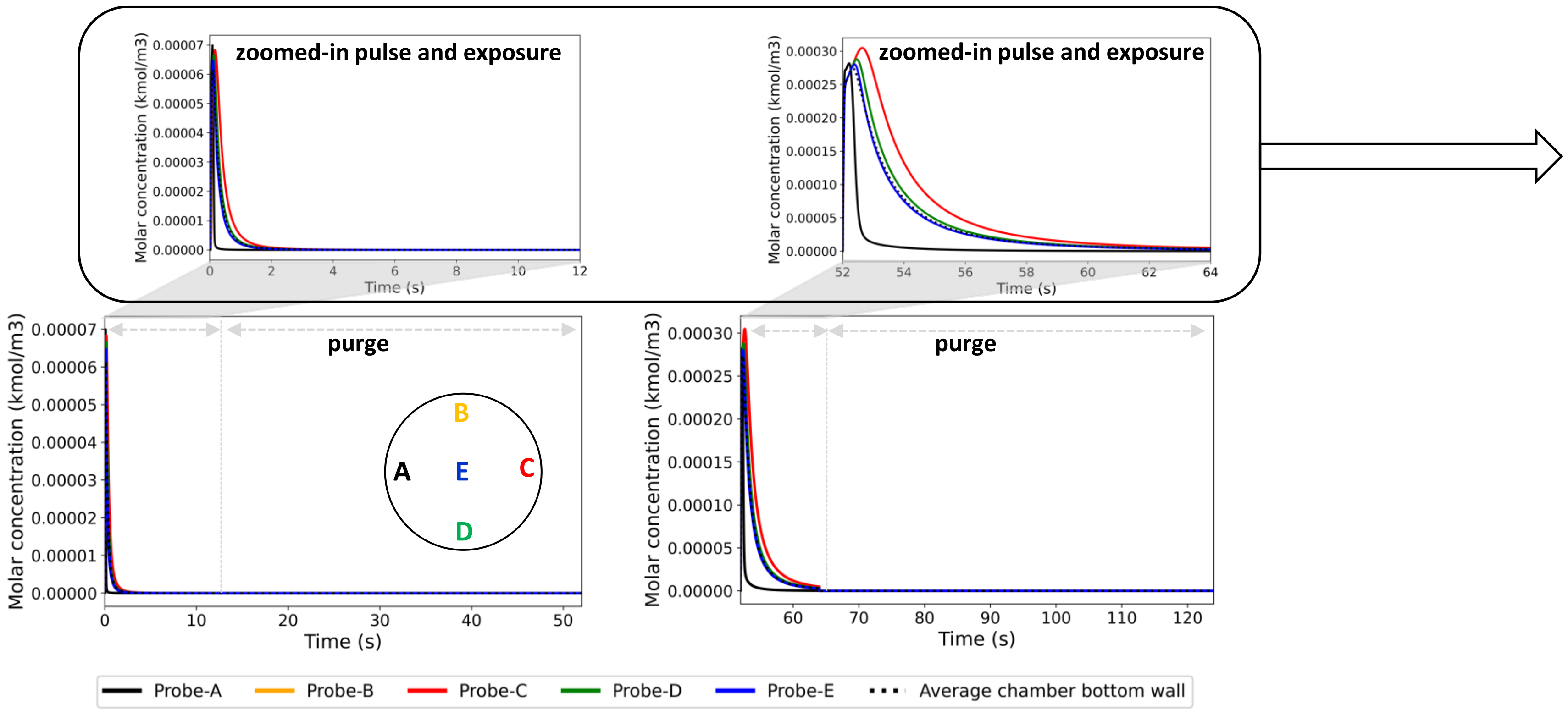
*Wenskat, Marc, Deyu, Getnet Kacha, et al. *Superconductor Science and Technology* 36.1 (2022): 01501 *Deyu, Getnet Kacha, et al. Chemistry of Materials 36.6 (2024): 2846-2856.*

Precursors distribution - thin film chamber

Precursors molar concentrations - probe points

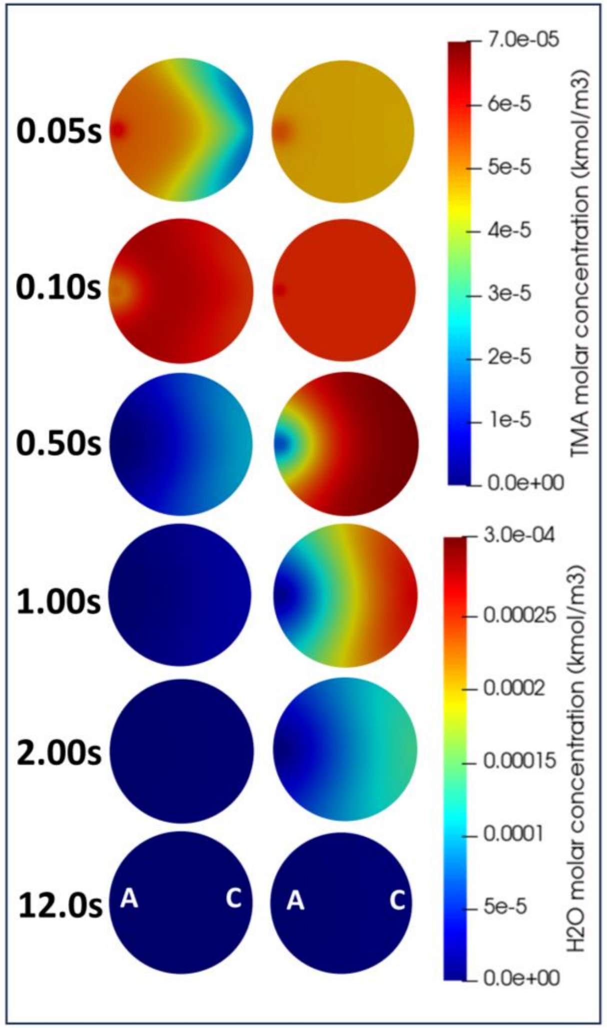
TMA

H_2O



Contour plots – exposure time

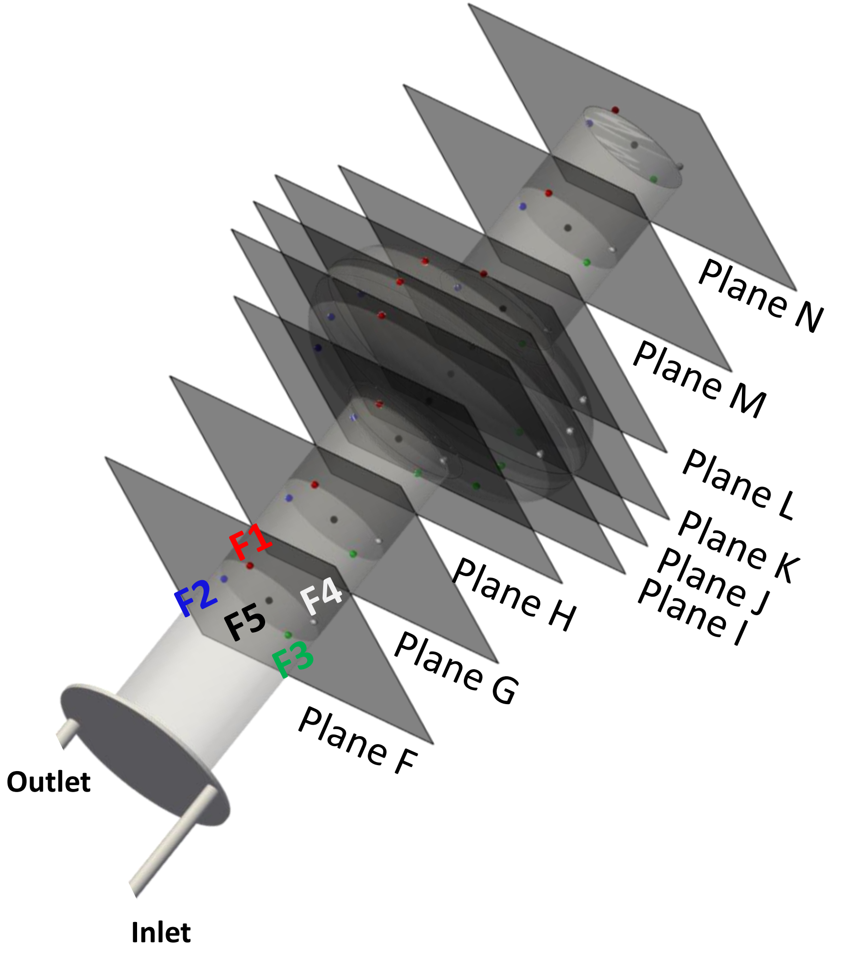
TMA H_2O



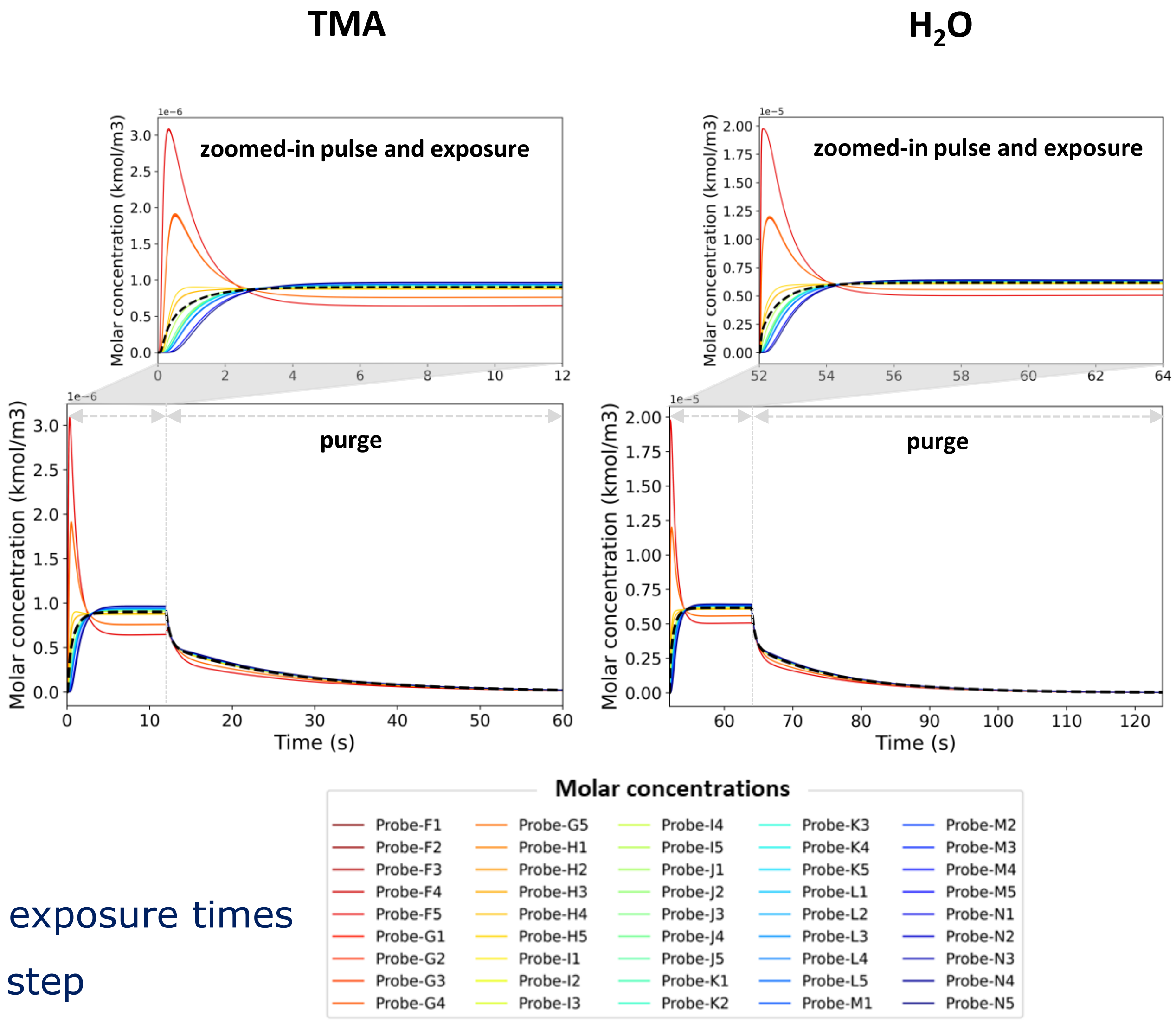
- ❑ Effective precursors distribution within given pulse and exposure times
- ❑ **Overestimated purging time, shorter purging is enough**

Precursors distribution - cavity volume

3D Computational domain-probe points



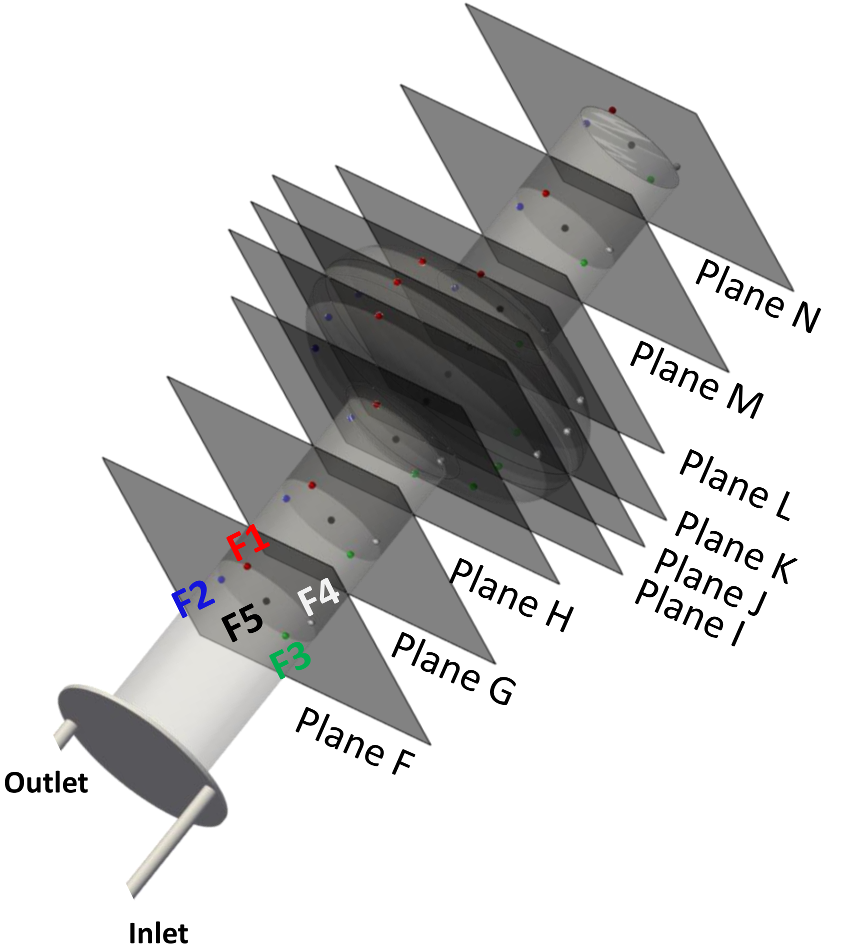
Precursors molar concentrations at probe points



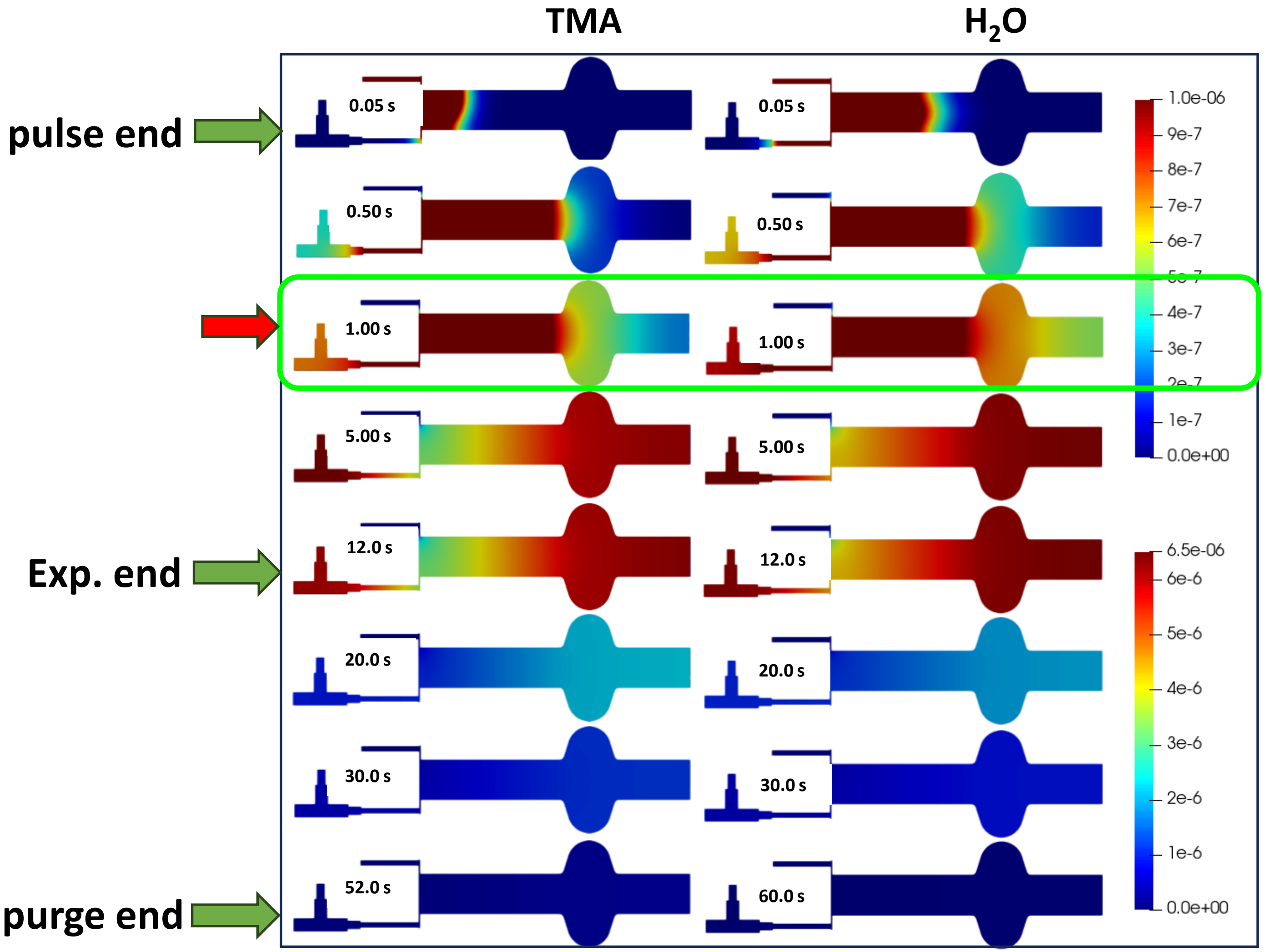
- Effective precursors distribution within given pulse and exposure times
- Successful decrease to near-zero levels during purging step

Precursors distribution - cavity volume

3D Computational domain-probe points



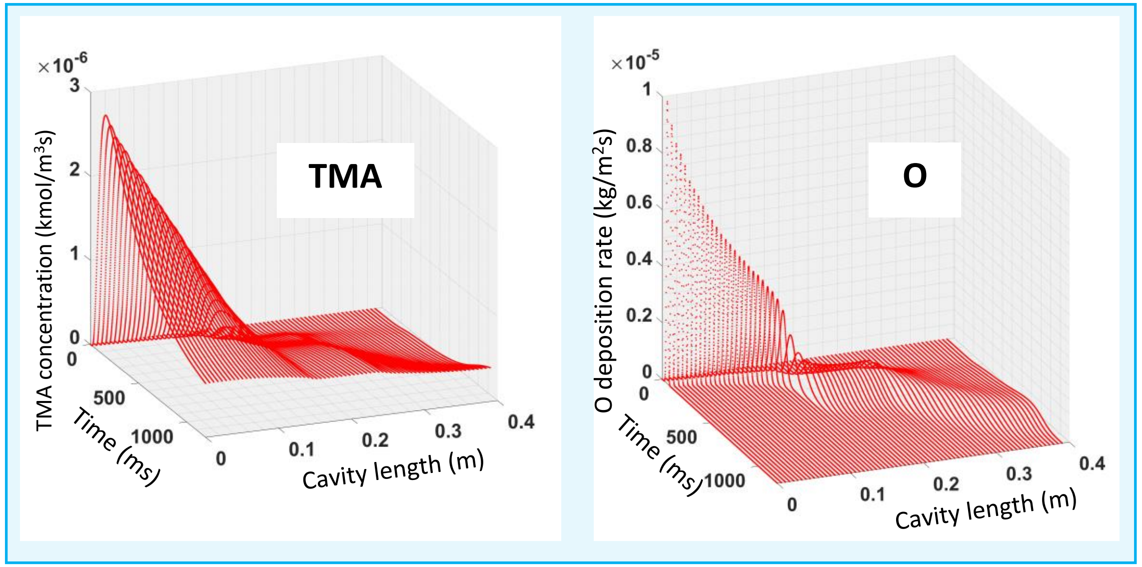
Contour plots



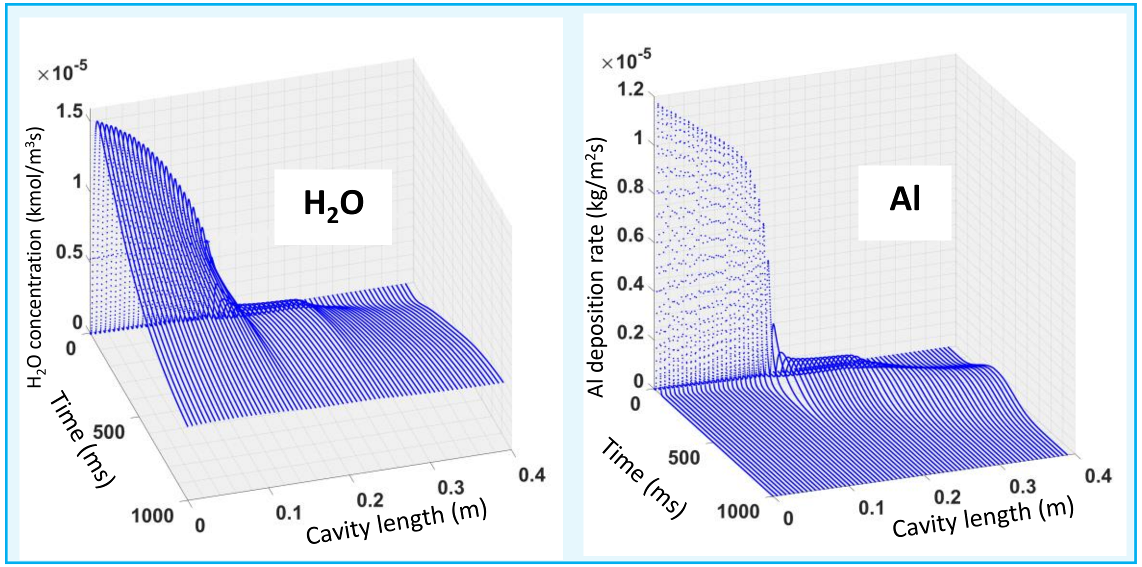
- ❑ Precursors effectively distributed and purged out within a given process time
- ❑ **~1 s of exposure time is enough for effective precursors distribution throughout the cavity**

Surface chemistry simulation shows fast saturation

TMA pulse:



H_2O pulse:



- $2Al(CH_3)_3\ (g) + 3OH^*\ (s) \rightarrow 3O^*Al(CH_3)_2\ (s) + 3CH_4\ (g)$
- $3H_2O\ (g) + O^*Al(CH_3)_2\ (s) \rightarrow 3OH^*\ (s) + 3CH_4\ (g) + Al_2O_3\ (s)$

- The pulse time for both precursors was set at 50 ms, with simulation running until saturation
- **TMA saturated at ~1 s and water at 750 ms**
- residual precursor concentrations required further purging to prevent unwanted deposition

Simulation observations for cavity geometry

- Precursors pulse for 50 ms
- TMA saturation in 1 s, H_2O in 750 ms, showing adequacy of brief exposure times
- **Simulated Al_2O_3 layer thickness ~1.2 Å per cycle**, consistent with standard ALD rates
- Short exposure and effective purging times reduce overall cycle time, ensuring uniform coating without compromising quality

Recipe Al_2O_3 coating @ 120 °C – Cavity volume

	TMA			H_2O			Cycle time /mins.
	Pulse /(ms)	Exposure / (s)	Purge /(s)	Pulse /(ms)	Exposure /(s)	Purge /(s)	
Simulation	50	1	-	50	1	-	-
Experiment *	500	60	120	500	60	120	6.02

- Experimental validation is needed to complement the simulation and ensure accurate, reliable findings

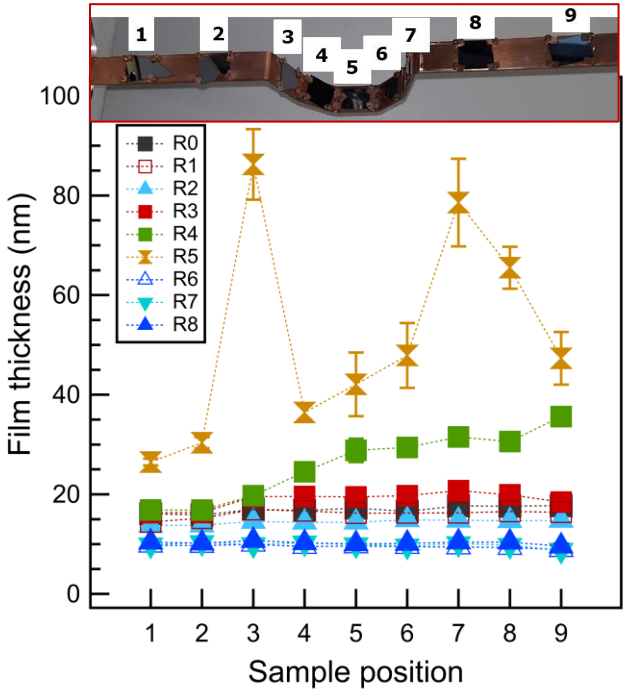
*Wenskat, Marc, Deyu, Getnet Kacha, et al. *Superconductor Science and Technology* 36.1 (2022): 01501, *Deyu, Getnet Kacha, et al. Chemistry of Materials 36.6 (2024): 2846-2856.*

Experiment agree with surface chemistry simulation

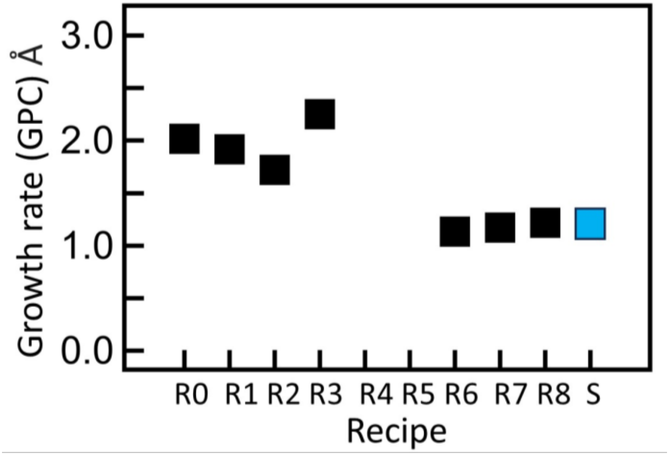
Recipe-cavity volume

	TMA			H_2O			Cycle	Time /hrs.
	Pulse /(ms)	Exposure / (s)	Purge /(s)	Pulse /(ms)	Exposure /(s)	Purge /(s)		
R0*–	500	60	120	500	60	120	84	8.42
R1–	500	30	120	500	30	120	84	7.02
R2–	500	1	120	500	1	120	84	5.40
R3–	500	1	90	500	1	90	84	4.16
R4–	500	1	60	500	1	60	84	2.52
R5–	500	60	30	500	60	30	84	4.13
R6–	50	1	120	50	1	120	84	5.38
R7–	50	1	90	50	1	90	84	4.14
R8–	50	1	60	50	1	60	84	2.50

Film Thickness



Growth Rate



- ❑ Consistent and uniform Al_2O_3 thin-film deposition across the cavity volume
- ❑ **Achieved predicted GPC of 1.2 Å with parameters suggested from simulation**
- ❑ Significant **reduction of up to 66.2% in overall process time**

*Wenskat, Marc, Deyu, Getnet Kacha, et al. *Superconductor Science and Technology* 36.1 (2022): 01501,

Deyu, Getnet Kacha, et al. Chemistry of Materials 36.6 (2024): 2846-2856.

Conclusions

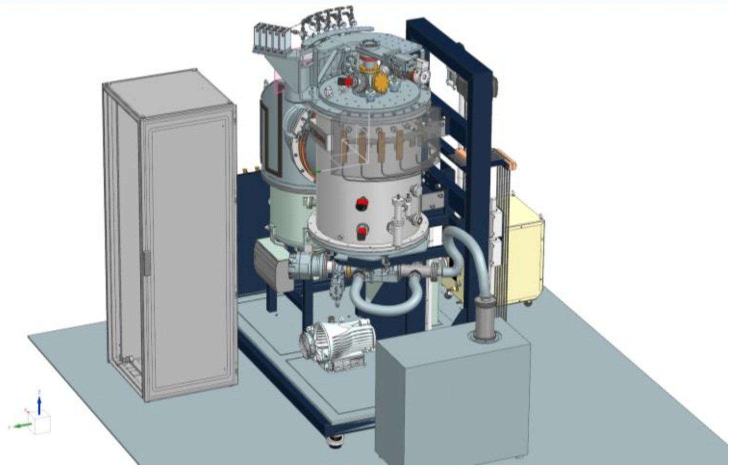
- ❑ **The study explored ALD of Al_2O_3 using both theoretical predictions and experimental verification**
- ❑ **A 3D computational domain was created using ANSYS Fluent software**
- ❑ **TMA and water were used as precursors with varying process parameters**
- ❑ **The precursors saturate at ~1 s, with a calculated GPC of 1.2 Å**
- ❑ **Experimental verification confirmed uniform Al_2O_3 coverage and a GPC of 1.2 Å**
- ❑ **The optimized recipe achieved up to 66.2% process time savings, reducing thermal impacts on the cavity**
- ❑ **The findings are transferable to modeling other important superconducting thin films, SIS structures, processes, and shapes of cavities**

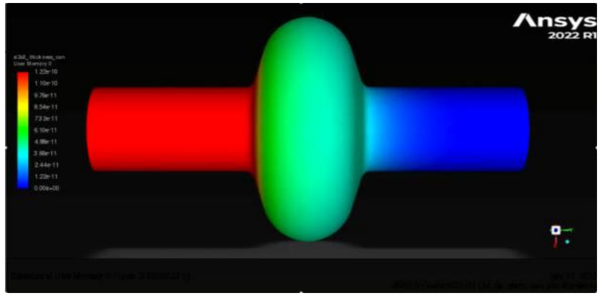
Next steps

- Use this toolbox for faster optimization of the next milestone
  → Simulation of ALD process for SIS structure on the cavity volume

- Face new challenges with new cavity coating boundary conditions*
  - New materials: NbTiN/AlN
  - Other precursors: TBTDEN, TDMAT, TMA and H_2/N_2 radicals
  - Plasma-Enhanced ALD
  - New coating system and vacuum conditions

PEALD





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* González Díaz-Palacio, Isabel, et al. *Journal of Applied Physics* 134.3 (2023).

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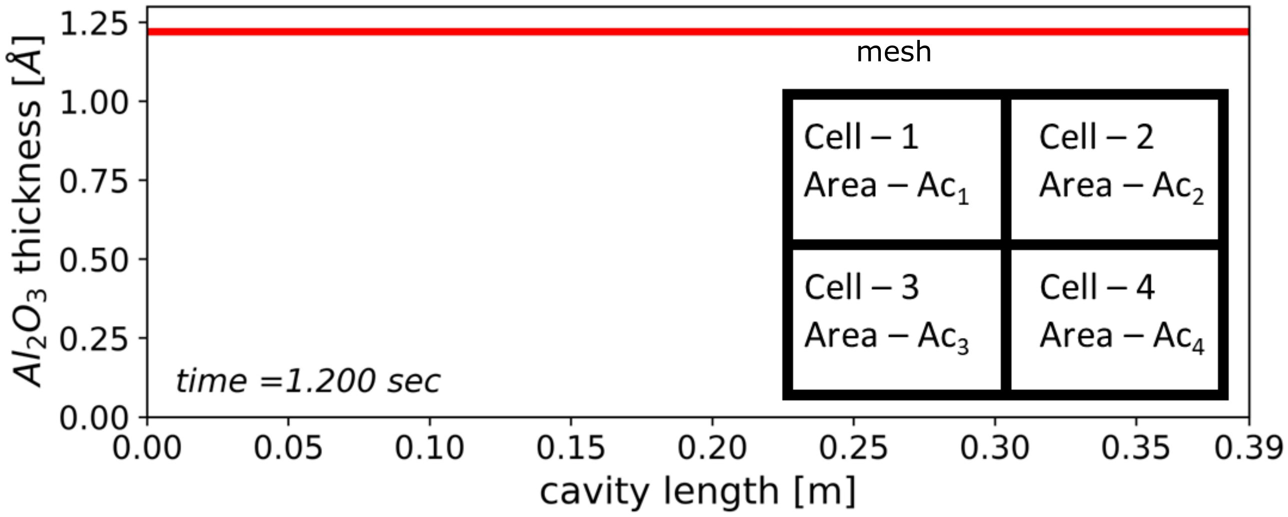
Thank you!

GPC calculation



$$\rho_{Al_2O_3} = 2 \times \sum_{c=1}^{N} \frac{M_{Al}}{AC_1 \times d_{Al}} + 3 \times \sum_{c=1}^{N} \frac{M_O}{AC_1 \times d_O}$$

$$M_O = D_O \times AC_1 \times t_O$$

where $M_{Al} = D_{Al} \times AC_1 \times t_{Al}$, $\rho Al_2O_3 = 3500\ kg/m^3$

- ❑ GPC of 1.2 Å, which aligned with typical ALD values

Recipe optimization – cavity volume

Dummy Cavity

- ❑ Temp=120 °C, N_2 – 20 SCCM

Recipe-cavity volume								
	TMA			H_2O			Cycle	Time /hrs.
	Pulse /(ms)	Exposure / (s)	Purge /(s)	Pulse /(ms)	Exposure /(s)	Purge /(s)		
R0* —	500	60	120	500	60	120	84	8.42
R1—	500	30	120	500	30	120	84	7.02
R2—	500	1	120	500	1	120	84	5.40
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R6—	50	1	120	50	1	120	84	5.38
R7—	50	1	90	50	1	90	84	4.14
R8—	50	1	60	50	1	60	84	2.50

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[*] Wenskat, Marc, et al. *Superconductor Science and Technology* 36.1 (2022): 01501, *Deyu, Getnet Kacha, et al. Chemistry of Materials 36.6 (2024): 2846-2856.*

ALD process modeling in ANSYS fluent

❑ Simulating ALD-Al_2O_3 in a thin film chamber and single-cell SRF cavity

Process breakdown

- Species transport
- Materials flow
- Surface reactions
- System heating

Surface reaction mechanism

TMA Pulse: $2Al(CH_3)_3\ (g) + 3OH^*\ (s) \rightarrow 3O^*Al(CH_3)_2\ (s) + 3CH_4\ (g)$

H_2O Pulse: $3H_2O\ (g) + O^*Al(CH_3)_2\ (s) \rightarrow 3OH^*\ (s) + 3CH_4\ (g) + Al_2O_3\ (s)$

PDEs

- Mass transfer (species transport)
- Surface reactions (chemisorption)
- Momentum transport (material flow)
- Heat transfer (system heating)

Finite Volume Method (FVM)

- Solve the defined PDEs

Coupling

- Couple PDEs to create a comprehensive simulation of the ALD cycle

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Simulation boundary conditions

Boundary Condition		Type	Value	Time	
Inlet	N_2	Mass flow inlet	20 SCCM	Continuous	
	TMA	Pressure inlet– P° at 25 °C	1257.23 Pa	50 ms pulse	
	H_2O	Pressure inlet– P° at 25 °C	3157.07 Pa	50 ms pulse	
Outlet	N_2	Base pressure	80 Pa	Continuous	
	TMA	Pressure outlet	Process dependent	Periodic behavior	
				Pulse -50ms	OFF
				Exposure-12 s	OFF
				Purge-40 s	ON
	H_2O			Pulse -50ms	OFF
				Exposure-12 s	OFF
				Purge-60 s	ON
Surface site density		-OH*	5/nm^2	Fixed	
Process Temp.		Chamber/cavity wall	120 °C	Continuous	
		Inlet feed pipes	75 °C	Continuous	

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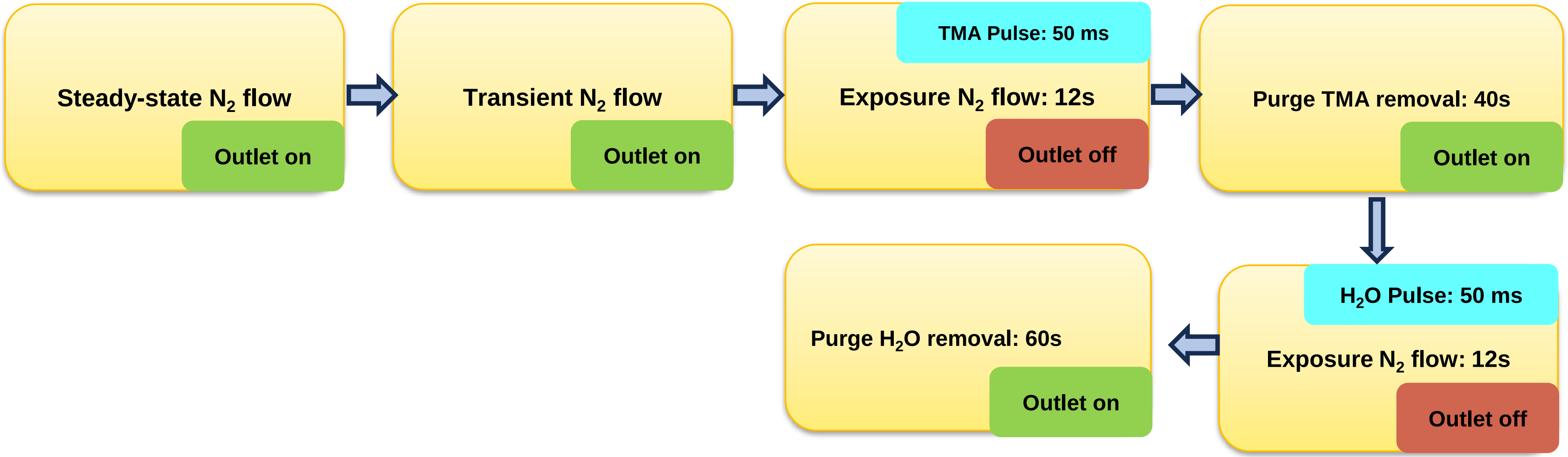
Simulation flow chart



Steady-state N_2 flow

Outlet on

Transient N_2 flow

Outlet on

TMA Pulse: 50 ms

Exposure N_2 flow: 12s

Outlet off

Purge TMA removal: 40s

Outlet on

H_2O Pulse: 50 ms

Exposure N_2 flow: 12s

Outlet off

Purge H_2O removal: 60s

Outlet on

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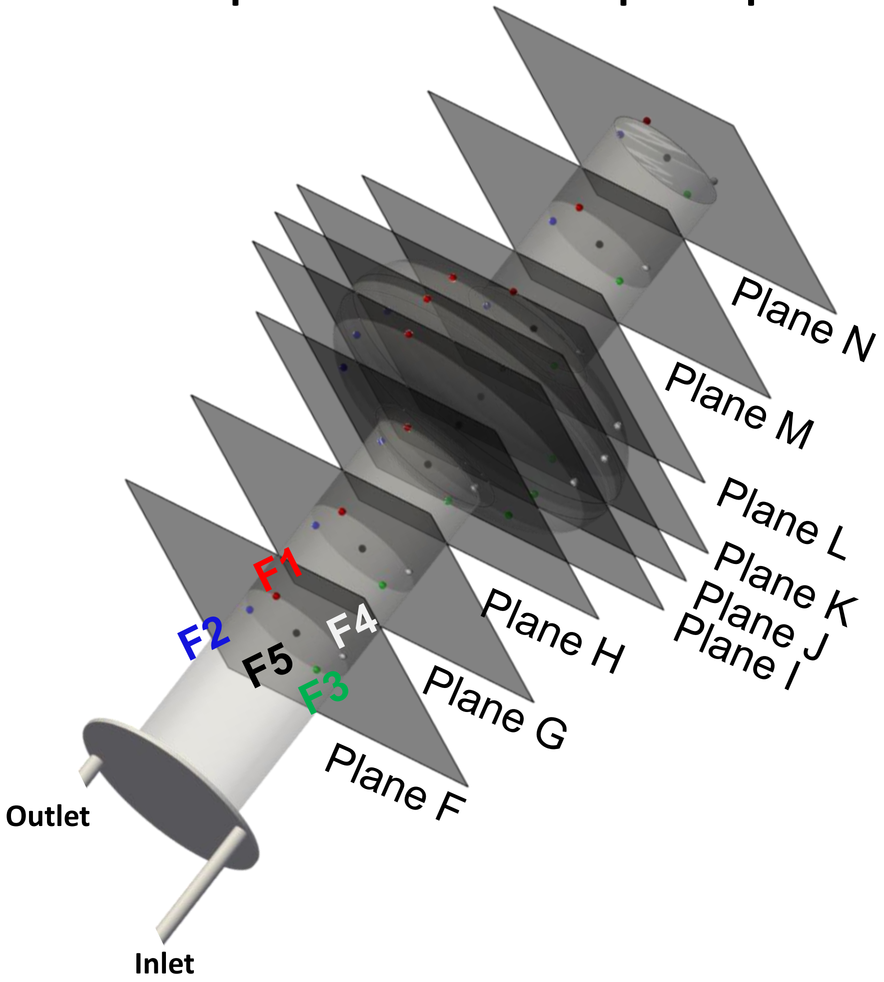
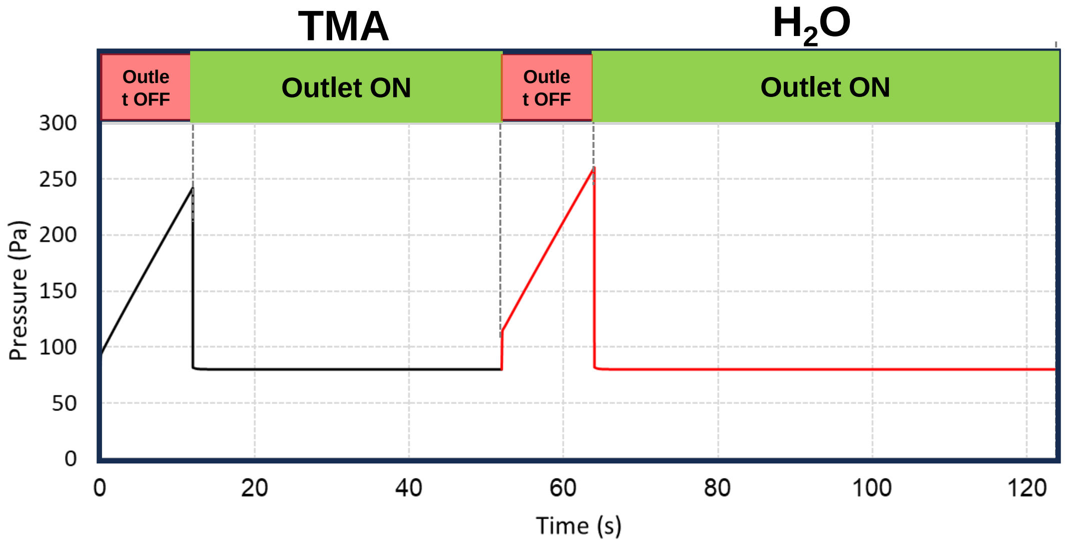
Precursors distribution-cavity volume

3D Computational Domain-probe points



Pressure Profile



- ❑ Boundary conditions:
  - ❑ Same as thin films chamber

Chemisorption reactions of ALD Al2O3

$$\|\text{–OH} + \text{Al(CH}_3)_3 \rightarrow \|\text{–O–Al(CH}_3)_2 + \text{CH}_4 \qquad (1a)$$

$$\|\text{–OH} + \|\text{–O–Al(CH}_3)_2 \rightarrow (\|\text{–O})_2\text{–Al(CH}_3) + \text{CH}_4 \qquad (1b)$$

$$\|\text{–OH} + (\|\text{–O})_2\text{–Al(CH}_3) \rightarrow (\|\text{–O})_3\text{–Al} + \text{CH}_4 \qquad (1c)$$

$$\|\text{–O–Al(CH}_3)_2 + \text{H}_2\text{O} \rightarrow \|\text{–O–Al(CH}_3)\text{OH} + \text{CH}_4 \qquad (2a)$$

$$\|\text{–O–Al(CH}_3)\text{OH} + \text{H}_2\text{O} \rightarrow \|\text{–O–Al(OH)}_2 + \text{CH}_4 \qquad (2b)$$

$$(\|\text{–O})_2\text{–Al(CH}_3) + \text{H}_2\text{O} \rightarrow (\|\text{–O})_2\text{–Al(OH)} + \text{CH}_4 \qquad (2c)$$

Activation energy - Ea

(1a) ? 0.35 eV

(1b) ? 0.72 eV

(1c) ? 1.05 eV

(2a) ? 0.44 eV

(2b) ? 0.67 eV

(2c) ? 0.26 eV

Limitations of simulation work

Simulation	**Aspect**	**Actual ALD Process**
Fixed	**Surface Site Densities**	Involve varying site densities
Constant	**Temperature**	May vary affecting reaction kinetics and film growth
Does not account	**Impurities and Contaminants**	Presence of impurities can impact surface reactions and film quality
Does not account	**Precursor Quality Variability**	Precursor purity and consistency can vary, affecting the outcome
Does not consider	**Surface Roughness**	Influences precursor adsorption and film deposition uniformity
Constant	**Sticking Probability**	Varies with surface conditions and temperature
Does not consider	**Long-Term Effects**	Critical for predicting the durability and performance of the coating

- These limitations highlight the need for experimental validation to complement the simulation results and ensure the accuracy and reliability of the findings.