Bipolar Plate Manufacturing and Reconditioning Using Next-Generation IMPULSE® HiPIMS Etching, Surface Preparation, and Pinhole-Free Deposition of Corrosion-Resistant, Low-ICR Coatings

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DOE AGREEMENT # DE-SC0023992, AMR PROJECT ID MNF-BIL015

Project Goal

Develop plasma processes utilizing Starfire Industries IMPULSE® HiPIMS power supply to deposit and etch conformal, high quality, corrosion resistant thin films on bipolar plates (BPPs) for hydrogen fuel cells (PEMFCs) to enable recycling of the BPP substrates to incrementally contribute to hitting the DOE HFTO manufacturing goal of $80/kW total cost of ownership.

Project Overview

Timeline

- Start: 06/26/2023
- End: 03/31/2024

Budget

- Total Project Budget: $200k
- Total DOE Share: $200k
- Total Cost Share: $0k
- Total DOE Funds Spent: $53k
- Total Cost Share Funds Spent: $0k

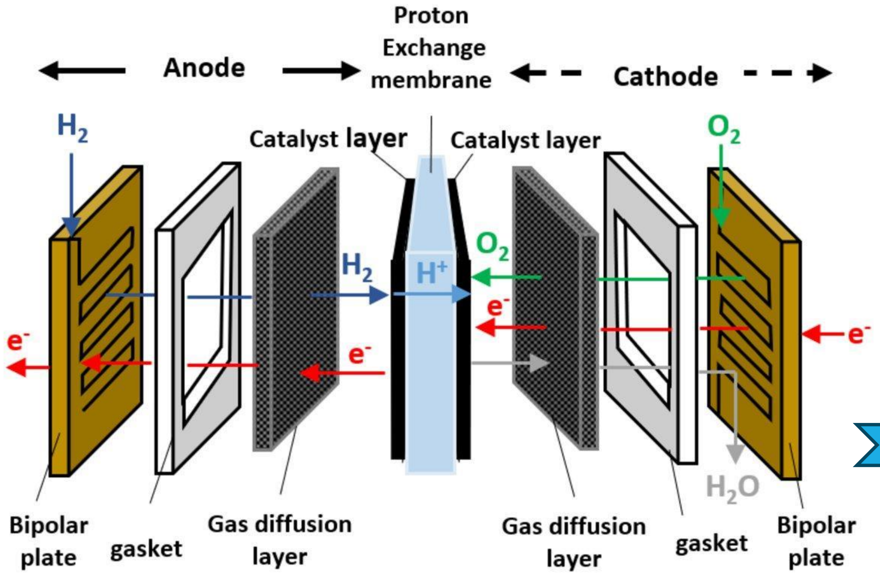
Barriers

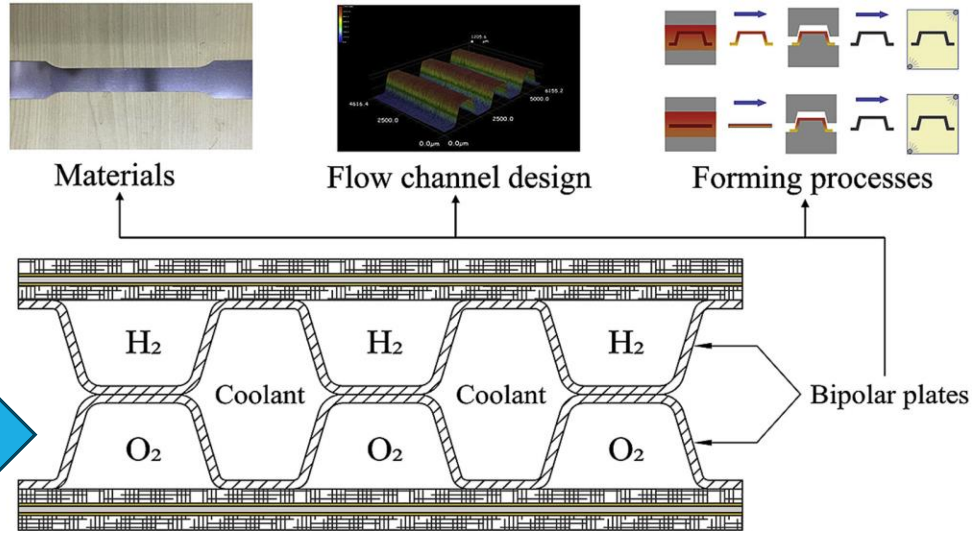
- Protective coatings are required for 316L stainless steel to be a viable bipolar plate (BPP) material in hydrogen fuel cells
- There is no innovative technology in effective recycling of corroded BPPs and redeposit protective coatings.
- At current manufacturing costs, BPPs with corrosion-resistant coatings would likely not meet DOE lifetime/performance targets

Partners

- Starfire Industries (Champaign, IL)
  - Brian Jurczyk (PI), Rajib Paul, Michael Hysick
- Center for Plasma-Material Interactions (CPMI) at the University of Illinois Urbana-Champaign (Urbana, IL)
  - David Ruzic, Amzad Hossain, Zach Jeckell, Nick Connolly
- Nano4Energy (Madrid, Spain)
  - Dr. Ivan Fernandez

Technical Overview: Bipolar Plates (BPPs) in fuel cell stacks





Bipolar plates (BPPs) are a critical component in proton exchange membrane fuel cells (PEMFCs) providing conducting paths for electrons between cells, distribute and provide a barrier for reactant gases, remove waste heat, and provide stack structural integrity.

- Material: (i) Stainless steel (316L) BPs possess high electrical and thermal conductivity, good gas impermeability, superior mechanical properties and formability.
  (ii) 316L BPPs as thin as 0.1 mm can be manufactured by plastic forming methods in mass at lower cost than Titanium (Ti).
- Problem: (i) Stainless steel (316L) has relatively lower corrosion resistance (gets corroded over time).
  (ii) It has higher interfacial contact resistance (ICR), that reduces overall cell-stack performance.
- Solution: (i) Reusing the corroded BPPs by etching and redepositing protective coatings to bring the cost lower (about $3/kW).
  (ii) Quasi conformal coating of stainless steel BPPs by TiN and amorphous carbon (aC) using a scaled-up HiPIMS technique.
  (iii) The TiN layer (with graded N content) will be on the side with the highest electrode potential to resist oxidation. aC is great for electrical conductivity. The keys are to not corrode and increase resistance, but also to avoid poisoning of the membrane, catalyst and transport layer in electrodes.

Potential impact of this project

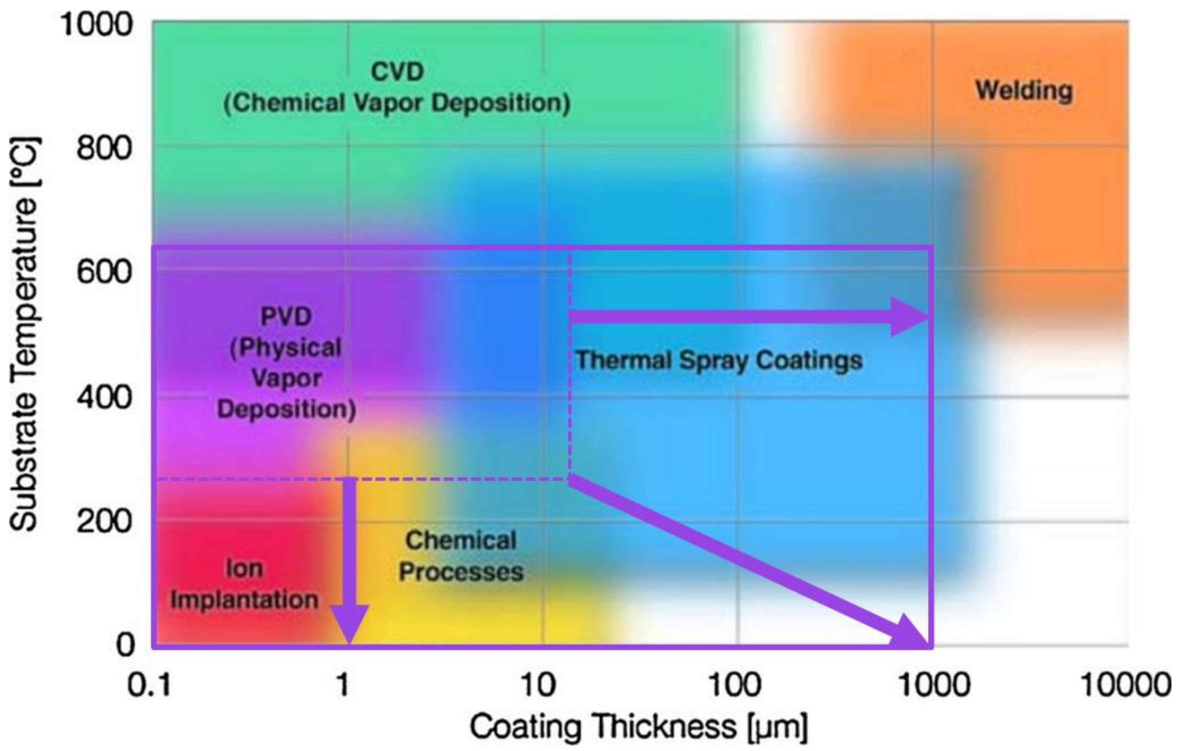
This project is relevant to DOE goals to:

- Achieve the Hydrogen Shot goal of $1 for 1 kg hydrogen by 2031.
- Lower greenhouse gas emissions and criteria pollutants by making technological advancement in PEMFCs.
- Create many good-paying jobs in the United States.
- Build clean energy infrastructure.
- Support and improve energy, environmental, or social justice.
- Strengthen U.S. manufacturing of PEMFCs.

Advantages and value proposition of this project/technology vs. current best practices or state-of-the-art.

- Current practice and problem: A reference class 8 heavy-duty vehicle utilizes 1,600 BPPs/vehicle with 275kW power rating. This represents **a significant recycling challenge for $3/kW 316SS raw material cost** before any forming, shaping, welding and coating take place.
- Our approach: Due to the quality of the HiPIMS coating (dense, non-columnar), nano-layering with mixed materials (DLC, nitride, carbide, etc.), and the ability of the IMPULSE® to achieve quasi-conformal deposition within the stamped BPP channels, **thinner anti-corrosion thickness will be required compared to conventional processes. This will lower overall cost for each BPP and enable dry-plasma etching for refurbishment.**
- DOE goal: If this SBIR is successful, we will incrementally contribute to the **DOE HFTO manufacturing goal to reduce ultimate system to the $80/kW target (@25khr durability)** with total cost of ownership. **Each reduction in cost encourages additional investment towards the hydrogen fuel cell transition**.

Approach: Next-Generation PVD (HiPIMS) deposition of suitable coatings



Generic trade space for coating processes
- Temperature
- Thickness

Physical Vapor Deposition (PVD) techniques traditionally were for ‘thin-films’
- 300-600°C temperature
- A few microns thickness

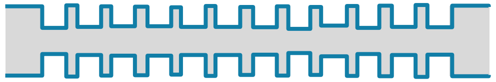
Precision Ion Energy Control & Layering
- Control Stress (Thicker Films)
- Coatings at Room Temperature
- Greater Control on Material Properties with High-Power Impulse Magnetron Sputtering

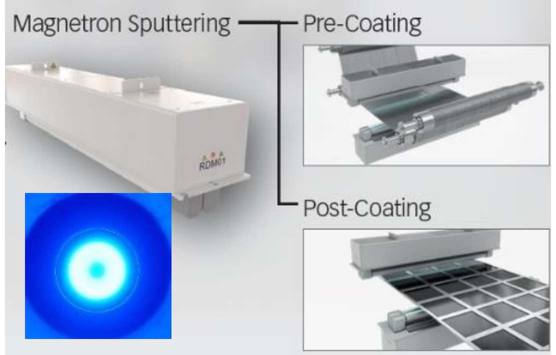
- Thin-film dc magnetron sputtering PVD will be used to put Ti/TiN and a-C layers on either side of the 316L (BPP).
- Our HiPIMS process allows etching onto the BPPs since it is high density plasma and it can REMOVE material.
- Corrosion products and prior coatings can be physically cleaned and then redeposited over 316L.
- Our IMPULSE will give quasi-conformal coatings, that will be better for sealing the 316L surfaces that are 3D pressed or shaped.

Full BPP Lifecycle: 316L Bipolar Plate Coating & Etching

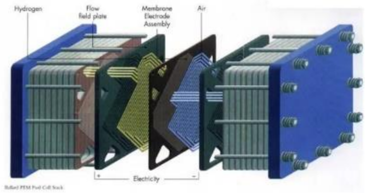
Fabricate 316SS BPP

IMPULSE® + Super Kick™
PVD Protection Coatings



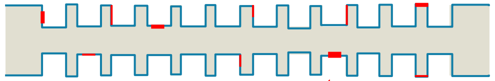


PEMFC Stack + Gen



MDV/HDV Use
25k Hrs

EOL Recycle



Bipolar Plate Recovery & Inspection
Coating Loss, Corrosion, Contaminants

IMPULSE® + Super Kick™ Dry-Plasma
Etch & PVD Surface Reconditioning

Starfire Innovation

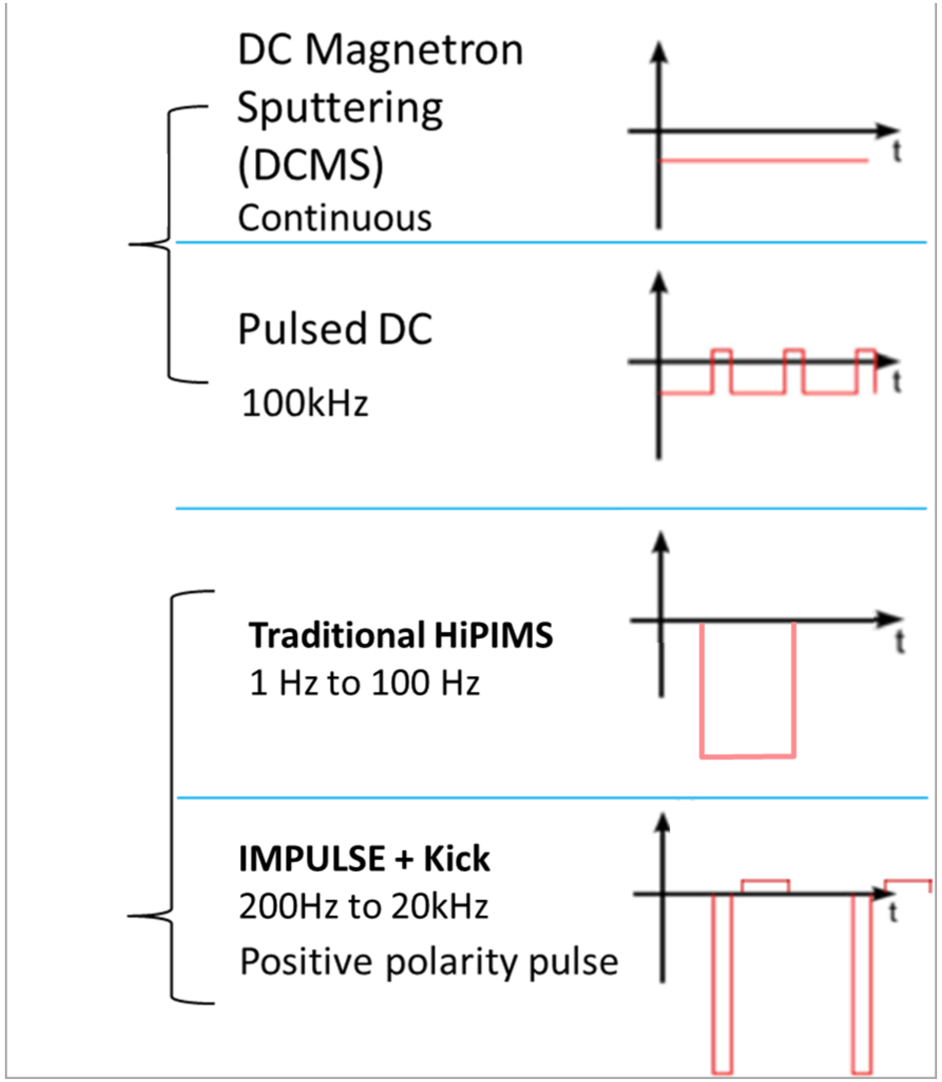
Starfire is **a user** of specialty PVD thin-films for particle accelerators—specifically Ti and Cu

We made the **IMPULSE® + Positive Kick™** initially to overcome traditional HiPIMS limitations **for our own products** → commercialization with *Kurt J. Lesker*

Improve deposition rate by accelerating metal ions to counter the "return effect" that limited HiPIMS adoption

Fast switching with parallel architecture to achieve 0.3—10 A/cm2 in **small, low-cost unit for R&D and small process**

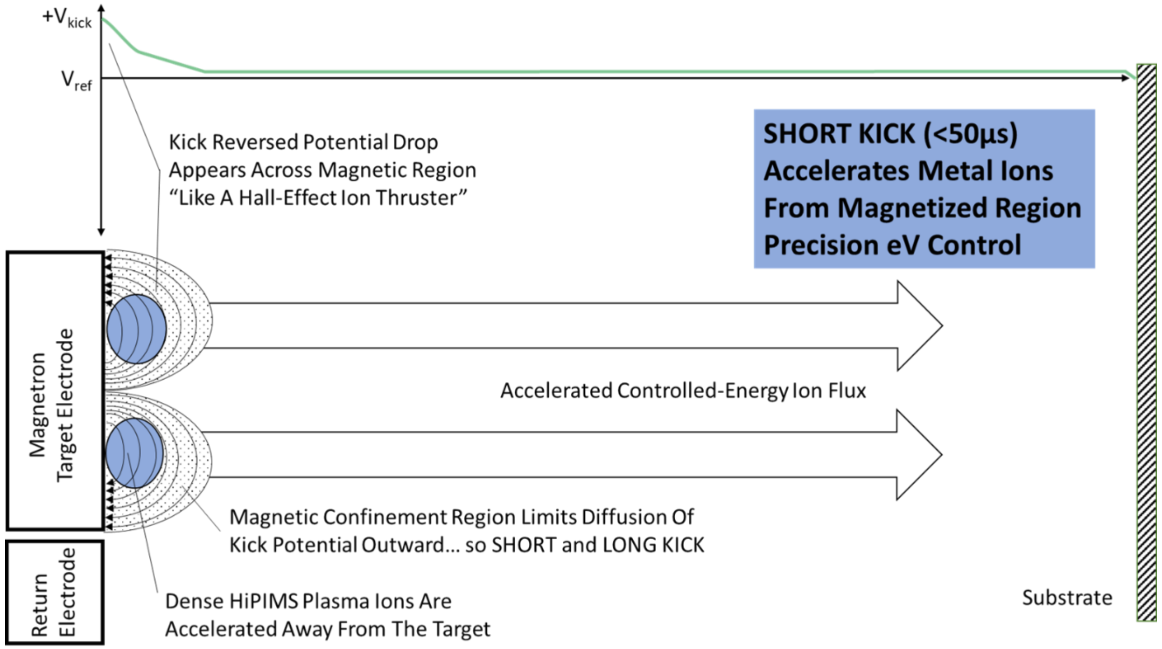
Enable **pulse synchronization with substrate bias** to improve Me/Ar ratios with world's first dual pulse module



IMPULSE® + Positive Kick™

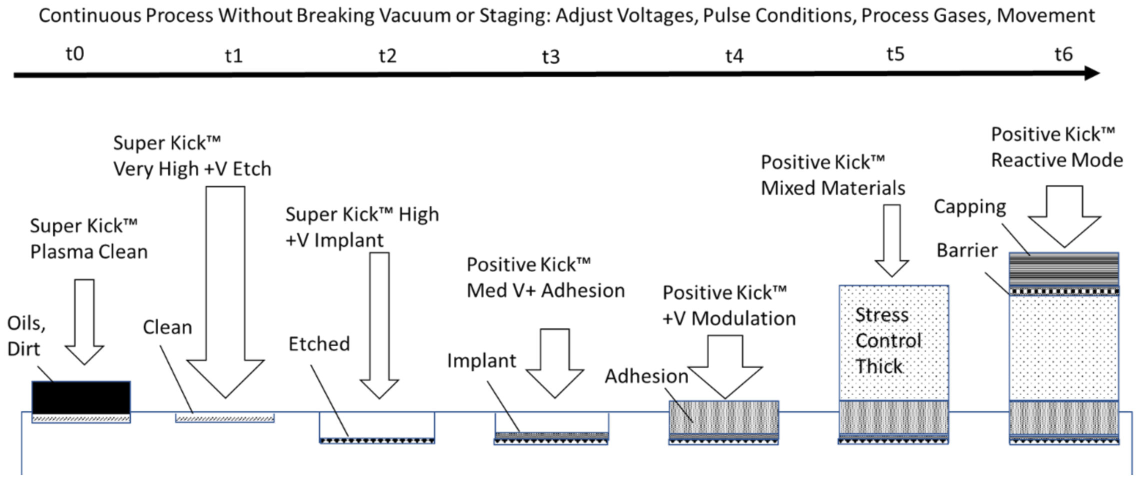
Quick Blurb on "bipolar HiPIMS"

- Intense main negative pulse to sputter target generates intense flux of sputtered metal ions
- Rapid positive voltage reversal to sputter target **"KICKS"** those metal ions towards the substrate with adjustable energy
- Dense HiPIMS plasma with extended Positive Kick leads to a **conformal sheath** on the substrate



The Positive Kick™ enables in-situ cleaning, etching, implantation, mixing and stress control

- Great for multilayer and graded properties



Allows movement around both axes of the Thornton-Anders Structure Zone Diagram

US11069515 patent & others

New Process Knobs

Customers responded very favorably to the **fully-adjustable Positive Kick™** + IMPULSE® technology for non-traditional areas (not hard coatings!)

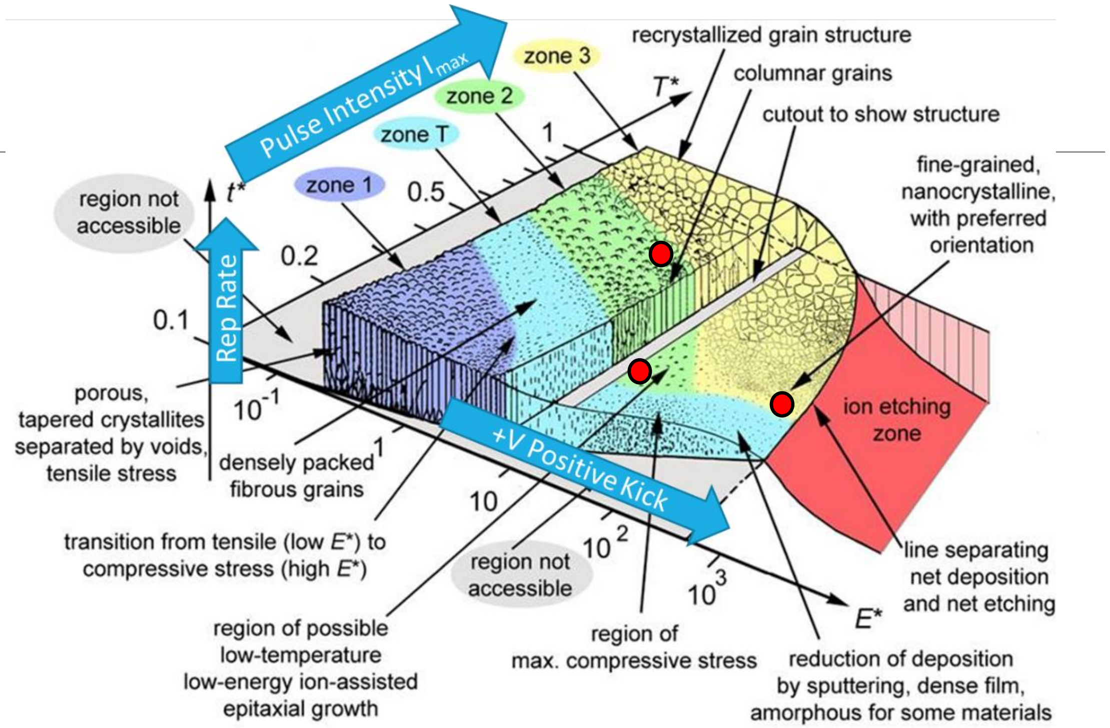
Materials scientists now had **additional independent knobs for T* and E* and t* for precision engineering** to enable manufacturing of new material properties

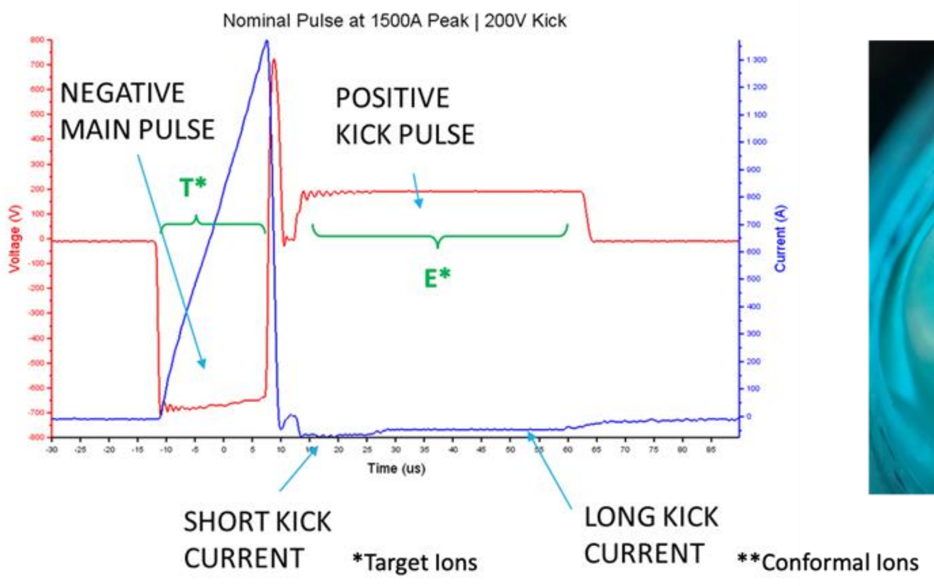
Our pulsing topology supports **very fast switching**

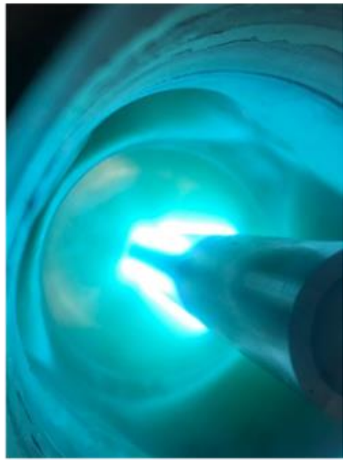
- Arc detect, mitigation, arrest and arrest with fast pulse termination <1µsec

Conventional HiPIMS power supplies (Huettinger) have minimum ~3µsec to 'start' to turn off

- **Result: major reduction in wafer particle counts for IMPULSE®**







Why Are Sputtered Ions Important?

Ions can be controlled and accelerated into the substrate to give the film surface **MORE ENERGY**

- Good for directionality too

Having a plasma present can add an additional eV's to ion energy in the "sheath"

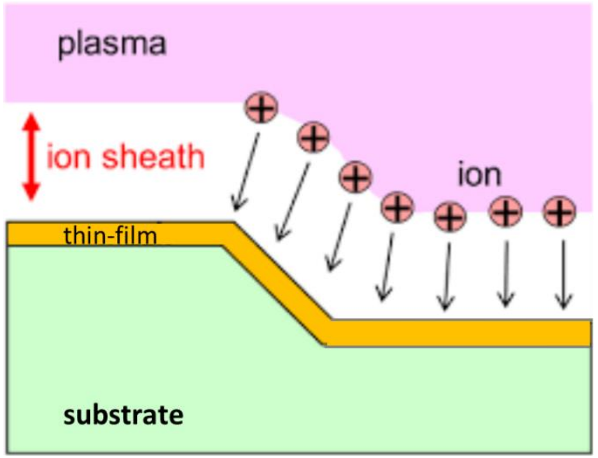
- Adding a controllable BIAS can make that even higher
- Ion energy allows sputtering at wider pressures

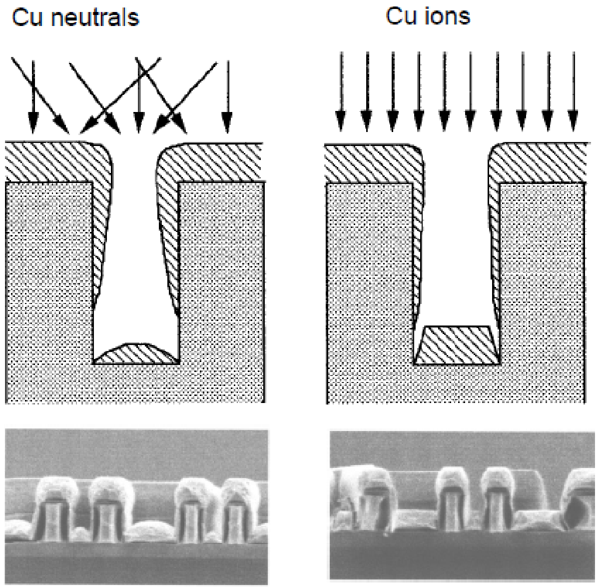
Energy transfer is critical for film adhesion, densification, microstructure, crystallinity, morphology, stress and electronic properties

Sputtered ions are even better—you are accelerating the material you want to deposit

- E.g. Metal^{+} ions vs. Ar^{+}

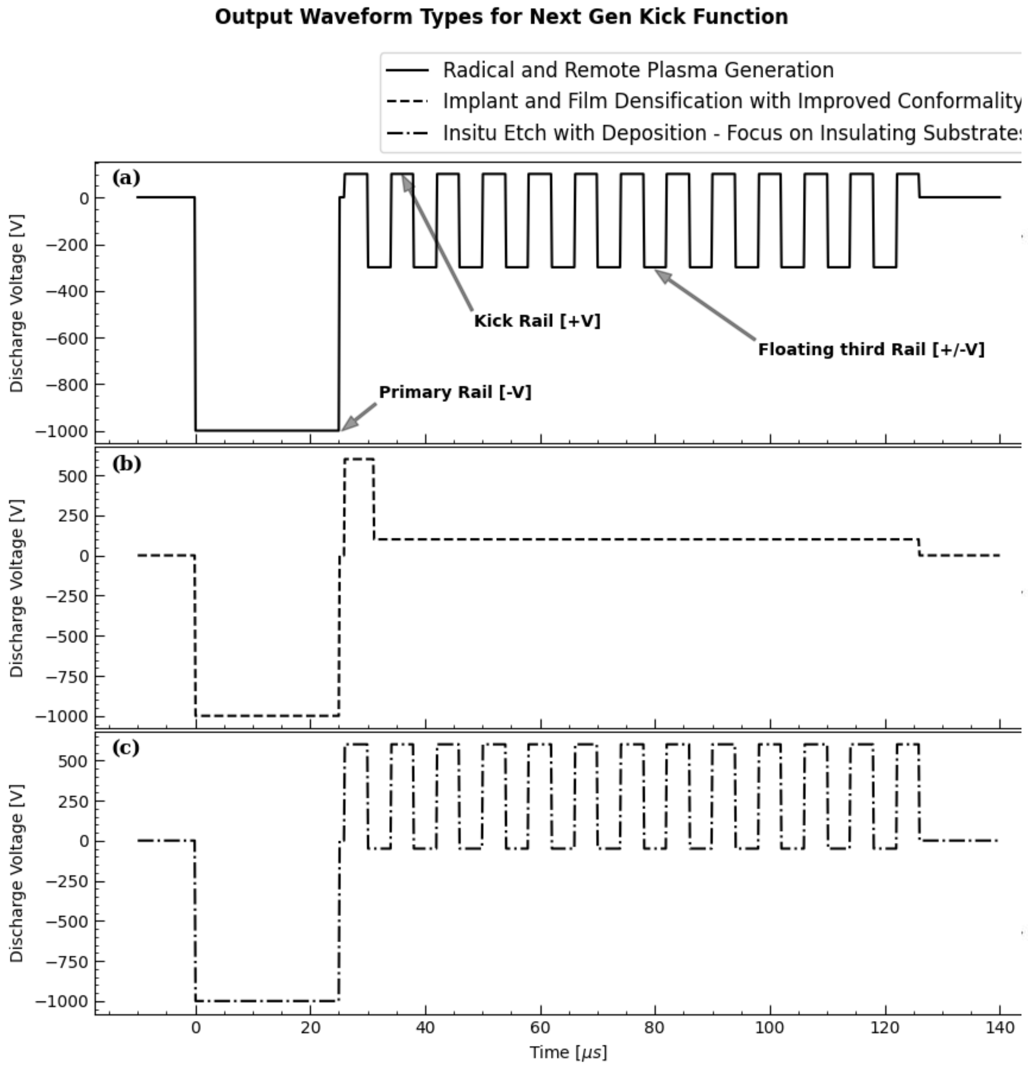
HiPIMS gives us lots of sputtered ions!

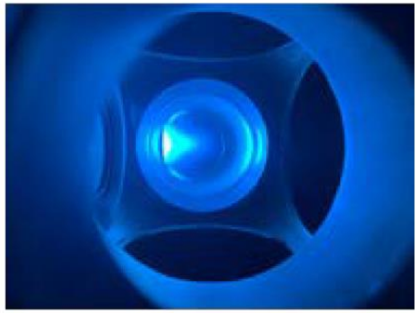


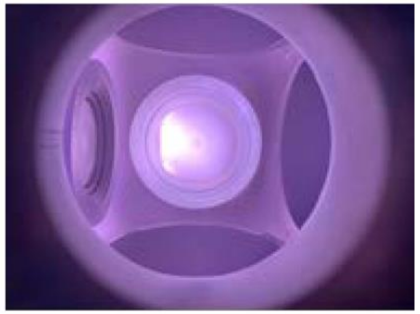


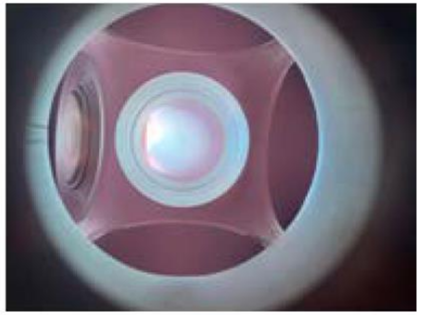
Z. J. Radzimski, J. Vac. Sci. Technol. B 16, 1102 (1998)

Varying SuperKick^{TM} Conditions = Different Plasmas









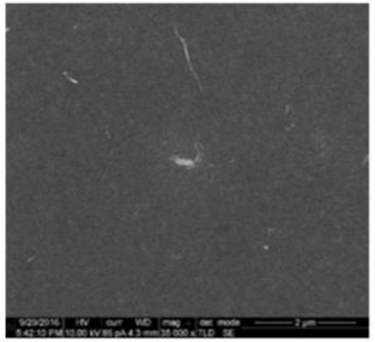
Adjusting the main pulse vs. positive kick affects EEDF, n_e

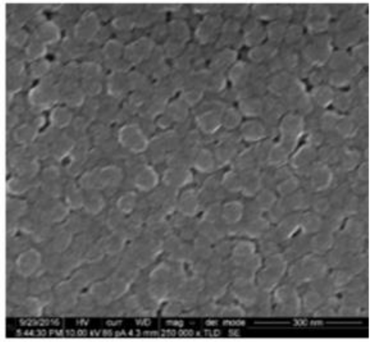
Very different plasma conditions at the substrate can be achieved

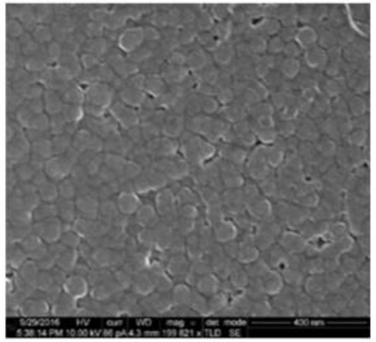
Etching, reactive deposition, even PECVD is observed with precursor injection near the substrate

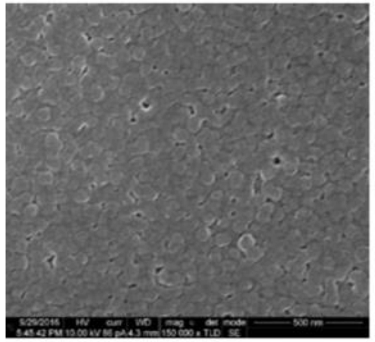
Select Adatom Mobility → Smoothness & sp^3 at-C

SEM Images of Carbon coating with DC magnetron sputtering

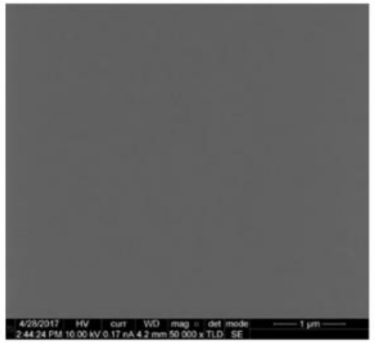

2µm

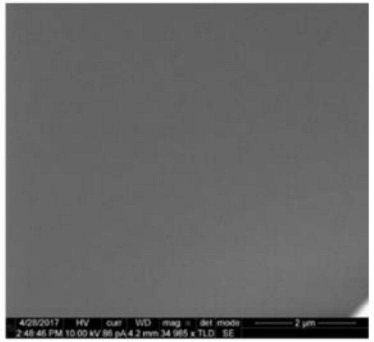

300nm

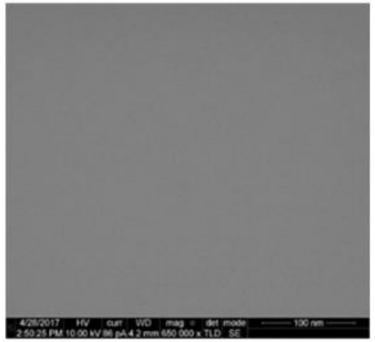

400nm

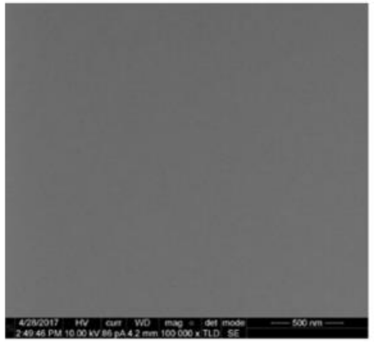

500nm

SEM images of Carbon coating with HIPIMS (IMPULSE power supply)


1µm

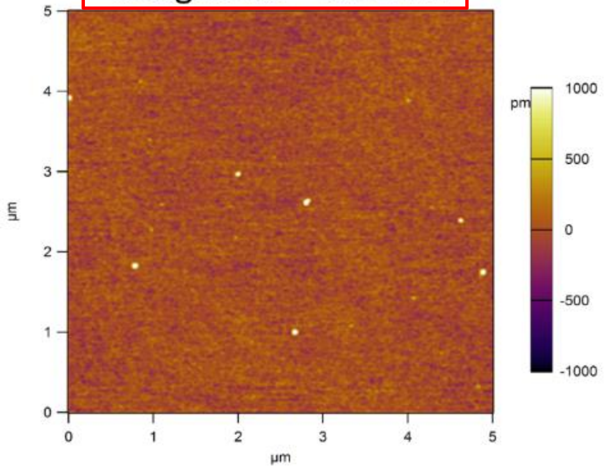

2µm


100nm


500nm

HiPIMS + Kick 500W

Roughness = 0.10nm



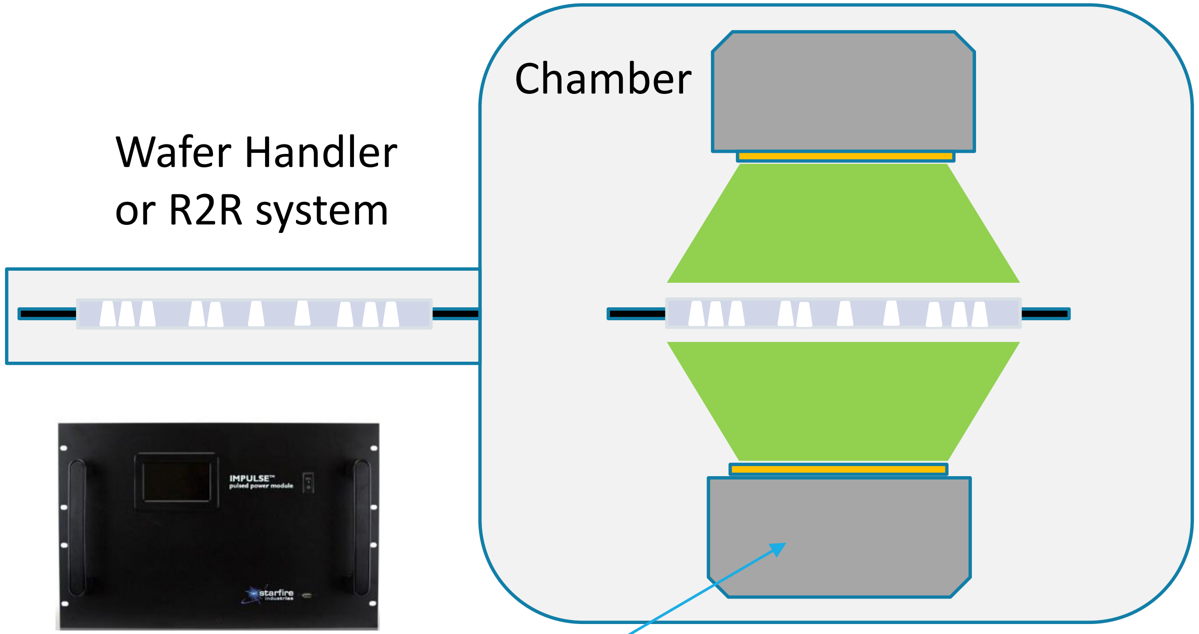
$+V_{KICK}$ precision control of adion mobility

Ultra-smooth AND fully dense

Preferentially break sp^2 bonds

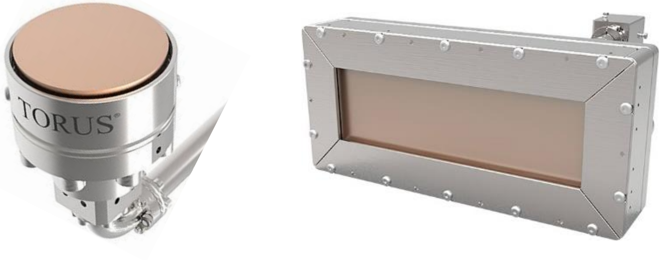
Coat Front/Back Of R2R Material w/IMPULSE®

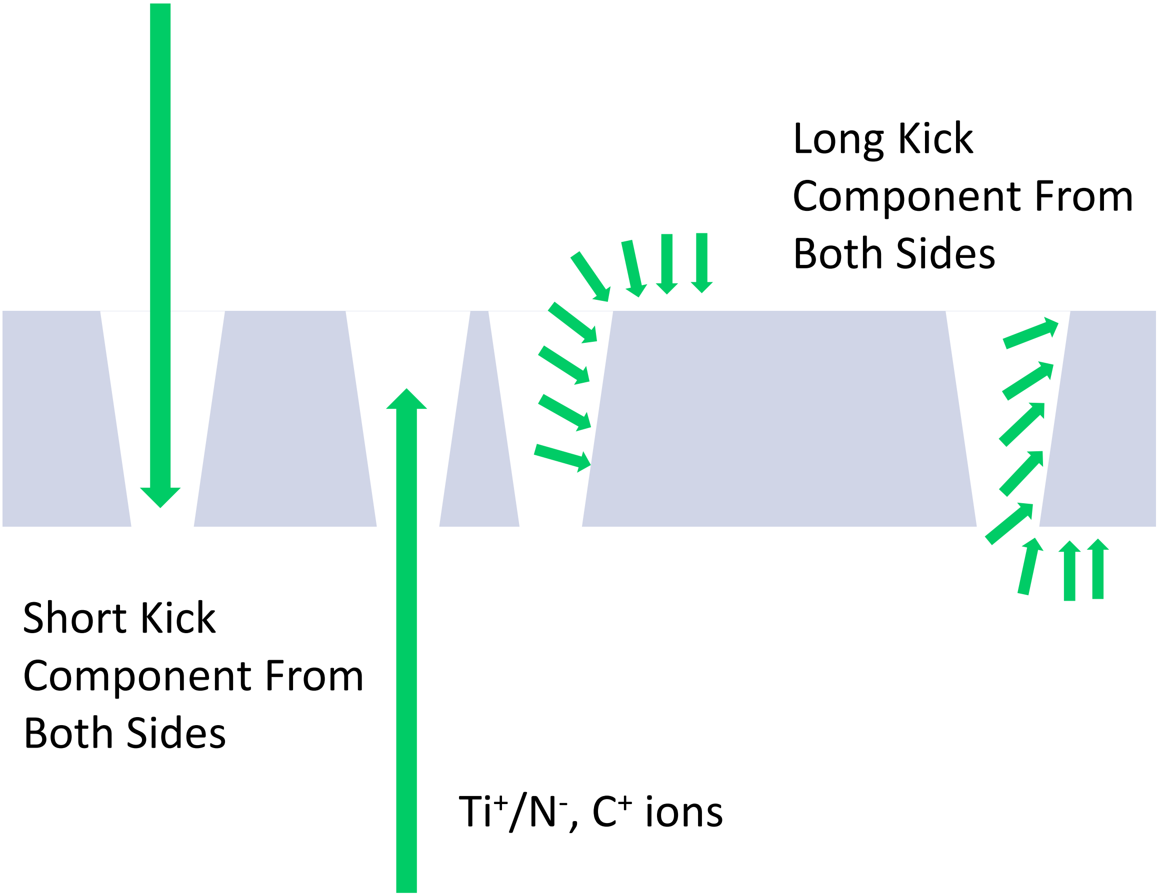
Use two systems to coat the front/back side of a wafer or R2R glass or polymer glass using Positive Kick™
High-Dep Rate, More Kick Pulses, Ion Energy/Densification From Both Directions, Adhesion, Throughput



IMPULSE®

Dual or Quad
Sputter Guns





Accomplishments and Progress

We have set up the instrumentation and identified other supply requirements

- aC deposition on ICARUS chamber
- TiN deposition and film etching on Starfire chamber
- ICR test stand

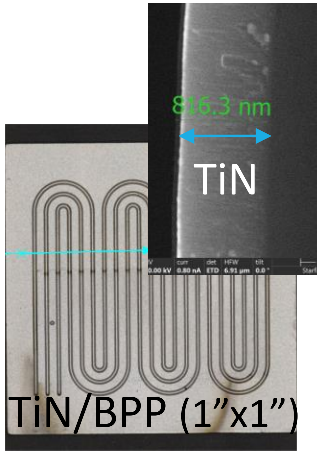
We have identified the materials and successfully deposited basic aC and TiN coatings

We have done preliminary characterization of the coatings utilizing:

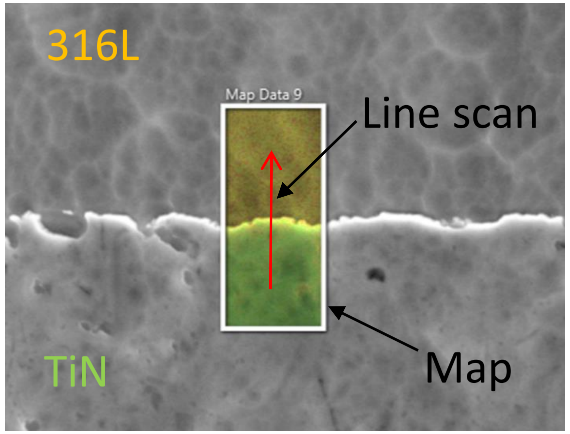
- SEM/EDS
- XRR

We have demonstrated complete etching of the deposited TiN, a key requirement for the proposed single-chamber solution

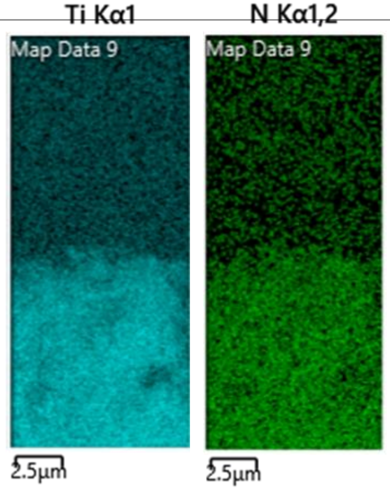
TiN/Ti deposition and etching on Bipolar Plate (316L)



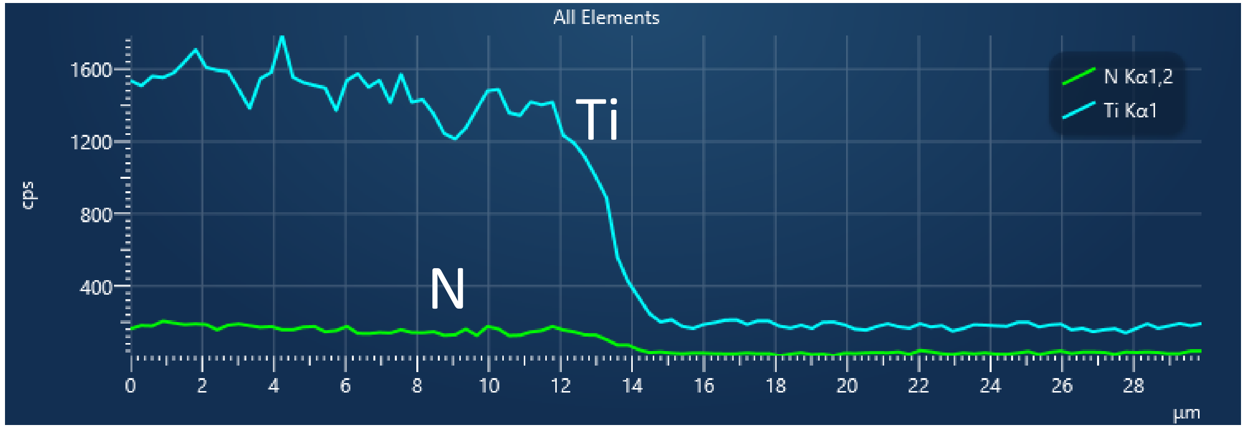
TiN coated BPP and Thickness of TiN



EDS elemental map



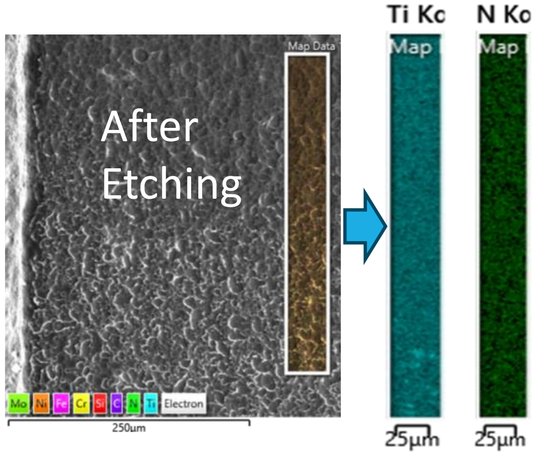
Ti map N map



Elemental Profiles from Line scan

- Etching of TiN/BPP was performed to calculate the etching rate
  - The substrate brought closer to target.
  - Kick power was maximized by changing kick width and voltage.
  - Etching rate of 816 nm thick TiN on BPP: 0.15 nm/sec

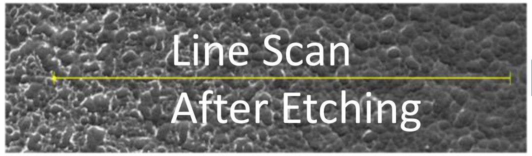
- With IMPULSE® PVD, we can functionally-grade the material and make layers. We can change the concentration of the mixture, to match CTE to the surface, provide a changing stoichiometric rate.

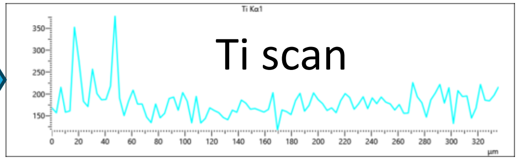


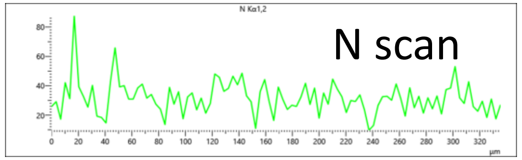
EDS elemental content

Element	Wt% Deposited	Wt% Etched
Ti	27.92	0.06
N	8.04	0.20
Substrate	64.04	99.74

No TiN after etching





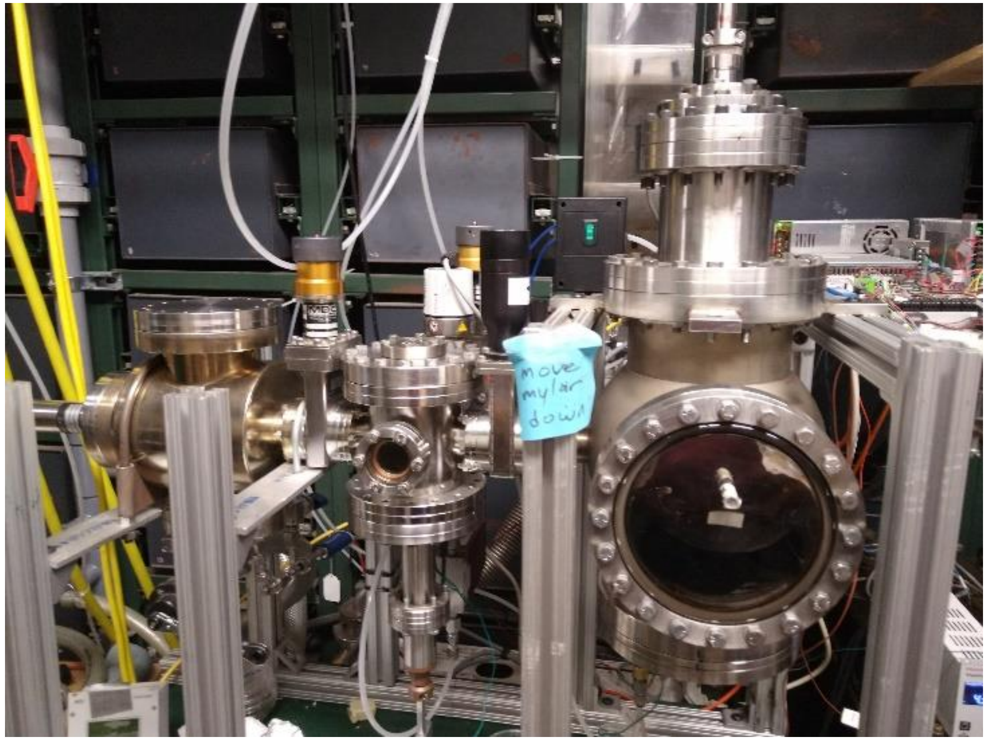


ICARUS Chamber for aC Deposition

High vacuum coating chamber with base pressure of 7e-8 Torr
- Equipped with load lock for increased purity
- Ability to heat sample stage during deposition

Sputter Deposition Equipment
- 2” TORUS Circular High Vacuum Magnetron Sputtering Source (Kurt J. Lesker) with graphite target
- 1.5 kW DC power supply
- Starfire IMPULSE® + Positive Kick™ HIPIMS supply

Available metrology techniques considered for film characterization:
- SEM- top-down film uniformity and film thickness
- Nano Indentor- hardness
- XRR- film thickness and density
- Raman spectroscopy- sp3 fraction in carbon



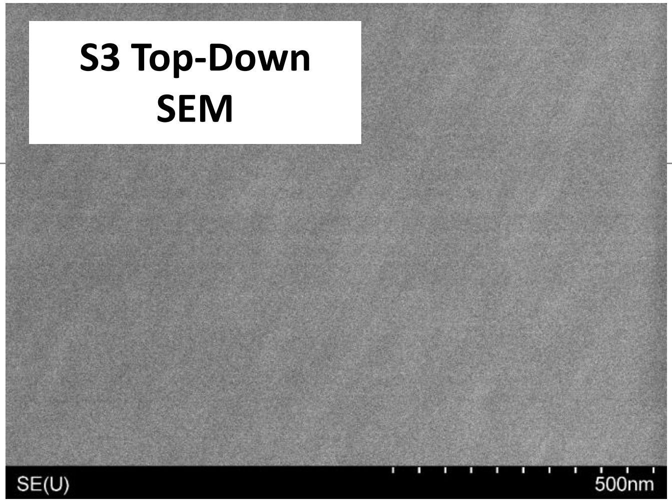
ICARUS Chamber

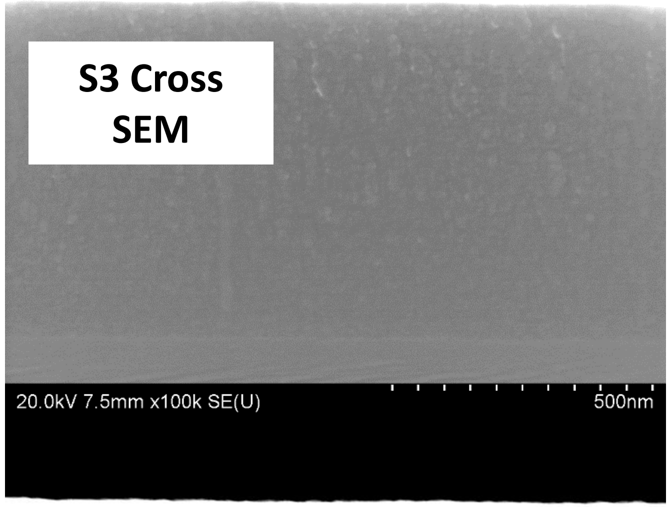
aC Film Process Development

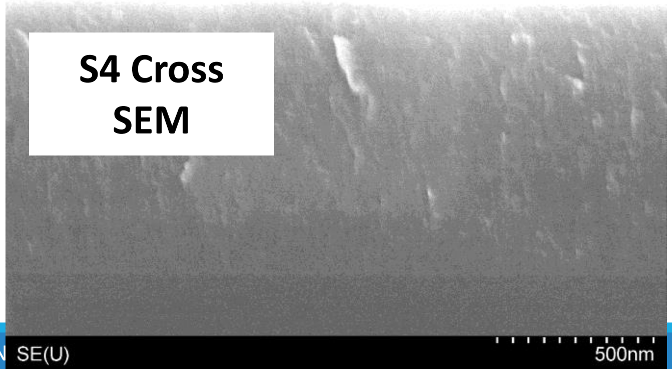
Sample	Pressure (mTorr)	DC Current (mA)	Main Pulse (µs)	Kick Pulse (µs)	Kick Voltage (V)	Rep Rate (Hz)
S1	4	216	30	100	100	800
S2	4	203	20	100	100	850
S3	4.5	250	35	20	20	1000
S4	4.5	250	75	20	20	1000
S5	4.5	250	75	100	20	1000

Targeting low pressure for low defectivity

High rep rate and short, low voltage kick allows for higher sp2 fraction, which enhances conductivity







Interfacial Contact Resistance (ICR)

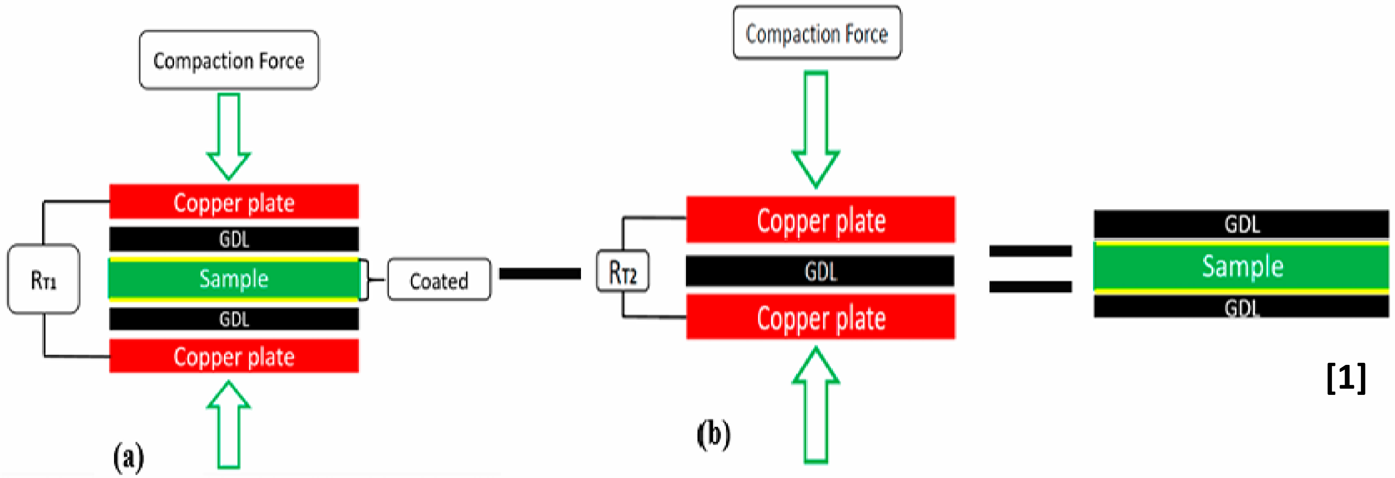
Bipolar plates should possess low Interfacial Contact Resistance (ICR)

- DOE target for ICR: <10 mΩ-cm^2

The proposed method to calculate the ICR of the bipolar plate is described in literature, used two measurements to determine contacts resistance between sample and gas diffusion layer (GDL)

ICR will be measured at 150 N/cm^2 compressive force, allowing for selection of promising coatings for dry etching

ICR Test Stand



[1]

Reference: [1] Forouzanmehr, M. et al. Sensors 2022, 22, 750. [CrossRef]

Collaboration and Coordination

The collaboration has become stronger between Starfire Industries and the Center for Plasma-Material Interactions (CPMI) at the University of Illinois at Urbana-Champaign through this project. The tasks for this work are split as follows:

- Starfire optimizes the Ti/TiN film deposition
- Starfire etches both the aC and Ti/TiN films
- CPMI optimizes the aC film deposition
- CPMI completes ICR testing and facilitates electrochemical corrosion testing

Starfire will informally consult with its colleagues at Nano4Energy in Madrid, Spain (Dr. Ivan Fernandez).

Remaining Challenges and Proposed Future Work

Remaining challenges:

- We do have a reasonable plans to attain the goals of this project on time.
- We will work sincerely to solve any/all challenges that might arise.

Proposed future work:

- We will change experimental parameters to deposit chemically variable/layered films to optimize the characteristic parameters for the applications (for example interfacial resistance, corrosion resistance, etc.)
- We will demonstrate that we can deposit the functional coatings on both sides of bipolar plates and we can etch out those coatings completely to redeposit fresh coatings.
- We have also planned to obtain corroded BPPs from a reliable source in future and actually remove the corroded materials from the BPP surfaces for depositing fresh barrier coatings. We will compare the results with fresh BPPs vs corroded BPPs.
- We will modify our plans as needed to accomplish the goals of this project and will try uplift our visionary goals further to make an impact commercially.

Summary and conclusions

- We have set plans to accomplish the goals of this project.
- We have arranged the instrumentational needs and obtained the materials, supplies, etc.
- We have successfully deposited the proposed coatings and obtained preliminary characterization results as presented in this poster.
- The preliminary results show that we have coated the BPPs with TiN (~800 nm thick) having graded N content which could be beneficial as corrosion barrier. We have also etched the TiN layer completely.
- We have also deposited aC (~800 nm) successfully and have made set-ups for ICR.
- We have identified our future works to attain the goals of this project through strong collaborations with University of Illinois at Urbana-Champaign and other industries.
- We are very optimistic that we will be able to achieve the goals set by DOE of about $3/kW clean energy sources (PEMFCs).
- Due to the high quality of the HiPIMS coating (dense, non-columnar), nano-layering with mixed materials (DLC, nitride, carbide, etc.), and the ability of the IMPULSE® to achieve quasi-conformal deposition within the stamped BPP channels, this project will lower the overall cost for each BPP and enable dry-plasma etching for refurbishment.
- This SBIR will incrementally contribute to the DOE HFTO manufacturing goal to reduce ultimate system cost to the $80/kW target (@25khr durability) with total cost of ownership. Each reduction in cost encourages additional investment towards the hydrogen fuel cell transition.