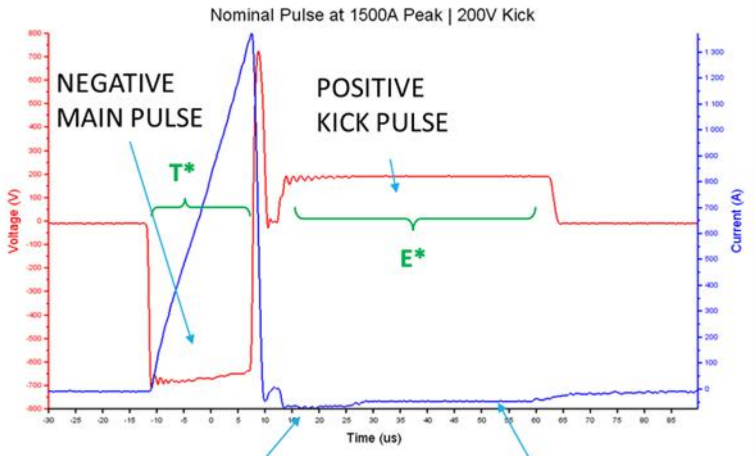
Innovations in High Power Impulse Magnetron Sputtering (HiPIMS)



NEGATIVE MAIN PULSE

POSITIVE KICK PULSE

SHORT KICK CURRENT

*Target Ions

LONG KICK CURRENT

**Conformal Ions

Presented by Frank Papa and the Starfire Impulse® Team

Overview

What is HIPIMS?

Why is this technology important?

Where can we use HIPIMS?

Note on Magnetics

Review: PVD Sputtering

PVD sputtering is an atom-by-atom process allowing thin films with tailored properties

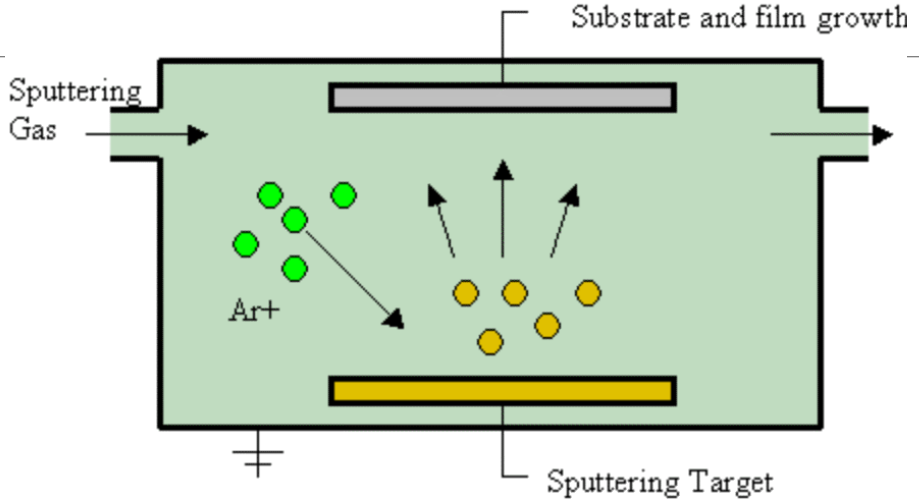
- Multiple layers / nanocomposites are possible

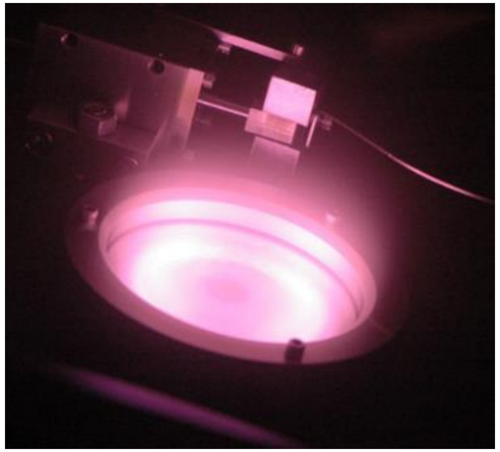
Sputtered atoms have a few eV of energy that assist with film growth

- Low pressure process to minimize scattering and slowing down

Some sputtered atoms are ionized (~1%) and controlled to the substrate

- Use substrate RF or DC bias to add energy to these ~1%





Traditional DC sputtering only has a few ions

What if… we could increase the fraction of the ionized sputtered material and control the energy of these ions?

Why Are Sputtered Ions Important?

Ions can be controlled and accelerated towards the substrate to add energy to the growing film

- Good for directionality too

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

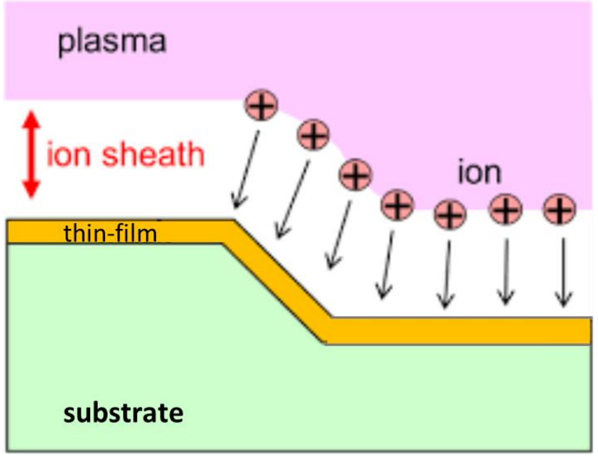
- Adding a controllable BIAS can make that even higher
- Ion energy allows sputtering over a wider pressure range

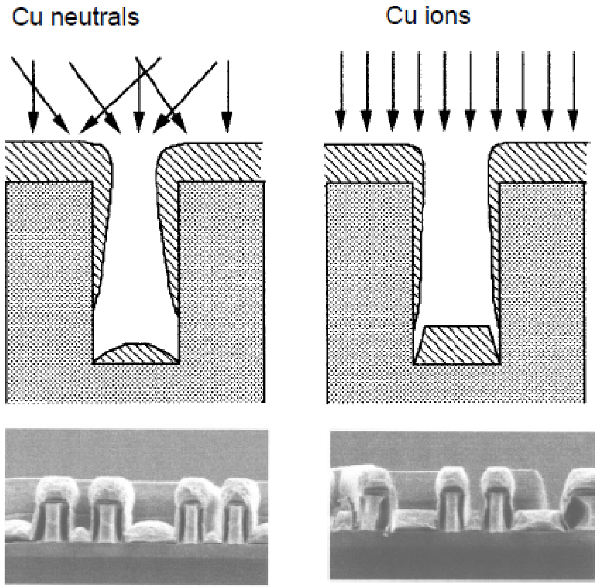
Energy transfer is critical for film adhesion, densification, microstructure, crystallinity, morphology, stress and electronic properties

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

- E.g. Nb$^+$ ions vs. Ar$^+$

HiPIMS gives us lots of sputtered ions!





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

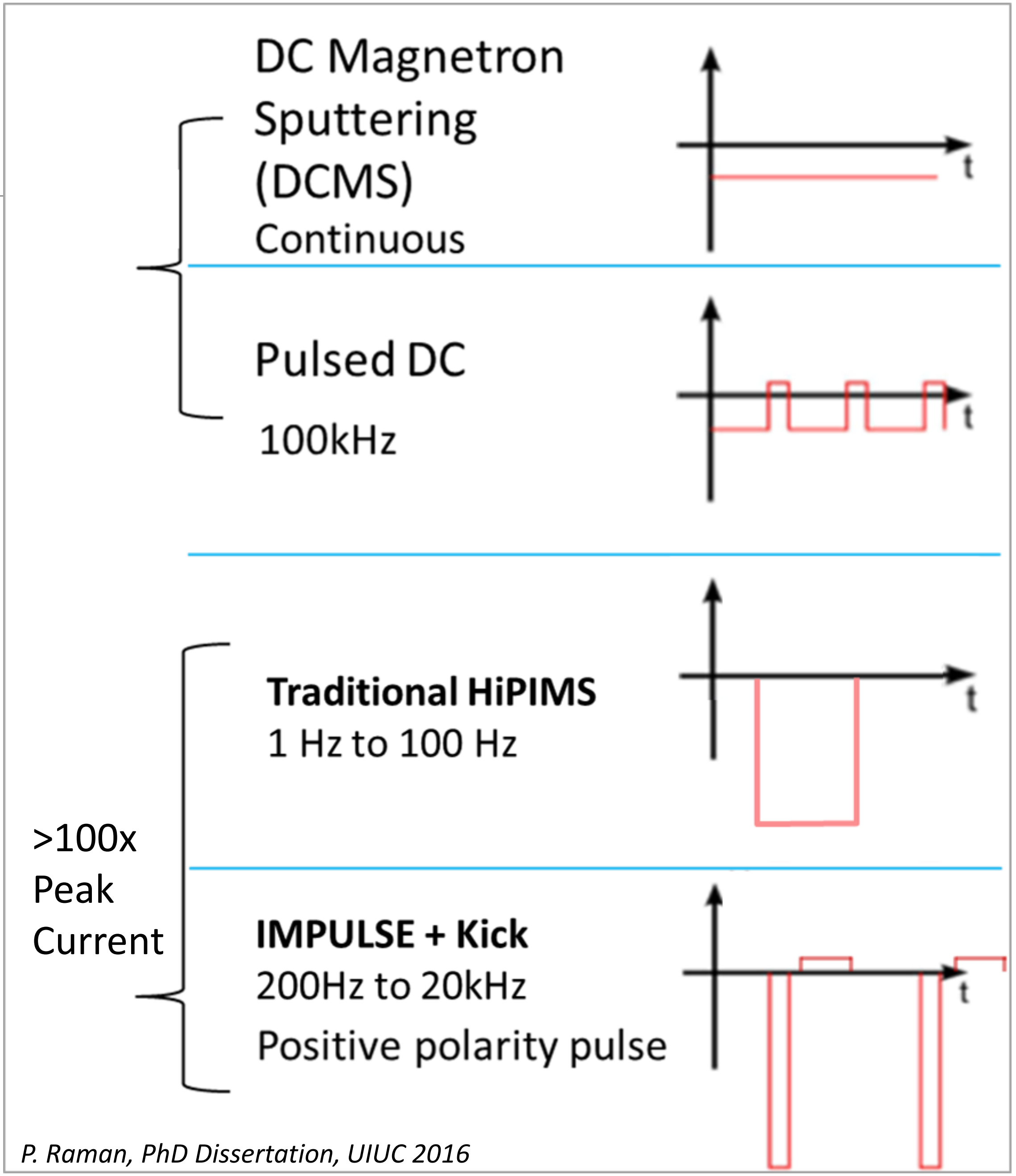
Comparing…

Traditional HiPIMS is 200-2000µs, 20-50Hz = 1% duty factor

- Long, hard pulses with long off time
- Energetic ions from localized plasma double layers
- Struggle to limit “hot spot” microarc formation

Traditional HiPIMS: a compromise between Cathodic Arc and DC/Pulsed-DC

- Much less “particles” than cathodic arc
- Medium ionization % for ion energy flux (more than pulsed DC)
- Lower deposition rate compared to either
- Current control limit pulses to ~0.1-1 A/cm^2 current density



DC Magnetron Sputtering (DCMS)
Continuous

Pulsed DC
100kHz

Traditional HiPIMS
1 Hz to 100 Hz

>100x Peak Current

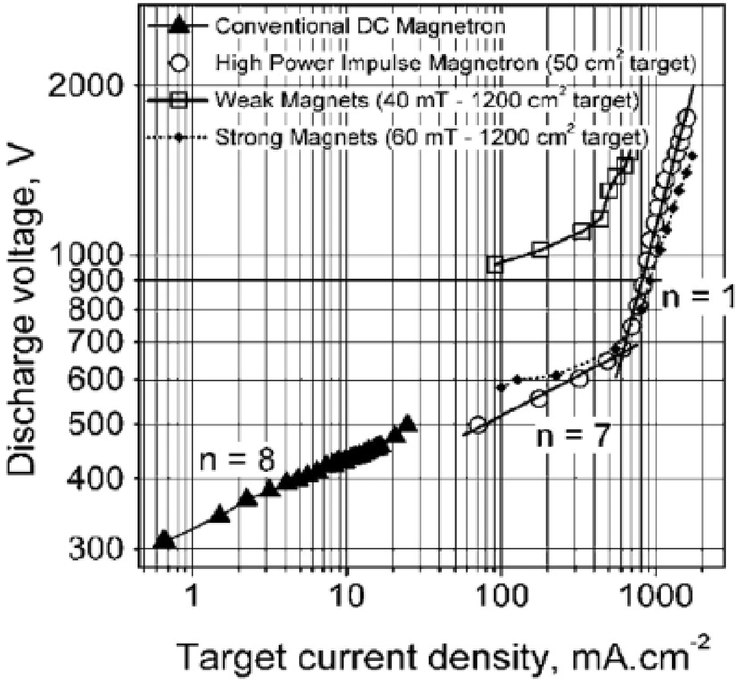
IMPULSE + Kick
200Hz to 20kHz
Positive polarity pulse

P. Raman, PhD Dissertation, UIUC 2016

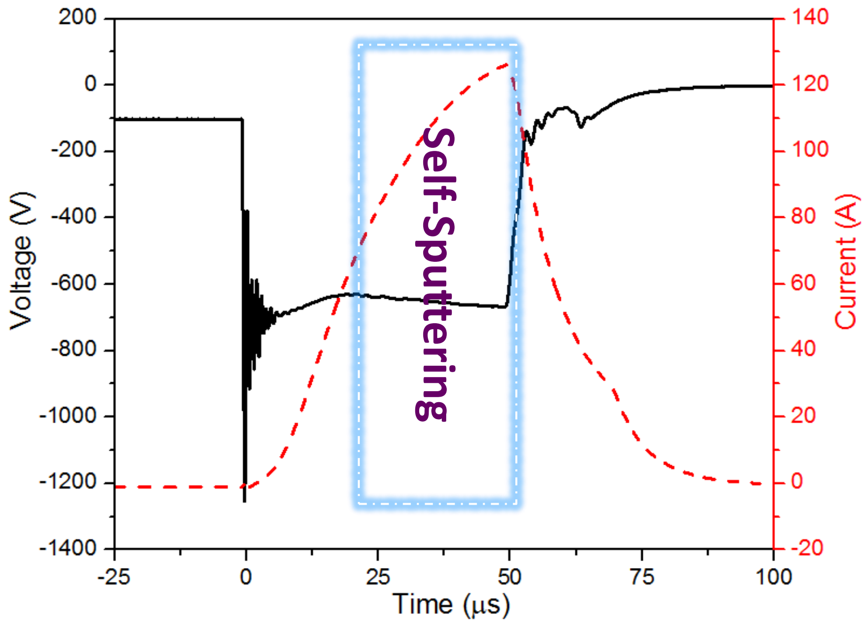
What is HIPIMS? HiPIMS is a type of iPVD technique

Technique	Discharge voltage(V)	Current density (A/cm²)	Peak power density (W/cm²)	Frequency (Hz)	Duty cycle(%)	Electron density(m^{-3})	Deposition Ion fraction (%)	Deposition ion energy (eV)
DC	**300-1000**	**<0.1**	**1**			**10^{15}-10^{17}**	~1	2-10
HiPIMS	**500-2000**	**3-4**	**1000-3000**	**50-5000**	**0.5-5**	**10^{18}-10^{19}**	>10	10-100

$I \propto V^n$



I–V characteristics Of Magnetron Discharges[1]



HiPIMS VI Oscillogram on a 4'' magnetron with an aluminum target.

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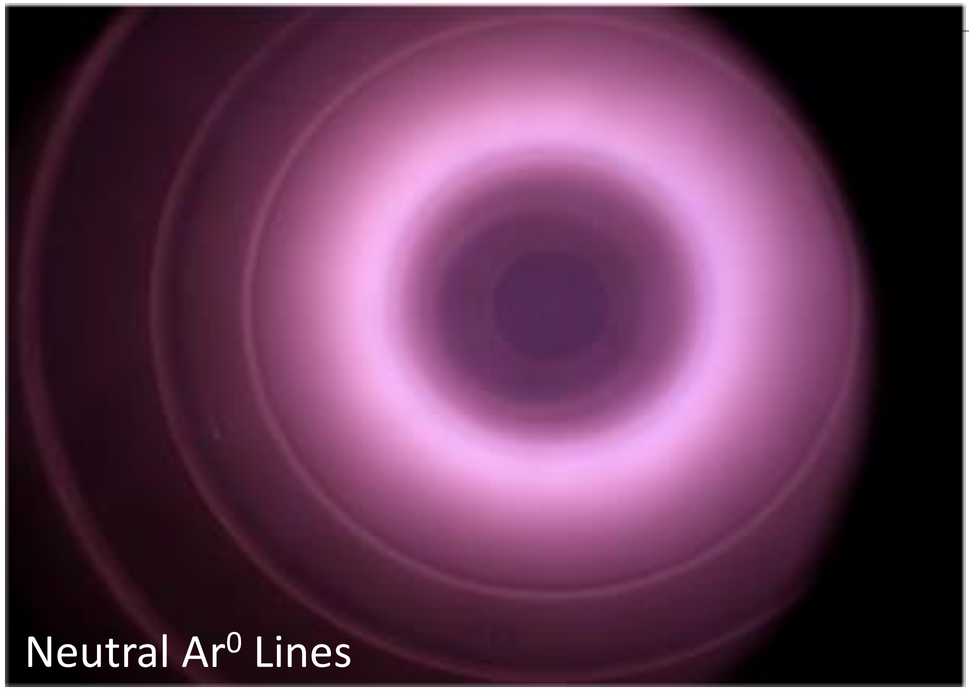
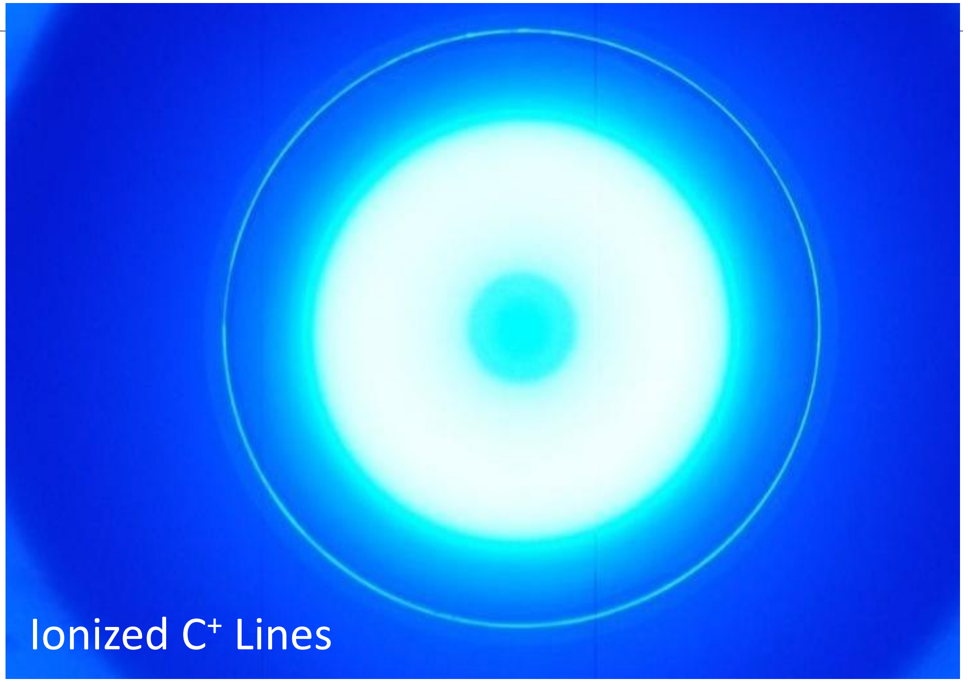
1. Ehiasarian, *Pure & Applied Chemistry* 82.6 (2010).

High-Power Impulse Magnetron Sputtering



DC Sputtering (dominantly pink argon plasma)
<$0.01 A/cm^2$ current density
0.1-1A current
~1-3% ionized sputtered metal

Pulsed Discharge
Striking HiPIMS
Color Change

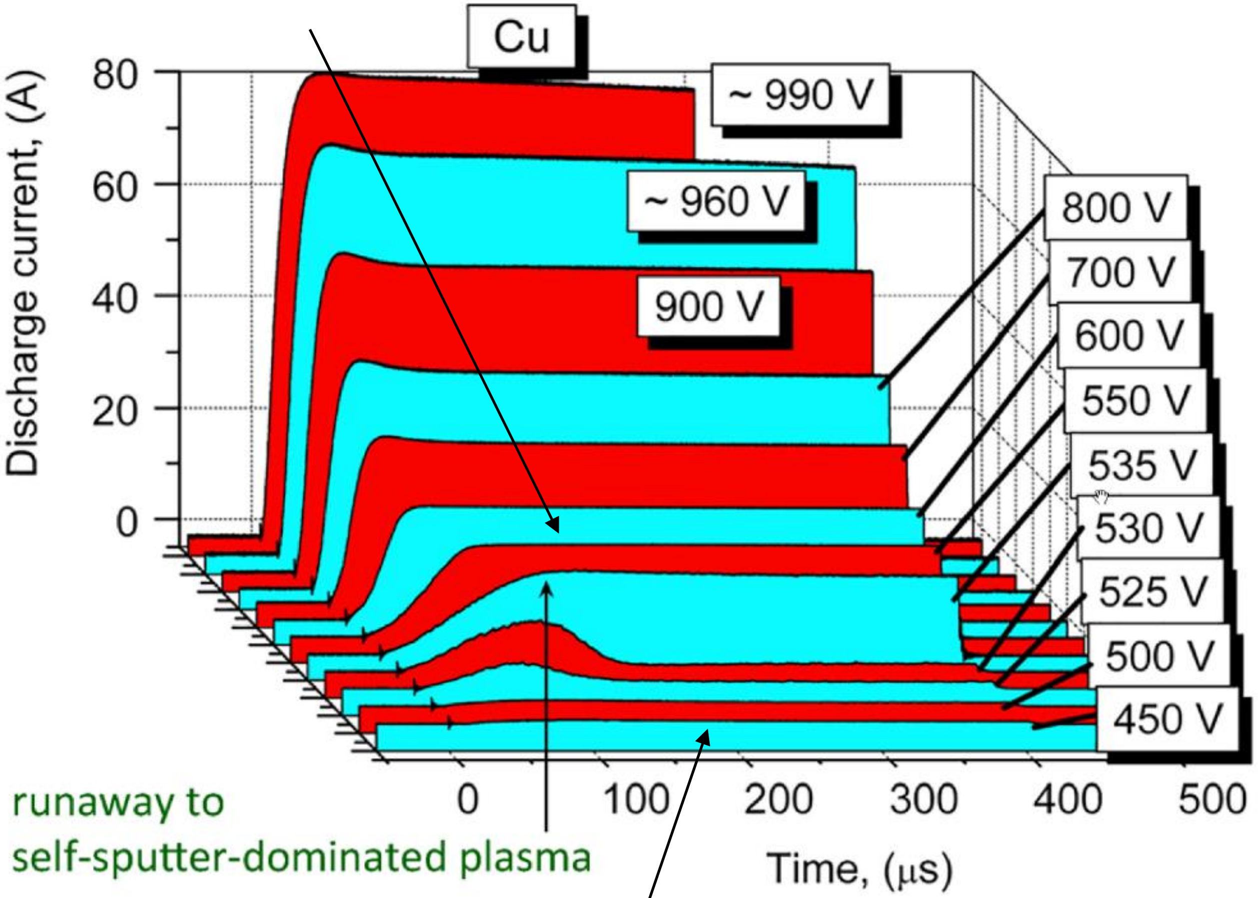


HiPIMS Sputtering (dominantly carbon plasma)
>$1A/cm^2$ peak current density
10-100's A currents
~10-90% ionized sputtered metal

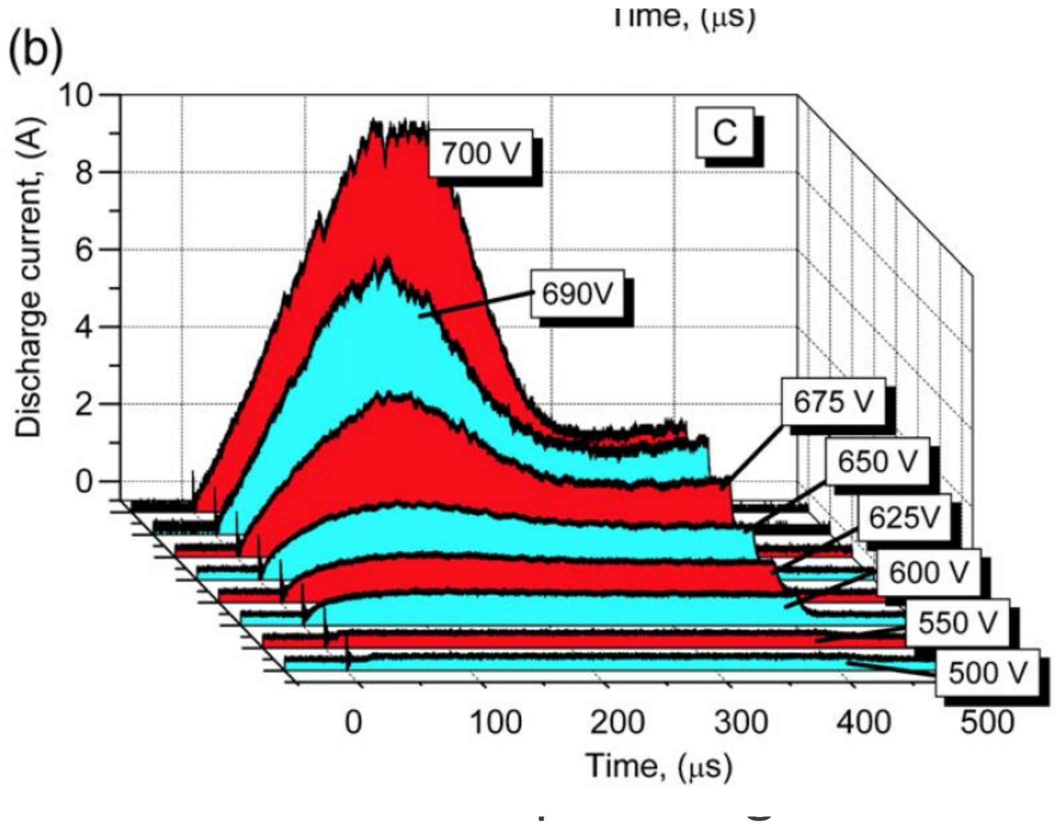
Same Sputter Gun, Time-Average Power, Material & Pressure → Completely Different Plasmas & Films

What Is Traditional HiPIMS?

HiPIMS Here



runaway to
self-sputter-dominated plasma



DC Sputtering Here

Anders et al, J. Appl. Phys. 102 (2007) 113303

Self-Sputtering & Recycling

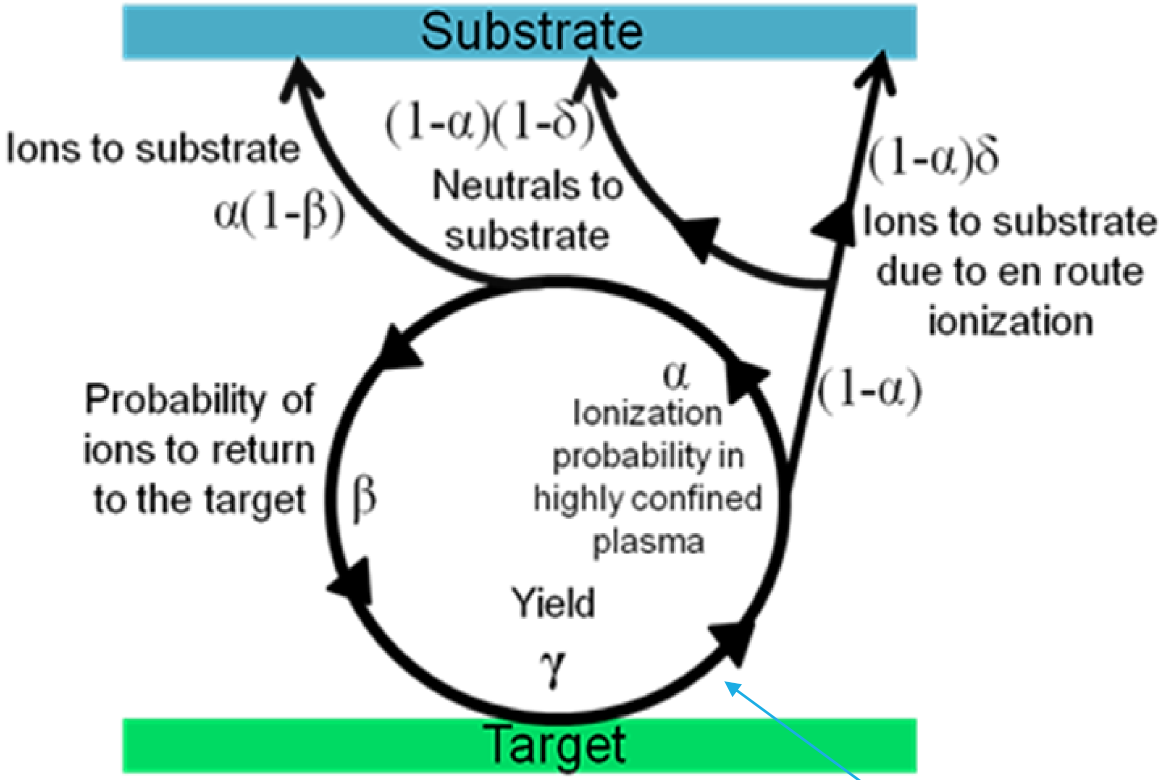
Traditional HiPIMS has a **LOWER** deposition rate due to RECYCLING

Self-sputtering:

- Target atom is ionized, and it returns to sputter more target atoms (yield > 1)
- Equal mass = maximum sputter yield & increase in current

Higher plasma density NEAR target → higher ionization → **greater recycling**

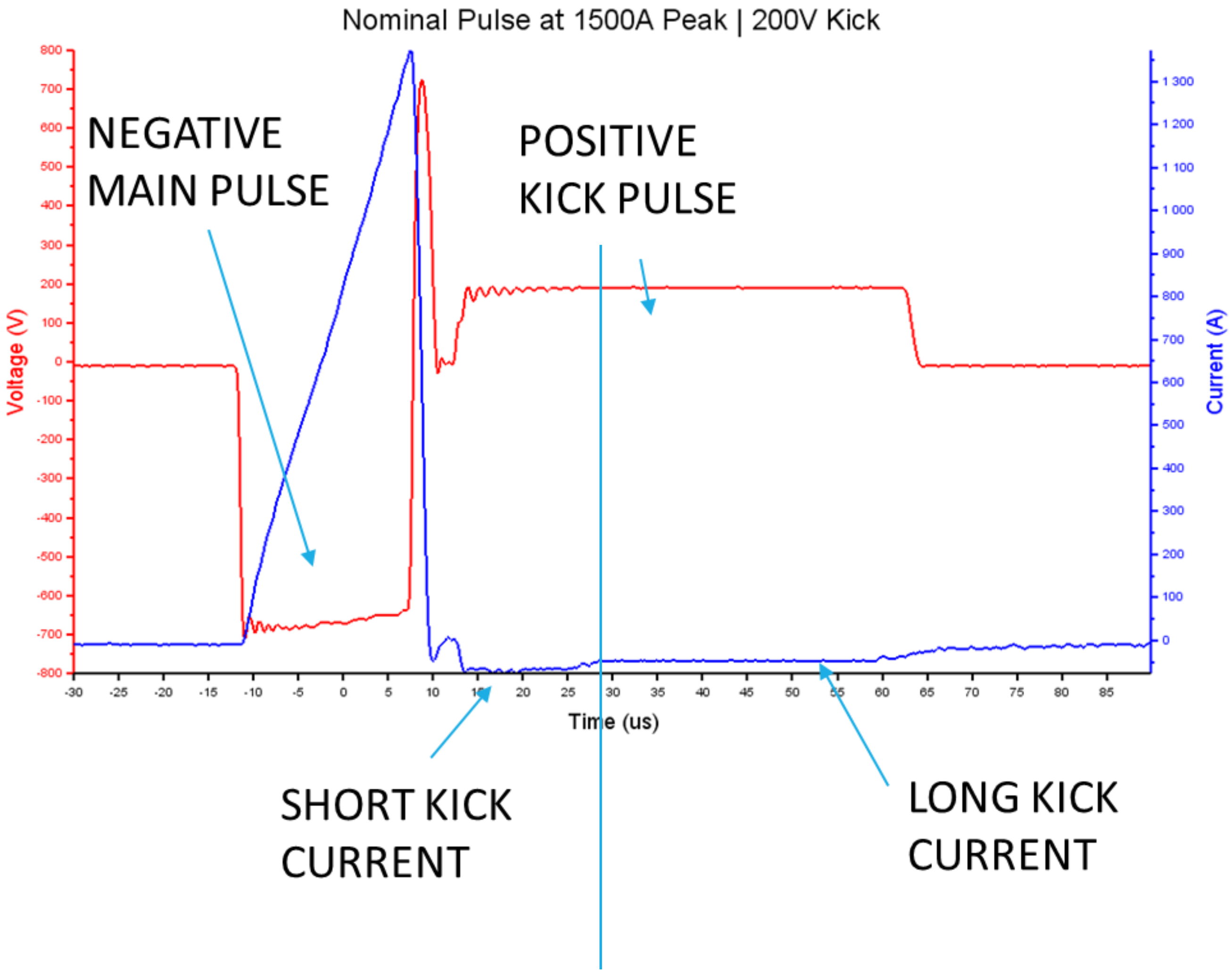
Recycled ions do not reach the substrate lowering deposition rate

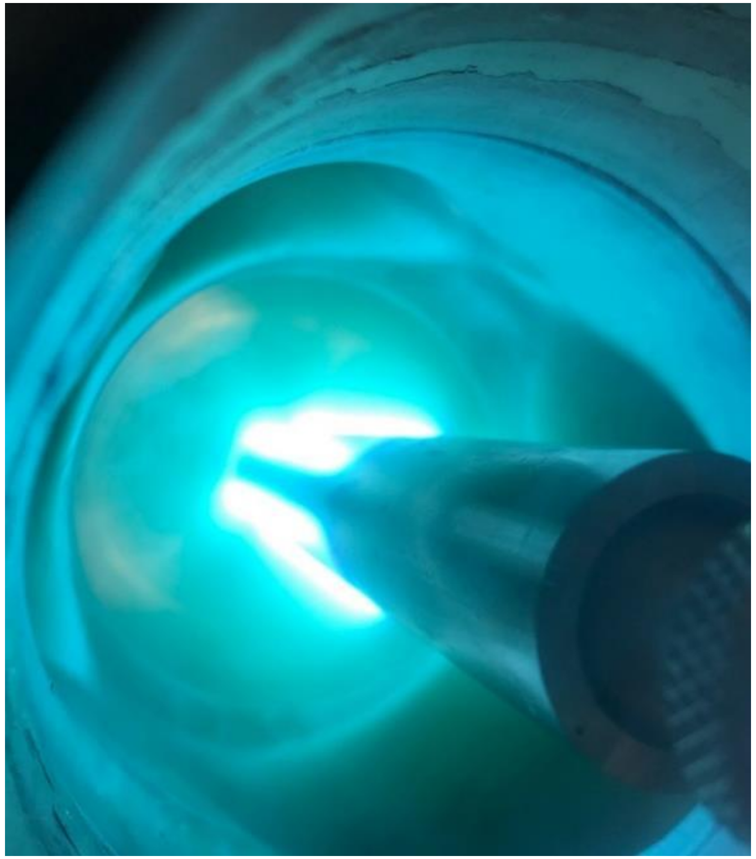


DENSE PLASMA IONIZES

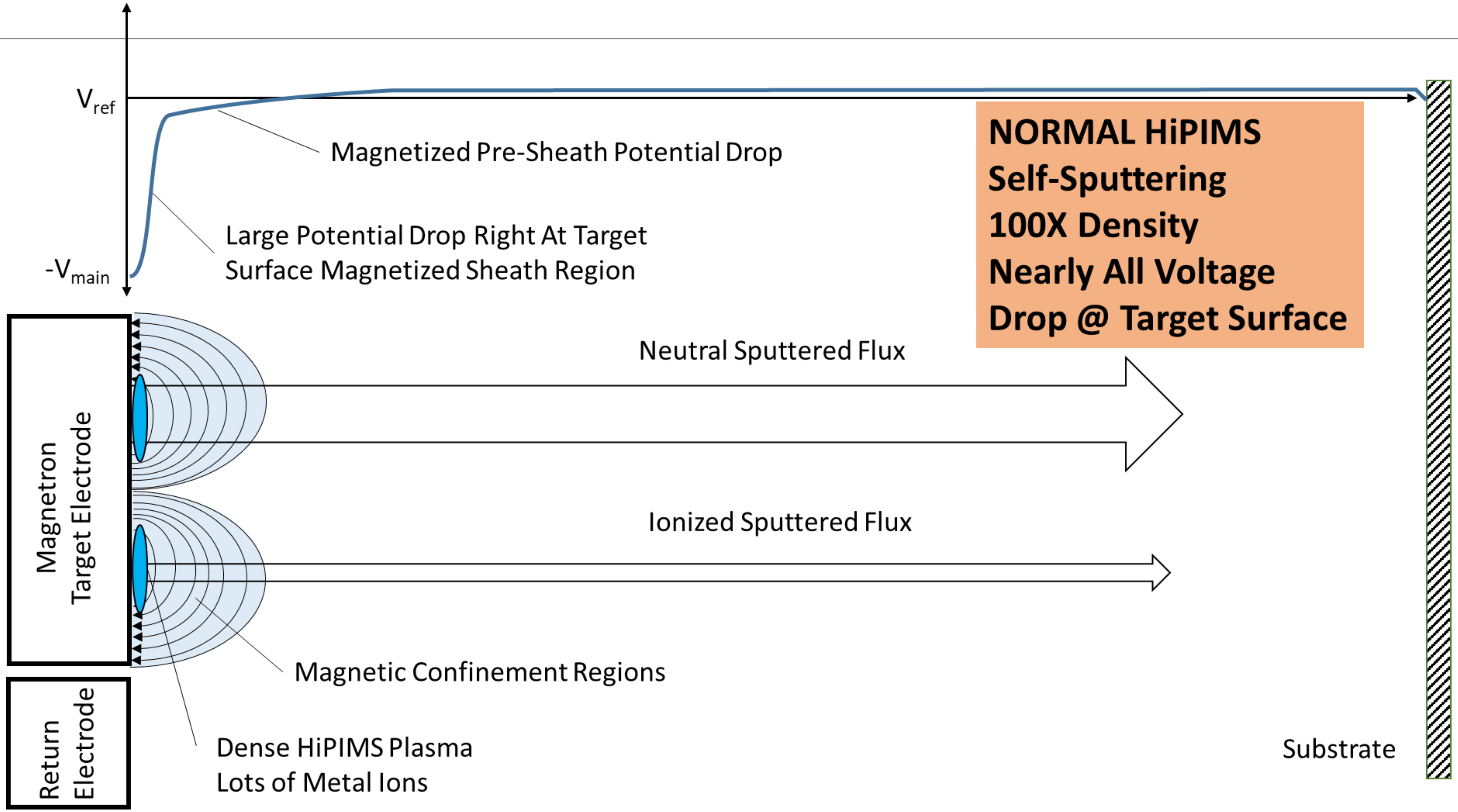
Raman et al, J. Appl. Phys., 120 (2016) 163301

20µs Triangular Pulse Waveform + Positive Kick™





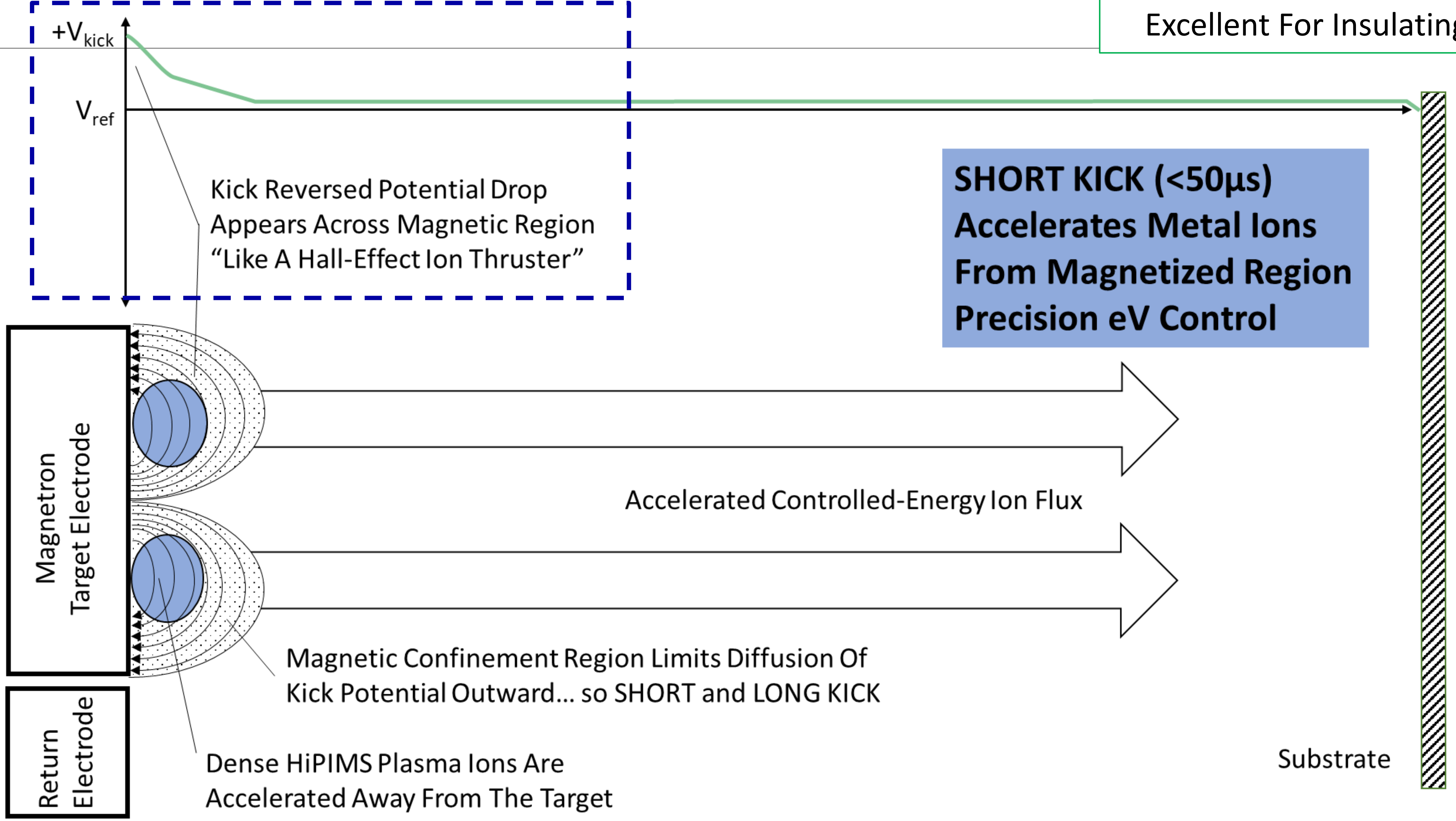
Normal HIPIMS Pulse



NORMAL HiPIMS
Self-Sputtering
100X Density
Nearly All Voltage
Drop @ Target Surface

Short Kick

Works Very Well At Short Working Distances Or Lower Pressure
Excellent For Insulating Substrates



Kick Reversed Potential Drop Appears Across Magnetic Region "Like A Hall-Effect Ion Thruster"

SHORT KICK (<50µs)
Accelerates Metal Ions From Magnetized Region
Precision eV Control

Accelerated Controlled-Energy Ion Flux

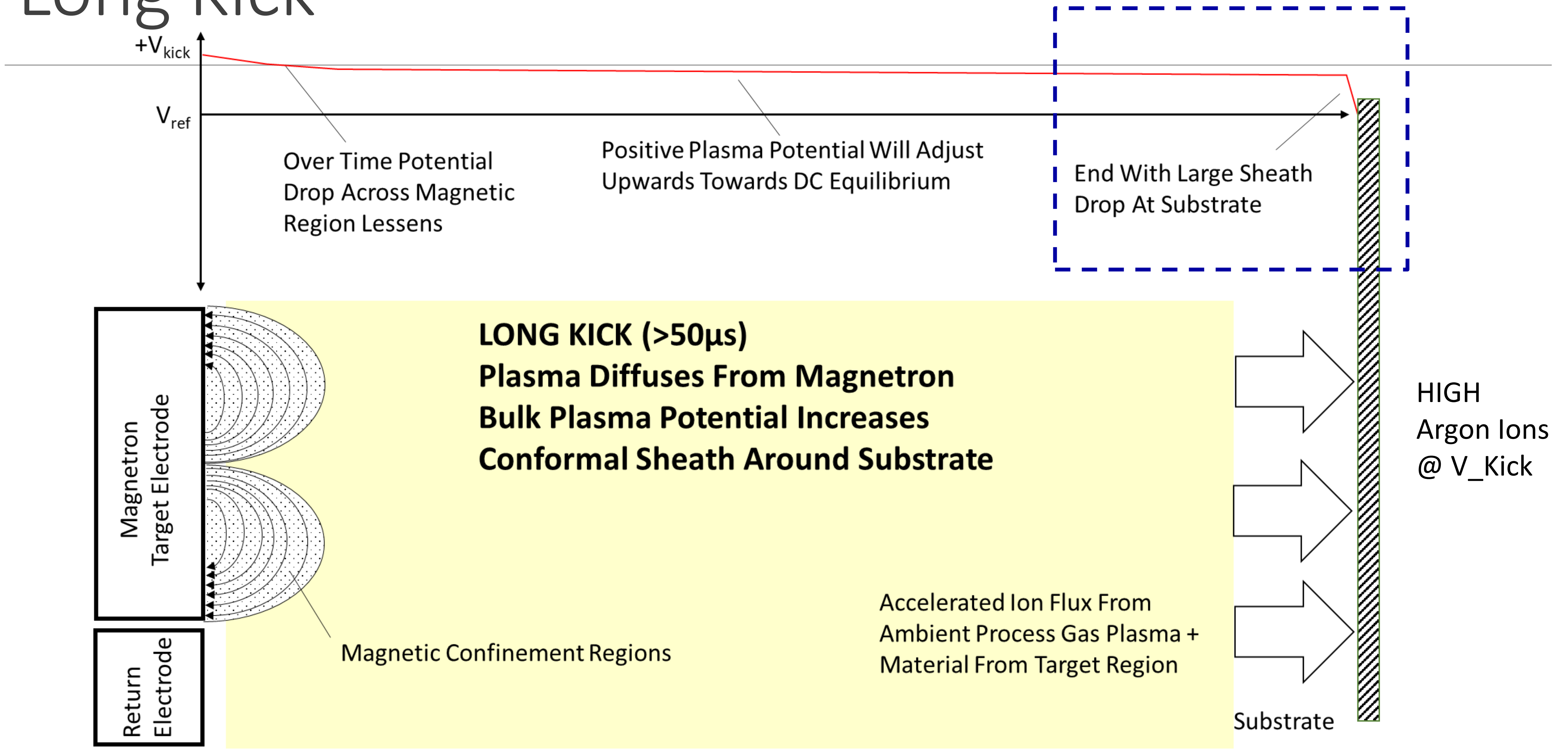
HIGH
Metal Ions
@V_Kick

Magnetic Confinement Region Limits Diffusion Of Kick Potential Outward… so SHORT and LONG KICK

Dense HiPIMS Plasma Ions Are Accelerated Away From The Target

Long Kick

Works Very Well At Higher Pressures



Over Time Potential Drop Across Magnetic Region Lessens

Positive Plasma Potential Will Adjust Upwards Towards DC Equilibrium

End With Large Sheath Drop At Substrate

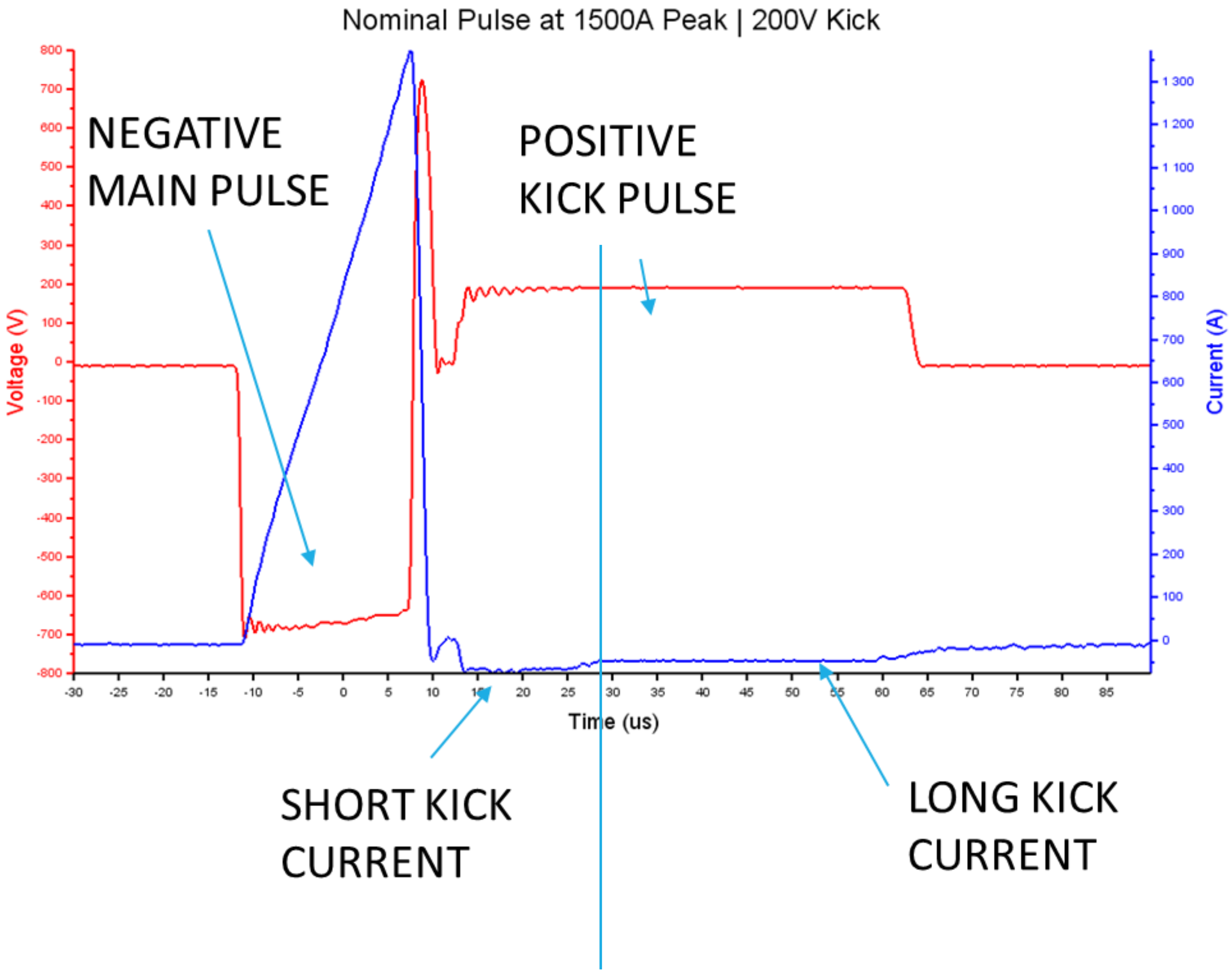
LONG KICK (>50µs)
Plasma Diffuses From Magnetron
Bulk Plasma Potential Increases
Conformal Sheath Around Substrate

Magnetic Confinement Regions

Accelerated Ion Flux From Ambient Process Gas Plasma + Material From Target Region

HIGH
Argon Ions
@ V_Kick

20µs Triangular Pulse Waveform + Positive Kick™

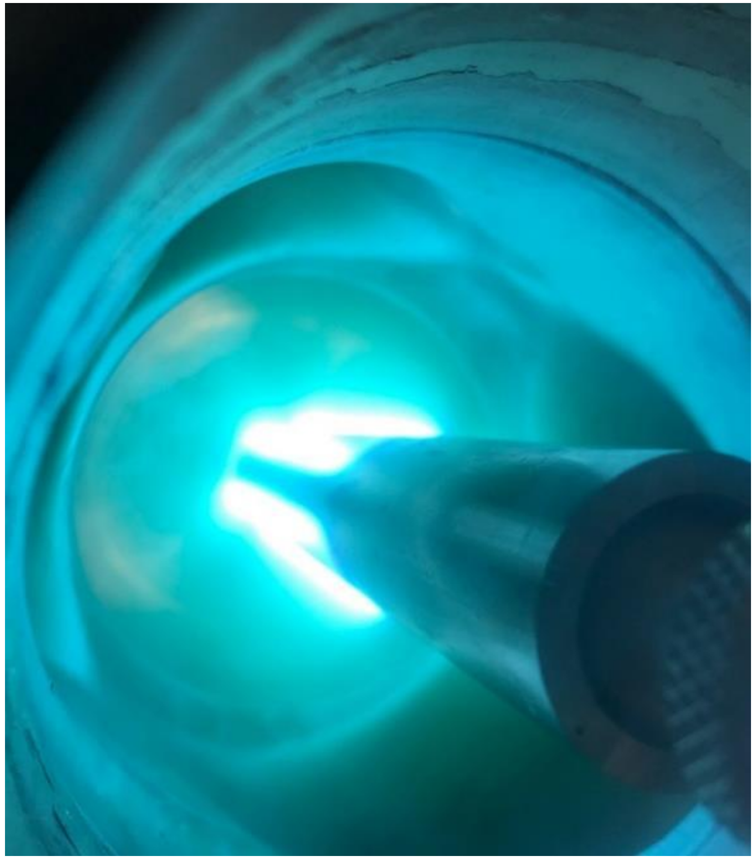


NEGATIVE MAIN PULSE

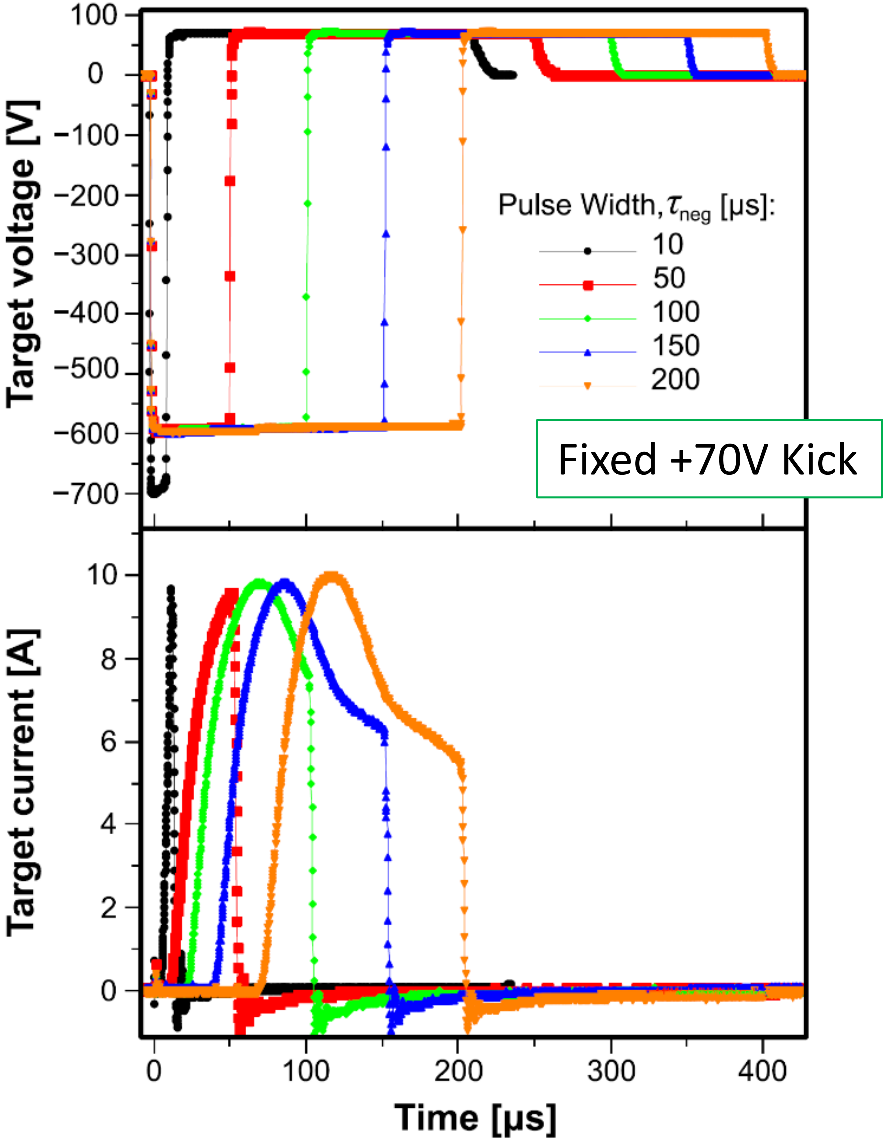
POSITIVE KICK PULSE

SHORT KICK CURRENT

LONG KICK CURRENT

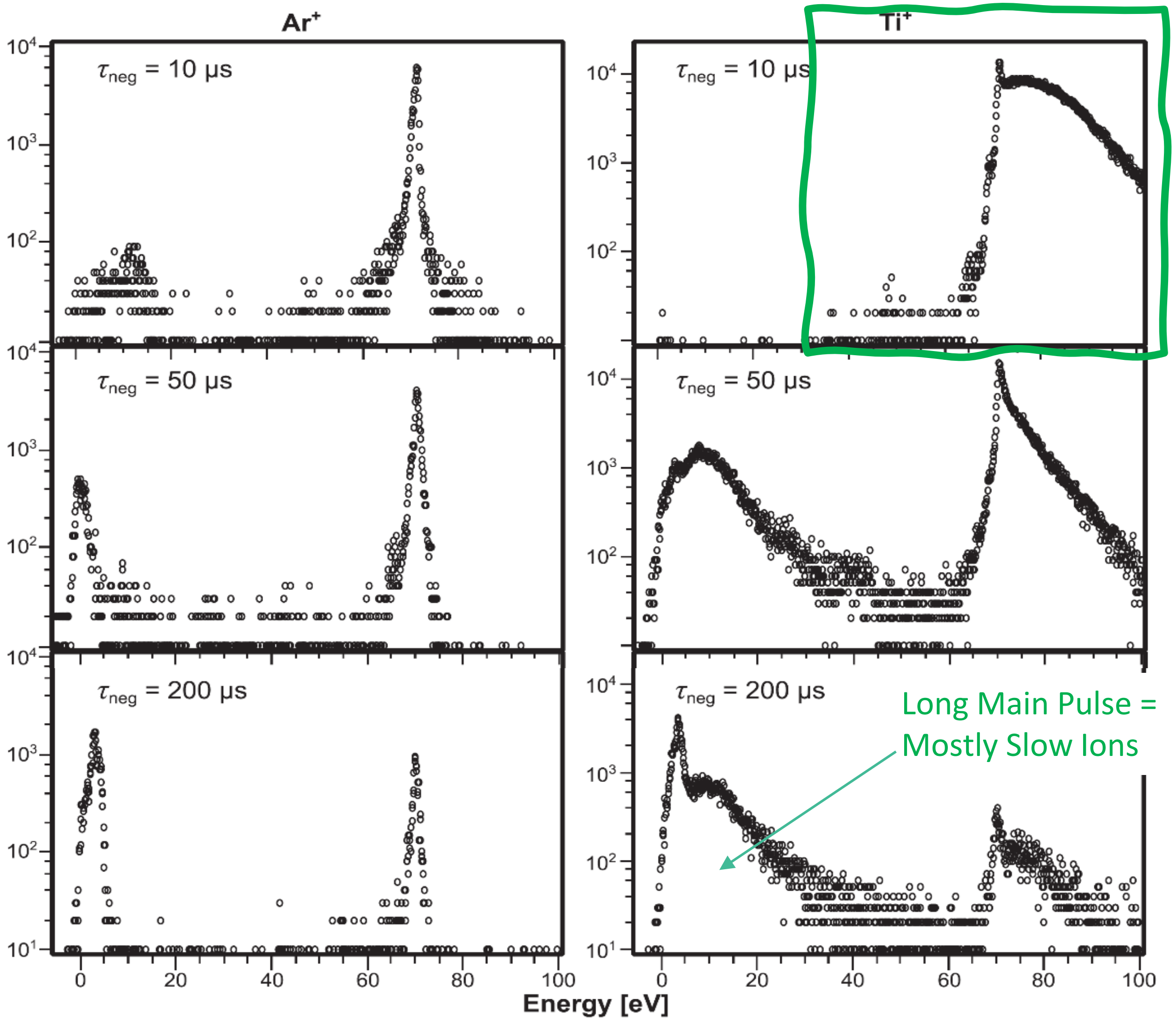


IEDF’s



Fixed +70V Kick

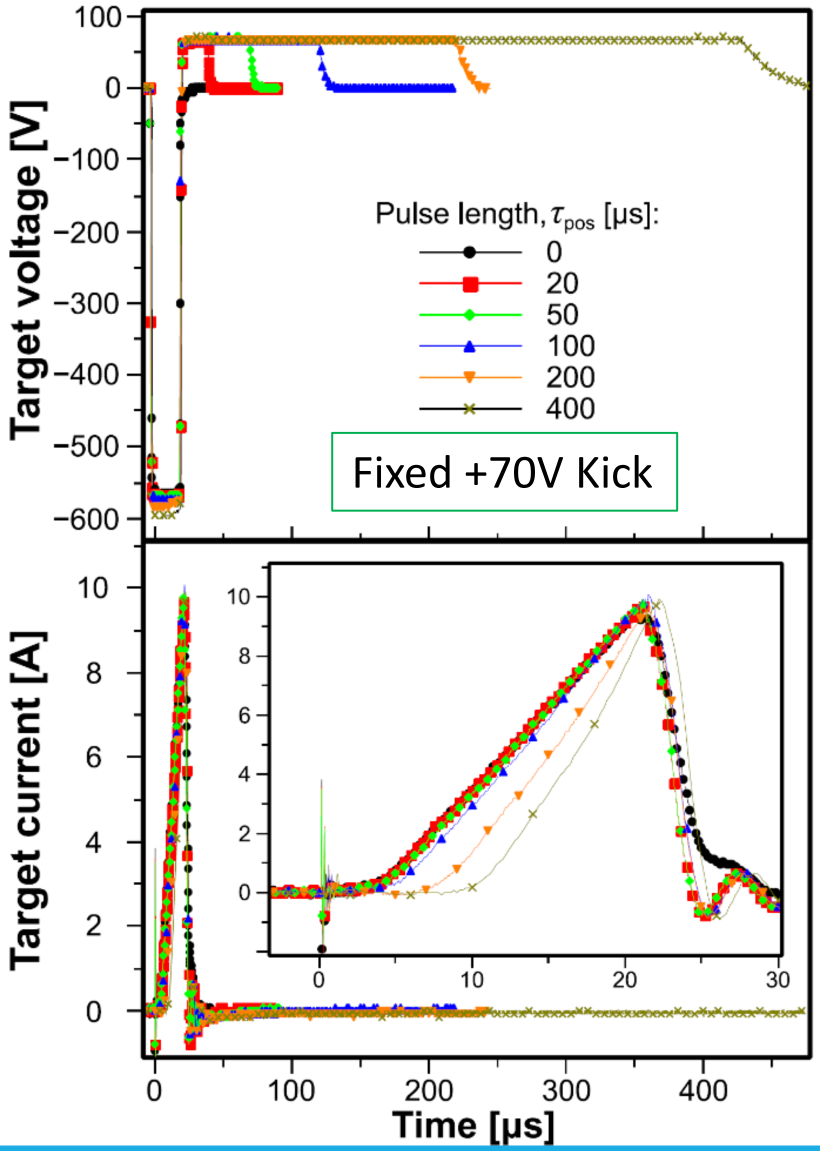
Short Main Pulse =
Only Kicked Metal Ions



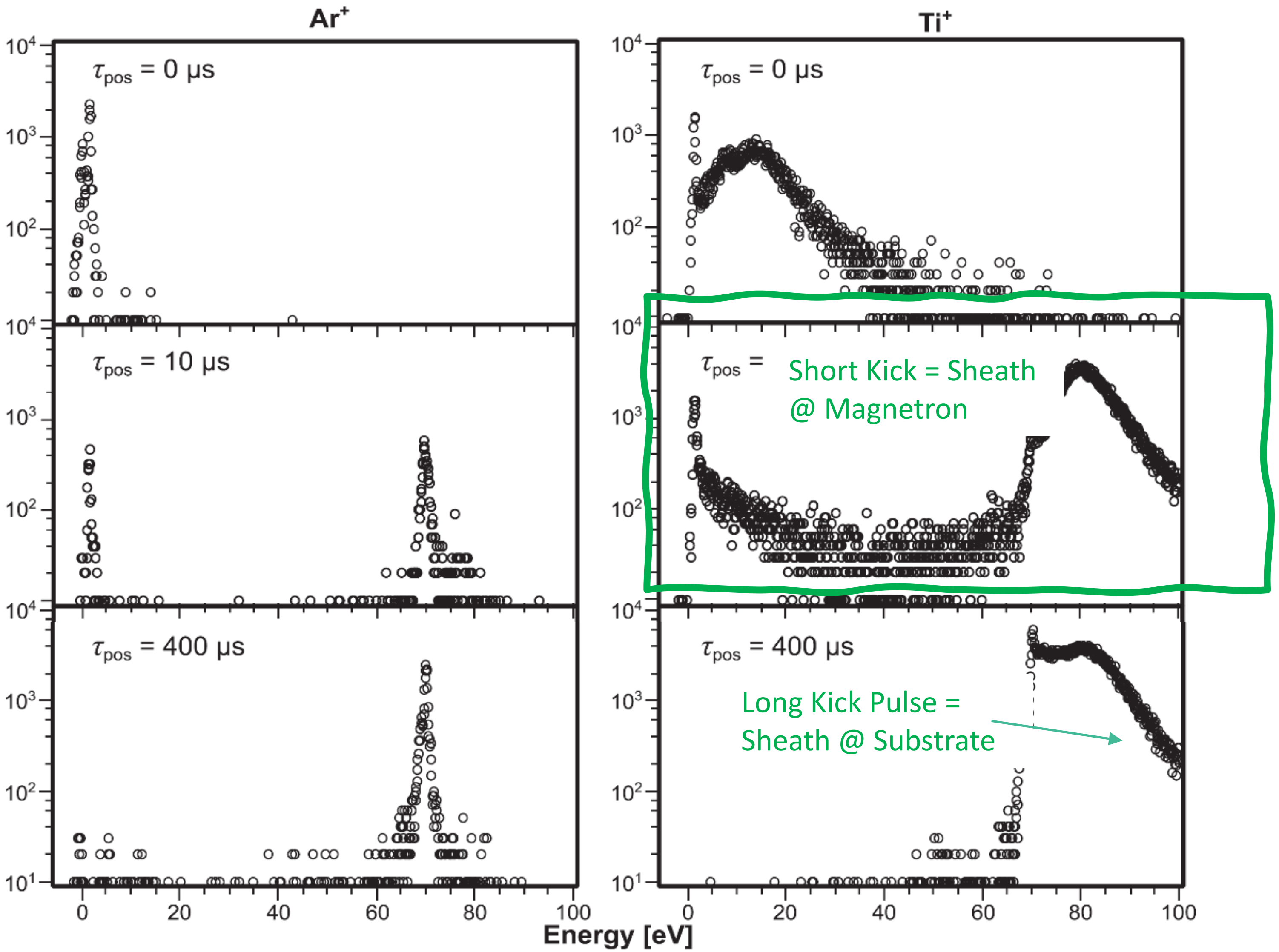
Long Main Pulse =
Mostly Slow Ions

Viloan *et al* 2020 *Plasma Sources Sci. Technol.* **29** 125013

IEDF’s



Fixed +70V Kick



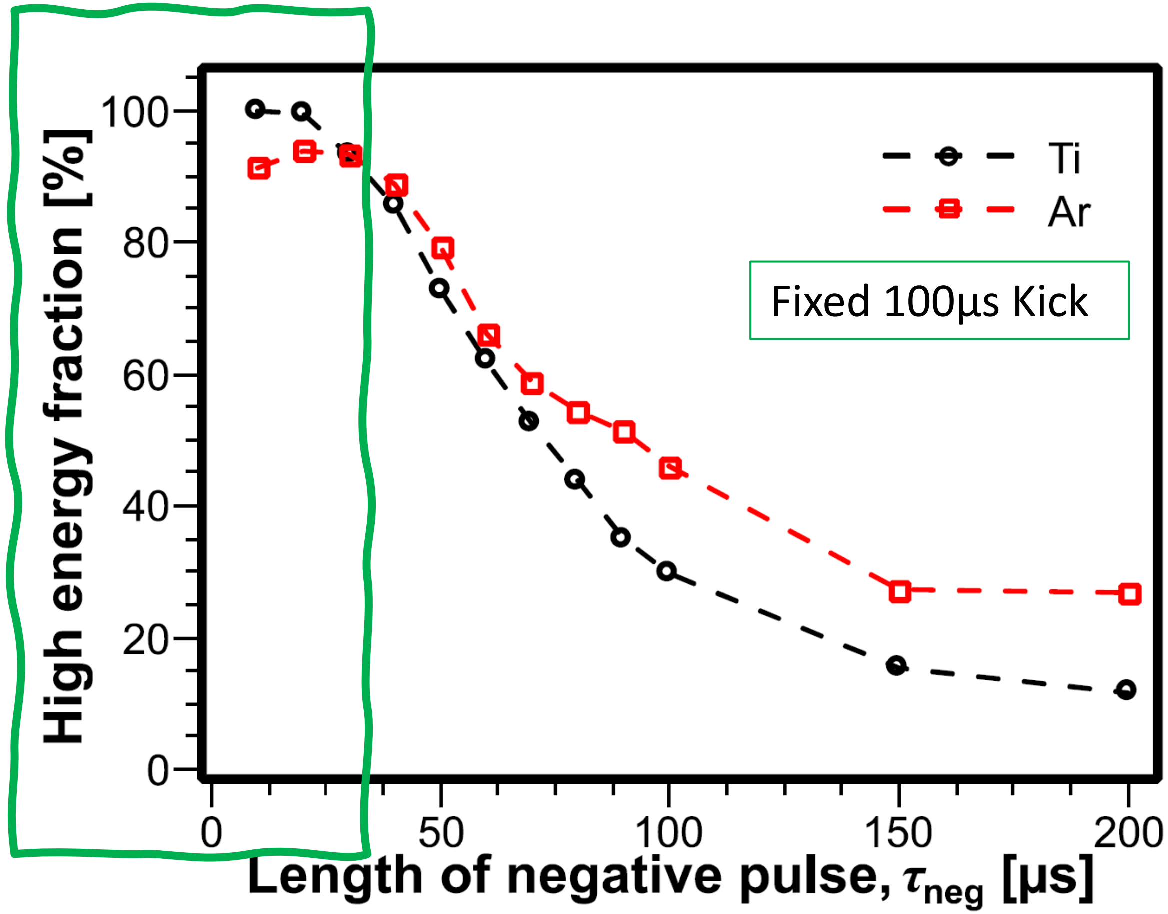
Short Kick = Sheath @ Magnetron

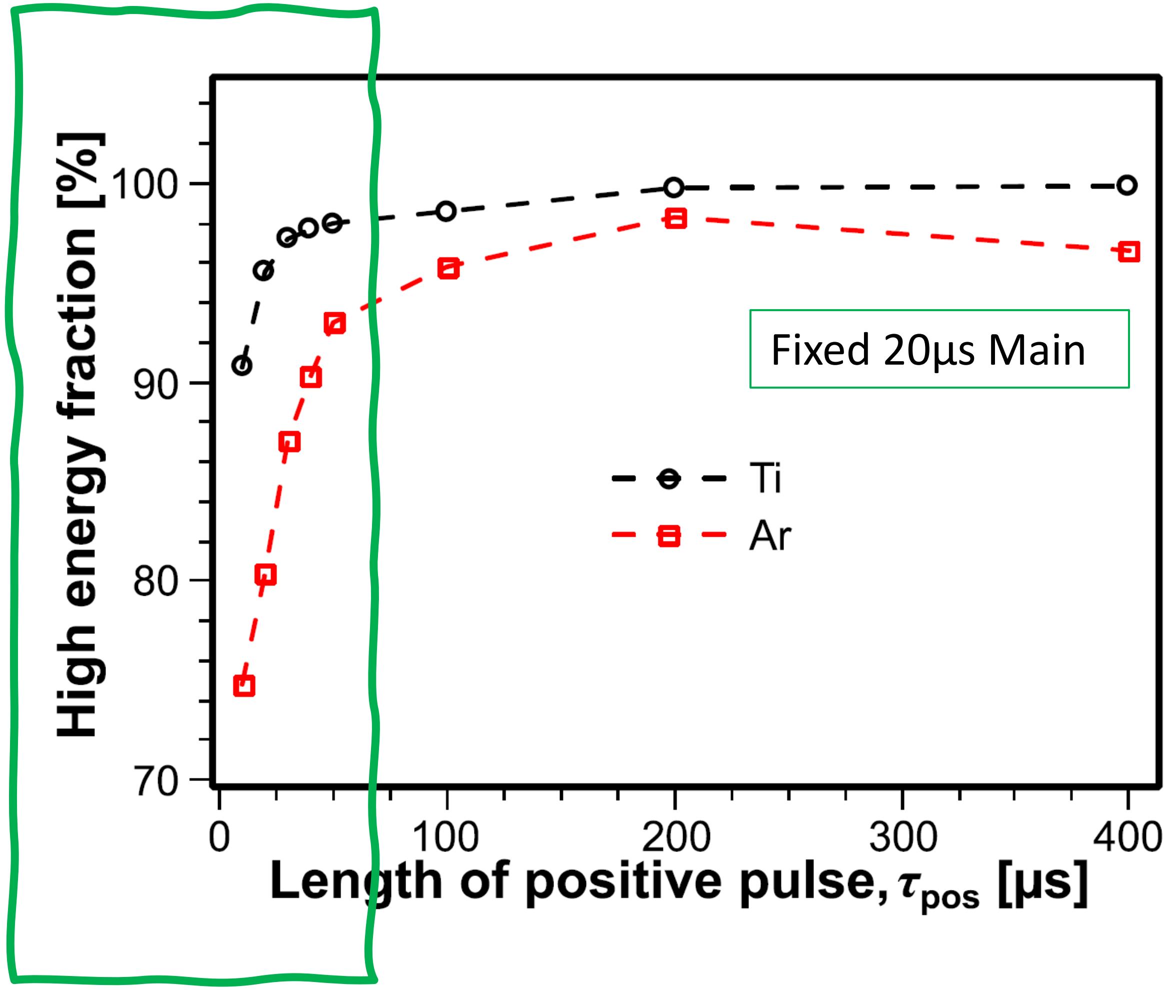
Long Kick Pulse = Sheath @ Substrate

Viloan *et al* 2020 *Plasma Sources Sci. Technol.* **29** 125013

Ion Ratios

Short Main Negative Pulse + Short Positive Kick → More Metal Ion % to Noble Gas Ion %





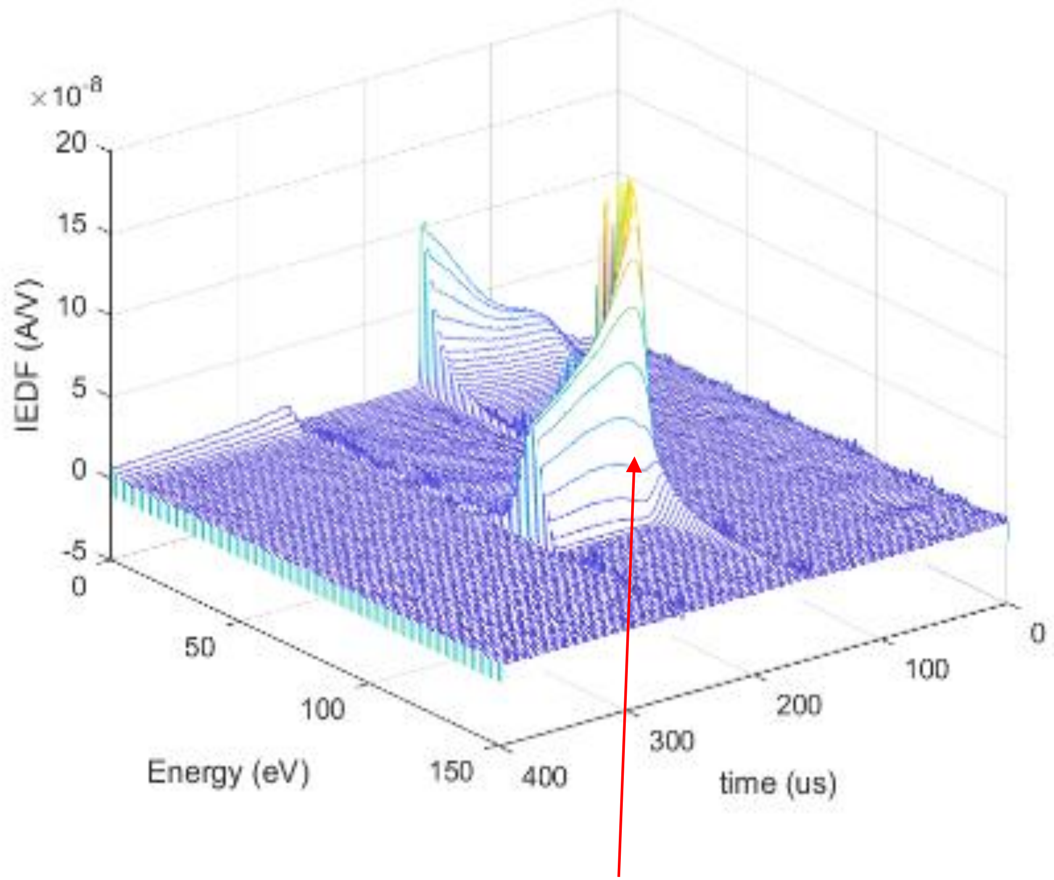
Viloan *et al* 2020 *Plasma Sources Sci. Technol.* **29** 125013

IEDF Measured

Upshift Ions By +V_{kick}

Short Kick Phase: 10-20µs

Precision Ion Energy Control



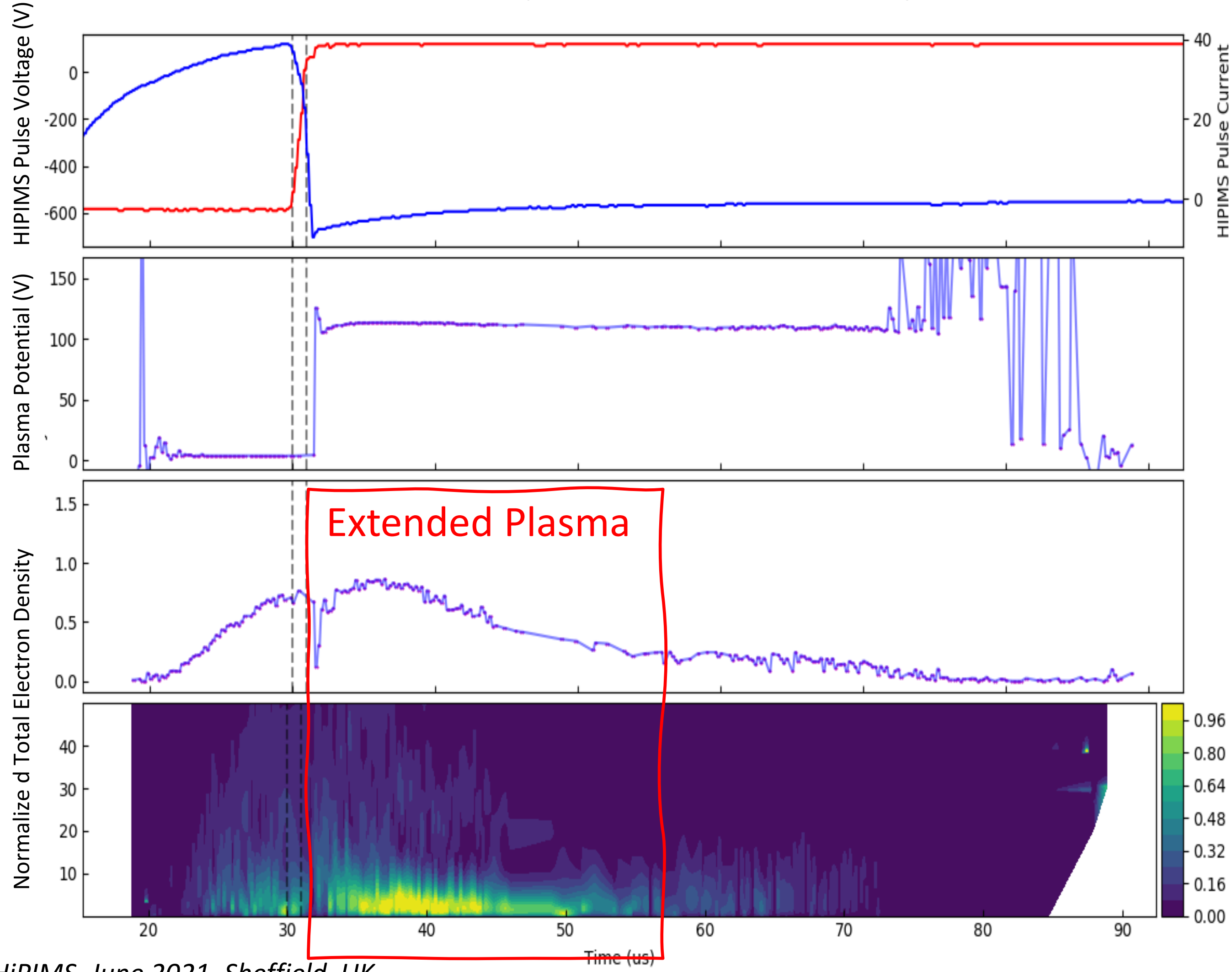
Short Kick Metal Ions

EEDF Measured

Increase In Plasma Density @ Substrate

Short Kick Phase: 10-20µs

Excellent For Reactive Deposition, Conformality, Vias



Extended Plasma

What Is The Positive Kick™ (Key Differentiator)

Rapidly turn off the main negative discharge pulse…and REVERSE it positive!

- The amplitude, duration and onset delay variables are set by the end user

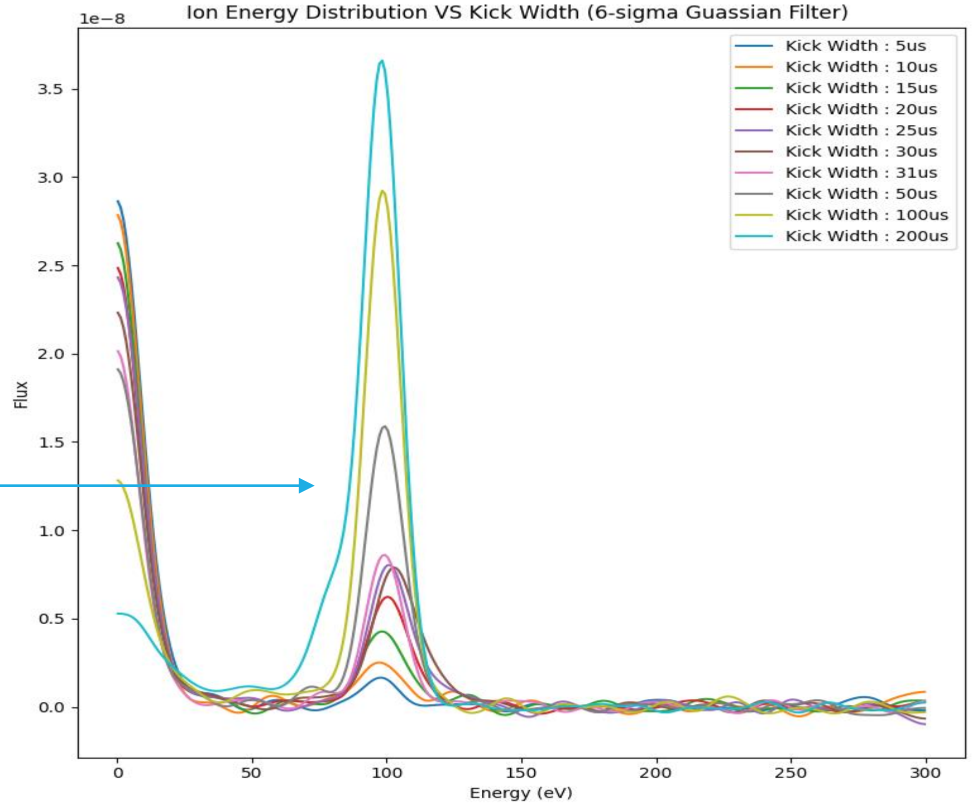
An accelerating potential develops across the magnetic confinement zone on the magnetron

- Like Hall-effect thrusters on satellites…
- Metal ions are KICKED towards the substrate for greater utilization and deposition rate

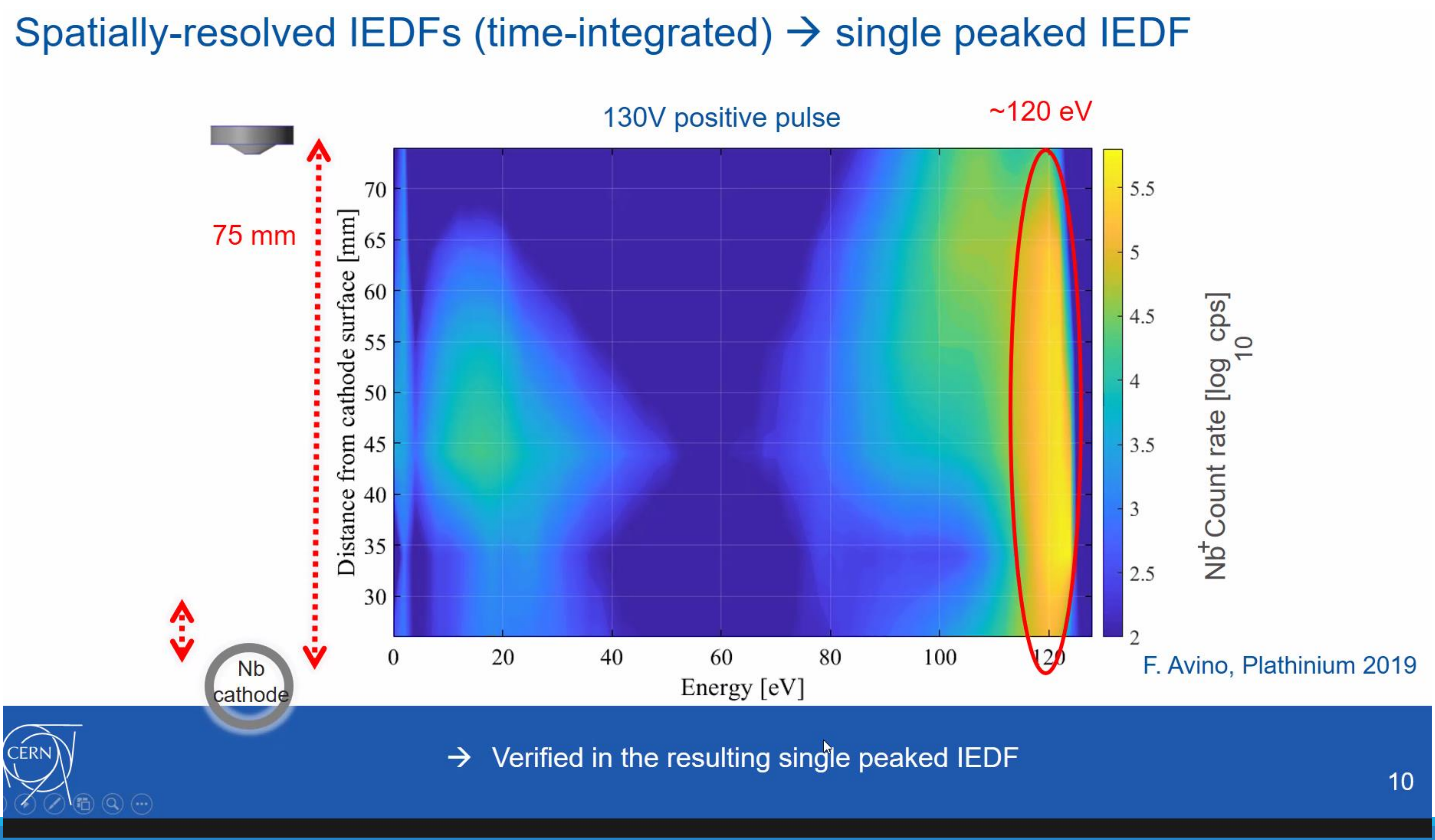
Plasma potential rises across the expanding plasma to generate a quasi-conformal sheath at the substrate

- Excellent ion energy control with eV's of precision
- **E***

D. Ruzic, 96th IUVISTA Workshop, Virtual, Jan 2021



Gridded Energy Analyzer: 100V Positive Kick™

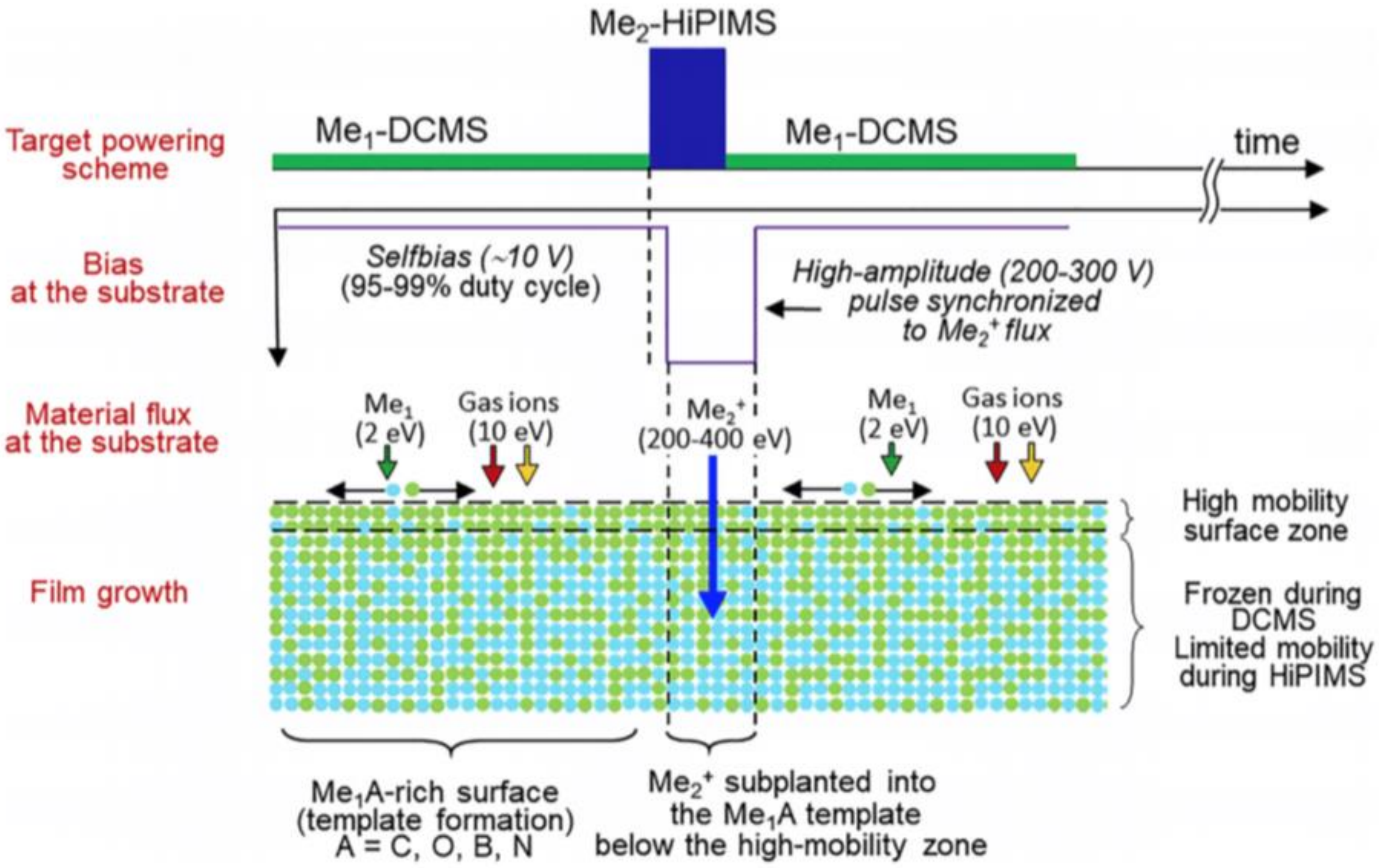


Spatially-resolved IEDFs (time-integrated) → single peaked IEDF

F. Avino, Plathinium 2019

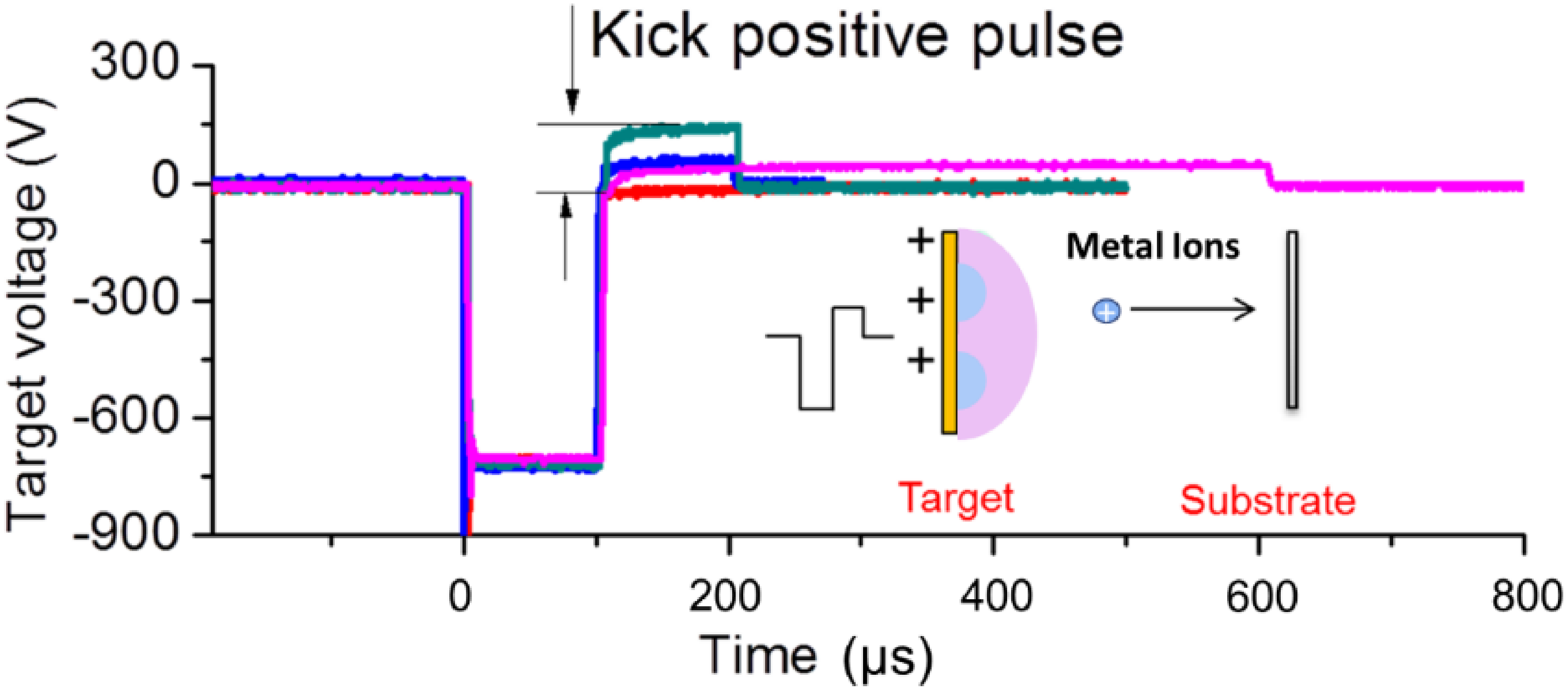
→ Verified in the resulting single peaked IEDF

HIPIMS with Synchronized Bias

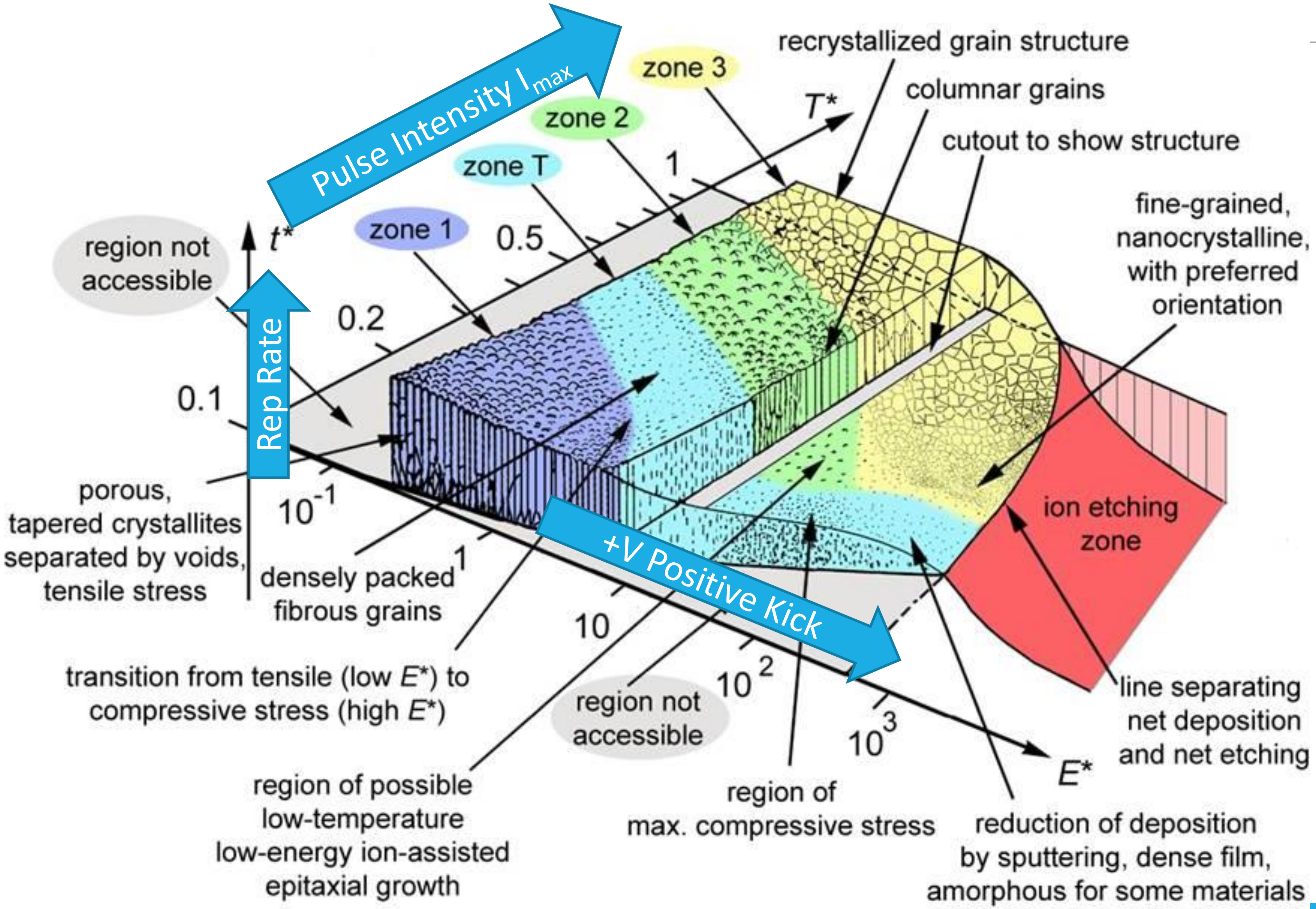


Greczynski J. Appl. Phys. **127**, 180901 (2020); doi: 10.1063/1.5141342

HIPIMS with Positive Kick



What Can We Do with HIPIMS



Access More Of The Thornton Diagram & Control Film Stress

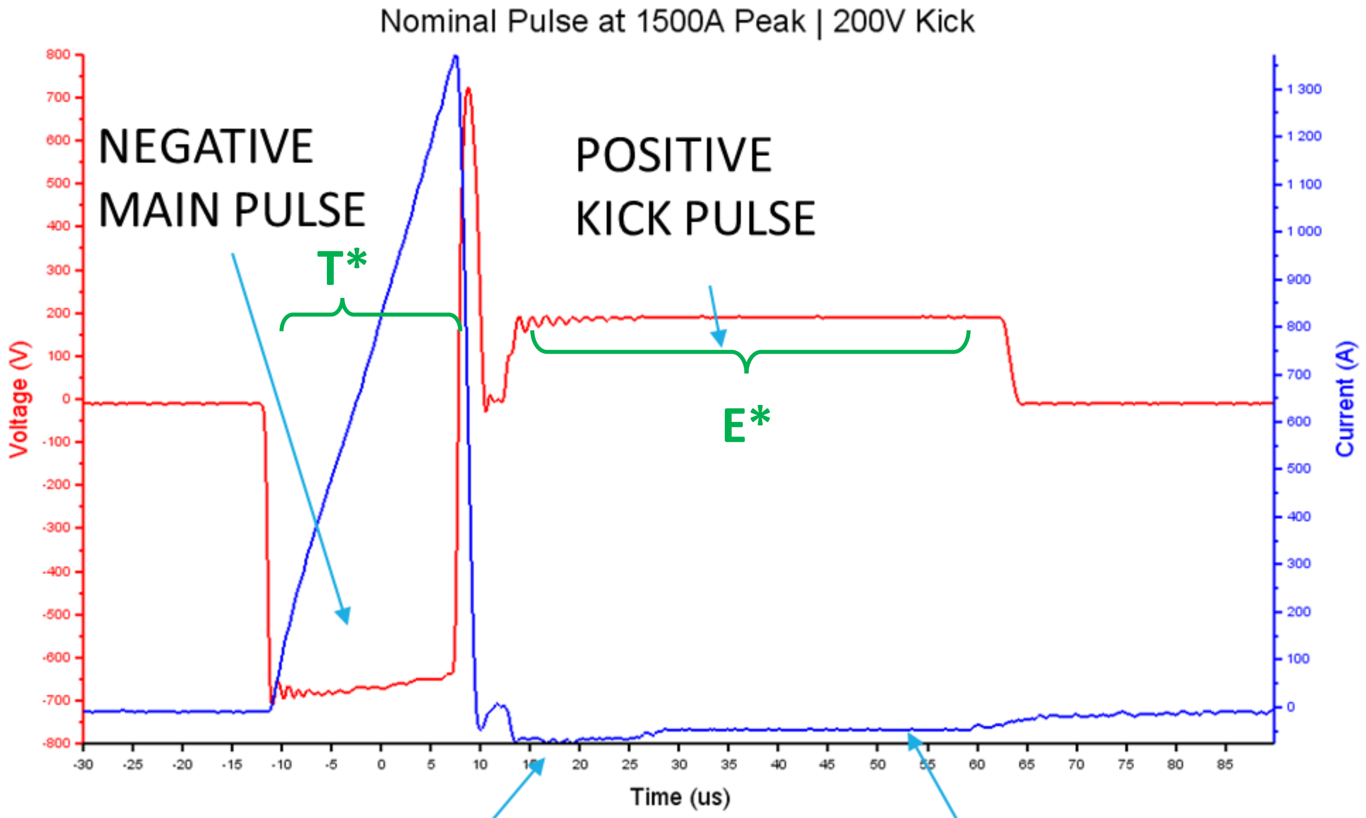
Positive Kick™ gives controlled ion energy *E axis control**

Ultra-Fast Pulsing gives larger IMPULSES of deposition flux… acting like *T control**

Higher Rep Rate = more Kick Pulses = more *t deposition rate**

Anders, Thin Solid Films, Volume 58 Issue 15, 4087-4090 (2010)

A Simplified View



NEGATIVE MAIN PULSE

POSITIVE KICK PULSE

SHORT KICK CURRENT

*Target Ions

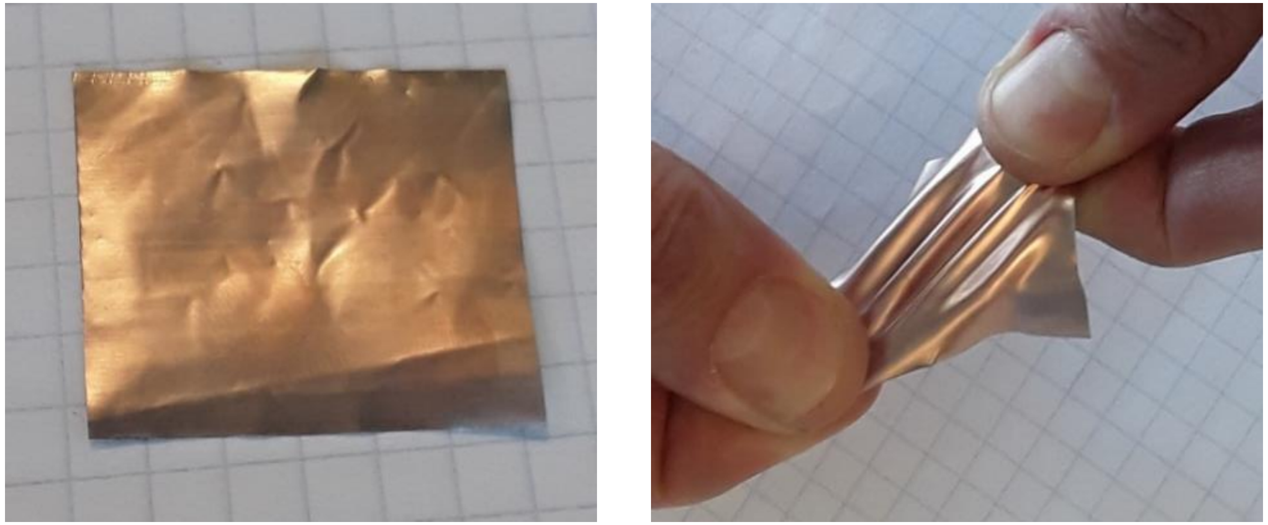
LONG KICK CURRENT

**Conformal Ions

Coating Plastics

Aluminum onto as-received PMMA sheet

- Well adherent, Scotch Tape Test
- Retains smoothness without thermal damage
- Single pass sputtering
- Very reflective

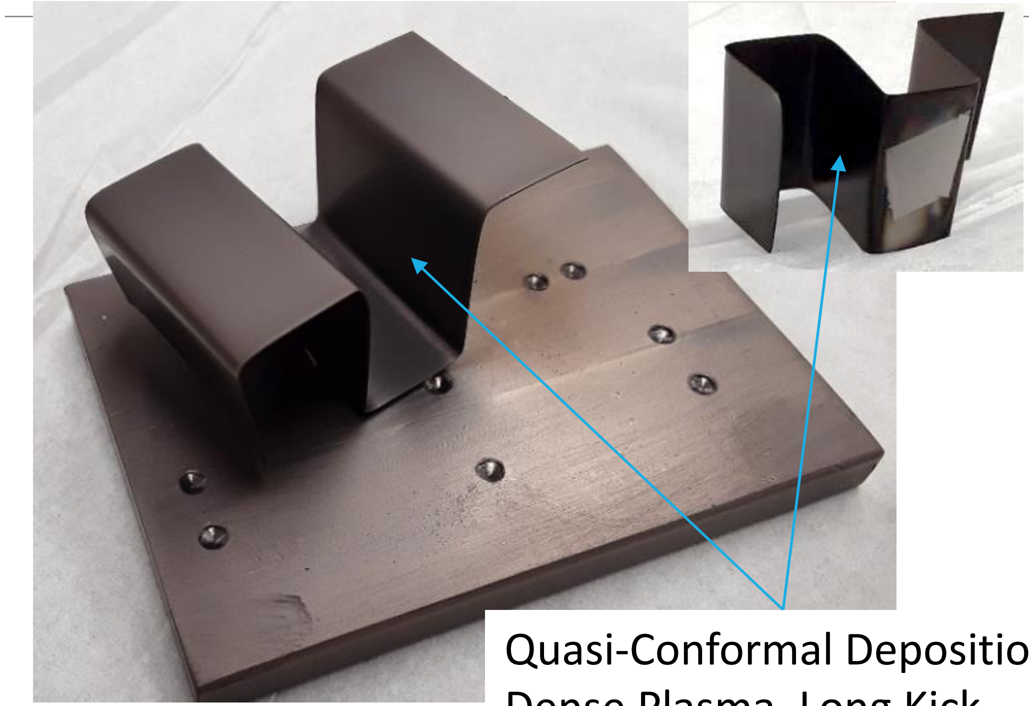


Cu/Cr on PTFE

Excellent adhesion

Stays flexible and conductive

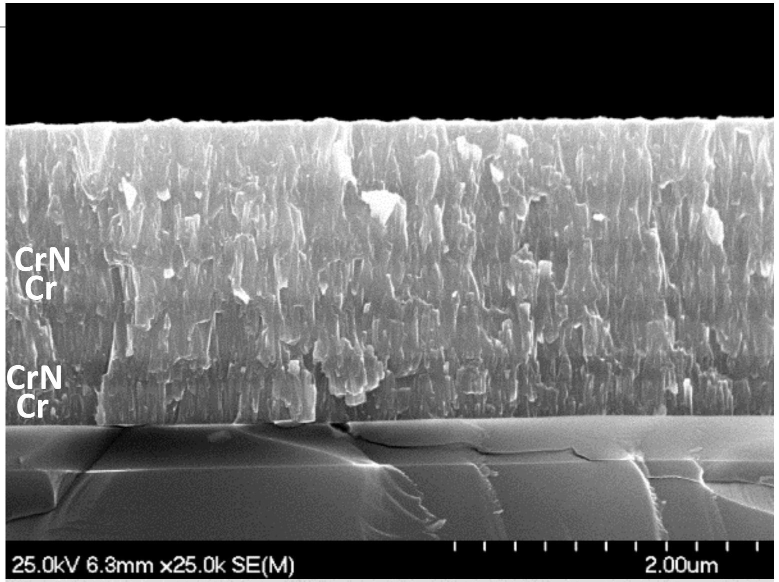
TiAlN/TiN Coatings & Cr/CrN Multilayers

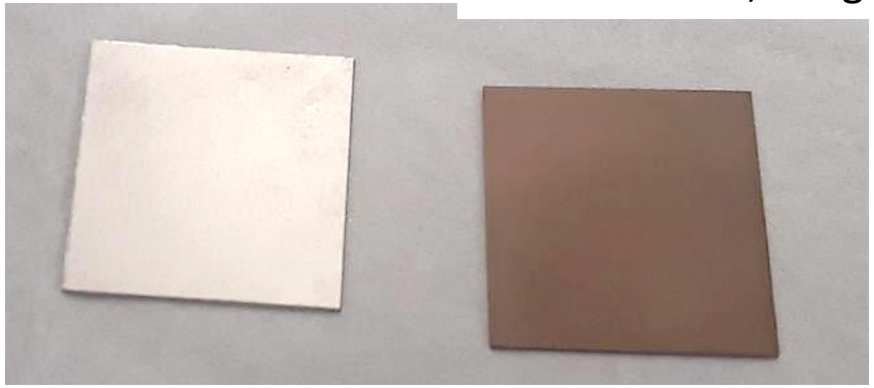


Quasi-Conformal Deposition
Dense Plasma, Long Kick

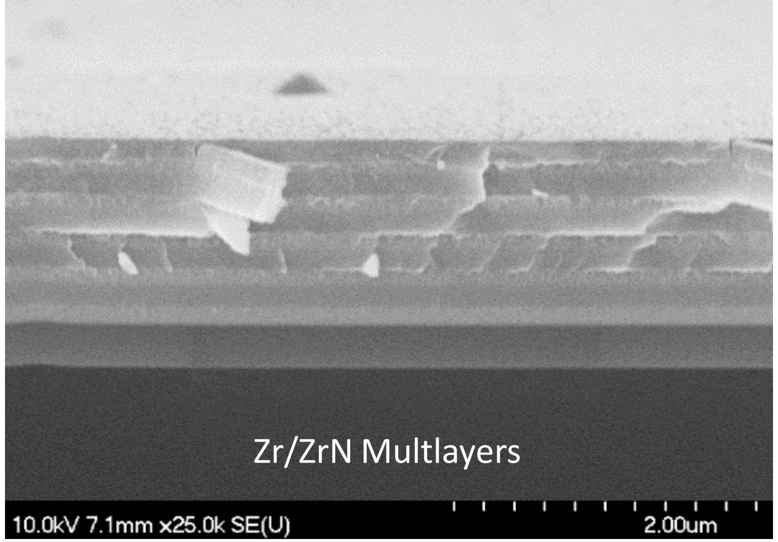
IMPULSE® is great for reactive sputtering since “metal” mode can be sustained over a wider N_2 flow regime.

The Positive Kick™ allows interface etching and ion energy control.



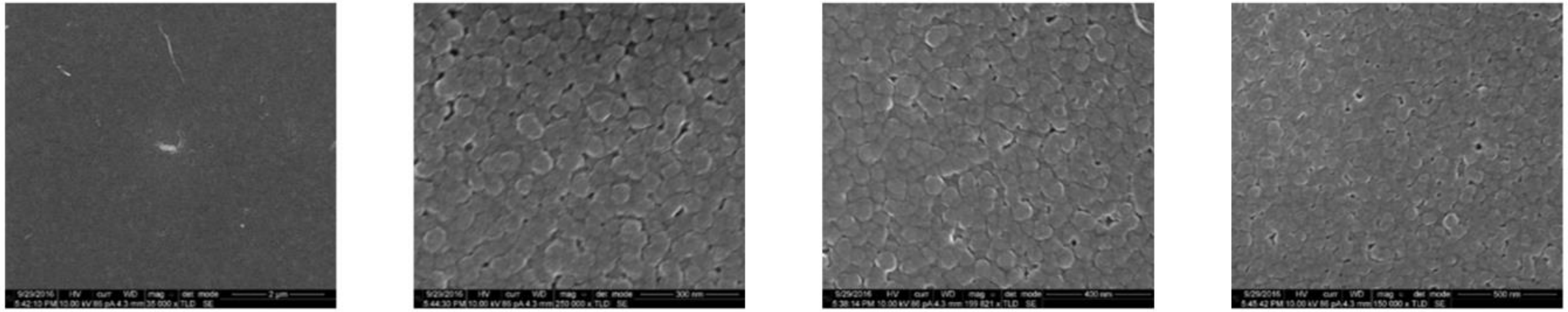


TiAlN/TiN, 20µm, 100bilayers
6—8x erosion resistance
vs. bulk Ti ASTM-G76-18



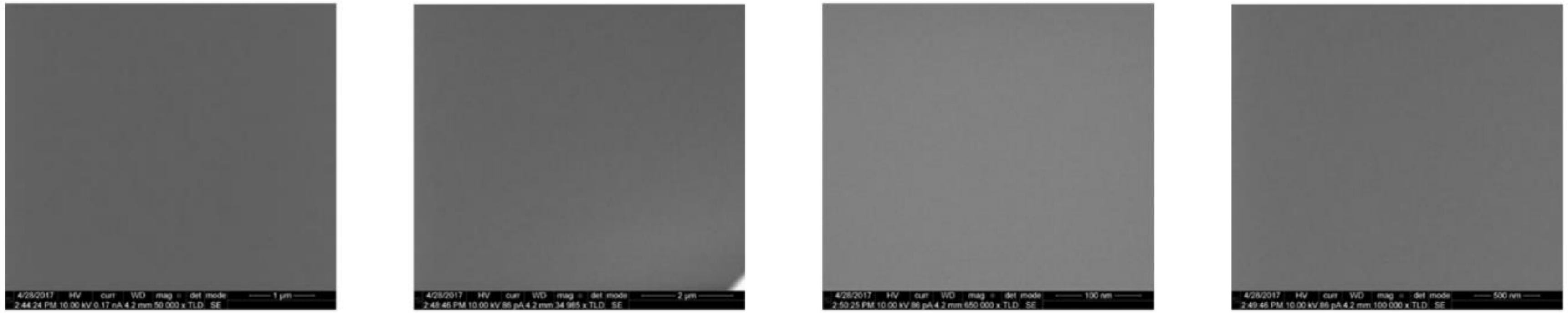
Select Adatom Mobility → Smoothness & sp^3 at-C

SEM Images of Carbon coating with DC magnetron sputtering



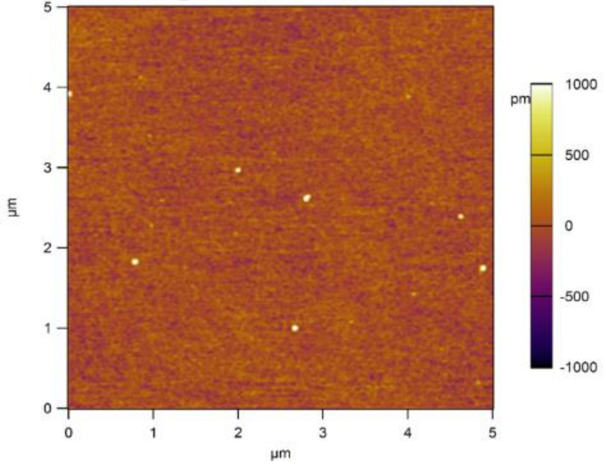
2µm 300nm 400nm 500nm

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



1µm 2µm 100nm 500nm

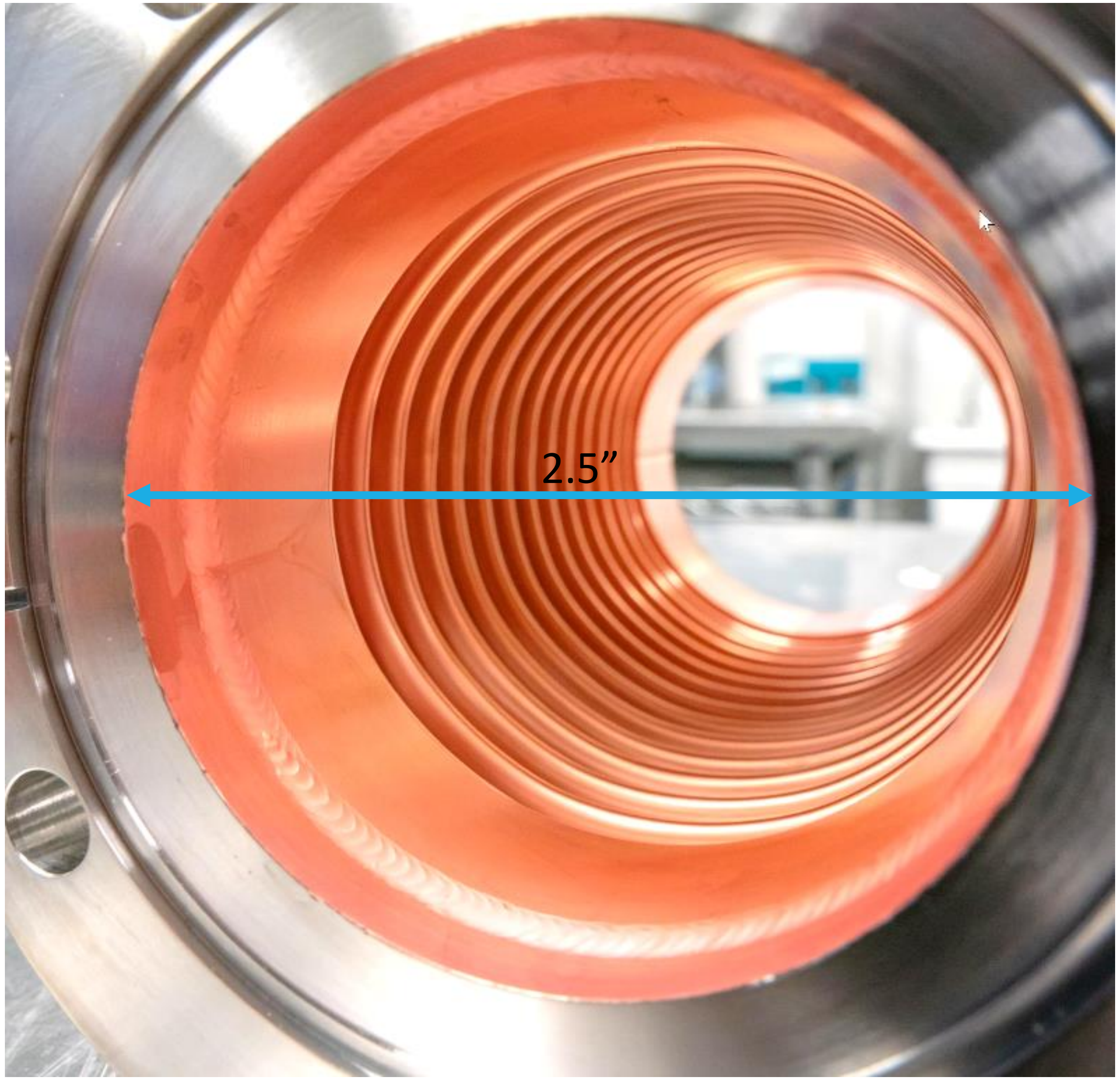
HiPIMS + Kick 500W
Roughness = 0.10nm

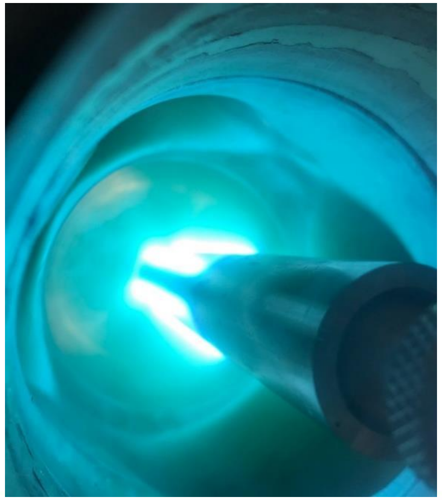


$+V_{KICK}$ precision control of adion mobility

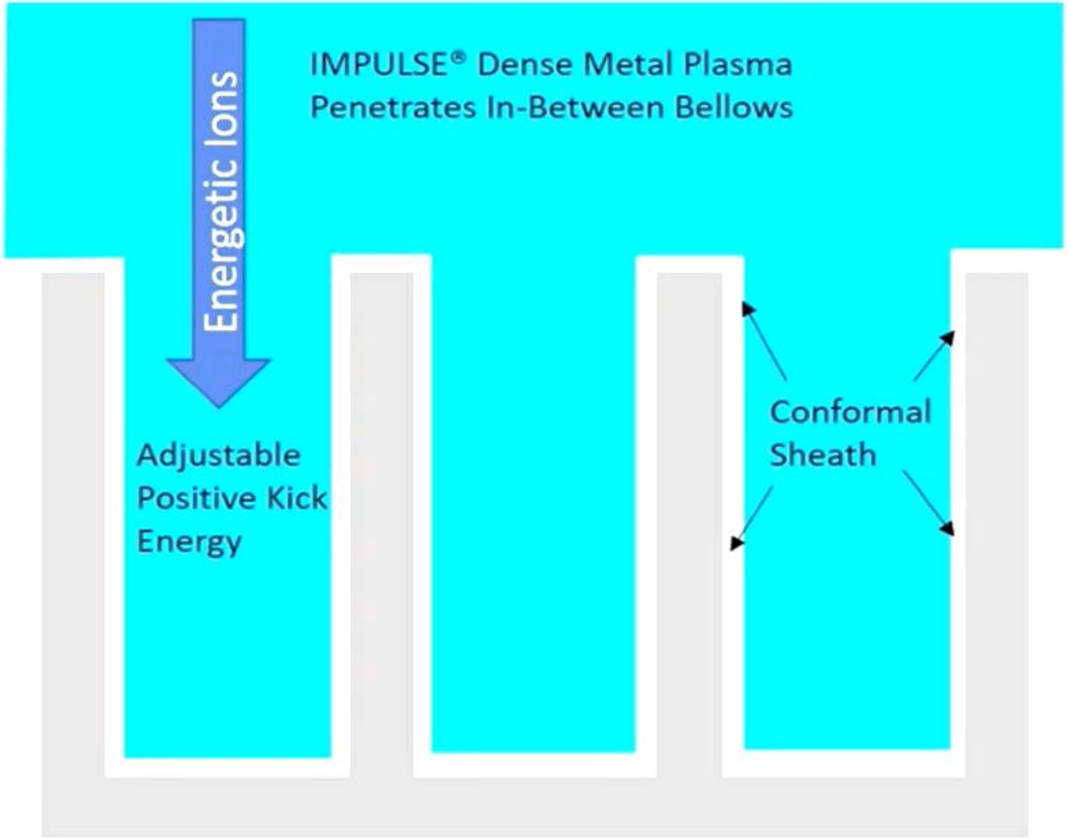
Ultra-smooth AND fully dense

Preferentially break sp^2 bonds





Ultra-Fast IMPULSE® HiPIMS
>90% Ionization Fraction
Dense Metal Plasma
Positive Kick™ Accelerates Ions
Elevates Plasma Potential
Conformal Sheath
Deposition Inside Bellows
Energetic Ion Bombardment
Dense Coating At 90° Incidence



IMPULSE® Dense Metal Plasma Penetrates In-Between Bellows

Quasi-Conformal Cu Deposition Bellows

Long Positive Kick™ penetrates into high-aspect ratio gaps for quasi-conformal deposition

Application: replacement of Cu electroplating for particle accelerators

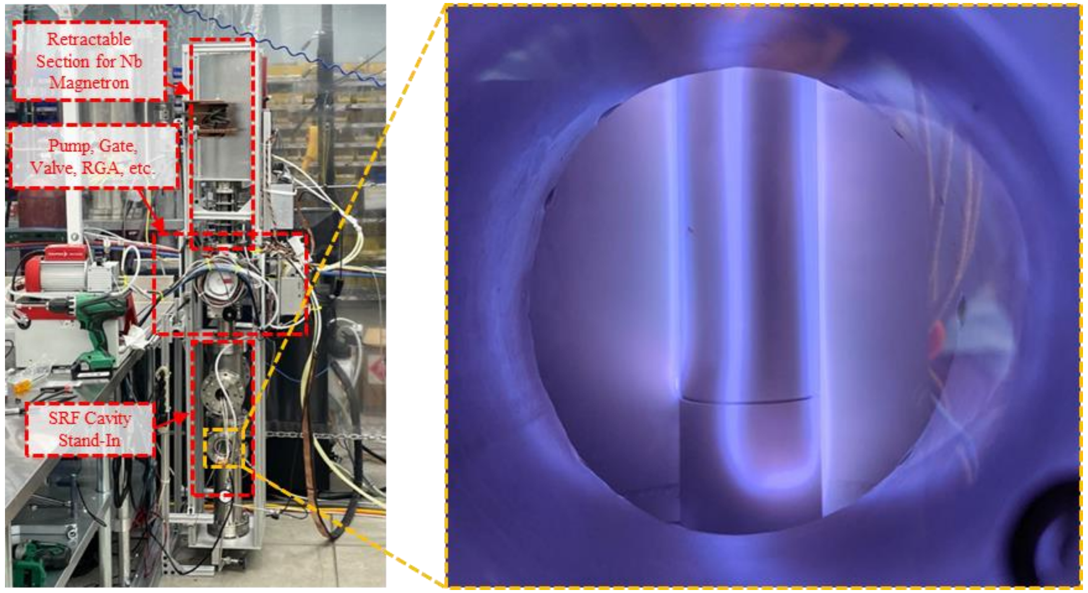
200°C bake and drop into LN_2
NO delamination, cracking or buckling = great film!

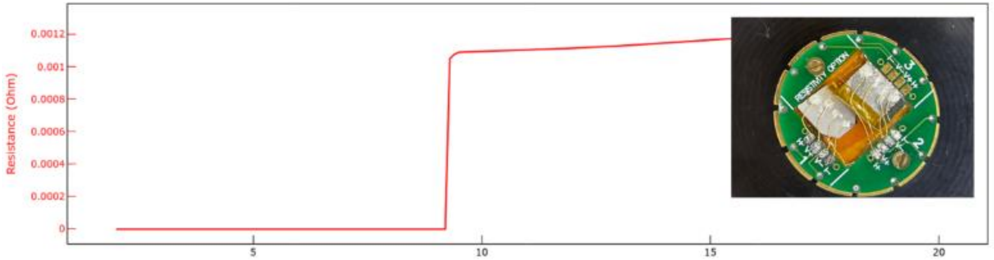
Superconducting Nb Conformal Deposition

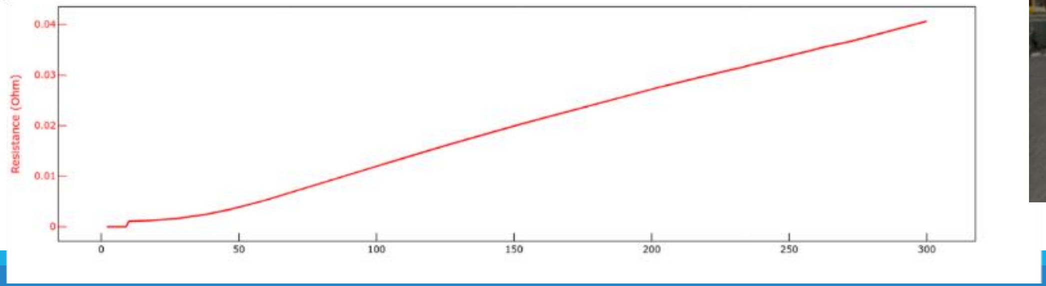
CRADA with the Thomas Jefferson National Accelerator Laboratory

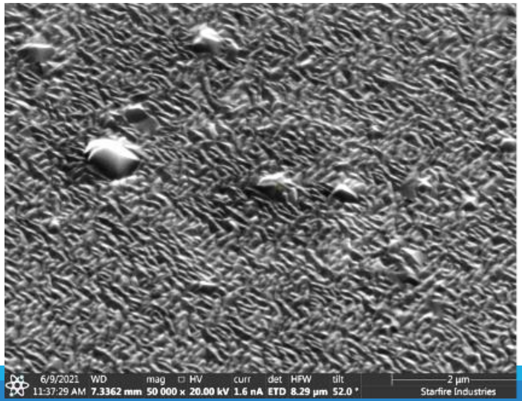
Radial Magnetrons™ for deposition/etch of cryogenic coatings onto elliptical SRF cavities, vacuum bellows, beamline sections, RF waveguides, 1” diameter cylindrical tubes and rectangular waveguide sections

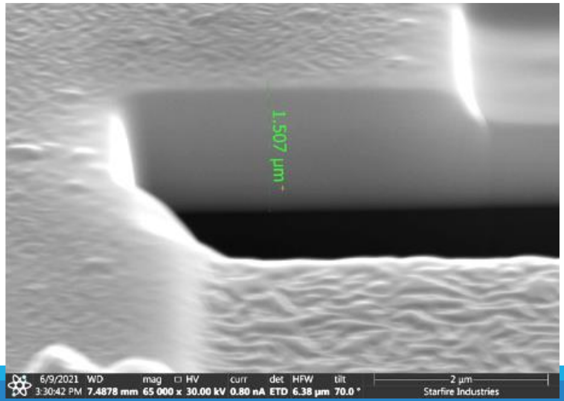
Preferentially etch Cu substrate, then deposit Nb to achieve 9.4K SC transition temperature







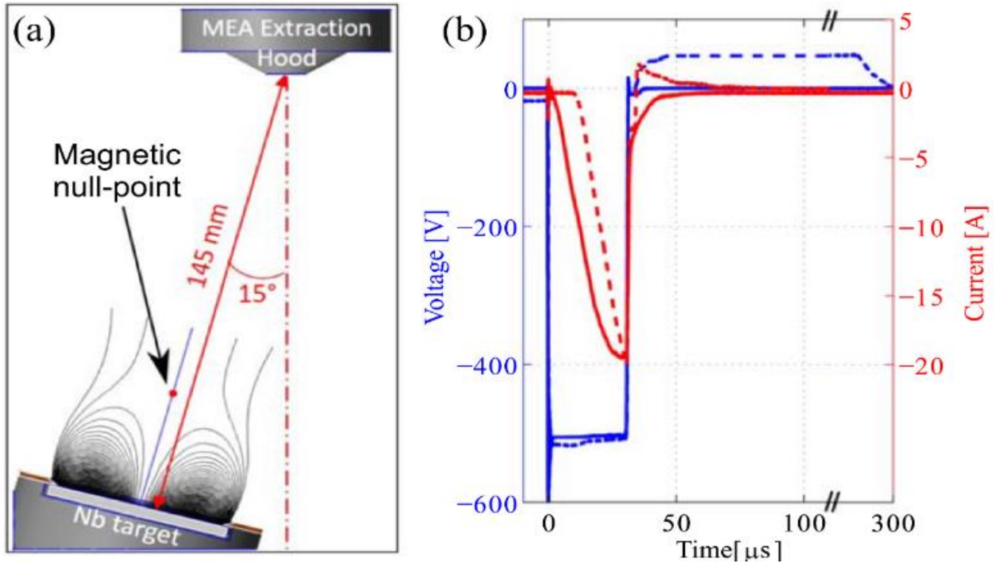


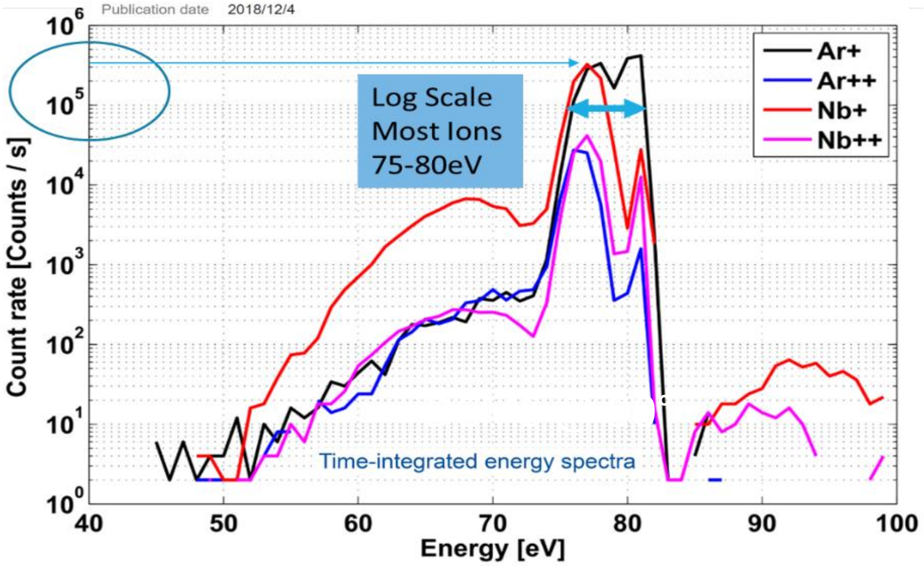


CERN Coatings @ 90° Grazing Incidence

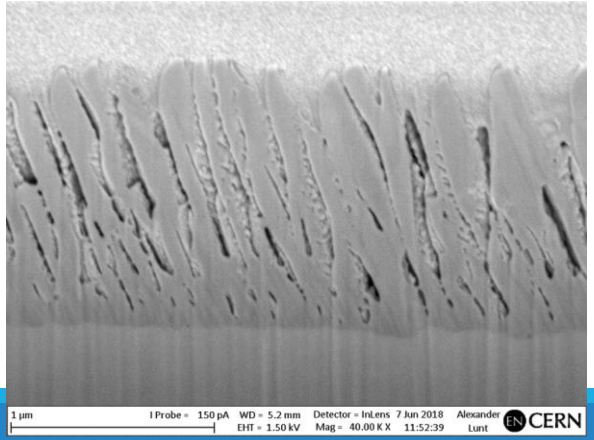
Plasma Sources Sci. Technol. **28** 01LT03

Grounded Substrate



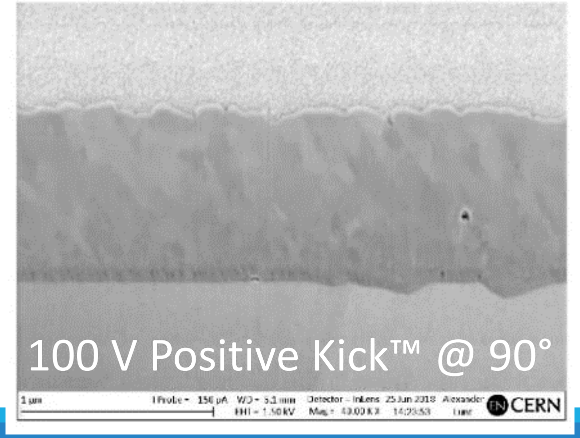


Traditional
HiPIMS
With grounded
substrate



Fully-Dense Niobium Thin-Films At 90° Incidence For 3D Superconducting RF Accelerator Cavities

Nb T_c = 9.1K
YES!



100 V Positive Kick™ @ 90°

Avino, HIPIMS 2018, Sheffield

Graded ZrC Layers Fission Gas Retention + Capping

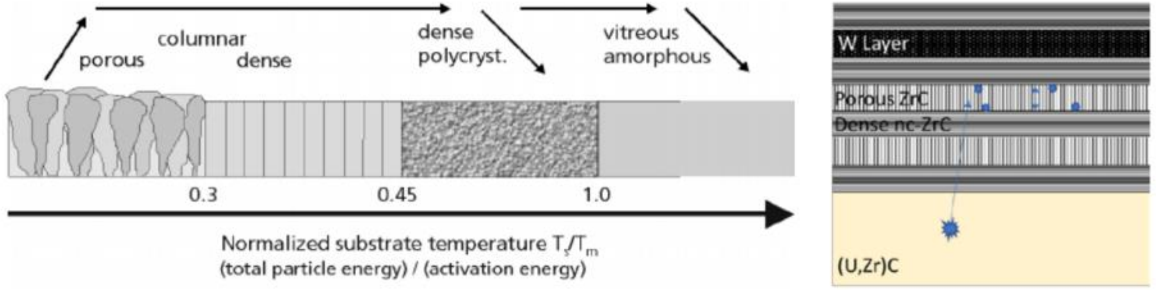


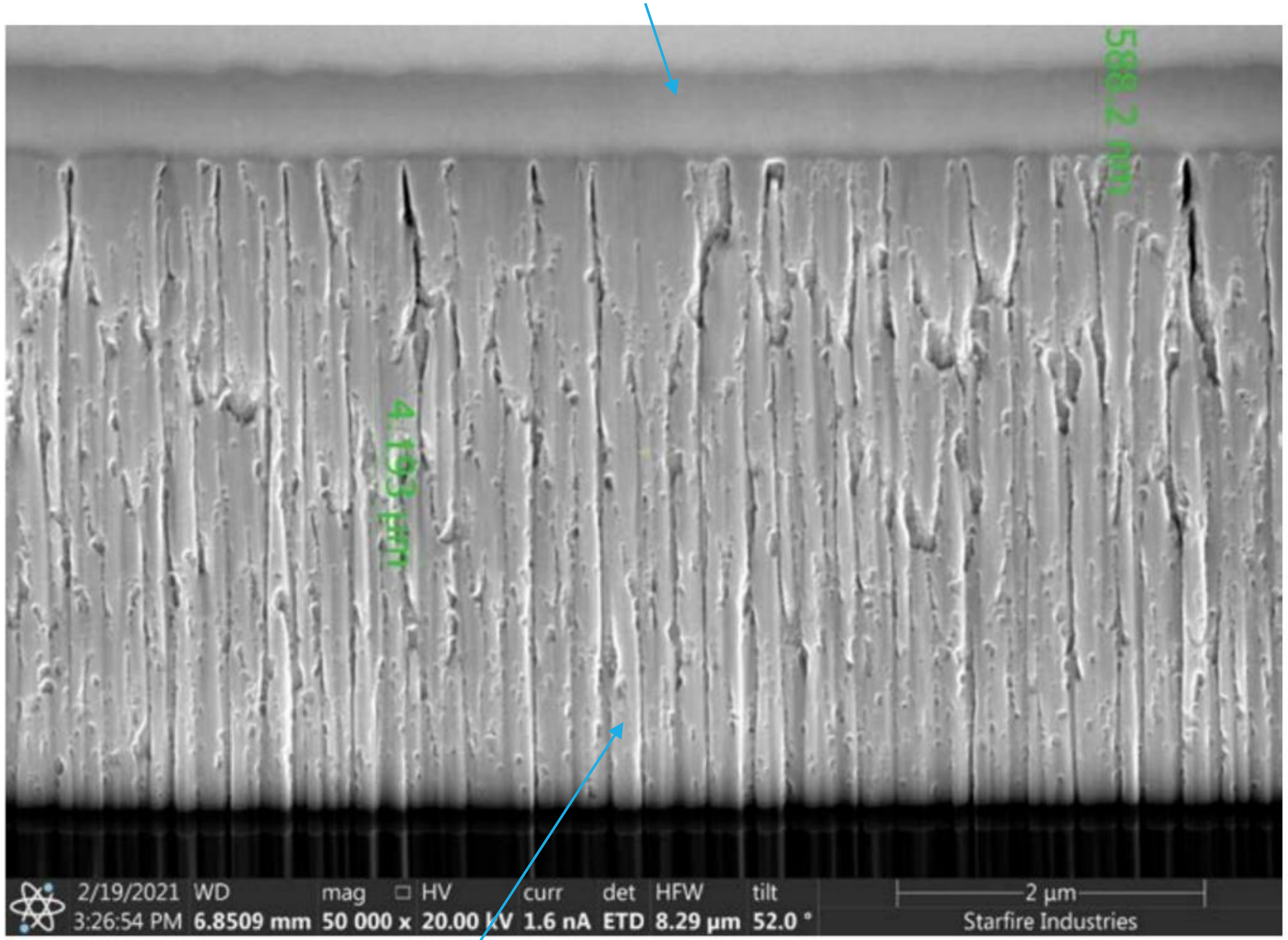
Figure 23: Adjusting IMPULSE® T* and Positive Kick™ E* for (1) porous columnar regions suitable for fission gas trapping and (2) dense, nanocrystalline non-porous compressive layers for sealing.

NASA project to coat nuclear fuel kernels with functional layers for high-temperature, corrosion resistance AND nuclear properties

- ZrO2 substrate
- Interface layer ZrC with implantation
- Porous Zone (engineered)
- Dense Capping Layer

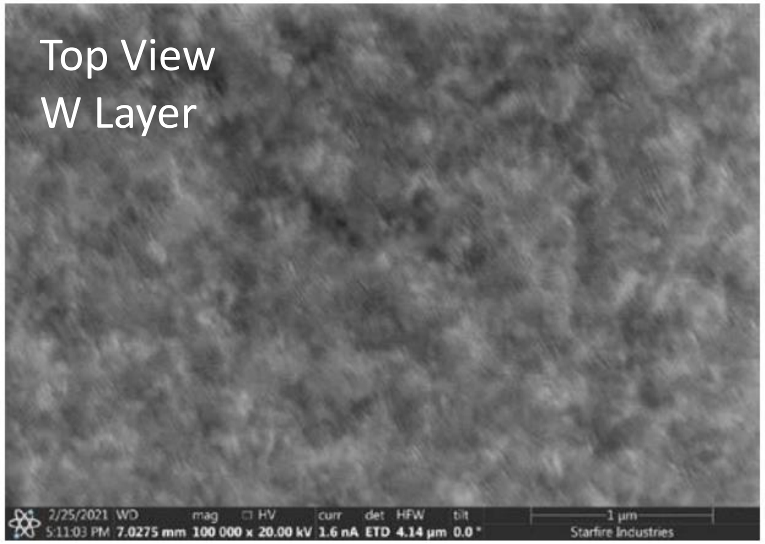
Change IMPULSE® + Positive Kick™ parameters on the fly to adjust or grade morphology

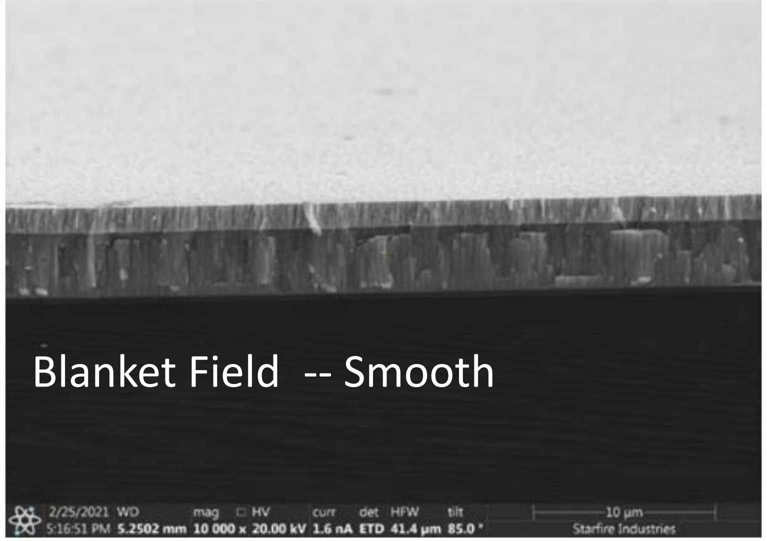
Fully-Dense, Amorphous ZrC -- Capping Layer

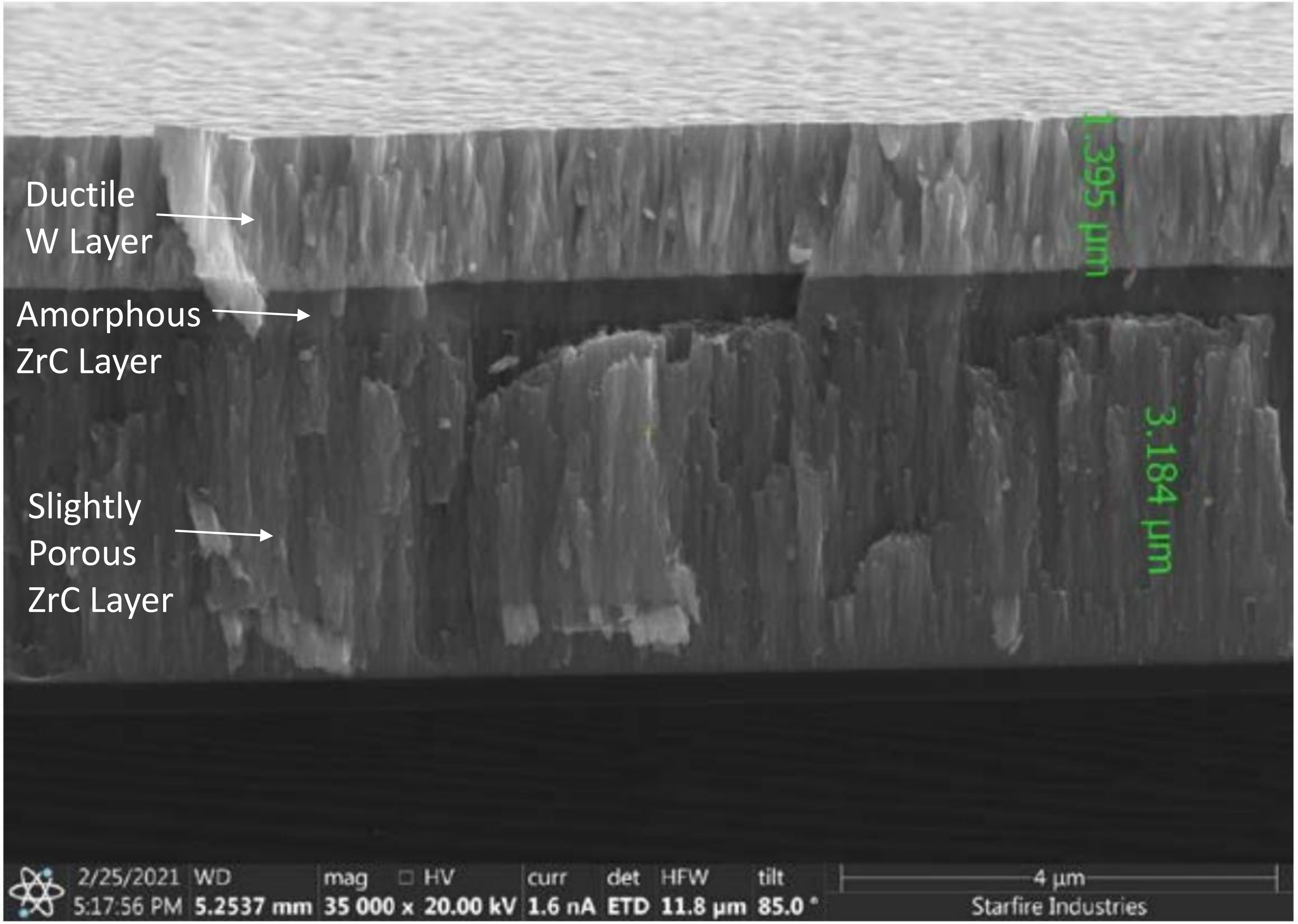


Porosity Zone ZrC -- Gas Trapping Layer

NASA Nuclear Thermal Propulsion Coatings


Top View
W Layer


Blanket Field -- Smooth


Ductile
W Layer

Amorphous
ZrC Layer

Slightly
Porous
ZrC Layer

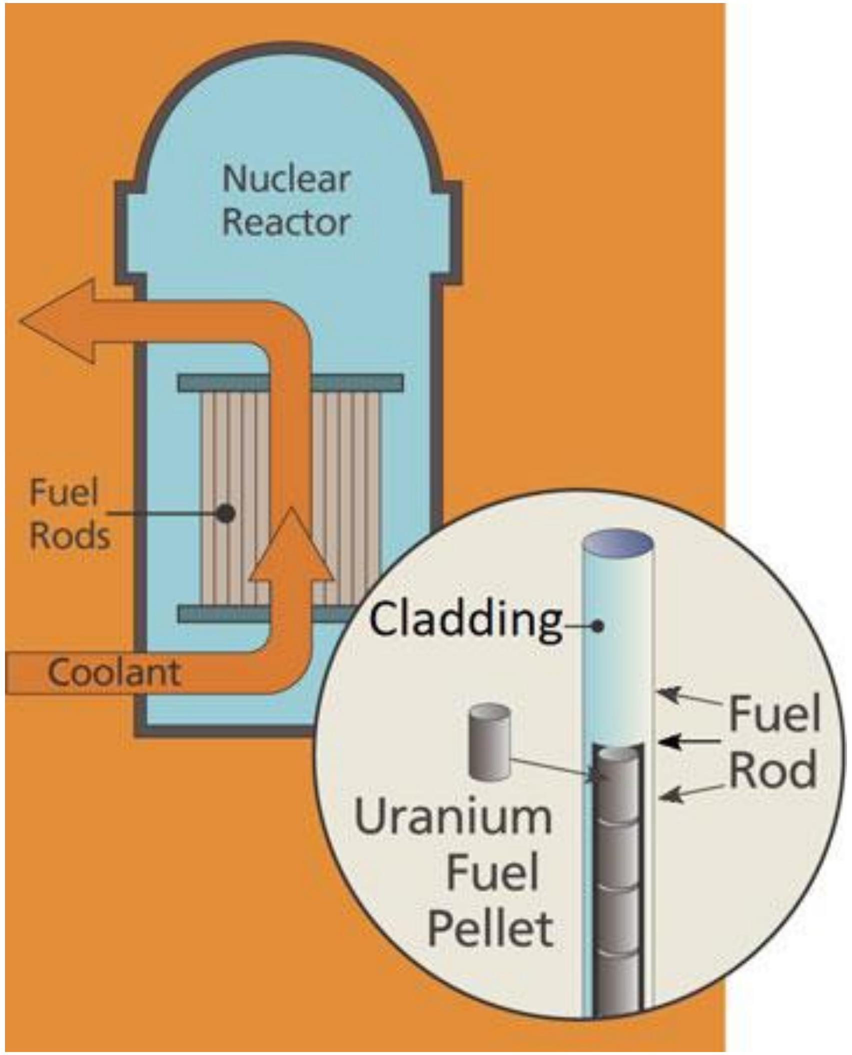
ATF Thin-Film Coatings

In many accident scenarios—like Fukushima, Japan—the zirconium-alloy cladding surrounding the fuel pellets is the weakest link for reactor core integrity.

The near-term ATF solution is fuel with the outside of the zirconium alloy cladding **coated with thin layer(s) of chromium** or other material to provide:

- Oxidation resistance and material behavior under harsh conditions
- Enhanced protection of fuel rods against debris fretting and wear
- Increase safety margins for higher power generation efficiency

<u>The goal is to preserve the underlying Zr bulk properties while improving tolerance under design-basis and beyond accident scenarios</u>



IMPULSE®: In-Situ Dep and Etch

Example recipe:

Operate IMPULSE® to clean/etch the substrate (Ar^+)

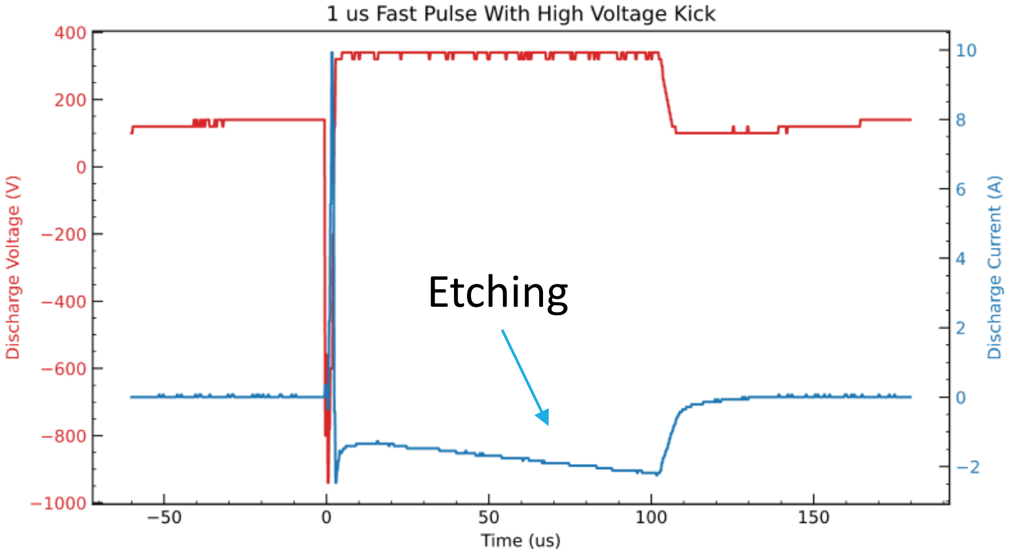
- Short main –HV pulse (1µs) with short kick pulse (40µs) at low kick voltage (+40V, then increase to +400V), ~8kHz rate

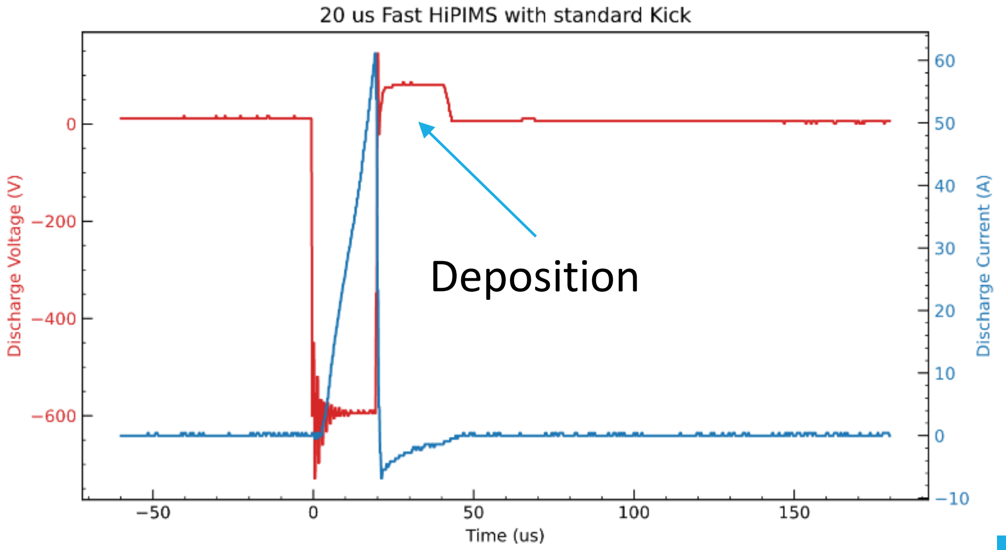
Increase main pulse for metal ion introduction for implantation/adhesion (Cr^+)

- Moderate –HV main pulse (20-100µs) with moderate kick pulse (20-200µs) at high kick voltage (+400V, then grade down +200V, +80V), ~1kHz rate

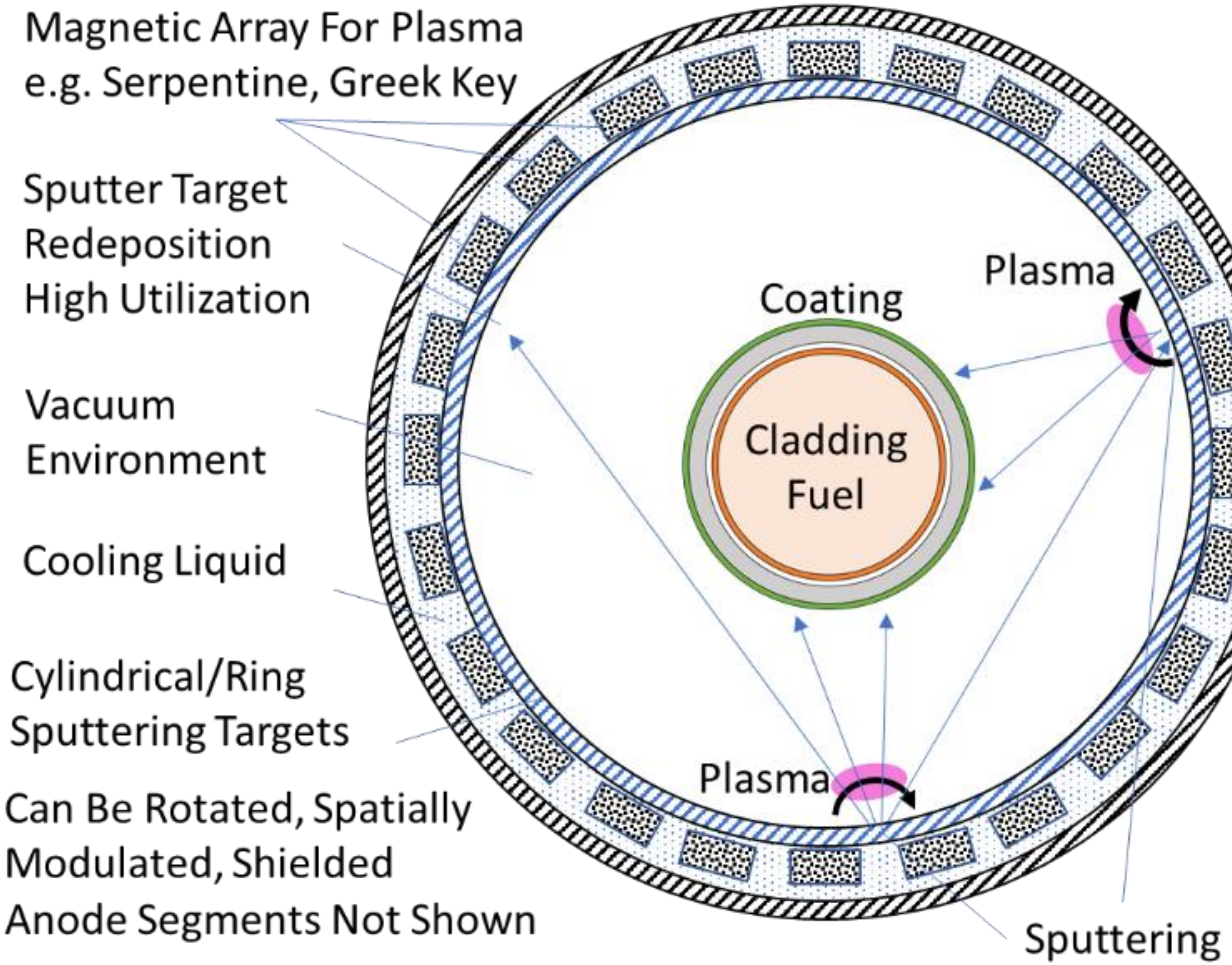
Alternate main/kick parameters for stress and morphology of main bulk layers

- Allow layering of different materials… start at 1 bi-layer
- Reactive chemistries, such as CrN are straightforward





Inverted Cylindrical Magnetron (pat. pend.)



Magnetic Array For Plasma
e.g. Serpentine, Greek Key

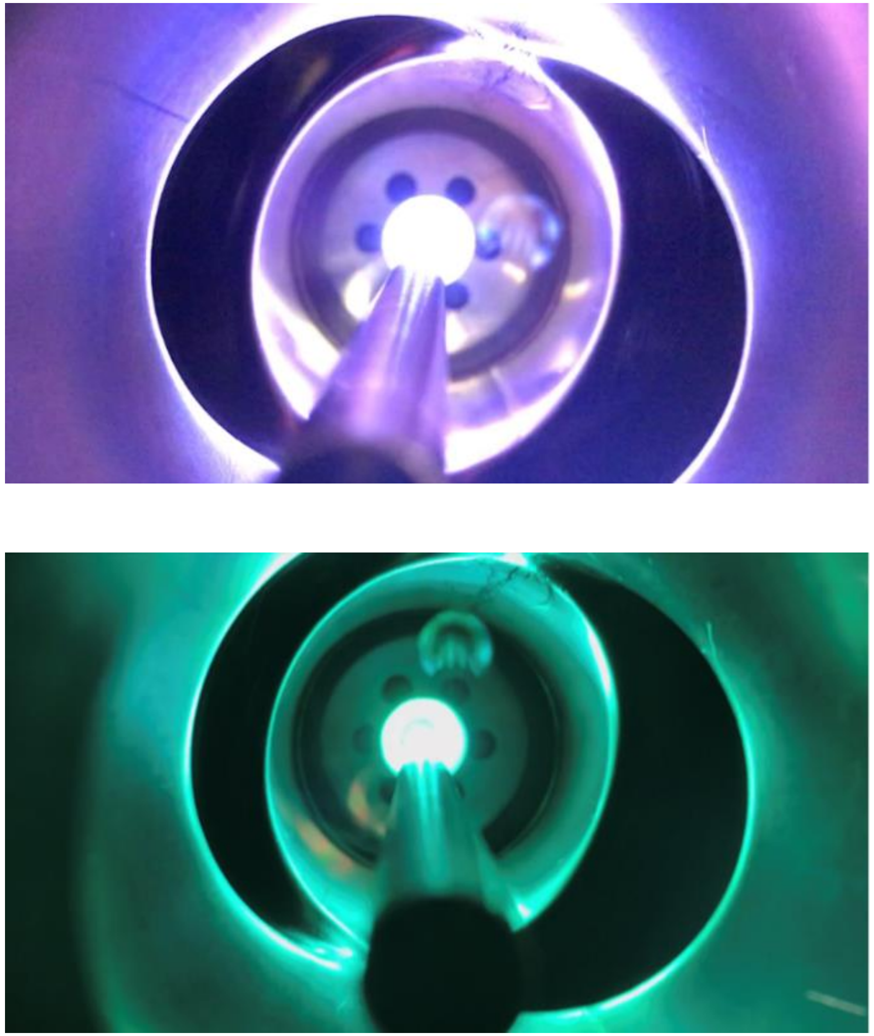
Sputter Target
Redeposition
High Utilization

Vacuum
Environment

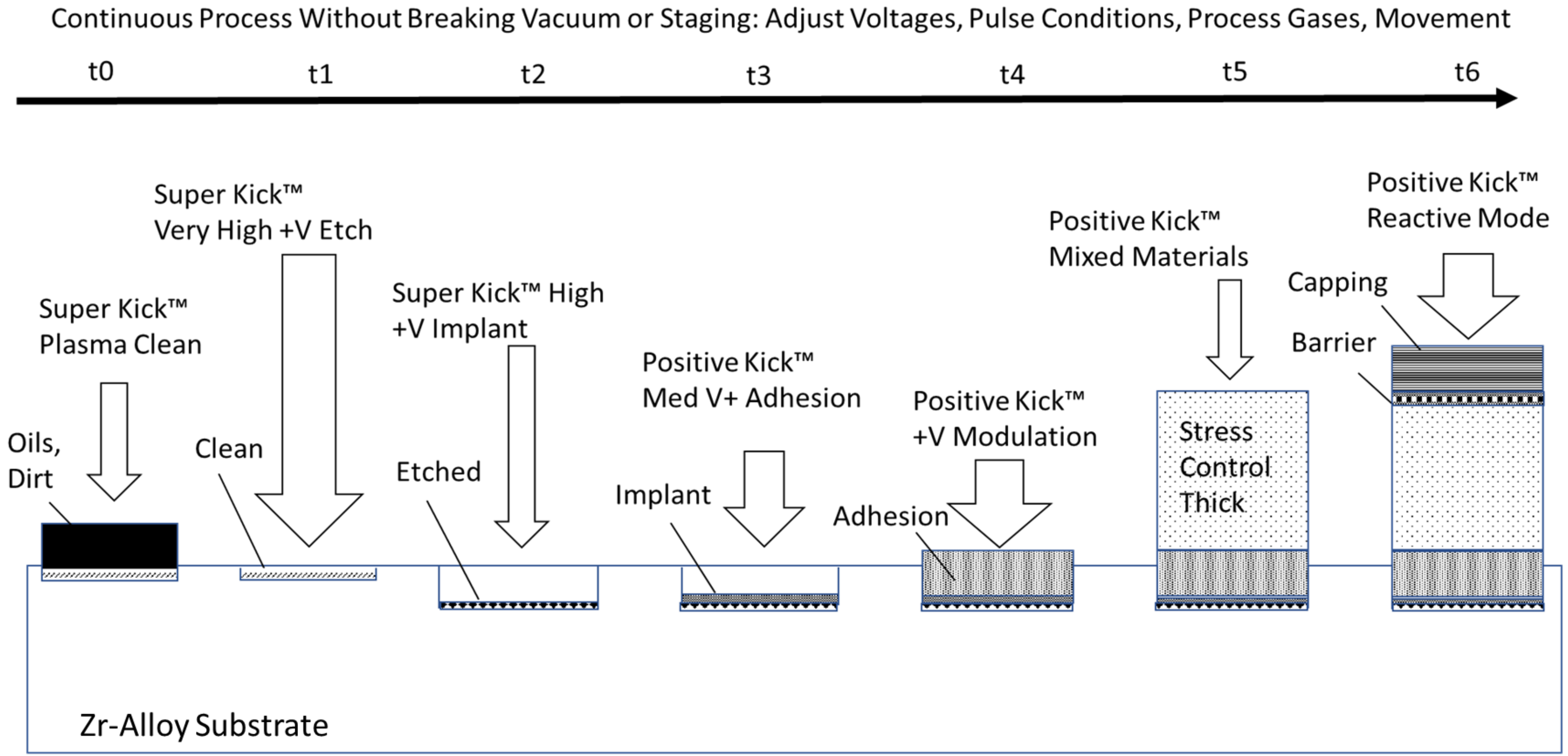
Cooling Liquid

Cylindrical/Ring
Sputtering Targets

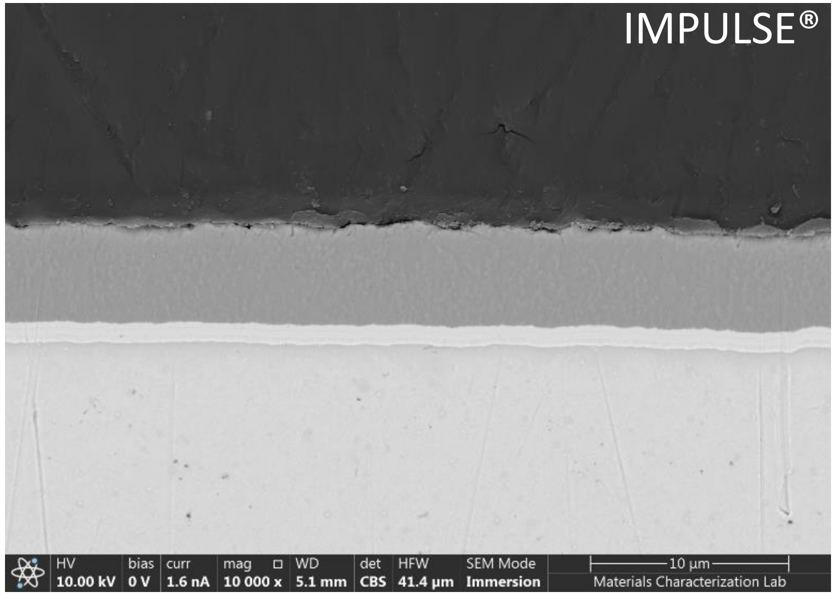
Can Be Rotated, Spatially
Modulated, Shielded
Anode Segments Not Shown

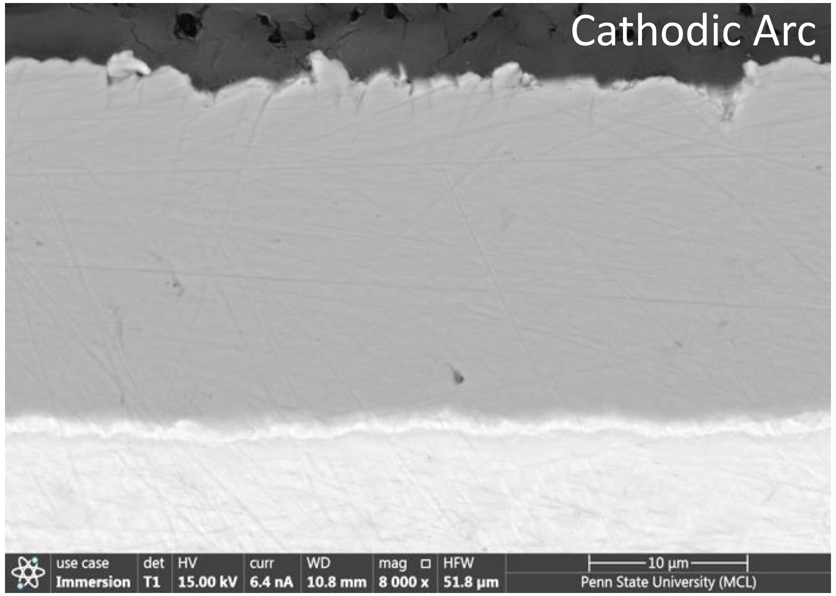


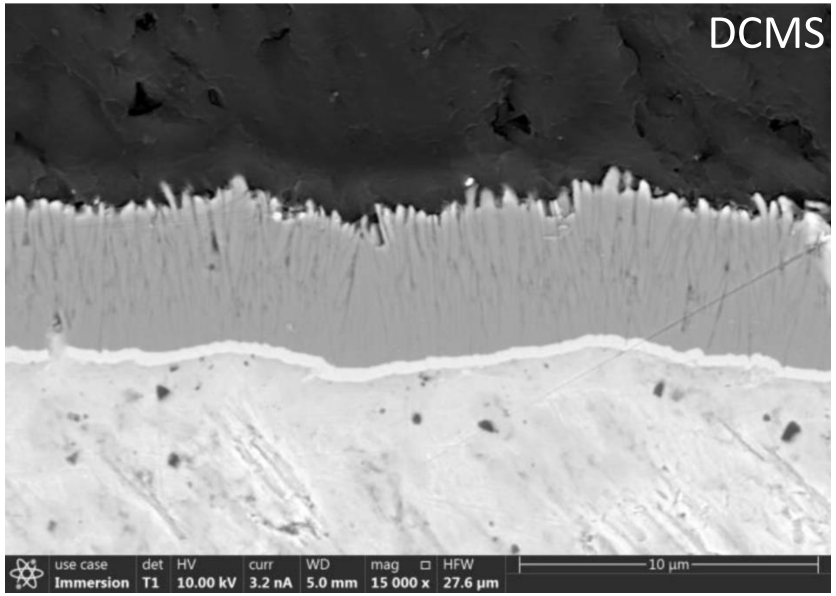
Continuous Processing w/IMPULSE®



SEM Analysis





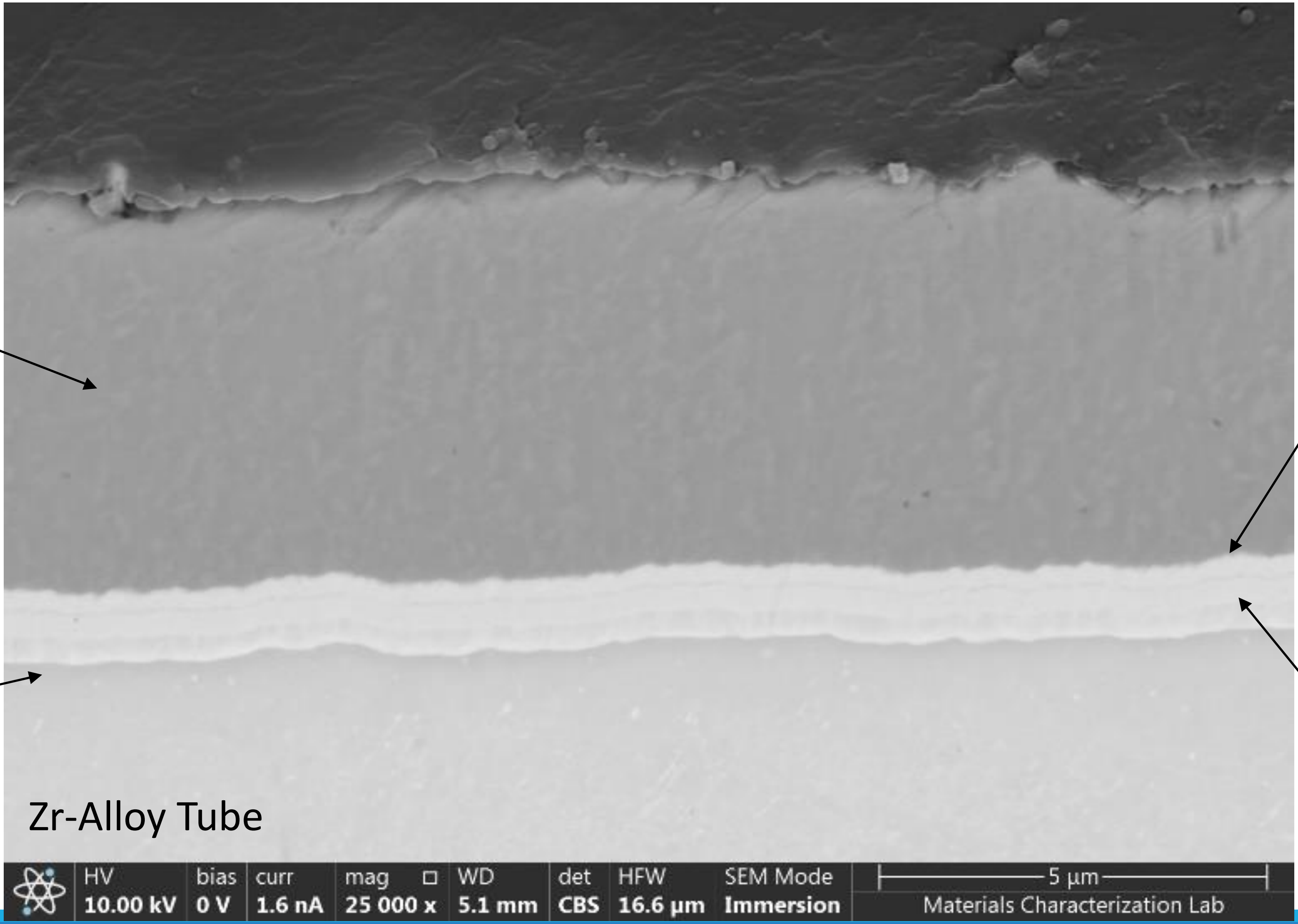


IMPULSE® + Kick™
Low Surface Roughness, Smooth
Well-Controlled Layer Interface
Full-Density, ~300nm grain
Stress-Controlled Bulk Film
Ductal Film

Cathodic Arc
Medium Surface Roughness
Some Defects Through Layer Interface
Near Full-Density, Some Voids
Stress-Controlled Bulk Film
Ductal Film

DCMS
High Surface Roughness
Defects Through Interfaces
Porosity (Many Pinholes)
Zone 1 Competitive Film Growth
Asperities, Crack Initiators

Etch/Implant/Stress Control w/Kick™



Cr Fully Dense
~300nm grains
Faint columnarity

Positive Kick™
Surface
Roughness
Reduction

eV Precision (E*)
Ion Energy Control

Pulse Current (T*)
Particle Flux Control

Nb Fully Dense
Implant/Mixing Layers
Variable Kick™ Energy

Corrosion Testing

Samples sent to Westinghouse for autoclave testing under representative LWR conditions

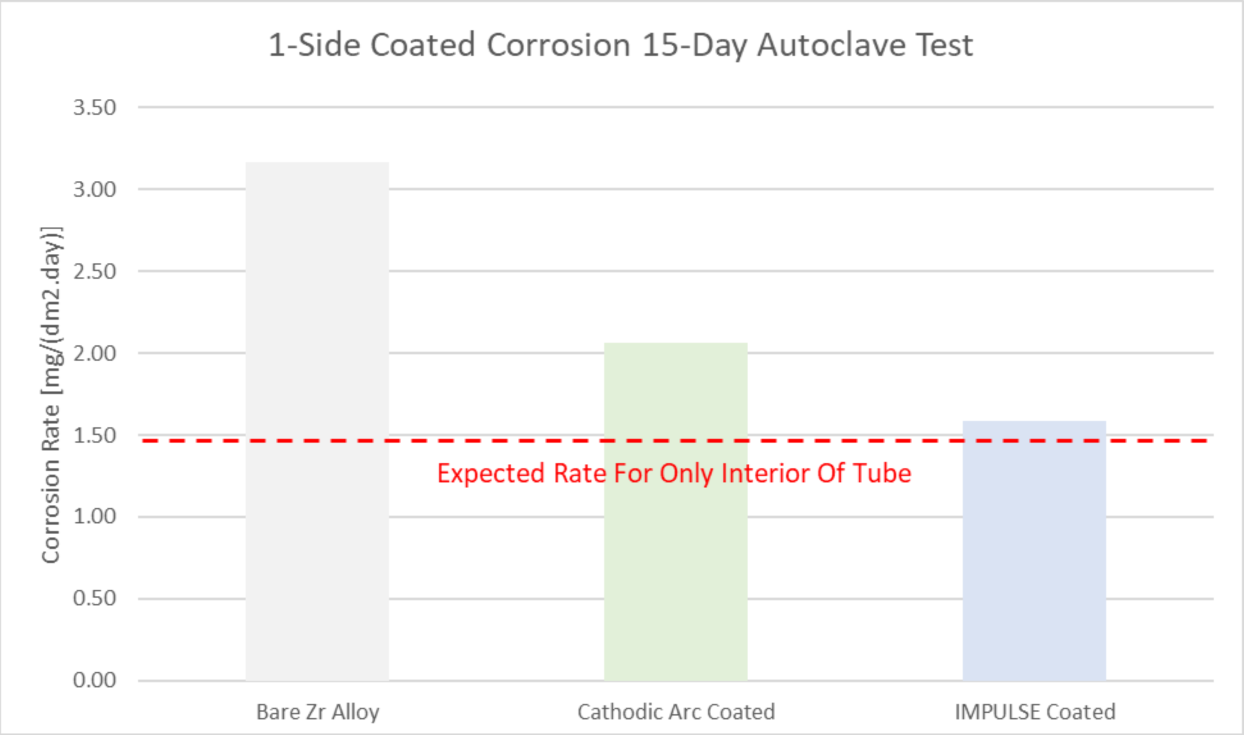
- 360°C, 18.7MPa, 0.5L/hr flow, 15 days
- Multiple CA, IMP coatings using good recipes

Coatings were applied on the exterior side of the Zr-allow tube (9.5mm OD, 8.36mm ID)

- Red-dashed line is 1.47, 46.8% anticipated from the control

IMPULSE® + Positive Kick™ samples exhibited the lowest corrosion rate

- Interior will show mass gain from oxidation less loss from spallation



Exposure	Sample ID	CTRL-9	CTRL-10	CTRL-11	CTRL-12	CTRL-13				AVG
14.9	Corrosion Rate (mg/(dm2.day))	3.14	3.20	3.20	3.18	3.10				3.16
days	No Coating	0.0								

Exposure	Sample ID	CA-20	CA-21	CA-34	CA-35	CA-26	CA-27	CA-30	CA-31	AVG
14.9	Corrosion Rate (mg/(dm2.day))	2.01	2.07	2.11	2.13	2.11	2.13	1.95	2.01	2.07
days	Nb (µm)	0.5--0.6				1.3				
	Cr(µm)	9.6--22.3				17.3--20.8				

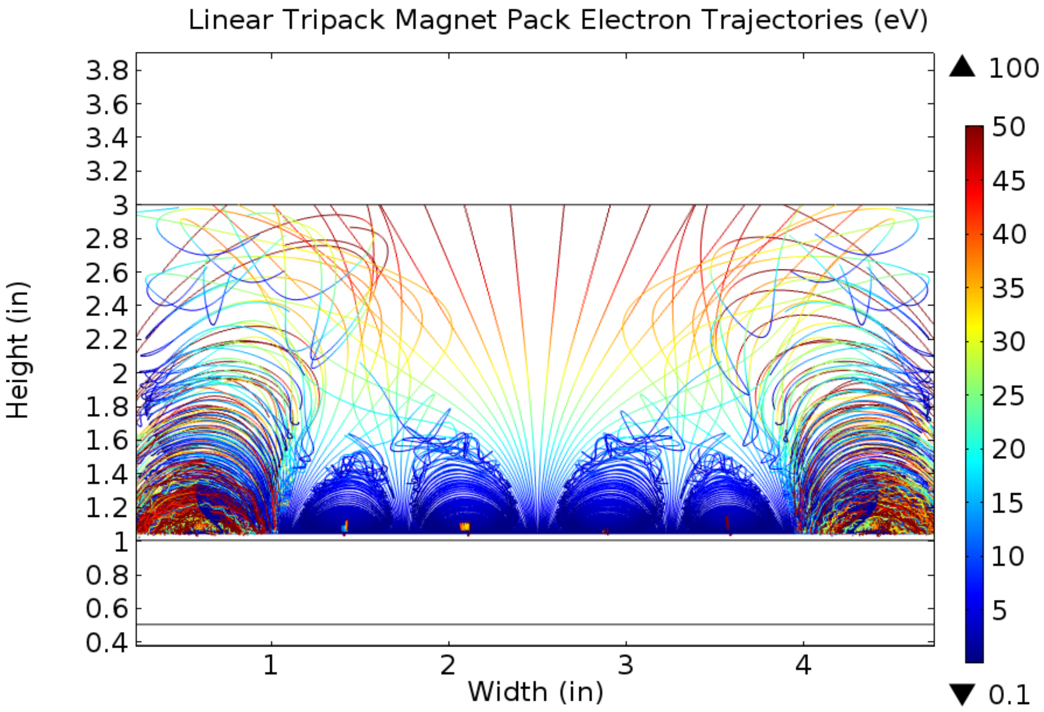
Exposure	Sample ID	IMP-47	IMP-49	IMP-50	IMP-51	IMP-52	IMP-53	IMP-54	IMP-55	AVG
14.9	Corrosion Rate (mg/(dm2.day))	2.19	1.47	1.57	1.46	1.54	1.52	1.47	1.46	1.59
days	Nb (µm)	0.5--2.5								
	Cr(µm)	4.5--6.5								

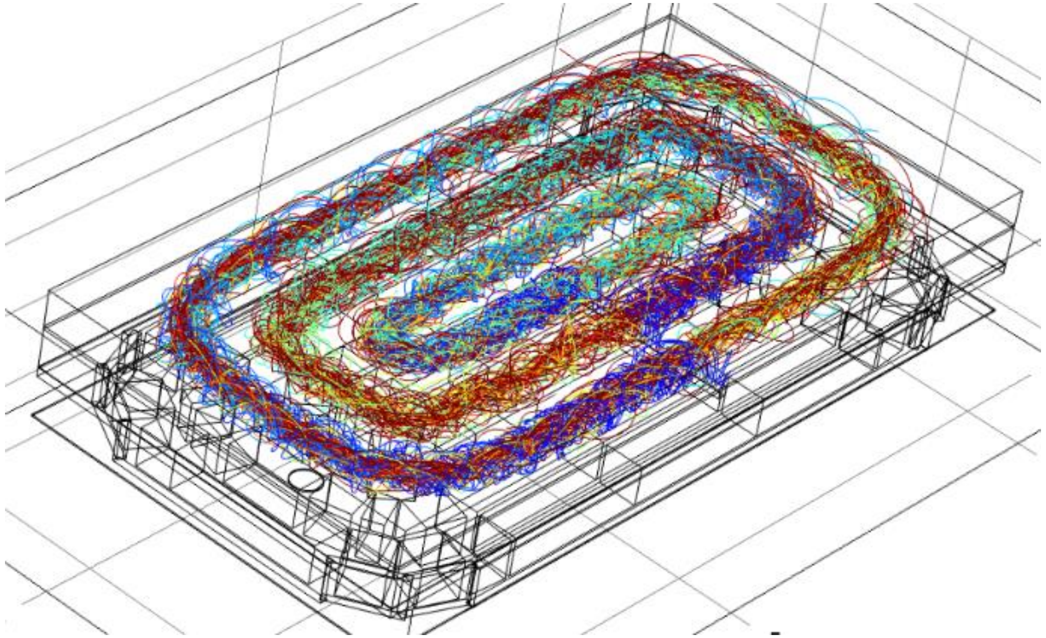
A Note on Magnetic Design

Magnetic field lines allow electron escape even at center line [3]

- Increased ion loss due to ambipolar diffusion
- Expanding plasma further from target surface

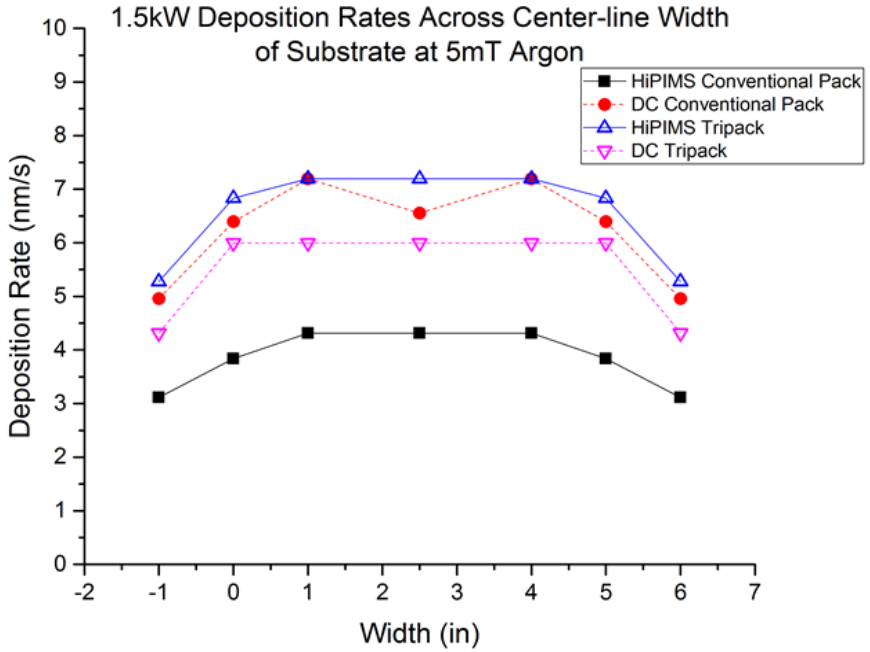
Decreased controlled confinement results in lower peak currents, but increased ion fractions

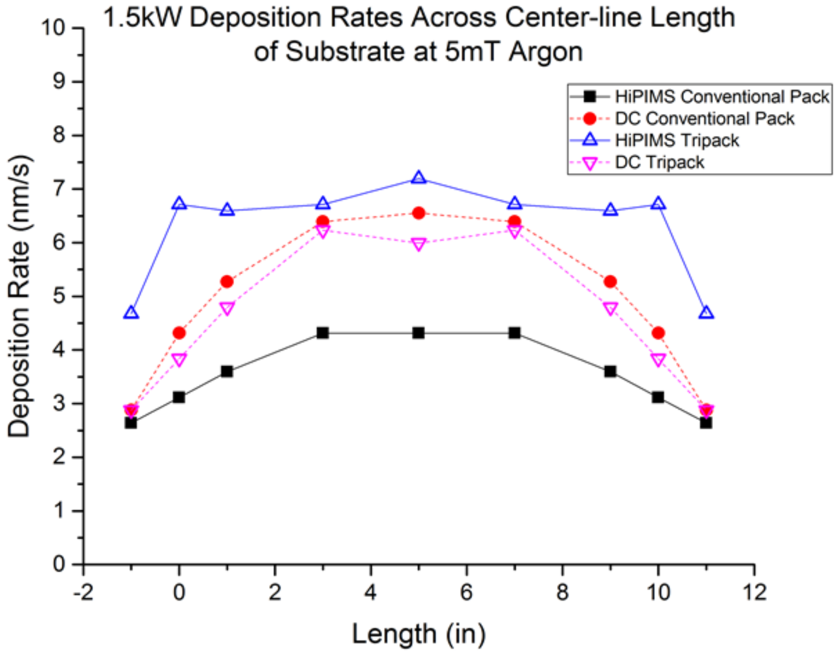




[3] Jake McLain, et. Al., Linear magnetron HiPIMS high deposition rate magnet pack, Vacuum, ISSN 0042-207X, https://doi.org/10.1016/j.vacuum.2018.06.023.

Higher Deposition Rates with Magnetics





- The results at 1.5kW show that the HiPIMS tripack has the highest deposition rates, where the conventional DC magnet pack produced the second highest. The smallest deposition rate is the conventional magnet pack HiPIMS.

- The error in these measurements fits within the data markers (0.08-0.2 nm/s)

[3] Jake McLain, et. Al., Linear magnetron HiPIMS high deposition rate magnet pack, Vacuum, ISSN 0042-207X, https://doi.org/10.1016/j.vacuum.2018.06.023.

IMPULSE® = Simple Ionized PVD

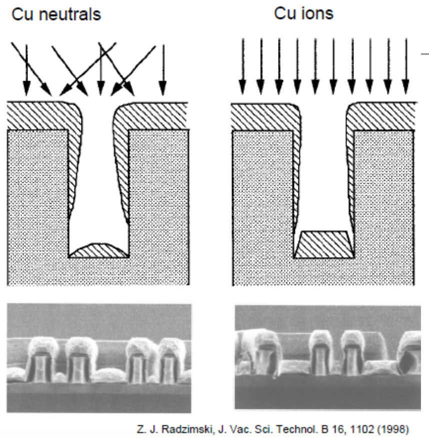
Positive Kick™ accelerates ions to the substrate

SHORT: metal ions from target following ∇B that works on insulating substrates

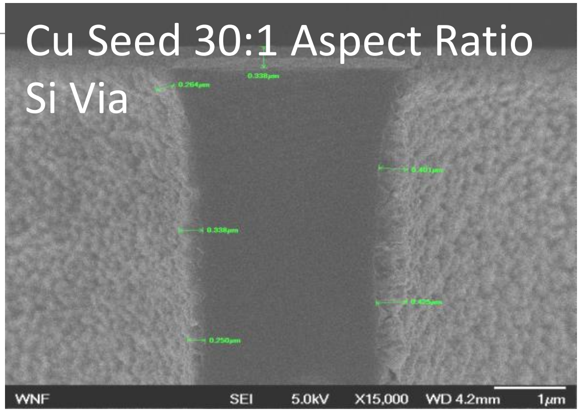
LONG: conformality; plasma potential at substrate for 3D substrates

IMPULSE® gives us lots of controlled-energy sputtered metal & gas ions!

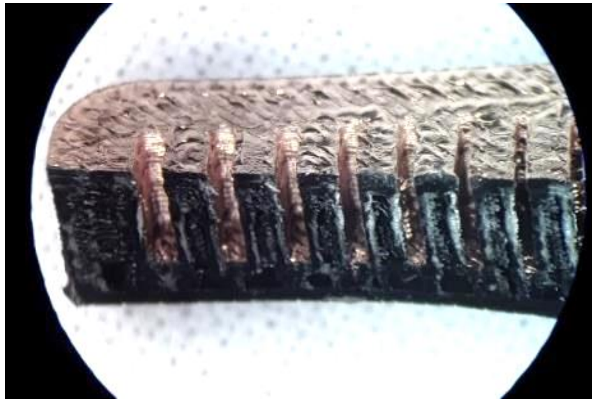
- Adjust ratios of metal ions / noble ions
- Sputter at higher pressures—e.g., 20mTorr!

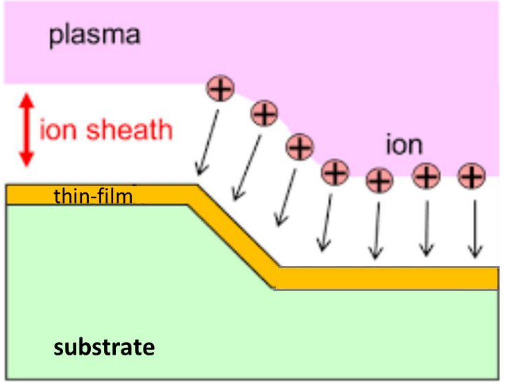


Z. J. Radzimski, J. Vac. Sci. Technol. B 16, 1102 (1998)



Cu Seed 30:1 Aspect Ratio Si Via





Copper directly on 3D printed PLA step wedge

- Excellent adhesion
- Good coverage of sidewalls and trench bottoms
- Good coverage of textured surface

Summary

- HIPIMS is a simple way to do Ionized PVD

- Can control Metal/Gas Ion ratio’s

- Can control Ion energies

- Tailored control over coating properties
  - Morphology
  - Stress
  - Conductivity
  - Adhesion

Current State of HIPIMS Technology

- HIPIMS power supplies currently available from 1 – 20 kW average power
  - Can stack supplies for large area applications in order to increase average output power
  - Challenge remains with peak currents > 2000 A

- Power supply “robustness” is at industrial level

- Extremely wide process window – need continued education and training

- Prices are slowly decreasing – need to reach critical manufacturing scale…

About Starfire Industries LLC

Champaign, IL USA (near the University of Illinois)

- ~35 employees, including 6 PhDs
- 14,000 ft^2 engineering, lab/test and production space
- Vertical integration from R&D, manufacturing, applications testing and support

Particle Accelerator Solutions:

- nGen® portable neutron generators
- Centurion® ultra-compact MeV particle accelerators

Plasma Processing Solutions:

- **IMPULSE® pulsed power modules for sputter/etch**
- RADION™ microwave plasma sources for PECVD/etch

Member of:

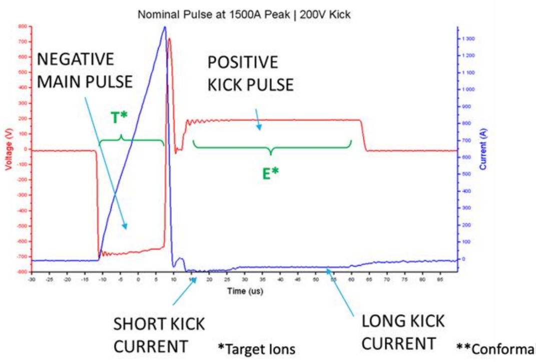
- Center for Plasma-Material Interactions
- Center for Lasers & Plasmas For Advanced Manufacturing

Two Business Groups Within One Organization

Products on 6 Continents!

Patent Portfolio Across Products

Innovations in high-power impulse magnetron sputtering (HiPIMS)



*Target Ions

**Conformal Ions

Q&A

For questions or advice:

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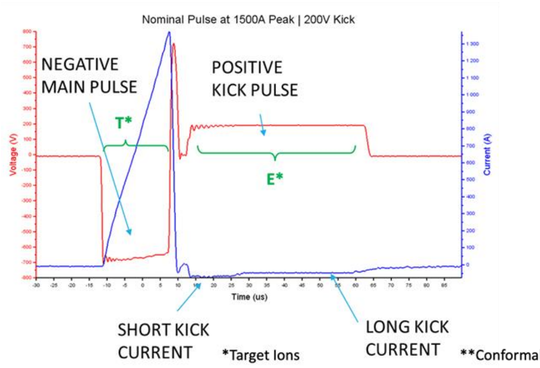
jgreer@pvdproducts.com
pvdproducts.com

Frank Papa
fpapa@starfireindsutries.com
www.starfireindustries.com

Innovations in high-power impulse magnetron sputtering (HiPIMS)



Thank you!

For questions or advice:

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fpapa@starfireindsutries.com
www.starfireindustries.com