DEVELOPMENT OF MATERIALS PROCESSING METHODS:

CATHODIC VACUUM ARC AND PLASMA IMMERSION ION IMPLANTATION COMBINED

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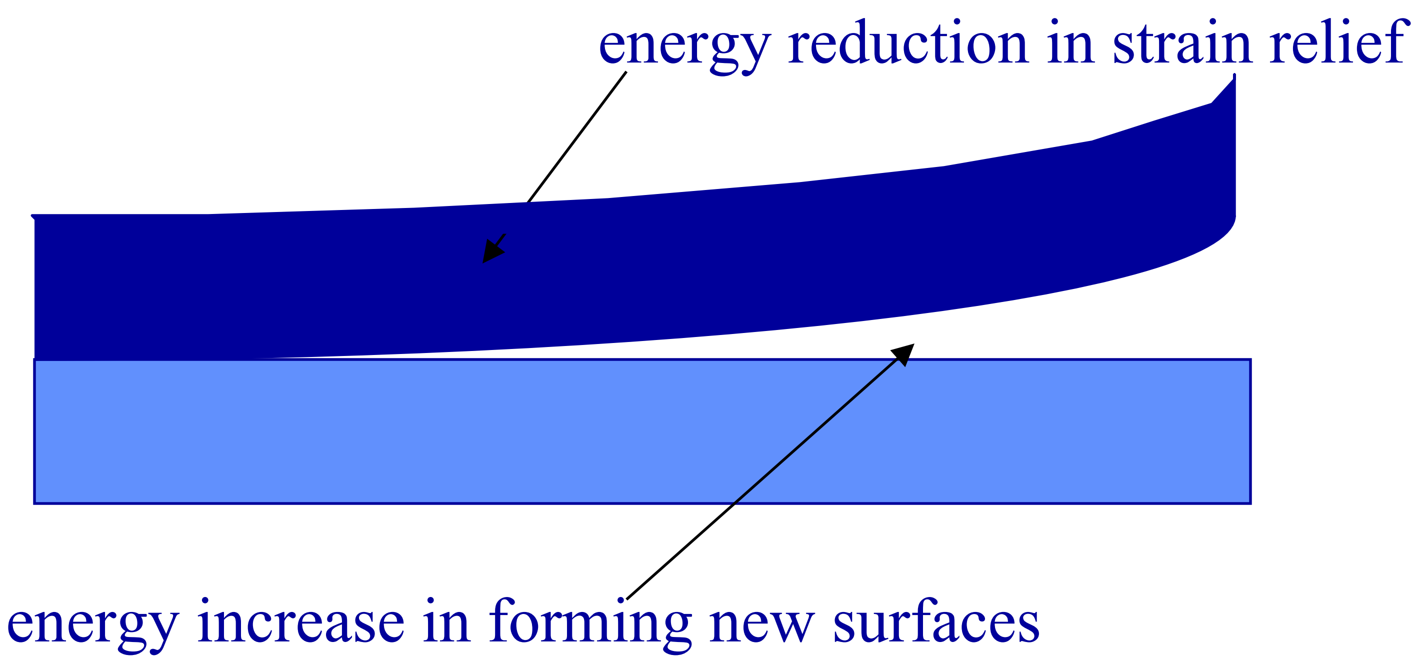
Requirements for Advanced Coatings

- No voids
- No cracking or resistance to crack propagation
- No delamination
- For some applications we need
  - Enhanced hardness
  - Enhanced toughness
  - Enhanced biocompatibility

Energetics of Delamination

- Griffith Criterion for crack propagation or delamination:

  If the strain energy relieved exceeds the energy required to create the two new surfaces a film will delaminate, once a nucleation point has formed



Our Strategies

- **Low stress and substrate mixing layers** for super adhesion
- **Nanostructuring** for enhanced hardness, resistance to cracking and supertoughness

Stress Generation in Thin Films

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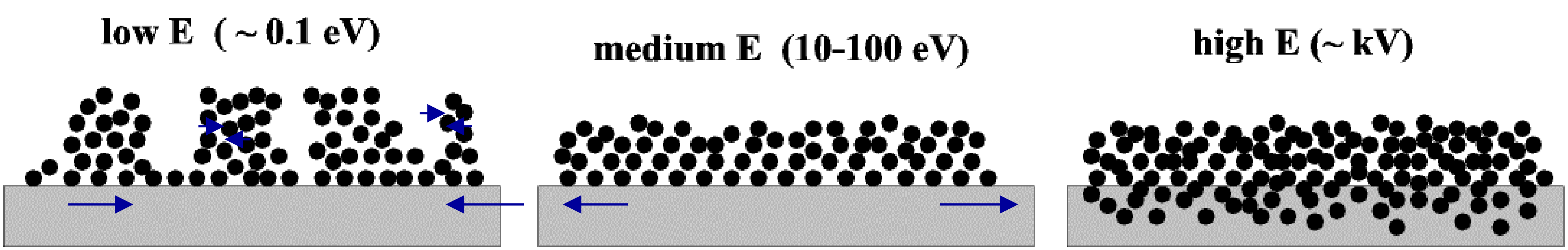
- Low -> voids (tensile stress)
- Intermediate -> dense, well connected (compressive stress)
- High -> observations show reduced stress and interface mixing



tensile stress compressive stress interface mixing

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Stress Generated by Ion Impacts

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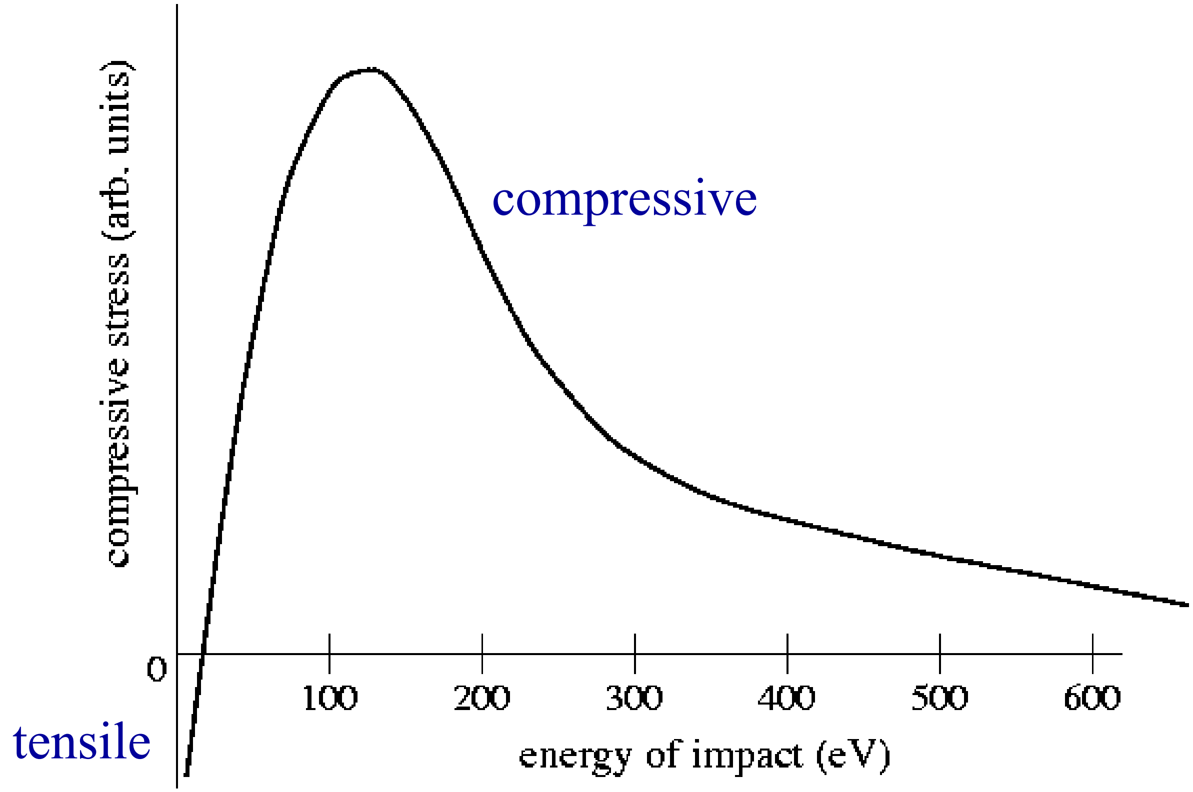
- Observed universal behaviour as a function of energy



High energy impacts can relieve the stress generated by lower energy impacts

The Universal Curve for AlN

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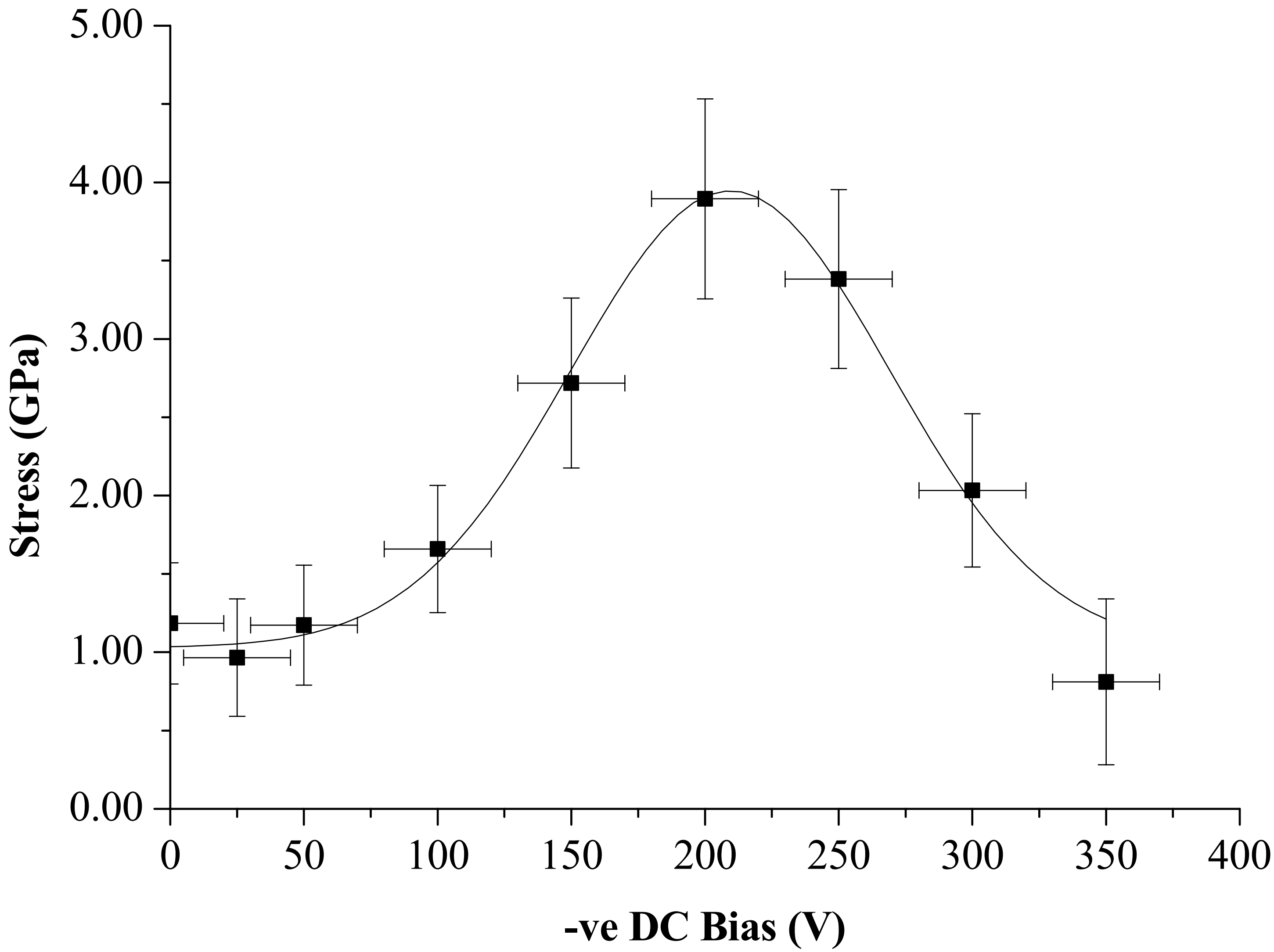

The Cathodic Vacuum Arc

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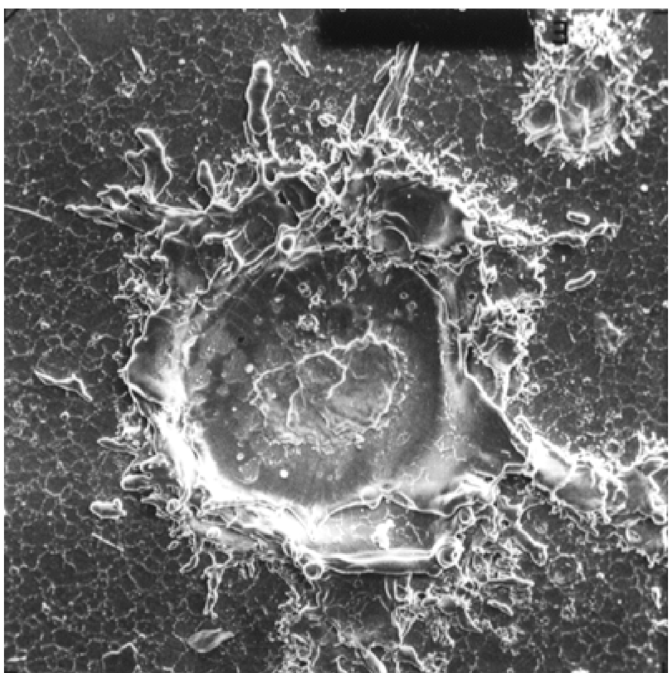
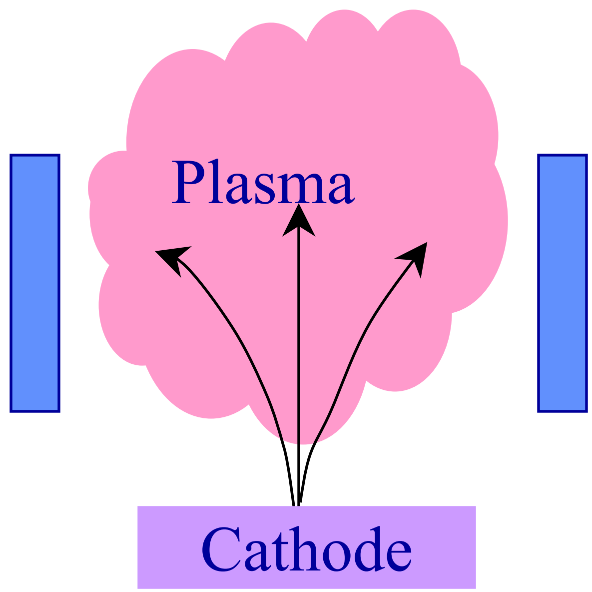
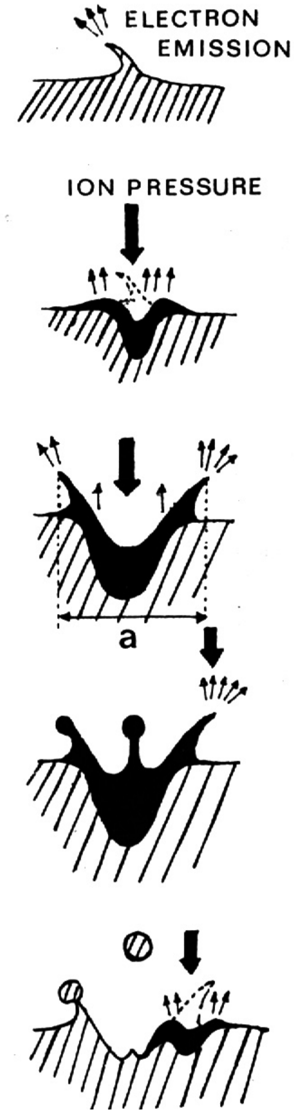
- Discharge triggered by direct contact or surface flashover
- Plasma drifts away normal to cathode surface
- FULLY ionized & energetic (10-100s of eV)



few hundred microns





Cathodic Arc Treatment of Cutting Tools

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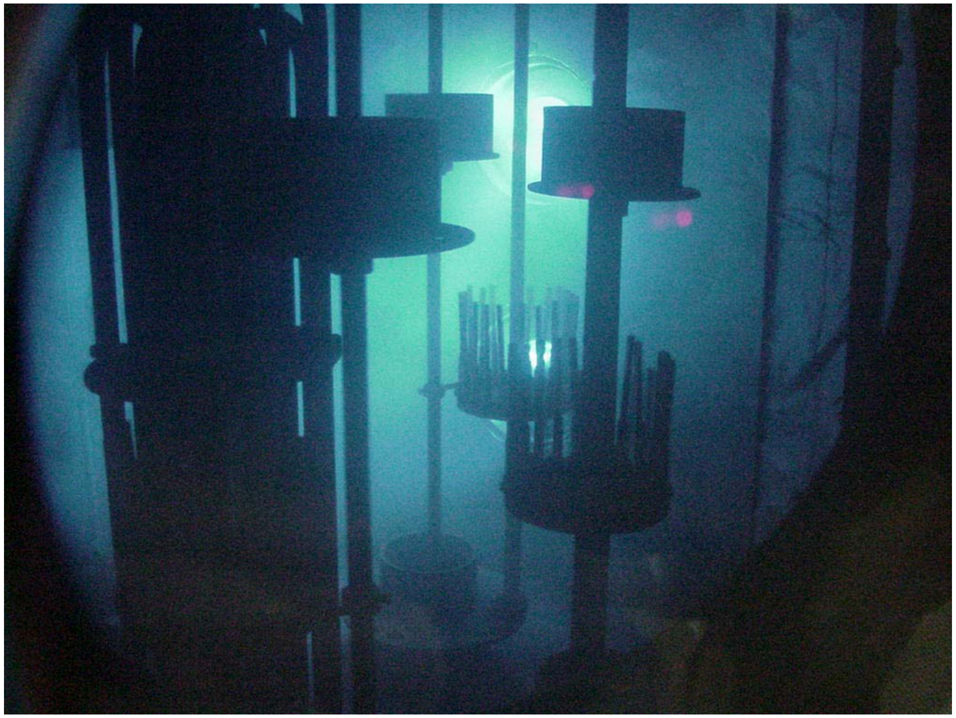
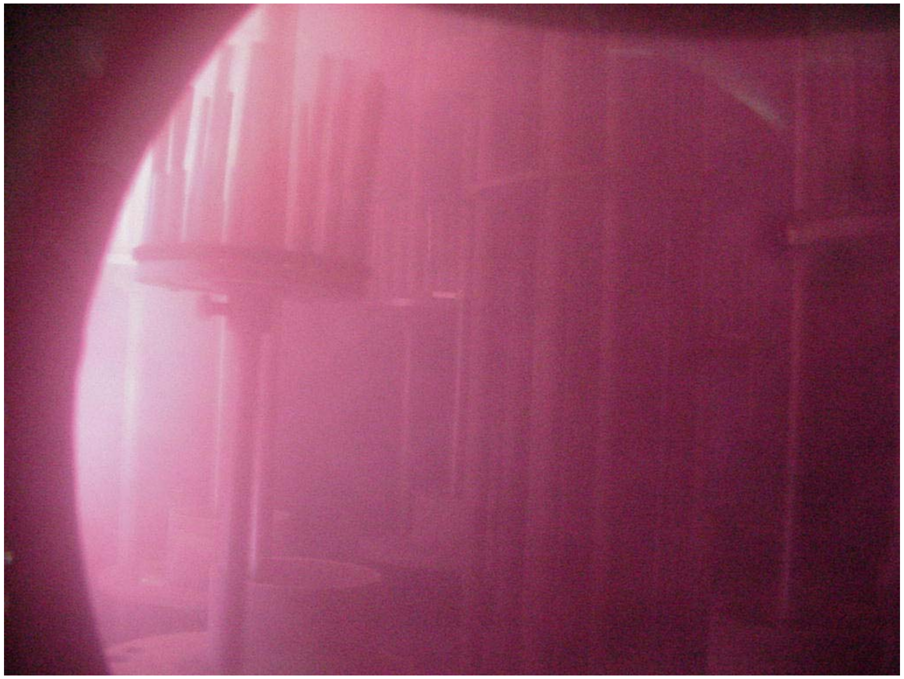
- Protective coatings for cutting tools produced using unfiltered arcs



Ti cathodes in nitrogen



Chromium cathodes in argon (etch)

Photographs courtesy of

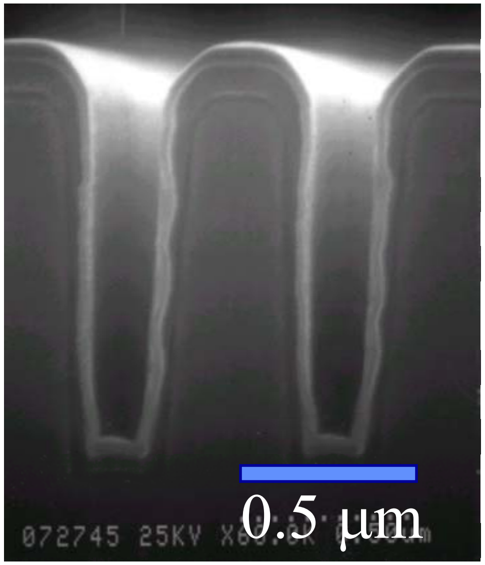
Sutton Tools

Magnetic Filter

- Curved solenoid used to guide plasma around bend while macro-particles go straight ahead
- Use arc current to establish magnetic field (~10-100 mT)

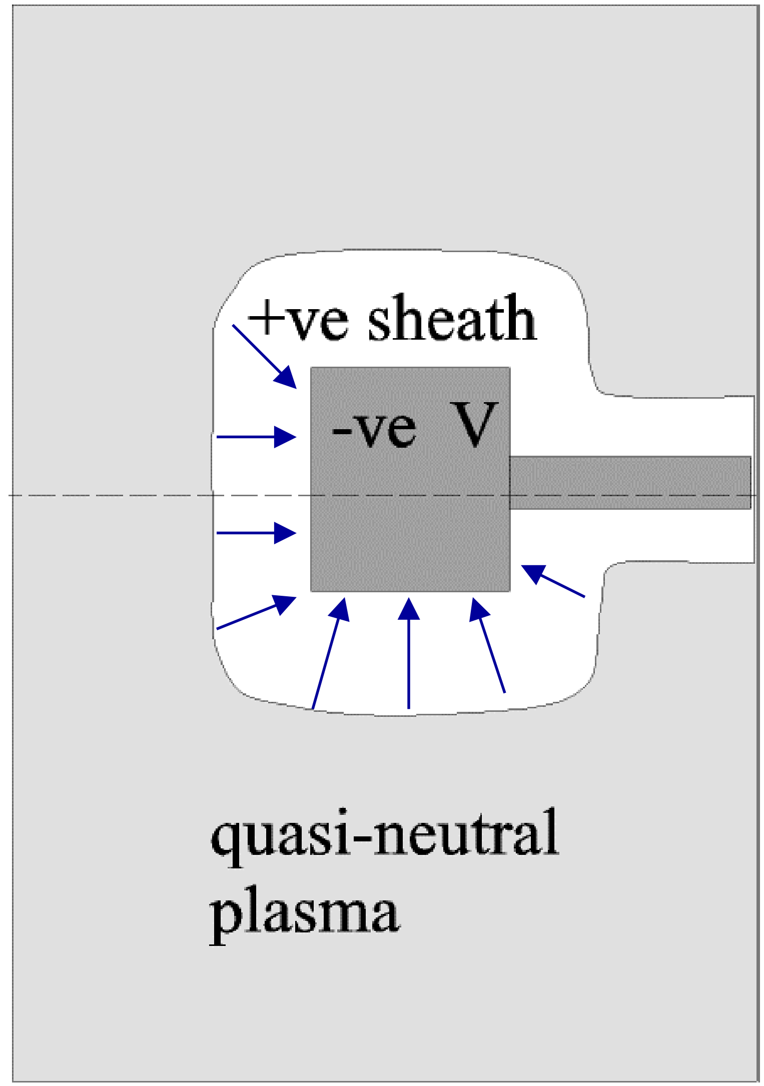
- Electrons magnetized & ions follow by electrostatic attraction

Andre Anders &
Othon R. Monteiro
Lawrence Berkeley National Laboratory
California USA



Plasma Immersion Ion Implantation (PIII)

- Bias applied to workpiece immersed in plasma (~10 kV)
- Arrows show electric field and direction of implanting ions
- Condensable plasma = bombardment during film growth
- Non-condensable plasma = sub-surface implantation



PIII&D Filtered Cathodic Arc System

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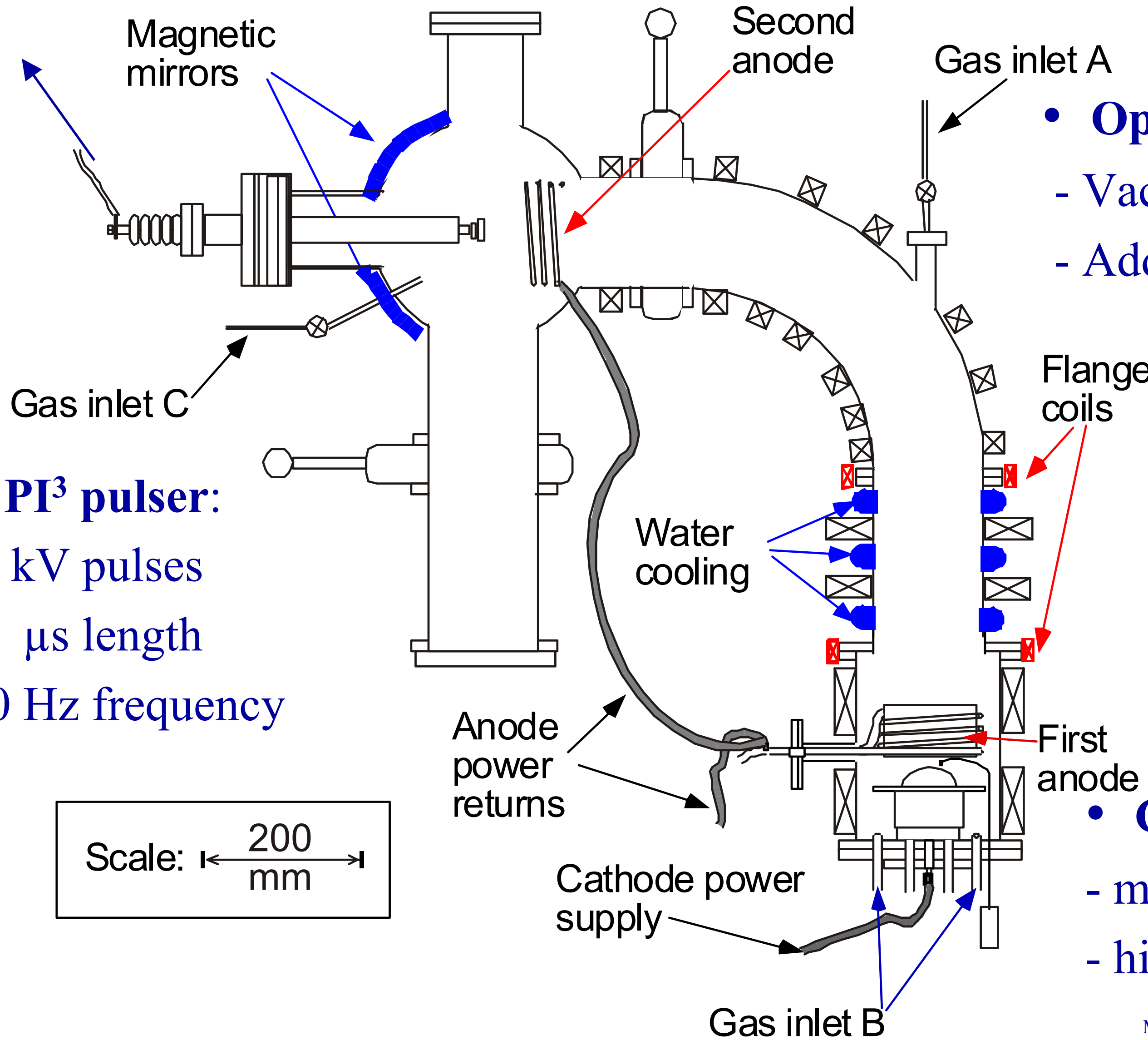
to HV pulsed power supply



- **Ansto PI³ pulser**:
  - 0 - 25 kV pulses
  - 5 - 150 μs length
  - 0 - 1200 Hz frequency

- **Operating conditions**:
  - Vacuum ≈ 10^{-6} Torr
  - Add process gases

- **Cathodic arc**:
  - metal or carbon
  - high ionisation rate

The PIII&D Process

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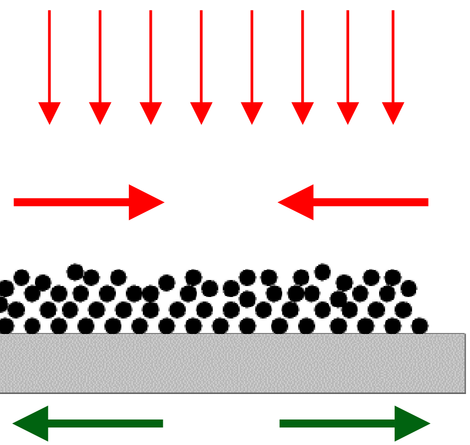
97.5 - 99.6 %
of cycle

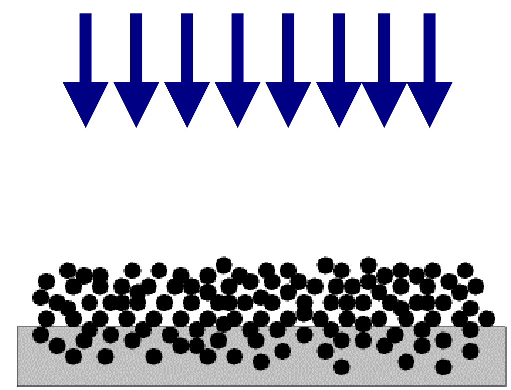
≈ 20-100 eV



Cathodic arc deposition

2.5 - 0.4 %
of cycle

1700 -
20,000 eV



PIII (20 μs, 200-1250 Hz)

Stress versus implantation energy

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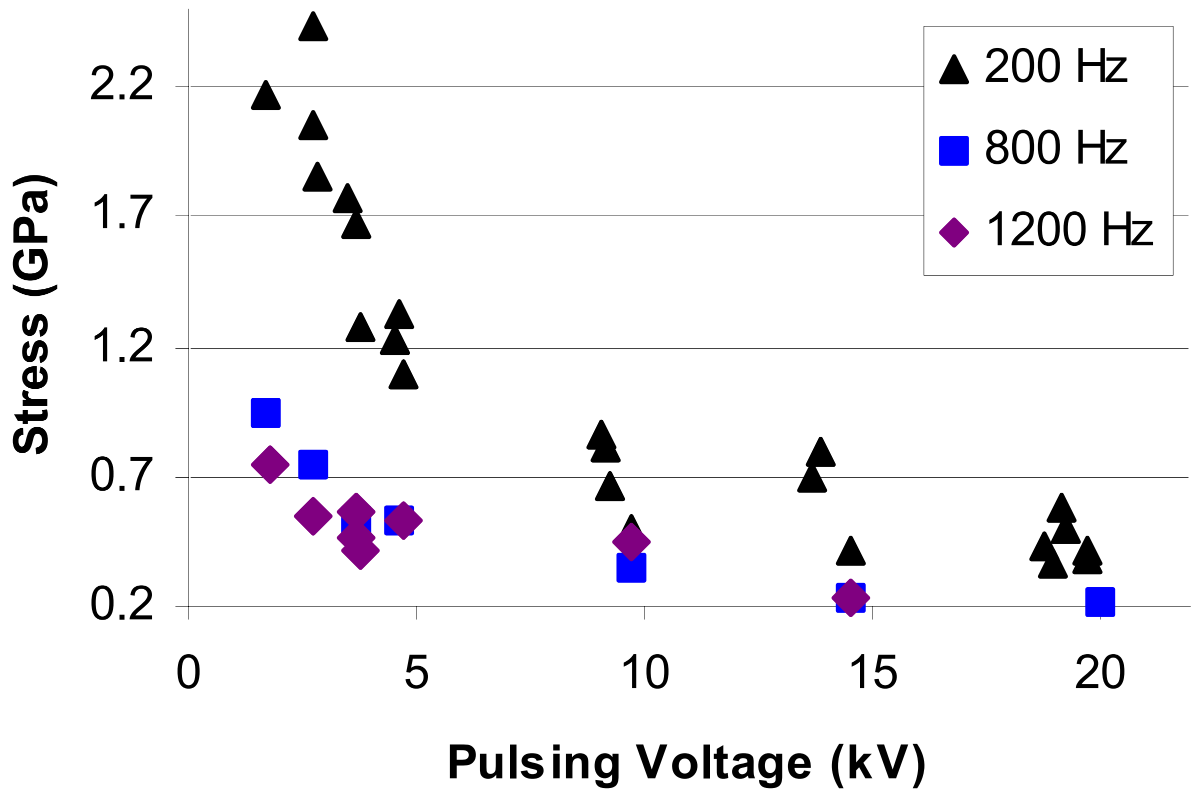
- stress versus high voltage bias energy for 20 μs applied at three different pulsing frequencies during the deposition of carbon films.

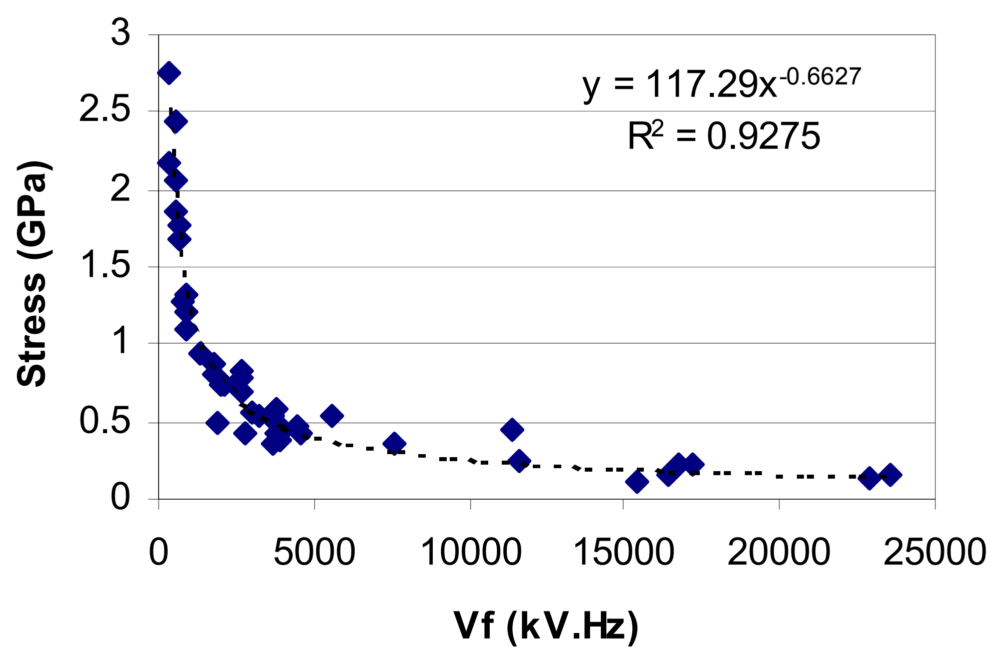


Macroscopic Stress Relief

- On a macroscopic scale, the film stress will be reduced as more of the film's volume is subjected to the high-energy thermal spikes
- Volume treated is proportional to *Ef* (or *Vf*)

relief to 0.75 GPa occurs around *Vf* ~ 2000 kV.Hz.

Can be achieved with pulses of:
10 kV @ 200 Hz
2.5 keV @ 800 Hz
1.7 kV @ 1200 Hz



The Vf relation in AlN

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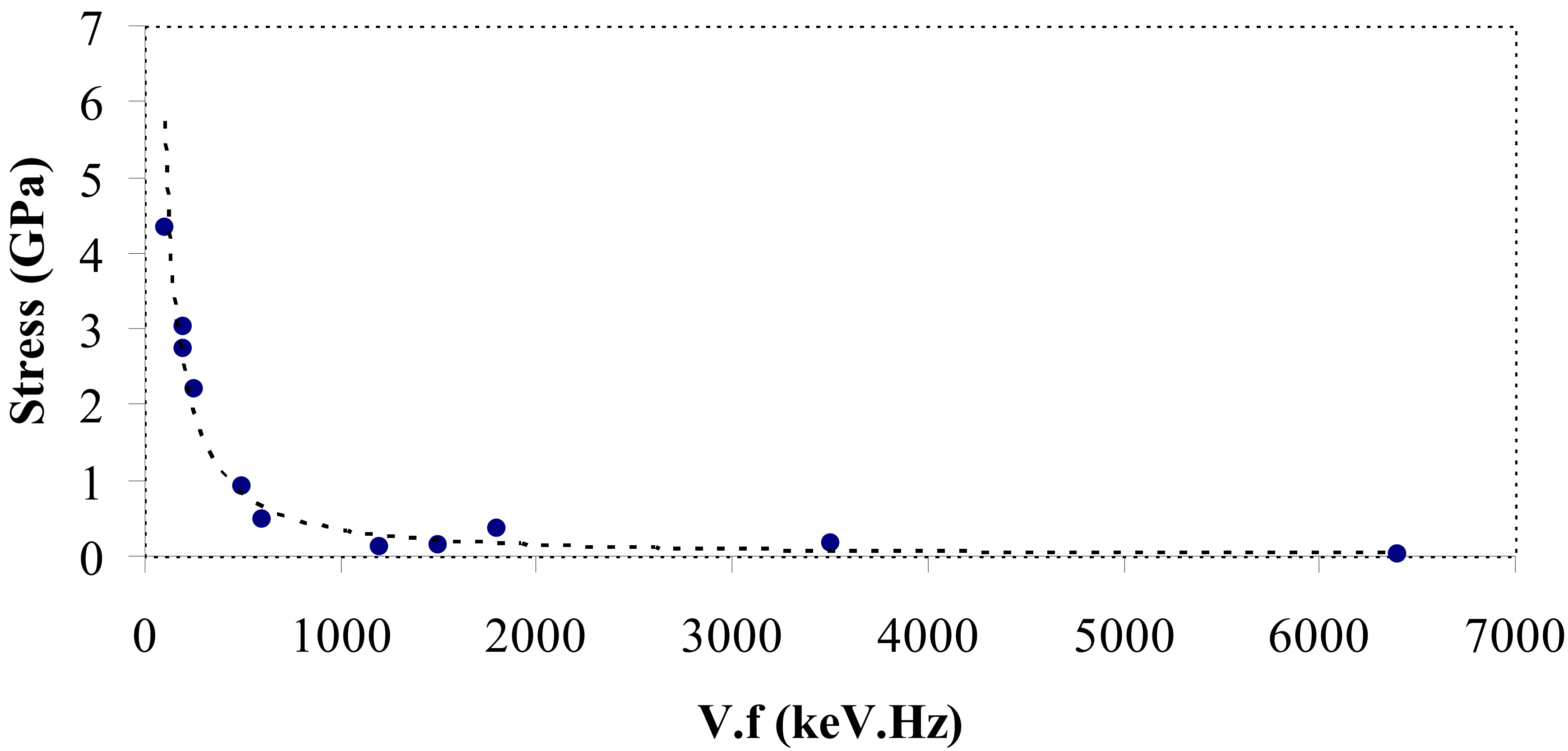
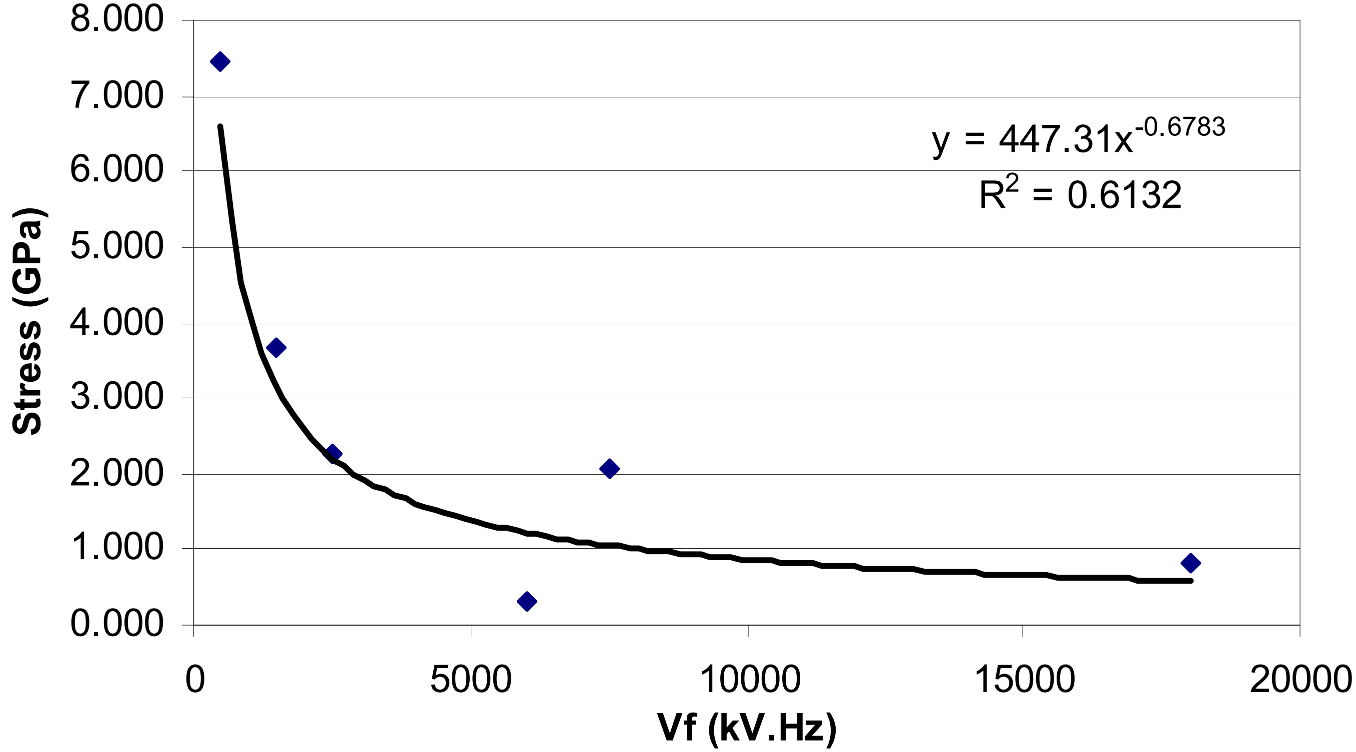
- PIII during deposition for bias voltages between 0.1 and 6.4 kV and frequencies ranging from 20 to 2000 Hz



Similar result found in TiN films

- **Data from titanium nitride films produced with PIII&D using energies of 5 and 15 kV and pulsing frequencies of 100 Hz, 500 Hz and 1200 Hz (20 μs pulse length as before)**



Stabilization of Metastable Phases

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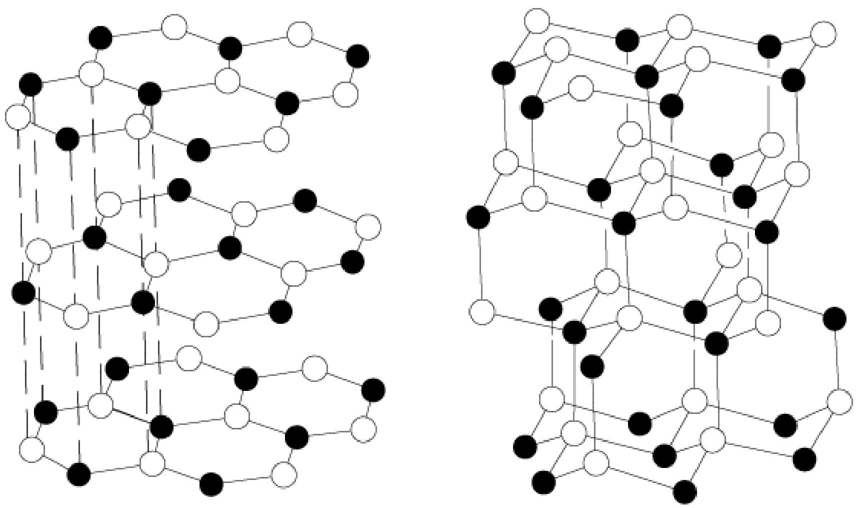
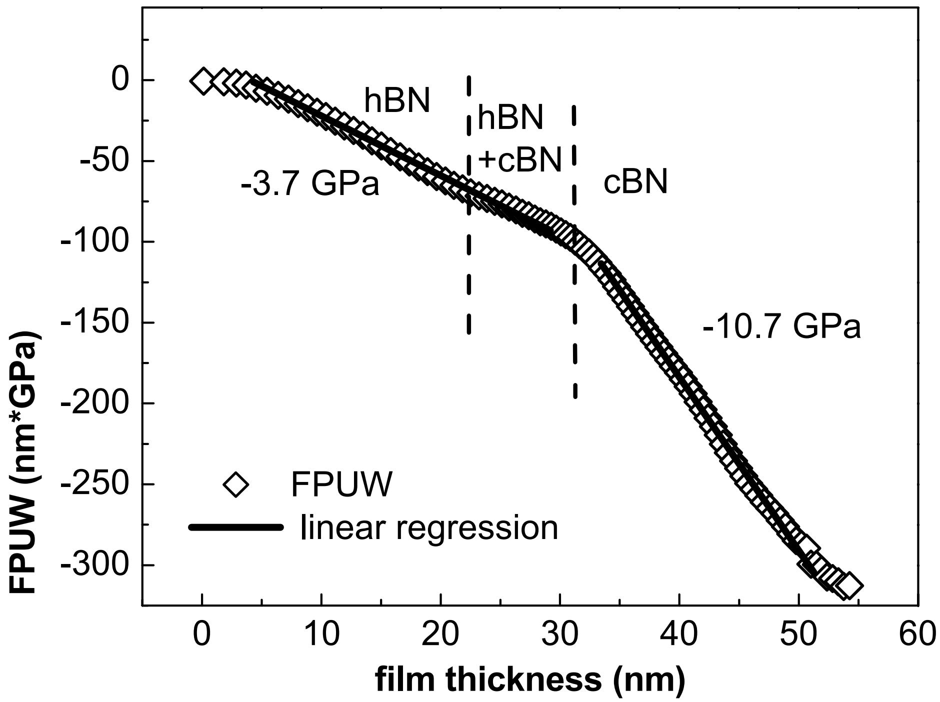
Structure of Boron Nitride



(a) Hexagonal Boron Nitride
Layers where nitrogen and boron atoms combined in a hexagonal network are superimposed and have a structure similar to graphite.

(b) Cubic Boron Nitride
Boron and nitrogen atoms combine three-dimensionally replacing carbon atoms in diamond.



B. Abendroth, R. Gago, A. Kolitsch, W. Möller, Institute of Ion Beam Physics and Materials Research, Forschungszentrum Rossendorf e.V., Dresden Germany

Remaining Challenges

- Uniform treatment of **complex shapes** avoiding breakdown

- Treating **insulating materials**

$$\Downarrow$$

SHEATH DYNAMICS

Practical Surfaces: Complex shapes

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Sheath Dynamics

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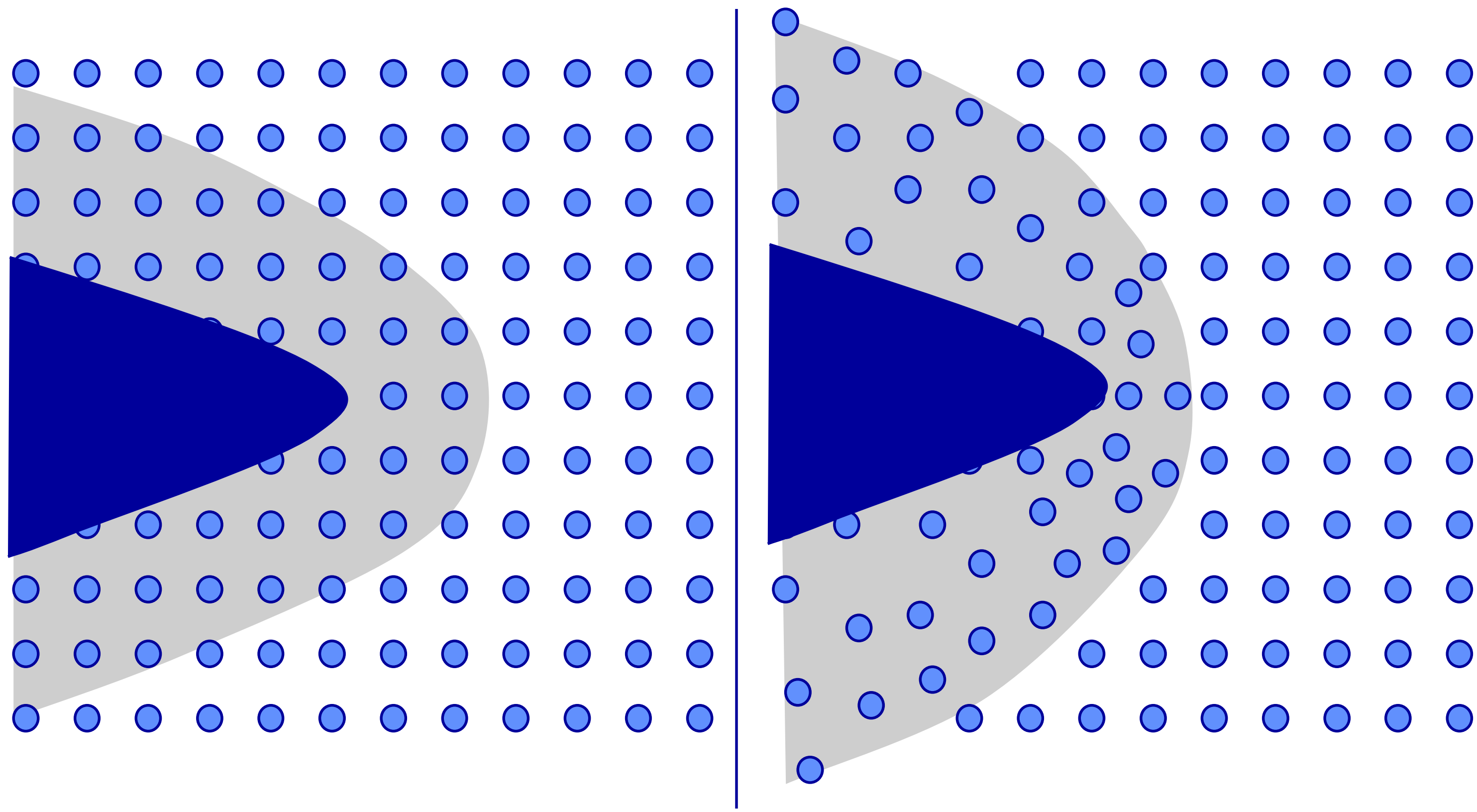
- Ion focusing occurs near tips increasing dose
- Small sheath width increases breakdown risk



Equilibrium Sheath

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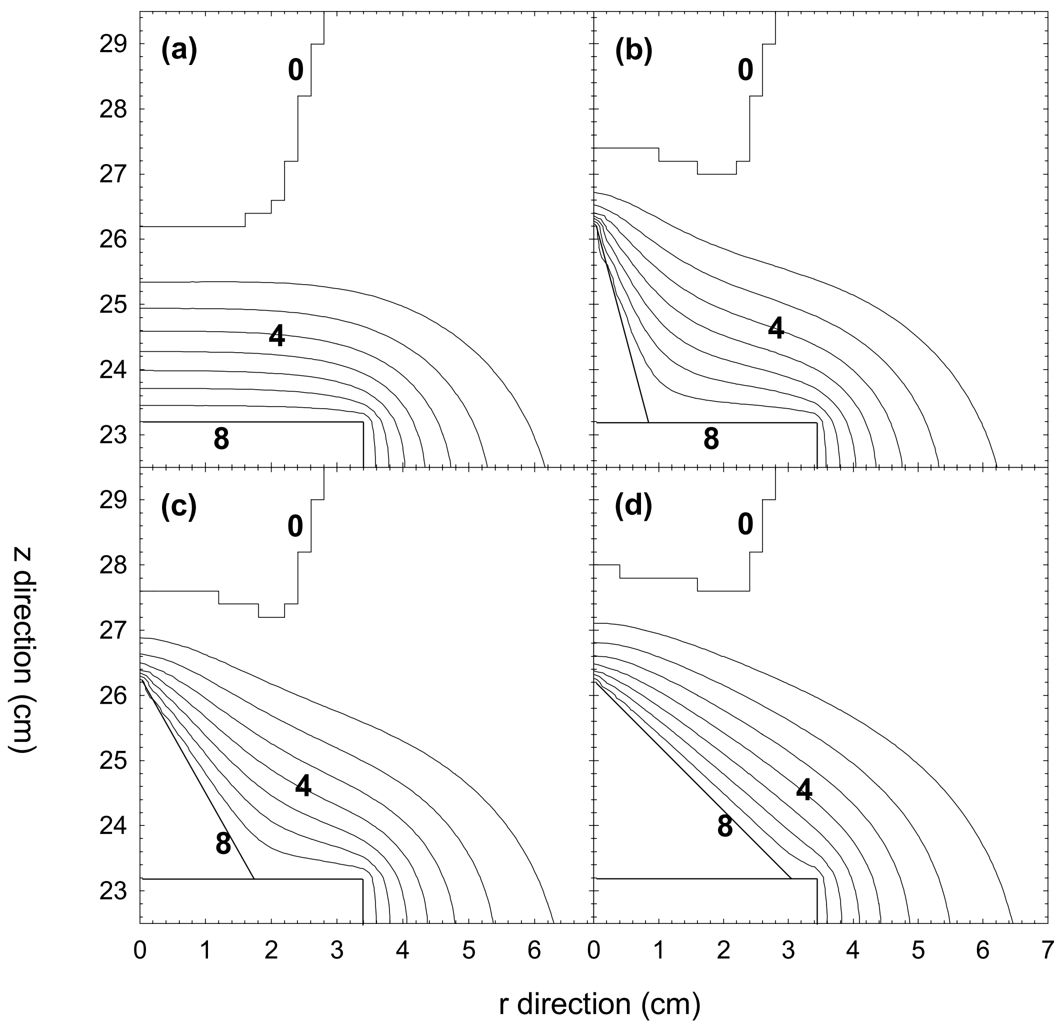

- PIC code to simulate sheath evolution in drifting plasma
- (a) Flat substrate
- (b) 30^{o} cone
- (c) 60^{o} cone
- (d) 90^{o} cone

Dose Effects

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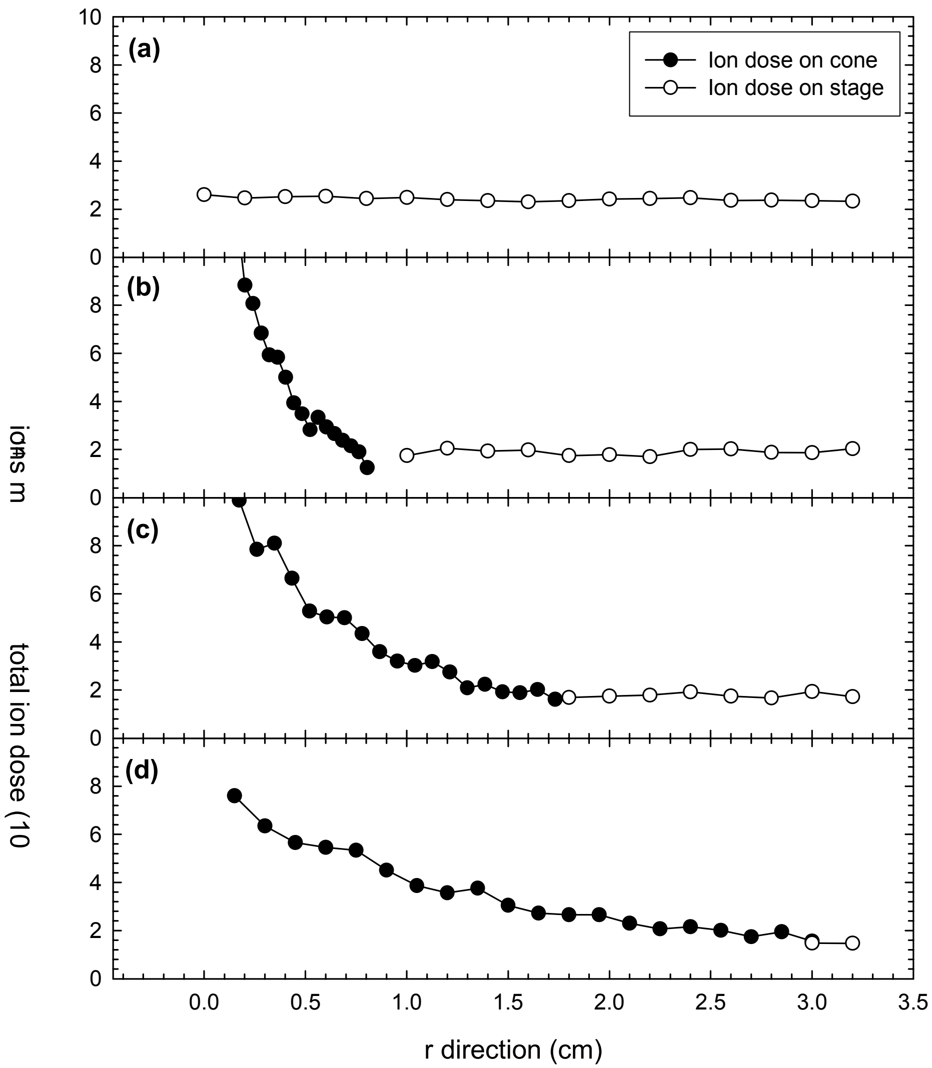
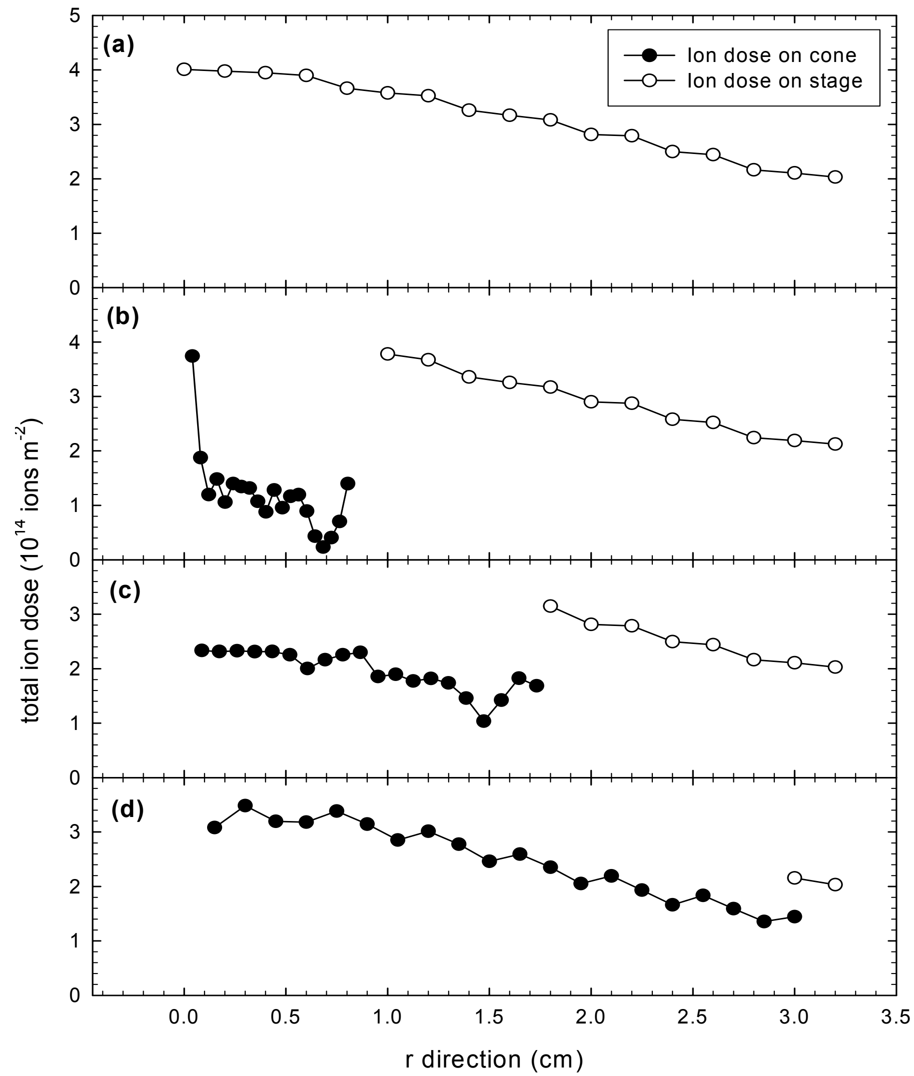
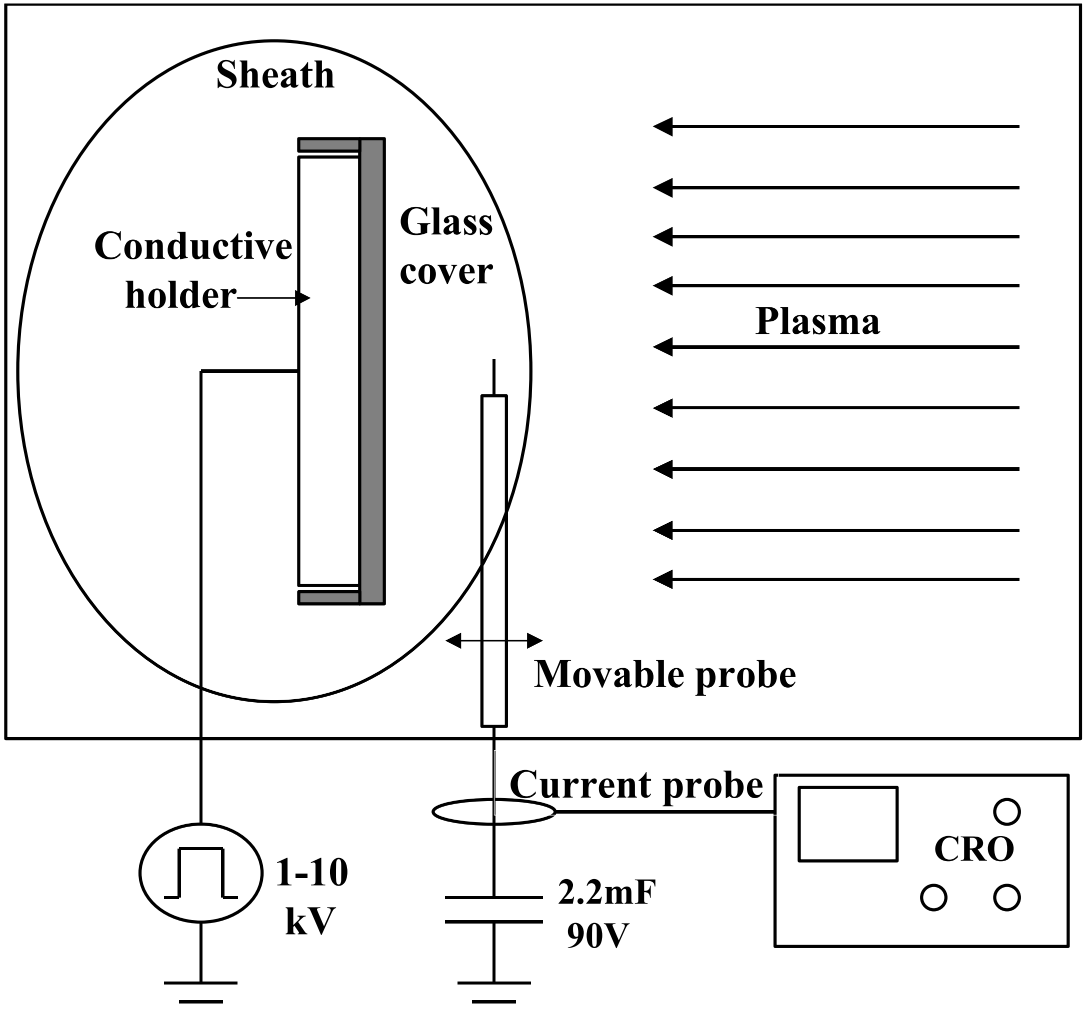
Implantation phase



Deposition phase



Measuring Sheath Collapse



Insulators: Charging Effects

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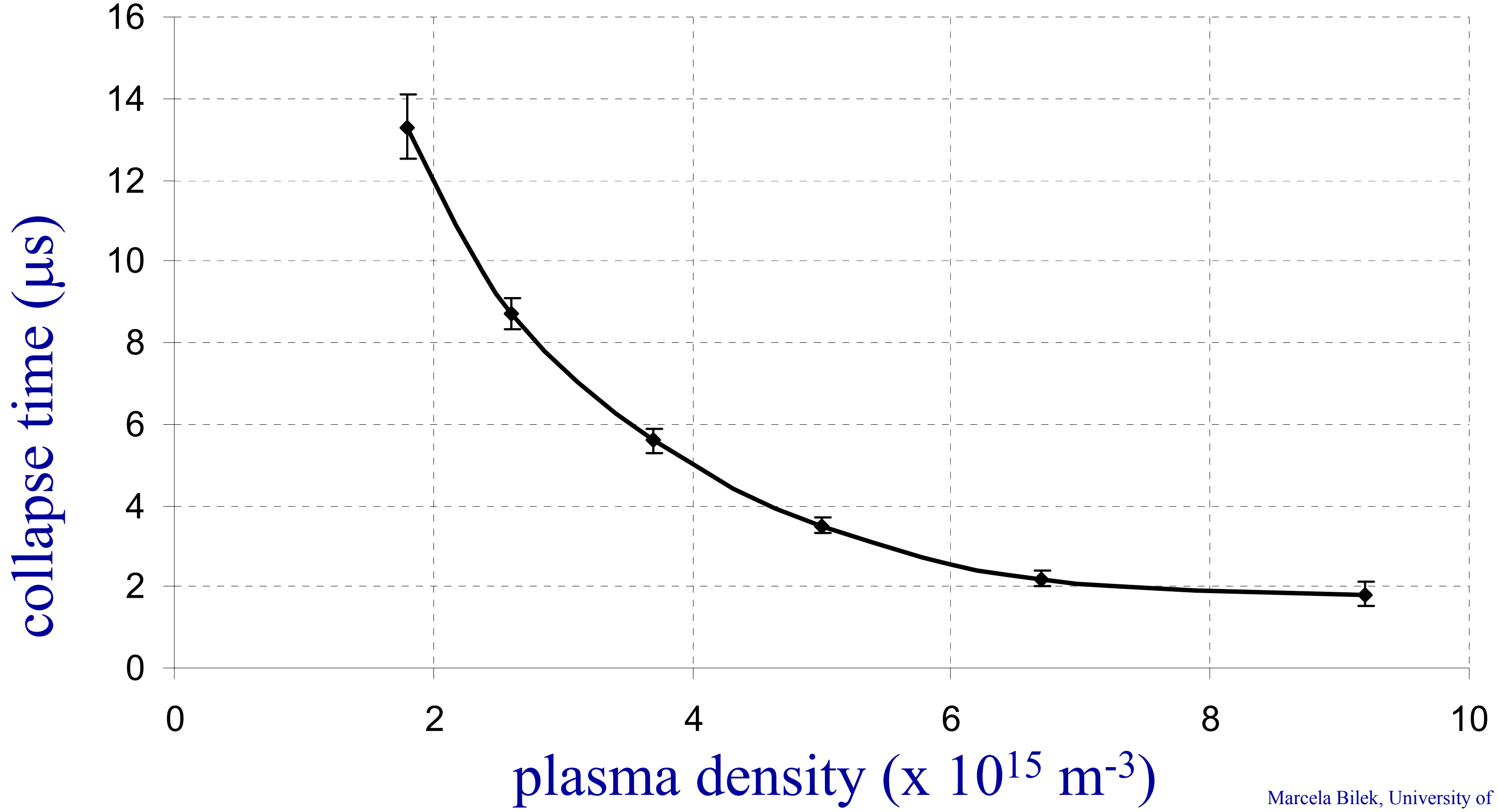
- Surface charging results in voltage droop (lower energy)
- Time for sheath to collapse down to 5 mm at an applied bias of 5 kV as measured by a Langmuir probe.



Solutions under study

- Thin conductive and ion transparent coatings stripped after treatment

- Ion implantation through mesh

Structure at the nanoscale

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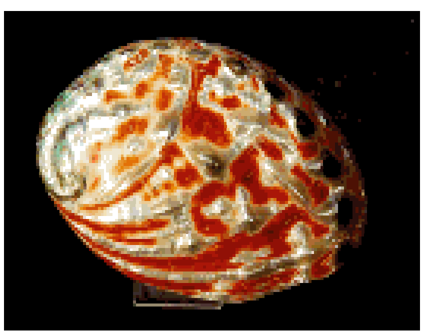
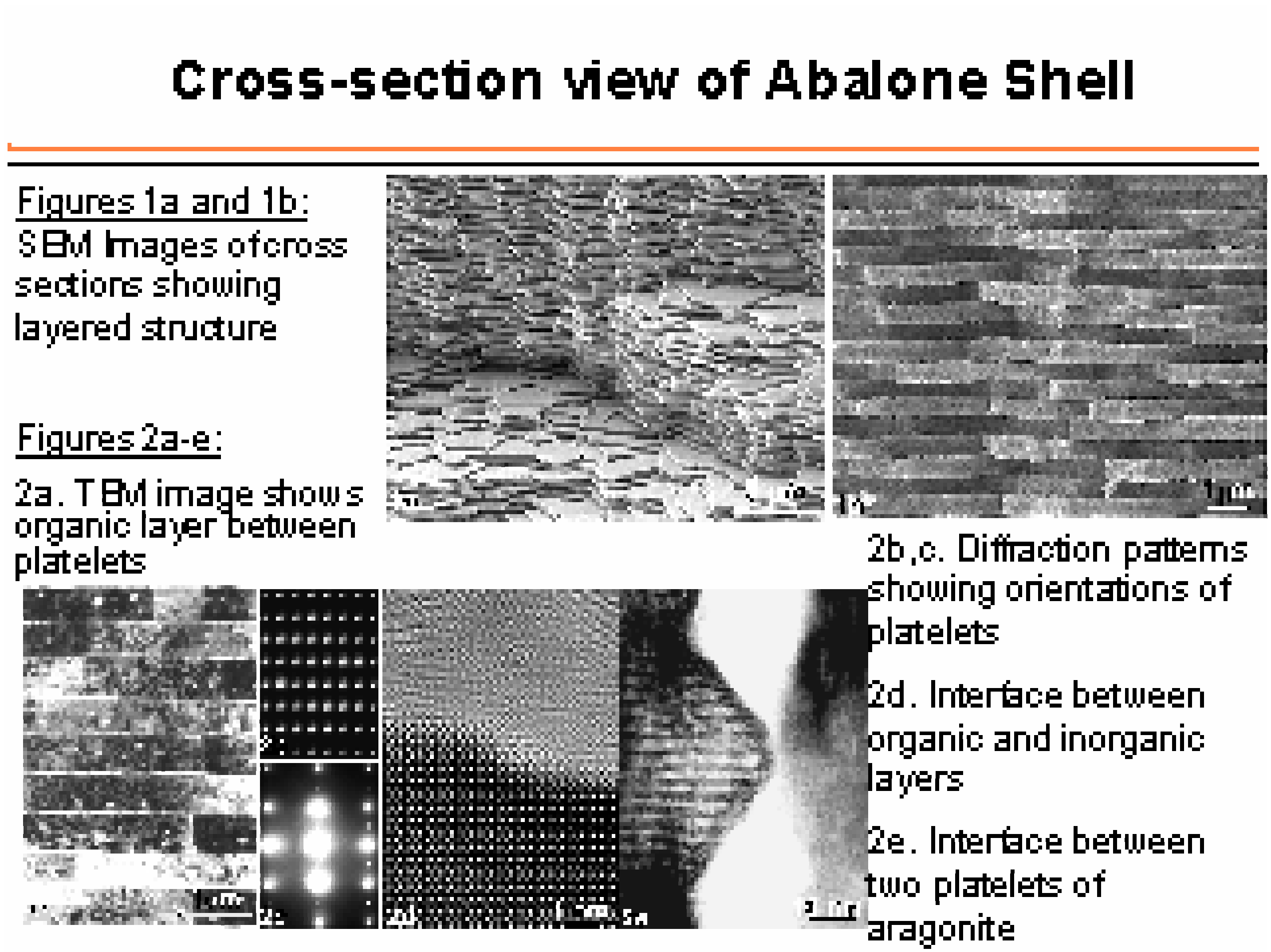
The structure of an abalone shell

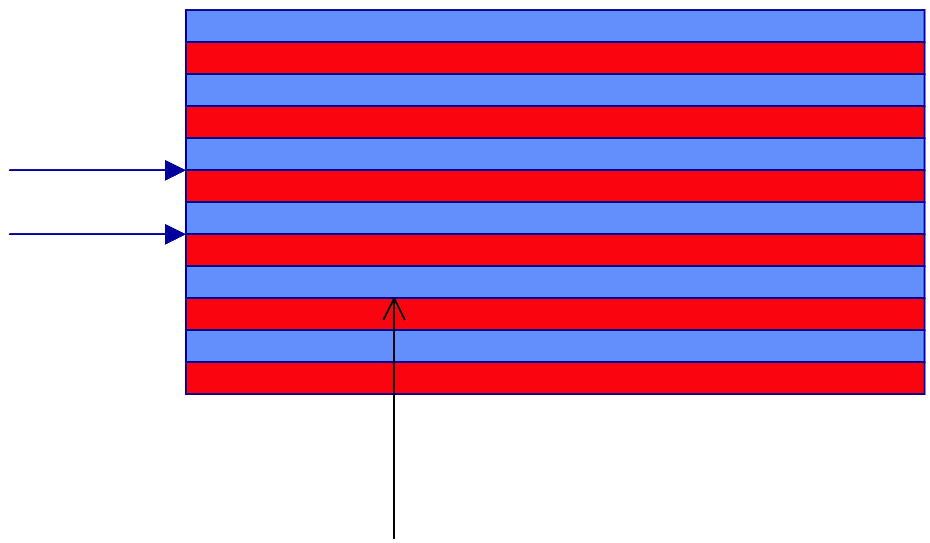


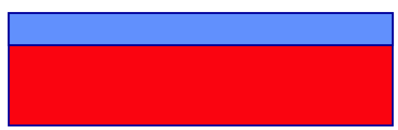


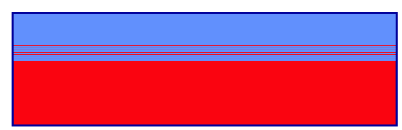
http://www.princeton.edu/~pmi/REU/presentations

A Multilayered Structure

Period

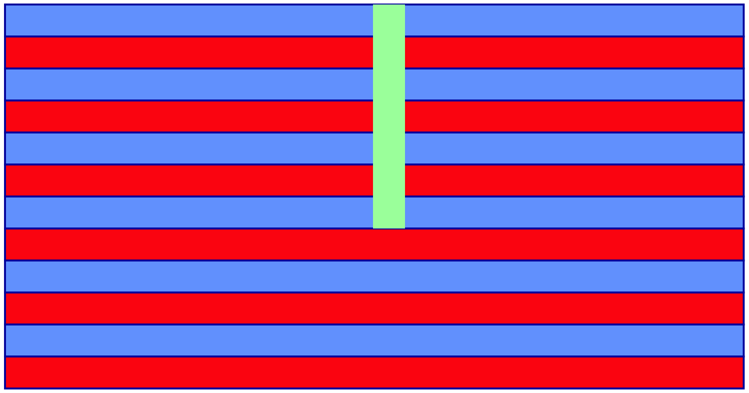






Sharp interface or Graded interface

Crack Propagation

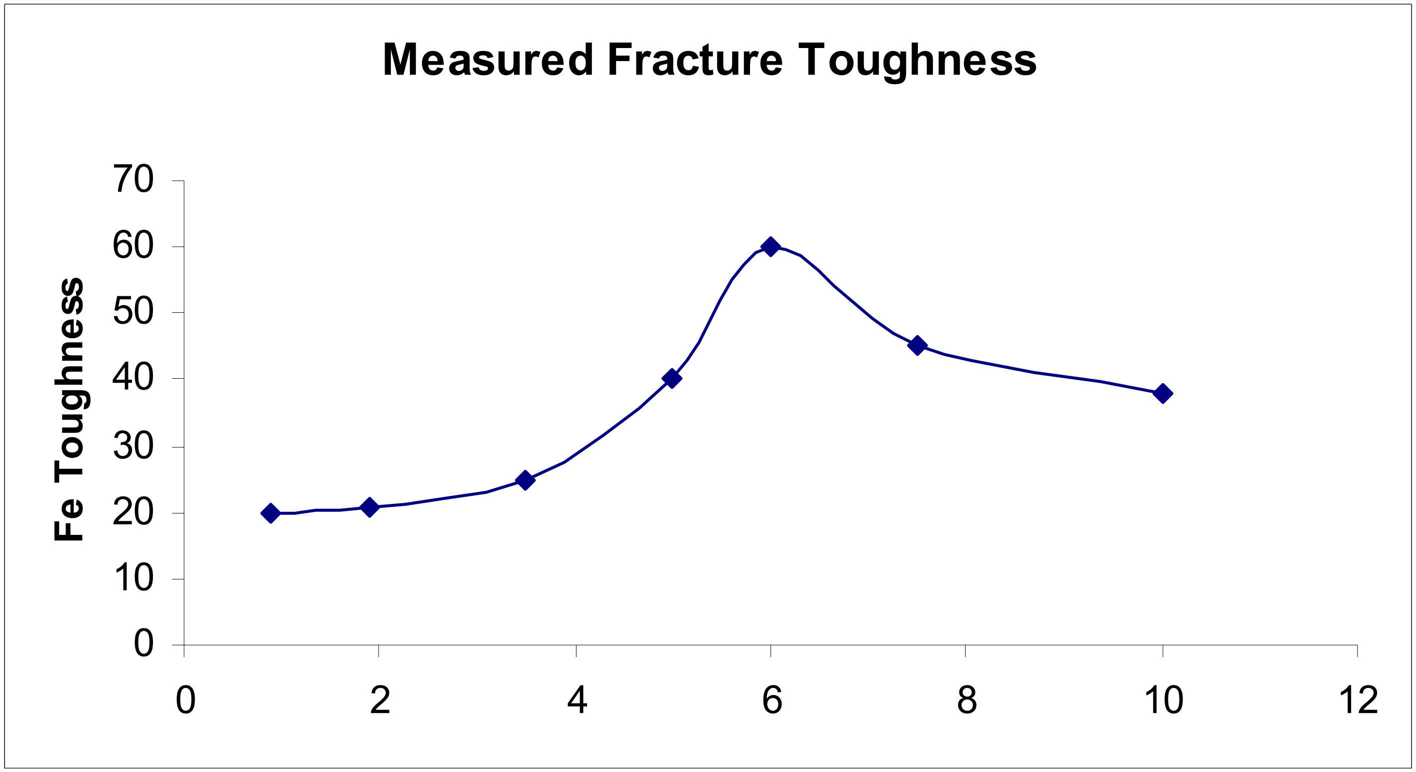


A crack propagating in a direction perpendicular to the layers is arrested at a soft layer since stress concentrated at the crack tip is reduced (*Okumura and de Gennes, European Physical Journal E, vol 4, p121, 2001*)

The Multilayer Advantage

- Increased fracture toughness
- possible mechanism
  - ➢Arresting of cracks at interfaces

TiC/Fe multilayer (*Liu et al, Mat. Sci. Eng. C4, 1996, p139*)



Surface Relaxation Method

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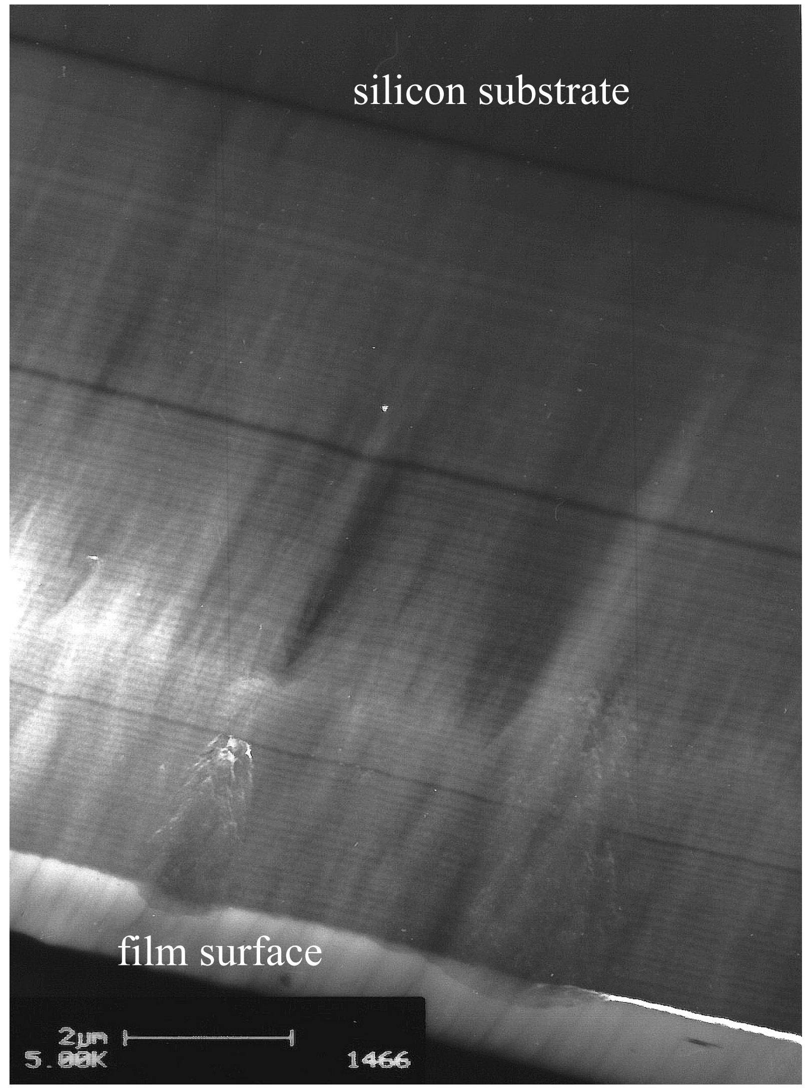
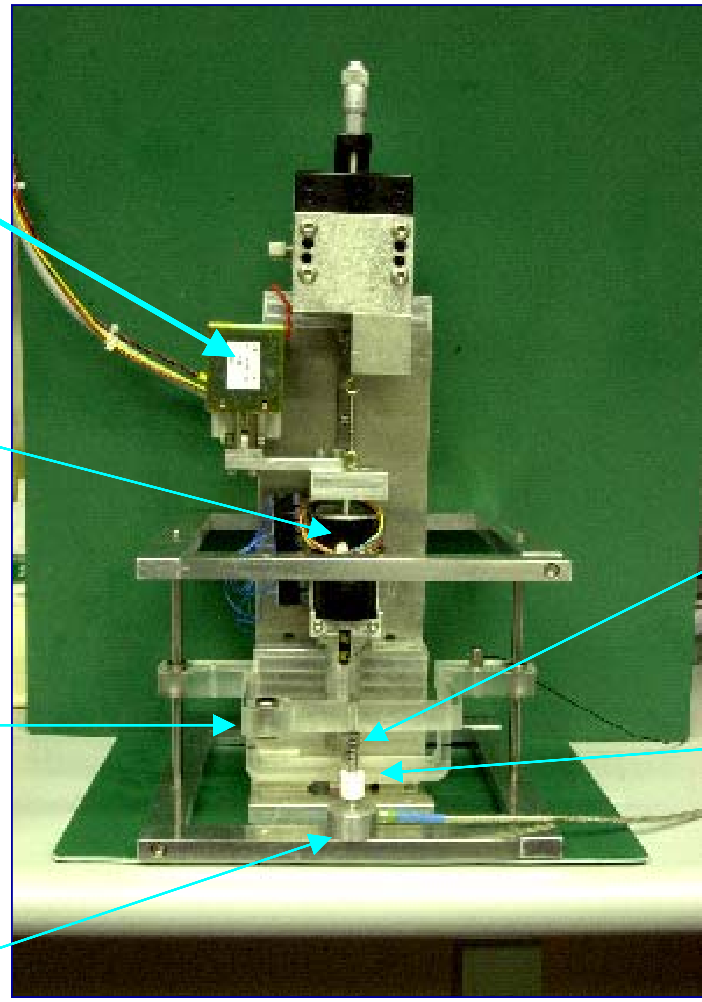
- 11.4 micron carbon film grown in the vacuum arc
- About 200 layers
- Dark layers result from surface relaxation when PIII&D stopped



Pin-on-disc wear tester + impact system



Combined wear test with Impacts

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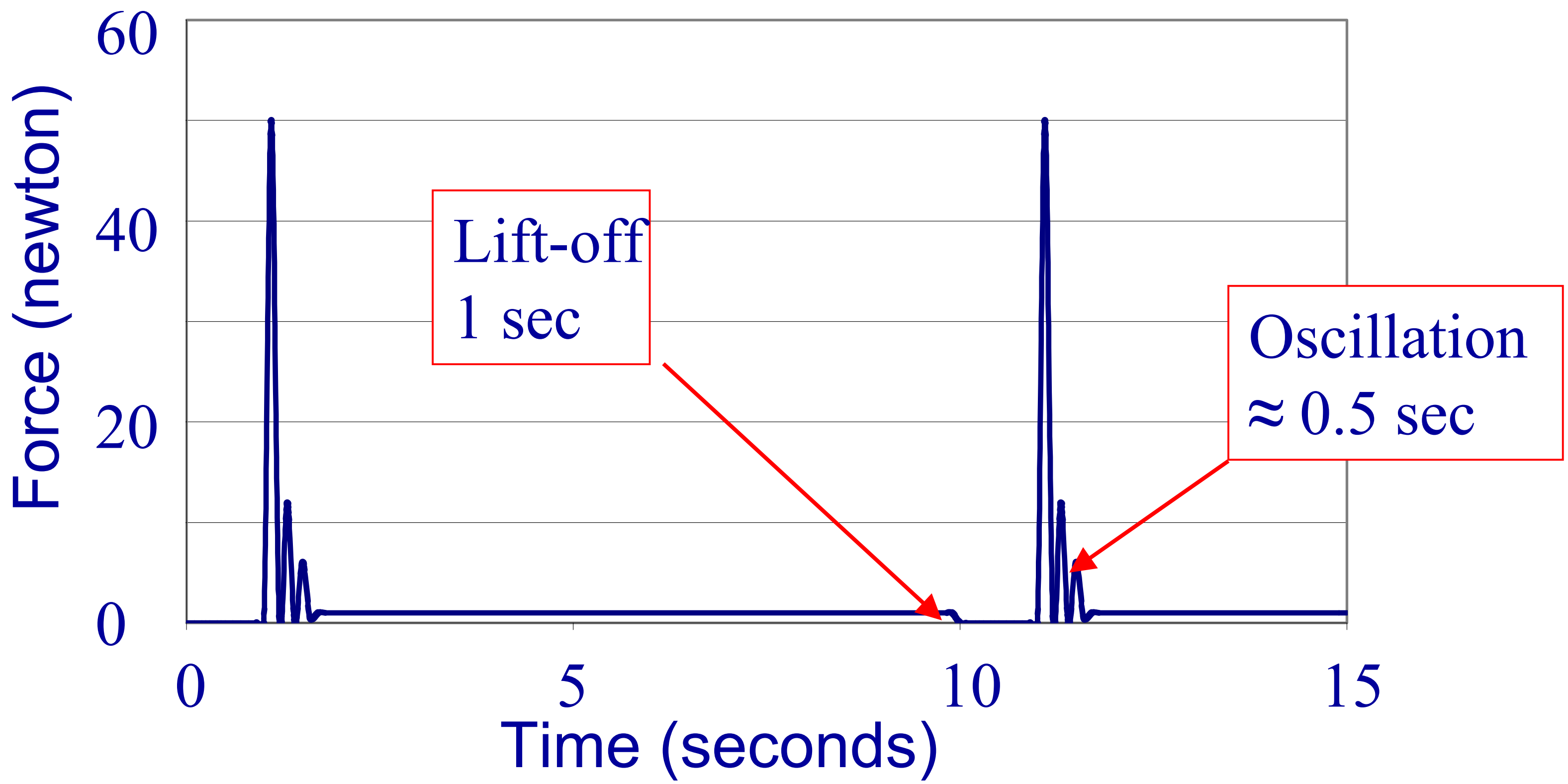

- 50 N impacts every 10 sec, ≈ 8.5 sec @ 1 N, 1 sec @ 0 N
- Disk at constant 2000 rpm rotation in Haemaccel®

Ti6Al4V pin on 2 μm thick (48 nm layers) carbon disc

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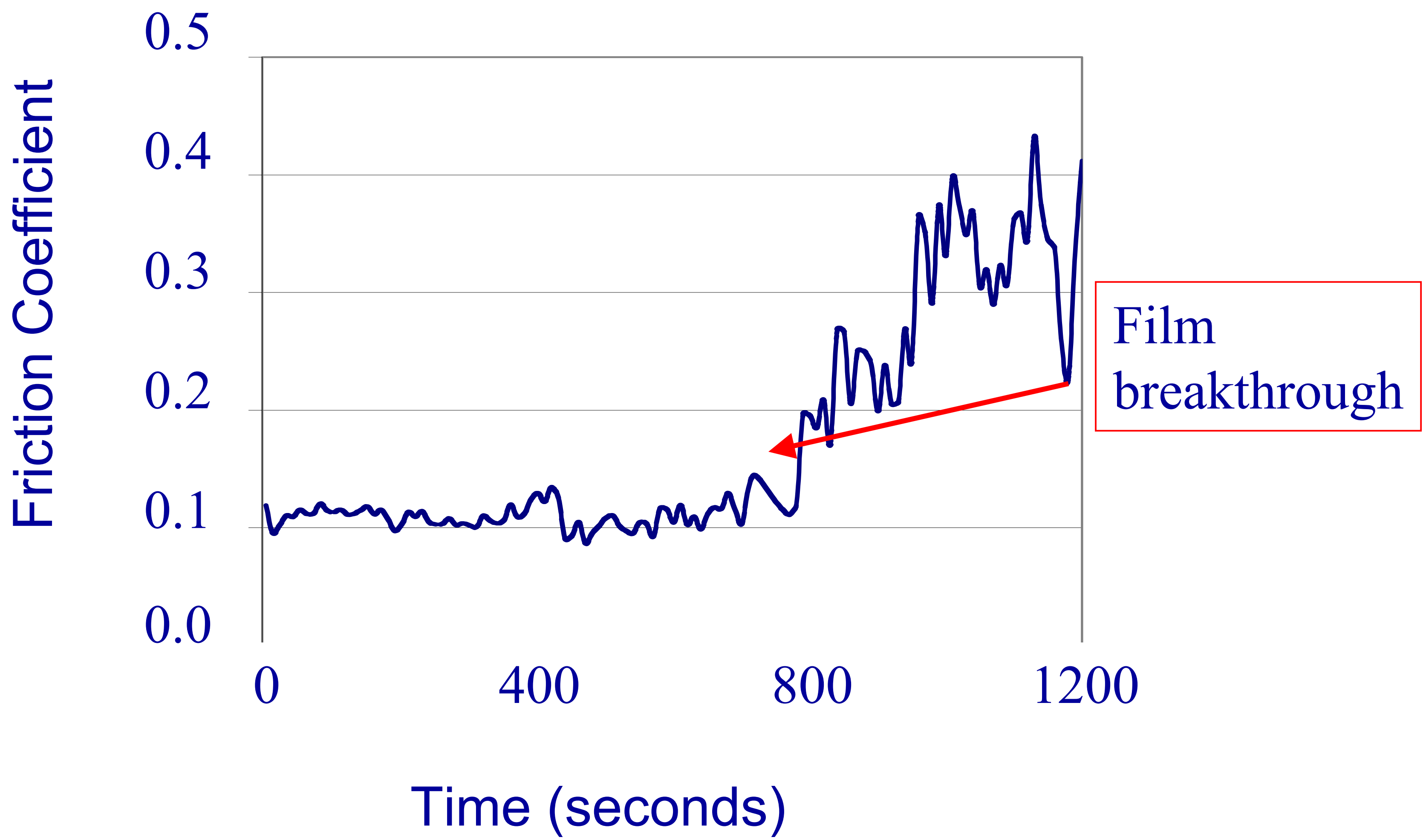

Ti6Al4V pin on 2 μm thick carbon disc: Wear + Impact

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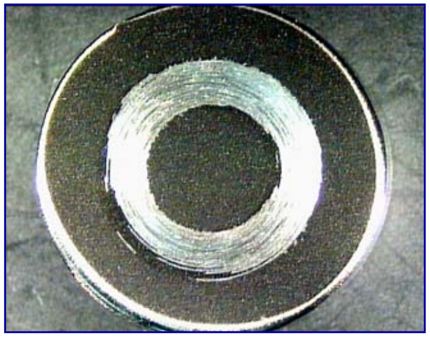
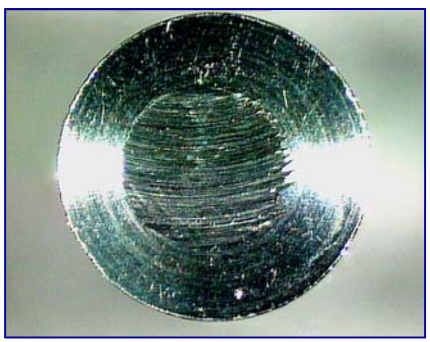


20 mm

Carbon (48 nm layers)



6 mm

Ti6Al4V pin

Pin and disc pair after 20 minutes wear + impact testing @ 2000 rpm

120 impacts @ 50 N

The disc has worn through to the metal, and the pin shows substantial wear

Ti6Al4V pin on carbon disc: Wear + Impact

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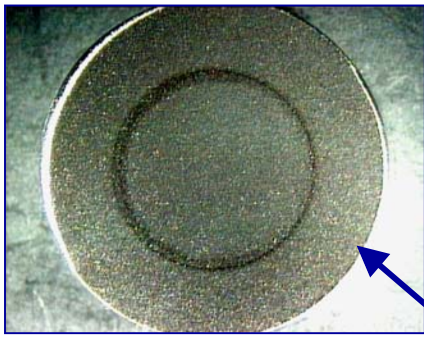
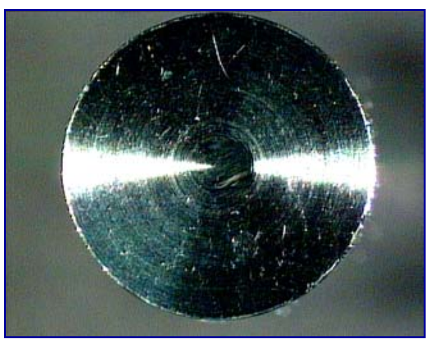


20 mm

carbon disc (24 nm layers)



6 mm

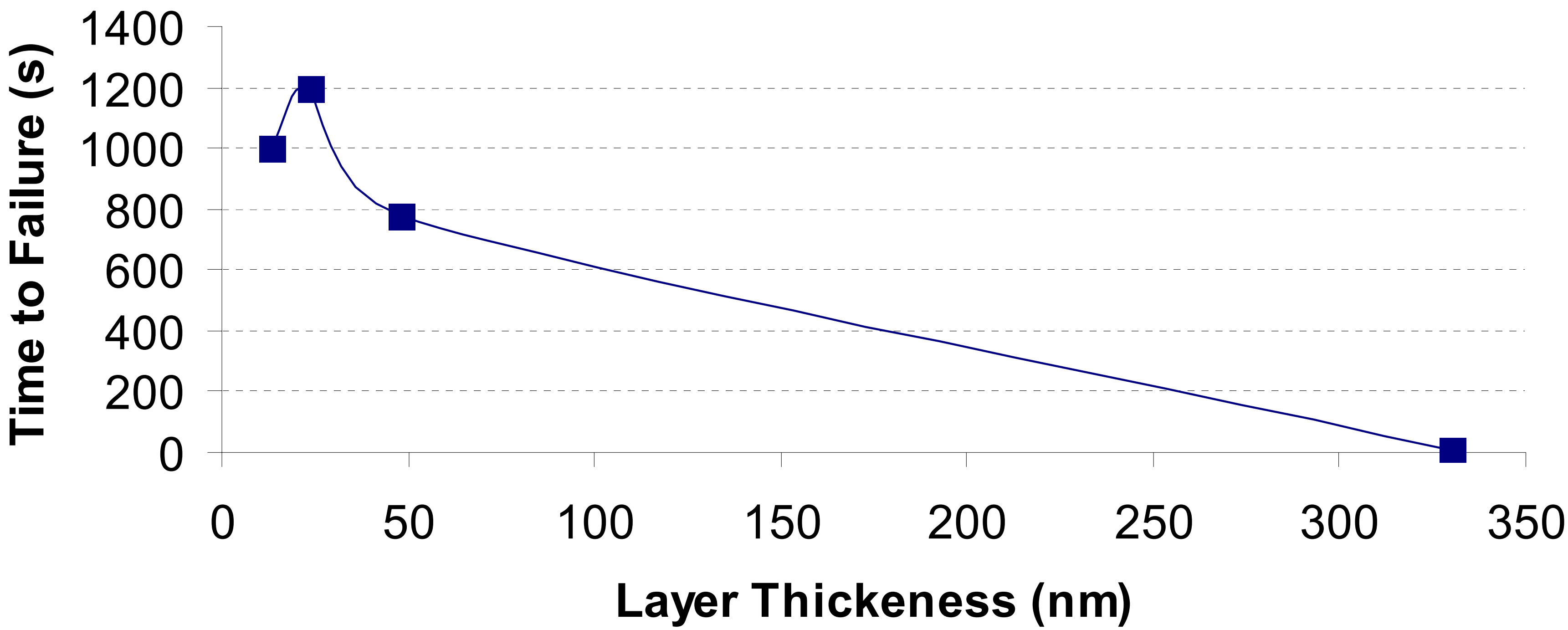
Ti6Al4V pin

Pin and disc pair after 20 minutes wear + impact testing @ 2000 rpm

120 impacts @ 50 N

Visual inspection of disc suggests mostly asperity wear, with little erosion into the bulk of the coating

Performance Enhancements by Multilayering



- Graph shows wear and impact time to failure for multilayered carbon films, 2 μm thick, on Ti6Al4V
- Interruptions to deposition produce a relaxed layers of higher density
- "Supertoughness" effect at optimum bilayer period

Nanoscale Multilayers:

Time variations in condensing species and surface mobility

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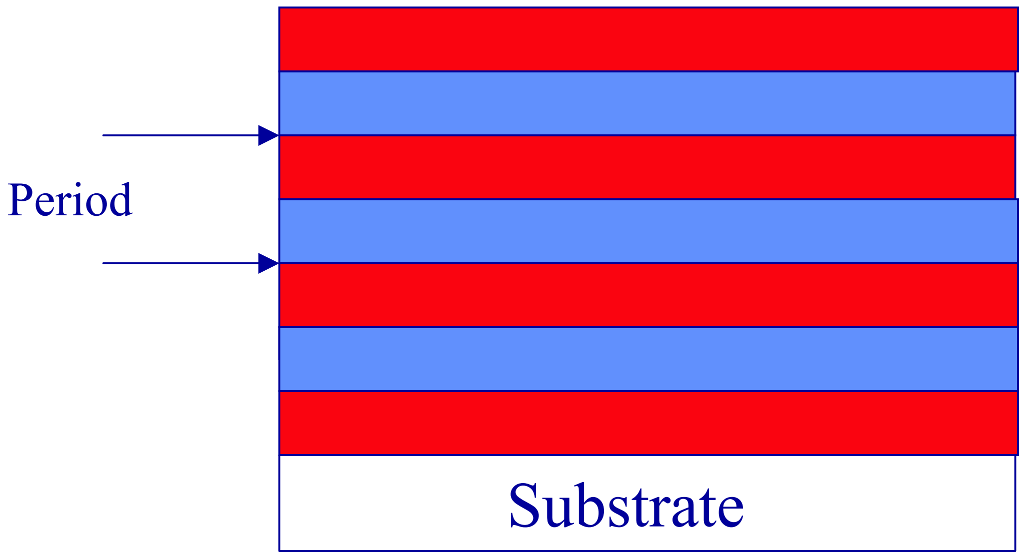
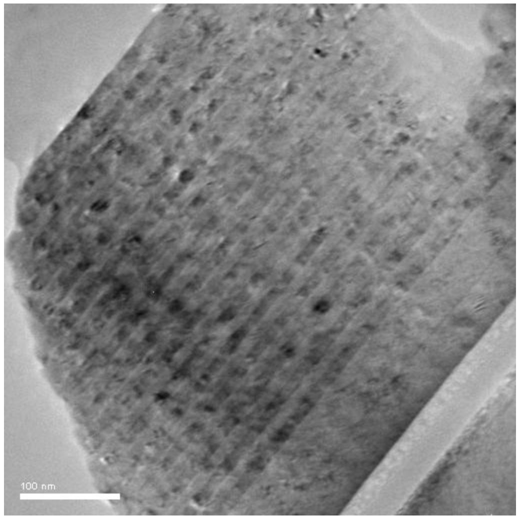
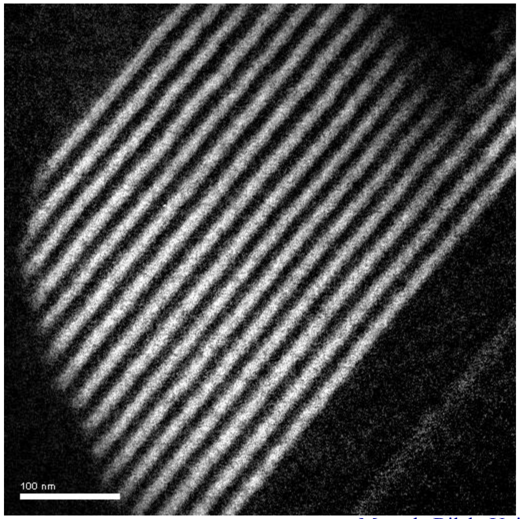
- Multilayered coatings
- 17 nm bilayer period





(a) TEM image (the scale bar represents 100 nm);



(b) shows a nitrogen elemental map from the same region.

Multilayer in the Ti/TiN System

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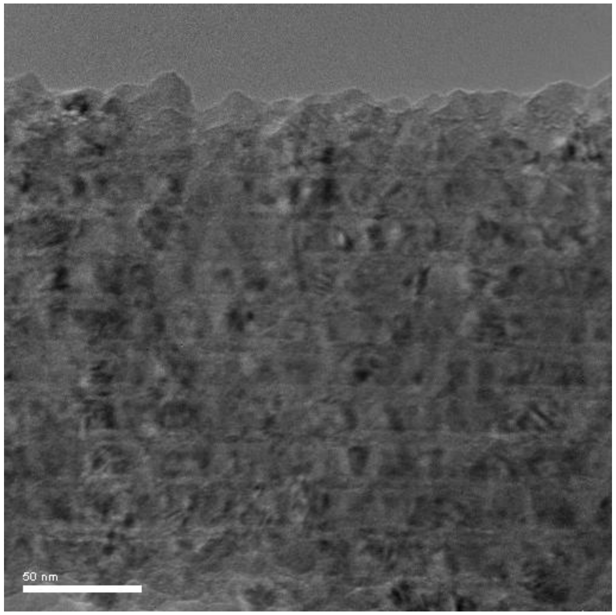
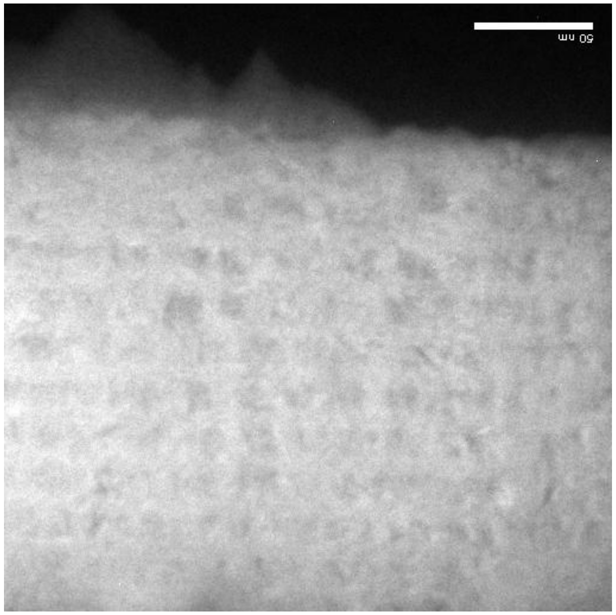
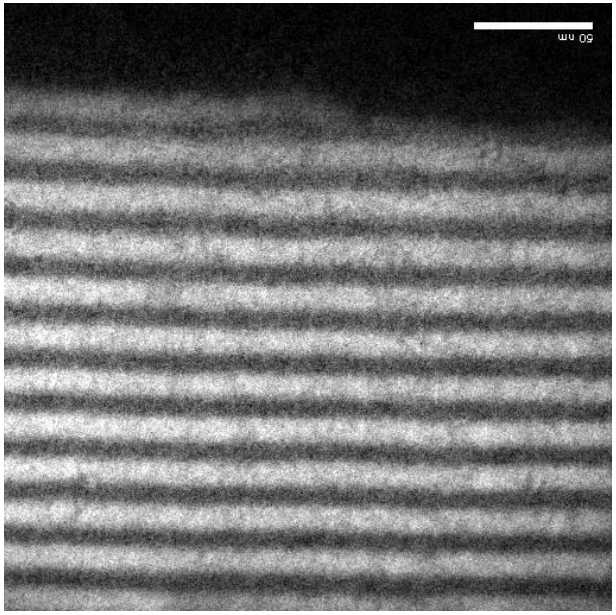
- Produced using cathodic vacuum arc PVD
- Ti provides a soft layer between alternate layers of TiN
- 17 nm bilayer period



BF image



Ti EELS map



N EELS map

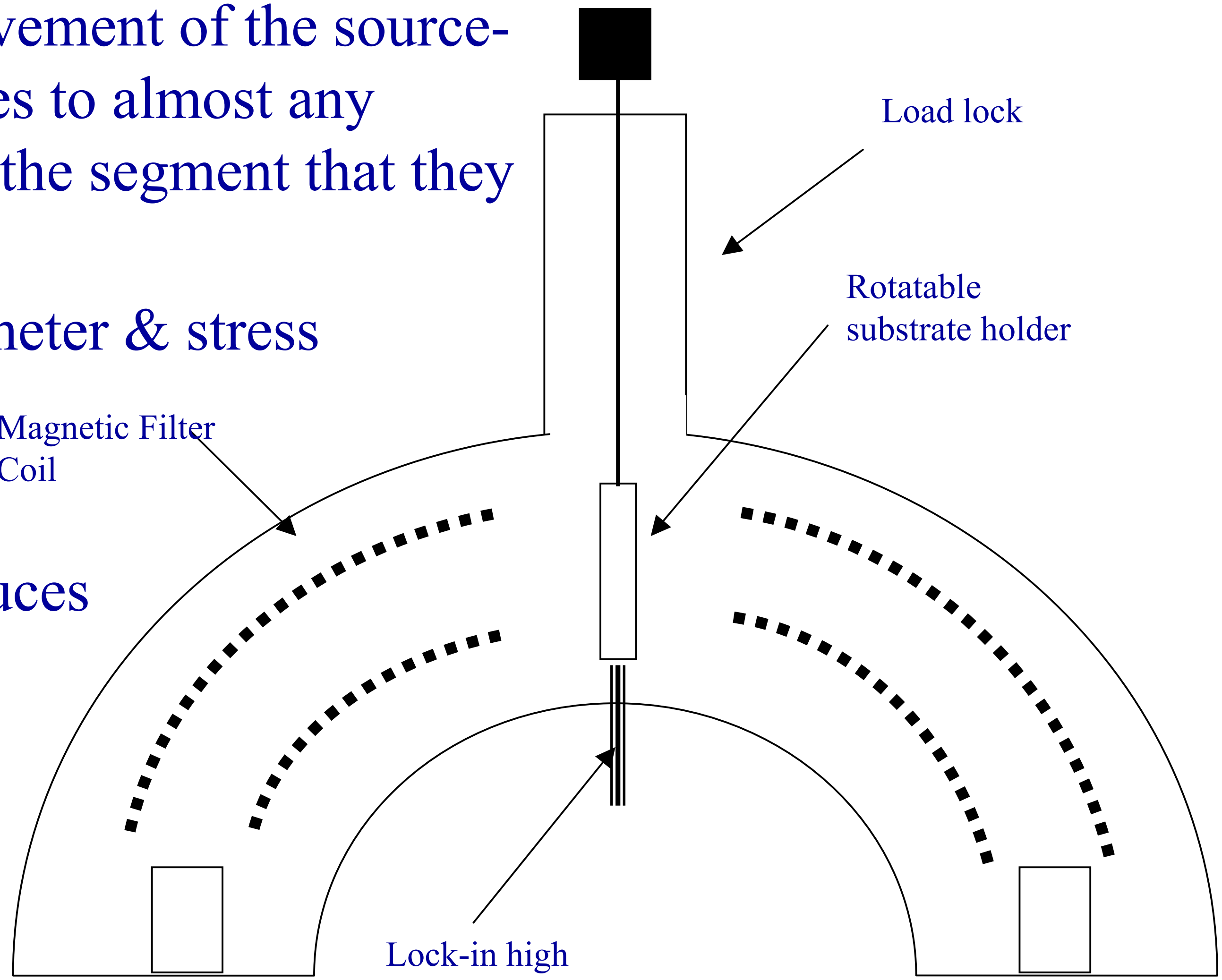
Limitations of Single Source dc Vacuum Arc

- single source limits the range of composition of constituent layers
- density of the dc plasma plume fluctuates strongly with the instantaneous arc current ⇒ deposition of precise layer thicknesses at the nanoscale difficult

- new system with two sources – pulsed
- pulsed sources deliver known current per pulse (easy to calibrate)
- lower macroparticle production in pulsed mode (I↑)
- currents of 1-5 kA ensures competitive rates

New System Design

- rails allow movement of the source-filter assemblies to almost any position along the segment that they subtend
- in-situ ellipsometer & stress



- open filter reduces macroparticle bounce
- dual sources in both arms

Source Design

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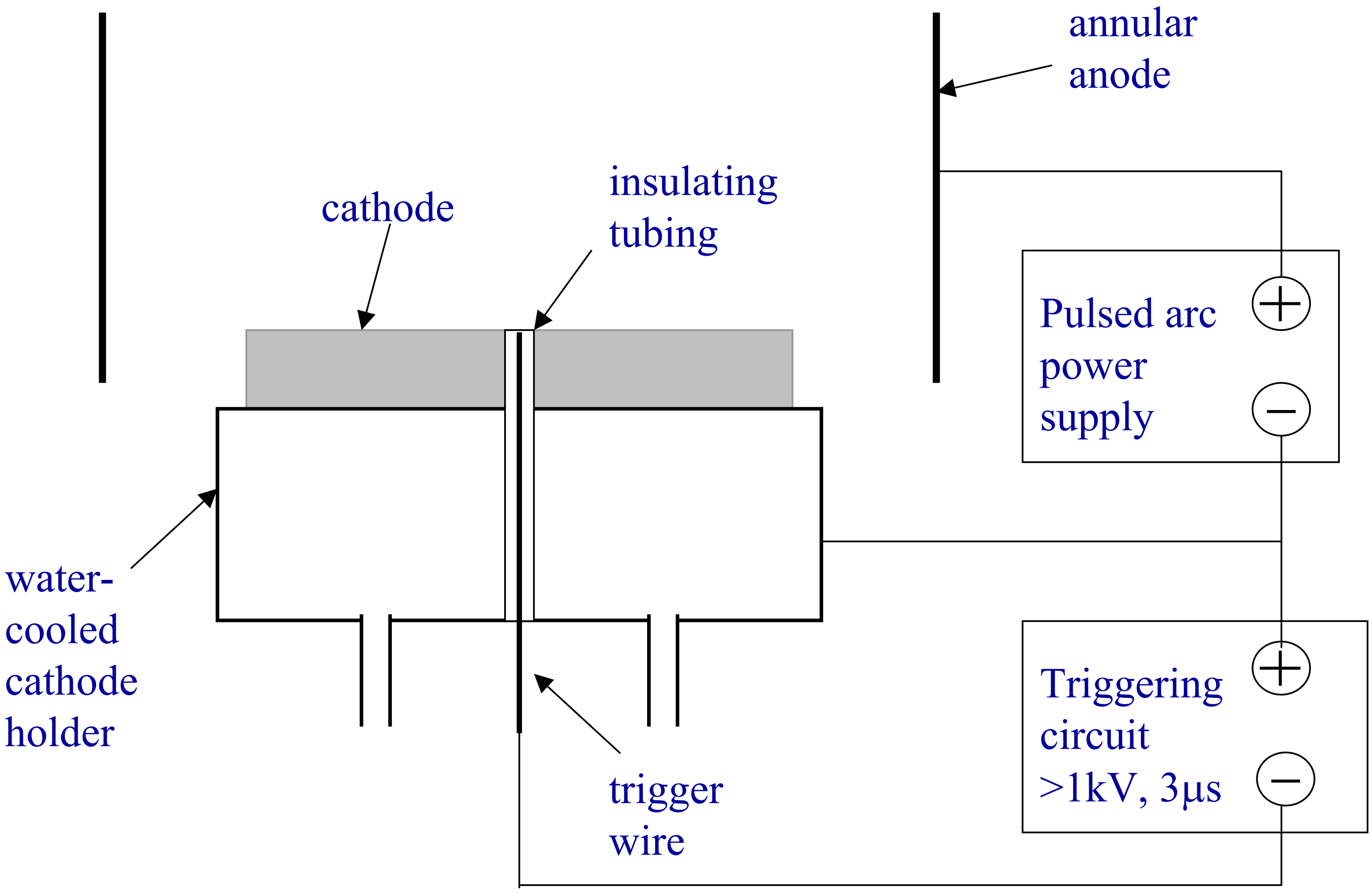

•based on design of Siemroth et al, *Surface and Coatings Technology*, **68/69**, 314-319, 1994

Centre trigger for uniform erosion

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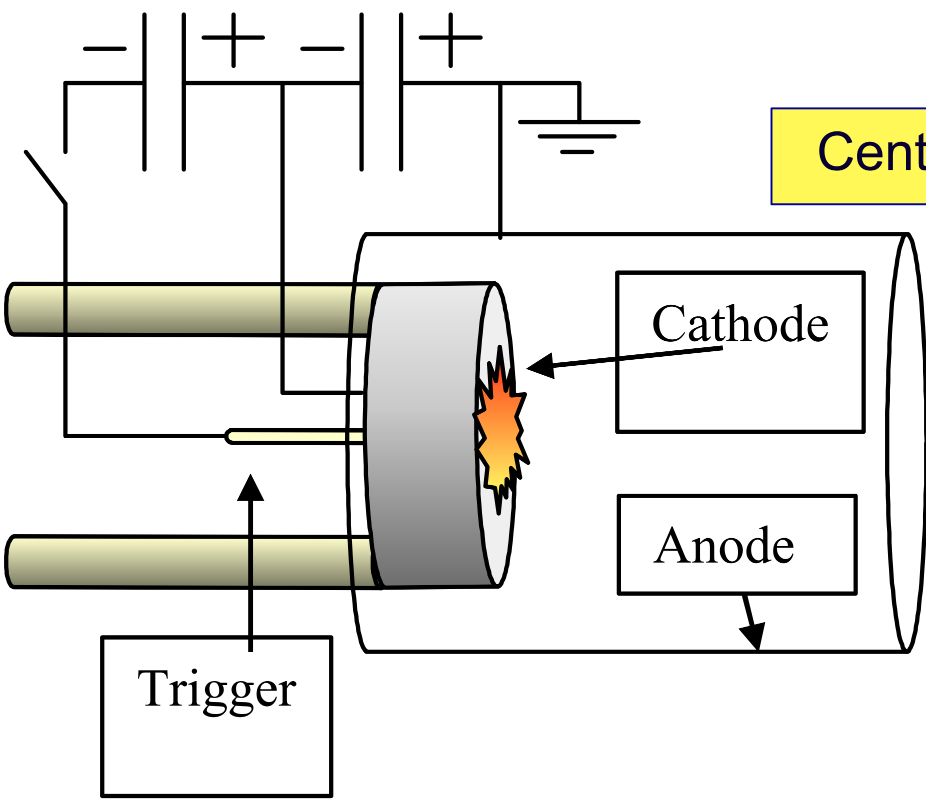
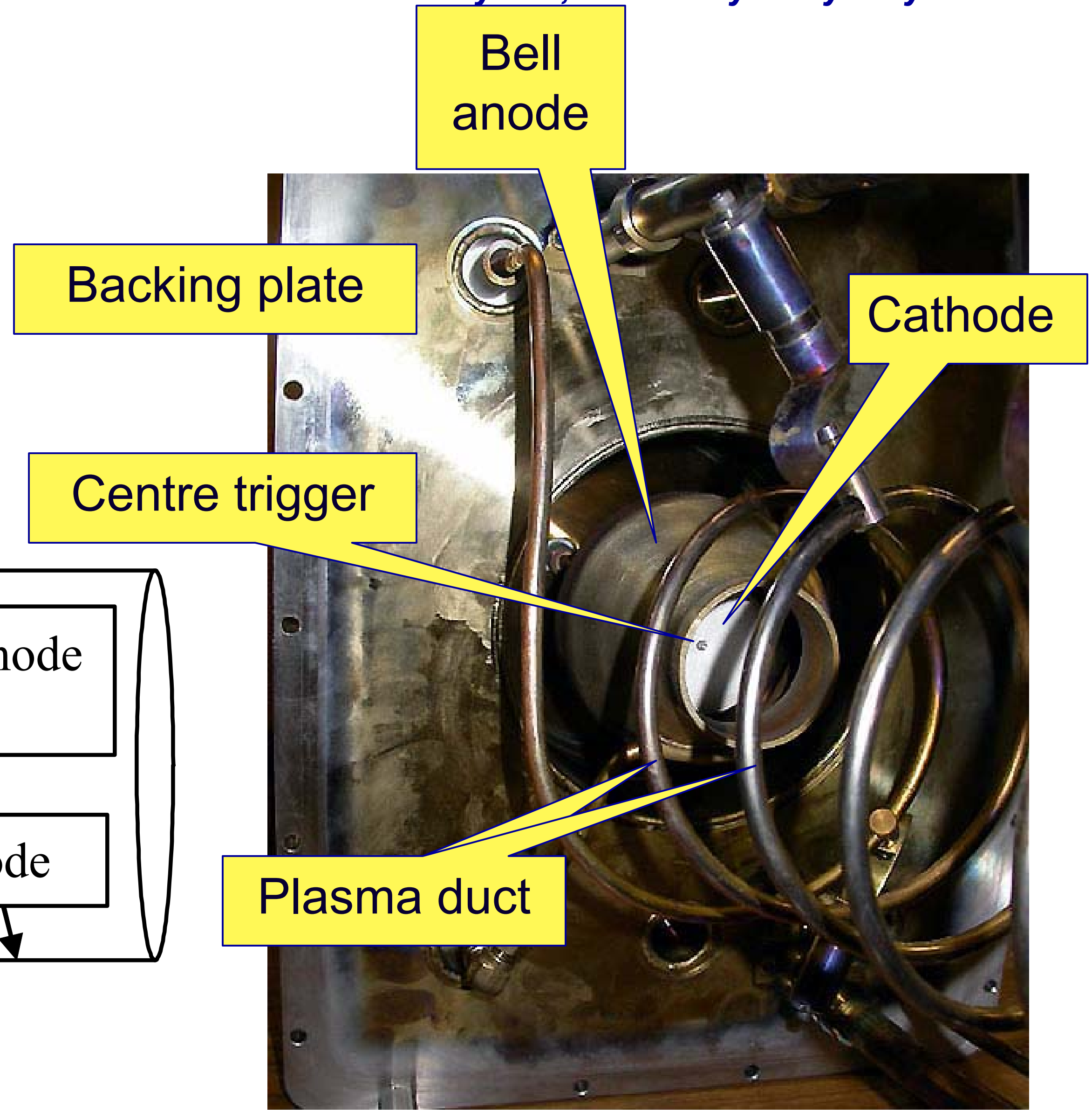
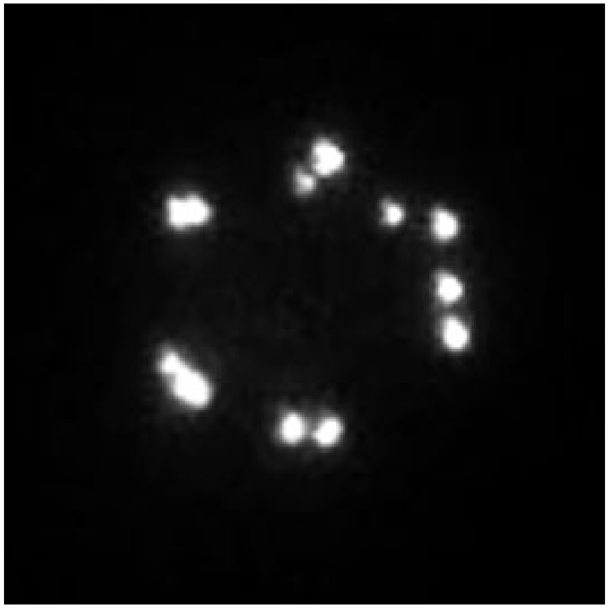
The key to a time stable deposition rate





Cathode spots

- Current is conducted through μm diameter spots on cathode surface
- Current limited to ~ 100A per spot. Arcs >100A exhibit multiple spots.
- Current density extremely high. $10^{9} – 10^{12}$ A. m^{-2}
- ~ 90% of plasma flux is electrons,~10% metal ions



Retrograde Motion.

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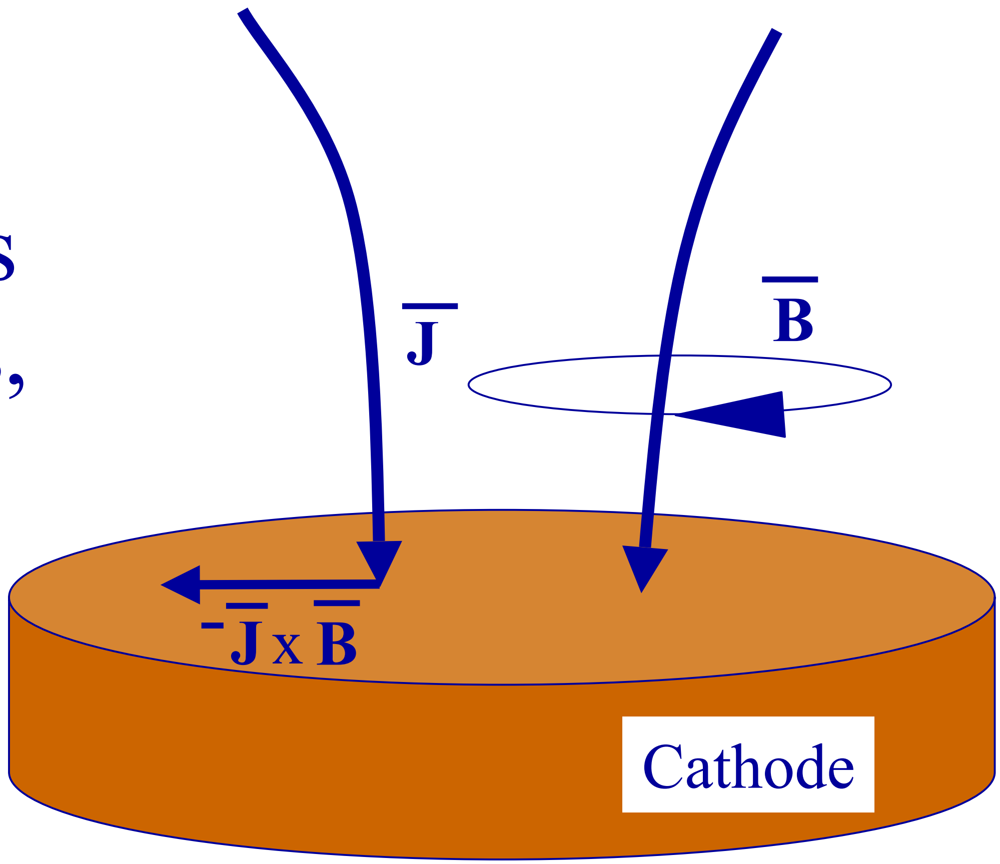
- In an external magnetic field, parallel to cathode surface, spots move in **-J** x **B** direction.

- In high current arcs with multiple spots, retrograde motion acts to repel spots away from one another.



1 ms exposures of cathode spots

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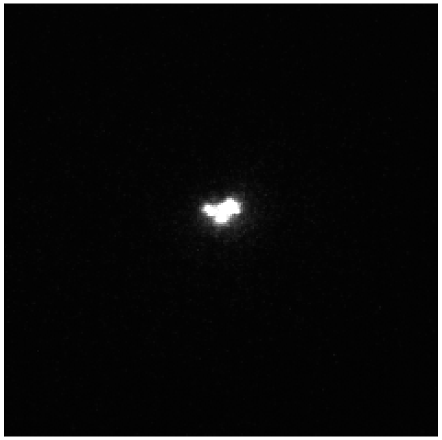
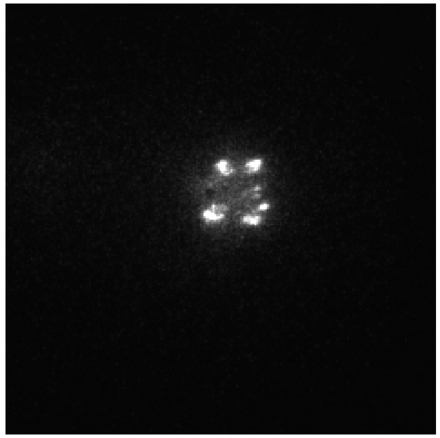
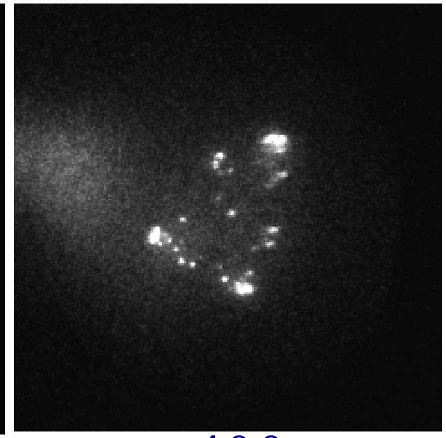
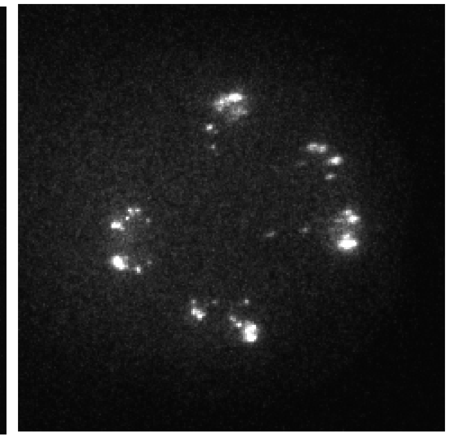
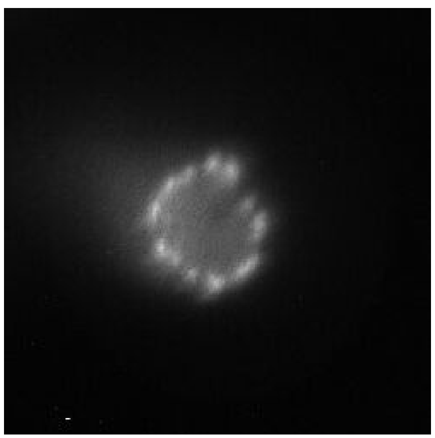
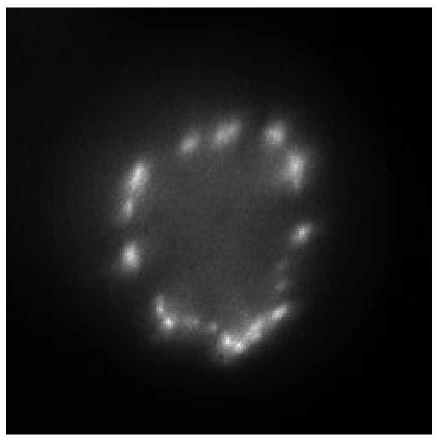
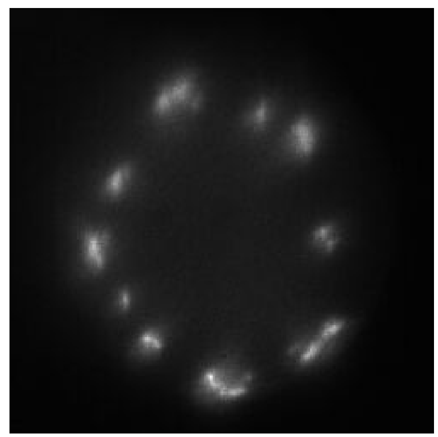
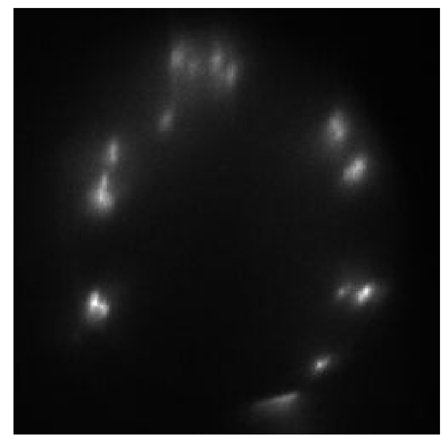
Al

100μs 200μs 400μs 600μs

Ti

200μs 400μs 600μs 800μs

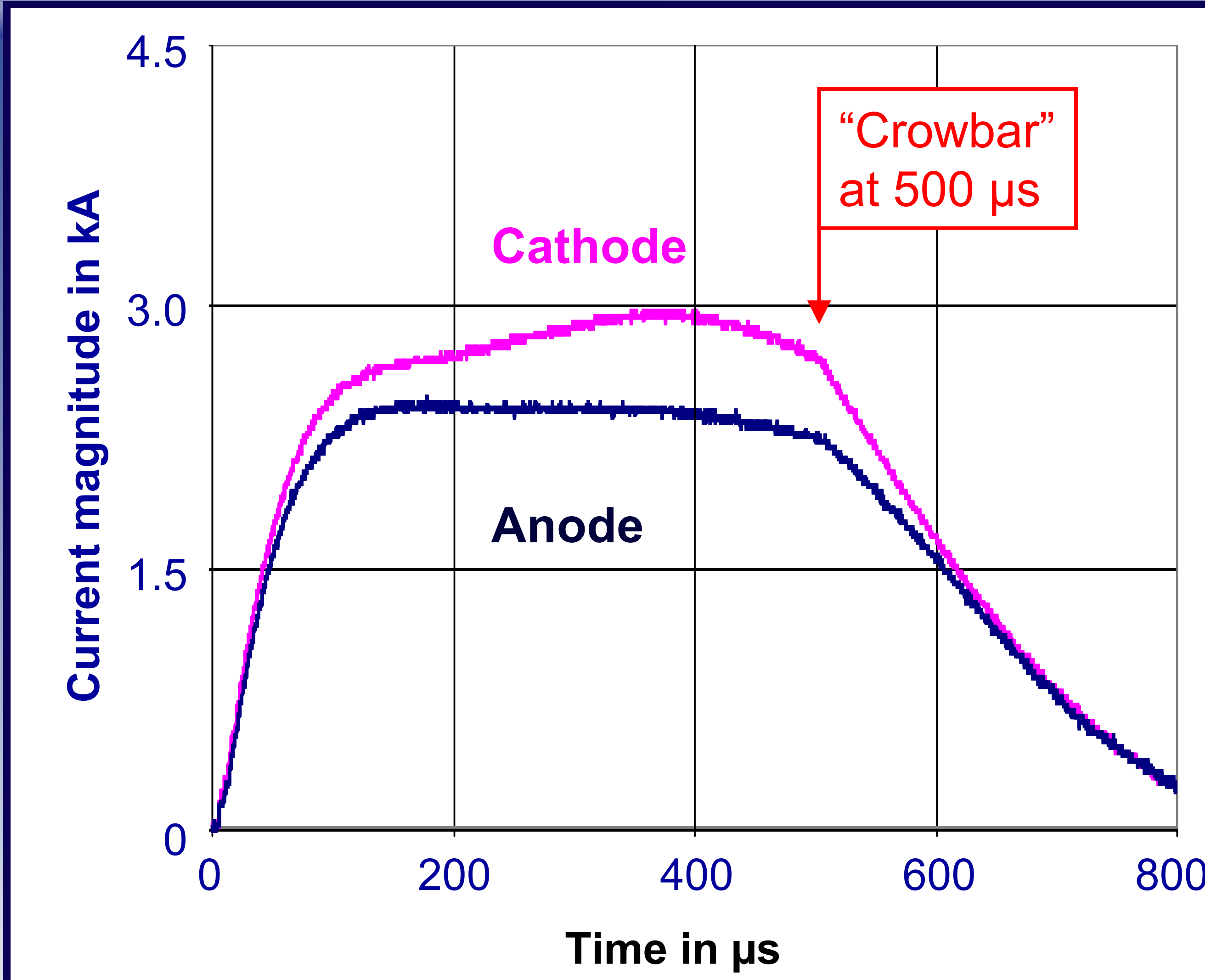
Image size 50mm square

Cathode and anode currents

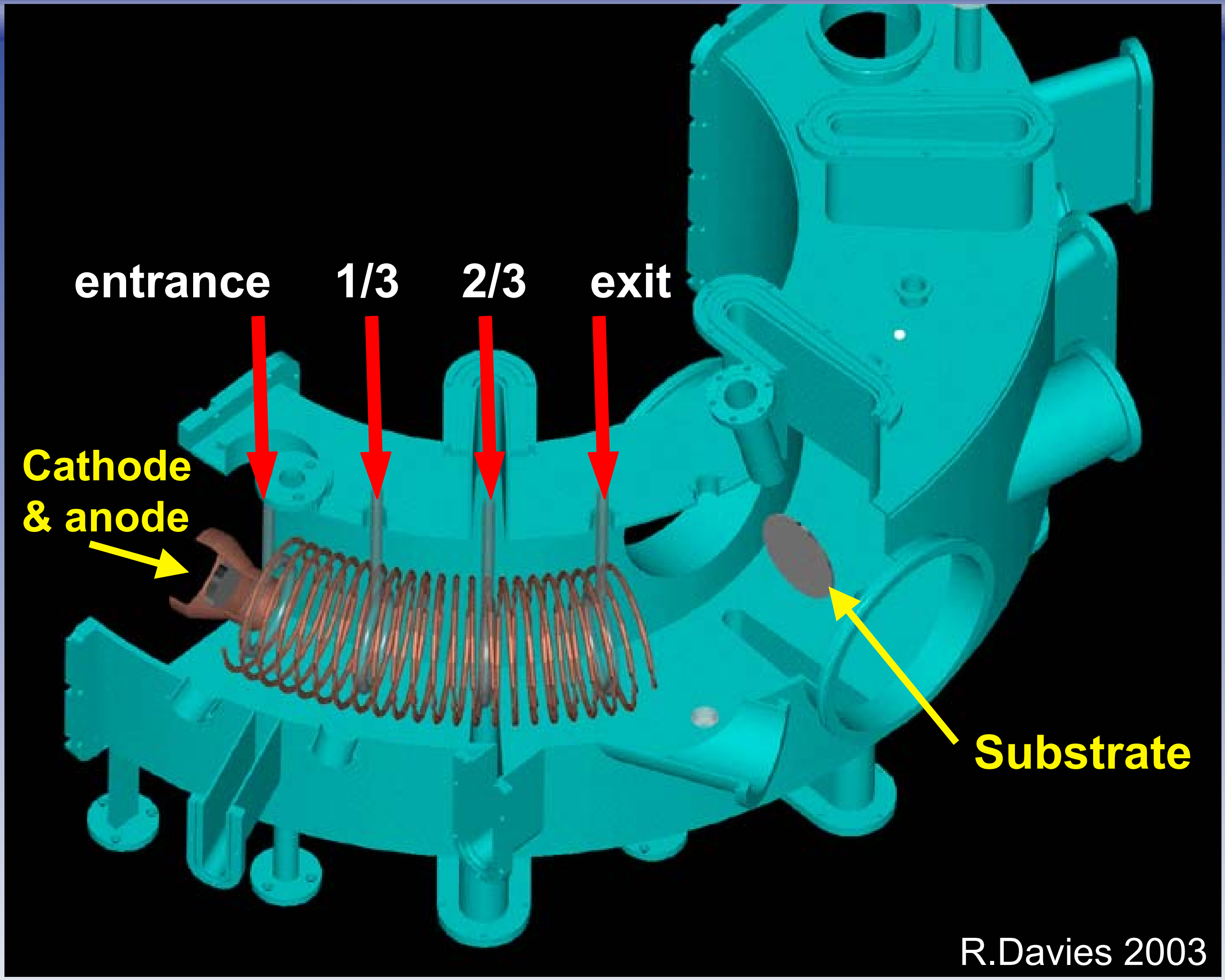
50 mm diameter Titanium cathode

177 mm diam. circular Al substrate biased at -90 V

Filter duct:
Initial field 43mT
Bias +35 V



Rogowski coil positions

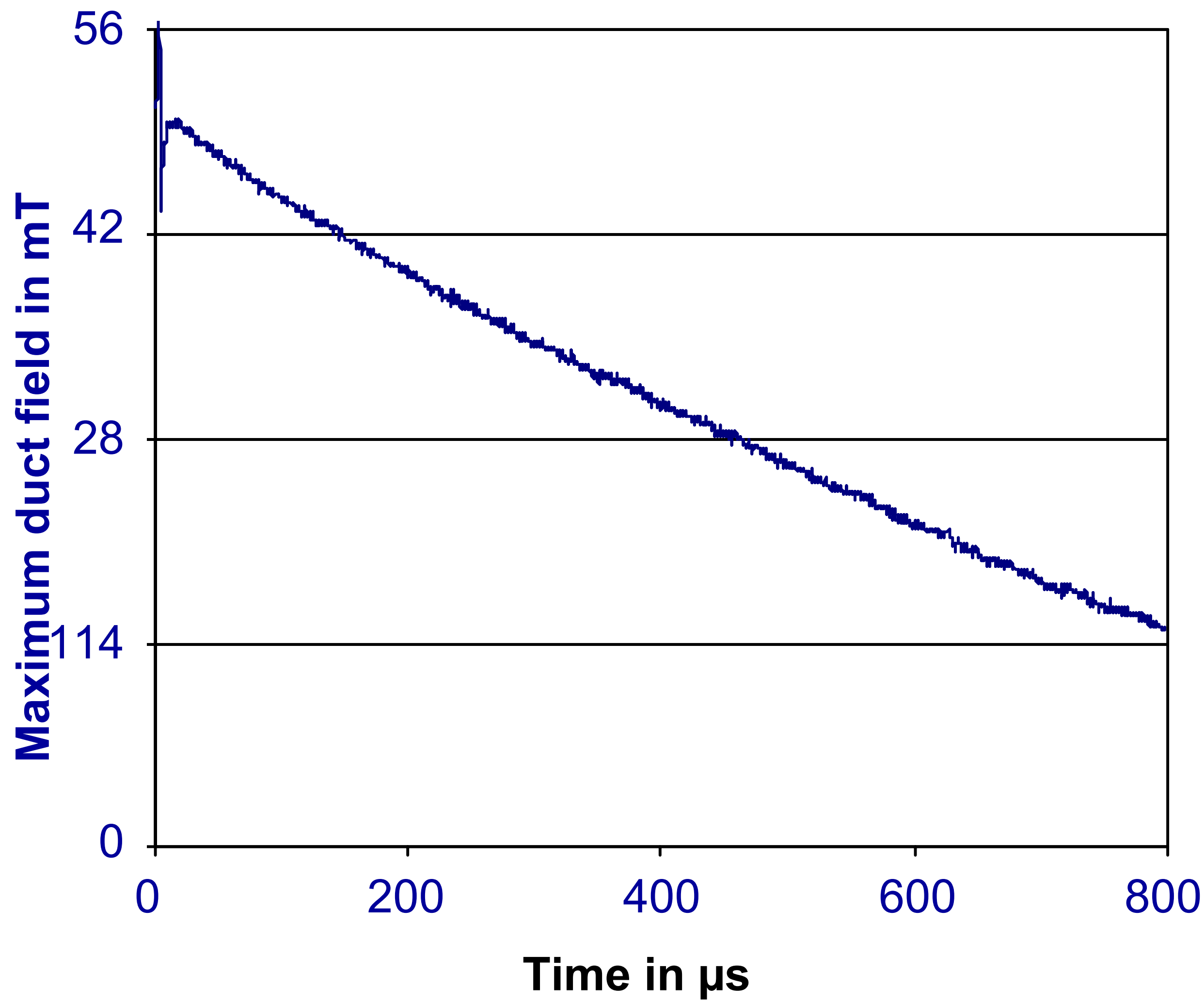


Falling axial duct field during pulse

177 mm diameter circular Al substrate biased at -90 V

Filter duct fields need to be matched to the plasma flux

Field triggered <u>before</u> cathode

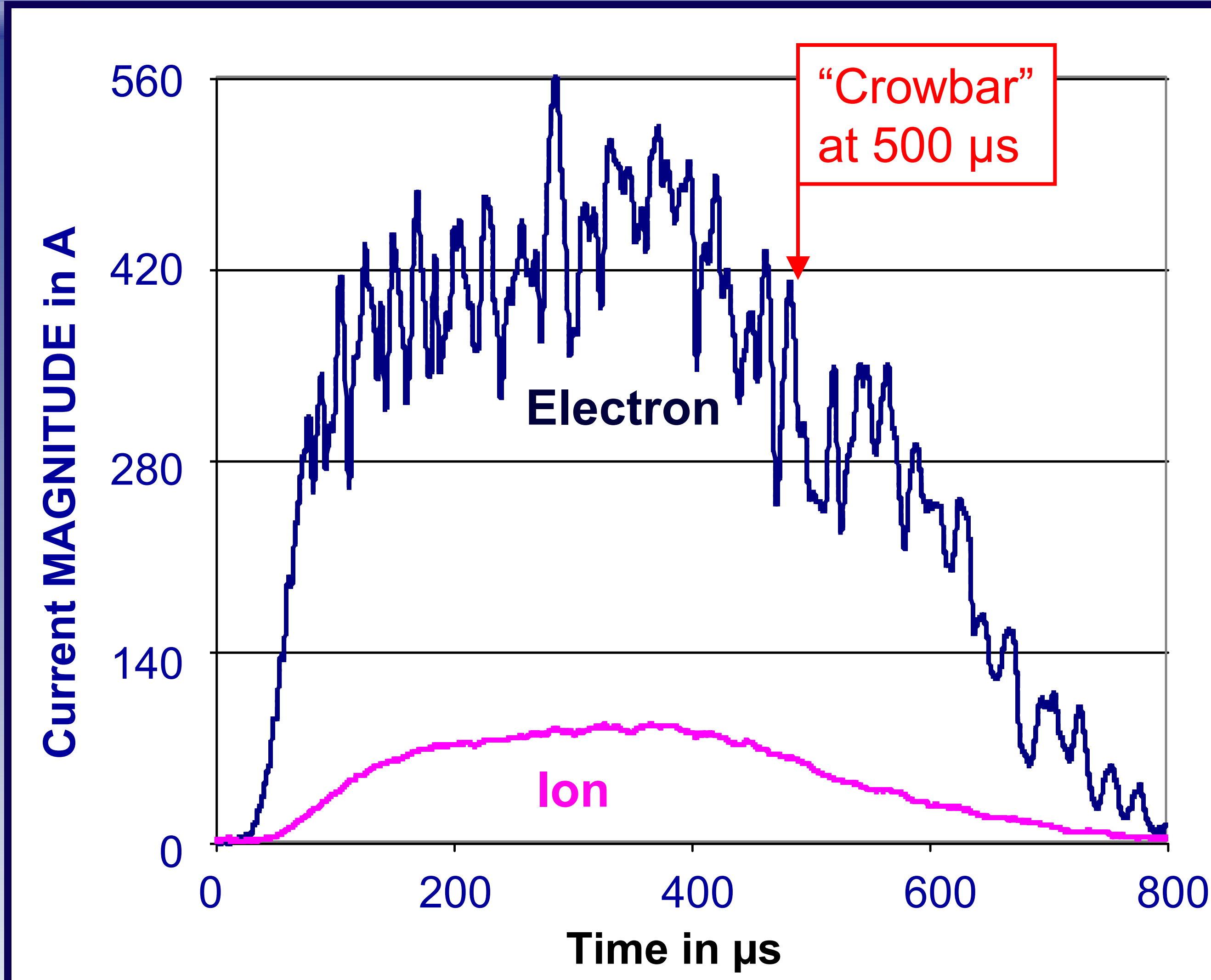


Ion and electron currents, measured at substrate

50 mm diameter Ti cathode

177 mm diam. circular Al substrate biased at -90 V & +90 V

Filter duct:
Initial field 43mT
Bias +35 V
Ion & Electron currents

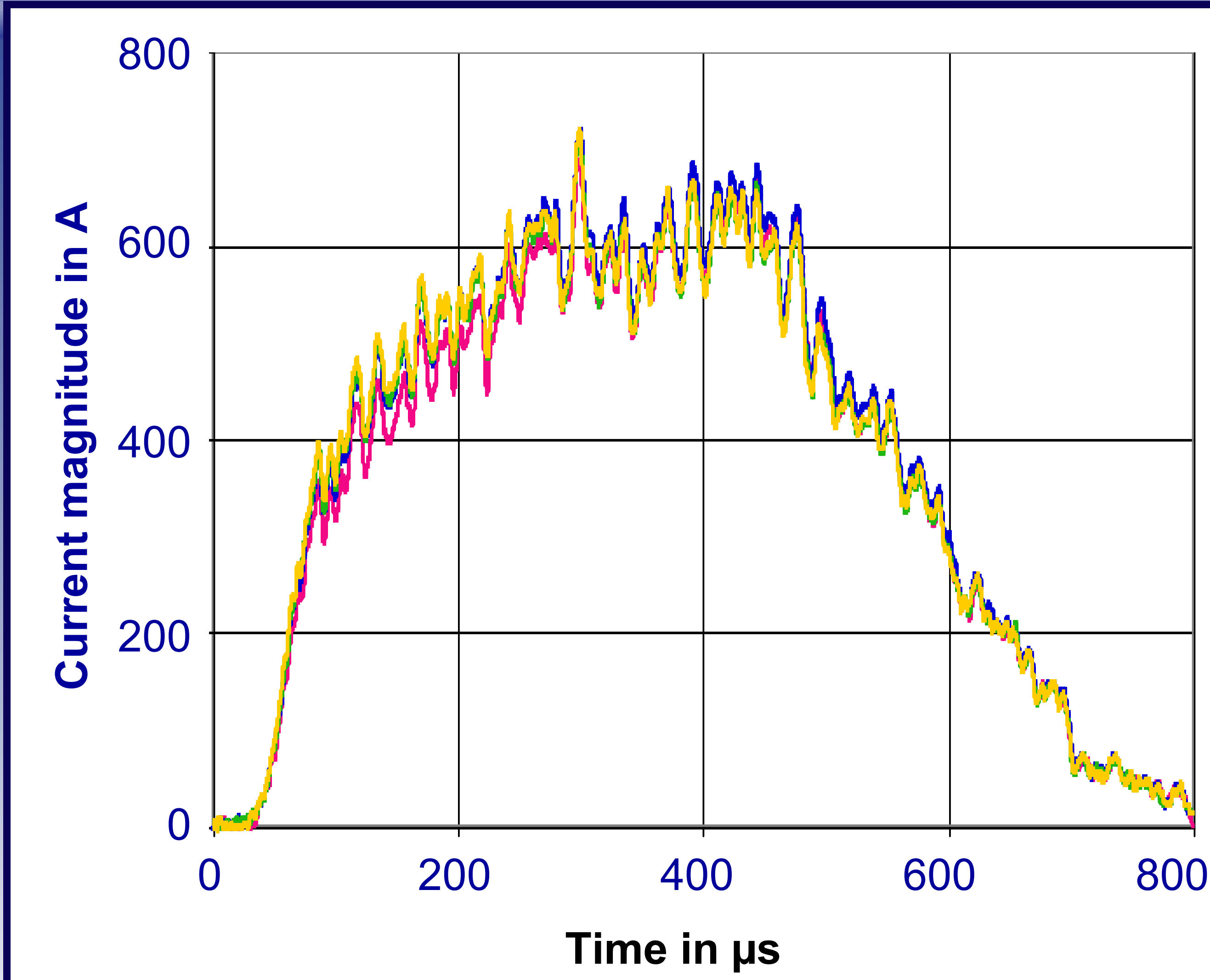


Plasma current (I_p) along filter duct- four Rogowskis

50 mm diam.
Ti cathode

177 mm diam.
circular Al
substrate biased
at +90 V

Filter duct
Initial field 43mT
Bias: +35 V



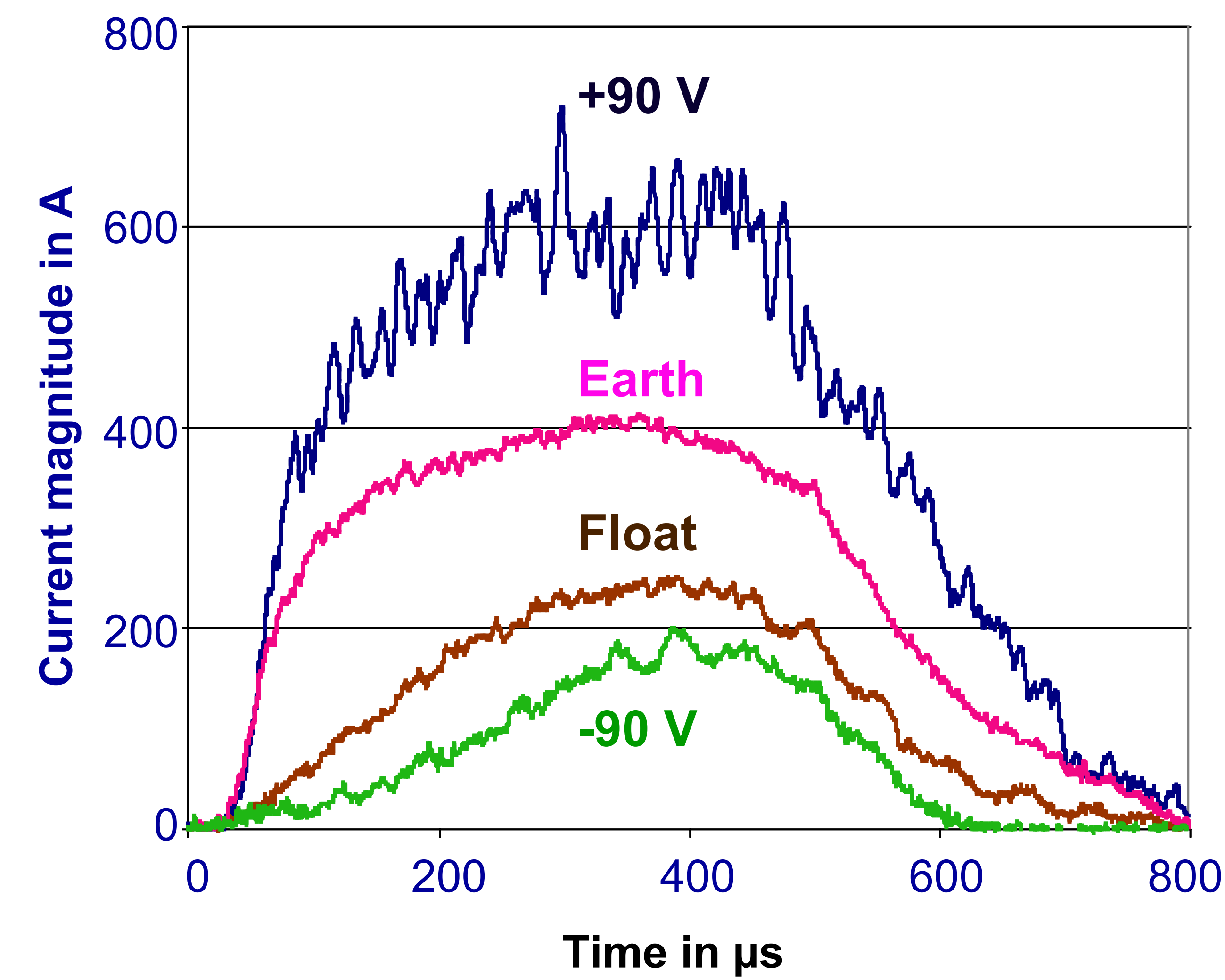
Substrate bias affects plasma current (I_p) in exit Rog

50 mm diam.
Ti cathode

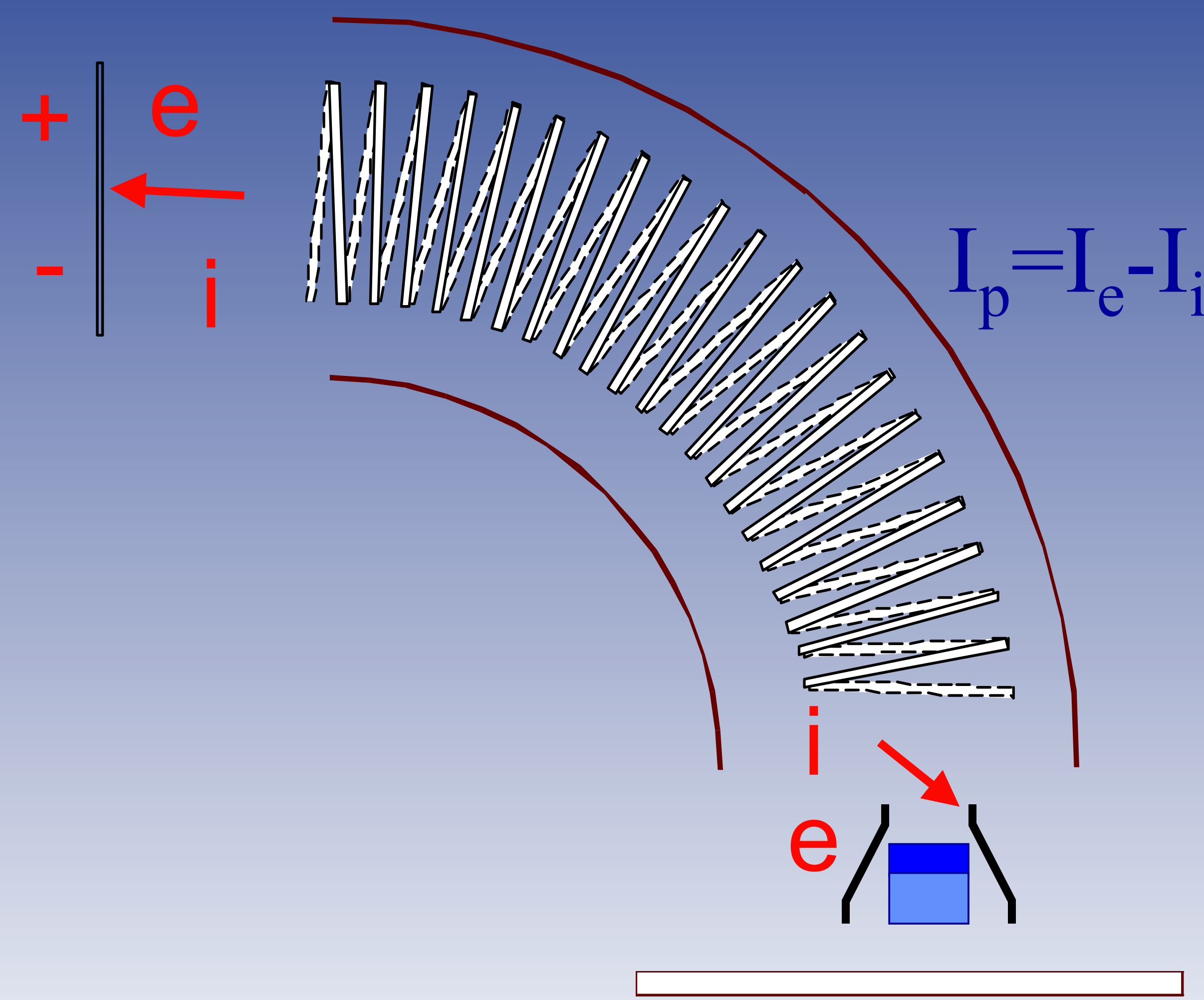
177 mm diam.
circular Al
substrate
biases:

+90 V, Earth,
Float, -90 V

Filter duct
Initial field 43mT
Bias: +35 V



Outline



Conclusions

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- Equivalence of the voltage and pulse frequency for achieving stress relief $\Rightarrow$ substitution of low bias with higher rep rates for high bias with low rep rates
  - 20 kV for 20 μs @ 200 Hz = 4 kV for 20 μs @ 1000 Hz
- Minimising the voltage requirements for feed-throughs and the potential for arcing (breakdown) on the substrates is useful for the coating of objects with complex shapes and sharp edges
- Superior performance can be achieved by nanostructured coatings such as nanoscale multilayers
- High current dual source pulsed arc system constructed
- High current fast moving spots reduce macroparticle emission
- Open filter to efficiently remove residual macroparticles
- Centre trigger ensures deposition rate stability over time

Acknowledgements

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Remaining Issues & Further Work

- Achieved deposition rates of around 0.25 nm per pulse = few tens of pulses per layer for nanolayered materials

- Pulses must be repeatable in composition and amount of material ejected (type 2 spots must be ensured)
  - cathode must always be properly conditioned
  - adsorption of gases between pulses must be controlled
  - linked to pressure when using background gas

Centre trigger for uniform erosion

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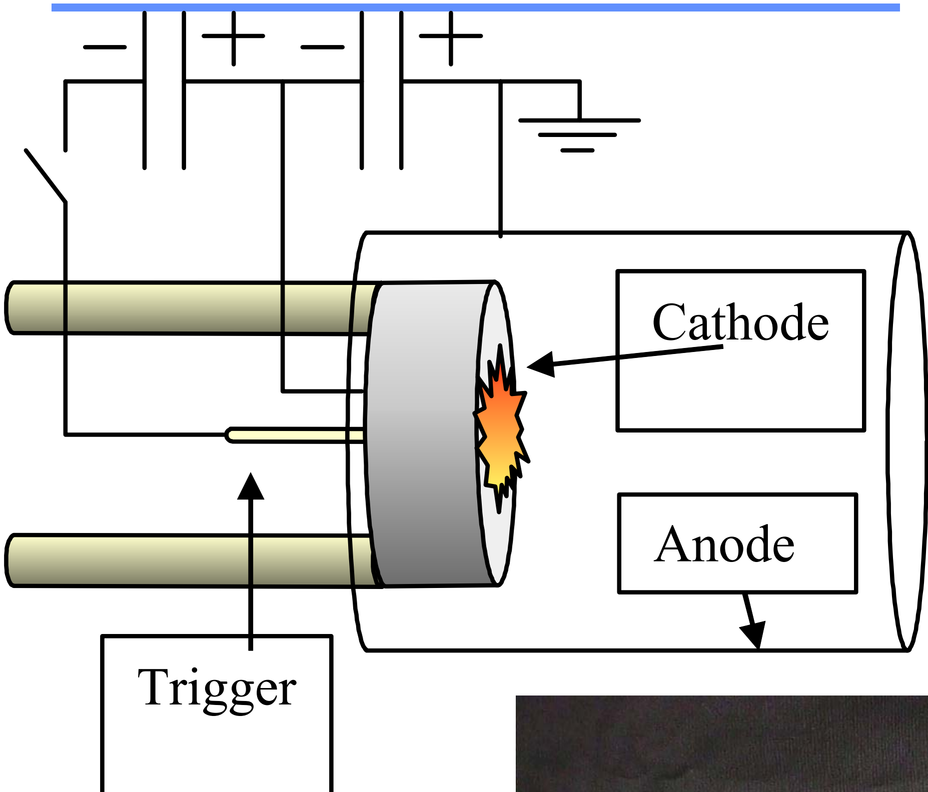

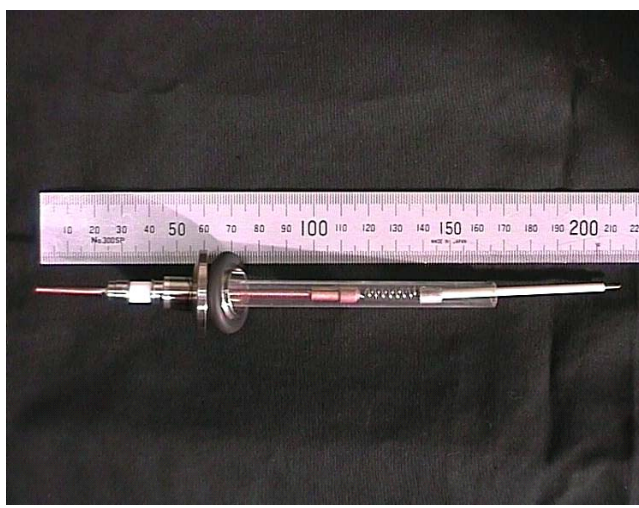

The key to a time stable deposition rate

Spot Types

- Contamination of cathode surface leads to variation in spot parameters.
- Type I spots: short lifetime, high velocity and small current per spot. Associated with surface contaminants
- Type II spots: longer lifetime, lower velocity and large current per spot. Associated with clean cathode surface.

Type 1 and 2 spot behaviours

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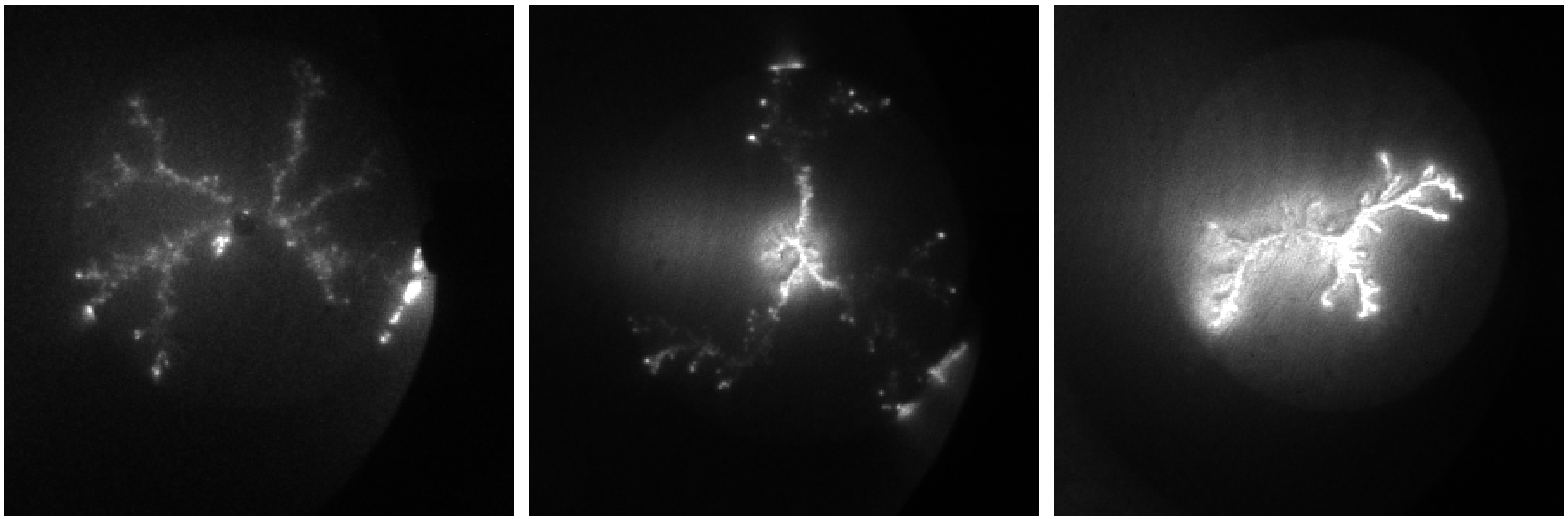
- In the deposition of multilayered films it will be important to ensure that only type 2 spots contribute to the plasma reaching the substrate

pulse # increasing



(a) type 1 arc - exp 100μs (b) type 1 and 2 arcs exp - 500 μs (c) type 2 arc - exp 2000μs
Al cathode. The power supply was the simple 12mF capacitor bank charged to 110V.

Notes: Anode spot in (a); Type 2 (brighter, slower moving) occasionally nucleate due to uneven cathode erosion

Wafer curvature with profilometer & Stoney's Equation

$$\sigma = \frac{1}{6} \bullet \left[\frac{1}{R_f} - \frac{1}{R_s} \right] \bullet \frac{E}{(1-\nu)} \bullet \frac{t_s^2}{t_f}$$

Where:

σ = stress in film after deposition

R_f = substrate radius of curvature post deposition

R_s = substrate radius of curvature pre deposition

E = Young's modulus

ν = Poisson's ratio

t_s = substrate thickness

t_f = film thickness

Proc. R. Soc., 1909

* 300 micron Si wafer and film grown to ~10 microns

Prototype Power Supply Designs

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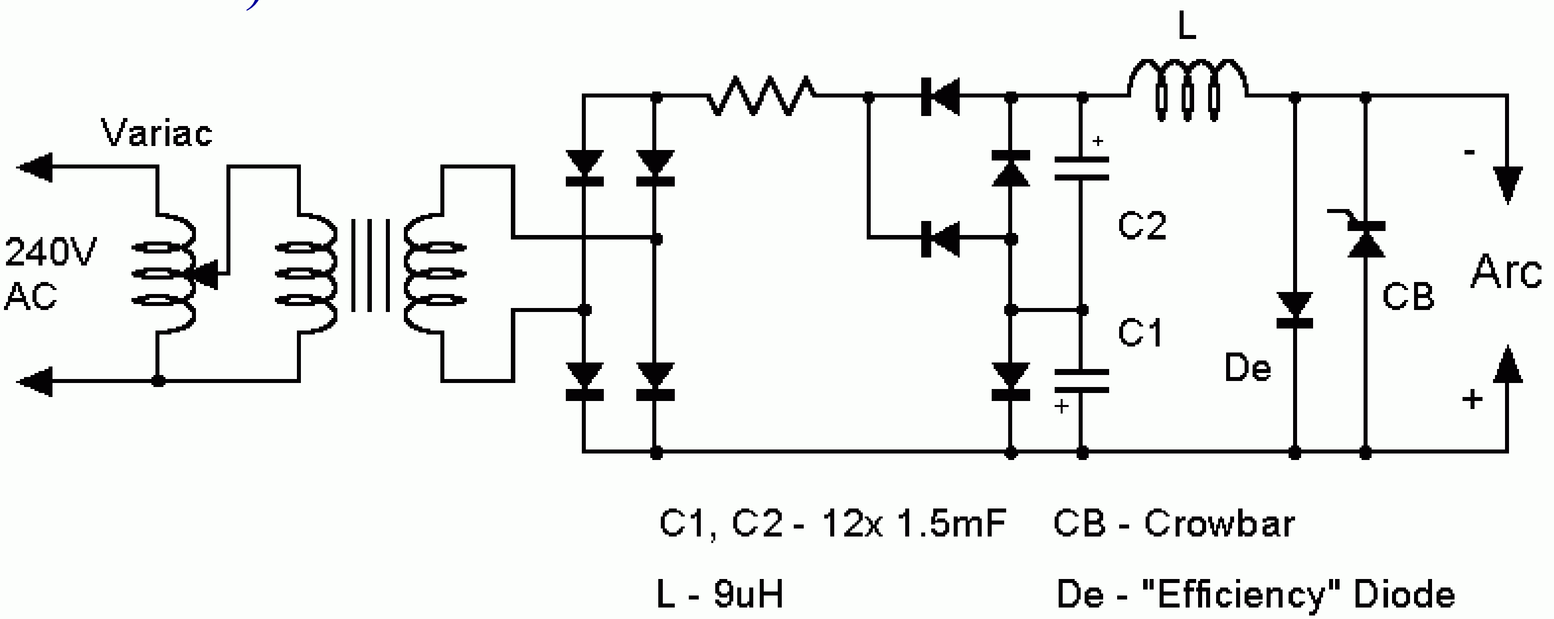
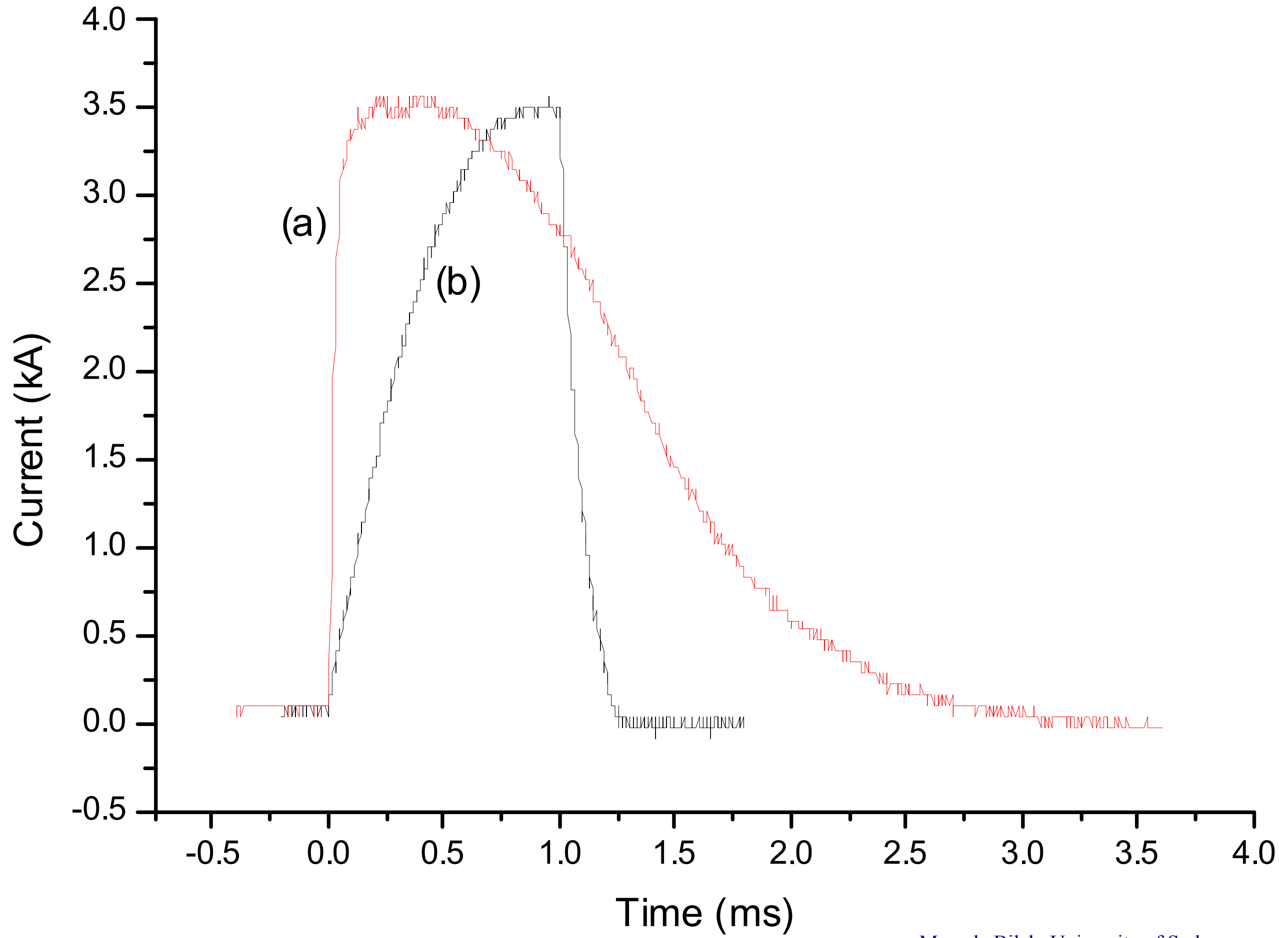
- First try (a) simple capacitor bank of between 6 and 12 mF, charged to between 100 and 400V
- Later (b) based on oscillating LC circuit used by Siemroth et al, adapted for electrolytic capacitors (for pulse shape control)



Current Profiles

- (a) simple 12mF, 400V capacitor bank
- (b) 300V LC pulse circuit, crowbarred at 1ms

Rising current pulse profile has much better cathode erosion characteristic

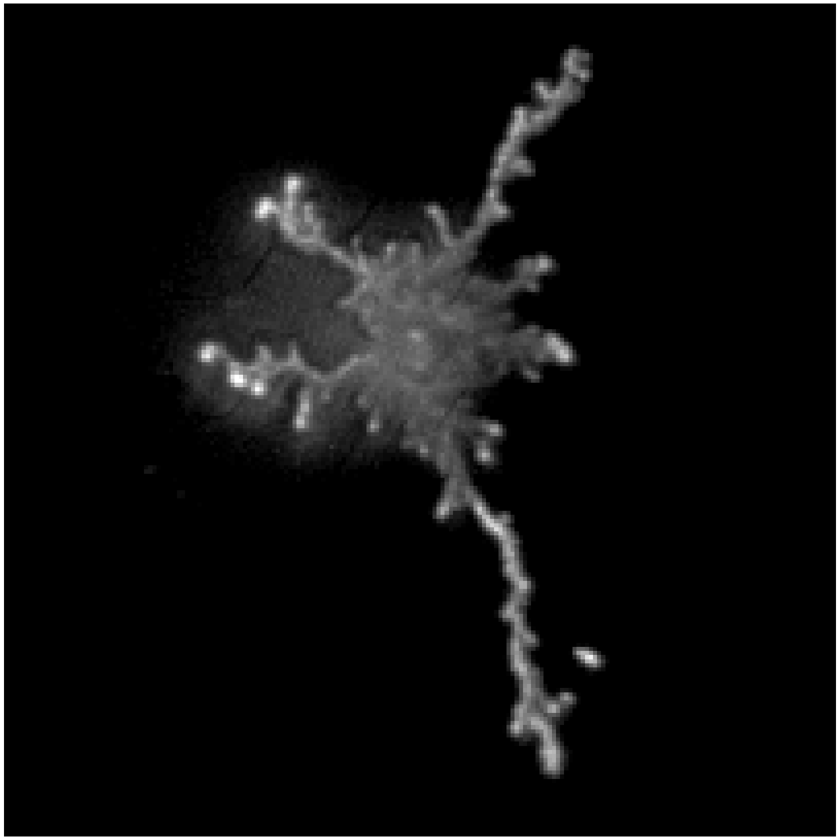


Design Issues

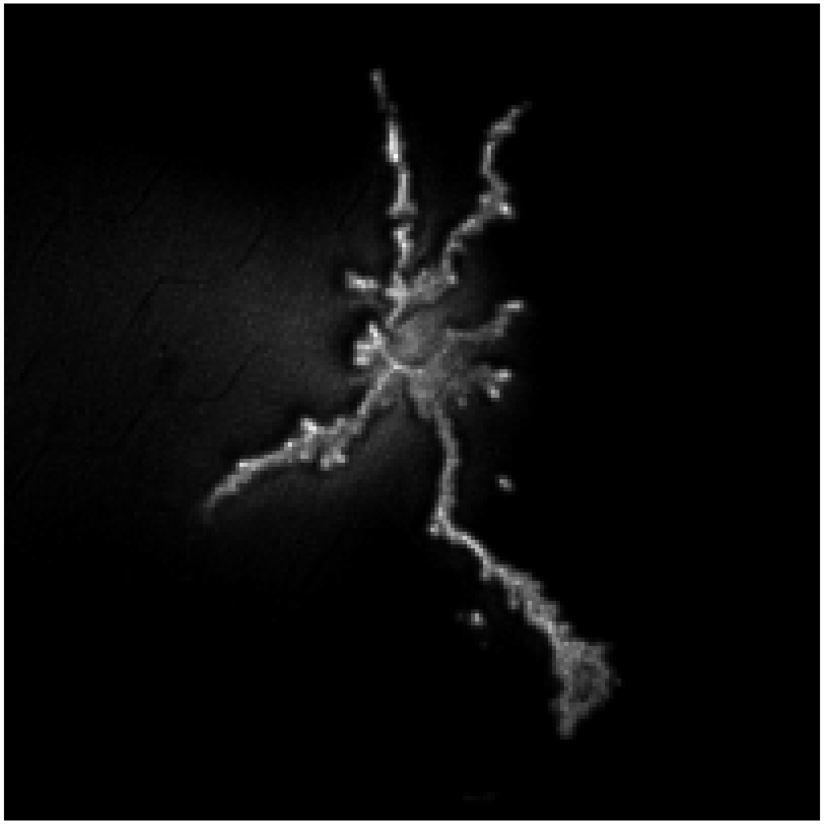
- Peak ion current – balance good magnetic confinement and fewer macroparticles with too much force on filter coil and losses scaling as I^2 (we chose 1-5 kA operation – CSD??)
- Pulse length is dictated by the radius of the cathode and the velocity of the cathode spots (metals 0.5 ms @ 3.5 kA peak I and reduce size of graphite target as would need 2 ms)
- Limits on pulse frequency set by tolerance of circuit components to heating. Designed for 10 Hz maximum pulsing frequency but may not be possible to achieve at high end of current range
- With a given L and C (resonant frequency) we adjust the charge voltage to vary peak I and crowbar time to vary pulse length
- This prototype dissipated only 400 W when running at maximum capacity of the wiring

Optimising for Cathode Erosion

- High speed CCD camera focused on carbon cathode
- Both charged to 300V, (b) crowbarred at 1ms



Current profile (a) – 2 ms exp.



Current profile (b) – 1 ms exp.

* complicated interplay between the current and the inter-spot distance

Faster type 1 to 2 transition with LC Resonator Supply

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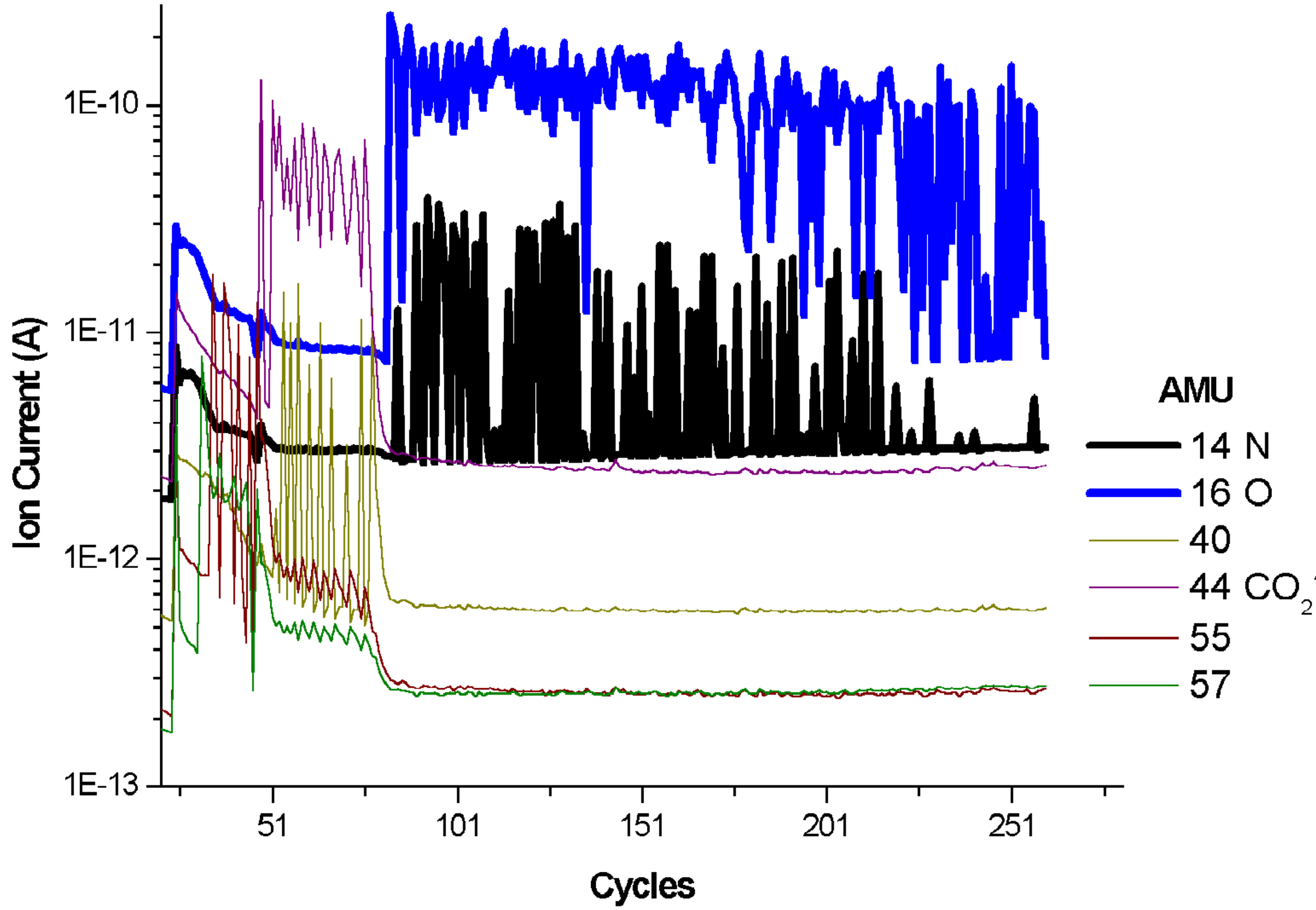
- occurrs within a few arc pulses
- ~ 0.5 Hz



Conclusions

- Design of dual source pulsed filtered cathodic arc for multilayer coatings constructed – further optimisation needed
- Important characteristics and operating parameters are:
  - time dependence of the arc current pulse is important in giving even erosion & sharp type 1 –2 transition
  - controlled rates of nonreactive deposition in vacuum due to the reproducible arc current pulse profile
  - controlled rates of deposition and controlled stoichiometry should also be achievable during reactive deposition processes when a background gas is used – need to balance pressure and rep. rate
- Effect of arc current and background gas pressure on the charge state distribution (CSD) of the plasma ions should be monitored to understand how the impact energy of ions will be affected by substrate bias