GENCOA

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Magnetron Based Plasma Substrate Pre-Treatment and Etching

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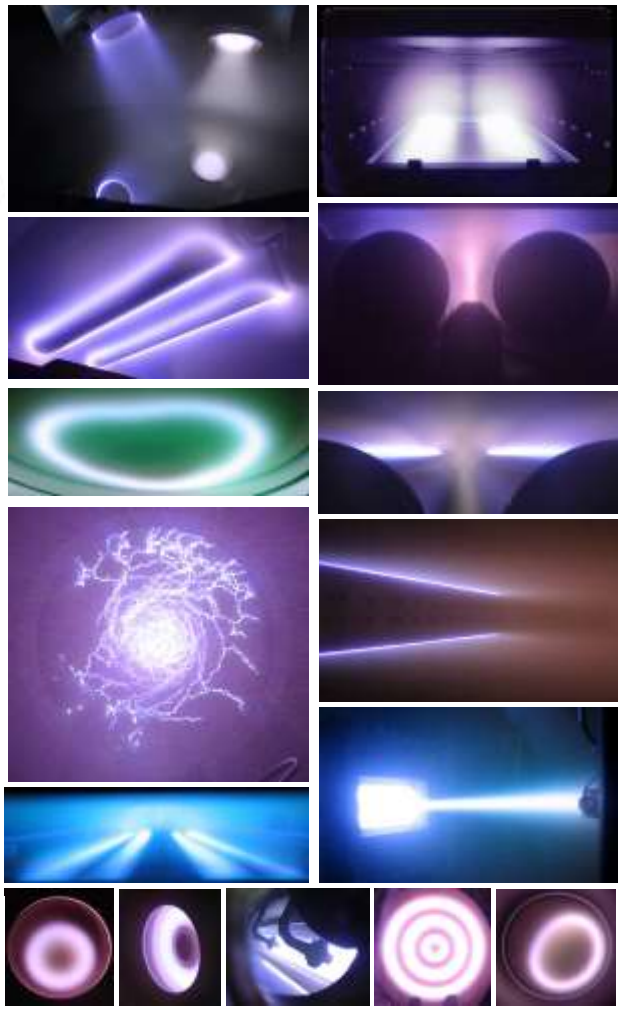
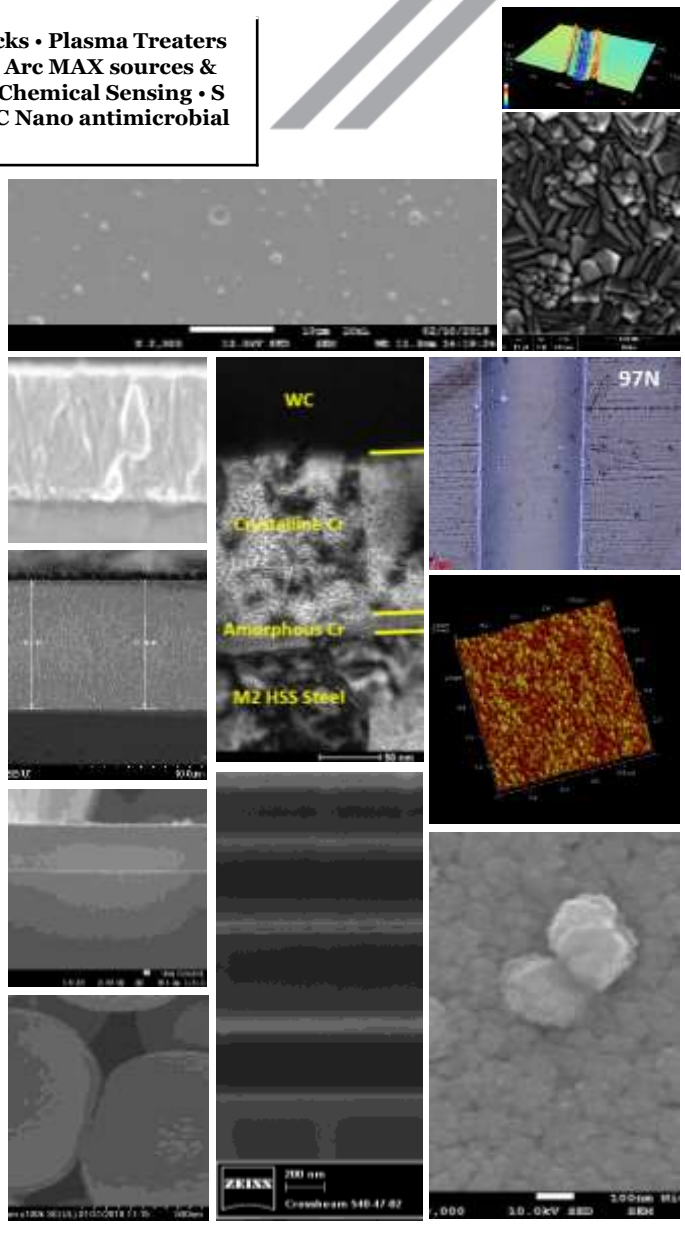
Presentation outline

- Different options for magnetron based vacuum plasma pre-treatment and etching compared
- The transition from DC to AC to +ve PDC to +ve Hipims
  - New Hip3+ positive pulse method for plasma treatment and etch
- Conclusions

27 Years of of Products and Technology from Gencoa

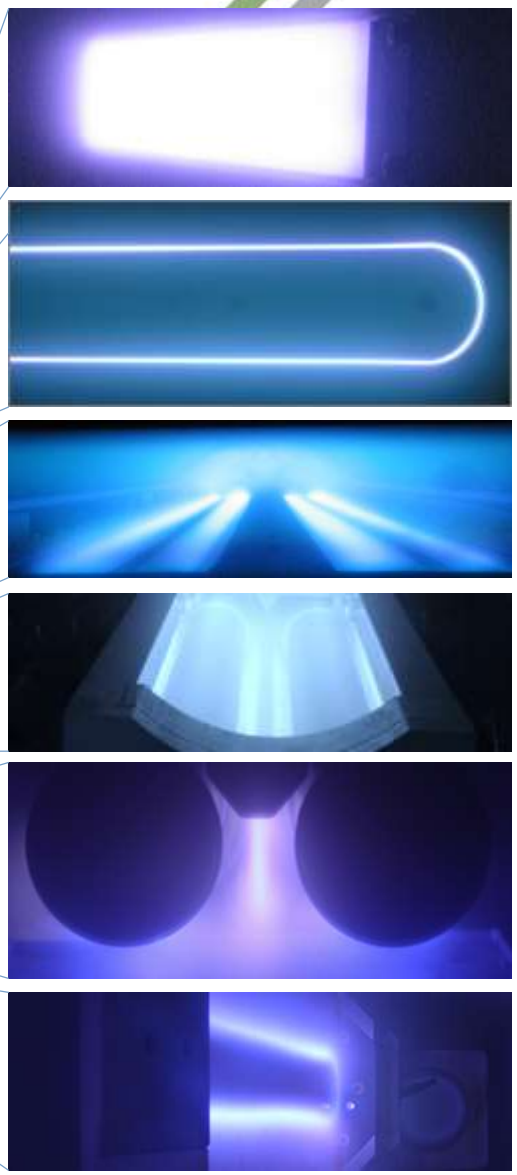
Rotatable & Planar Magnetron Sputter Cathodes • Retrofit magnetic packs • Plasma Treaters • Speedflo Reactive Gas Controllers • IM Ion Sources & power supplies • Arc MAX sources & power supplies • Active Anodes and Gas Delivery Bars • OPTIX Gas and Chemical Sensing • S and Se Sensor • PEC Pulsed Effusion Cell • V⁺DLC - Transparent DLC • IC Nano antimicrobial layer technology • Process implementation & tuning •





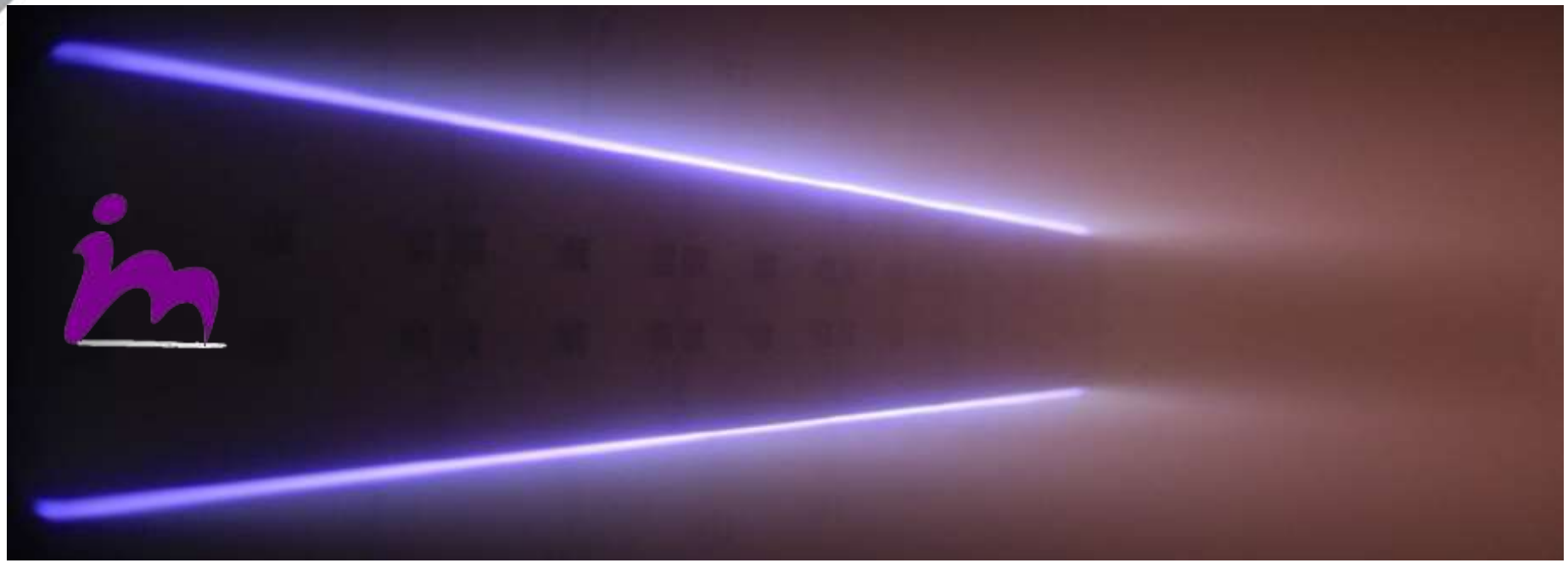
Plasma Generation and Pre-treatment options available

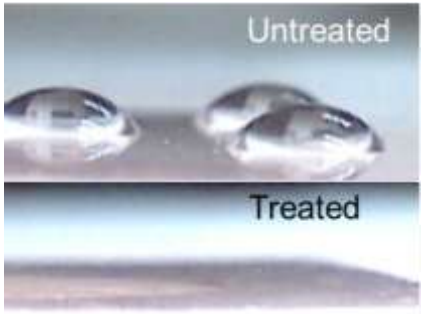
Plasma Treatment Product Categories:	**Application / use**
Glow Discharge	Low speed plastics
DC inverted magnetron linear ion sources	Low speed metallics, plastic web & glass
DC magnetron based plasma treaters	Low to High speed plastic web
AC type plasma treatment sources	High speed plastic web
AC type gas activation sources – O2 plasma generation for reactive gas reactions	High speed radical O2 gas production
New positive pulsed power inverted magnetron plasma source	*Metallic etch, glass and plastic pre-treat, ion irradiation*



Gencoa series linear ion sources

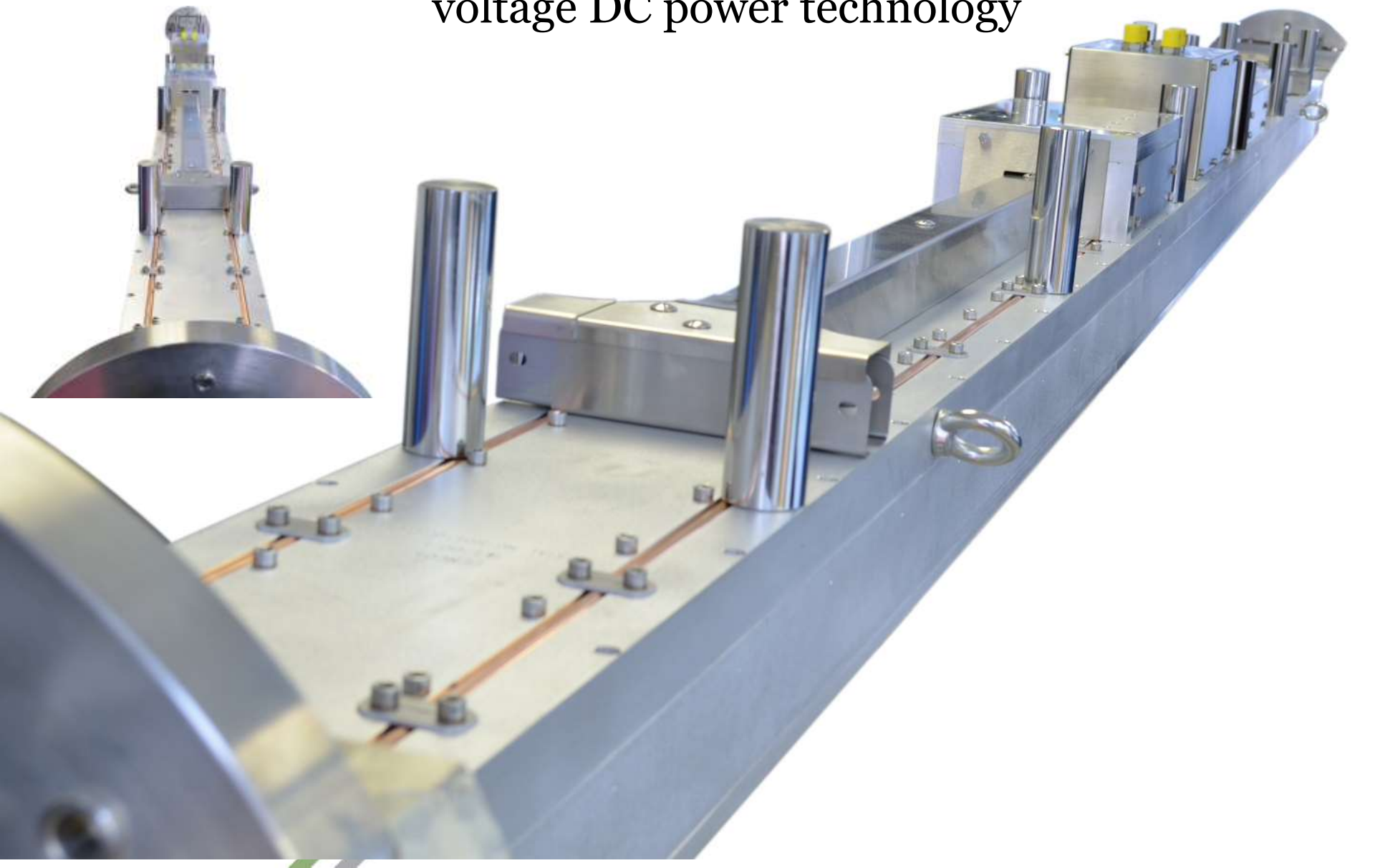
Based upon inverted magnetron End Hall type design





Ion sources - Lengths from 200 to 5000mm beams and internal, external or cantilever mounting

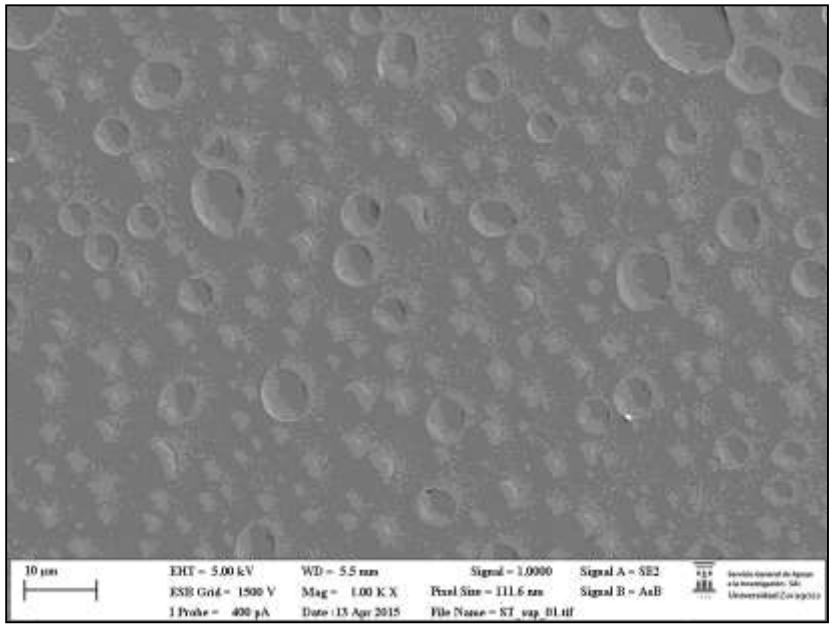
Internal mounting *im*4700 easily scalable technology as based upon +ve voltage DC power technology



Comparison of tempered glass with and without the use of a single pass plasma pre-treat with linear ion source

Parallel on-axis in-lens secondary electron detection SEM

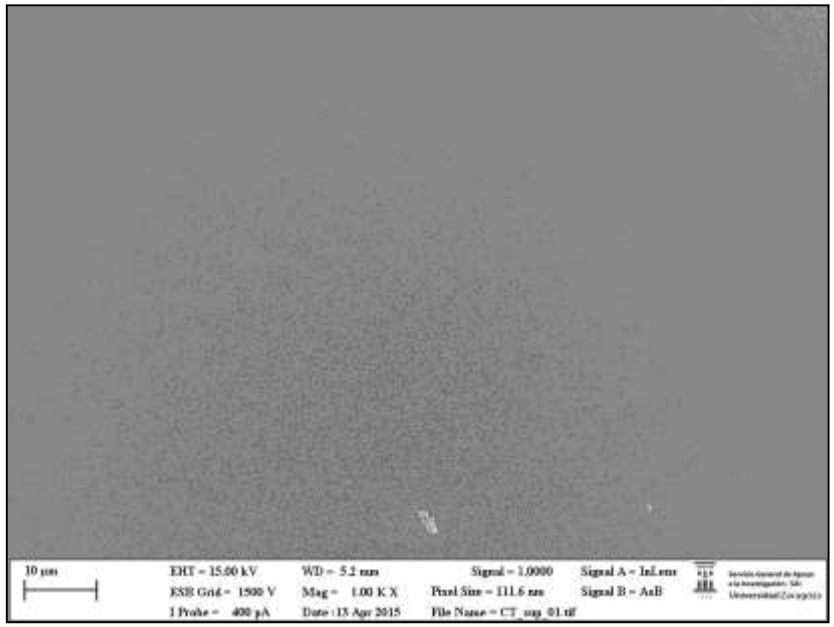
Sample not treated by ion beam



Samples without ion beam pretreatment show a hazy reflection.

Due to small bubbles (5 mm) in the coating.

Sample with ion-beam pre-treatment



After the tempering process no visible defects were detected on the coating.

SEM analysis confirm the good state of the coating.

VISTA Telescope – Parana Chile

Flame Nebula (VISTA -ESO)

VISTA Telescope mirror coater

Ion Source IM1500 At VISTA

Large mirror ion etching

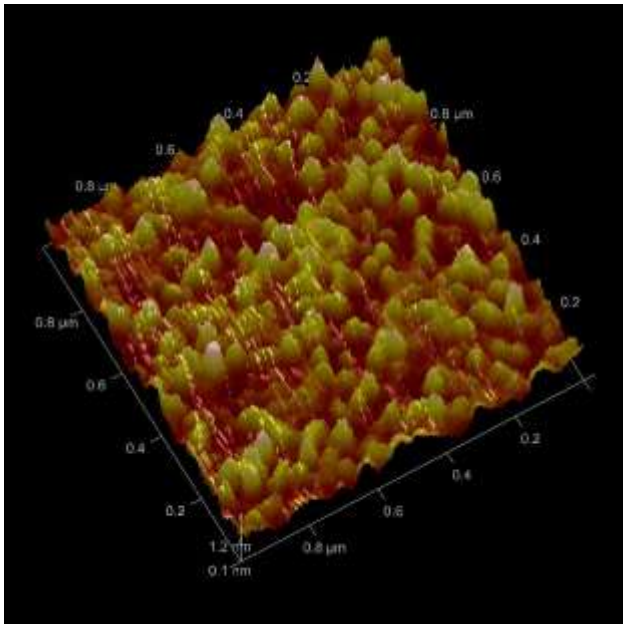
Large mirror coaters

Ion source

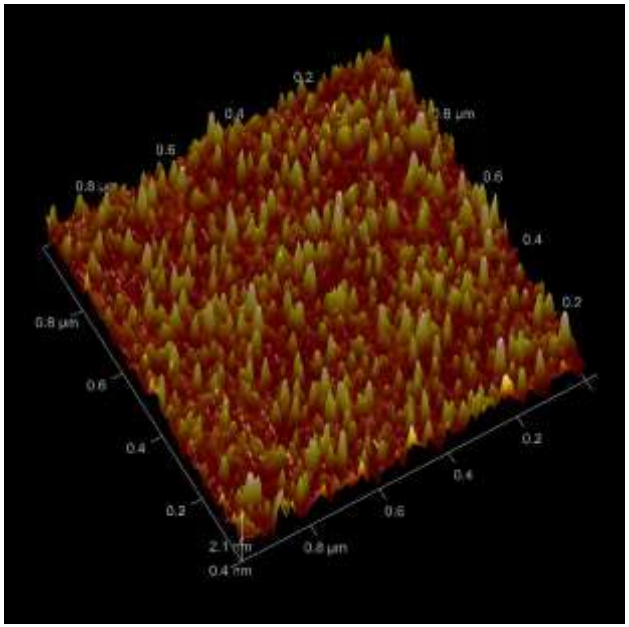
Linear ion sources are controllable and ‘gentle’ – typically 1 atom removed per pass and no surface roughening

AFM 3D Mapping – 1h Treatment

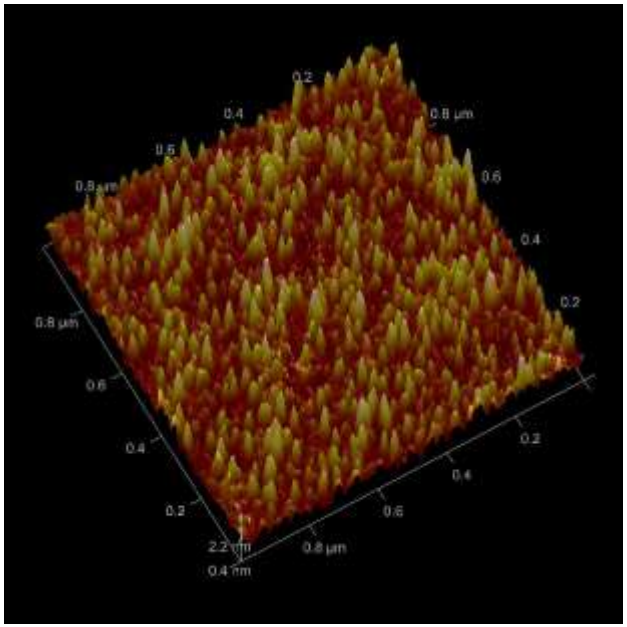
T-1K-R01



T-1.5K-R02



T-2K-R03



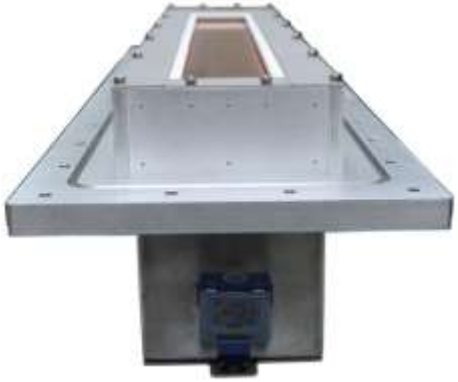
Treatment of Zerodur composite ceramic glass. The overall surface roughness doesn’t change substantially with the ion bombardment, however composite nanotopography is enhanced

Advantages of linear and circular DC inverted magnetron plasma sources

Linear Ion Source pros and cons	**Other points of note**
Very controllable and convenient but ***low current***	Self-neutralised beam; electron chanelling effect from beam ejection slot design
Limited anode and cathode lifetime – using carbon materials greatly enhances life.	Metal anode and cathodes will sputter much more quickly. Replacement more expensive and could require complete source strip-down
Automated regulation for the gas to maintain constant current & voltage – ensures constant beam energy	Beam properties will change constantly with varying vacuum conditions – gas feedback control an advantage
DC power suppler technology	Gas regulation feedback control within power supply is ideal. Gas done by separate MFC control less automated
Any length up to 5m in 50mm	Very easy to scale as DC power based

DC magnetron based plasma treaters for surface pre-treatment

Internal and external DC magnetron based plasma treating designs

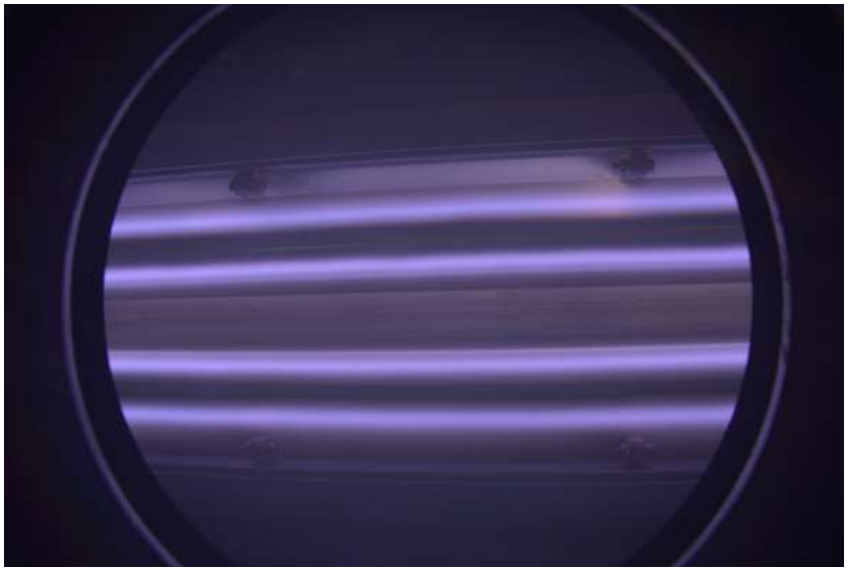


Advantages of DC magnetron based plasma source -Pulsed DC more effective than DC in some applications

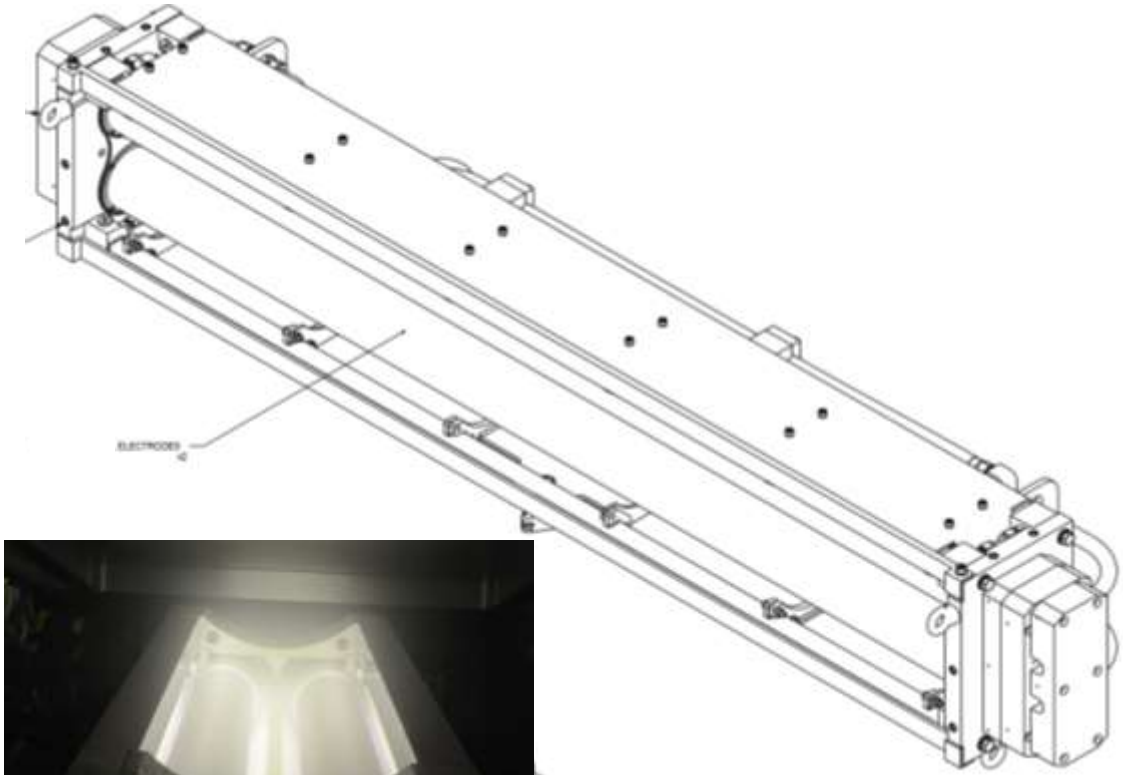
Magnetron pros and cons	Other points of note
Uses the same robust design as all planar magnetrons plus extra insulation for operation at high pressure – if in unwind zone	Low cost power technology
Ceramic insulation used in critical areas to prevent burning at high pressures	Polymers can be problematic due to the harsh environment
Many design and size options depending upon system / application	
High power capacity – high water flow and direct target cooling optional. Stainless Steel targets used typically.	Stainless Steel has a 'gettering' effect for moisture – Ti also good but higher cost.
Option of gas feedback control for automatic power output to react to different substrate types	Feedback control self-regulates and can adapt to the web conditions
Plasma & gas confinement front box with viewing window required	Best to confine the plasma and provide a 'purer' localised discharge

High power plasma gas source for Pre-treating and Radical Assisted Sputtering Processes

- Modern alternative to RF and Microwave powered active gas sources – no power or scaling issues – 0.2 to 4m lengths
- Up to 40 Amps of plasma electrode current per m length
- Highly activated gas species with 70 eV energy
- Added kinetic energy of gas to aid layer oxidation & pre-cleaning
- Pure gas plasma – no etching of electrodes
- No maintenance
- Uses Gencoa DLIM patent - Active Anode gas excitement



High power AC plasma treaters (4kV) for surface pre-treatment - Dual 75mm dia electrodes, magnetron enhanced medium frequency switching power

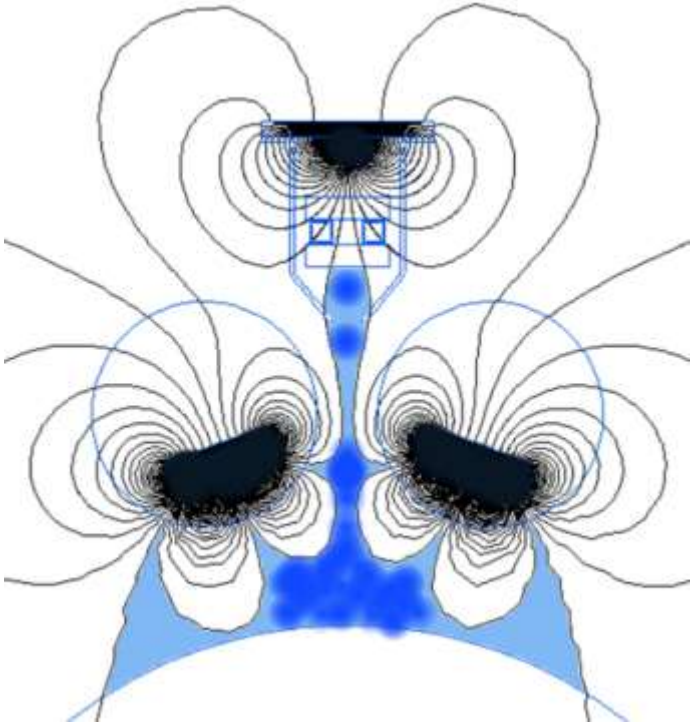


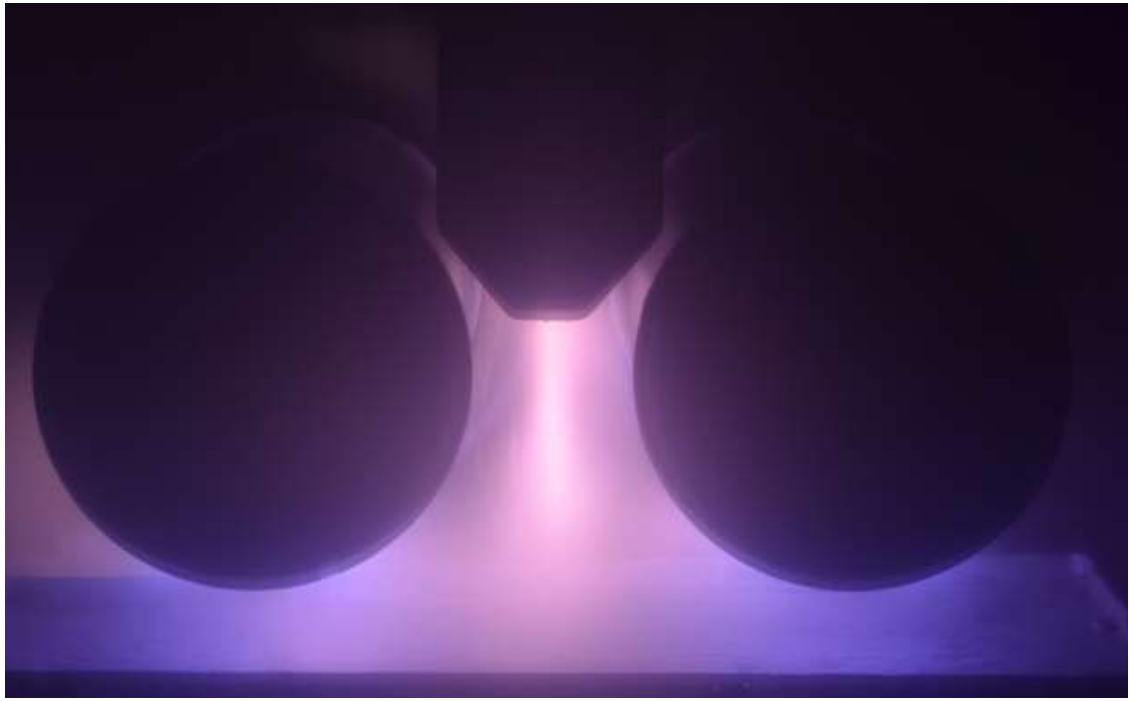
Magnetic packs angle adjustment for plasma – web interaction adjust

AC power provides excitation and easy to scale in length compared to RF and MW

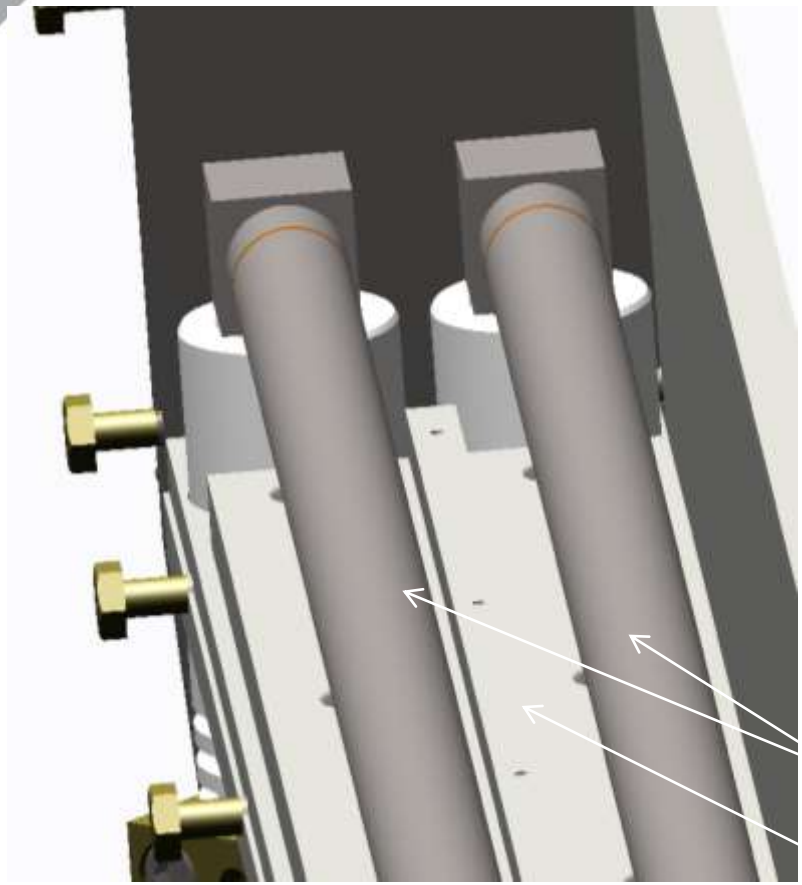
Uses both magnetics in the electrode tubes as well as magnetics in the remote active anode

A dual rotatable magnetron with Active Anode and switching power and a mix of Ar and O2 gas, creates an enegetic plasma with + & -ve bombardment of the substrate





ULTRA COMPACT possible
AC powered dual electrode operates with a medium frequency generator
This switches electrons and drives the plasma generation



The AC dual output power supply will provide 40 kHz frequency of switching at upto 7kV and 5 kW maximum power. The power is switched between 2 water cooled electrodes in the presence of argon gas and a magnetic field. The resulting plasma intensity will provide effective pre-treatment of the passing web.

Water cooled dual electrodes

Pre-distributed gas injection

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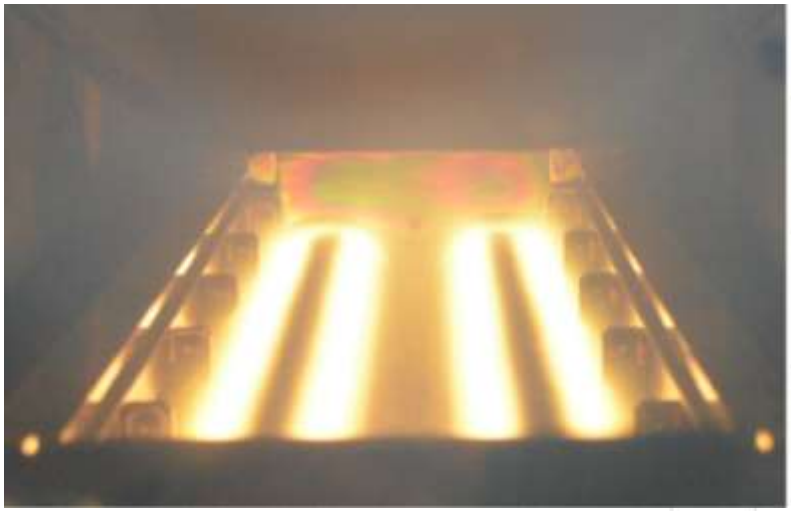
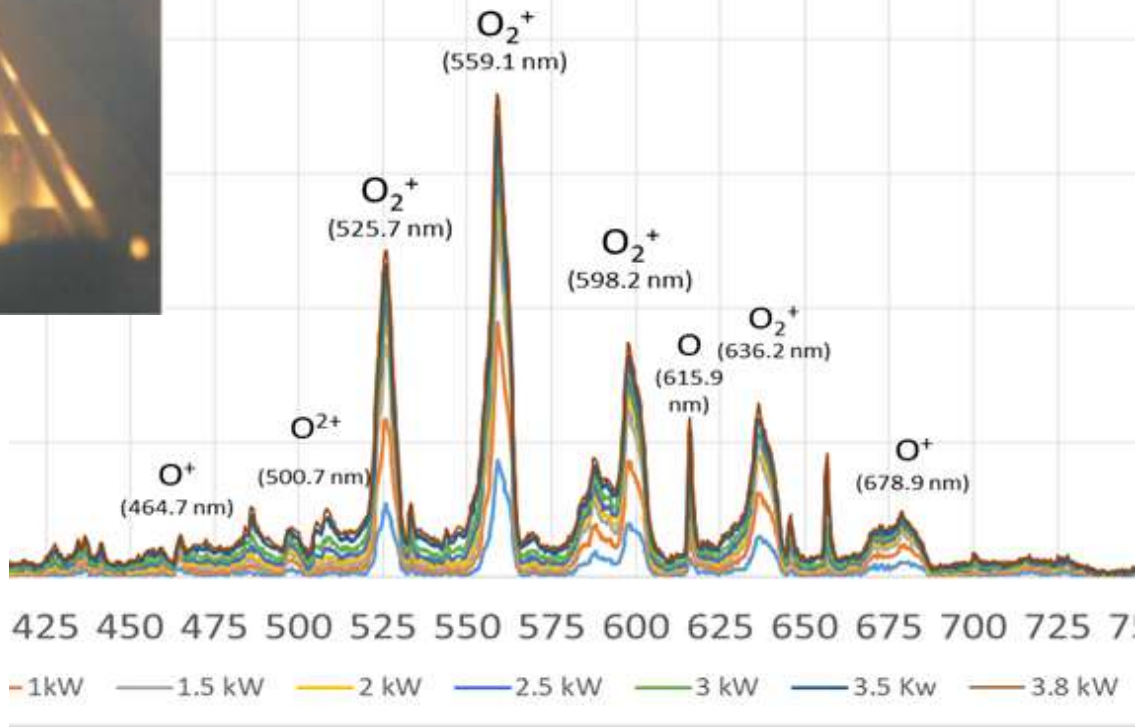
The AC plasma and active anode provides single and double ionisation of the Oxygen atoms and molecules for extra reactivity of the sputtered metal surface

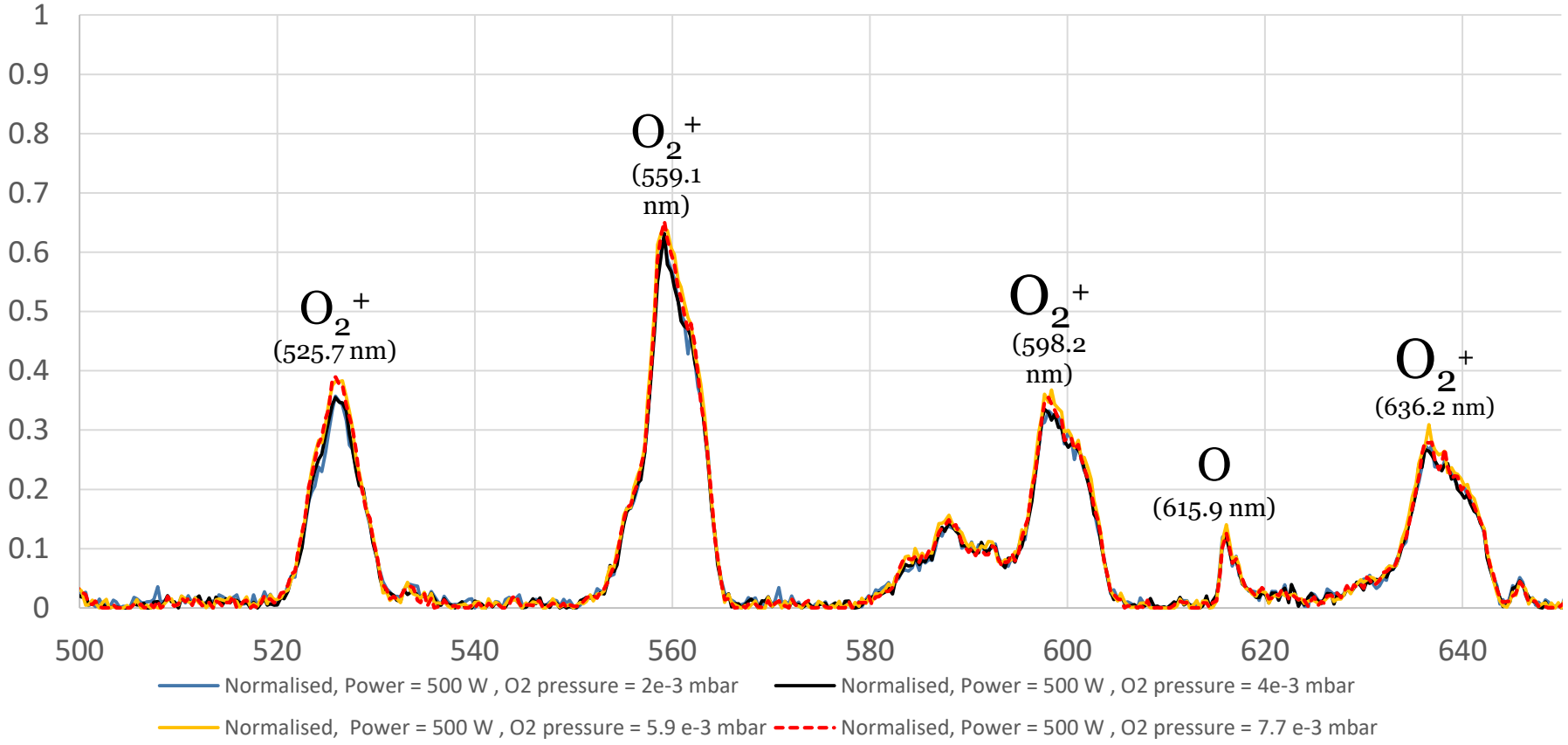


Plasma Emission Spectra at varying powers for 400mm long electrodes at varying powers



Plasma Spectrometry with changes in O_2 pressure at 500 W

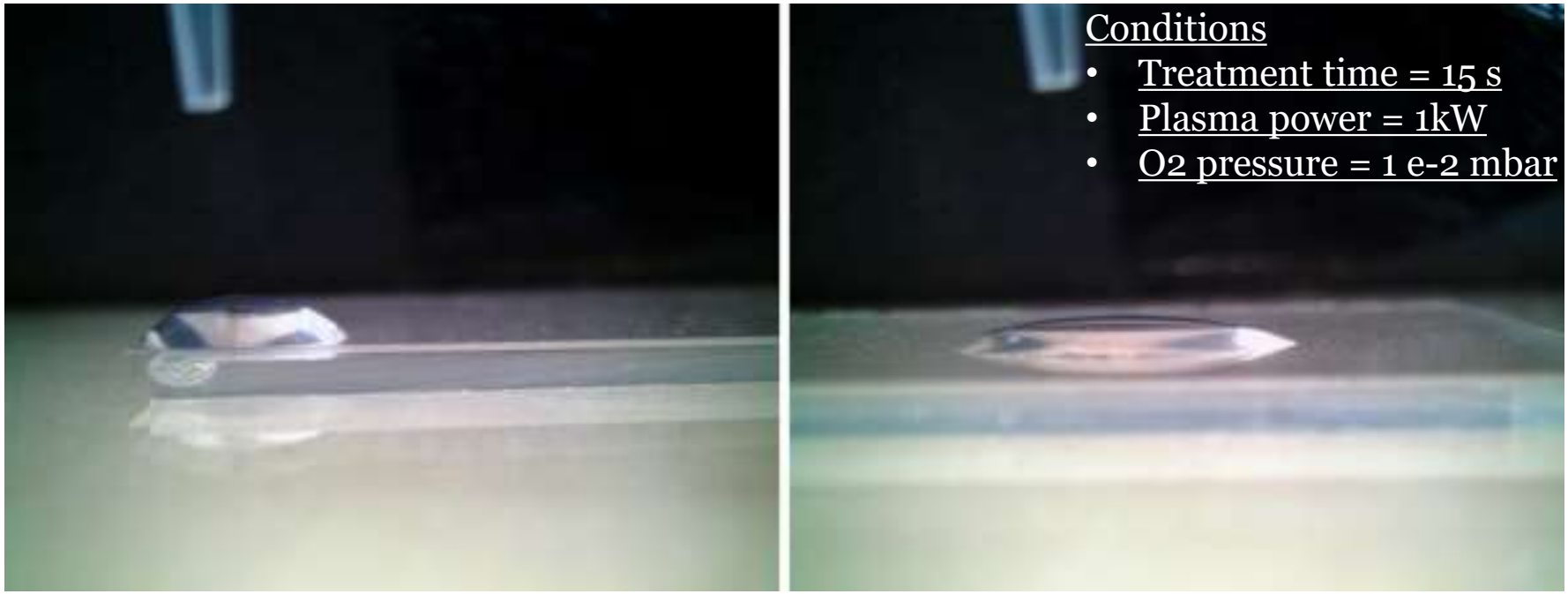
- there is little change in the ion/neutral ratio over the O2 pressure range



Contact angle measurements

Untreated Surface

Treated Surface



- The oxygen plasma provides 70eV bombardment of the surface plus kinetic energy as ions repelled from electrodes as power switches to +ve potential.
- Hence can be used to pre-clean the substrates prior to coating

Comparison with other gas plasma sources

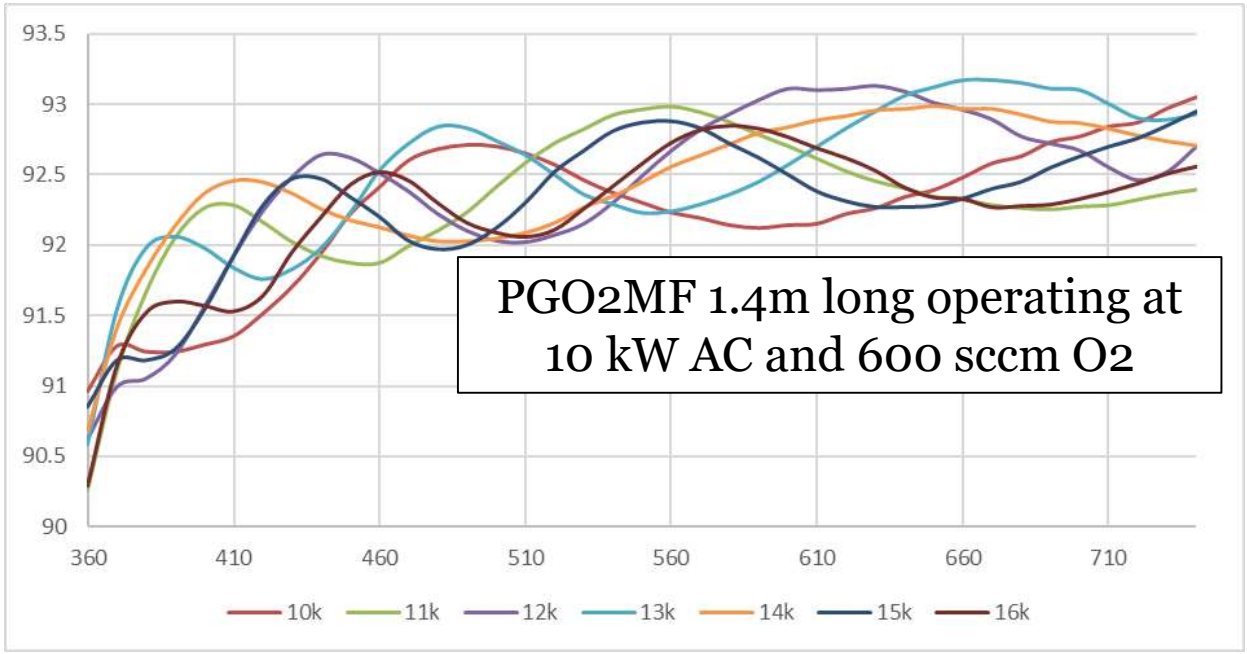
Plasma Source Type	Plasma Power (kW)	Current Density (mA/cm^2)	Plasma Density (m^{-3})	Reference
$GPgO_2400$	3.8	4	10^{15}	30mm away from the source
$GPgO_2400$	3.8	2	10^{15}	110mm away from the source
Microwave ECR	0.4	1	$10^{15} – 10^{16}$	https://www.robeko.de/wp-content/uploads/2019/07/robeko_miro-200-cl.pdf, https://www.sciencedirect.com/science/article/pii/S0042207X08003527
RF	1-5	1-5	$\sim 10^{18}$	https://www.ccrtechnology.de/copras-basics/

Comparison of Microwave plasma source and Gencoa PgO2MF

- PgO2MF produces same uniformity & optical layer quality as MW
- Rate is 10% higher for the PgO2MF at the same sputter target power
- MW cannot operate above 14kW sputter power, PgO2MF has no sputter target limit (increase the AC power and O2 gas flow), at 16kW, rate is 20% higher than MW max rate

PGO2MF

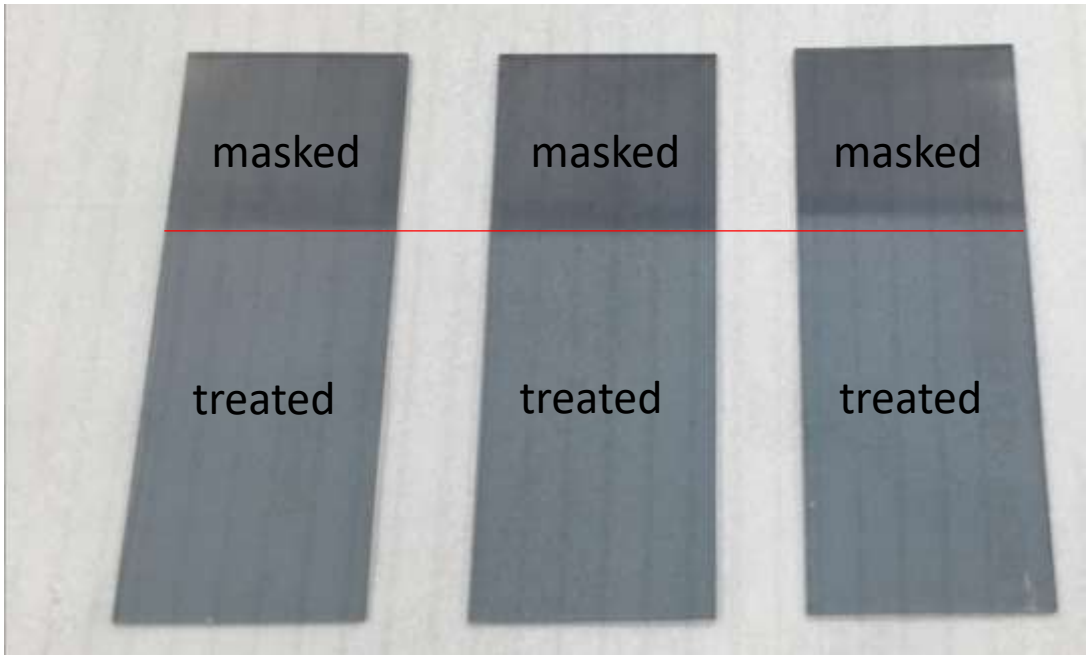
PGO2MF can also pre-clean the substrates in 5-10 minutes

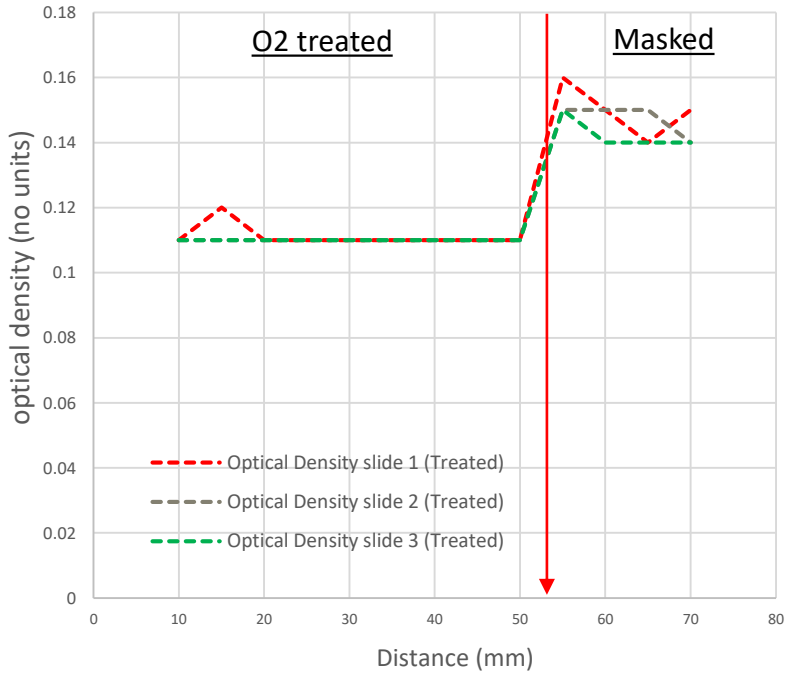


SiO2 transparency at different Si target sputter powers

O_2 activation of Al coatings

- 15nm of Aluminium was pre-coated onto glass slides which were then exposed to O2 plasma at 2kW for 30 minutes





- The results show a decrease of ~30% in the optical density between the masked and treated regions of the Al pre-coated slides
- A surface depth of pre-coated Al has been oxidised – source can be used for pre-cleaning of substrates as well as radical assisted sputtering

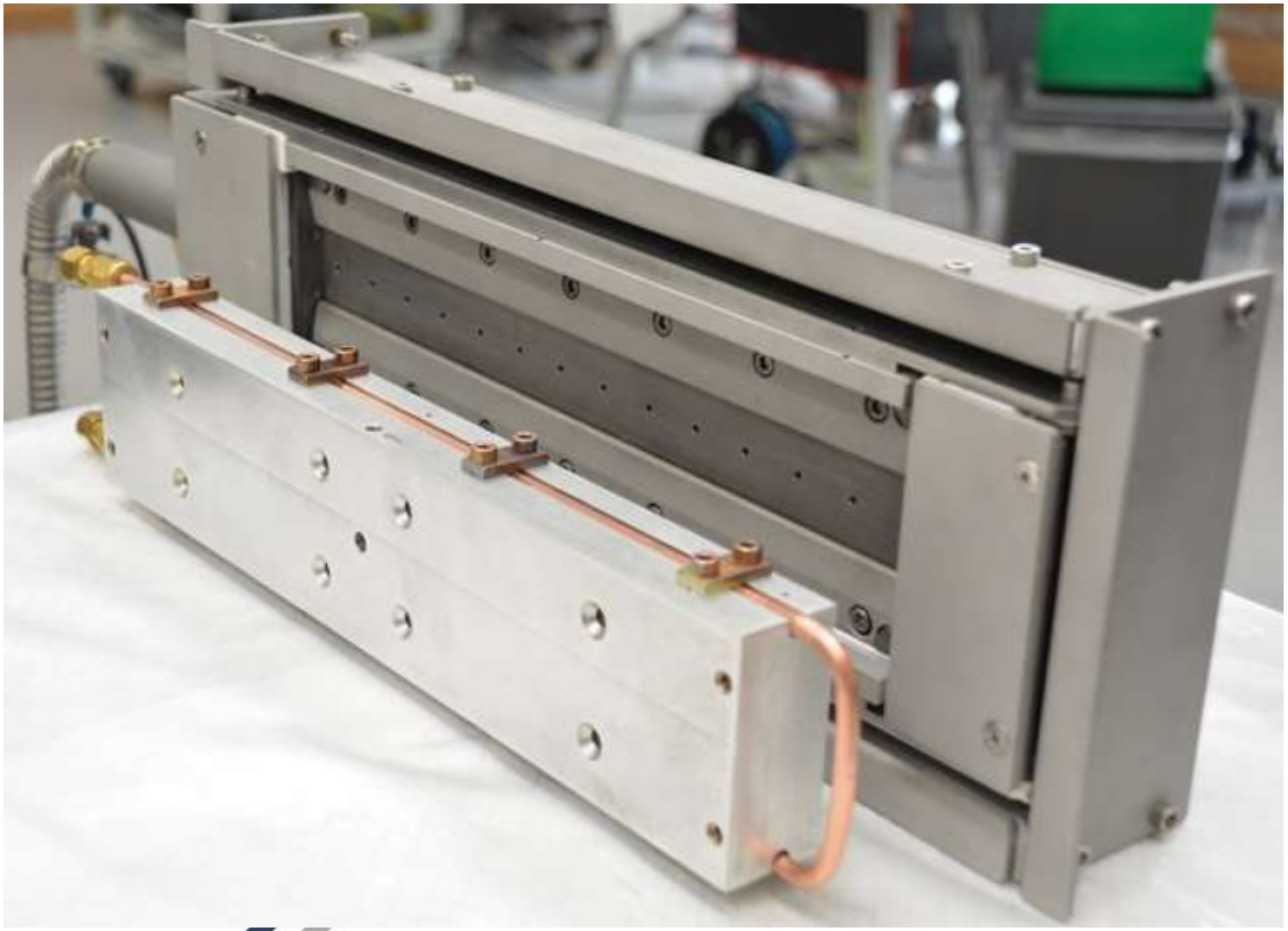
Pros and Cons of AC based magnetically enhanced plasma sources

Plus Points	**Weakness**
Switching AC plasma with active anode enhancement produces a high intensity plasma for pre-treatment or O2 plasma production	Could damage the substrate if power is too high or substrate speeds too low
Self-neutralized switching plasma potential – no charge build-up on substrate or target – more robust in 'dirty' environments	Higher cost compared to single electrode DC
Double electrode – switching from positive to negative so stable anode and cathode	Not able to etch material from the substrate as only 70eV energy of bombardment
Highly scalable and controllable plasma & can run at high substrate speeds and powers	
Can run in poisoned mode or 'gettering' mode	

GENCOA

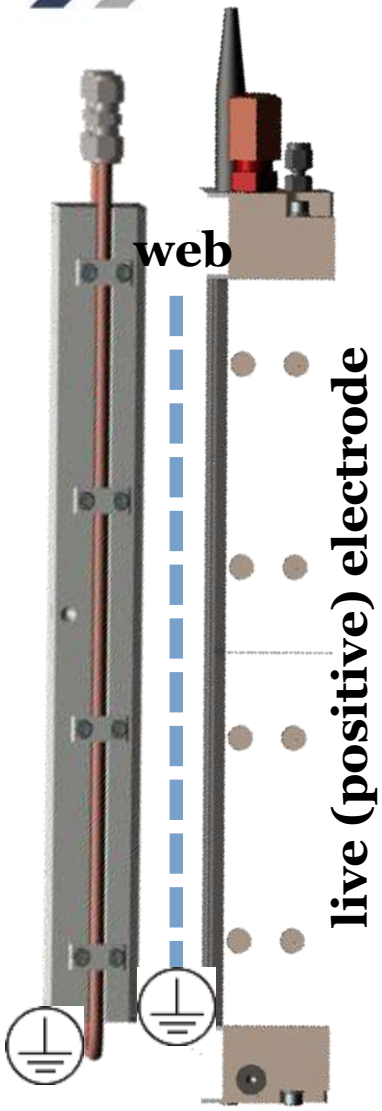
Introducing new magnetron plasma pre-treatment and etch method, based upon Positive voltage pulses to magnetically enhanced electrodes

Inverted Magnetron Metal Sheet Etcher
Initial use of positive voltage pulses to etch sheet metal and plastic



Inverted magnetron metal etcher - principles

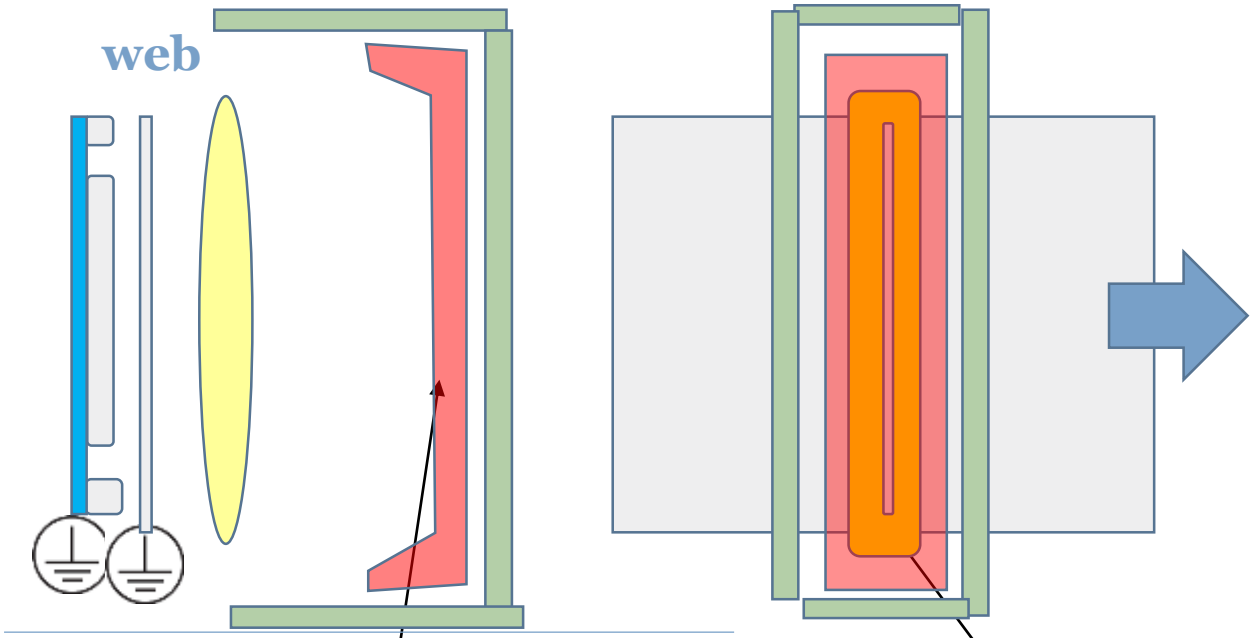
- Two-electrode discharge
- One electrode is grounded, one is live (positive pulse V+)
- Magnets create a magnetic field trap over a grounded electrode.
- The web/substrate to be treated is kept in contact with ground
- A (positive) pulsed mode is used for the discharge, for improved effectiveness in etching the web surface
- Due to the pulsed nature even dielectric layers on substrate could be removed by this method.



Inverted magnetron - principles

Gas injection (internal)
via this fitting only.
Argon to be used

Both electrodes need
water cooling

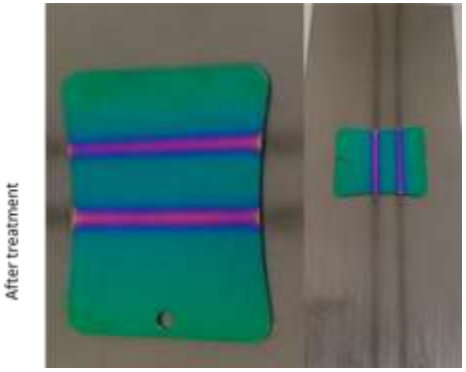


grounded electrode with permanent magnets

live (positive) electrode

Plasma is generated in this zone, and it's confined via electric and magnetic field

IMME – Plasma discharge and fast etching of different materials – the metal roll is the target

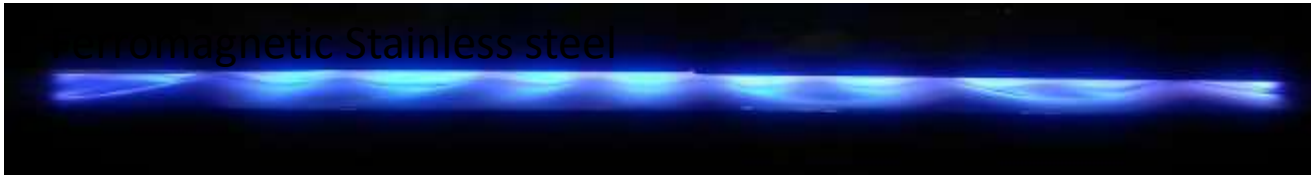


On TiOx-coated stainless steel

(Power 0.1 kW, for 60 secs)

Etching rate estimated at 50nm/min

Gap 25 mm, 0.4 kW

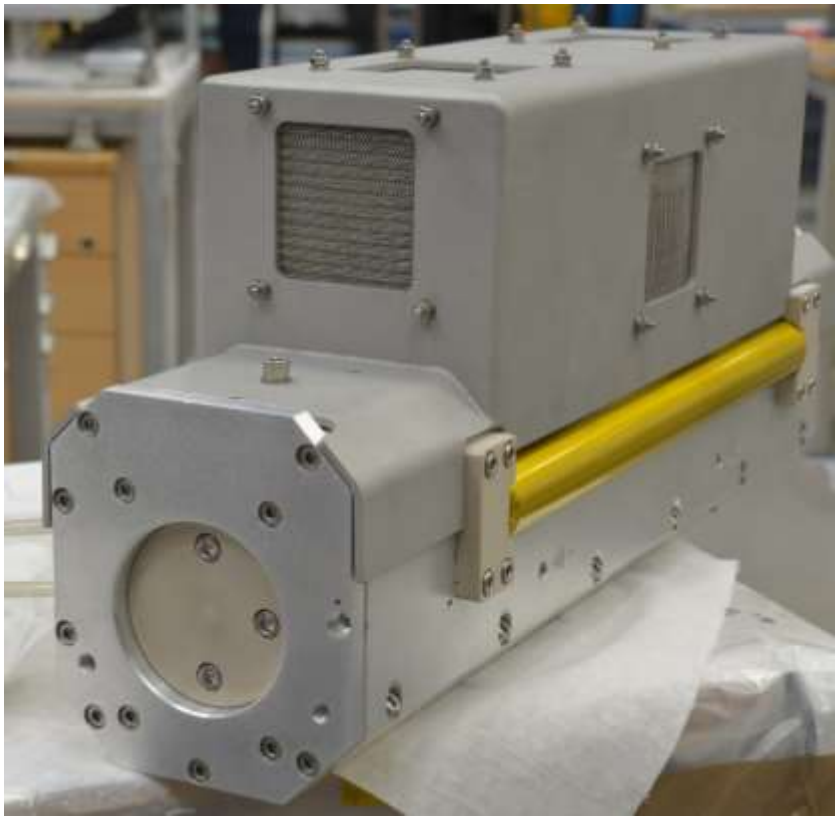


Gap 11 mm, 0.5 kW
Substrate heat effect.
Plasma is affected my magnetic web material

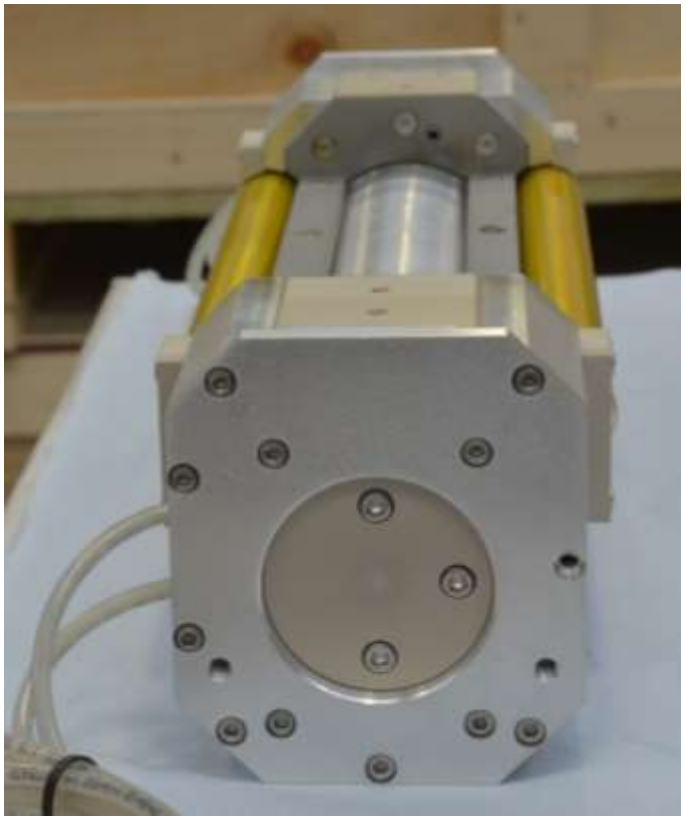
Gap 11 mm, 0.5 kW

Etching Unit – Roller design

A similar method can be applied to a powered roller

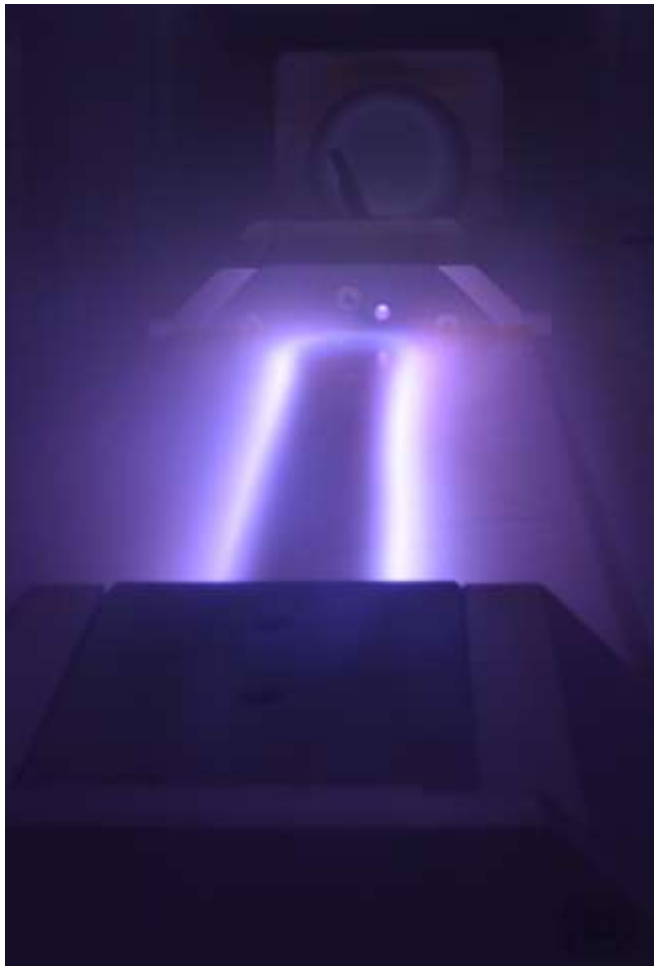


Full assembly - encapsulated



With roller exposed

Plastic web on roller Plasma Treatment Roller Electrode



Electrode power couples through the plastic web material to establish a discharge

Full plasma power directly on the web (not a remote source). Roller cools the web

Moisture liberated and pumped away

Space saving as can act as a guidance roller – driven – needs to integrated at the system design phase – hard to retrofit and applying power and cooling through the roller not easy

Hip³

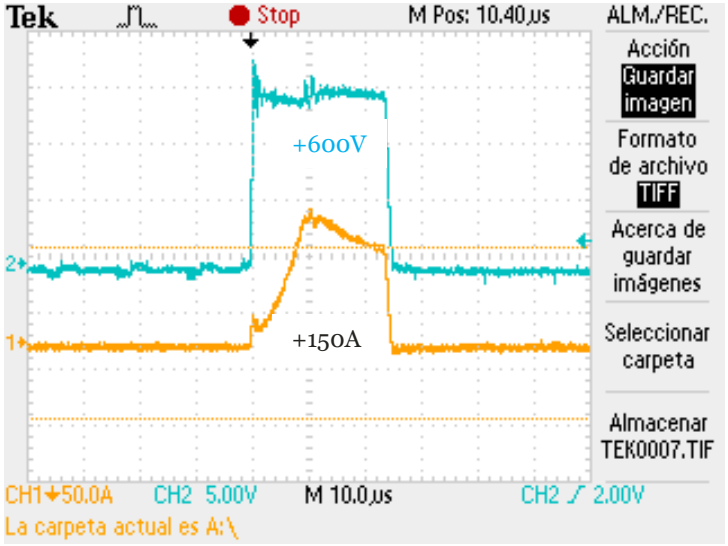
High Rate Ion Etching Technology
'The Power of Positive'

Rapid coating removal and surface preparation based upon positive voltage Hipims – patent pending

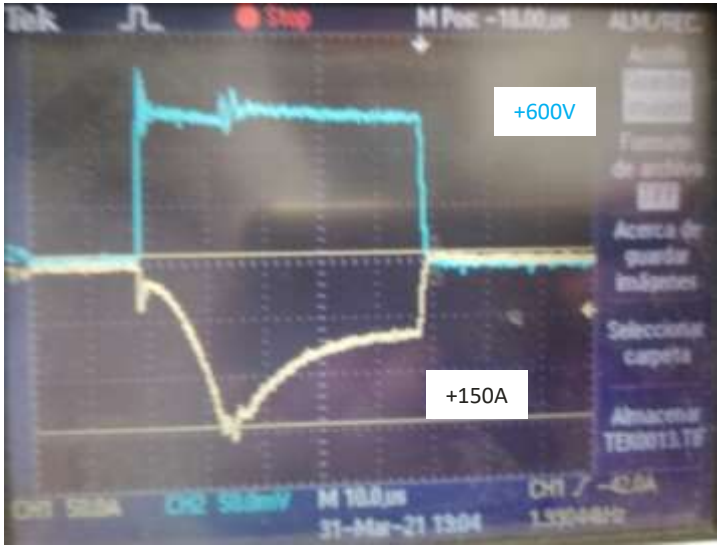
Hip³ Pulsing Parameters

Pulse width as high as 120us with stable peak current around 150A. No negative phase to the pulse.

MAG Ion Source– Voltage pulse



22us pulse width
Max. frequency – 2kHz
Max. Average Power – 20kW



50us pulse width

Etching tests – conductive substrates in a batch coater with 2 planar magnetrons (100 x 400mm)

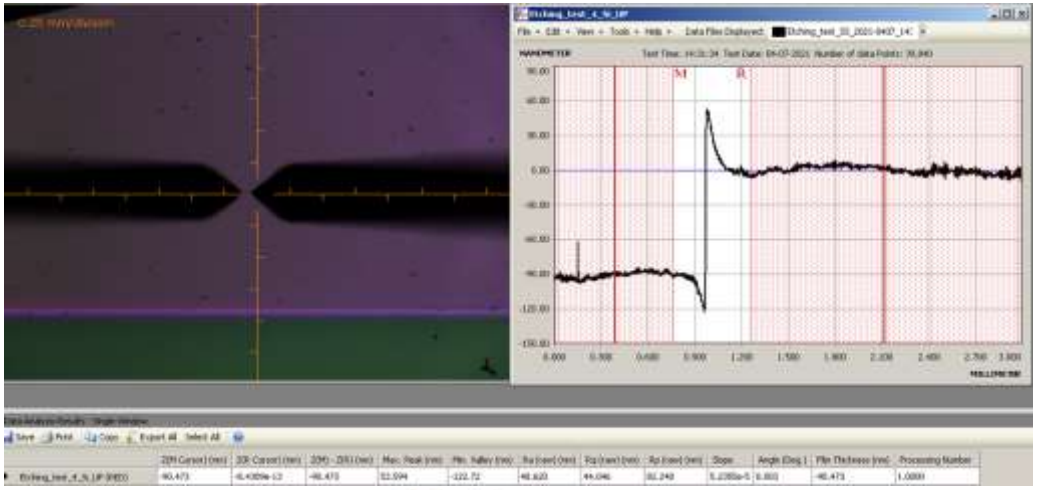
Total distance in 3-fold rotation (approx.):

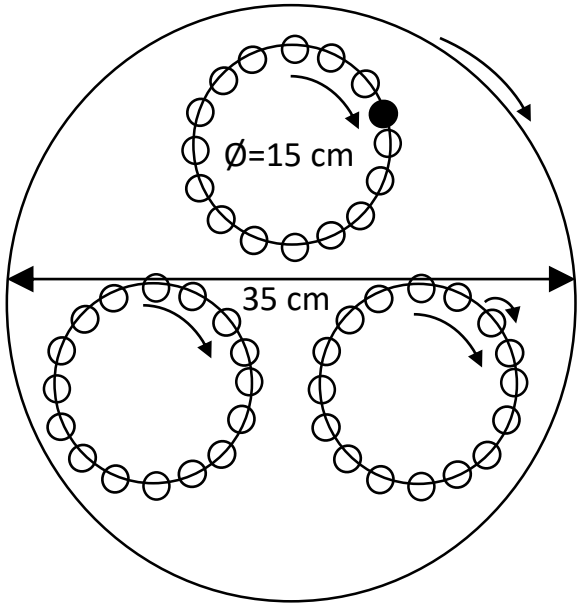
3 times 2*p*(7.5) = 140cm = 1.4m

Time : 1min @1rpm

Speed (@1rpm) = 1.4m/min = 1pass/min
(@5rpm) =7.0m/min = 5 pass/min

If etching rate (Carbon) equal to 50nm in 60min then:
50nm * 1.4m /60 min = 1.16nm*m/min





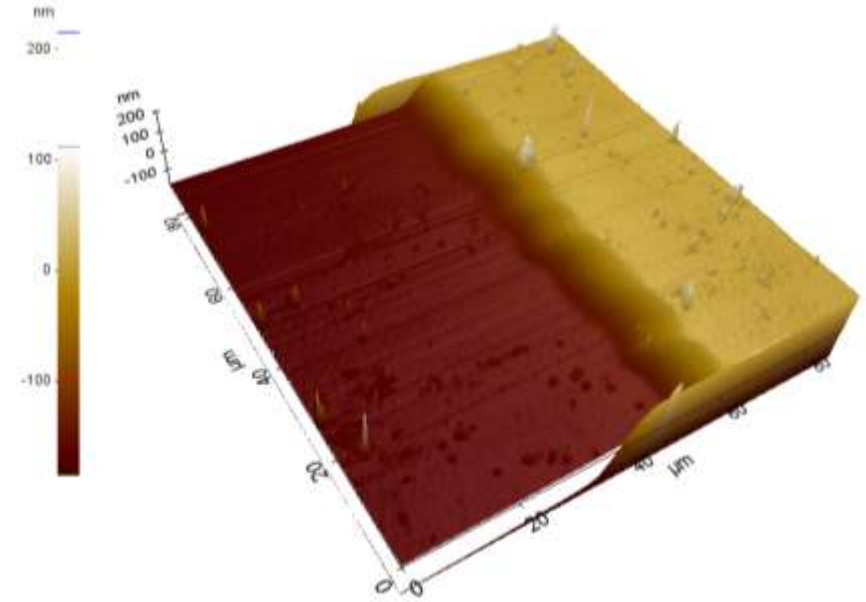
Hip³ Source
(100 x 400mm target)

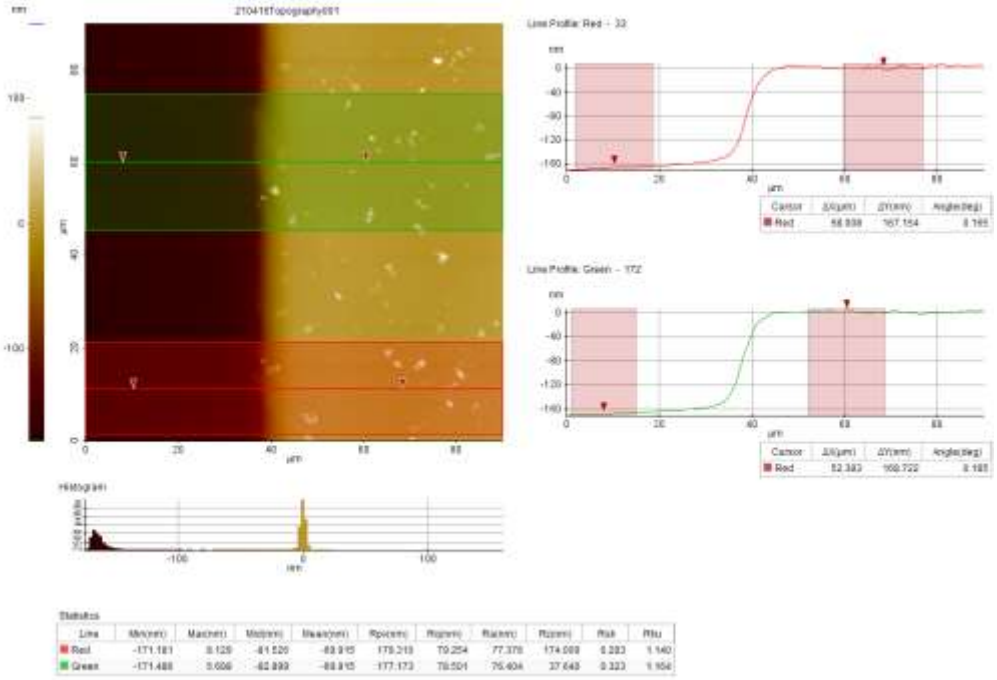
Etch depth measured by surface step profile and AFM

Etching assessment by AFM

ION SOURCE:
3kW average (145A peak, 660V peak)
22us – 2kHz

SUBSTRATE
Bias DC-200V
Ar gas 50sccm – P(Ar) = 5e-3mbar
Etching time = 60min





Hip3 etching rates – comparison with DC-Pulsed Argon Glow discharge

ETCHING RATE FOR STAINLESS STEEL

Ion source + DCP (200V, 100kHz – 250W) = 160nm in 60min
TOTAL = **192nm/hr (2.24nm*m/min)**

DCP (350V*, 100kHz – 350W) = 6-12nm in 60 min TOTAL = **0.1 to 0.2 nm*m/min**

* Minimum Voltage and frequency to ignite Plasma in chamber

DC-P Glow discharge

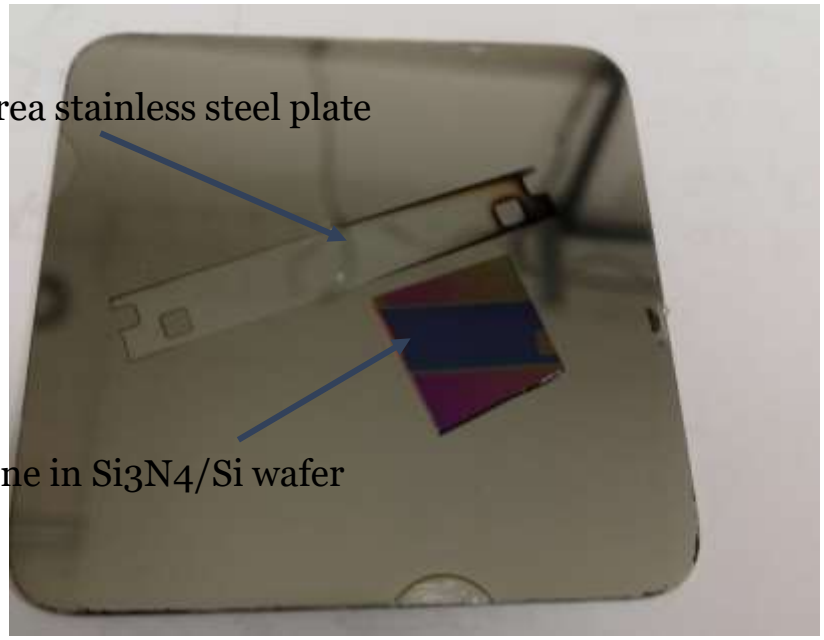
Hip³ discharge

Ar gas 60sccm – P(Ar) = 6e-3mbar
Bias Pulsed DC-250V – 150kHz

Etching of Carbon & Si_3N_4 3 axis rotation for 60 min

ION SOURCE:
3kW average (145A peak, 660V peak) 2us – 2kHz
Ar gas 50sccm – P(Ar) = 5e-3mbar
DC Bias -200 V

Etching Rate Stainless Steel = **90nm/hr (1.05nm*m/min)**



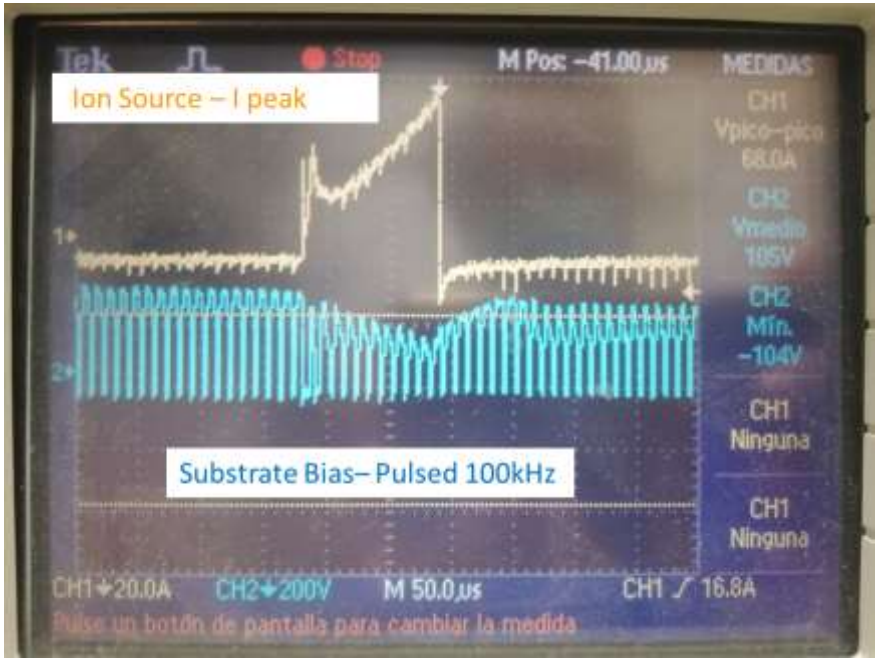
Etching Rate Si3N4 on Silicon wafer = **38nm/hr (0.44nm*m/min)**

80nm taC on Stainless Steel (before etching)

taC sample after 60 mins etching

Etching of Carbon & Si_3N_4 Pulsed DC 50 min

ION SOURCE:
3kW average (145A peak, 660V peak) 2us – 2kHz
Ar gas 50sccm – P(Ar) = 5e-3mbar
Pulsed DC Bias -250 V 150 kHz



Etching Rate Si3N4 on Silicon wafer measured by AFM = **160nm/hr (1.86nm*m/min)**

Etching Rate Stainless Steel = **192nm/hr (2.24nm*m/min)**

Etching Rate Stainless Steel = **192nm/hr (2.24nm*m/min)**

<u>ETCHING RATE ESTIMATION FOR STAINLESS STEEL FOR HIGHER APPLIED POWERS</u>

If power is raised to 10kW = **7.46nm*m/min**
If power is raised to 20kW = **14.91nm*m/min**

Hence at 20 kW approx is equivalent to **150** times faster than a linear ion source.

Summary Hip³ etching process for metallic substrates with pulsed substrate bias applied

- High Power Positive Pulses on a magnetron source to perform etching in combination with Negative DC or Pulsed Bias, and a second magnetron operating at very low power.

- A steady peak current state is achieved, allowing operation at high average power (up to 20kW) at low frequencies (as low as 2kHz) – typical HiPIMS conditions.

- Etching rates as high as **2.24nm*m/min on 3D rotating parts** were demonstrated for Stainless Steel with 3kW average operation on a 100 x 400mm ion source (magnetrom).

- Etching rates as high as **1.12nm*m/min** were demonstrated for Si3N4 with 3kW average operation and pulsed DC Bias (100kHz).

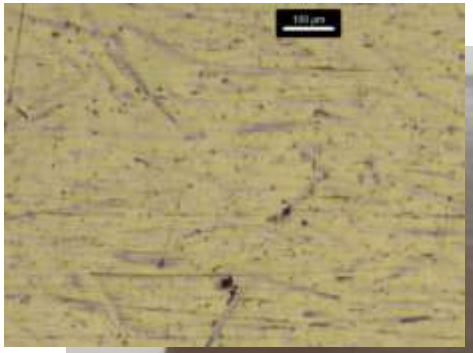
- Etching rate can be estimated to be above **15nm*m/min** on Stainless Steel using Ar and a rectangular magnetron with 400cm2 with 20 kW applied power.

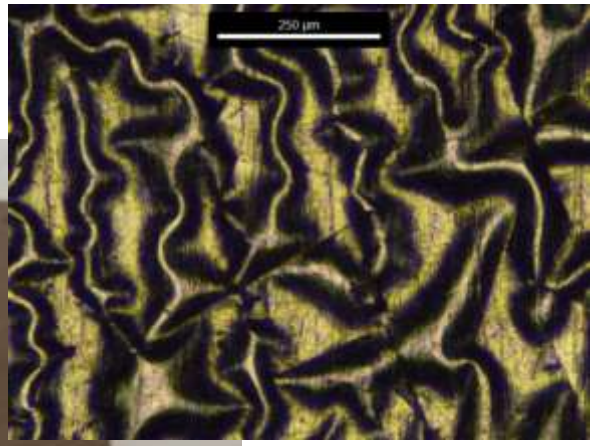
- The combination with reactive gases boosts the etching rate (observed for DLC etching using Ar+O2 plasma).

Test on plastics – Ryton PPS-GF in the same batch coating chamber

- Hip³ can be used with argon and oxygen to rapidly pre-treat plastics
- No substrate bias possible with insulating substrate materials
- But treatment still effective

- Etching time – 5minutes
- P (Ar+O2) – 1.3 e-2mbar (Ar:O2 – 50:50)
- HiP³ parameters : 550V 40us 2000Hz, 130W





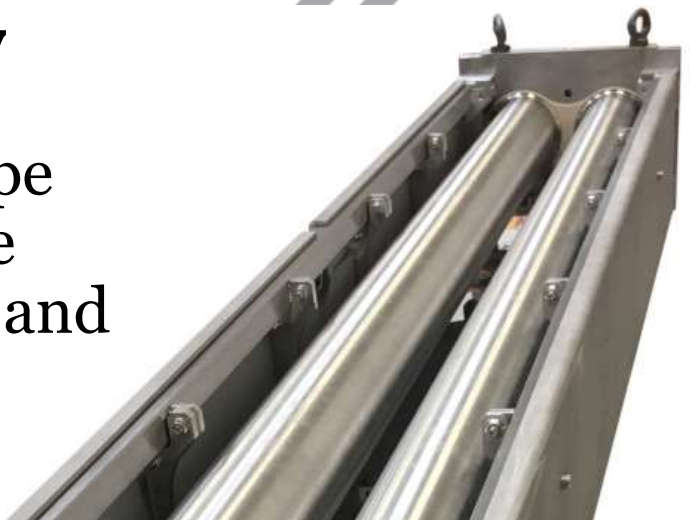
Plasma treated prior to TiN deposition

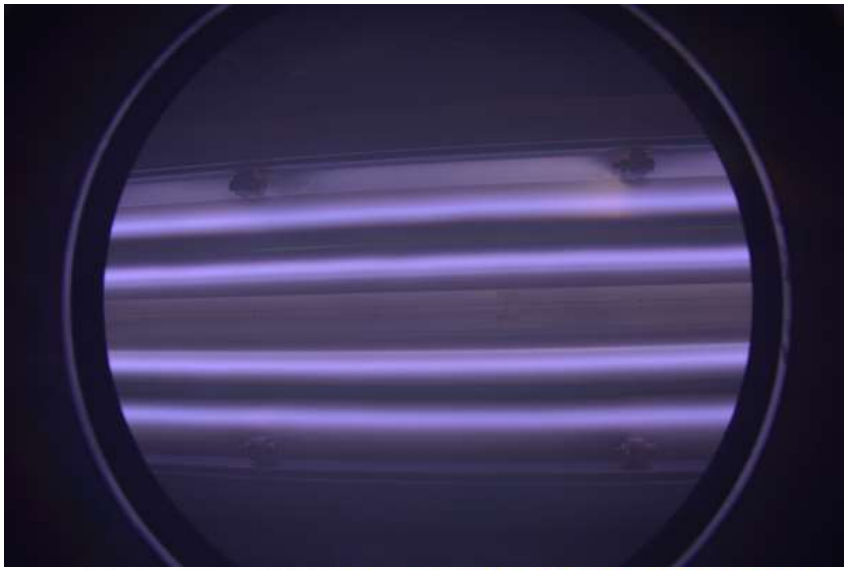
TiN deposition with no pre-treatment

Hip³

High Rate Ion Etching Technology

Exploring the use of **Hip³** Hipims type positive pulses with a dual electrode plasma source to treat and etch metals and plastics

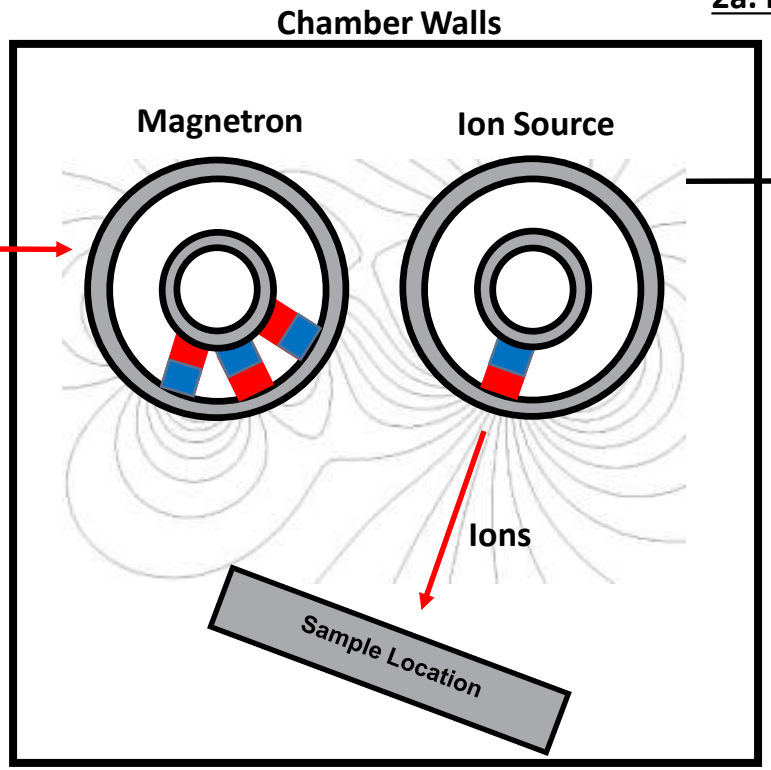




Hip³ applied to the dual electrode plasma source

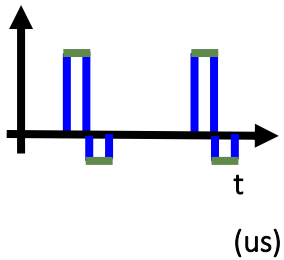
1. Magnetron Power

Magnetron discharge produces electrons which neutralizes ion source discharge



2a. HIPV Power Supply – positive pulsing

2b. Waveform on Ion Source

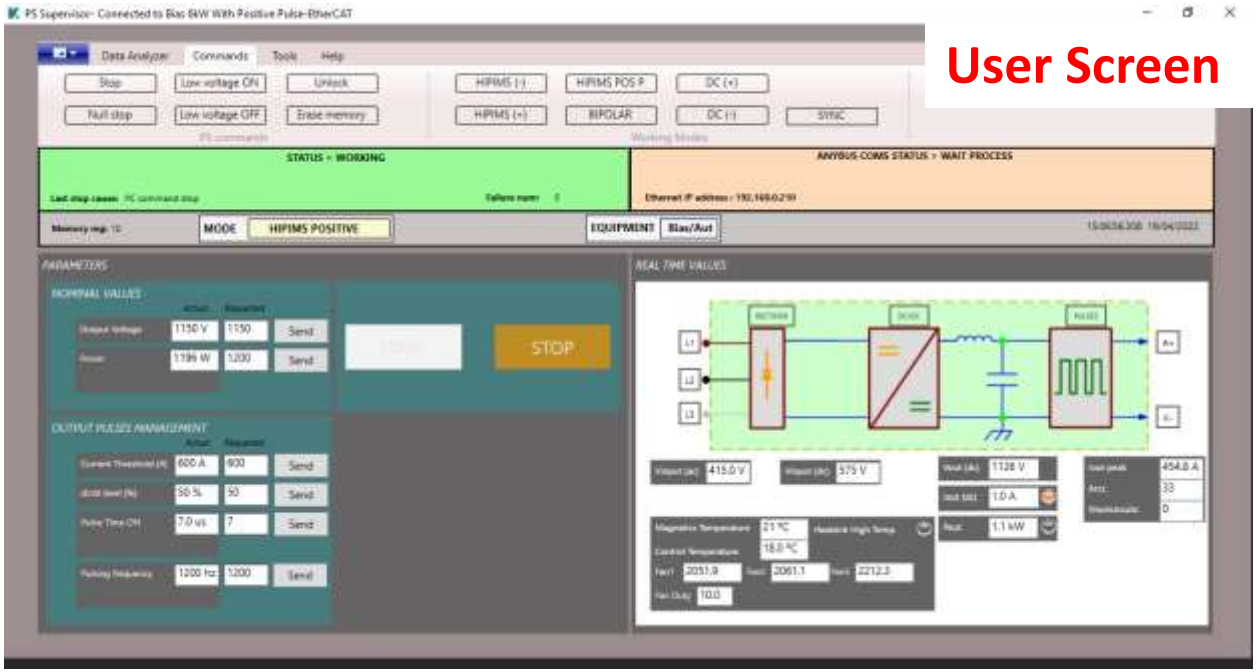


3. Plasma on magnetron and ion source

Hip³ etch process parameters

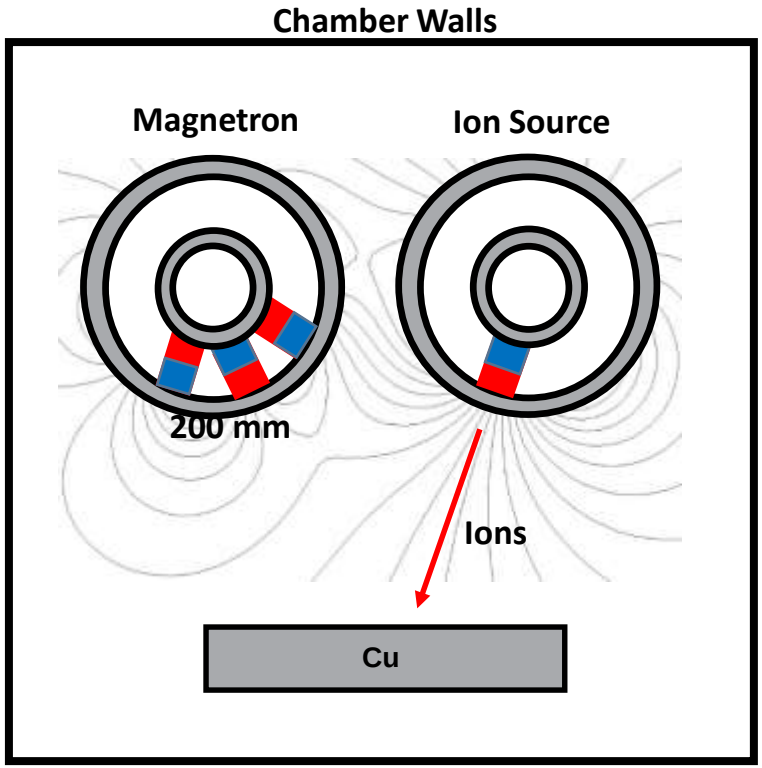
- Probe charges up positively – positive bombardment occurs!

Yellow = target voltage
Green = grounded probe
Red = Rogowski coil

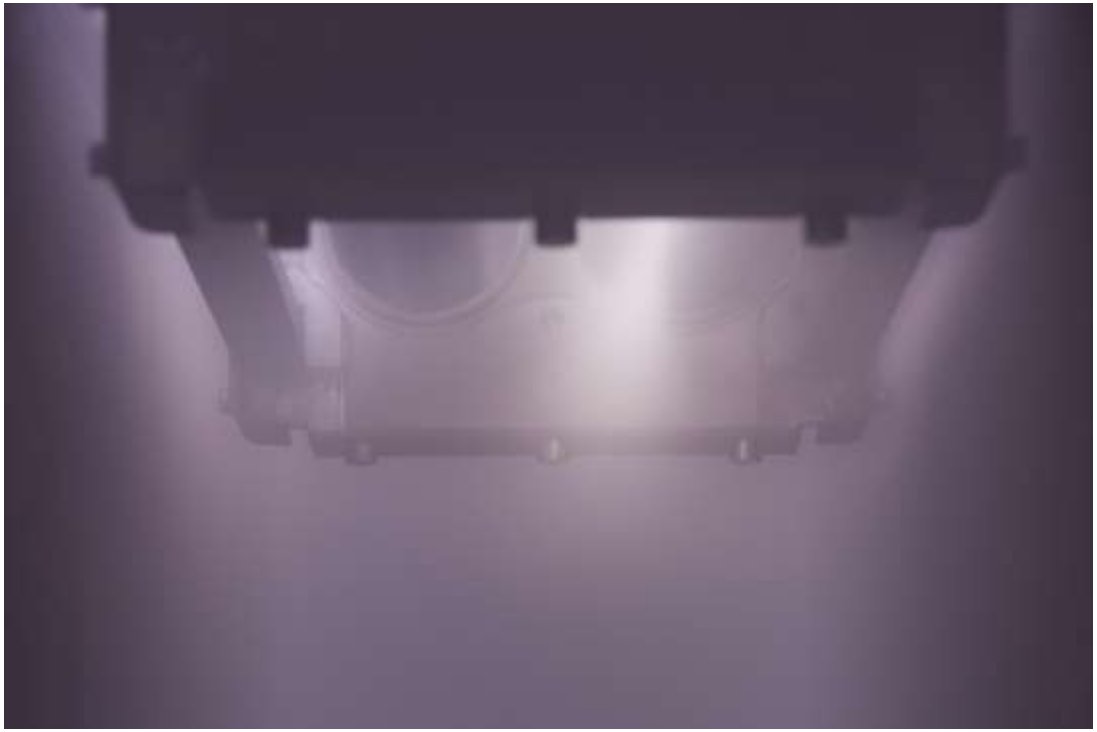


❑ Ion Source – 1.2 kW (600 A peak, 1200 V peak), 7 us - 1250 Hz

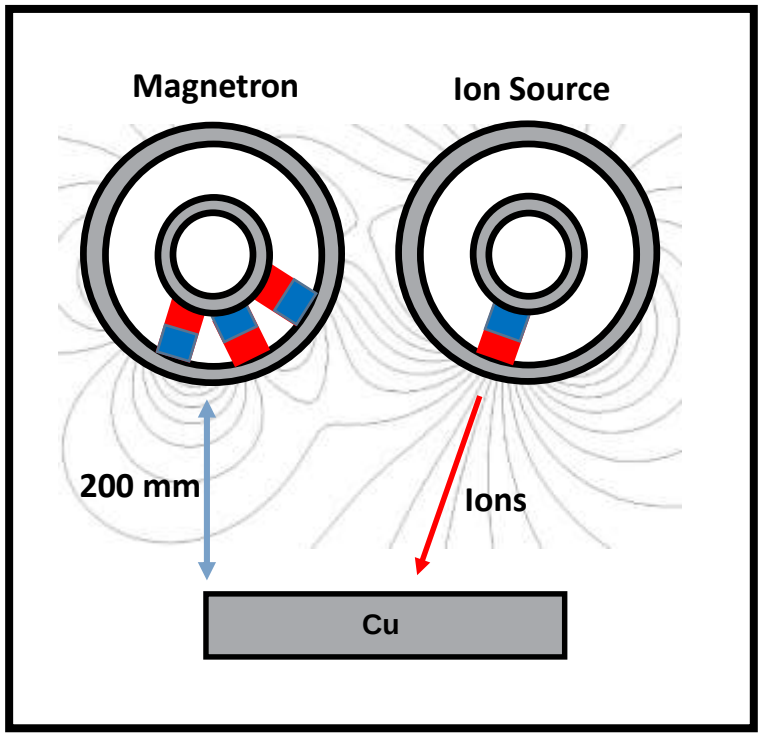
Hip³ Cu etch process with an Argon Plasma



- Ar plasma



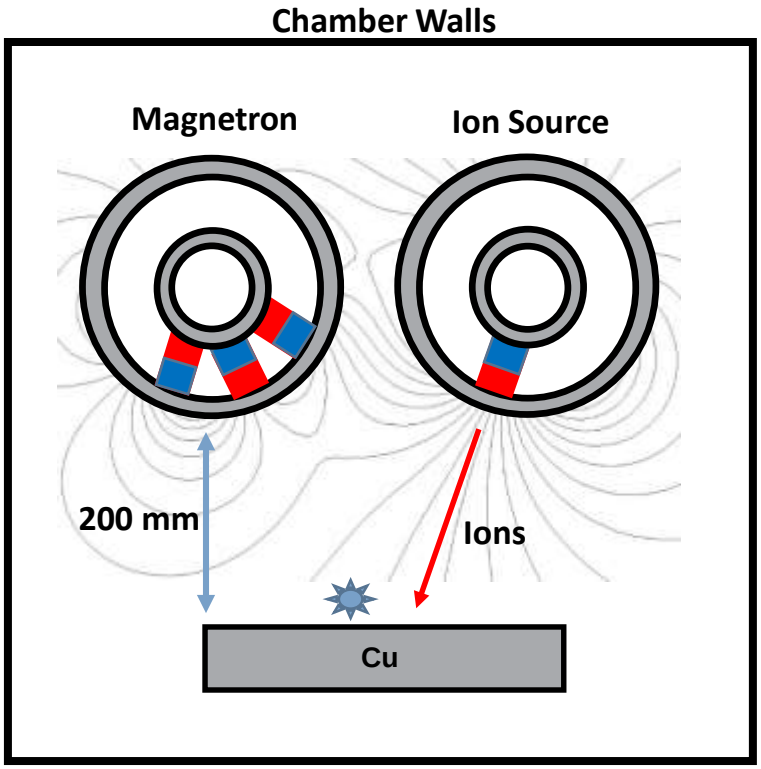
Hip³ Cu etch process with an Oxygen Plasma

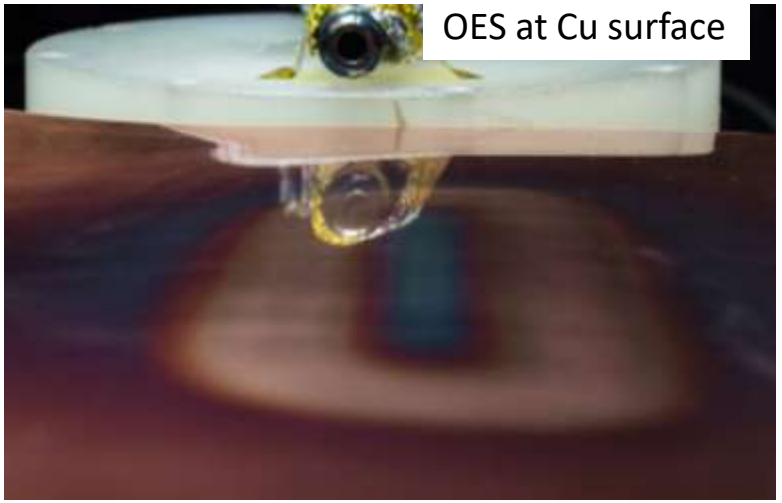


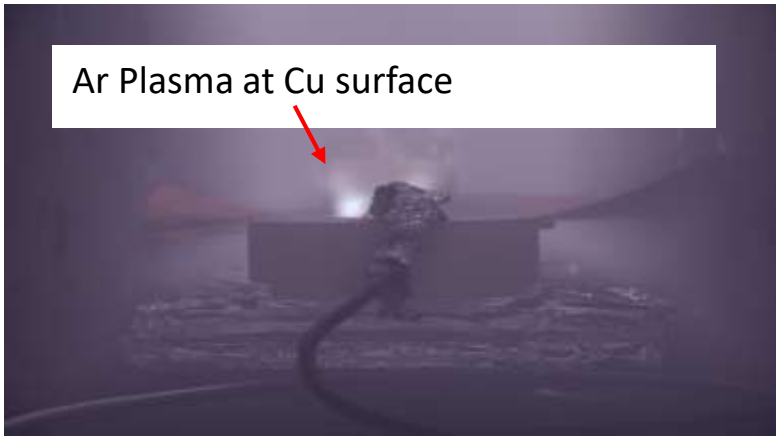
❑ **Pure O2 plasma**

❑ Auxiliary magnet placed behind Cu sheet to confine electrons near plate – copper plate at earth potential

Hip³ Cu etch process monitored by optical emission spectroscopy





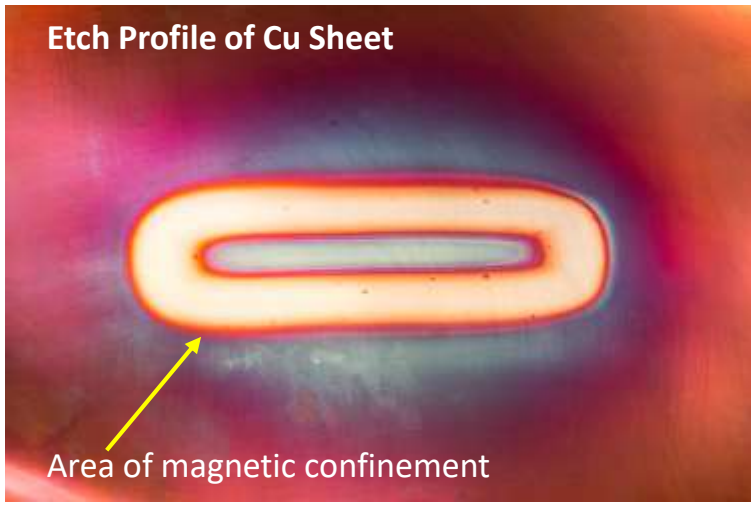


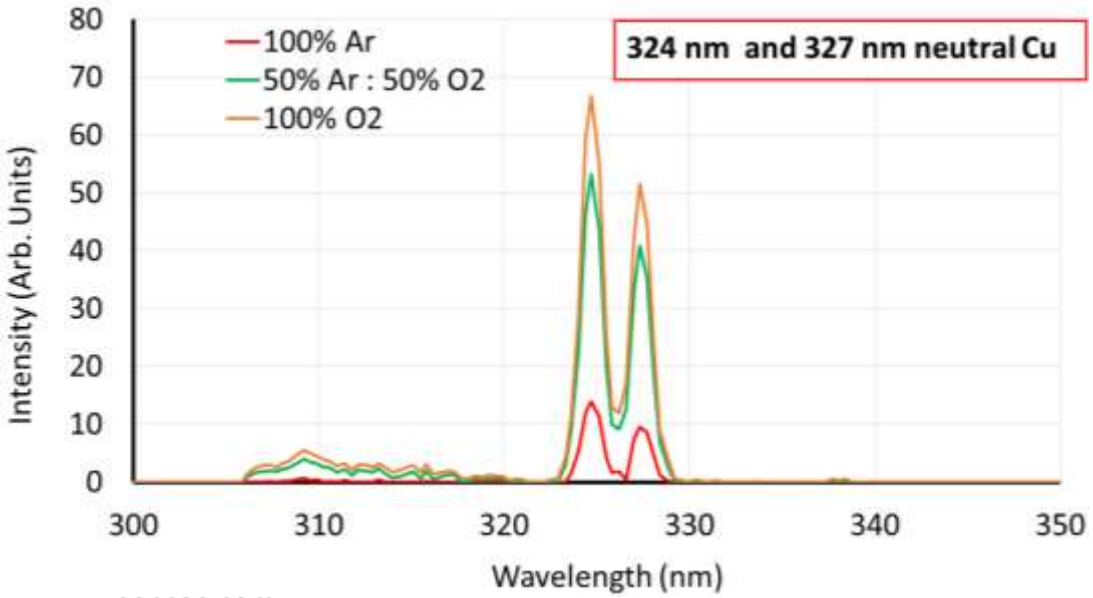
- Optical Fibre allows Cu emission to be viewed through OES

Hip³ Cu etch process monitored by optical emission spectroscopy, gas Ar/O2

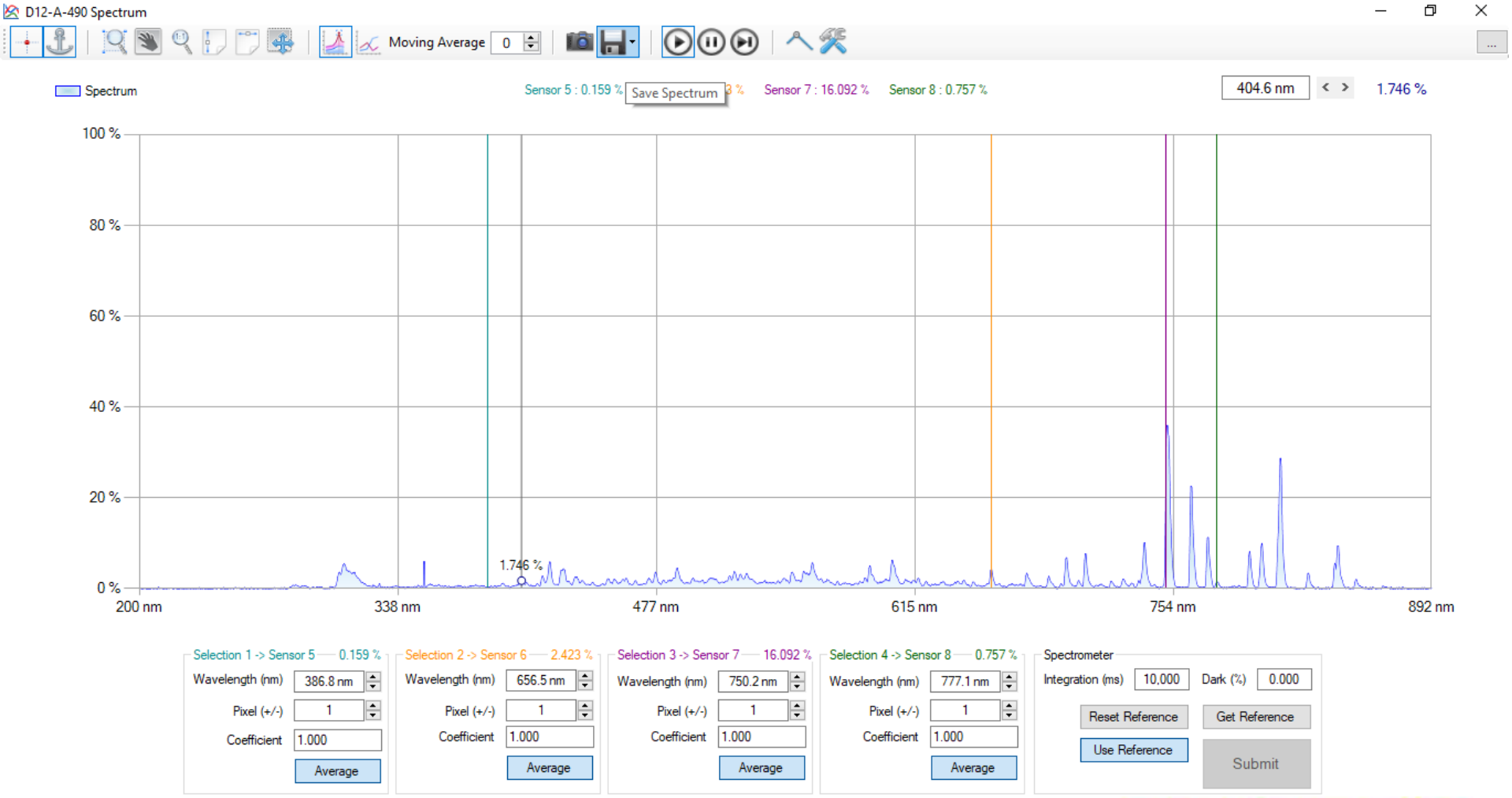
Hip³ Cu etch process monitored by optical emission spectroscopy

- **Clear etch profile** visible on earthed Cu sheet after 1 hour etch at 1.2 kW
- **Cu emission varies** with Ar and O2 % in plasma
- **O2 presence enhances Cu emission** intensity – implies **greater Cu etch with O2** in plasma discharge



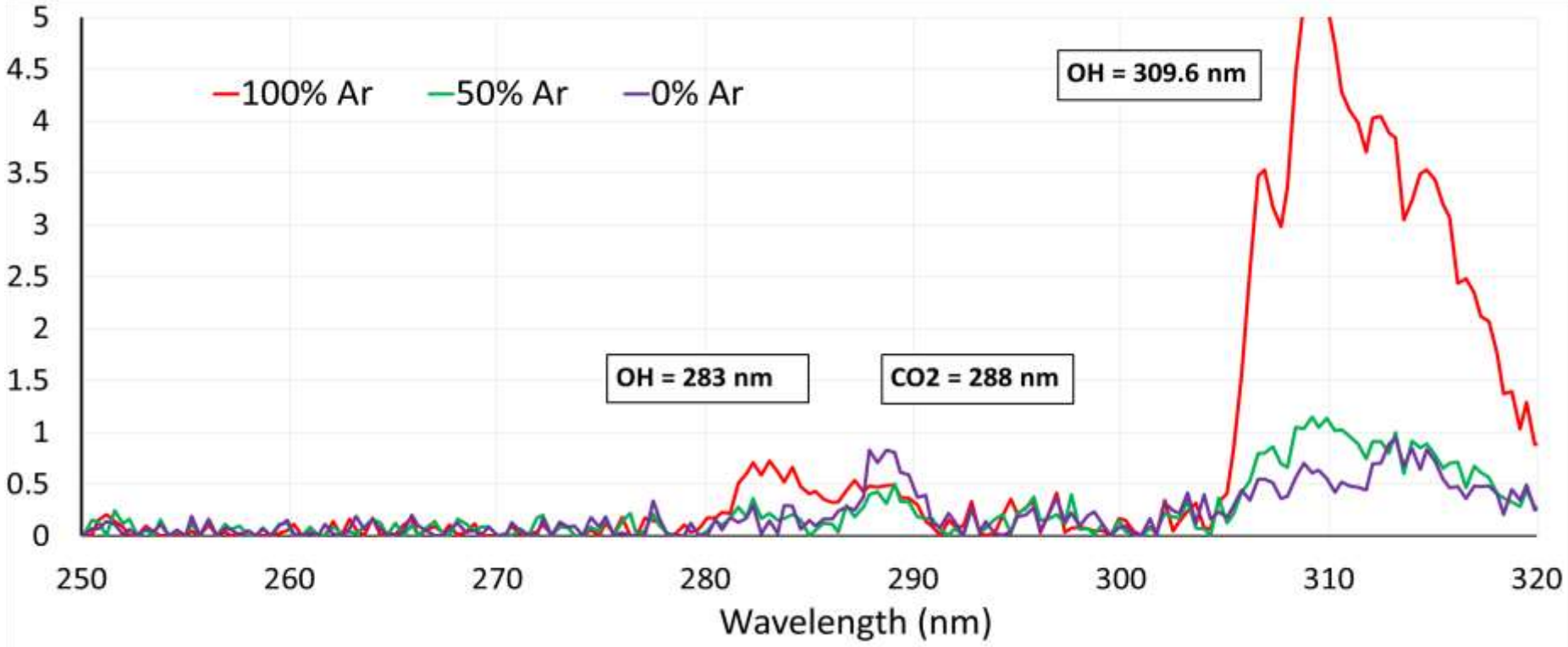


Hip³ PET etch process monitored by Speedflo based optical emission spectroscopy



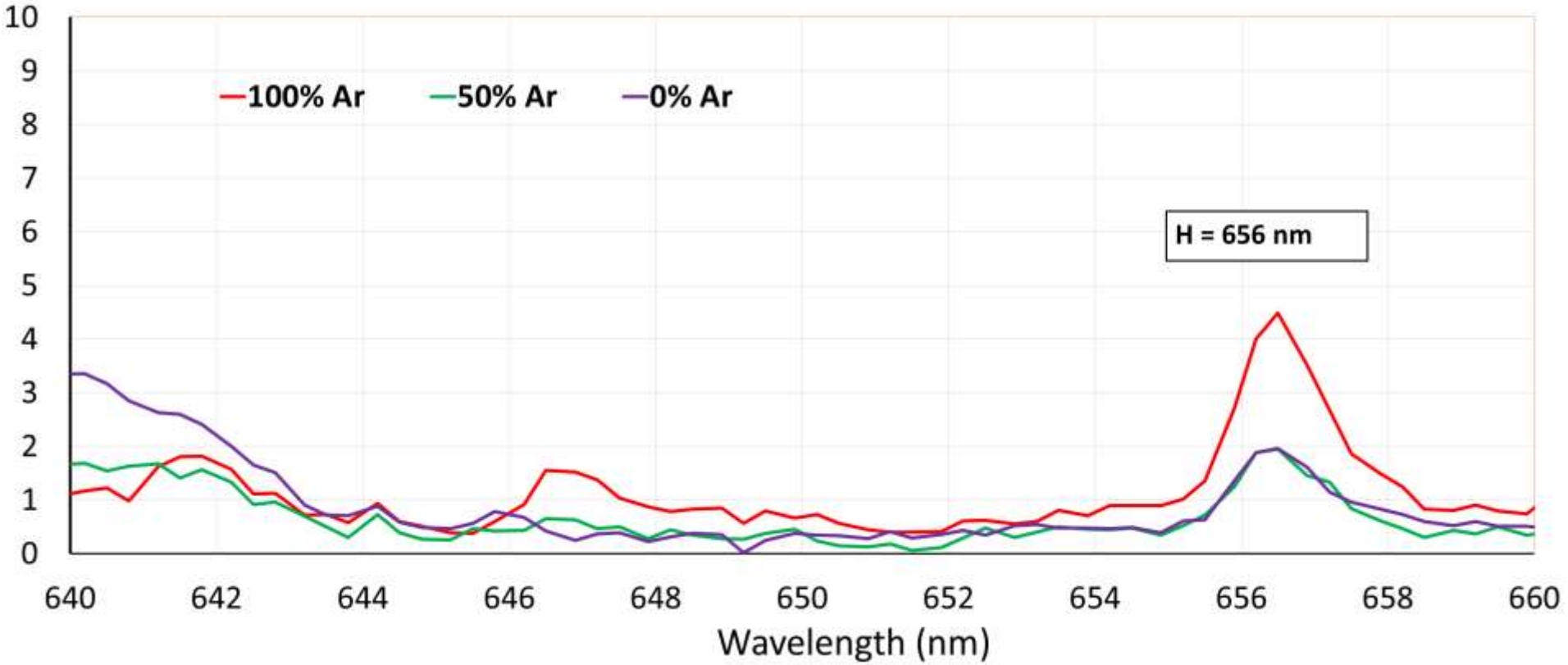
Hip³ PET etch process monitored by optical emission spectroscopy

- OH emission increases when Ar plasma is used, relative to O_2



Hip³ PET etch process monitored by optical emission spectroscopy

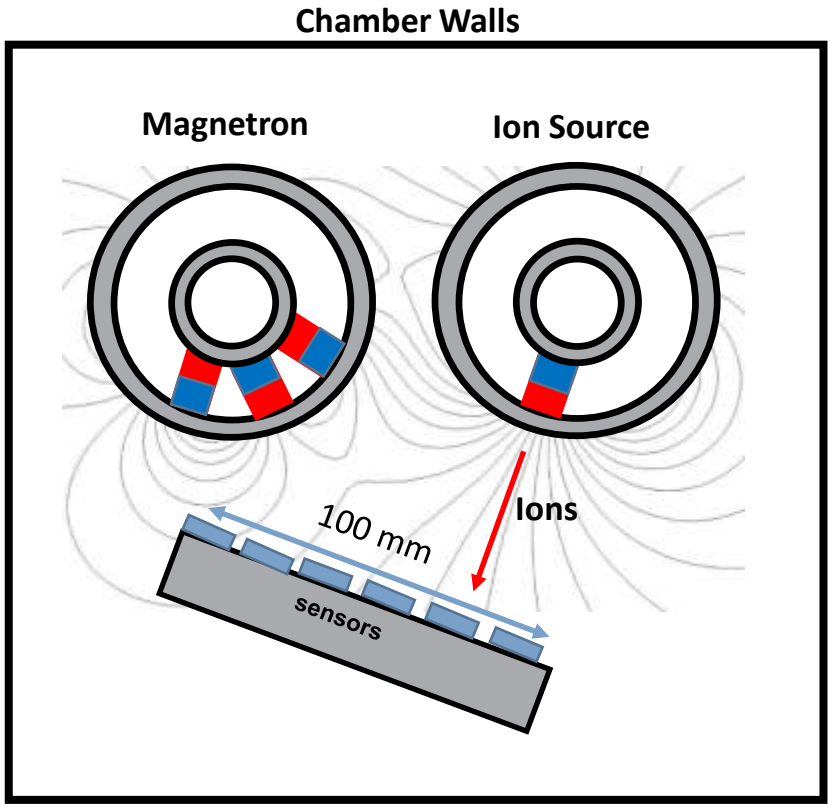
- H emission similarly increases with increasing Ar relative

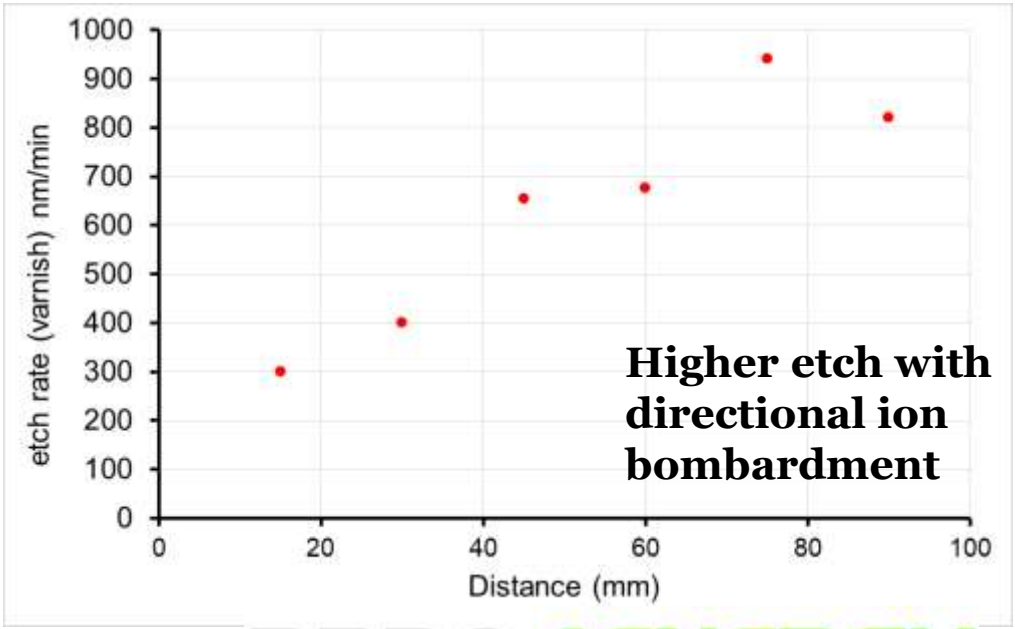


Hip³ Acrylic etch process monitored by crystal sensors

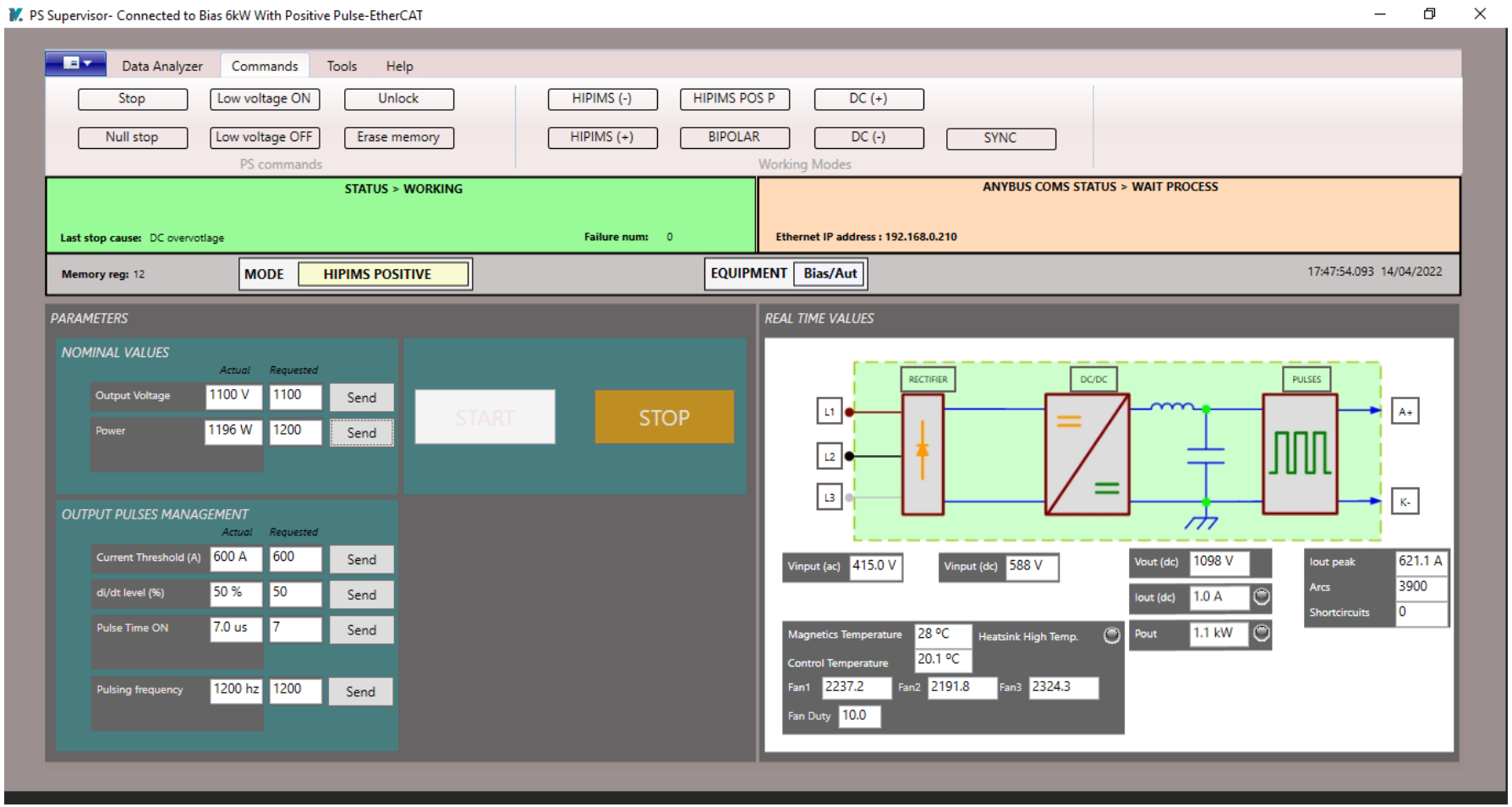
- Acrylic removal rate, crystal sensors

Cured acrylic varnish coated crystal sensor



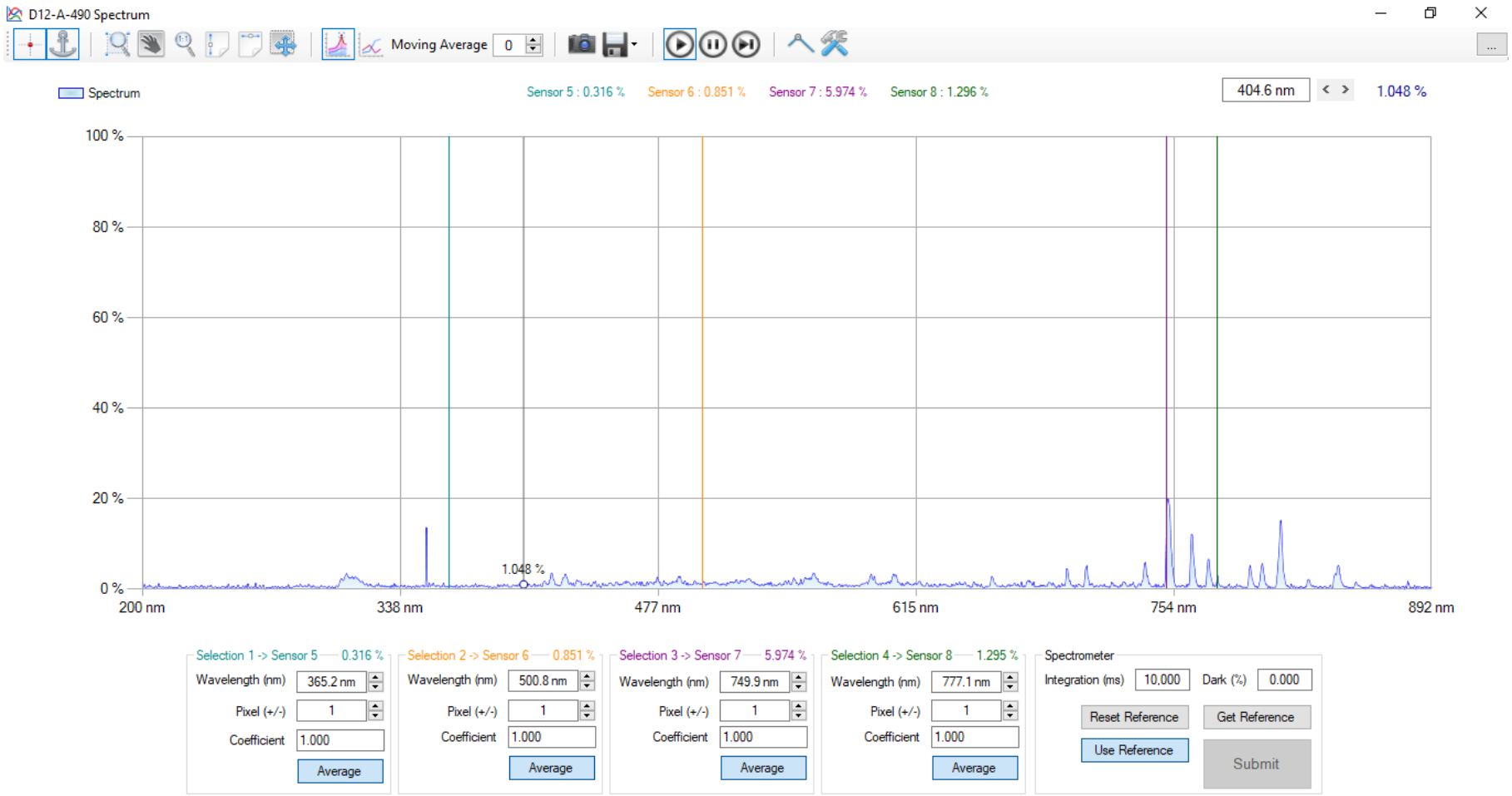


Hip³ Ti on glass etch process ion source HipV power supply settings



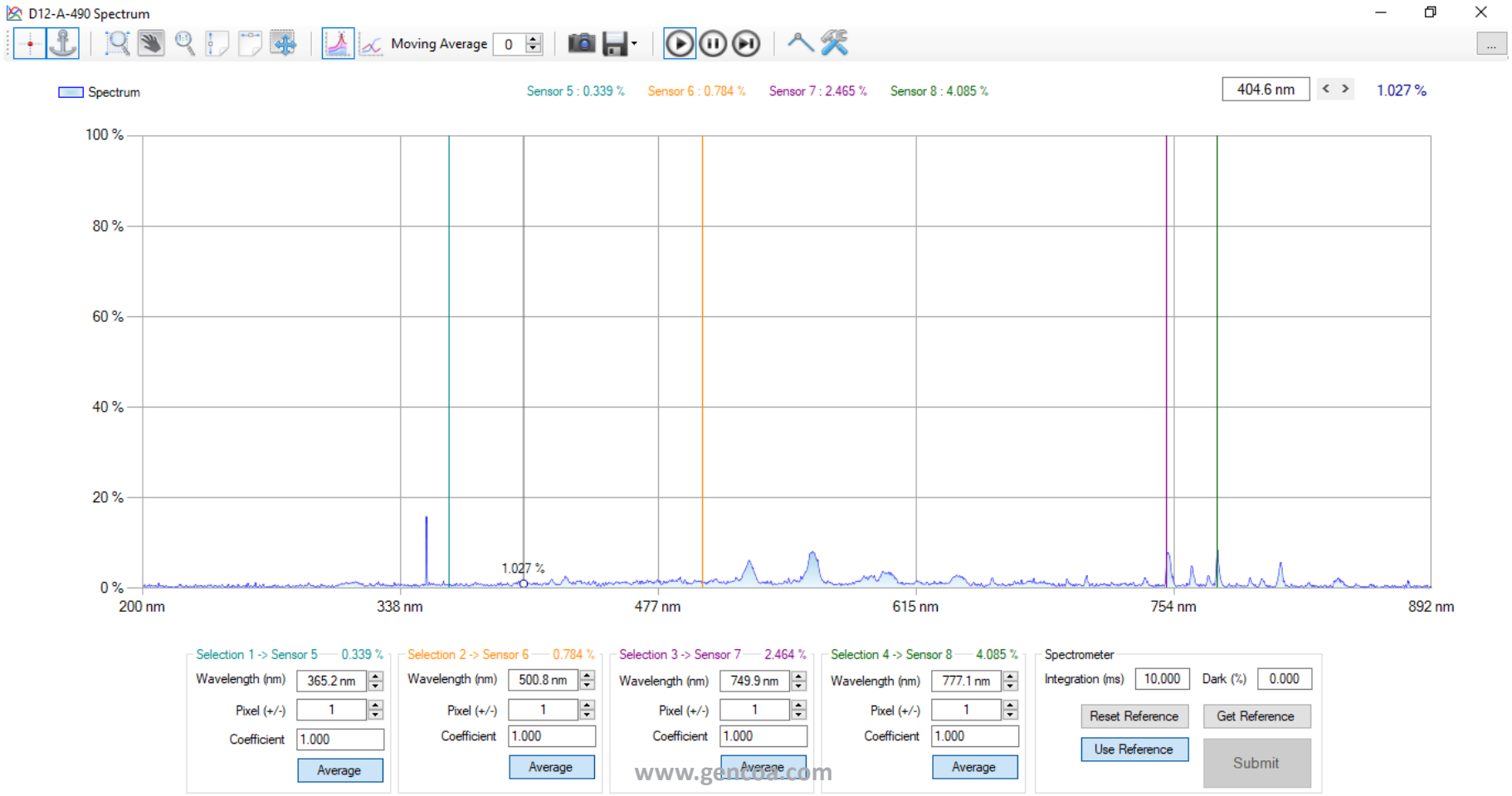
Hip³ Ti on glass pure argon etch process monitored by optical emission spectroscopy

- ❑ Pure Ar plasma – little to no evidence of Ti emission at 365 or 500 nm
- ❑ Some OH emission



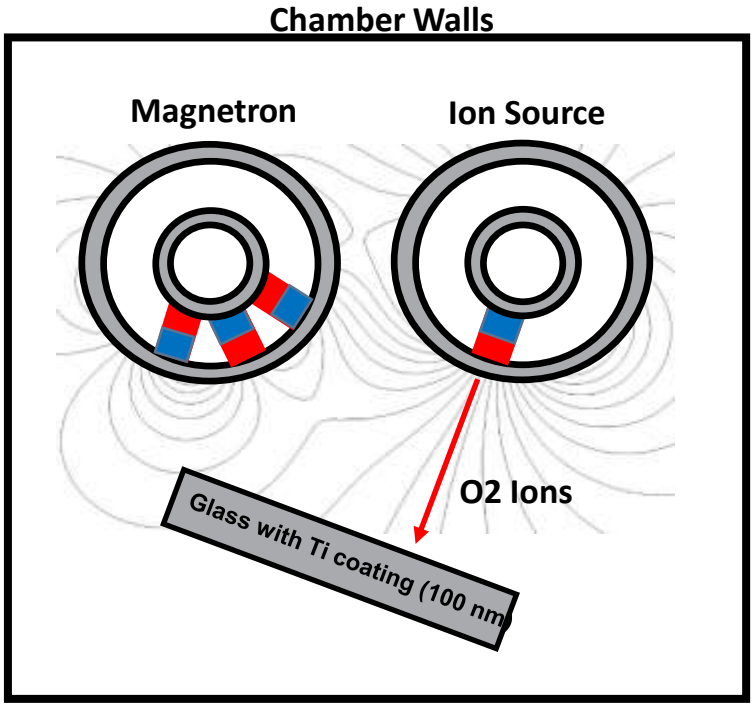
Hip³ Ti on glass pure oxygen etch process monitored by optical emission spectroscopy

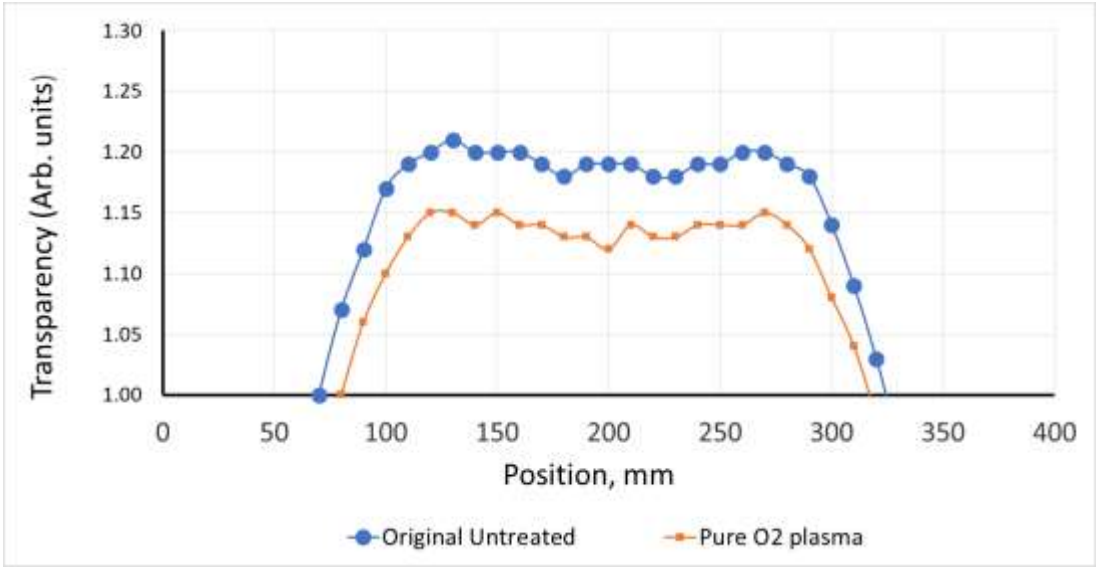
- Pure O2 plasma – little to no evidence of Ti emission at 365 or 500 nm



Hip³ Ti on glass oxidation process monitored by change in transparency

- Optical transparency change was used to interpret O2 activation of Ti on glass
- **Lower optical density through Ti coated glass** after O2 plasma exposure

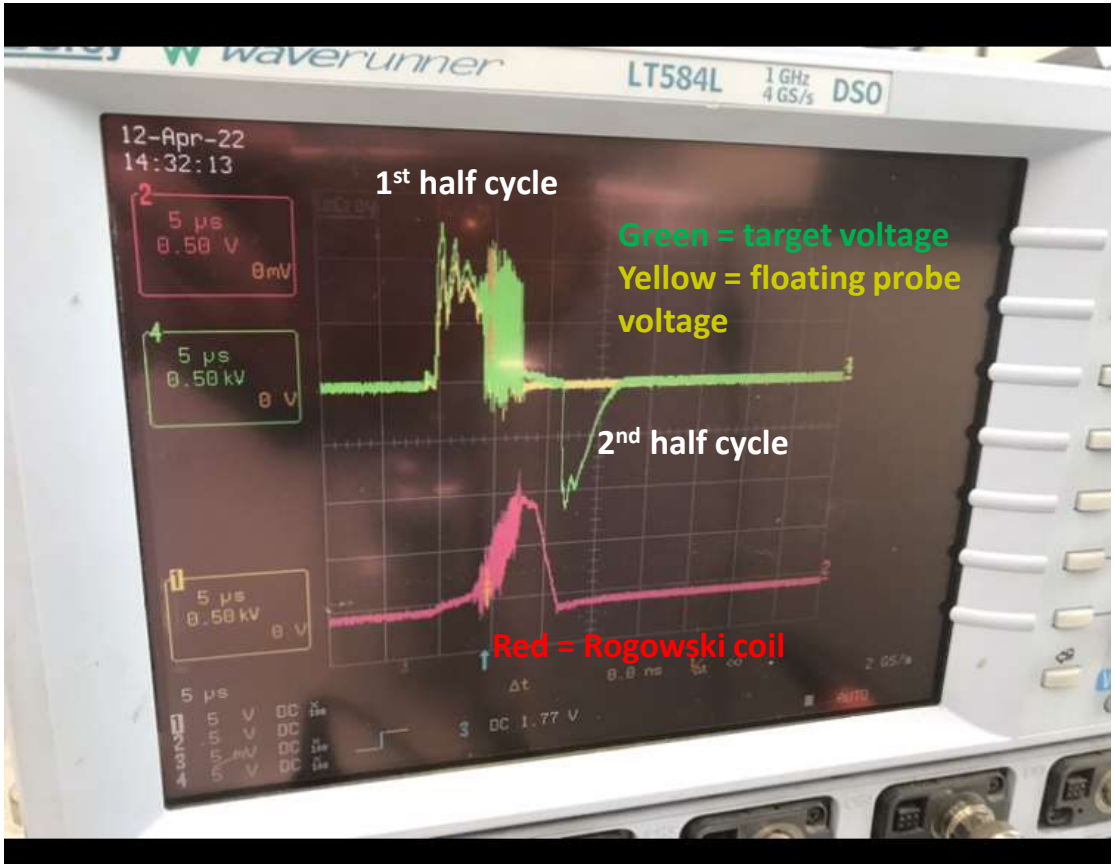




Power = 1.2kW, 600 A peak current, peak voltage = 1100 V

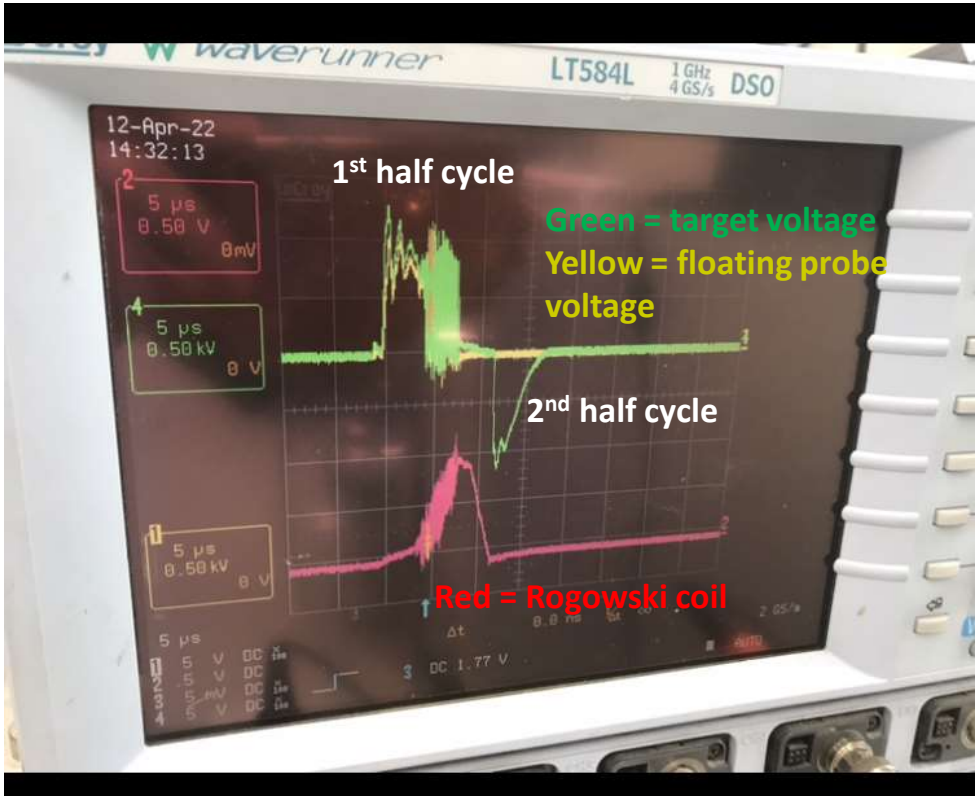
Hip³ Ti on floating glass plasma monitored by floating probe

- Symmetric voltage waveforms on both **target** and **floating** probe
- **Floating** probe shows ions reach the surface and charge positive within **1st half cycle of pulse**
- Glass doesn't discharge on its own during **2nd half cycle of pulse**, needs electrons to neutralize the positive ion bombardment



Hip³ Ti on glass ion irradiation repulsion effect

- Positive voltage charges the electrically floating glass, hence incoming ions are slowed down \ repelled hence no metal **etch effect** on glass
- However the energy level of the oxygen ions is sufficient to change the metal surface to oxide to approx. 10nm depth



Summary

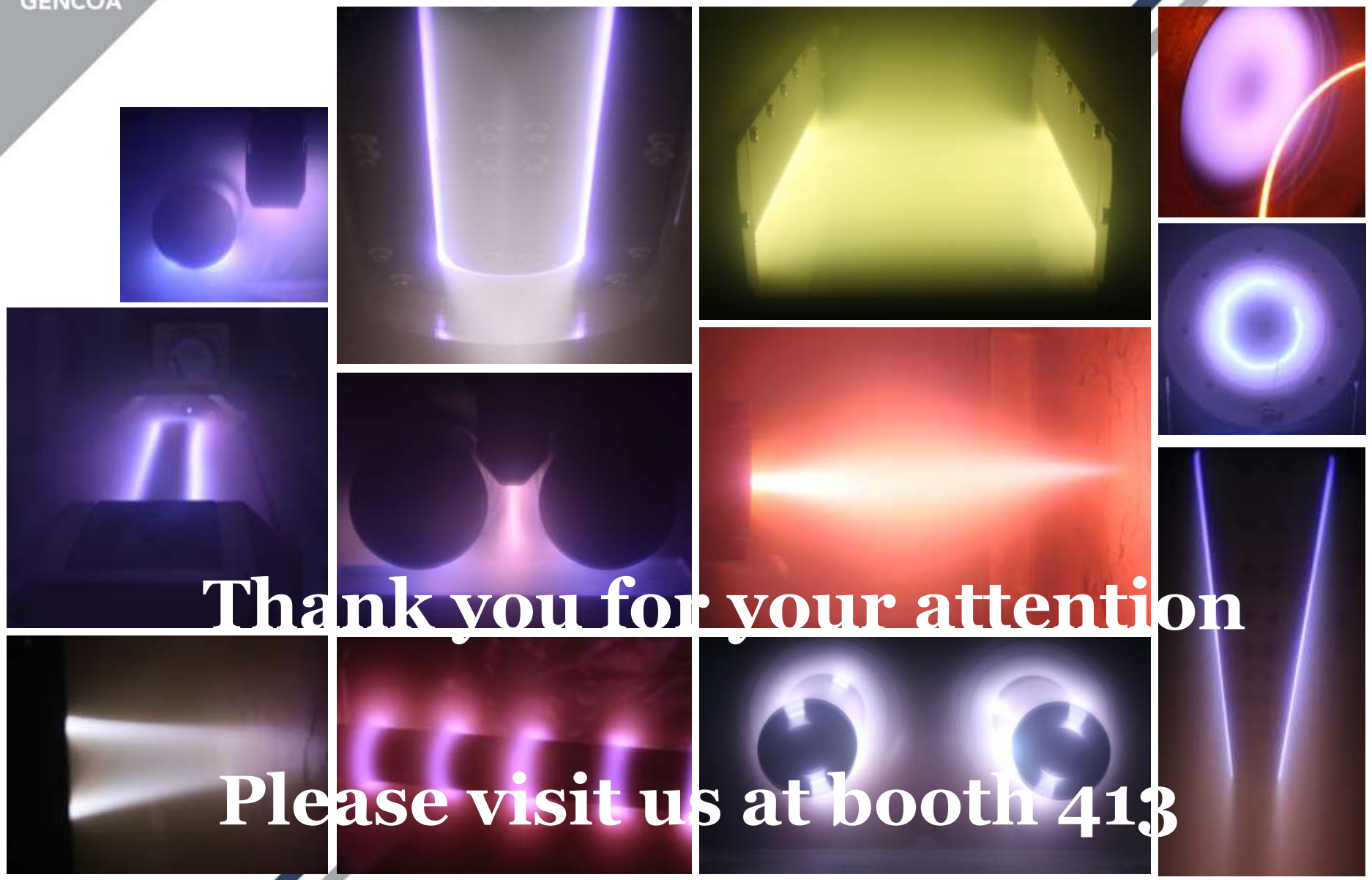
- There are many choices for plasma pre-treatment devices depending upon the speed, type of substrates to be treated, and why the pre-treatment is required.

- DC magnetron plasmas are effective but AC plasma excitement offers many additional benefits.

- A new generation of etch, pre-treatment and oxidation devices based upon high current positive pulses are a reality.

- Positive pulsed hipims type plasma use ion irradiation to more rapidly pre-treat and etch materials compared to DC and AC methods.

GENCOA



Thank you for your attention

Please visit us at booth 413