

Atmospheric Plasma for Surface Modification and Nanoscale Embedding of Chemistry

Project WP-2742

Santanu Chaudhuri
University of Illinois at Chicago

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14. ABSTRACT The technical objective of this project is to develop an atmospheric plasma based, scalable solution for a single-pass process that can clean, modify, and deposit a thin gradient coating on aluminum alloys with nanoscale control of morphology for optimum control of bonding, adhesion and corrosion performance.					
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Project Team



University of Illinois at Chicago

Prof. Santanu Chaudhuri

Arash Samaei

Dr. Pikee Priya

Starfire Industries

Dr. Brian Jurczyk

University of Illinois at Urbana-Champaign

CPMI

Prof. David Ruzic

Dhruval Patel

Dr. Lucia Bonova

Nirbhav Chopra

Weikun Zhu

Zachary Jeckell

Dr. Chisung Ahn

ARI

Dr. Dan Krogstad

Dr. Joe Osborne

MatSE

Prof. Jessica Krogstad

Project supported three graduate students, two undergraduate researchers, three postdoctoral fellow, two research engineers, and three faculty members

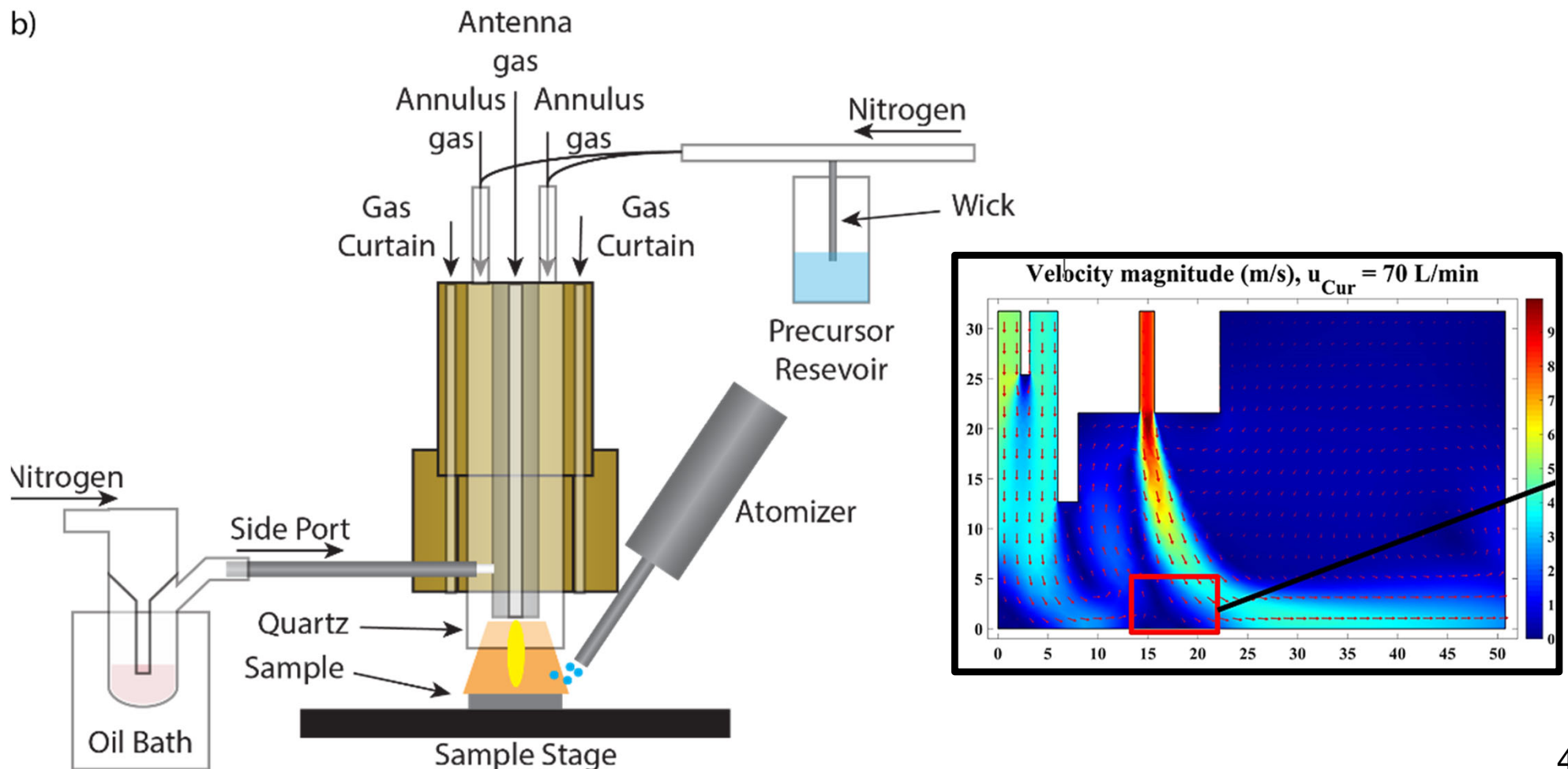
Background

- Funding approved 05/2017 and project started in 10/2017
- **WPSON-17-03:** Surface morphology modification by non-chemical methods to enhance coating adhesion and mechanical bonding on metal surfaces
 - ◆ Proposed technologies must maintain paint adhesion and mechanical bonding durability as well as improve the corrosion resistance of the target substrate material
 - ◆ Proposed treatment process should be a single-step process that does not require any chemical processing or treatments
 - ◆ Surface treatments for coating adhesion applications must meet the adhesion and long-term corrosion requirements of the total coating
 - ◆ Developing an understanding of the physical mechanisms to improve adhesion and corrosion protection by altering the surface structure and morphology is necessary to effectively transition non-chemical methods
- **Expected Benefits of Proposed Work:** Reduce the environmental impact of chemical surface treatments used in the manufacture and maintenance of DoD weapons systems

Technical Objective

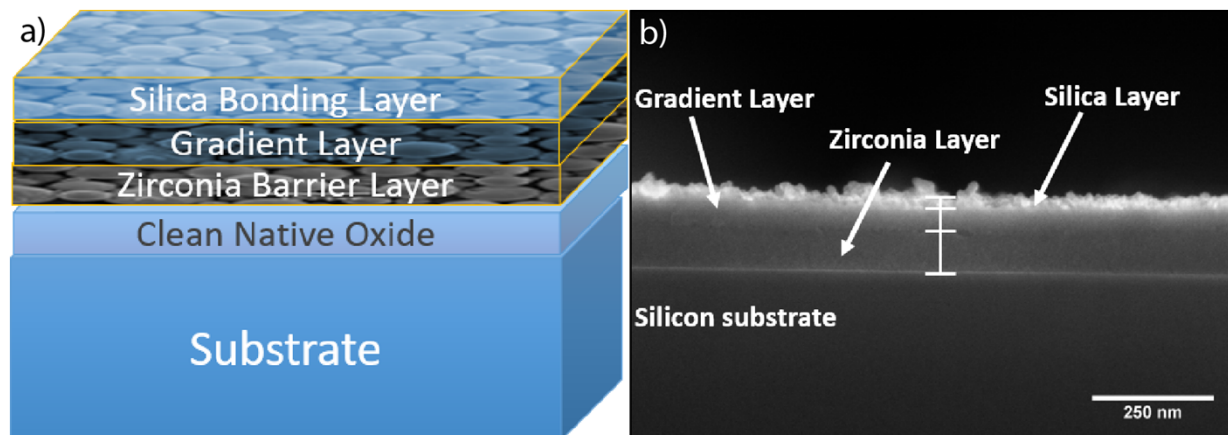
Develop an **atmospheric plasma based, scalable solution** for a single-pass process that can clean, modify, and deposit a thin gradient coating on aluminum alloys with **nanoscale control of morphology** for optimum **control of bonding, adhesion and corrosion performance**.

b)



Technical Approach

- **Combined experimental-computational approach to decrease the developmental cycle**
 - ◆ Identify viable processing windows using experiments
 - ◆ Develop models and simulate the effects of these processing parameters on the AP effectiveness
 - ◆ Validate the results with experiments
- **The Zirconia-Silica Gradient Coating**
 - ◆ Zirconium oxide coatings provide a water barrier and provide corrosion protection
 - ◆ Silica coatings provide improved adhesion of the paint to the zirconia coatings
 - ◆ Gradient provides a better management of stress

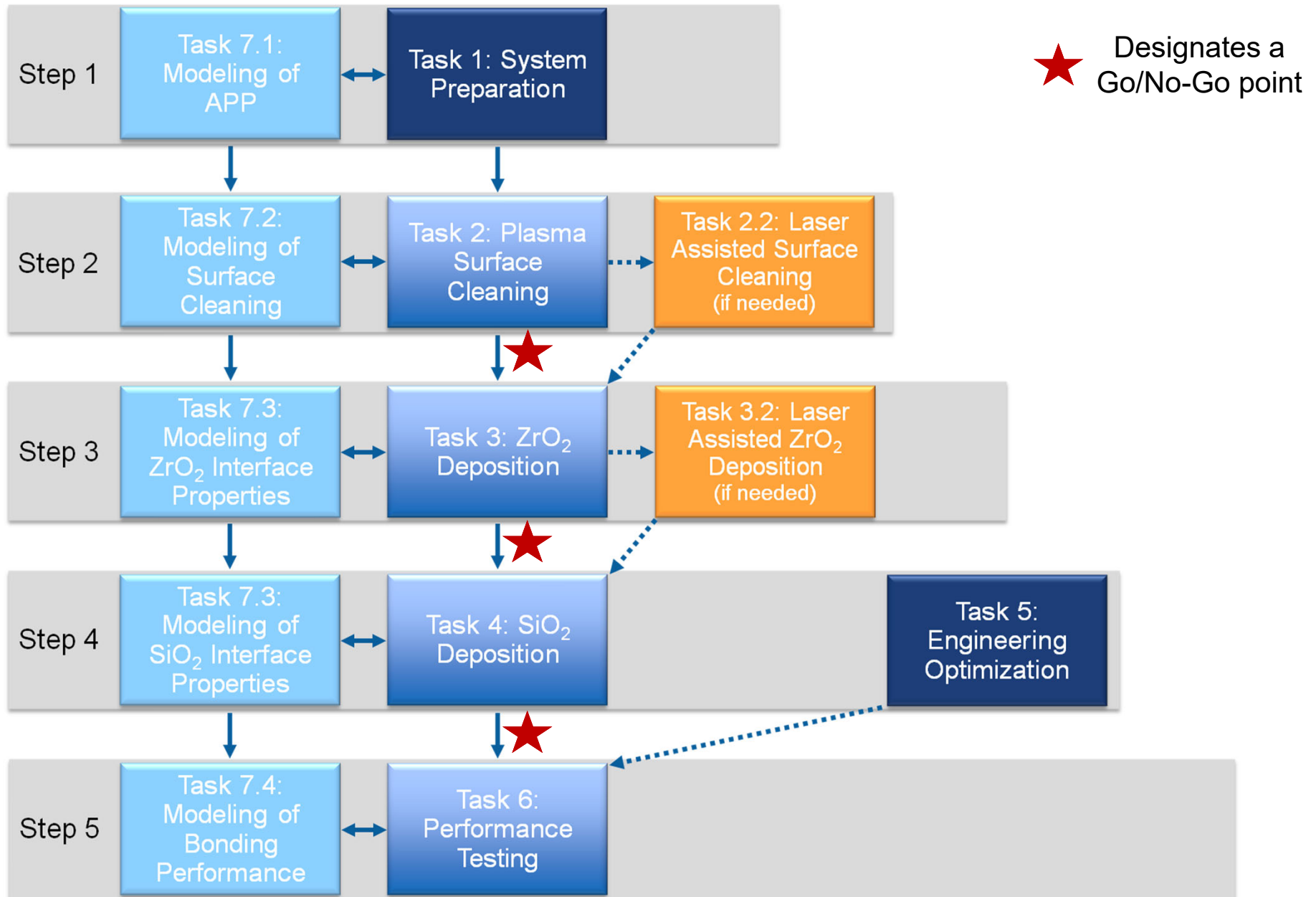


Overall Project Plan

Tasks	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1: System preparation												
Task 1.1 Substrate design with moving stage												
Task 1.2: Laser integration to enable LAPCAP method												
Task 2: Cleaning and Activation												
Task 2.1: Standalone ECAP process												
Task 2.2: Standalone laser process (Optional)												
Task 2.3: Combination of laser and ECAP (Optional)												
Task 2.4: Verification and qualification tests												
Task 3: Optimization of the Al₂O₃-ZrO₂ layer												
Task 3.1: Microwave or Laser-assisted Surface texturing												
Task 3.2: Characterize substrate after surface texturing												
Task 3.3: Volatile precursor mediated ZrO ₂ deposition												
Task 3.4: Laser-assisted ZrO ₂ deposition												
Task 3.5: Interface characterization												
Task 4: ZrO₂ and SiO₂ co-deposition												
Task 4.1: SiO ₂ on alumina												
Task 4.2: Deposition of SiO ₂ on Al-ZrO ₂ substrate												
Task 4.3: Development of ZrO ₂ -SiO ₂ -organosilane layers												
Task 4.4: Interface characterization												
Task 5: Engineering Optimization and CGCAP system integration												
Task 5.1: Integration of dual deposition source and modification												
Task 5.2: Optimization for gradient coating development												
Task 5.3: Characterization of gradient coatings												
Task 6: Performance testing												
Task 6.1: Performance testing: corrosion protection												
Task 6.2: Performance testing for the painted coupons												
Task 7: Multiscale modeling of CGCAP												
Task 7.1: Multiphysics model of atmospheric plasma system												
Task 7.2: Chemistry model for plasma and plasma-surface reaction												
Task 7.3: Mesoscale and FEA model of coating-substrate interfa												
Task 7.4: Bonding performance model of the CGCAP layers												
Task 8: Program Management and Tech Transfer												
Task 8.1: Reporting, coordination and dissemination												
Task 8.2: Scalability, manufacturing cost and tech transfer study												



Technical Approach: Outline and Steps

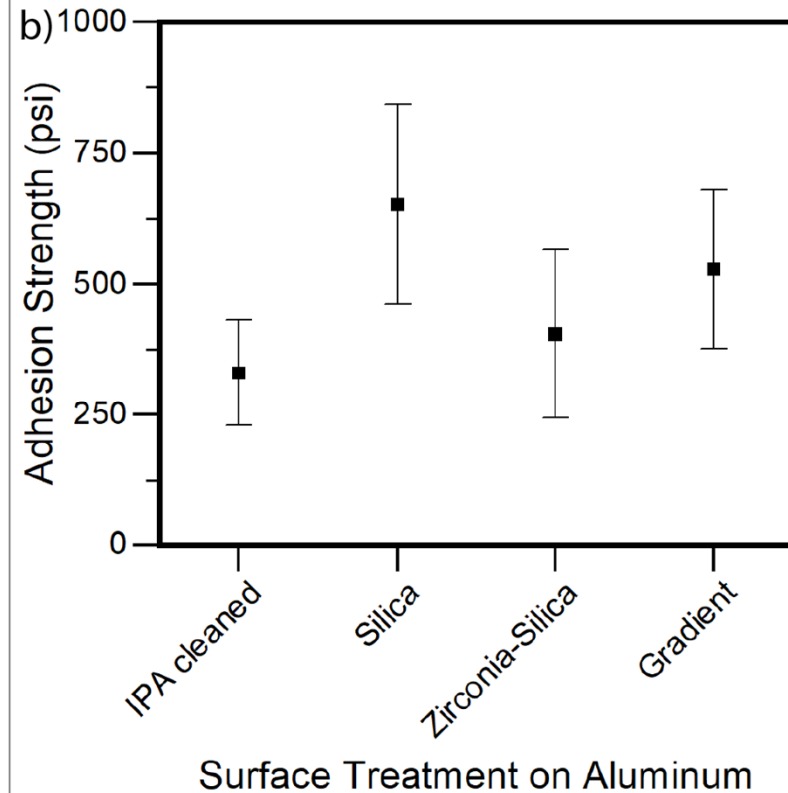
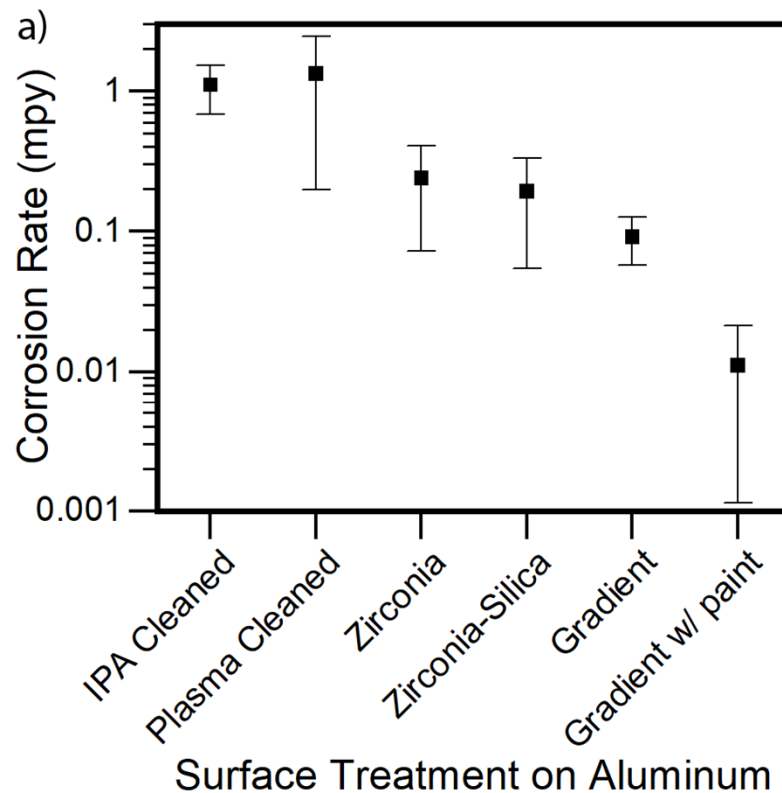


Overview of the Work

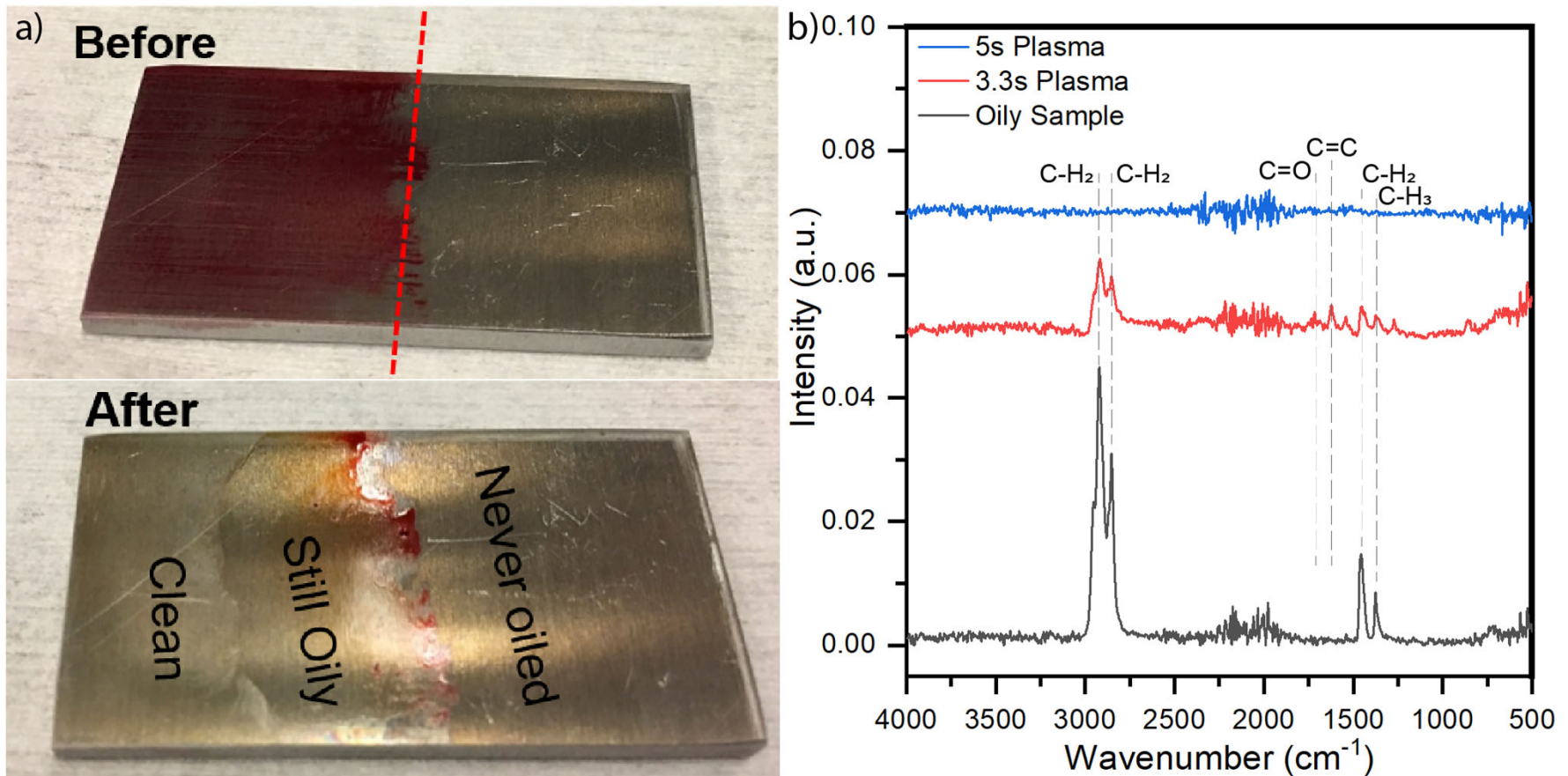
- **APP surface cleaning** – A successful and clean process
- **Modeling of the cleaning process** – Optimization for efficiency
- **Development of Zirconia Coating** – Precursors are key
- **Development of Silica Coating** – Porosity control is key
- **Development of gradient Aluminum/Zirconia/Silica coatings**

Results

- Developed chemical waste-free Al substrate cleaning and gradient coatings deposition method with APP
- The results show improvement of adhesion and corrosion resistance



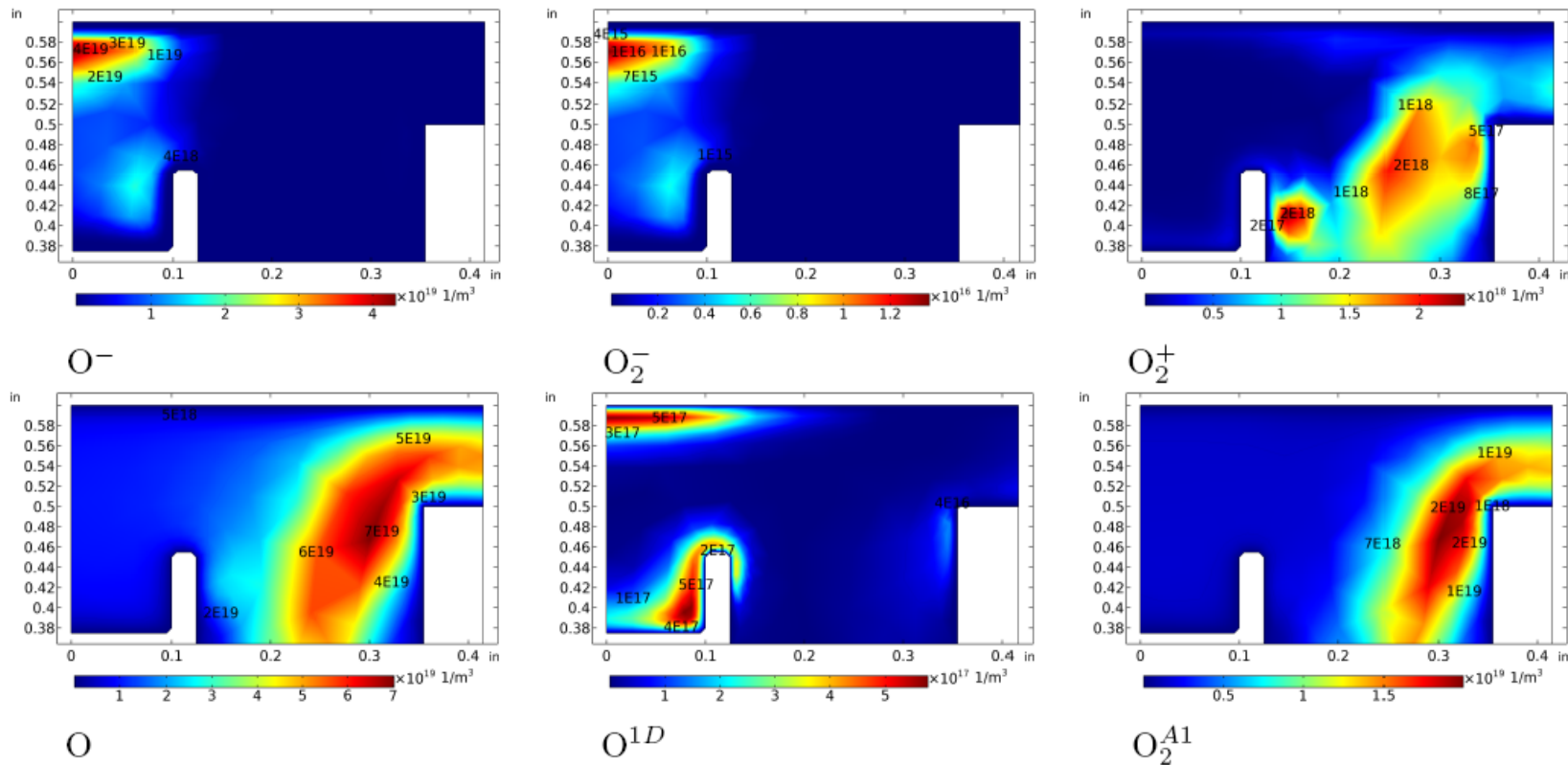
Step-1: Surface Cleaning



- APP cleaning of a thick layer of oil (with red dye) before and after plasma cleaning during a single pass at 600 W 20 L/min air and a speed of 0.83 mm/s.
- ATR-FTIR spectrum of oil cleaned samples showing that the plasma fully cleans the sample within 5 s (5 mm/s).

Optimizations: APP chemistry

- A full coupling of gas-phase plasma chemistry and contaminant removal kinetics⁽¹⁾ is powerful for optimization of plasma source and chemistry for surface cleaning

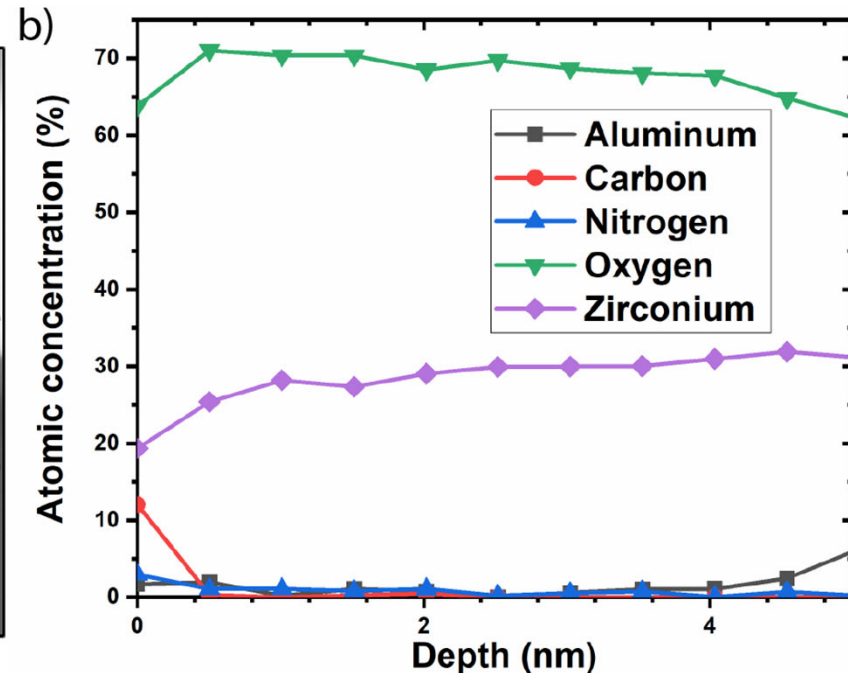
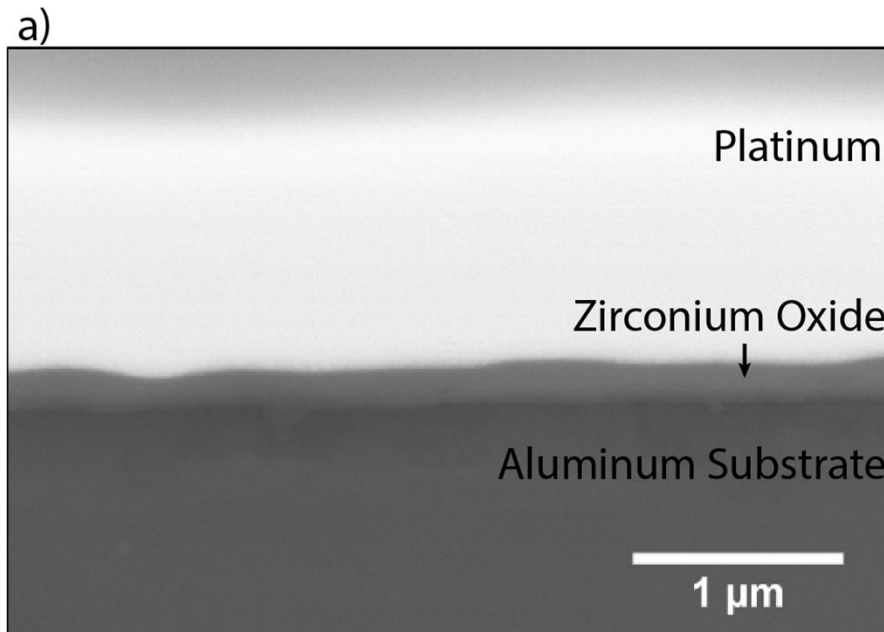


(1) Samaei A, Chaudhuri S. Multiphysics modeling of metal surface cleaning using atmospheric pressure plasma. *Journal of Applied Physics*. 2020;128(5):054903.

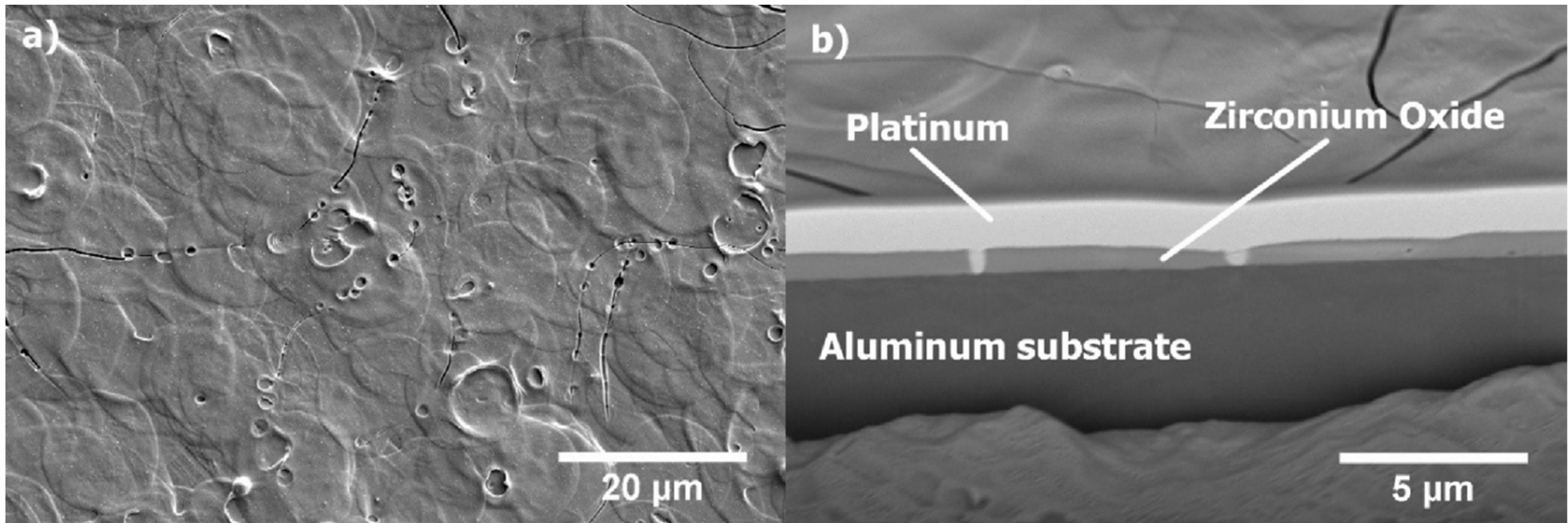
<https://doi.org/10.1063/5.0011769>

Step-2: ZrO₂ Deposition

- AP processing has been used as a chemical waste-free process to deposit zirconium oxide coatings on aluminum
- The coating produced at a thickness of ~115 nm were able to pass a scratch test, based on ASTM C1624
- A multiphysics model that incorporates heat transfer, plasma chemistry, gas-phase and surface-chemistry reactions has been developed

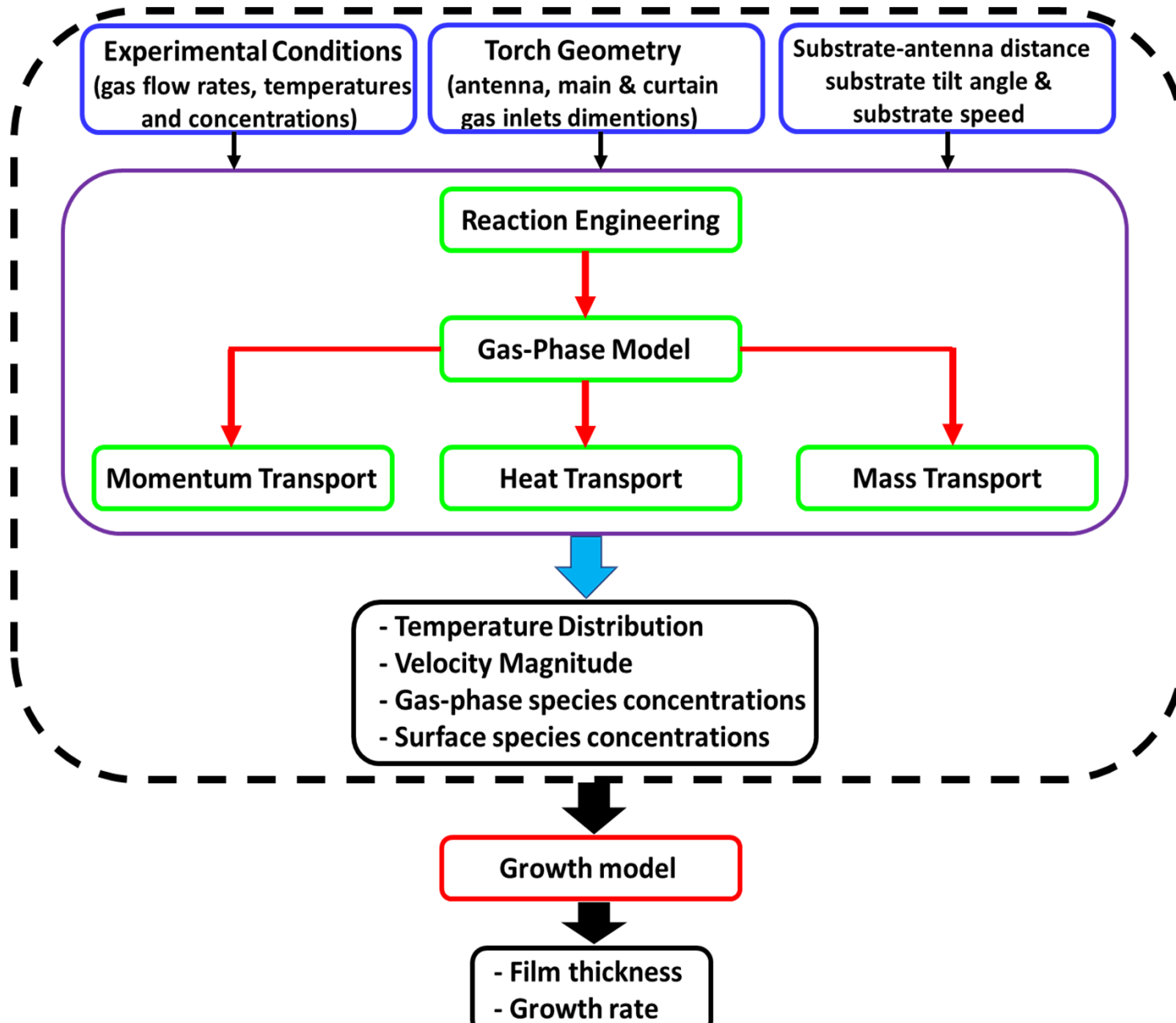


Step-2: ZrO₂ Deposition



SEM and cross-section of coatings deposited from aerosolized ZrO(NO)₃ solution.

Step-2: Multiphysics Modeling of ZrO_2 Deposition

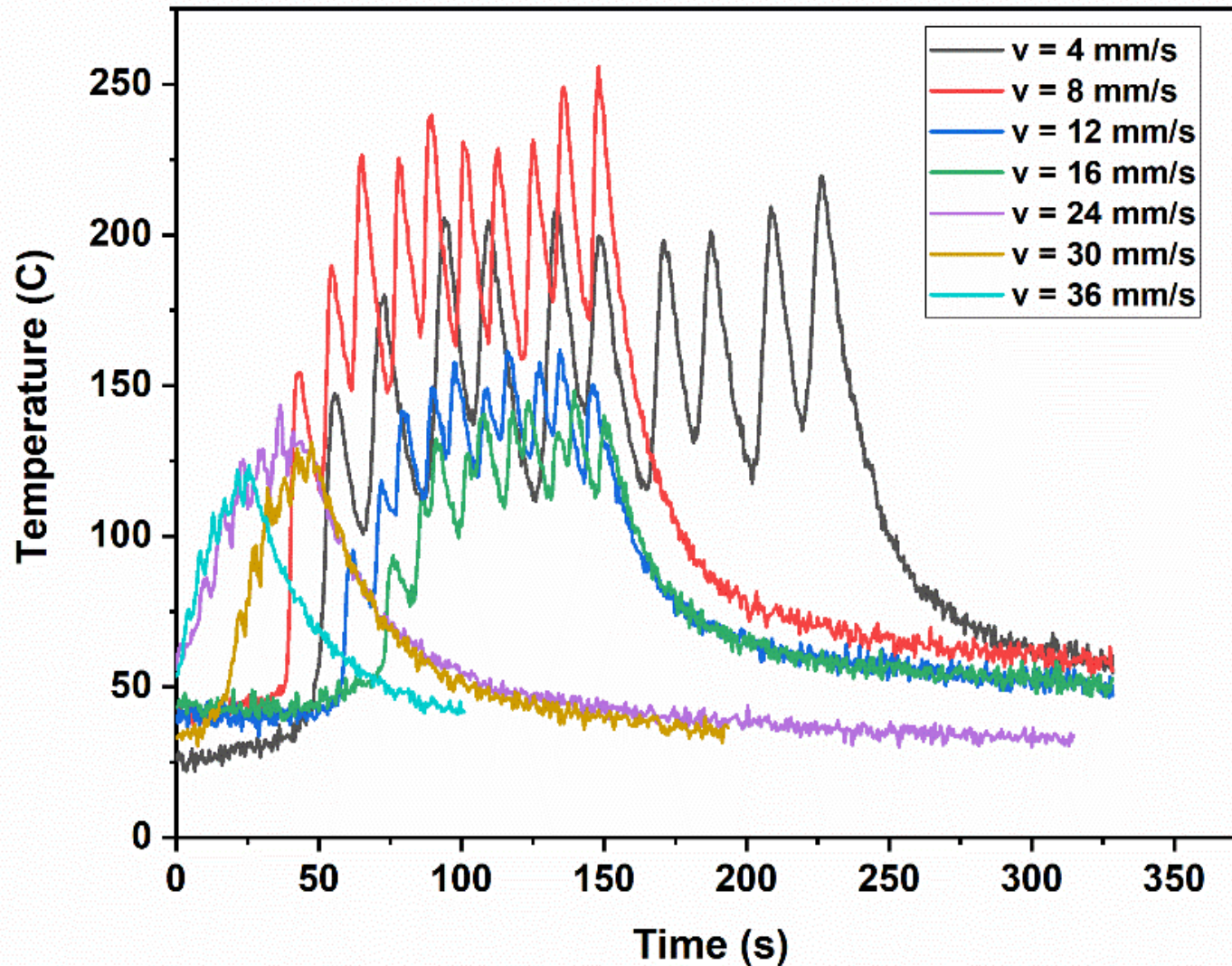


Step-2: Corrosion rate measurements

Corrosion data from the linear polarization resistance experiments for select aluminum and zirconia coated aluminum samples

Sample	E _{corr} (V)	I _{corr} (μA)	Corrosion Rate (mpy)
Aluminum	-0.773	33.84	1.108
Plasma Cleaned	-0.789	40.65	1.331
600 W, 0.25 M ZrO(NO ₃) ₂	-1.033	8.53	0.279
1000 W, 0.25 M ZrO(NO ₃) ₂	-0.972	7.34	0.241
600 W, 0.5 M ZrO(NO ₃) ₂	-0.788	23.86	0.781
1000 W, 0.5 M ZrO(NO ₃) ₂	-0.885	32.89	1.077

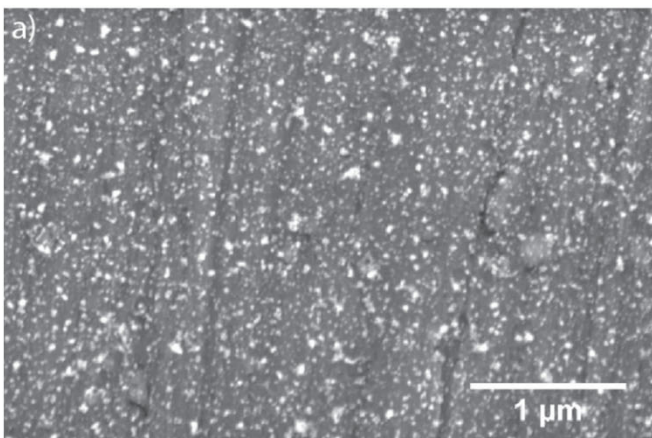
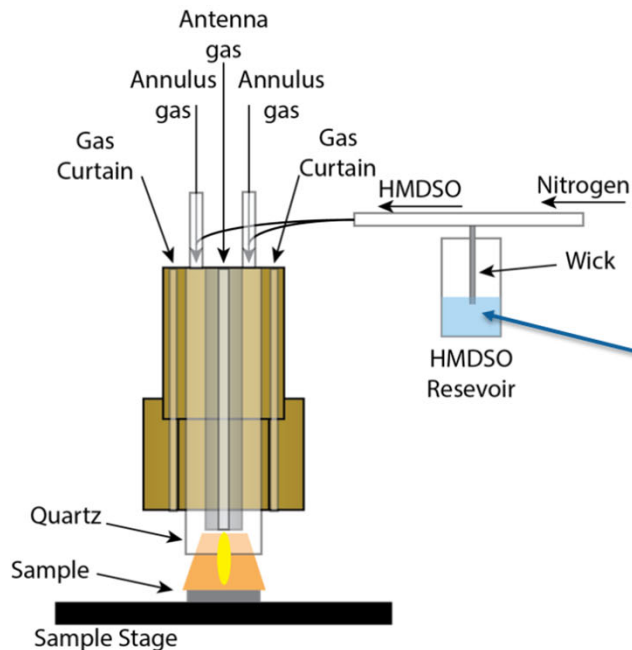
Step-2: Temperature change during ZrO₂ Deposition



Step-3: Task 4 and 7 - Silica Deposition

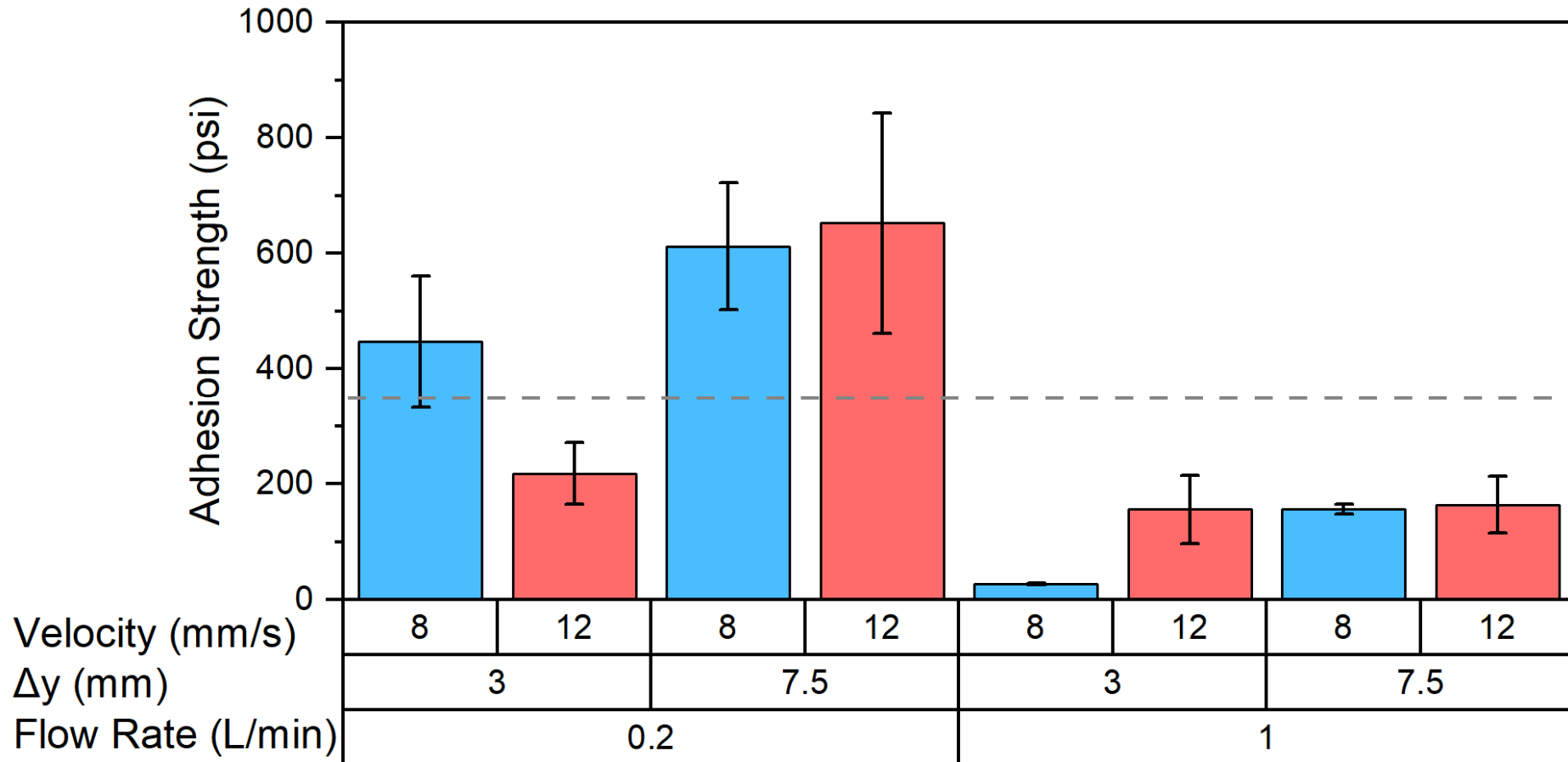
- AP processing has been used to deposit silicon oxide coatings on aluminum
- The effects of the microwave power, the gas composition, the silicon precursor containing gas flow rates and the number of coating passes were explored
- Silica coatings can be produced ranging from ~ 40 to 200 nm
- The multiphysics model was adapted to include the silicon precursor chemistry

Step-3: Silica Deposition



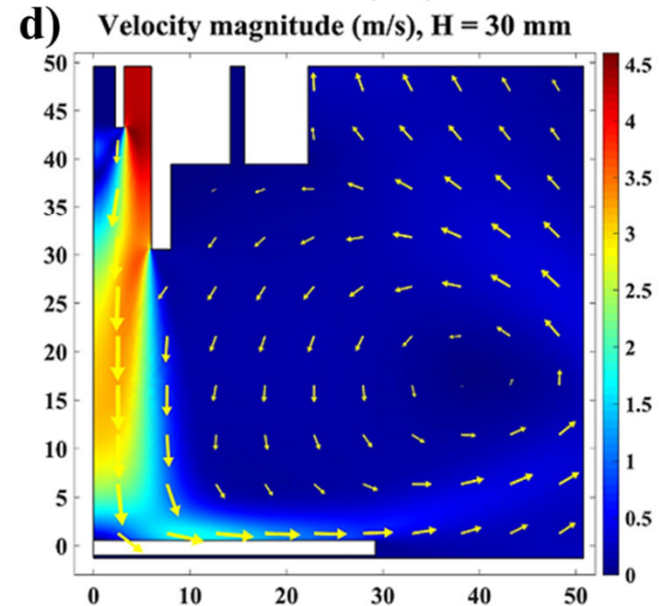
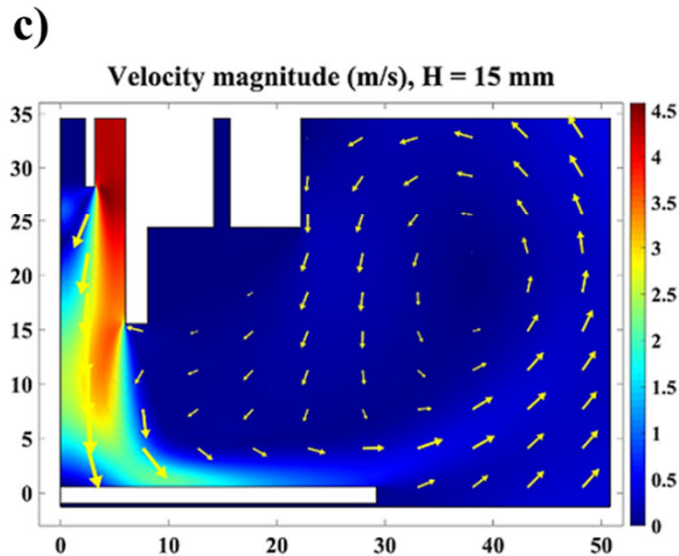
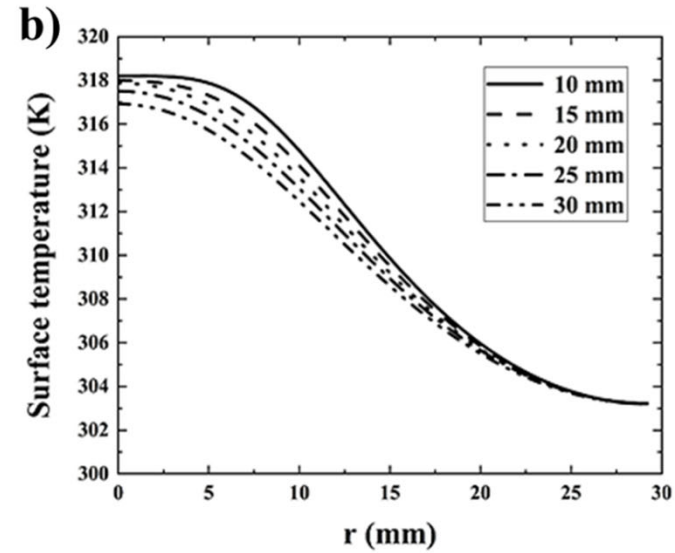
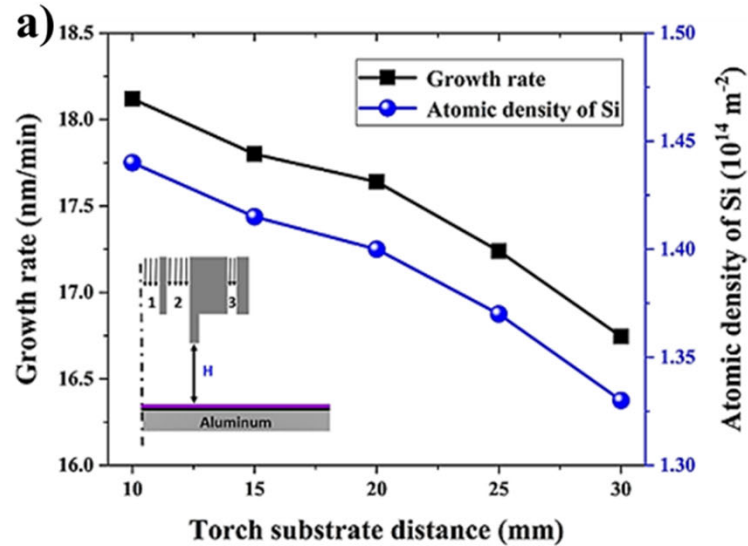
SEM and b) FIB images of the silica coated samples produced from 800 W, 17/4 L/min N₂/Ar, 0.03 mL/min HMDSO, 2 cm deposition height and a speed of 4 mm/s.

Step-3: Silica Surface - Adhesion Test

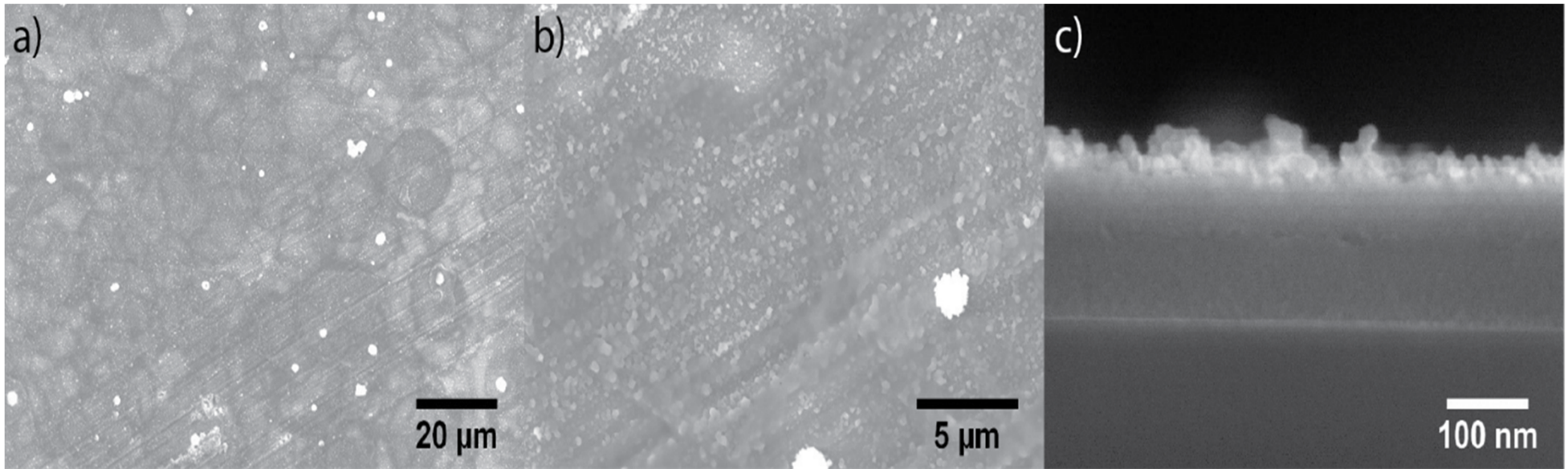


Results from pull-off adhesion tests using epoxy primer on silica-coated aluminum. All samples were deposited with TEOS that was delivered through the antenna. The dashed gray line represent the results from the chemically cleaned bare aluminum control.

Step-3: Silica Surface – Modeling Growth

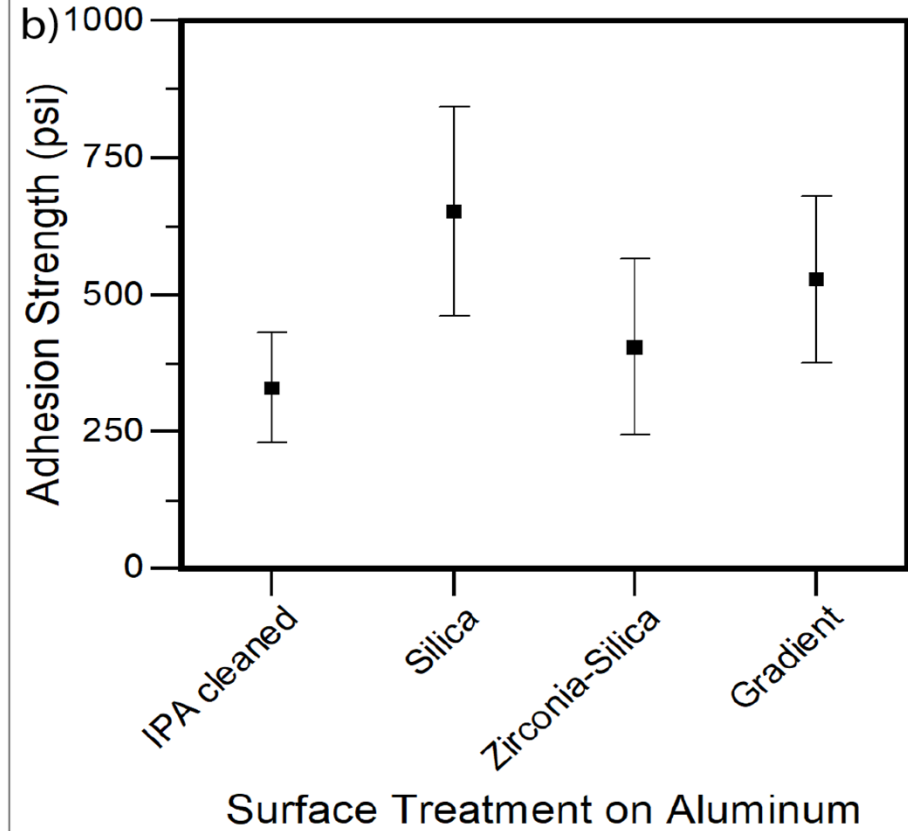
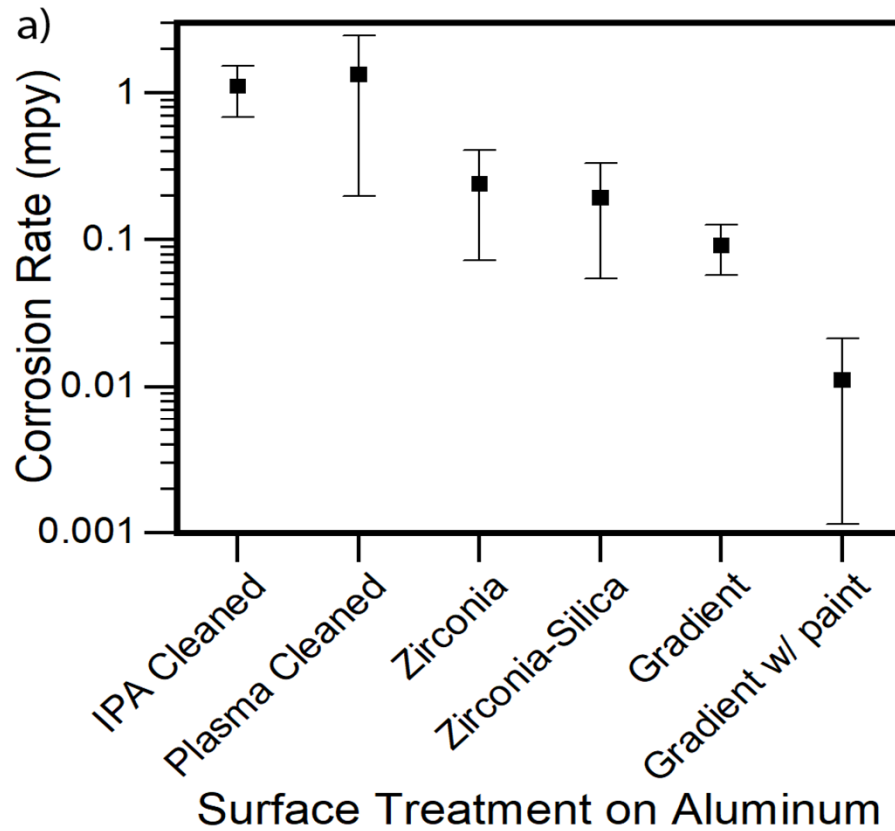


Step-4: Gradient Coatings



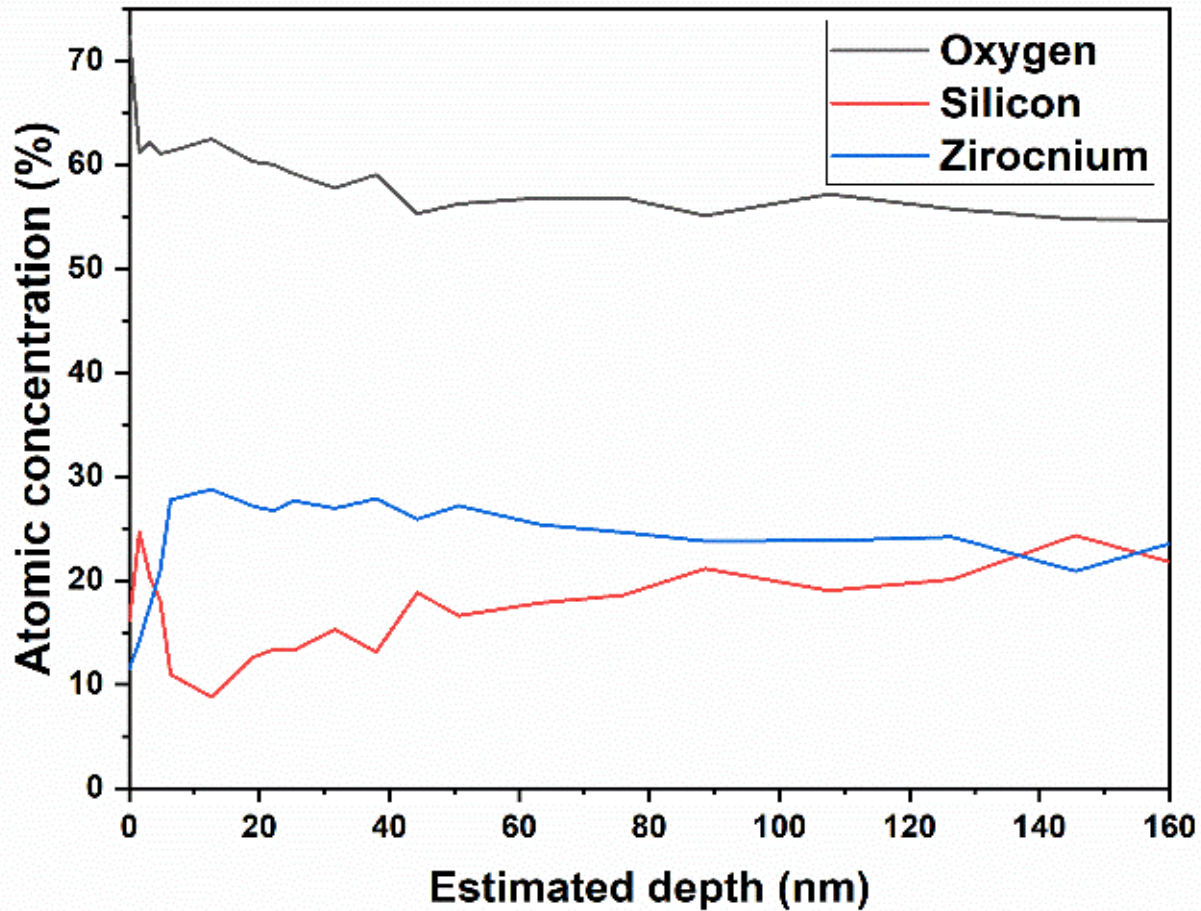
The a,b) surface and c) cross-section micrographs of the gradient coatings were collected using SEM. The surface micrographs shown were collected on coated aluminum samples using a) 1000x and b) 5000x magnification. c) The cross-section micrographs are of cleaved silicon wafer with a gradient coat were obtained using 200kx magnification.

Results – Corrosion of Samples with Gradient Coatings



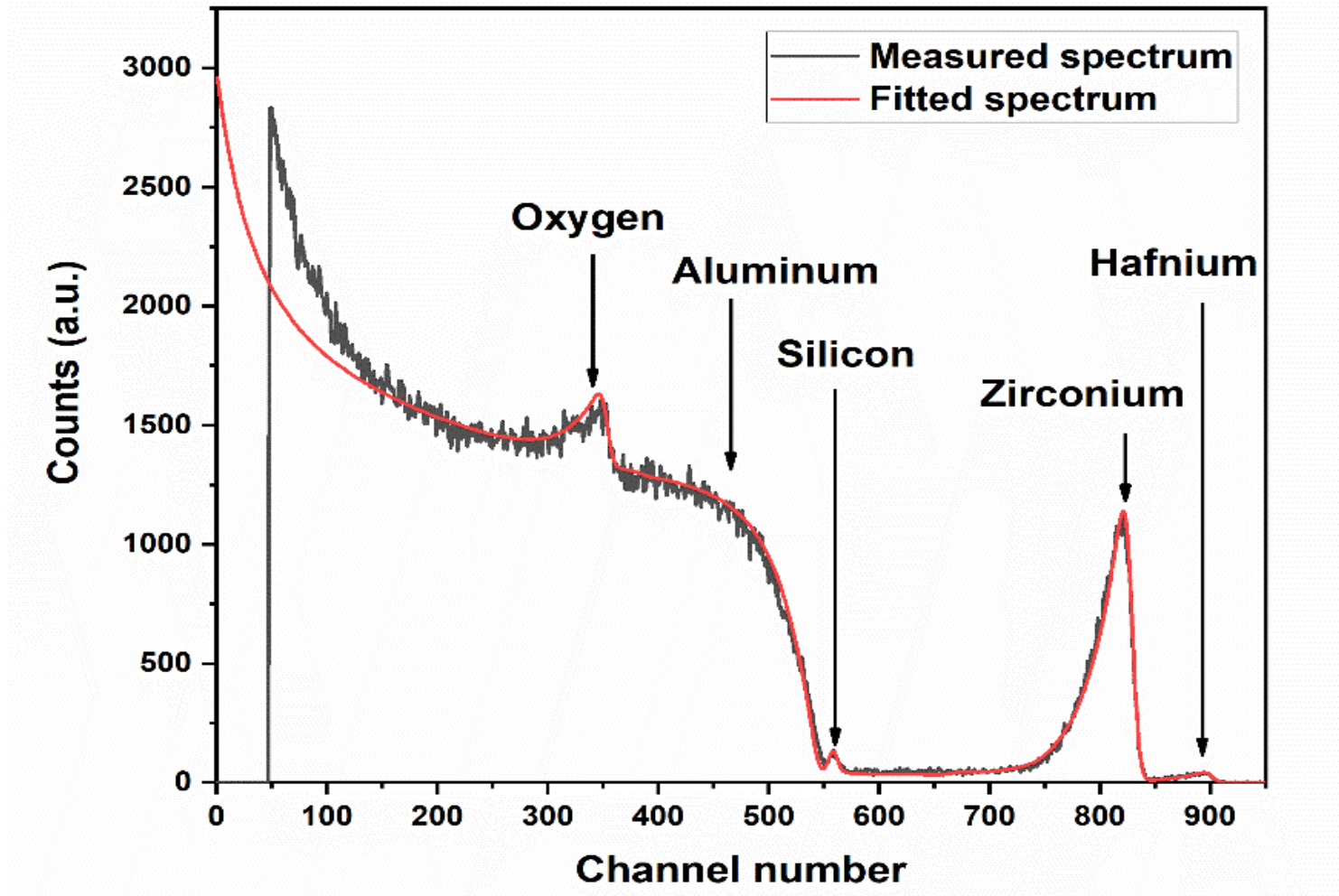
Shown here: (a) Corrosion rates measured by linear polarization of the cleaned, coated and coated/painted samples. (b) Adhesion strength measured by pull-off adhesion testing of the cleaned and coated aluminum samples using an epoxy primer.

Results – Gradient Coatings



XPS results showing top Silica and bottom zirconia layers

Results – Gradient Coatings



RBS data confirming the integration of corrosion control capabilities by introducing Hf into the zirconia layer as impurity

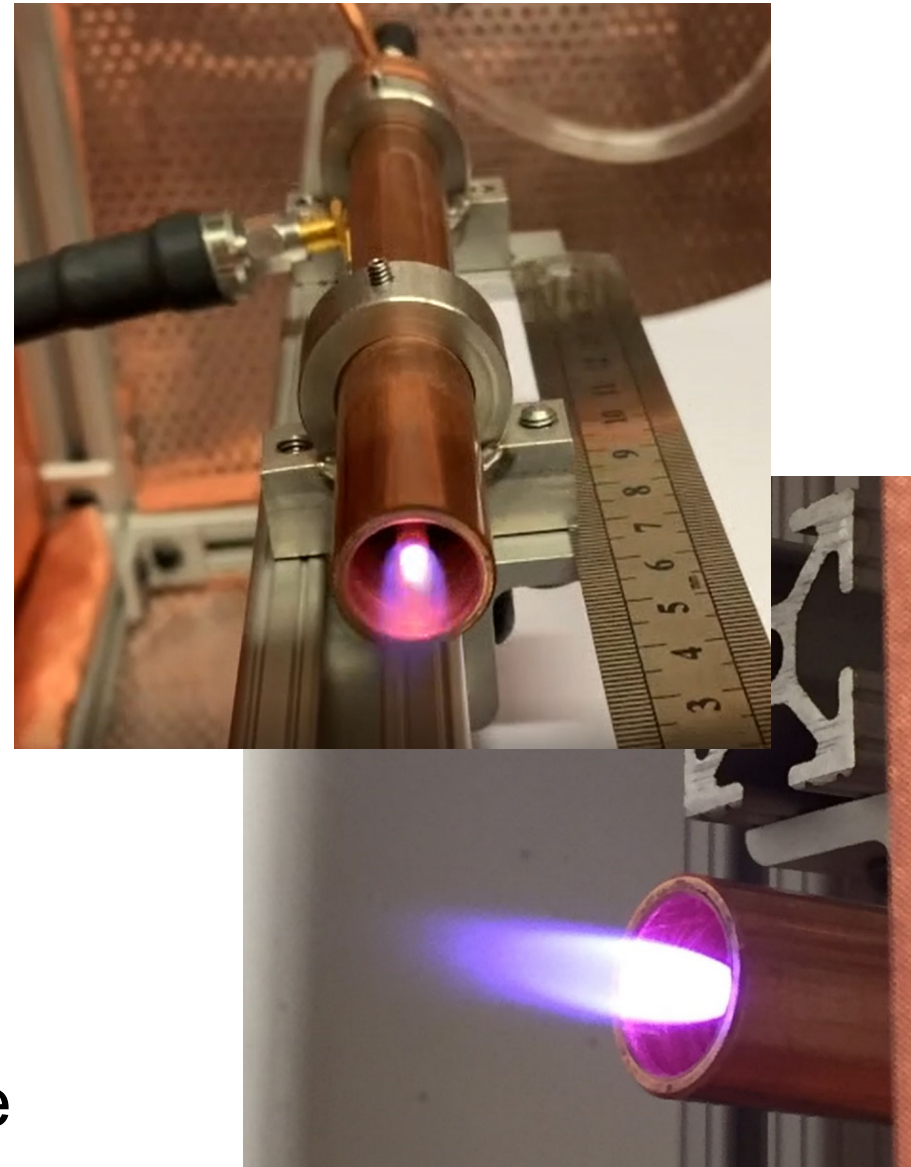
Transition Plan – Starfire Industries

RADION™

- Small microwave plasma applicator for hand-held or small robotic-arm applicator
 - ◆ ~100W power levels
 - ◆ Cold plasma, low temperature
 - ◆ High-efficiency HEMT transistors
 - ◆ Multizonal flow for *OnePass*SM

- Patent-pending pulsed potential for improved film adhesion, densification

- Parallelizable, pulsed, adjustable afterglow chemistry



Transition Plan – Starfire Industries - Cost

100-200W RADION (SMALL SPOT SIZE)			300-500W RADION (MEDIUM SPOT SIZE)		
CapEx Calculation			CapEx Calculation		
Microave Plasma Applicator	\$30,000	per unit	Microave Plasma Applicator	\$45,000	per unit
Precursor Delivery System	\$15,000	per unit	Precursor Delivery System	\$15,000	per unit
Amortized Lifetime	10	years	Amortized Lifetime	10	years
WACC Discount Rate	6%		WACC Discount Rate	6%	
Effective Captial Cost	\$50,562	per unit	Effective Captial Cost	\$67,416	per unit
Plant Days/Year	300	days	Plant Days/Year	300	days
Plant Availability	90%	uptime	Plant Availability	90%	uptime
Capital Equipment Cost	\$0.780	amortized cost/hr	Capital Equipment Cost	\$1.040	amortized cost/hr
OpEx Calculation			OpEx Calculation		
TEOS Consumable cost	\$0.011	\$/mL	TEOS Consumable cost	\$0.011	\$/mL
mL/hour	2.76	mL/hr	mL/hour	11.04	mL/hr
plasma coating width	1	cm	plasma coating width	2	cm
plasma coating speed	1	cm/sec	plasma coating speed	2	cm/sec
m2 coated per hour	0.36	m2/hour	m2 coated per hour	1.44	m2/hour
time to coat 1m2	2.78	hours	time to coat 1m2	0.69	hours
Precursor canister size	1000	mL	Precursor canister size	1000	mL
Change out frequency	362.32	hrs	Change out frequency	90.58	hrs
Canister cost	\$145.83	1L/unit	Canister cost	\$145.83	1L/unit
TEOS Consumable Cost	\$ 0.403	precursor cost/hr	TEOS Consumable Cost	\$ 1.610	precursor cost/hr
Ar/N2 gas consuption	0.84	L/hr	Ar/N2 gas consuption	0.84	L/hr
Cost per L (std gas cylinder)	0.009412	\$/L	Cost per L (std gas cylinder)	0.009412	\$/L
Gas Consumable Cost	\$0.008	gas cost/hr	Gas Consumable Cost	\$0.008	gas cost/hr
Electrical Unit Price	\$0.15	kW/hr	Electrical Unit Price	\$0.15	kW/hr
RADION Power Use	0.4	kW	RADION Power Use	0.75	kW
Power Consumable Cost	\$0.0600	power cost/hr	Power Consumable Cost	\$0.1125	power cost/hr
Electrode Unit Price	\$40.00	per applicator	Electrode Unit Price	\$40.00	per applicator
Change Out Time	500	hours/change	Change Out Time	500	hours/change
Electrode Consumable Cost	\$0.0800	power cost/hr	Electrode Consumable Cost	\$0.0800	power cost/hr
CapEx Cost Per Hour	\$ 0.780	\$/hr	CapEx Cost Per Hour	\$ 1.040	\$/hr
OpEx Cost Per Hour	\$ 0.550	\$/hr	OpEx Cost Per Hour	\$ 1.810	\$/hr
Total Cost Per Hour	\$ 1.33	\$/hr	Total Cost Per Hour	\$ 2.85	\$/hr
Levelized Cost Per 1 m2 Coverage	\$ 3.70	\$/m2	Levelized Cost Per 1 m2 Coverage	\$ 1.98	\$/m2

Transition Plan – Large Scale Systems with Robotics



- Fraunhofer IFAM Robot-guided atmospheric pressure plasma nozzle assembly treating the surface of an aluminium die casting component.
- We are in discussion with Fraunhofer Germany, US counterparts, and DoD labs for an ESTPC project

Key Points

- Improved a complex but environment friendly technology for environment friendly surface modifications
- Process control and design of torch are key to performance
- A version of the technology transferred to Starfire and currently manufacturable as custom system
- The values for corrosion performance has higher error bars indicating further improvement in the uniformity of the coatings possible

BACKUP SLIDES

Publications

- ◆ Bonova, L., Zhu, W., Patel, D.K., Krogstad, D.V. and Ruzic, D.N., 2020. Atmospheric pressure microwave plasma for aluminum surface cleaning. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*, 38(2), p.023002.
- ◆ Patel, D., Bonova, L., Jeckell, Z., Barlaz, D.E., Chaudhuri, S., Krogstad, D.V. and Ruzic, D.N., 2021. Deposition of zirconium oxide using atmospheric pressure plasma enhanced chemical vapor deposition with various precursors. *Thin Solid Films*, 733, p.138815.
- ◆ Samaei, A.; Chaudhuri, S. Understanding the Dynamic Growth Environment of Silicon Dioxide in Atmospheric Pressure Plasma Using Multiphysics Modeling. *Surfaces and Interfaces* 2020, 21. <https://doi.org/10.1016/j.surfin.2020.100739>.
- ◆ Samaei, A. and Chaudhuri, S., 2021. Mechanical performance of zirconia-silica bilayer coating on aluminum alloys with varying porosities: Deep learning and microstructure-based FEM. *Materials & Design*, 207, p.109860. [ps://doi.org/10.1063/5.0011769](https://doi.org/10.1063/5.0011769)
- ◆ Samaei, A. and Chaudhuri, S., 2020. Multiphysics modeling of metal surface cleaning using atmospheric pressure plasma. *Journal of Applied Physics*, 128(5), p.054903.

WP-2742: Atmospheric Plasma for Surface Modification and Nanoscale Embedding of Chemistry

Performers: *University of Illinois at Chicago, University of Illinois at Urbana-Champaign and Starfire Industries*

Technology Focus

- *Develop an atmospheric plasma (AP) based scalable solution that can clean, modify, and deposit a thin gradient coating on aluminum alloys for optimum control of bonding, adhesion and corrosion performance.*

Research Objectives

- *Develop a combined computational and experimental framework to design an AP surface cleaning and modification methodology*
- *Establish a processing-structure-property-performance model using multiscale simulations with detailed plasma chemistry and a model for the conversion layer to speed up the process development cycle.*

Project Progress and Results

- *Atmospheric air plasma can be used to clean aluminum panels*
- *Zirconia and silica coatings can be deposited from organometallic precursors*

Technology Transition

- *Starfire Industries has been developing a small plasma applicator unit for use in cleaning and coating deposition based on this project.*

