Science and Technology of Materials, Interfaces, and Processing

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40 Years of magnetron sputtering: Still an exciting field for discovery

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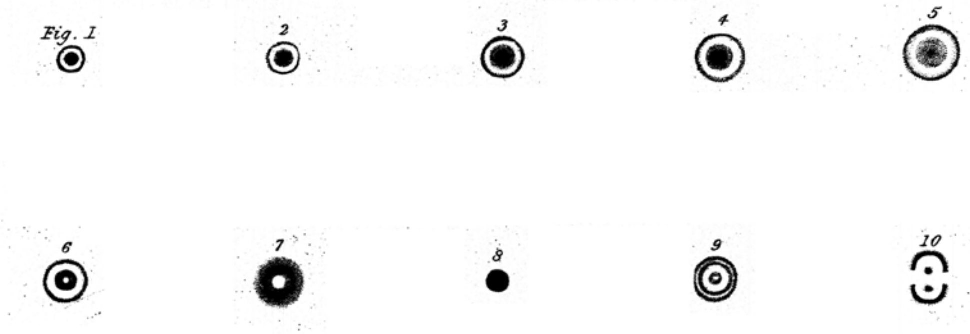
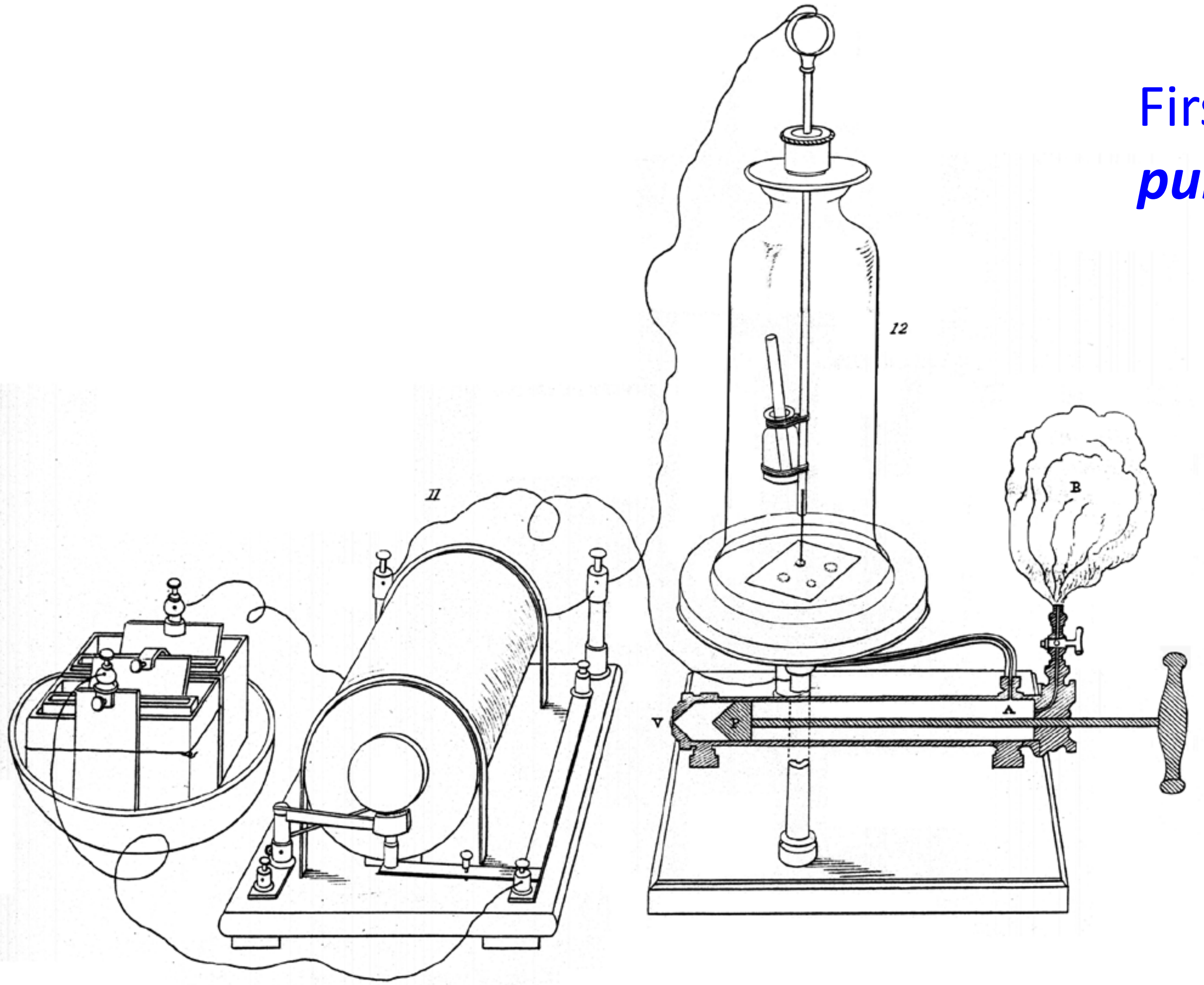
American Institute of Physics Publishing

Volta’s birthday, 2015-02-18

Grove 1852: Sputtering



First sputtering was ***pulsed*** sputtering!



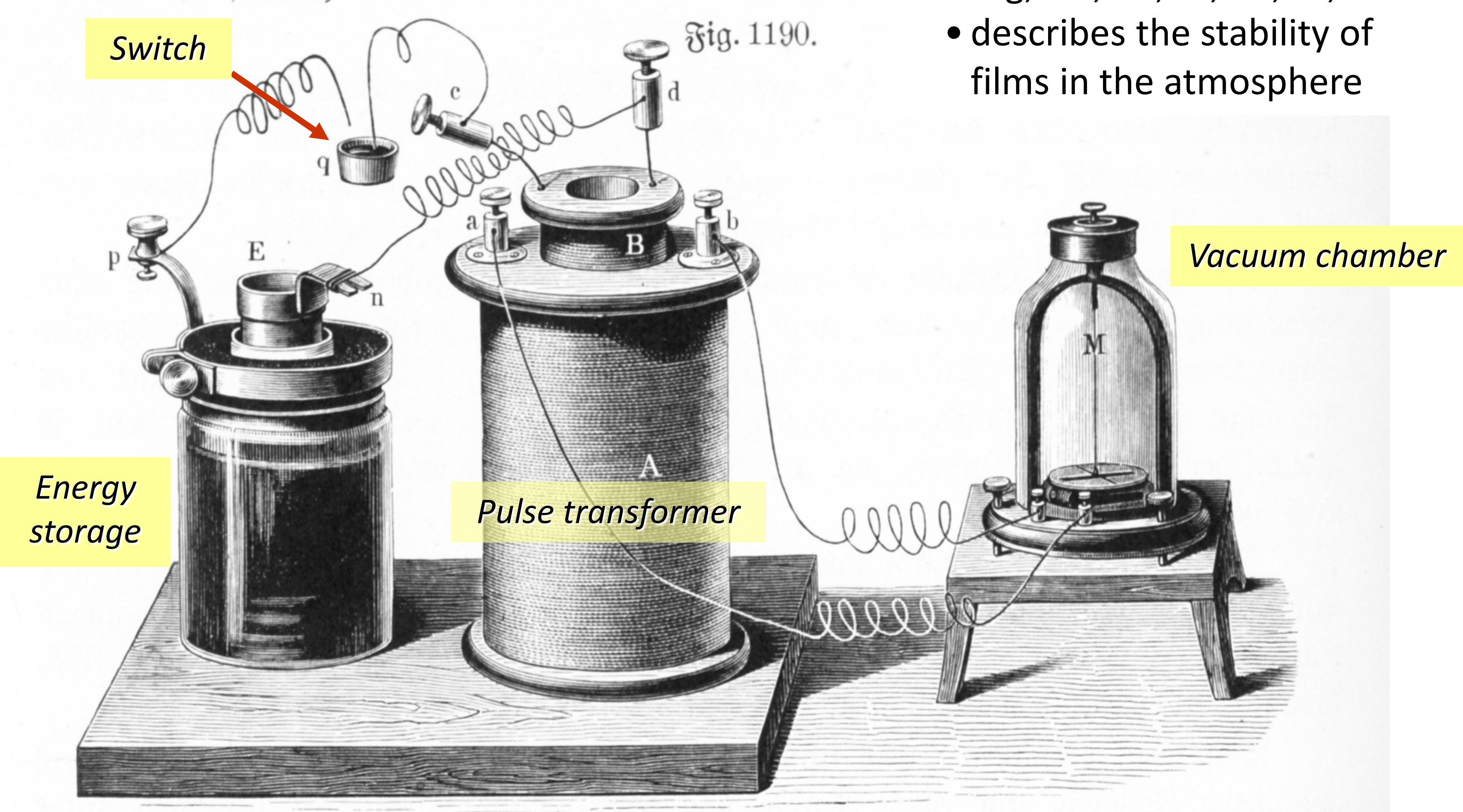
W. R. Grove, Phil. Mag. (1852) 498

Pulsed Diode Sputtering (at relatively high pressure)

Many elements of modern pulsed processing

Arthur Wright, 1877 deposited numerous films:

- Pt, Au, Co, Bi, Pd, Pb, Al, Sn, Mg, Zn , Cd, Ni, Co, Te, Fe
- describes the stability of films in the atmosphere



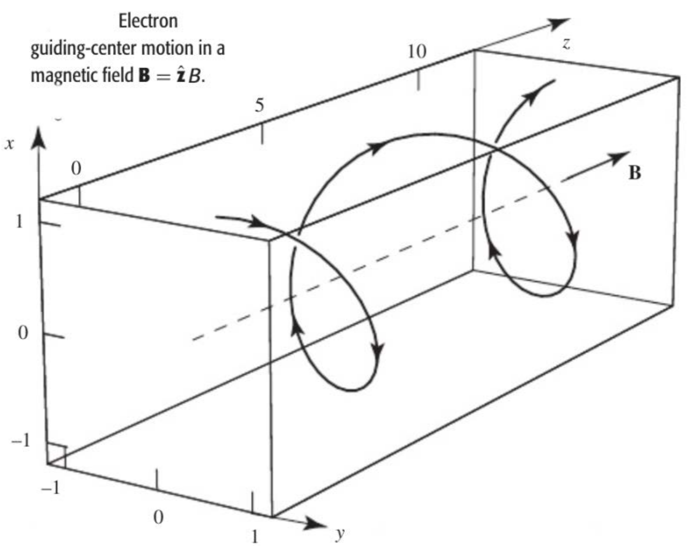
A.W. Wright, American J. Sci. - Third Series, vol. XIII, no. 78 (1877) 49

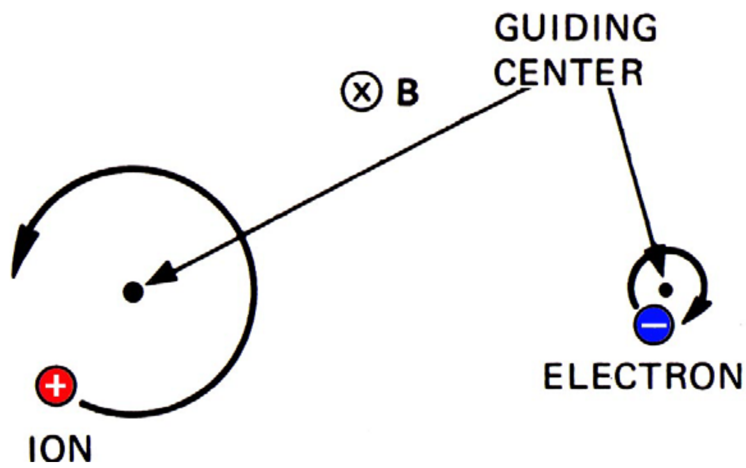
Single Particle Motion

- Gyration of charged particles in a magnetic field
  - Larmor radius
  - Cyclotron frequency
  - right hand rule for electrons

$$\boxed{r_L = v_\perp / \omega_c}$$

$$\boxed{\omega_c = |Q| eB / m}$$





Joseph Larmor
(1857-1942)

M. A. Lieberman and A. J. Lichtenberg, Principles of Plasma Discharges and Materials Processing, 2nd ed., Wiley, Hoboken, NJ, 2005

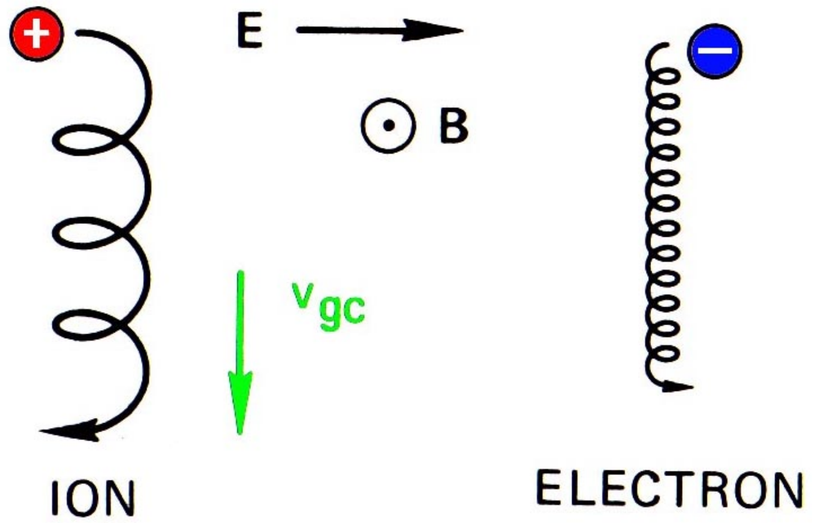
Single Particle Motion

- Equation of motion in a magnetic and electric field

$$m\frac{d\mathbf{v}}{dt} = Qe\left(\mathbf{E} + \mathbf{v}\times\mathbf{B}\right)$$

- motion is superposition of Larmor gyration and ***drift of the guiding center*** with a velocity

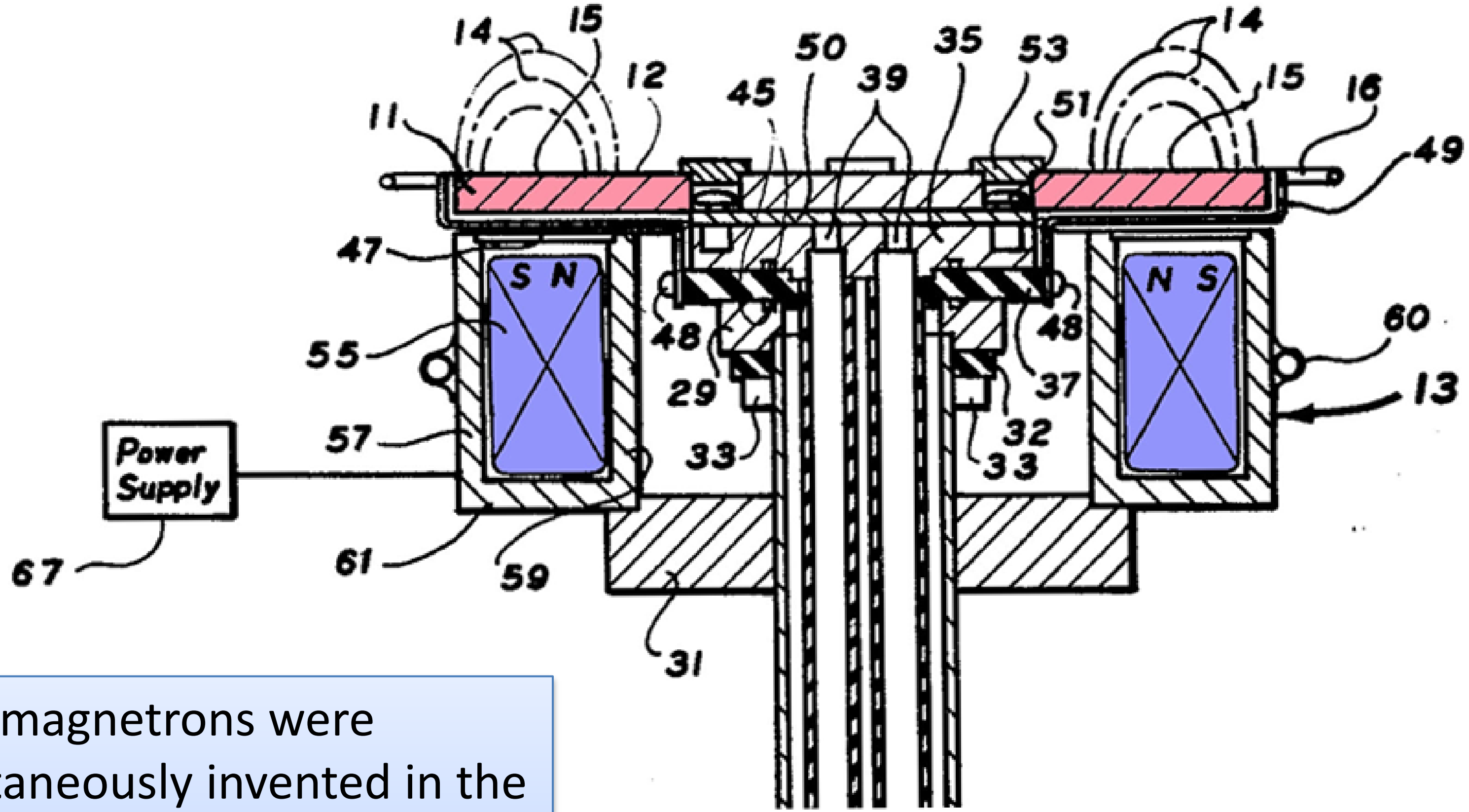
$$v_{\perp gc} = \frac{\mathbf{E}\times\mathbf{B}}{B^2} \equiv v_E$$



Notes:

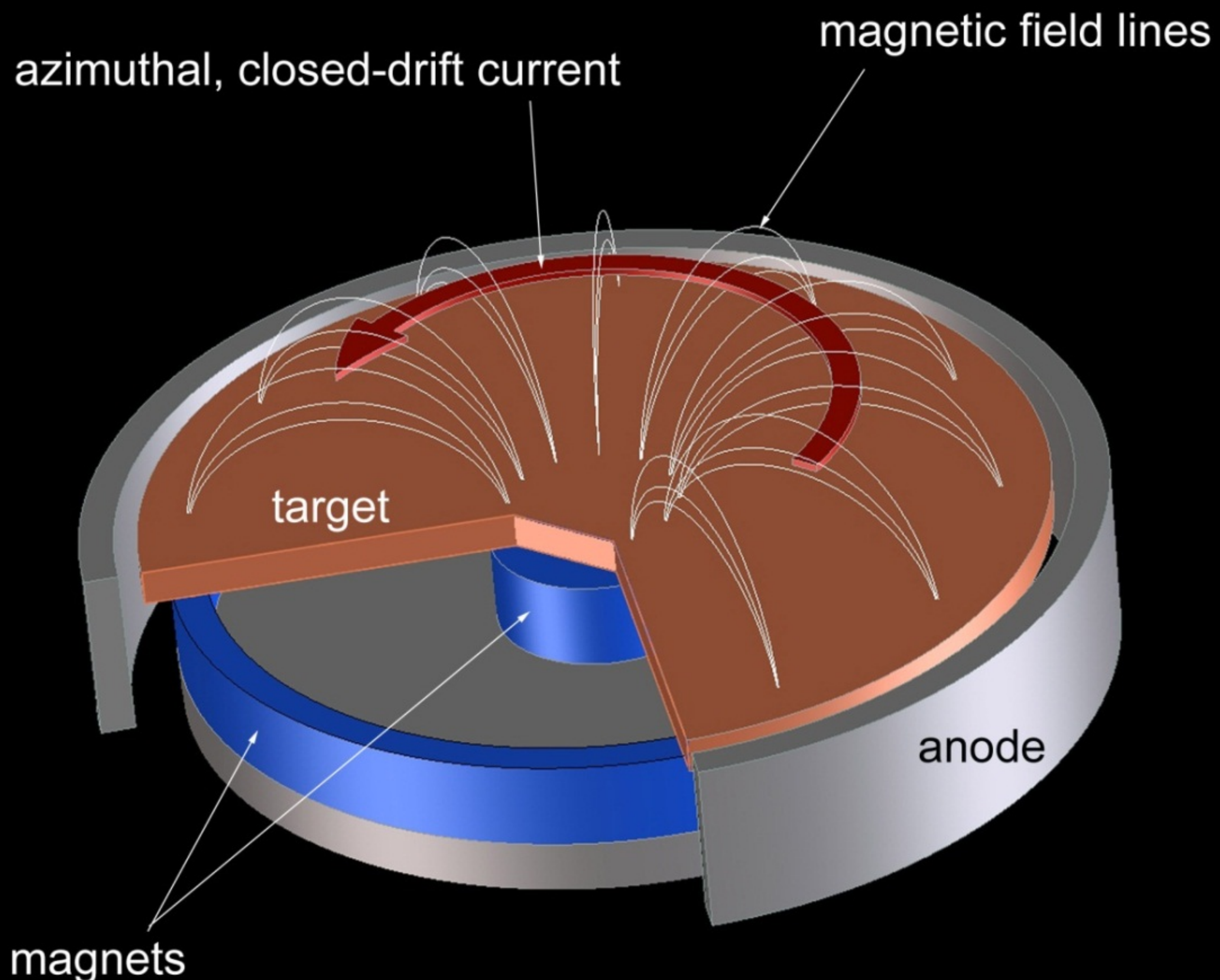
1. drift is independent of charge sign
2. drift is perpendicular to both **B** and **E** vectors
3. in laboratory plasmas, only electrons are magnetized

Early 1970s: Planar Magnetron



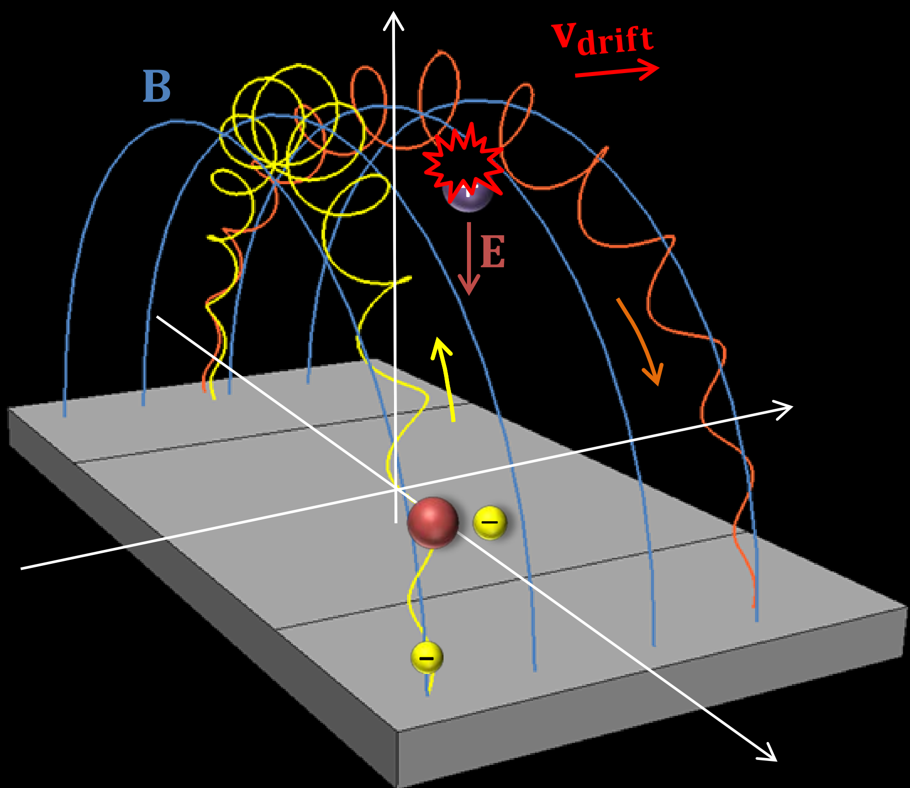
various forms of magnetrons were practically simultaneously invented in the early 1970:
Clarke, Mullaly, Gorbani, Chapin,…
see for example D.M. Mattox, The History of Vacuum Coating Technology, Society of Vacuum Coaters, Albuquerque, 2002.

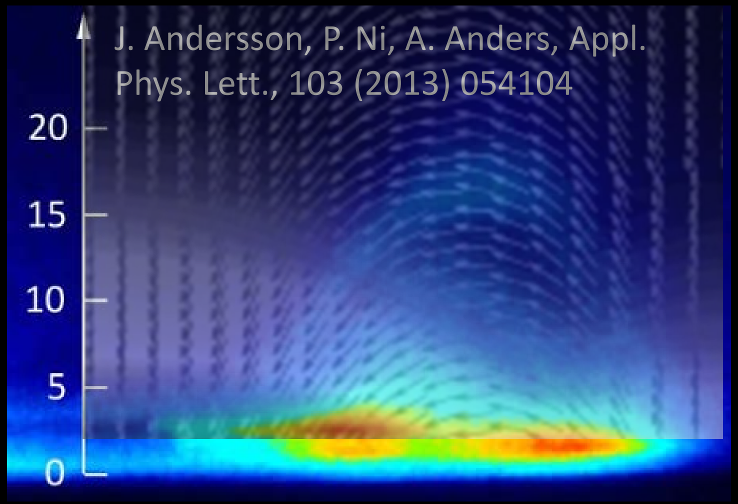
J. S. Chapin, "Sputtering process and apparatus," US 4,166,018, (filed 1974).



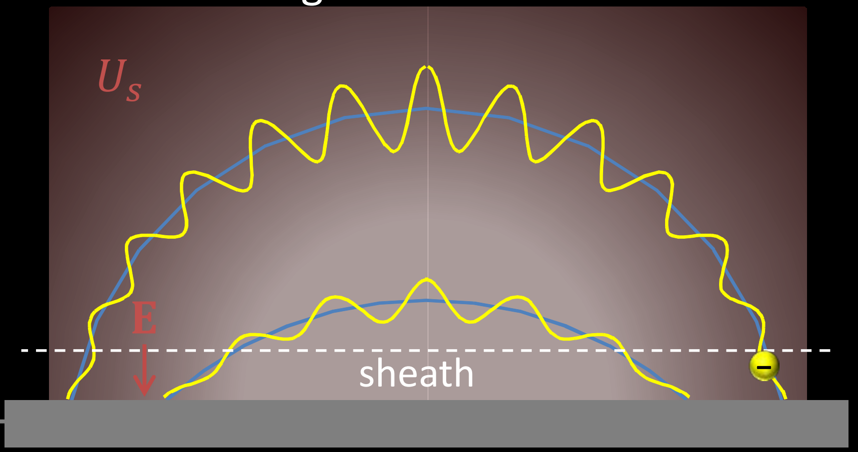
A. Anders, Surf. Coat. Technol. **205** (2011) S1.

Motion of electrons in magnetic trap of magnetron





"Bouncing" motion of electrons



- Formation of secondary electrons in the sputtering process and energization of electrons in the sheath and pre-sheath provides necessary energy to sustain the magnetron discharge

Slide design by Matjaz Panjan.

Magnetrons

Gencoa.com

High current is not always HIPIMS

- Magnetrons serving alternatingly as cathode and anode
- Medium frequency sputtering
- high power but not high power density, hence it is not HIPIMS

Photo courtesy of VON ARDENNE

Large Area Coatings

http://www.vonardenne.biz/

Unbalanced Magnetron:

A first step to using the plasma of the magnetron to assist film growth

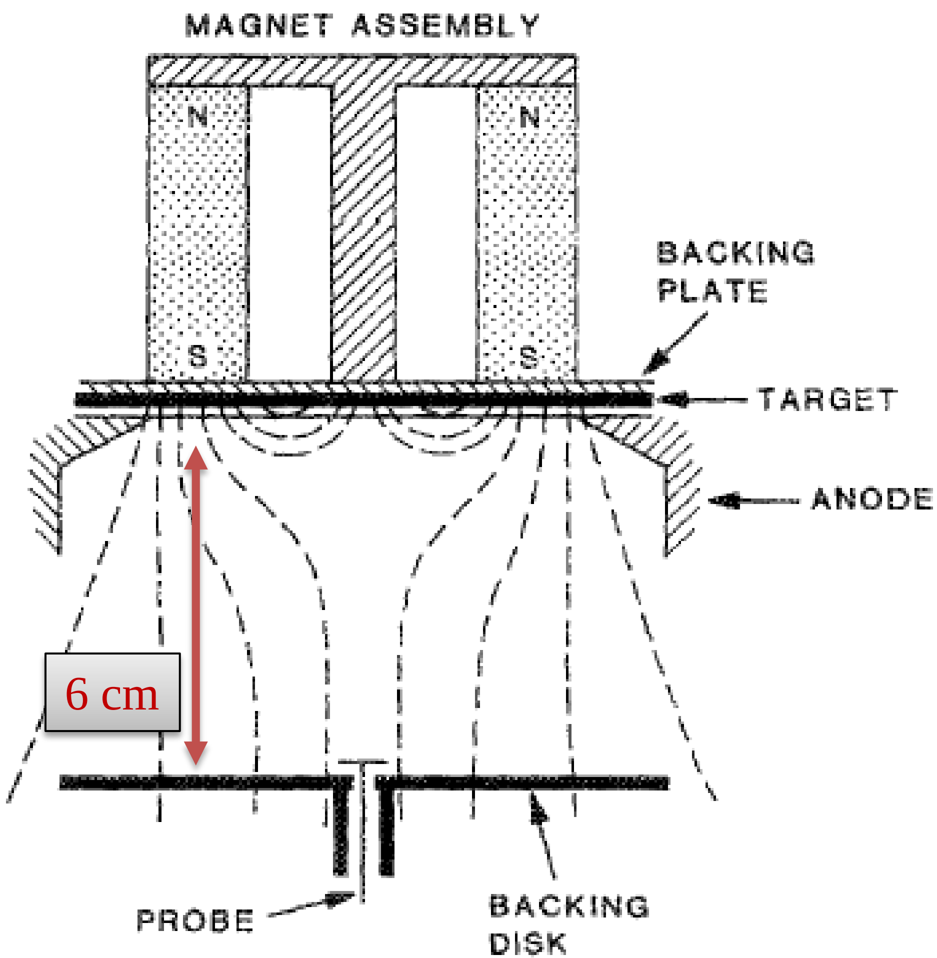


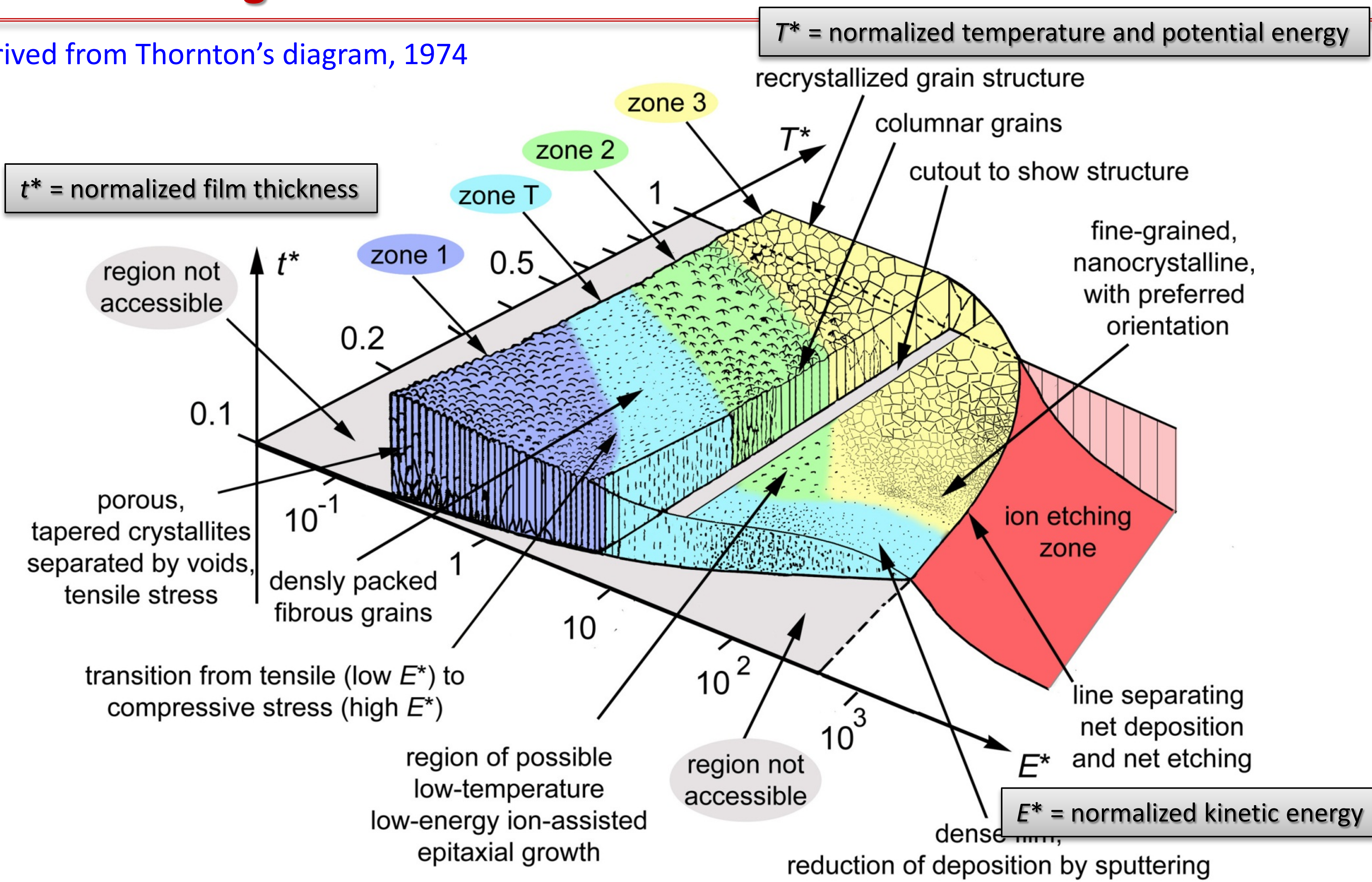
FIG. 1. Magnetron and probe assembly are shown schematically. For the measurements reported here the target to probe distance was maintained at 60 mm.

- Unbalanced magnetic field allows electrons and ions to escape from target region, providing a means of ion assistance to film growth
- $n_e \sim 10^{12}$ cm^{-3}, for up to a distance of 10 cm.

B. Windows and N.Savvides, J. Vac. Sci. Technol. A **4**, 453 (1986)

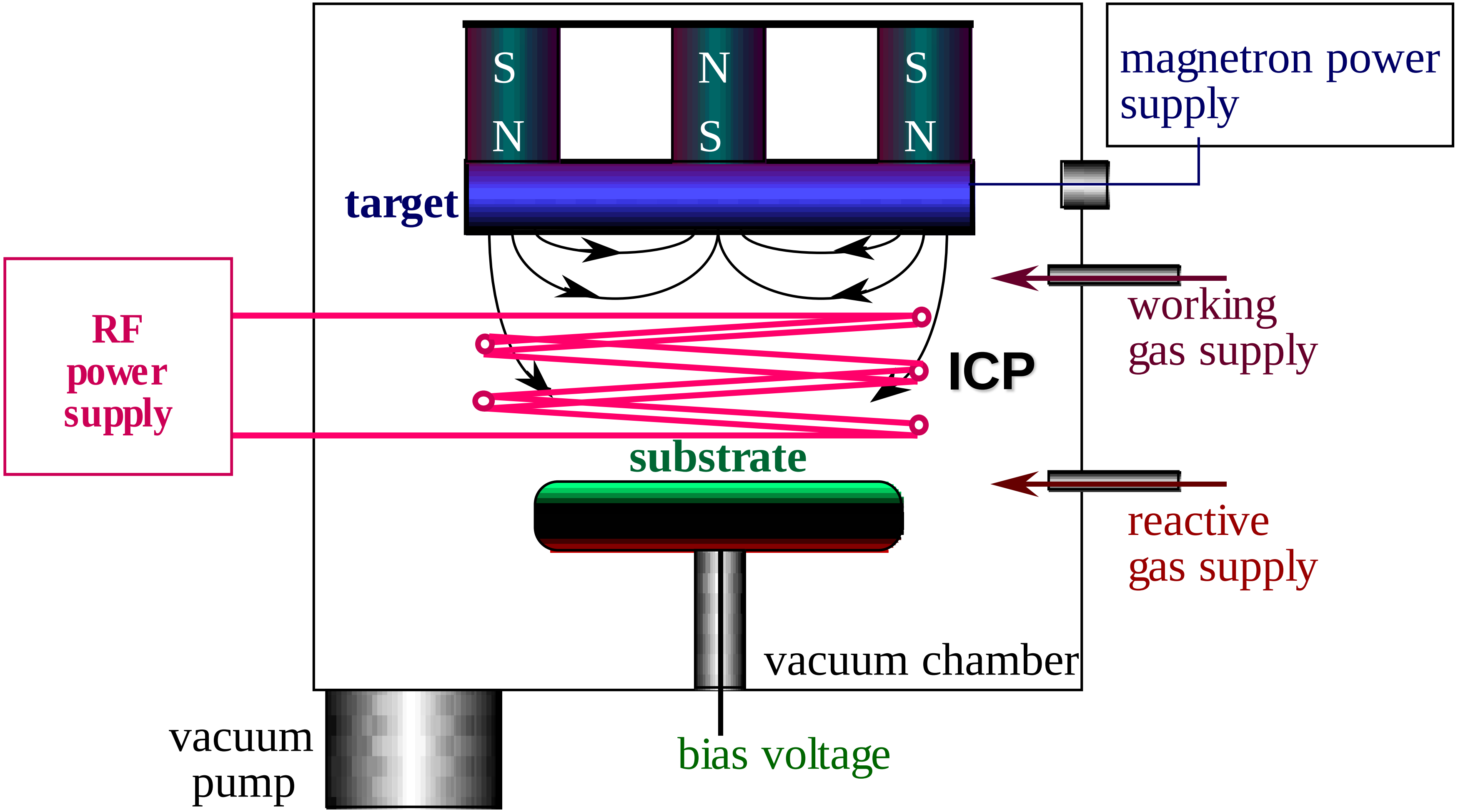
Motivation Illustrated by a Generalized Structure Zone Diagram including the Effects of Plasma Assistance to Film Growth

derived from Thornton's diagram, 1974



A. Anders, Thin Solid Films **518** (2010) 4087

1990s: i-PVD
Magnetron Discharge with Ionization



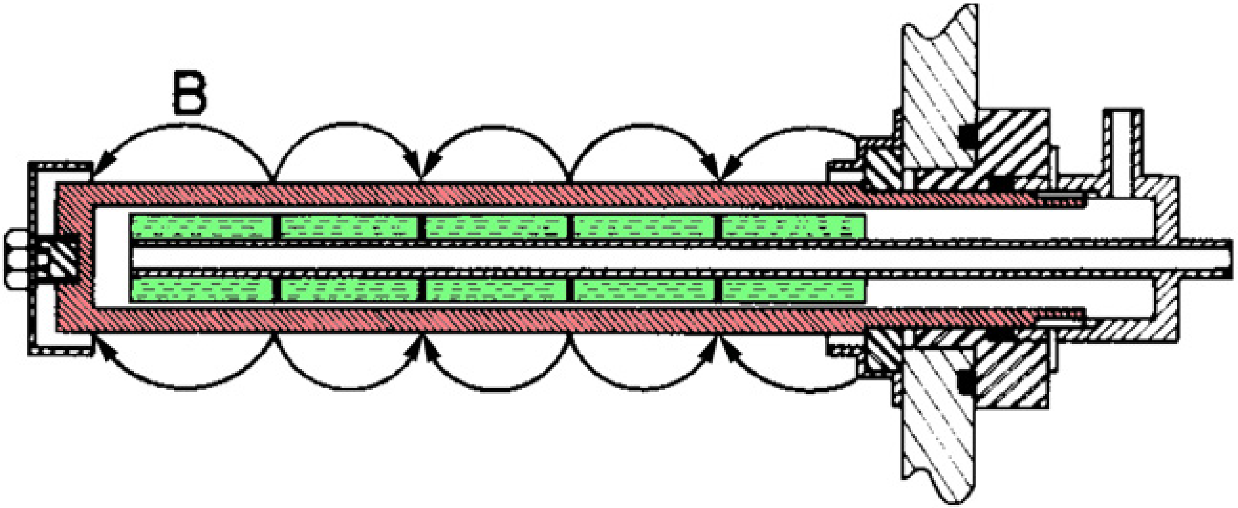
S. M. Rossnagel and J. Hopwood, Appl. Phys. Lett. 63 (1993) 3285-3287

Ionized Physical Vapor Deposition; *Vol.*, edited by J. A. Hopwood (Academic Press, San Diego, CA, 2000).

1977: Early Report on Self-Sputtering

- Self-sputtering = sputtering of a target by ions of the target material

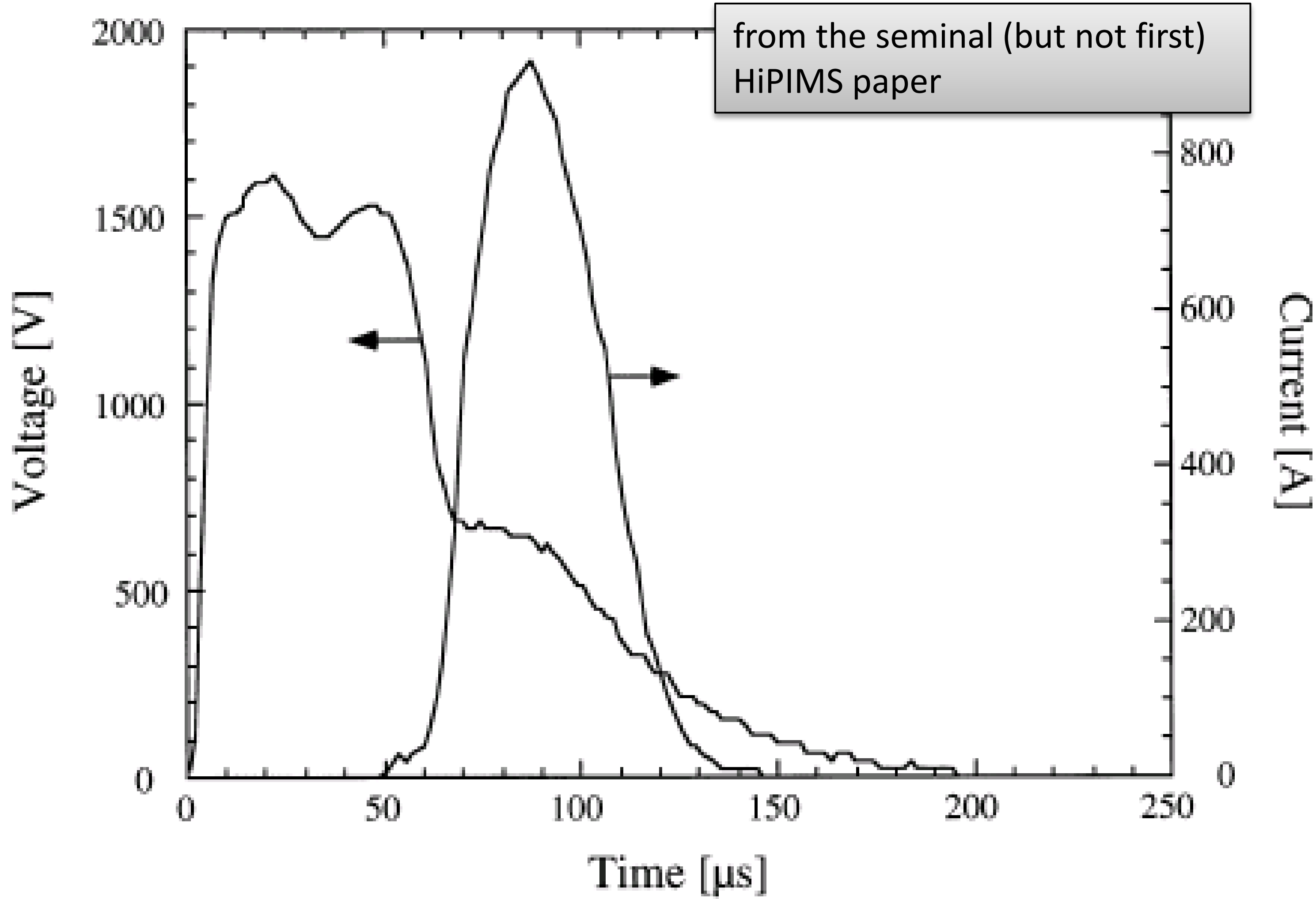
cm^2. It is concluded, from comparison of the experimental reslts of power efficiency with calculated values from sputtering yield data, that a significant fraction of the sputtered atoms must be ionized upon passing through the dense plasma region and that these ions are accelerated back to the target. More than 18% of total ion current is estimated to be ionized



N. Hosokawa, T. Tsukada, T. Misumi, J. Vac. Sci. Technol. 14 (1977) 143.

Turning the Magnetron into a Plasma Source

from the seminal (but not first) HiPIMS paper

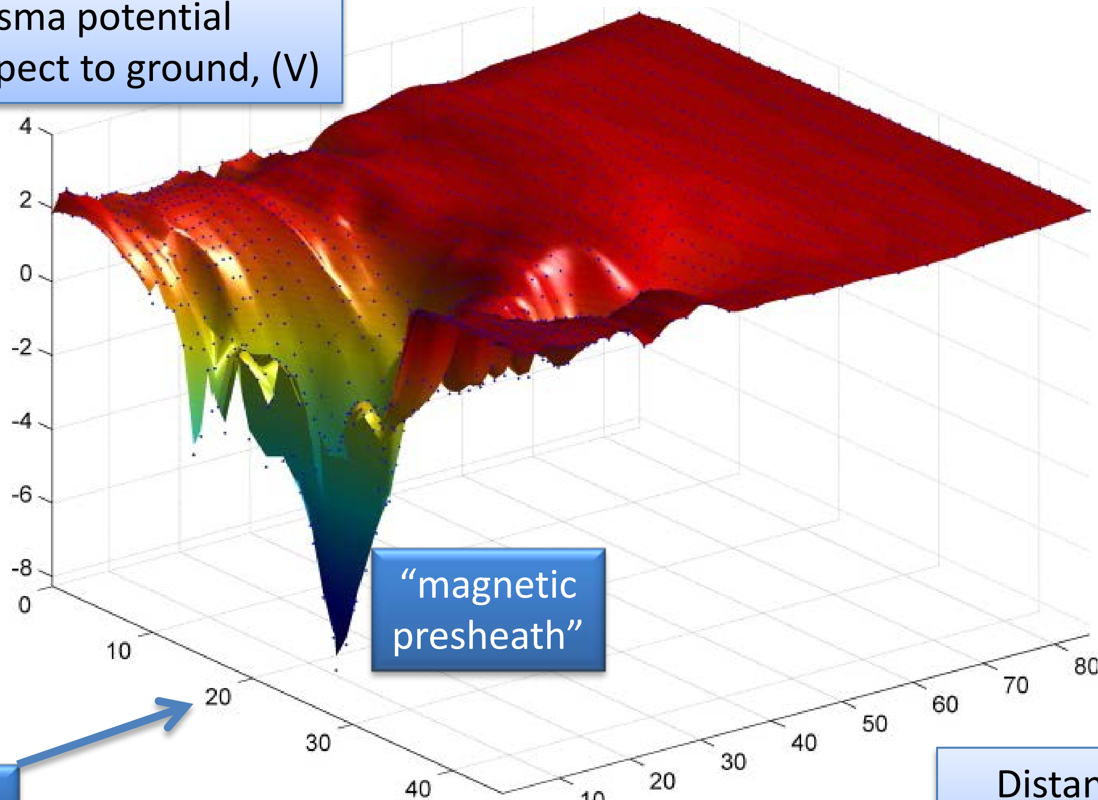


V. Kouznetsov, *et al.*, *Surf. Coat. Technol.* **122**, 290-293 (1999)

Pulse-Averaged Electric Field in Plasma with Magnetic Field

Plasma potential in front of a racetrack of a magnetron (Nb sputtered in Ar), measured with emissive probe → Average ion acceleration is mostly toward to target

Plasma potential with respect to ground, (V)



data best seen in [video clip]

"magnetic presheath"

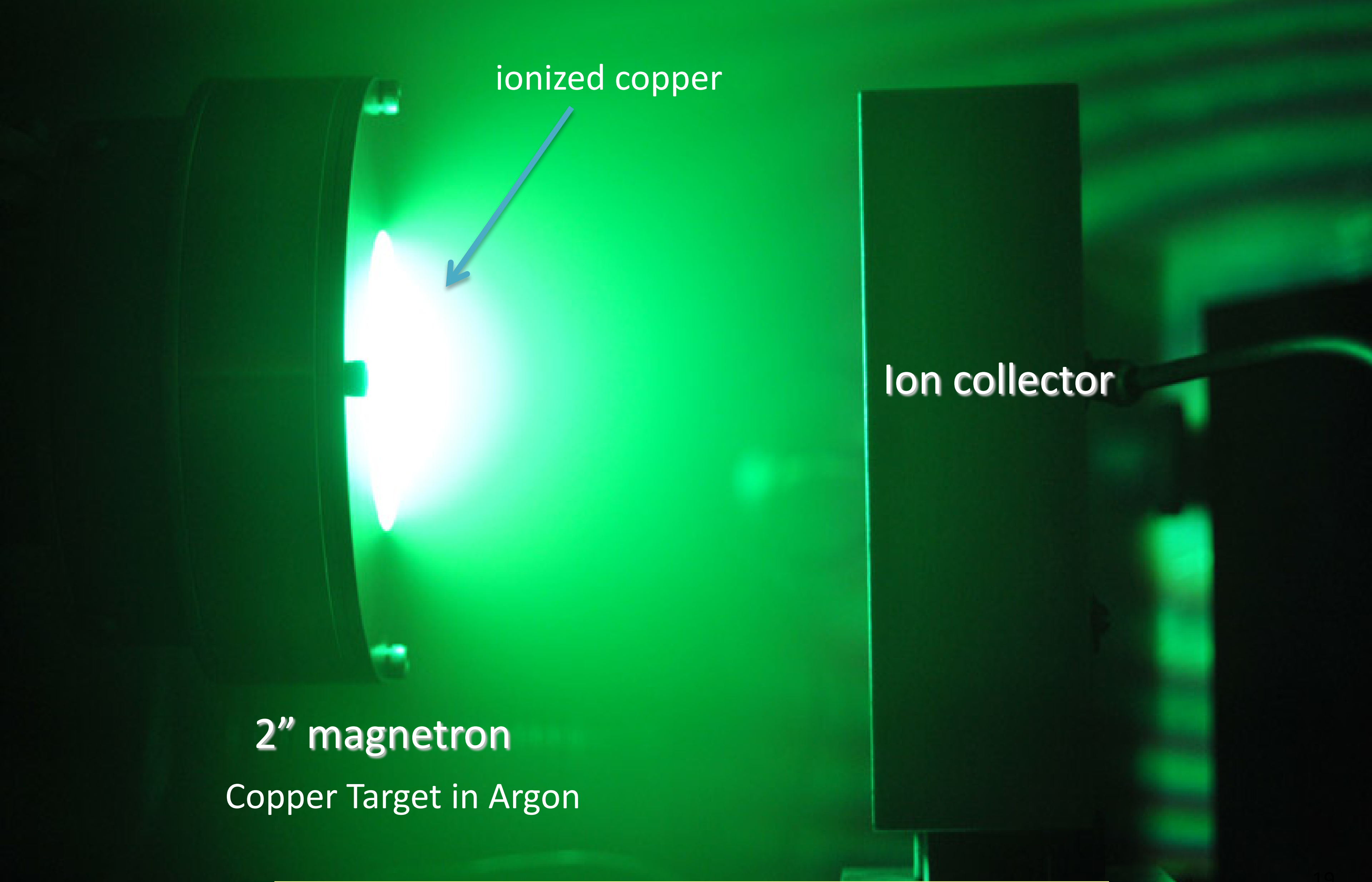
"racetrack"

Distance *r* from target center, (mm)

Distance *z* from target surface, (mm)

J. Sanders, *et al.,* Rev. Sci. Instrum. **82** (2011) 093505; A. Rauch *et al.,* J. Appl. Phys. **111** (2012) 083302.

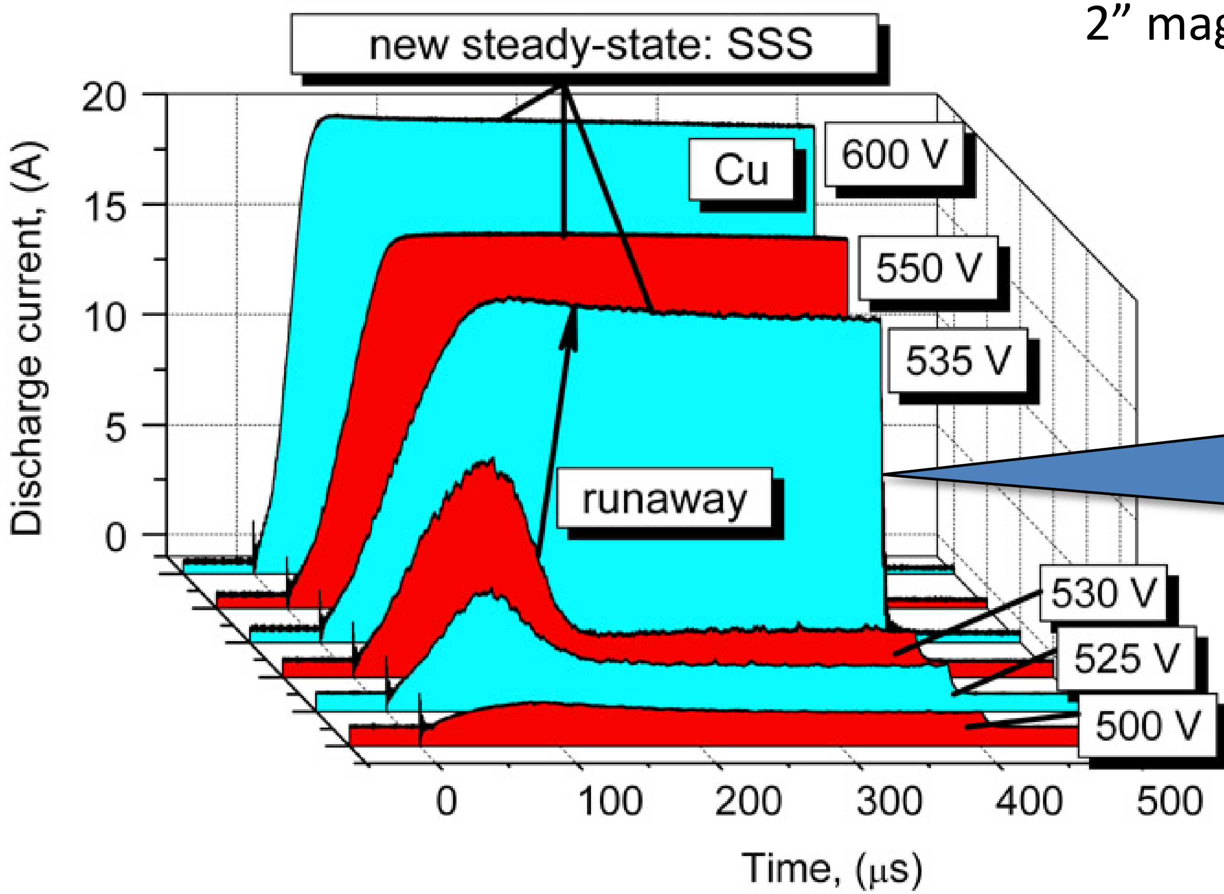
HiPIMS



J. Andersson and A. Anders, Phys. Rev. Lett. **102** (2009) 045003.

Runaway of Self-Sputtering

Copper target,
2” magnetron

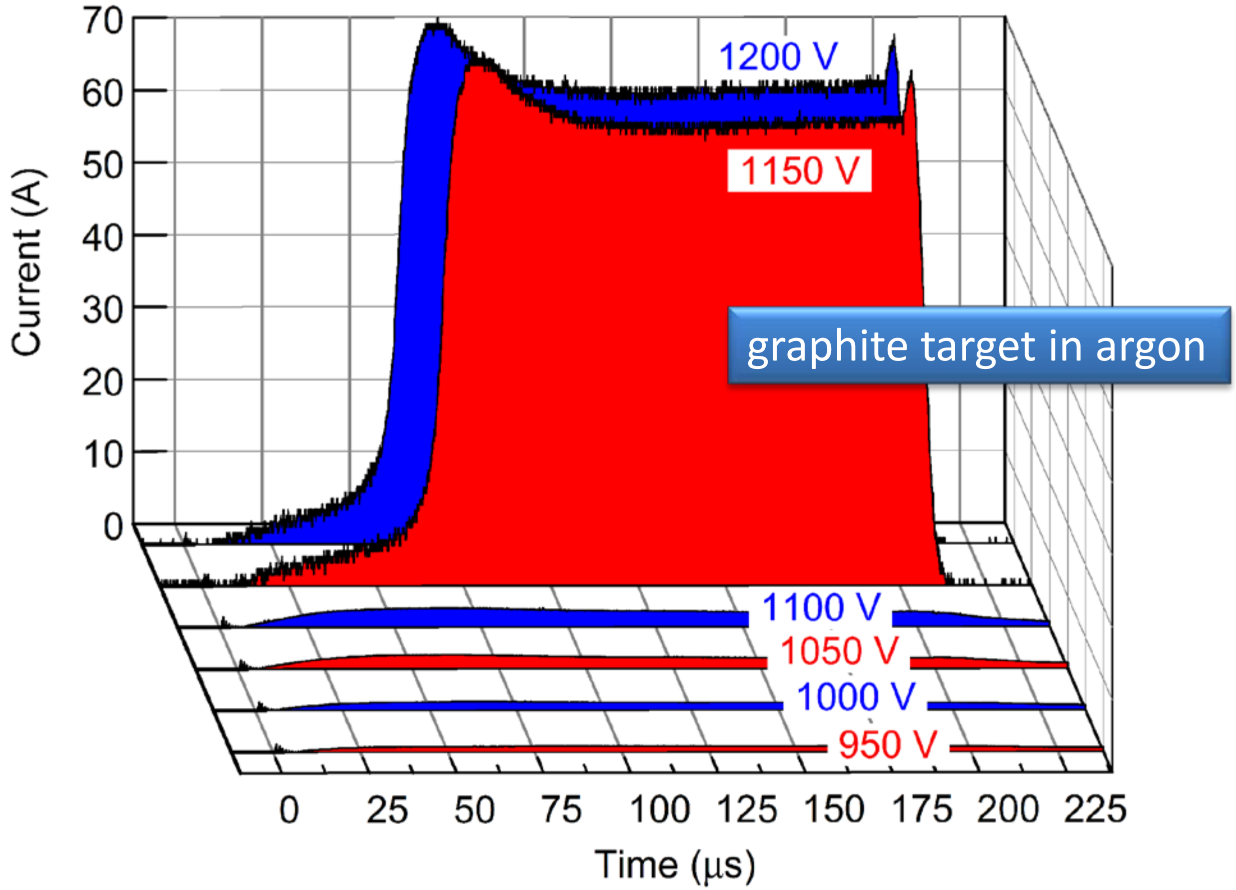


Look for this small change in voltage but huge effect in current!

A. Anders, *et al.*, J. Appl. Phys. **103** (2008) 039901

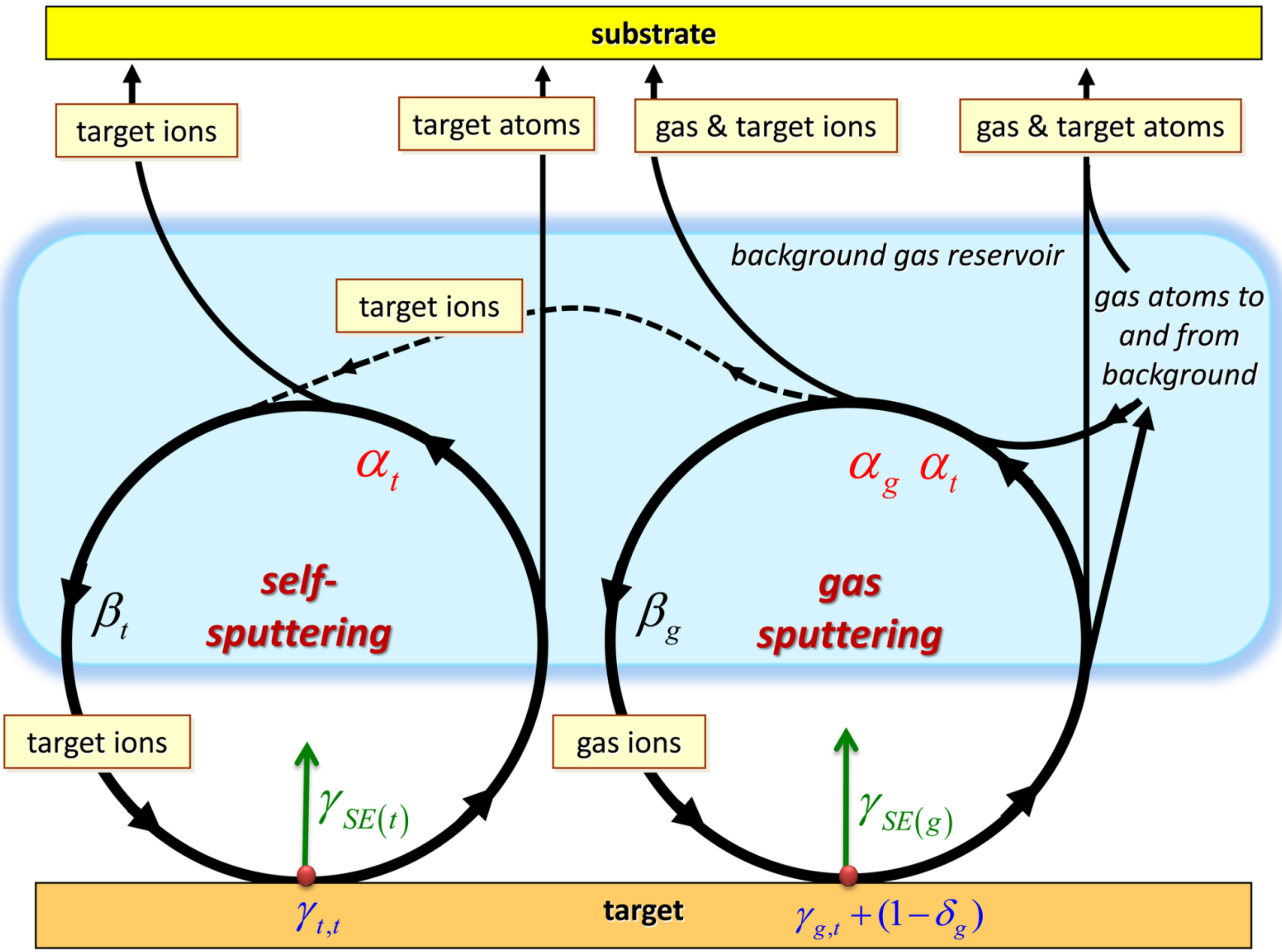
Runaway can be observed for all target materials

- including those with extremely small self-sputtering yield, which was initially surprising



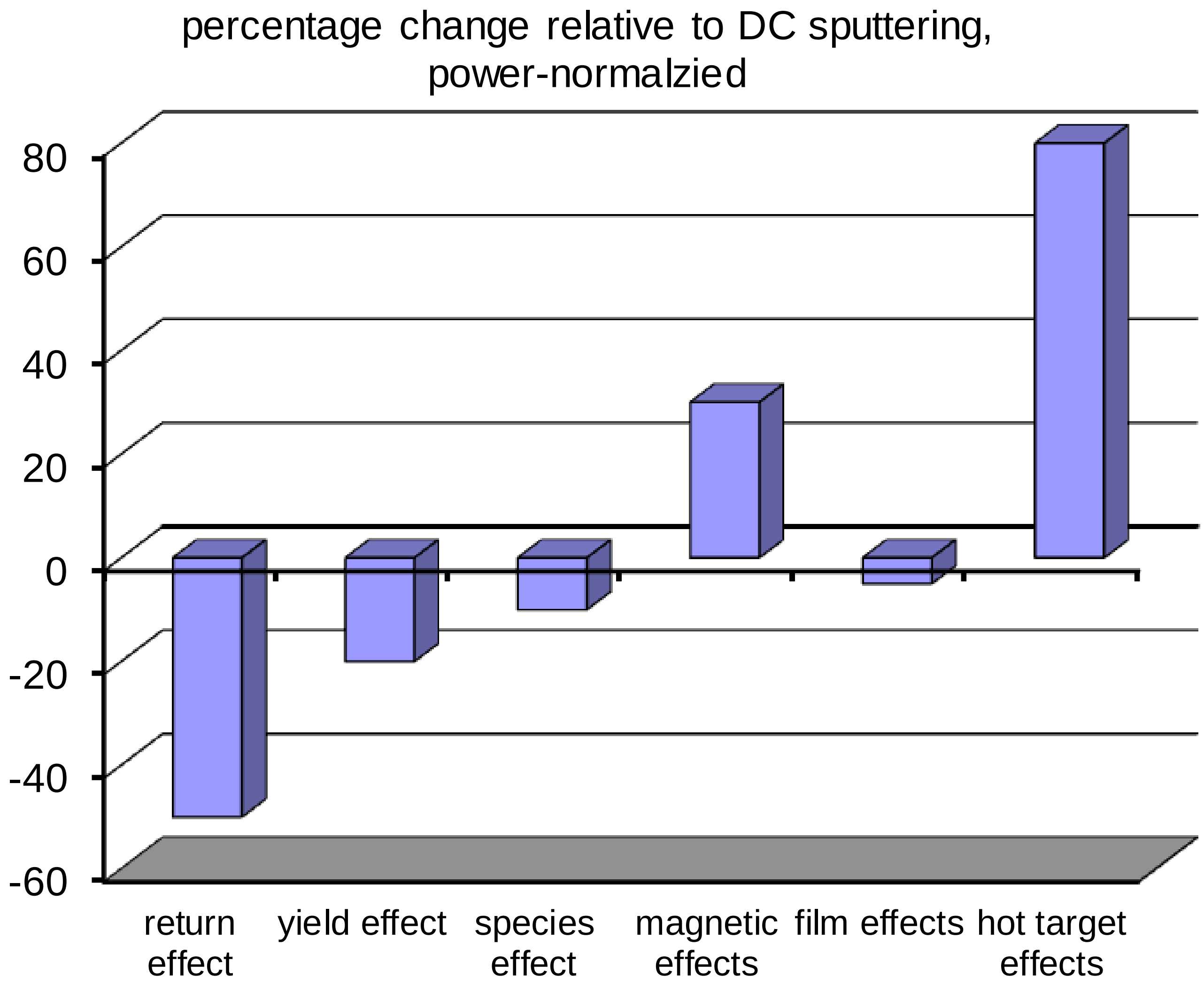
A. Anders, *et al.*, J. Phys D: Appl. Phys. **45** (2012) 012003.

Generalized Flux Model for HIPIMS



A. Anders, *et al*., J. Phys D: Appl. Phys. **45** (2012) 012003.

Deposition Rates of HIPIMS Are Affected by Several Features

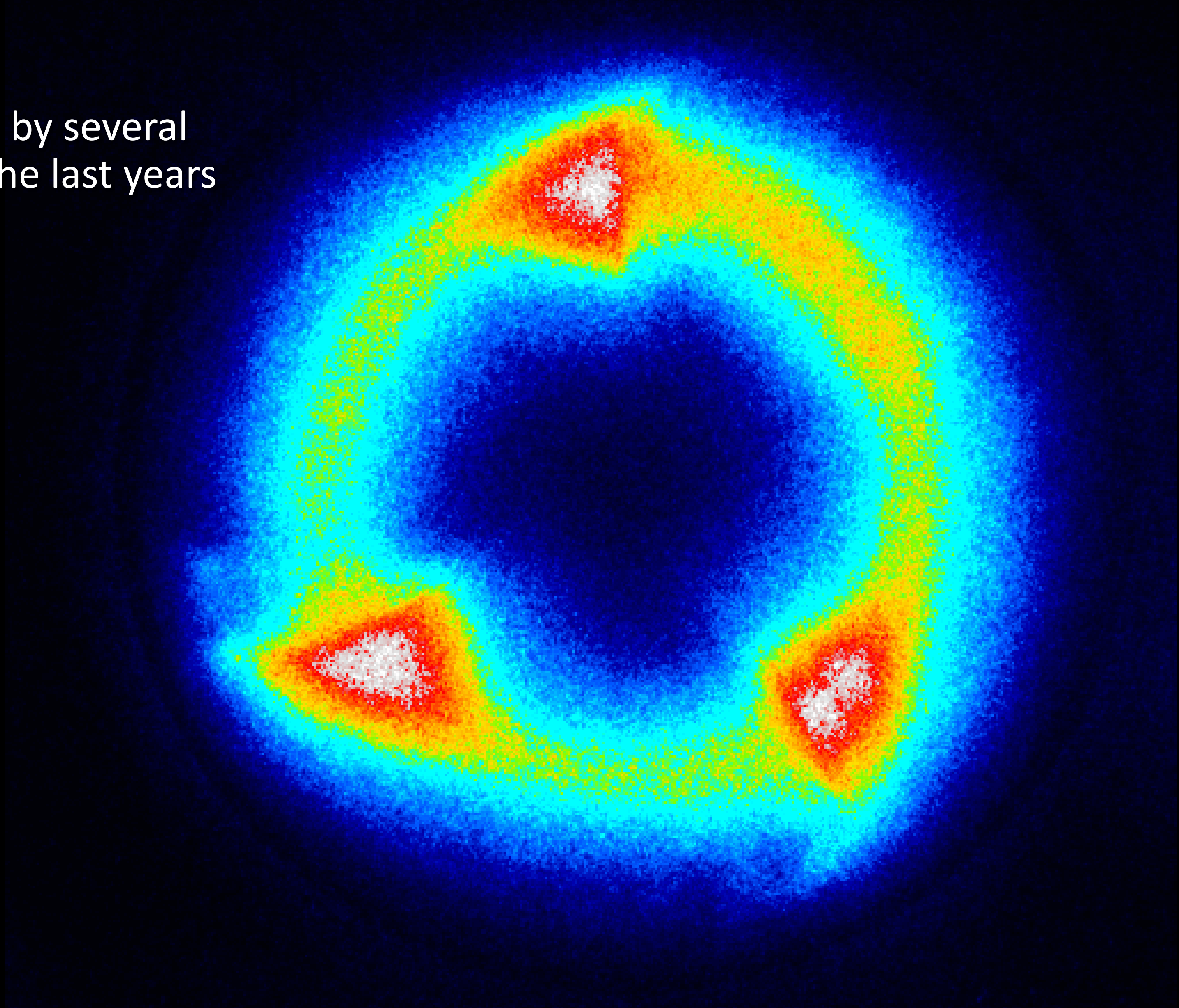


Example.
The specific effects depend on the material system and other parameters!

A. Anders, J. Vac. Sci. Technol. A **28** (2010) 783.

Localization of Ionization and Self-Organization

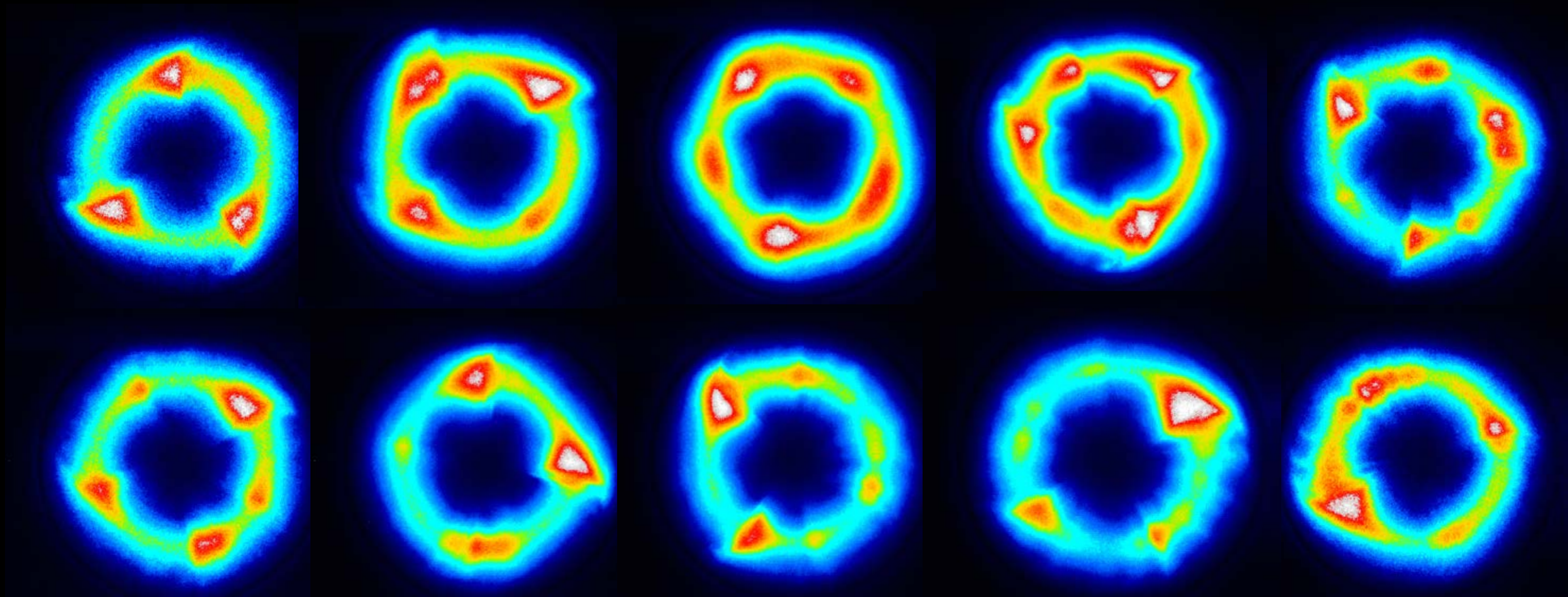
observed by several groups in the last years



A. Anders, *et al.*, J. Appl. Phys. **111** (2012) 053304

Self-organization and Turbulence

<u>ALL</u> of those images were taken with Nb target, 0.27 Pa Ar, 50 µs pulse, 350 A peak.



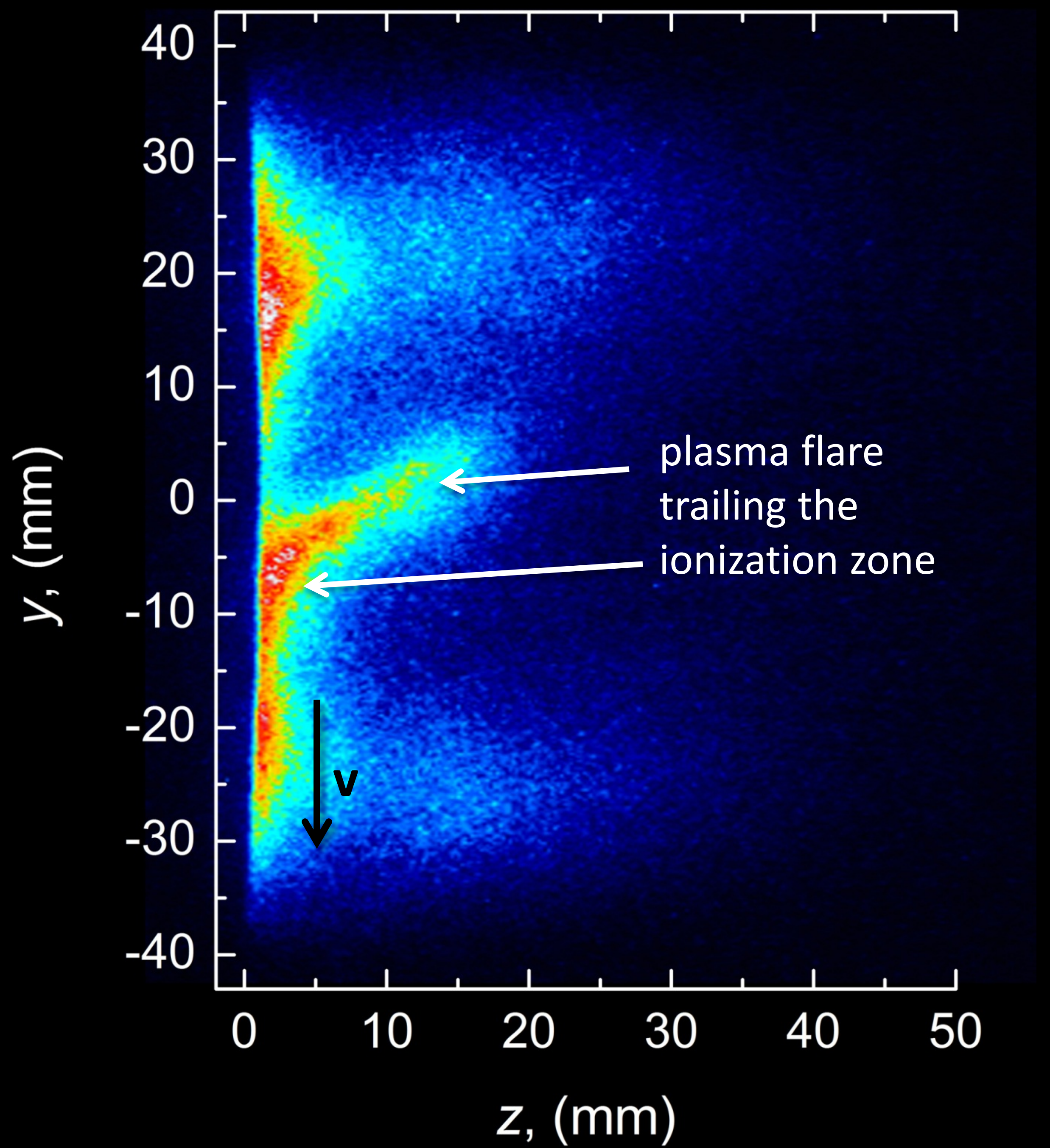
Each image is from a different pulse → similarities and differences suggest that structures

- show some interaction (self-self-organization)
- show strong changes, evolution, turbulence

A. Anders, *et al.*, J. Appl. Phys. **111** (2012) 053304

Side-on view frame image

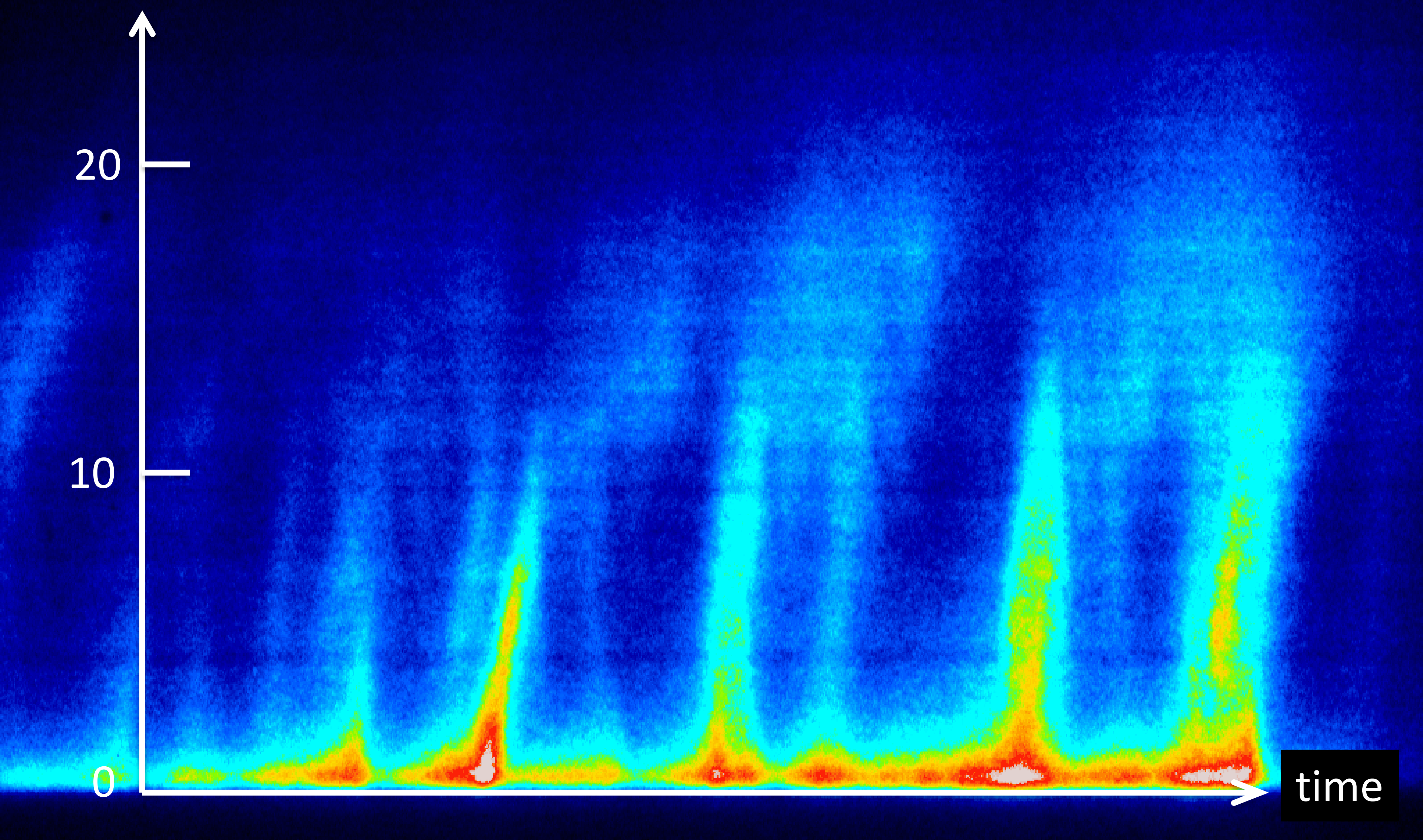
(10 ns snapshot)



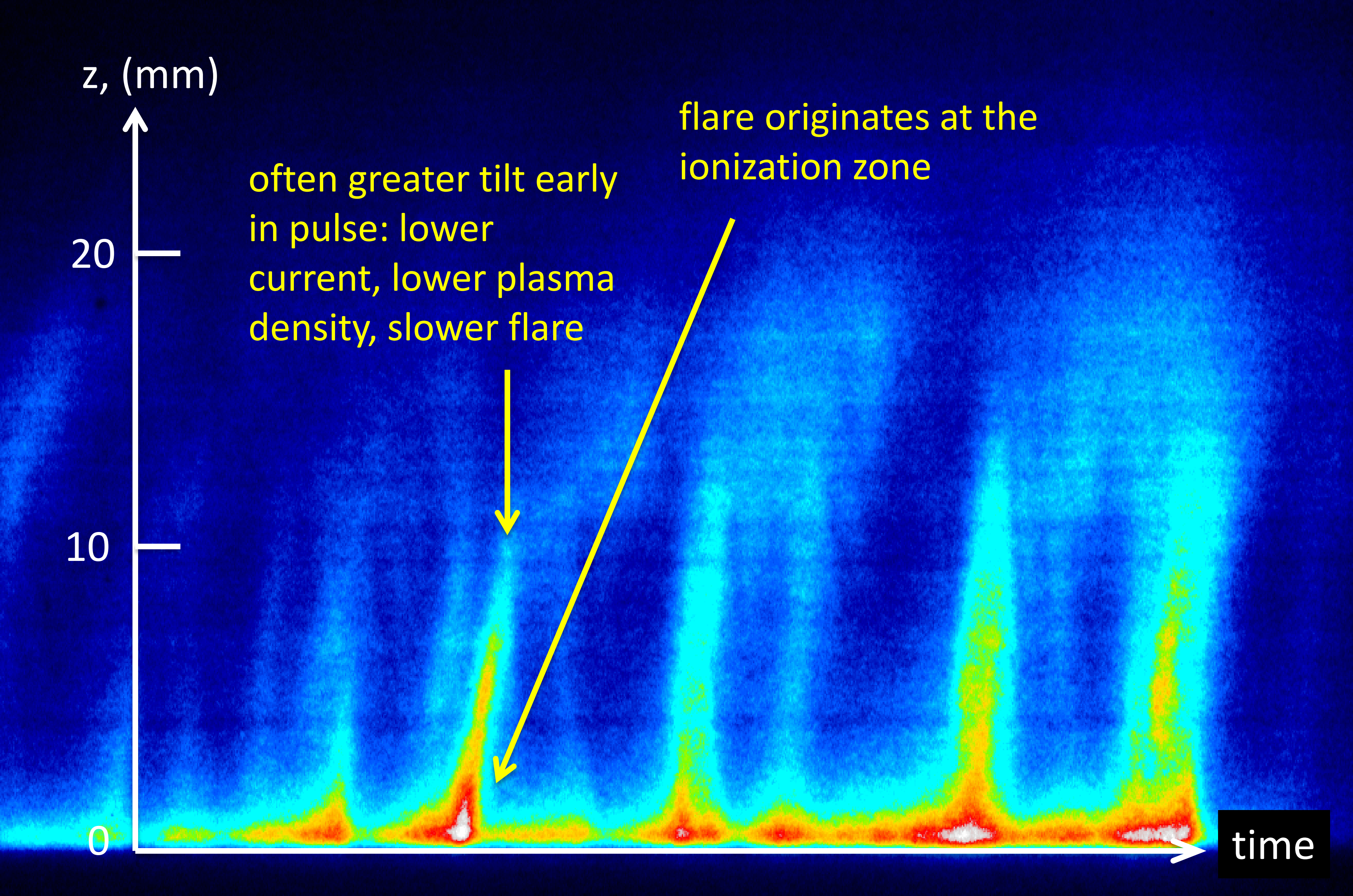
A. Anders, *et al.*, J. Appl. Phys. **111** (2012) 053304

Streak image sequence, 20 μs sweep time

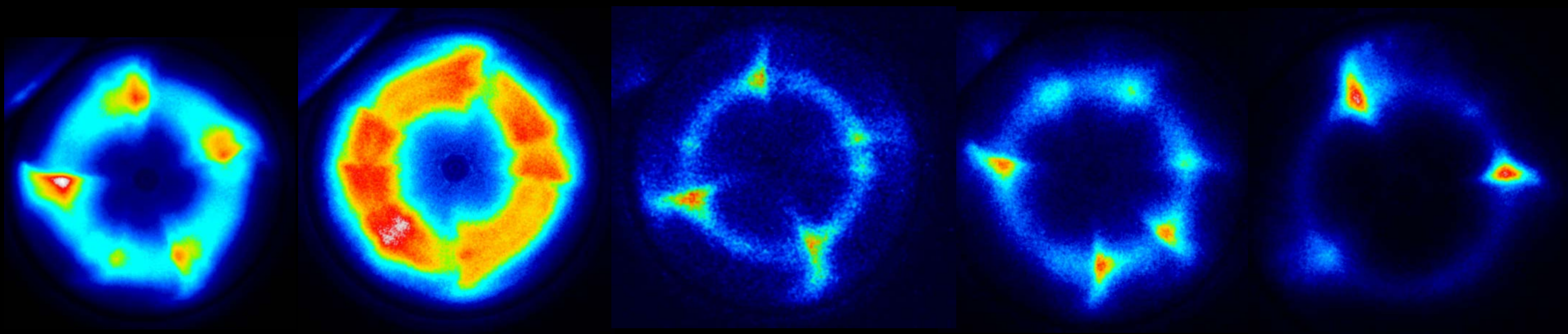
A. Anders, *et al*., J. Appl. Phys. **111** (2012) 053304



Example of Streak Image, 20 μs sweep time



Spectroscopic Imaging:
End-on view through Spectral Filter.
→ Evidence for Concentration of Ionization.



300-800 nm

Al I, from 3.14 eV

Ar I from 13.3 eV

Al II, from 15.06 eV

Ar II, from 19.22 eV

Al, 0.25 Pa Ar, 100 A, 150 ns snapshots

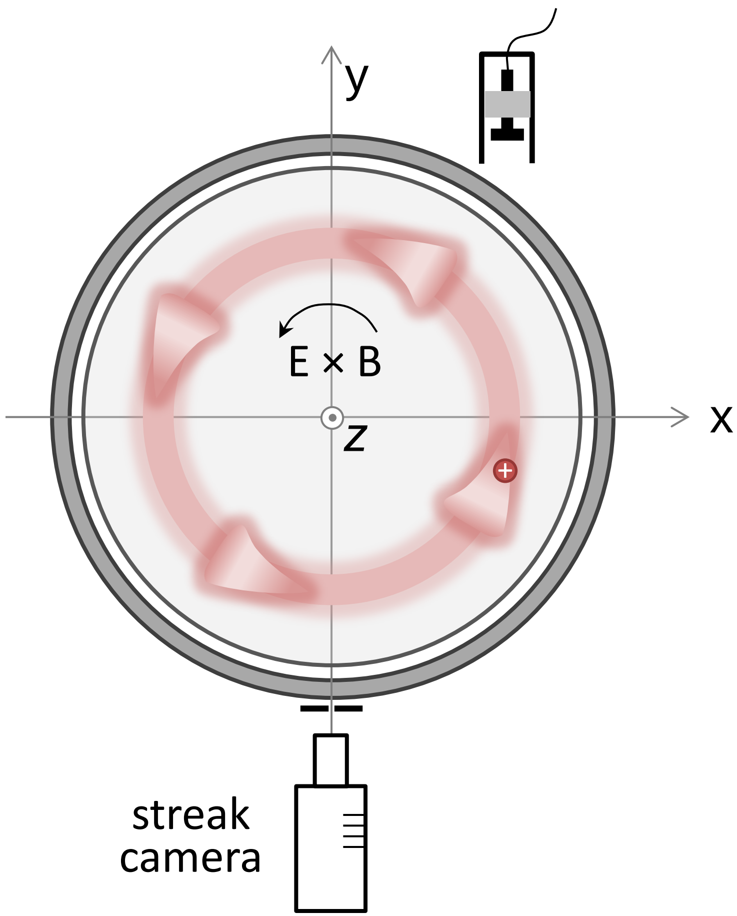
→ ionization occurs primarily in the ionization zones, little elsewhere

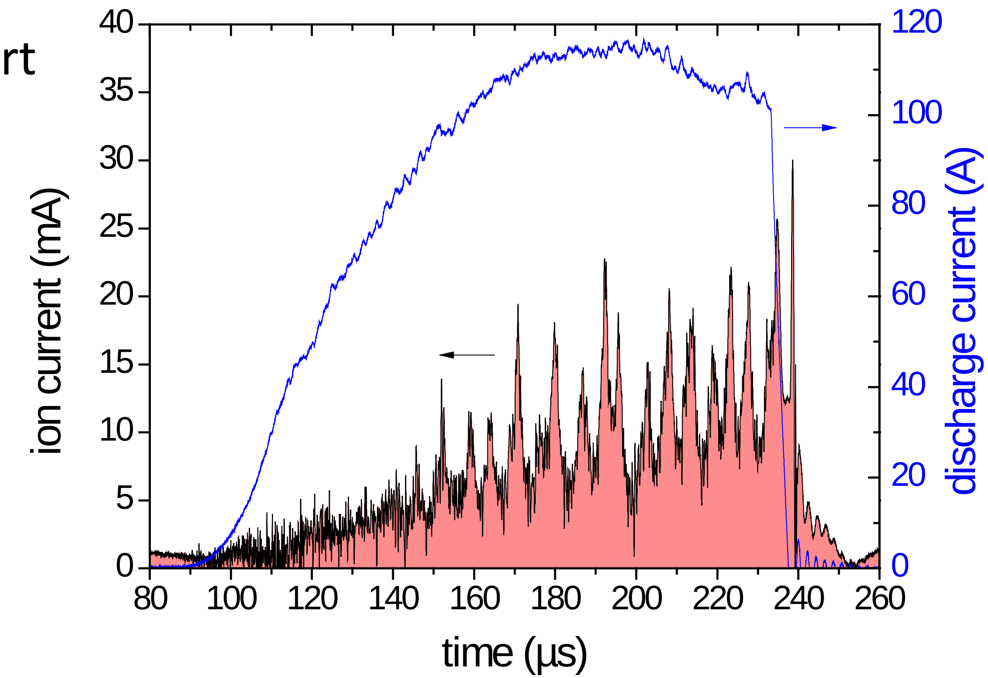
→ the higher the upper excitation level the more focussed appears the plasma

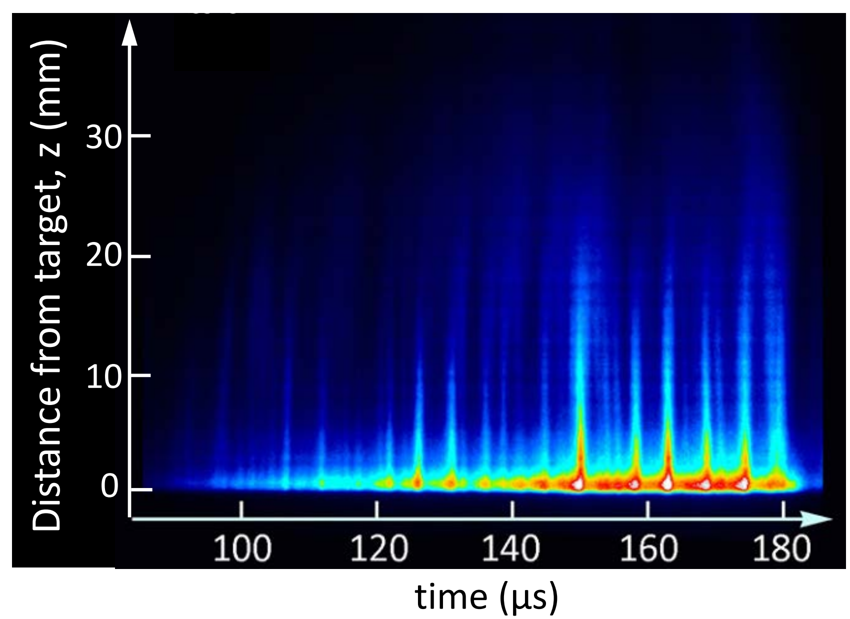
A. Andersson, *et al.*, Appl. Phys. Lett. **103** (2013) 054104.

Ionization zones and transport of charge

Ionization zones contribute to transport of charge across magnetic field lines





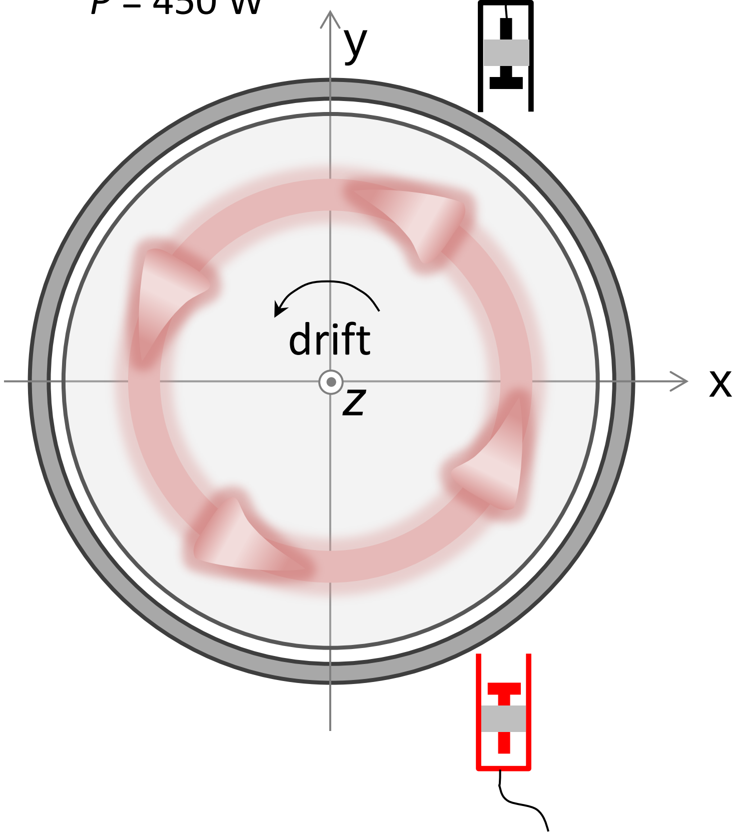


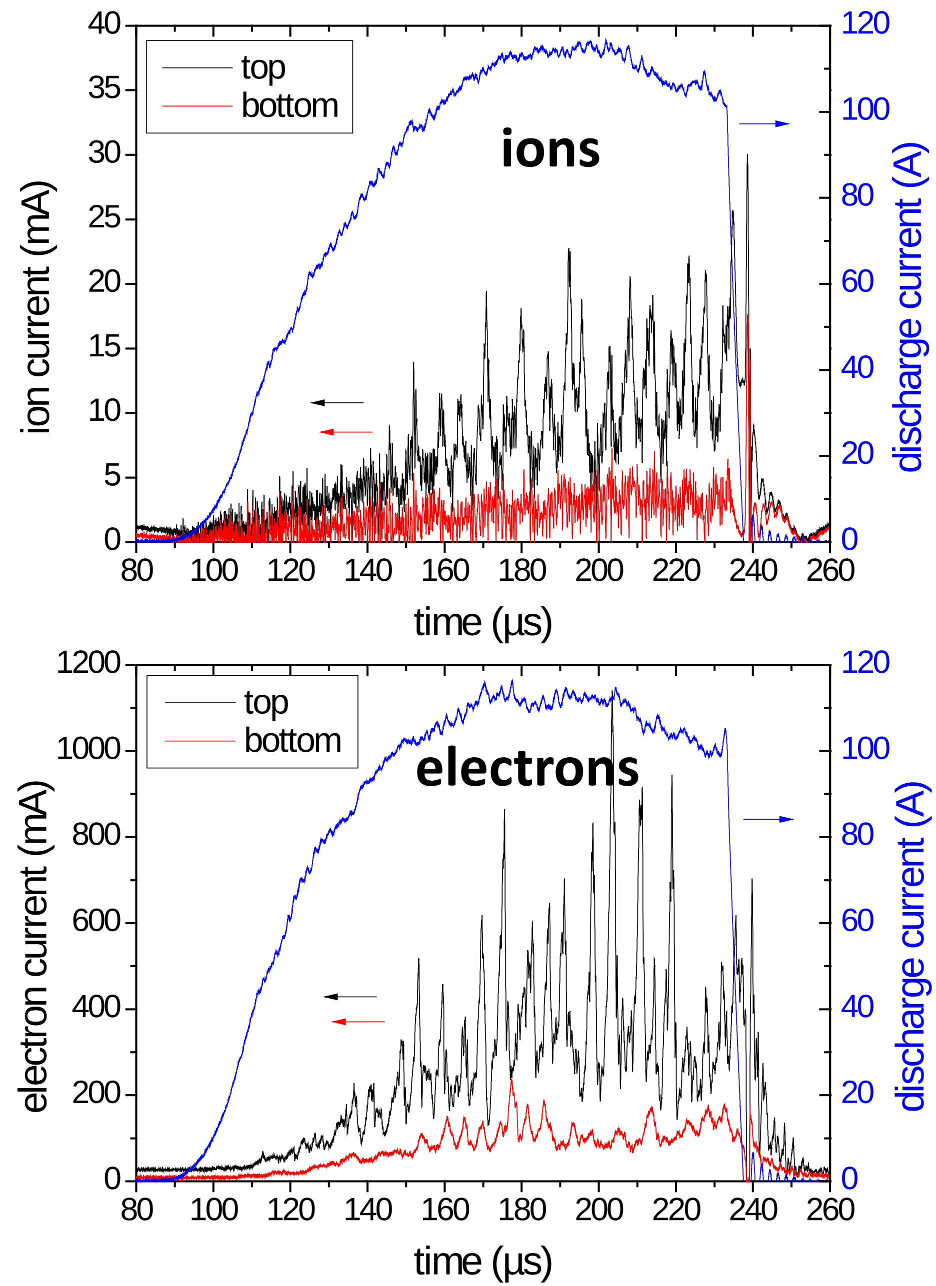
M. Panjan, *et al.*, Plasma Sources Sci. Technol., **23** (2014) 025007.
P.A. Ni, *et al.*, Appl. Phys. Lett., **101** (2012) 224102.

Ionization zones and transport of charged particles

HiPIMS discharge

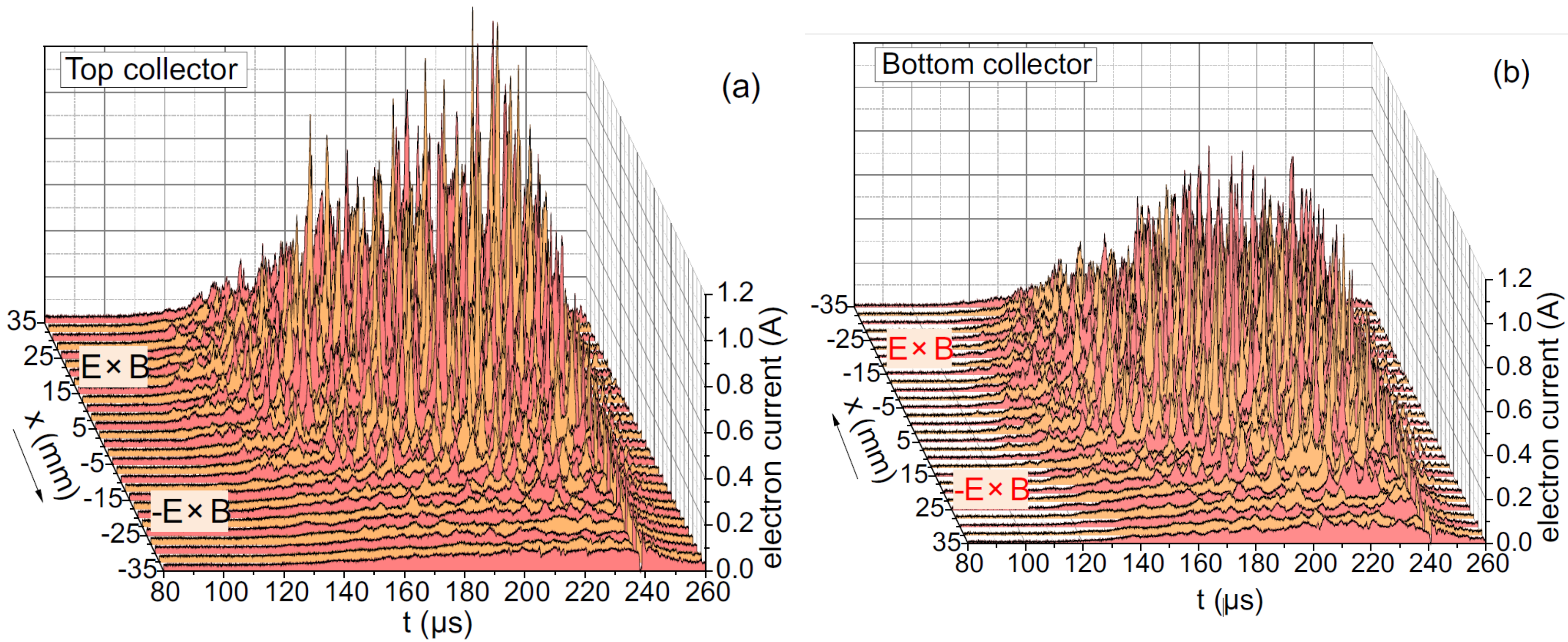
U = 390 V
I_{av} = 1.25 A
P = 450 W





M. Panjan, *et al.*, *Plasma Sources Sci. Technol.*, **23** (2014) 025007.

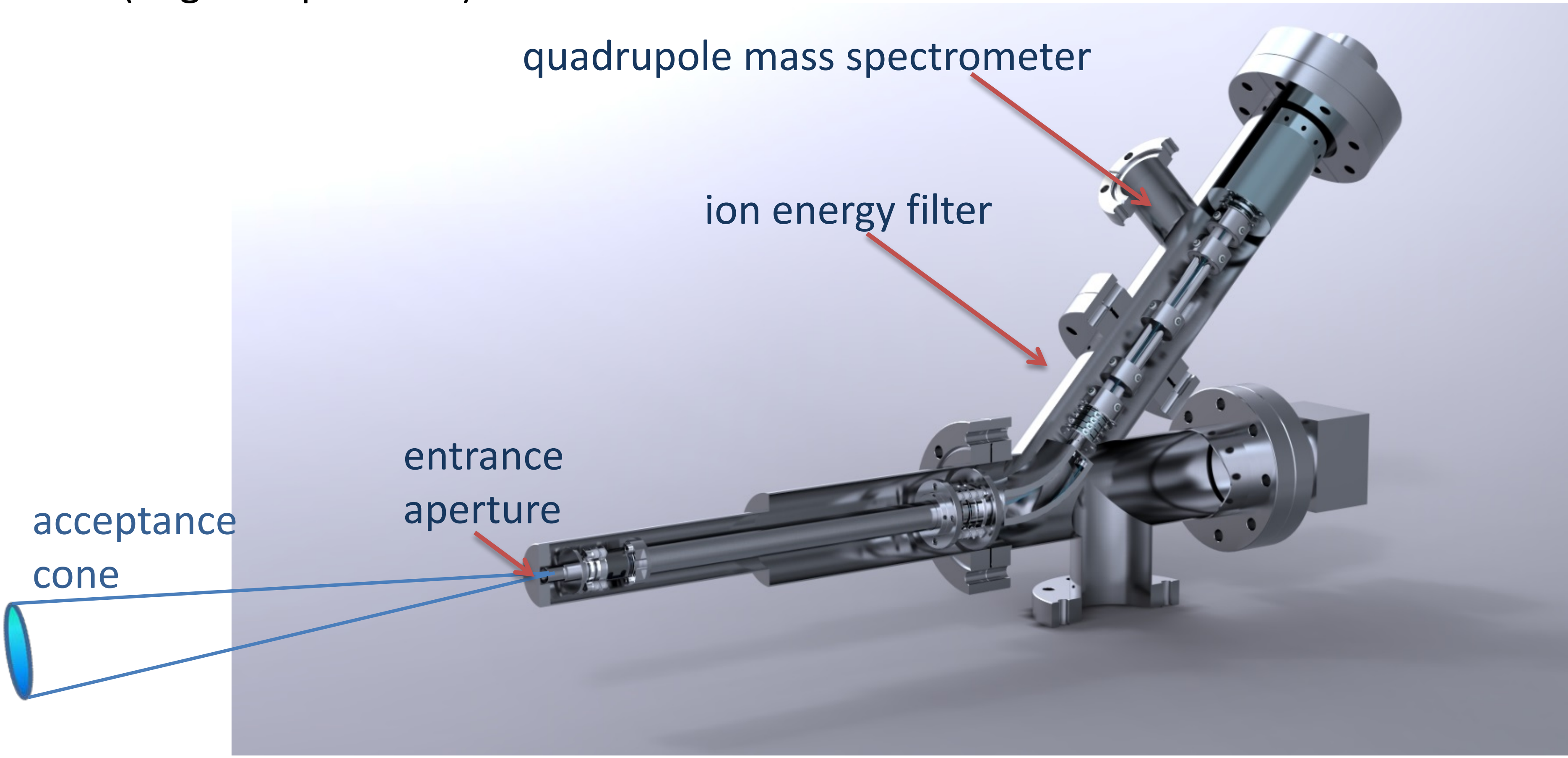
Biased Probes Indicate Flux Contains Jets, and Suggest Asymmetry Related to ExB Direction



M. Panjan, *et al*., Plasma Sources Sci. Technol. **23** (2014) 025007.

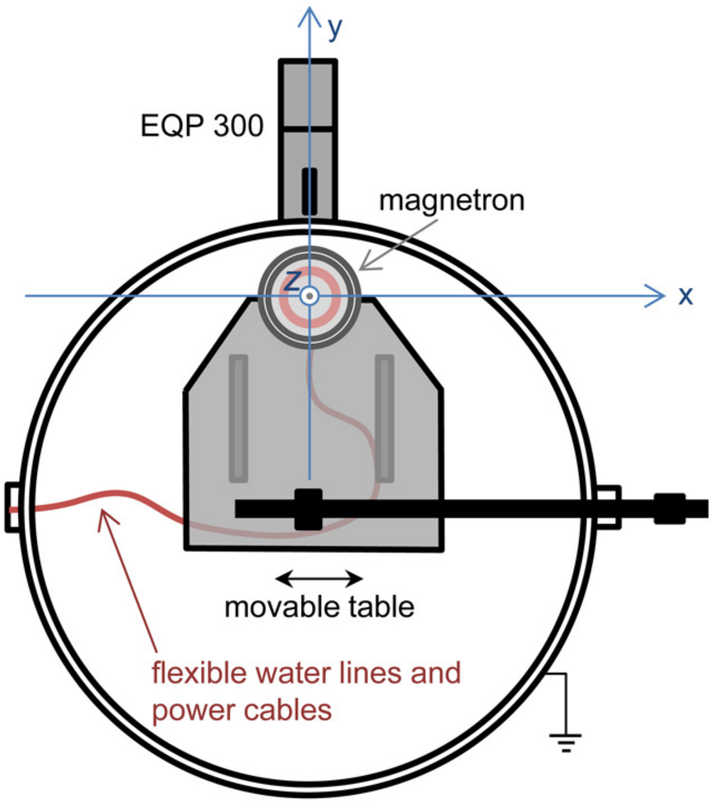
Measurements of Ion Energy Distributions

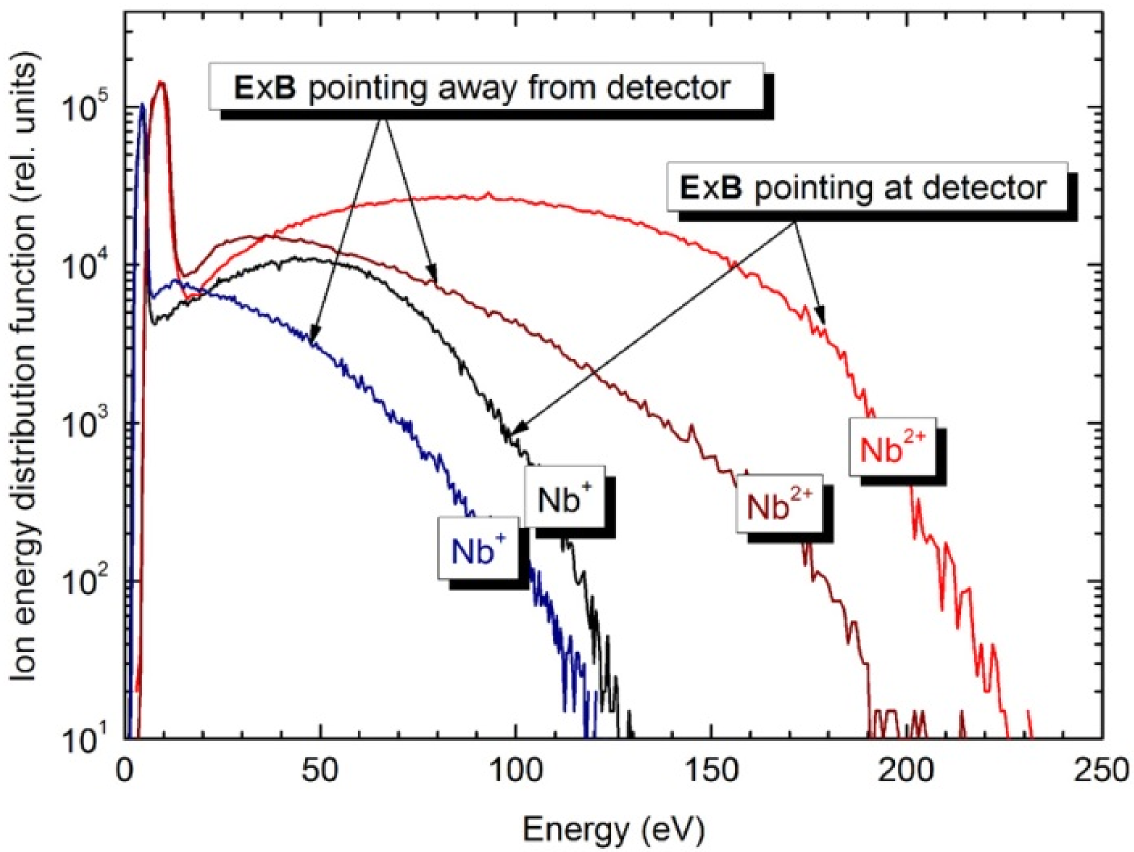
We use EQP300 by Hiden Ltd.; scan mass up to 300 amu and energies up to 1 keV (neg. and pos. ions)



Instrument transmittance function has a greater acceptance cone angle for small (especially < 10 eV) ion energies

Ion Energy Distribution Function – measured azimuthally

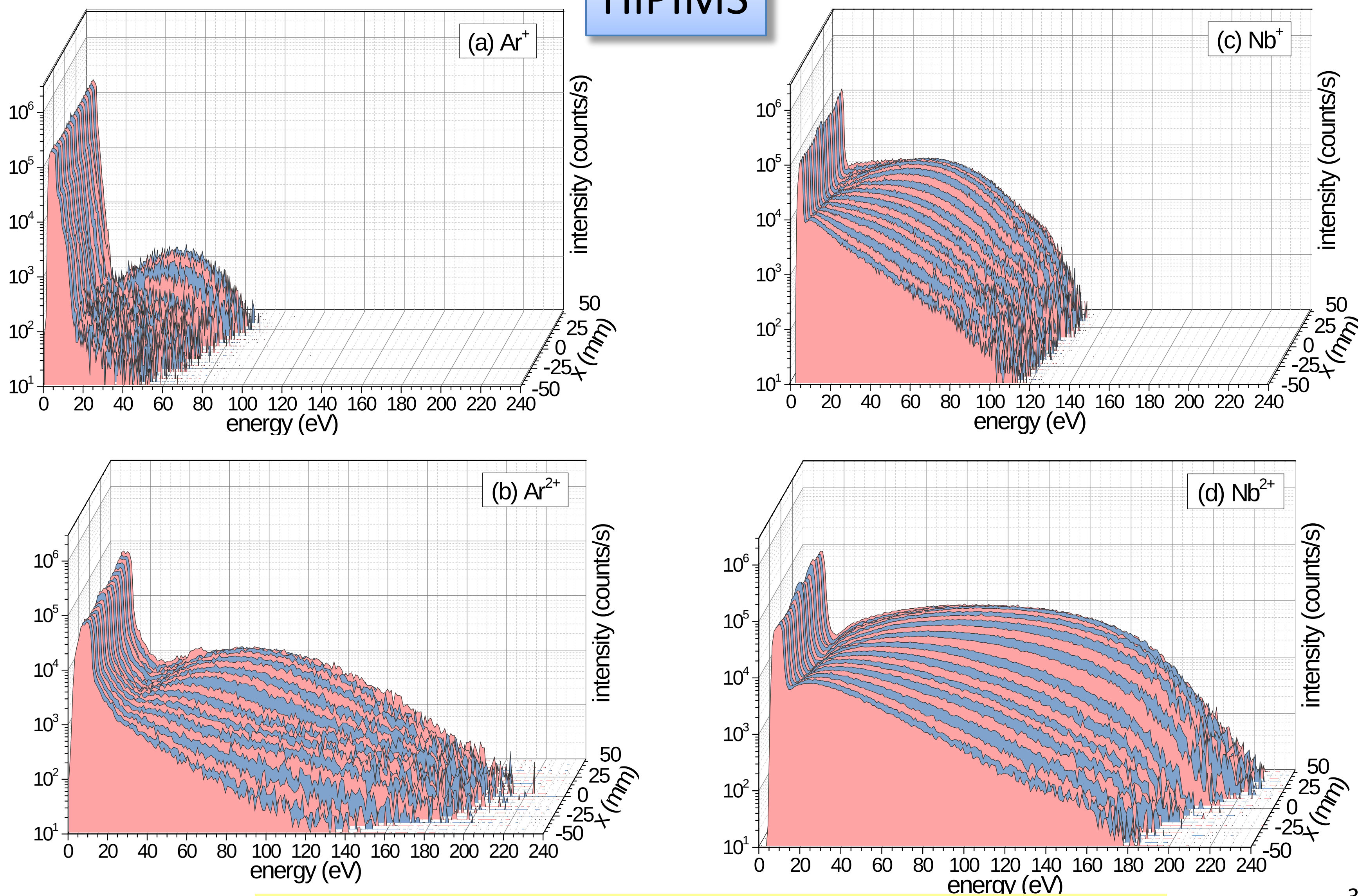




A. Anders, *et al*., Appl. Phys. Lett. **103** (2013) 144103;
M. Panjan, *et al*., Plasma Sources Sci. Technol. 23 (2014) 025007.

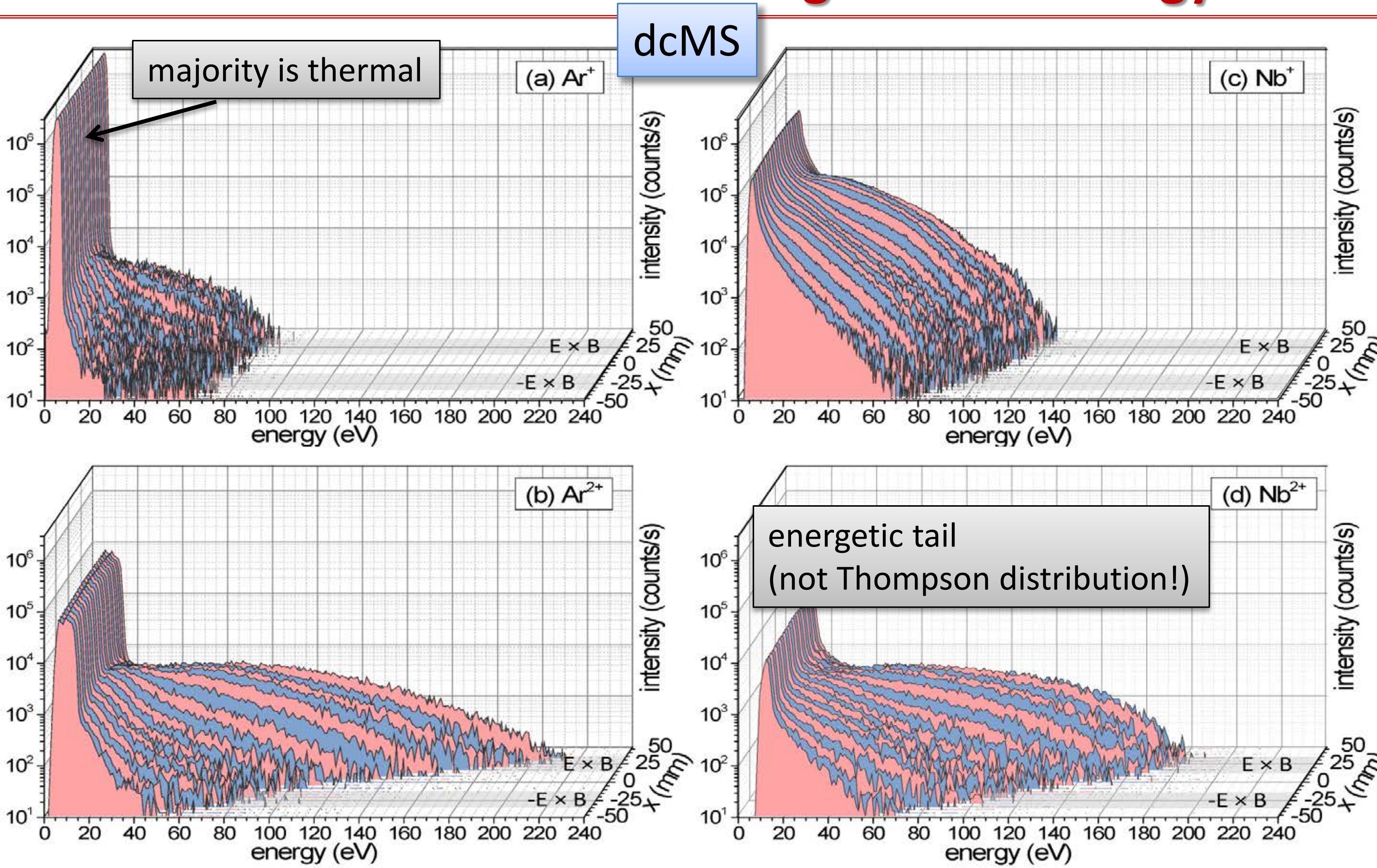
Examples of Ion Energy Distribution Measurements

HiPIMS



M. Panjan, *et al.*, Plasma Sources Sci. Technol. **23** (2014) 025007.

Recent Research: Ionization Zones are Regions of Elevated Potential → Ions gain extra energy

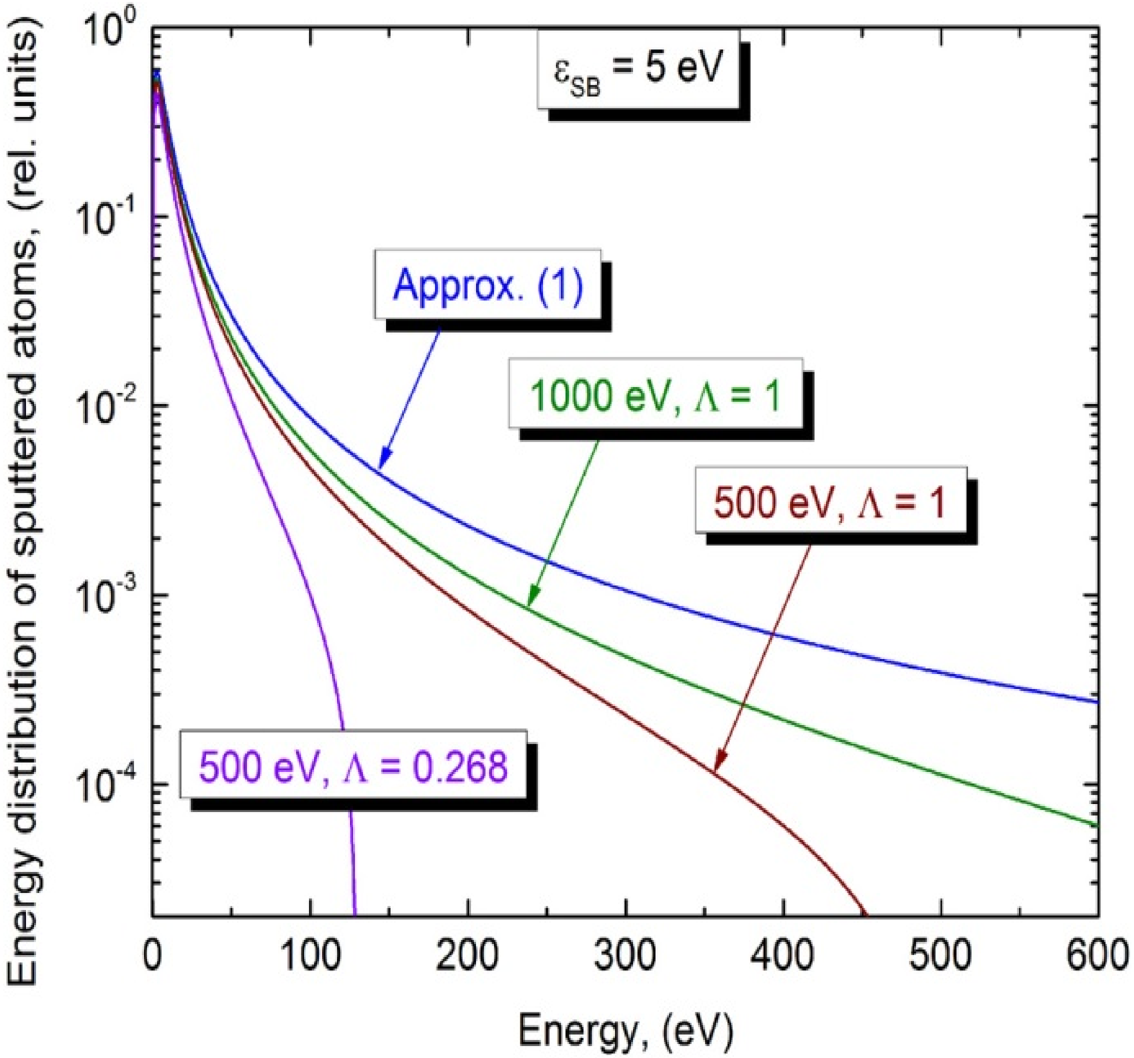


M. Panjan, *et al.*, Plasma Sources Sci. Technol. **23** (2014) 025007.

Thompson-Sigmund Binary Collision Theory

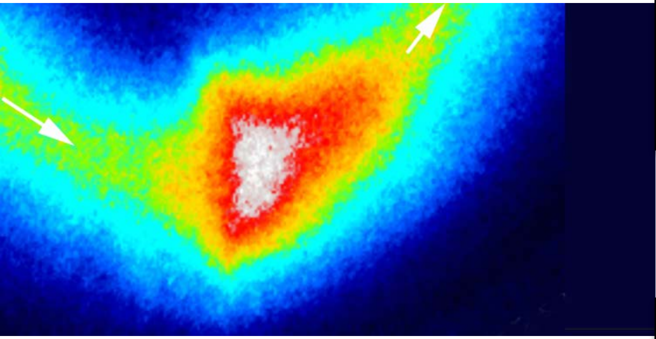
approximation:

$$f_{\text{Thompson}}\left(\varepsilon\right) \propto \frac{\varepsilon}{\left(\varepsilon + \varepsilon_{SB}\right)^3}$$



A. Anders, *et al.*, Appl. Phys. Lett. **103** (2013) 144103.

Potential Humps at Ionization Zones are like "Propeller Blades"

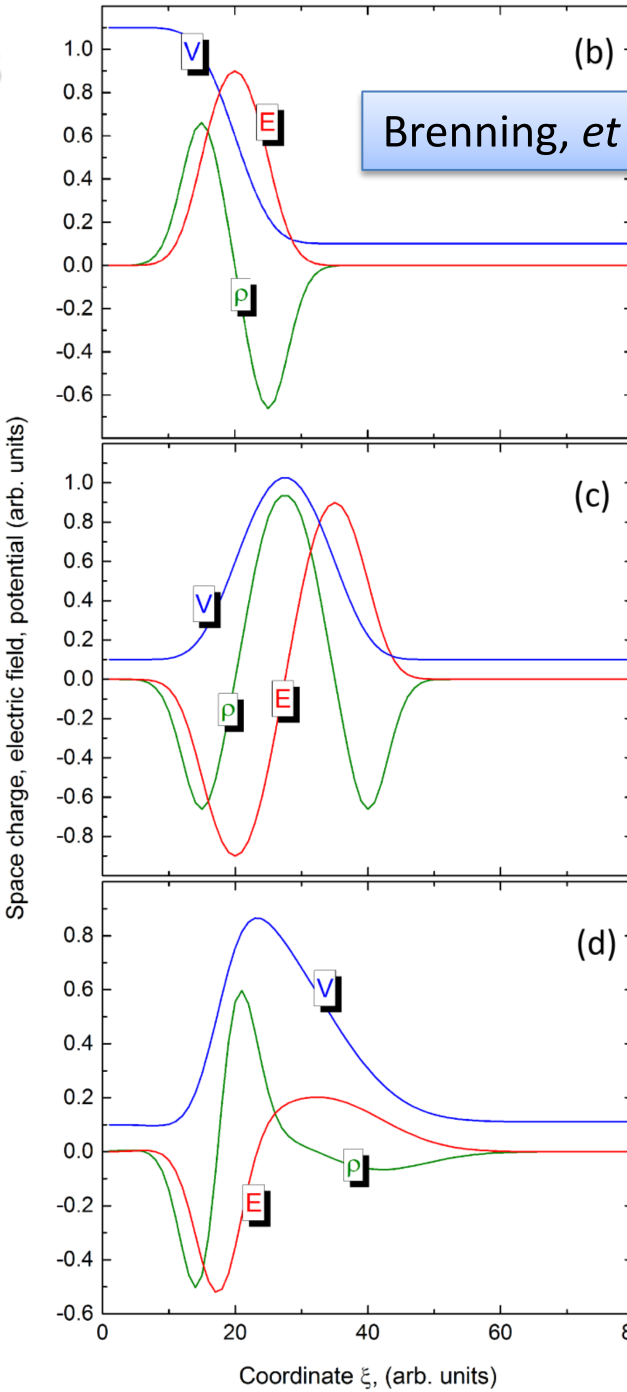


simple double layer:
→ potential step

2 double layers:
→ potential hump

$$V\left(\xi_{start}\right) \approx V\left(\xi_{end}\right)$$

Asymmetric double layers:
→ asymmetric potential hump.
Hump height is several 10 V.

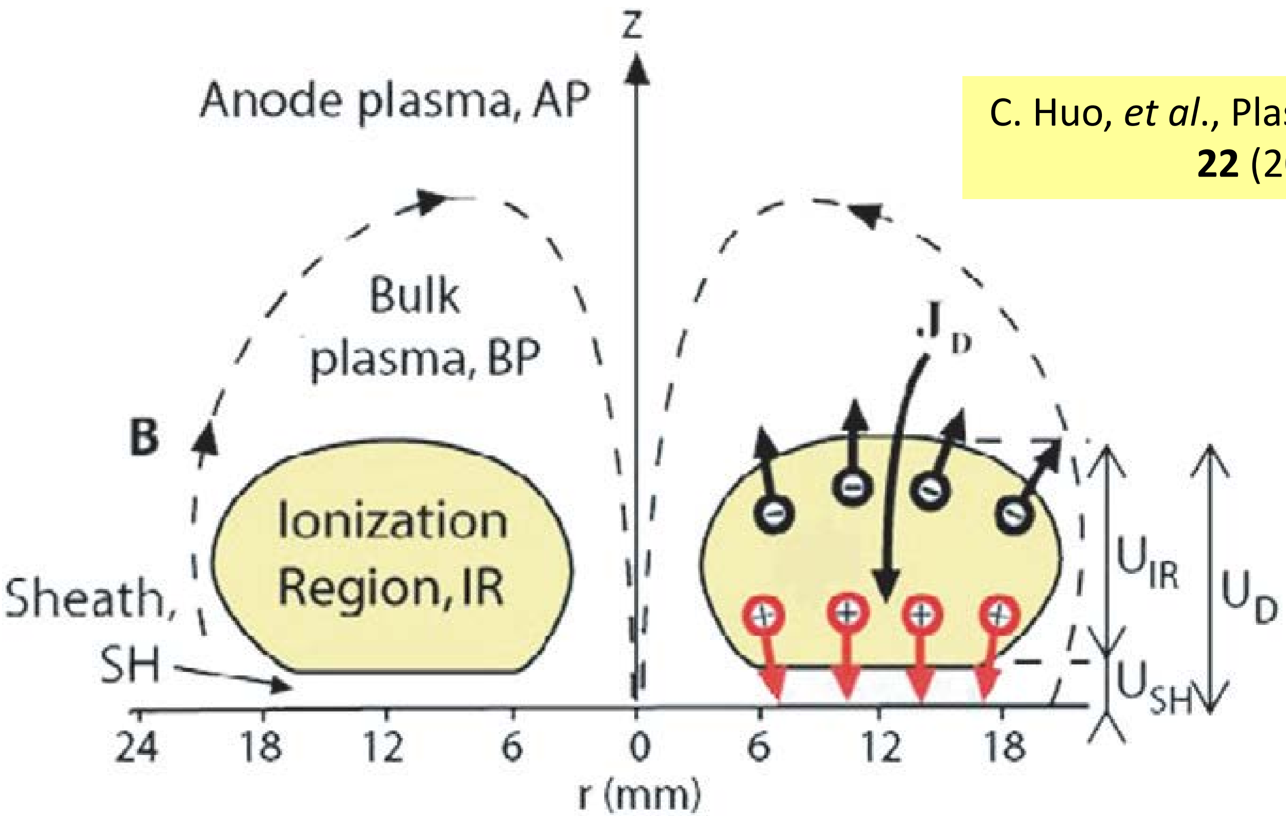


Brenning, *et al.*

A. Anders, *et al.*, Appl. Phys. Lett. **103** (2013) 144103.

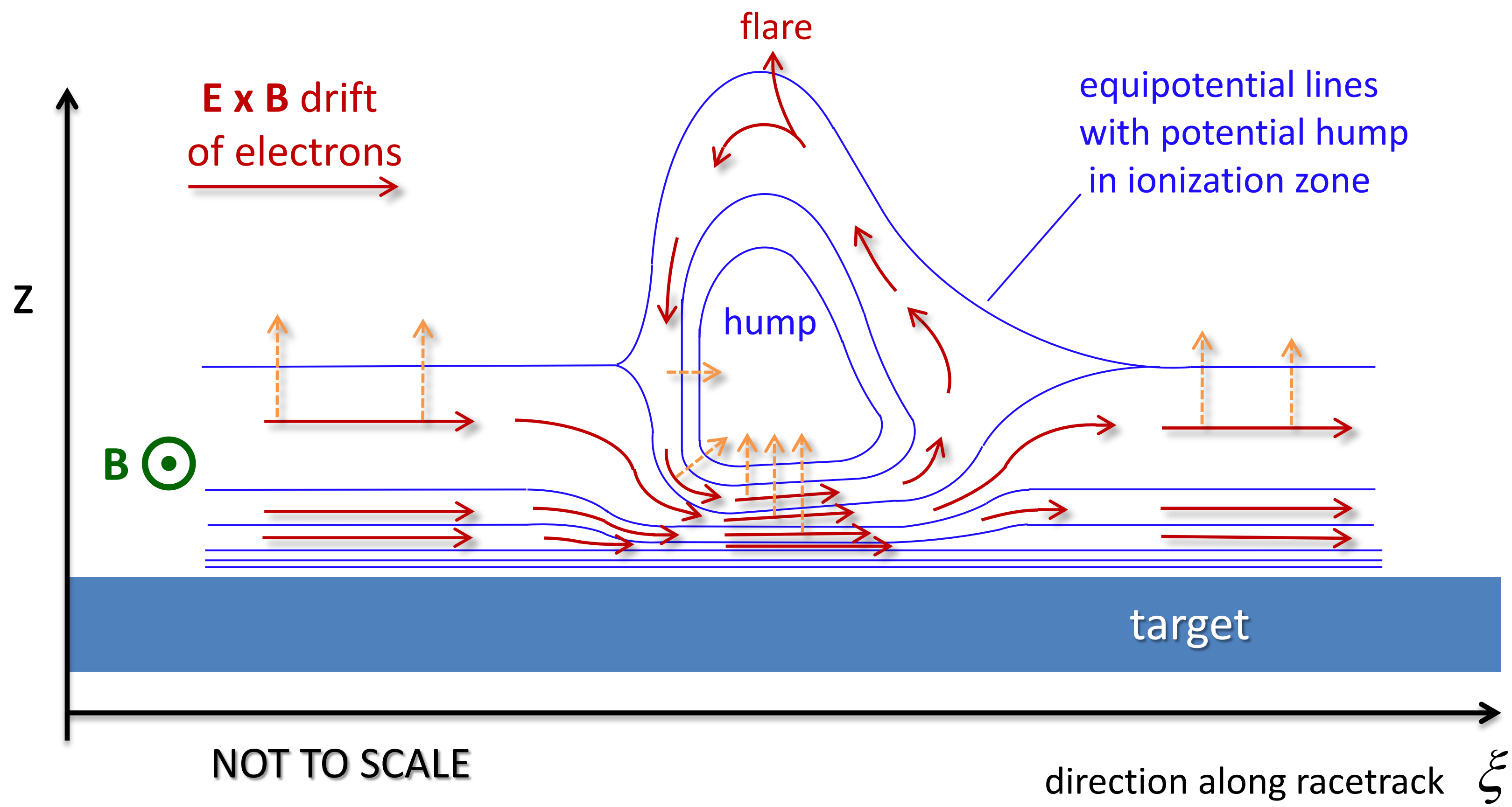
Energizing Electrons in the Sheath Versus in Presheath

- **Penning-Thornton paradigm**: $E_{SE} = eV_{sheath}$ and all electron heating results from hot (secondary) electrons
- However, even as the voltage drop in the magnetic presheath is smaller than in the sheath, the electron current in the presheath is much greater and than in the sheath → *energy dissipation and electron heating can be greatest in the presheath*



C. Huo, *et al*., Plasma Sources Sci. Technol. **22** (2013) 045005.

Localized Energizing of Drifting Electrons



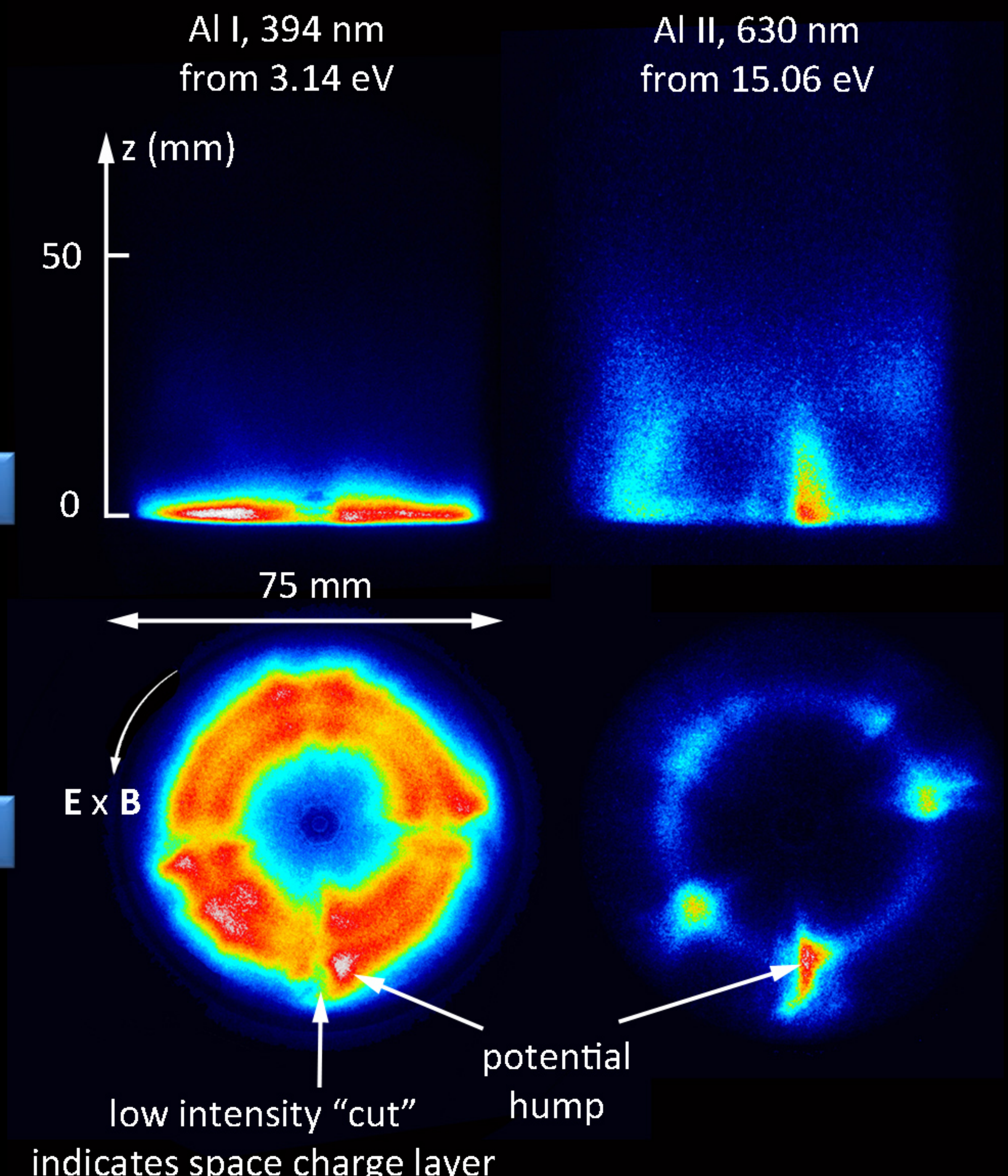
- electrons drift according to the local **E** and **B** fields
- ions are not magnetized, follow **E**-field

A. Anders, Appl. Phys. Lett. **105** (2014) 244104.

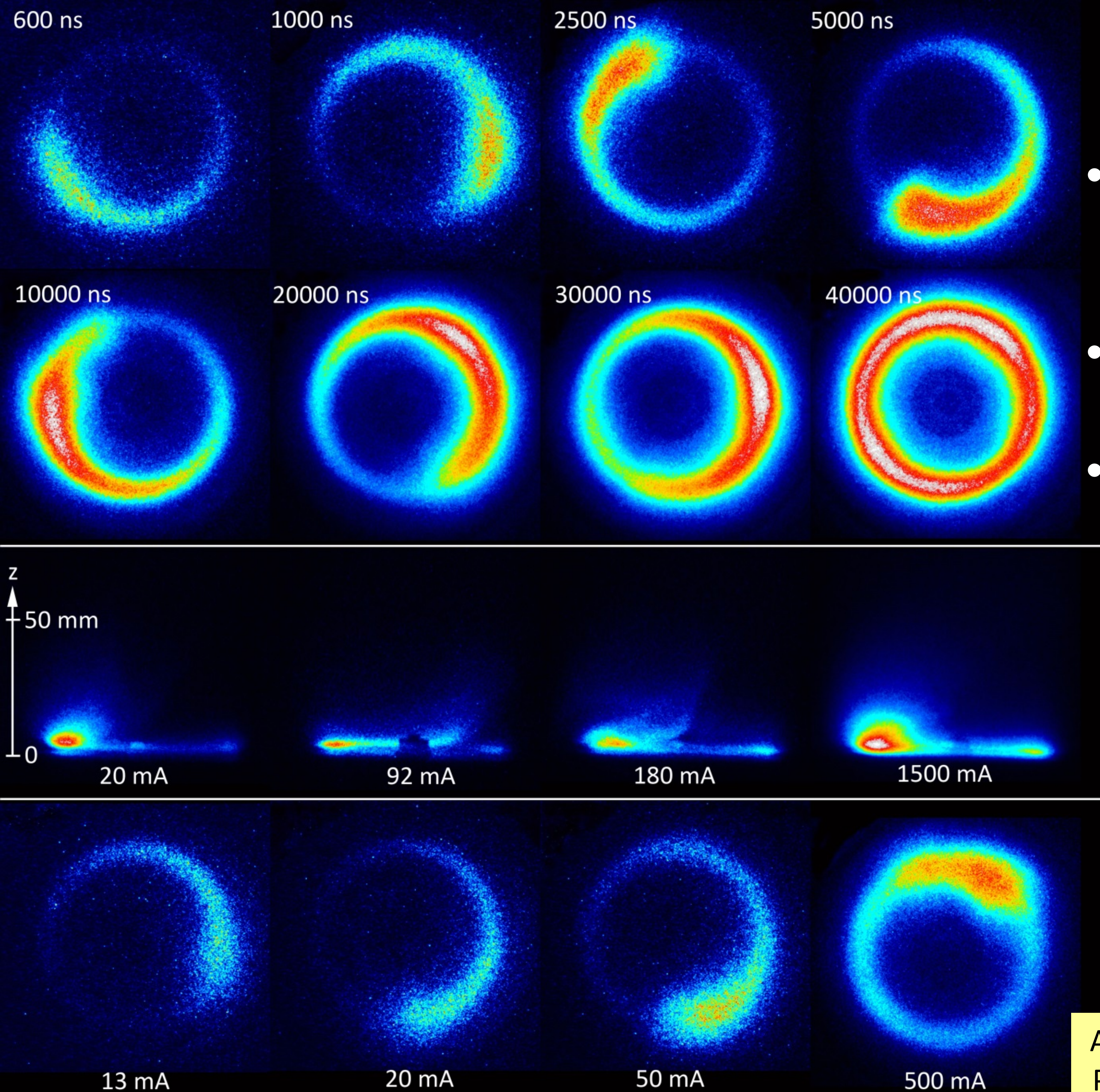
Light can be seen as strongly related to the potential hump structure

side-on view

end–on view



A. Anders, Appl. Phys. Lett. **105** (2014) 244104.



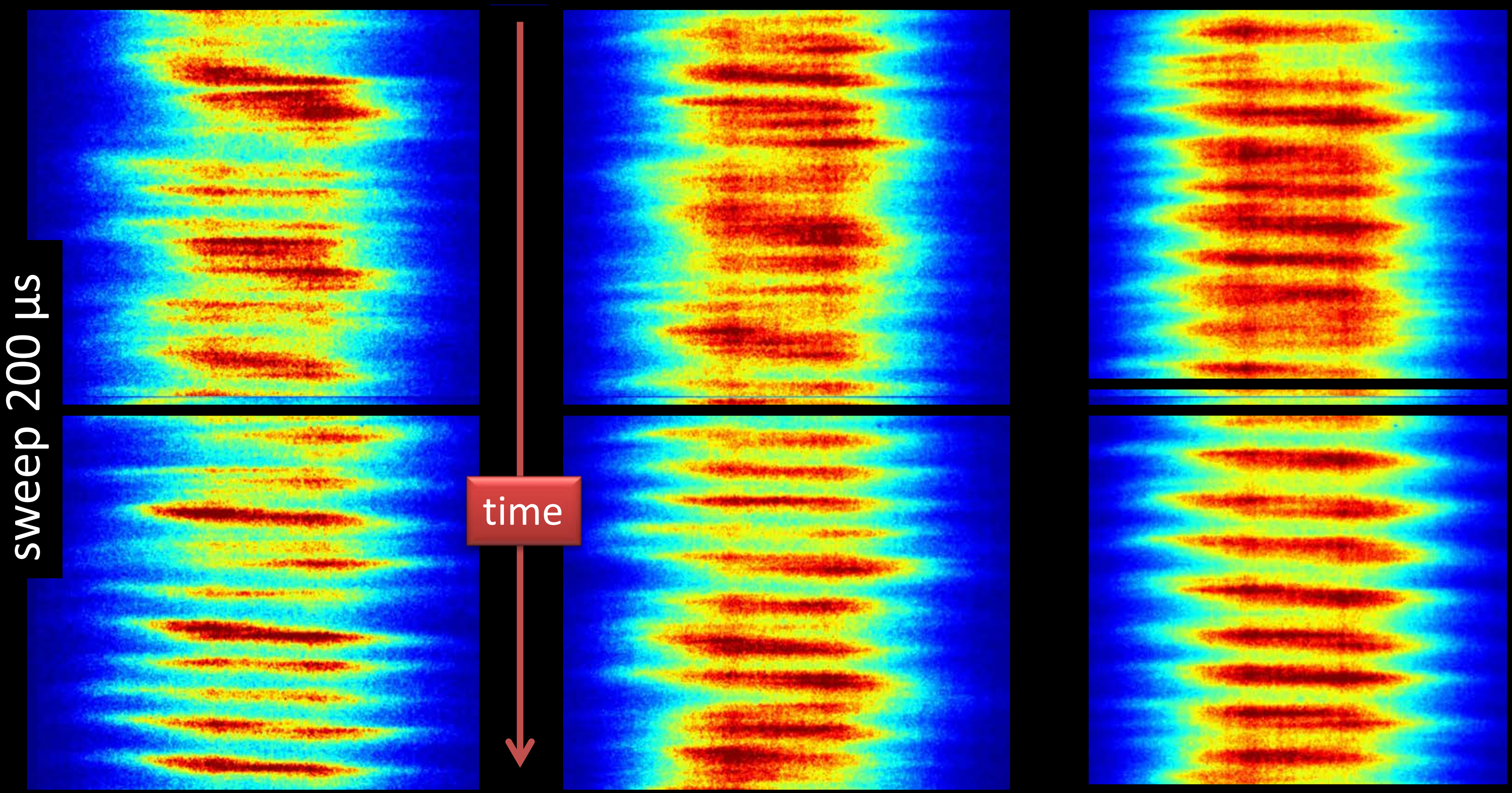
Ionization zones exist:

- even DC at low current, all the way to 4 mA!
- also in reactive systems
- with much slower motion than HiPIMS

Nb in Ar

A. Anders, *et al.*, IEEE Trans. Plasma Sci. **42** (2014) 2578.

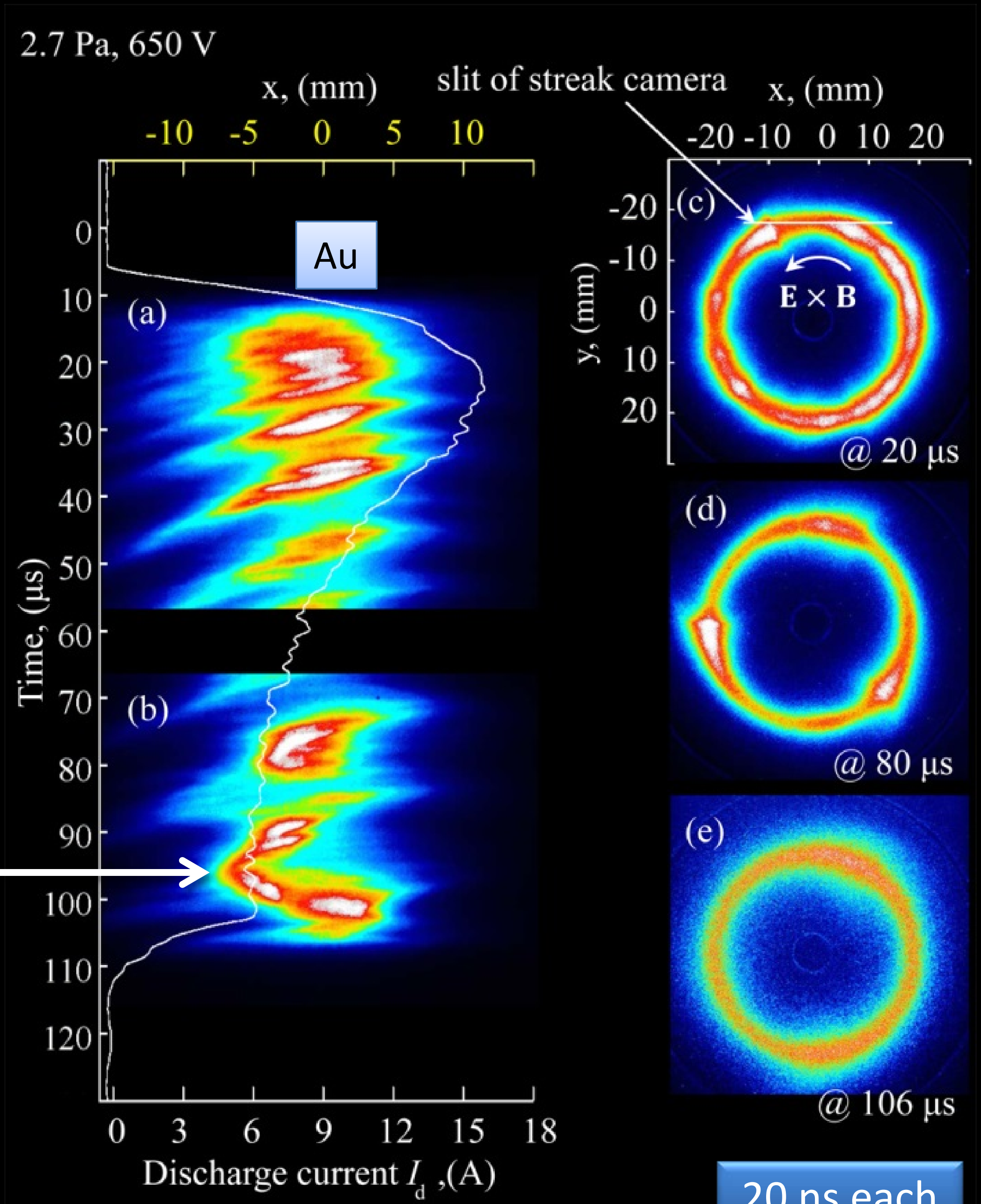
Evolution of Ionization Zones seen for DC Magnetron Discharges (3” Nb in Ar)



examples of streak camera images, illustrating zone stability vs. change

Y. Yang, *et al.*, Appl. Phys. Lett. **105** (2014) 254101.

Pulsed dc: Transition Region



Reversal of direction!
From E x B to - E x B
at about 6 A.

20 ns each

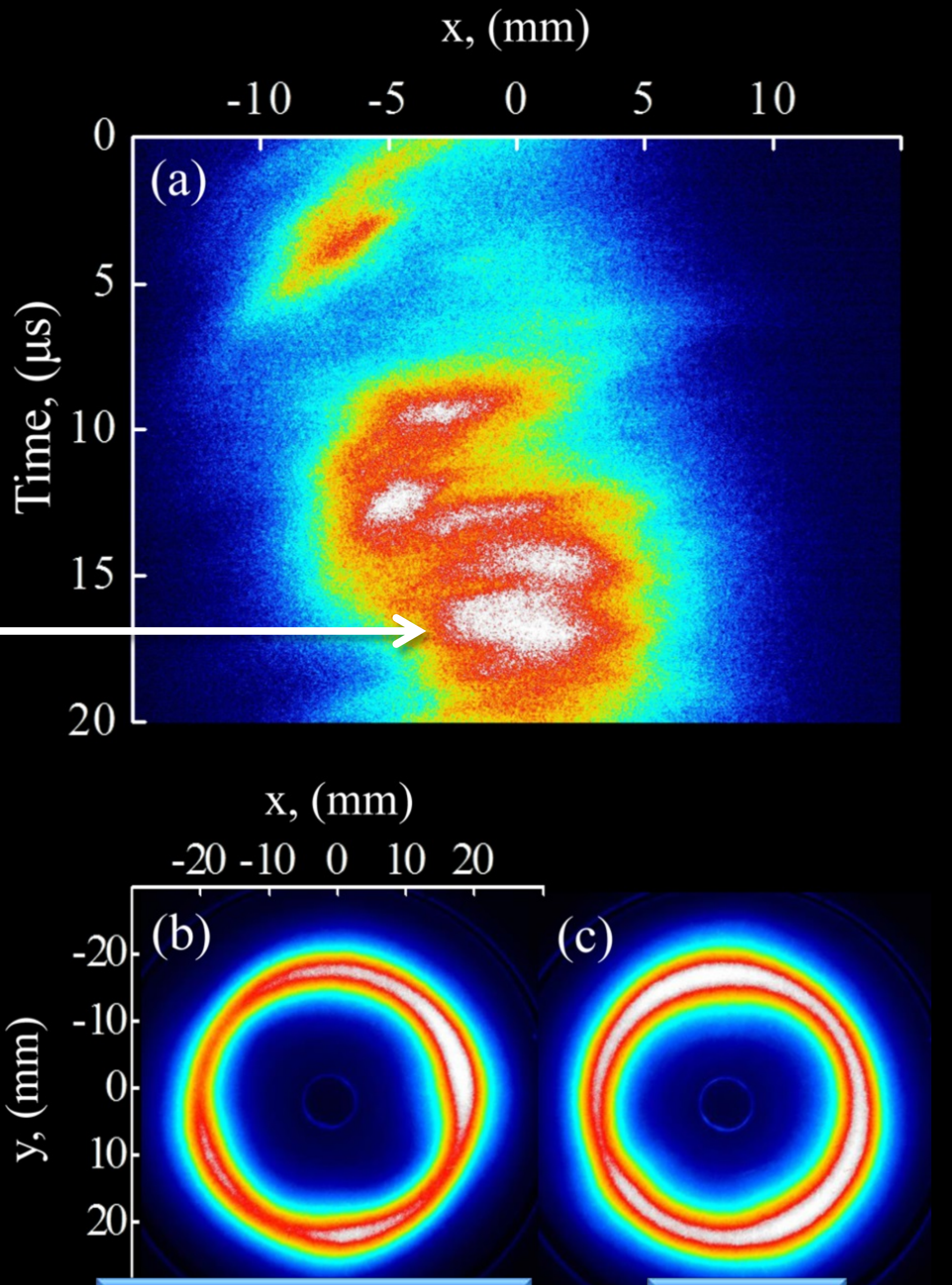
Y. Yang, *et al*., Appl. Phys. Lett. **105** (2014) 254101.

Pulsed dc:
Transition region to high current

0.1 Pa Ar, 5 A, 700 V

Au

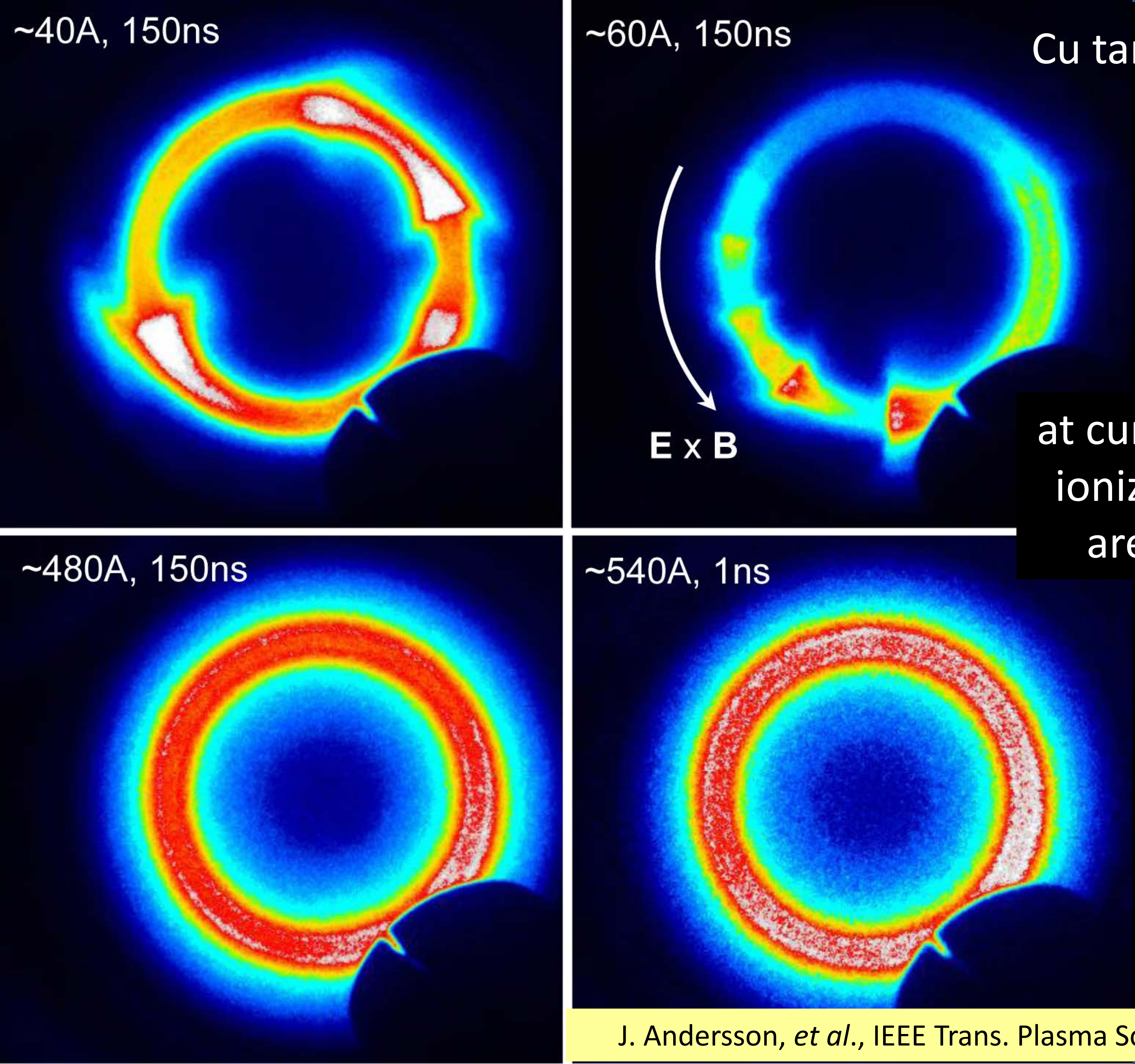
Practically stationary



exposure 30 µs

100 µs

Y. Yang, *et a*l., Appl. Phys. Lett. **105** (2014) 254101.

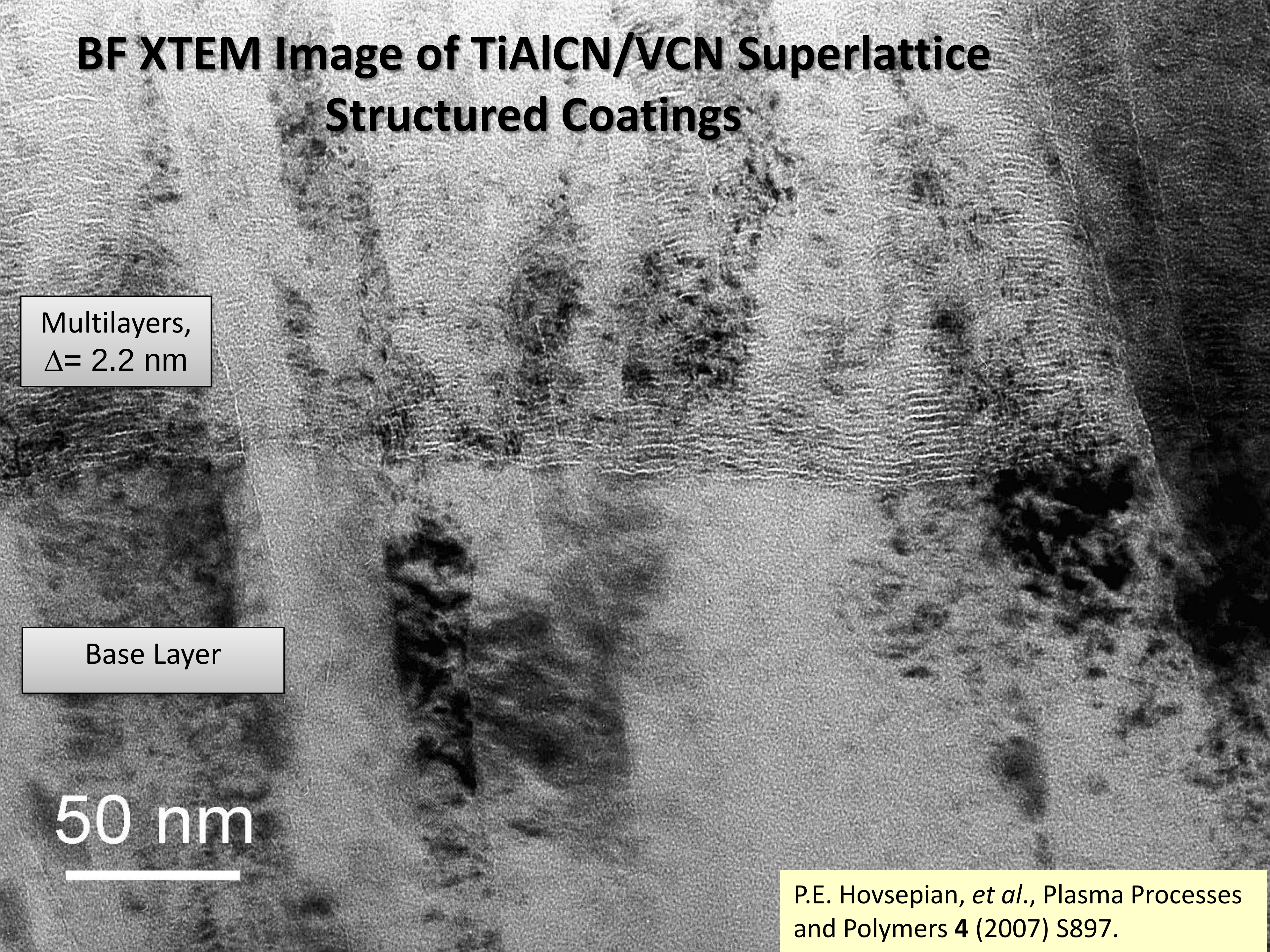


Cu target, gasless

at current > 300 A ionization zones are lost! (!?)

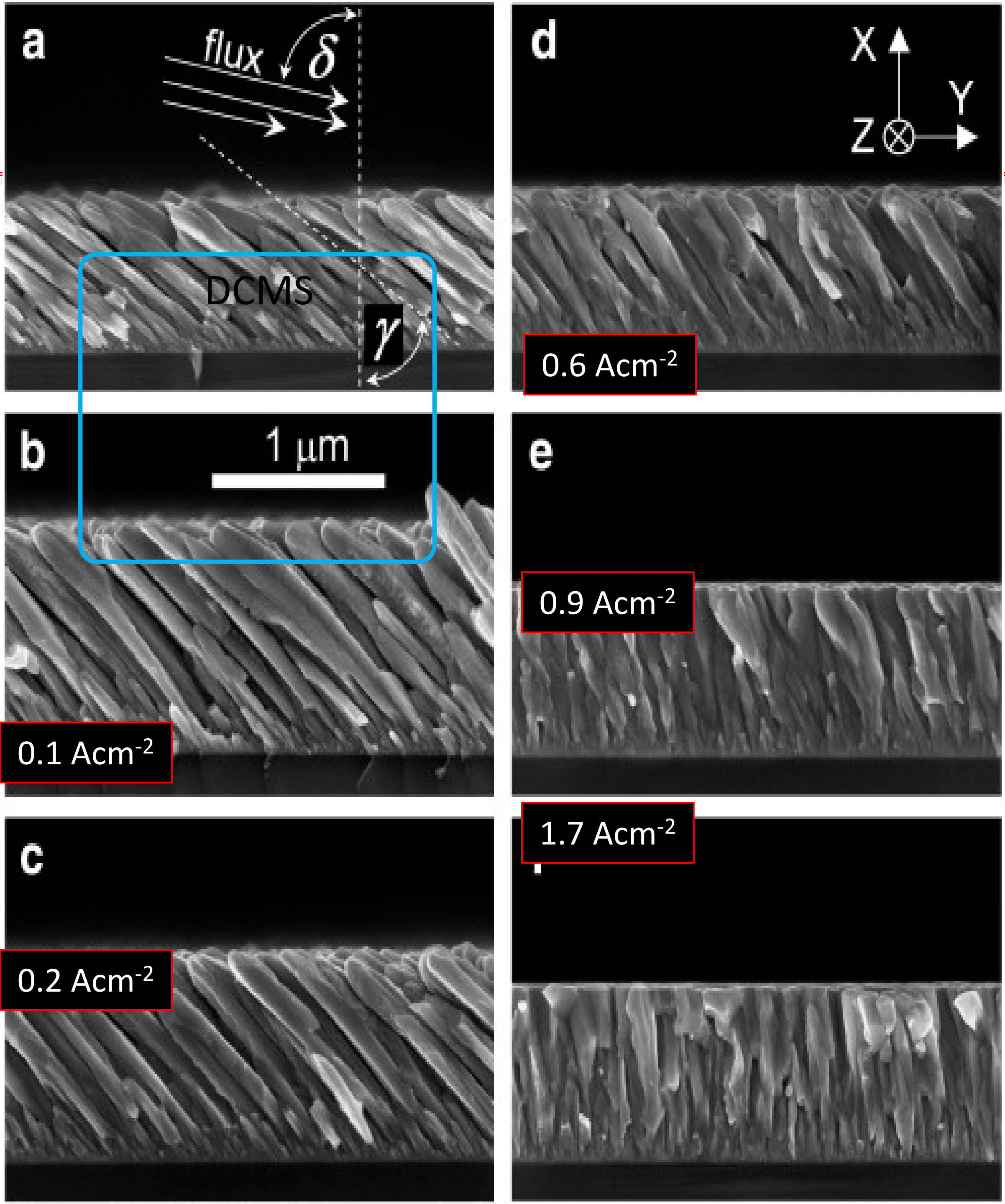
J. Andersson, *et al*., IEEE Trans. Plasma Sci. **42** (2014) 2856.

BF XTEM Image of TiAlCN/VCN Superlattice Structured Coatings

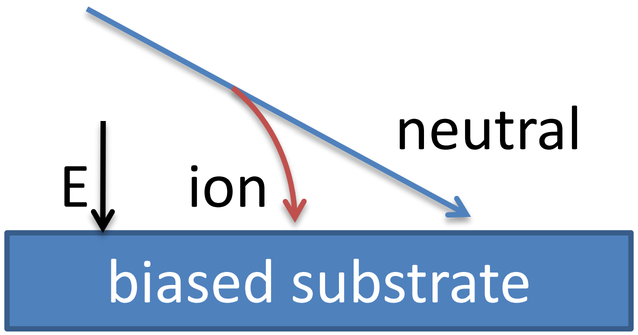


P.E. Hovsepian, *et al*., Plasma Processes and Polymers **4** (2007) S897.

CrN Glancing Angle Deposition

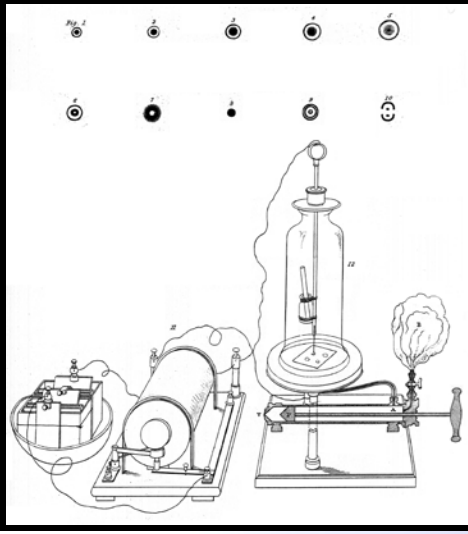


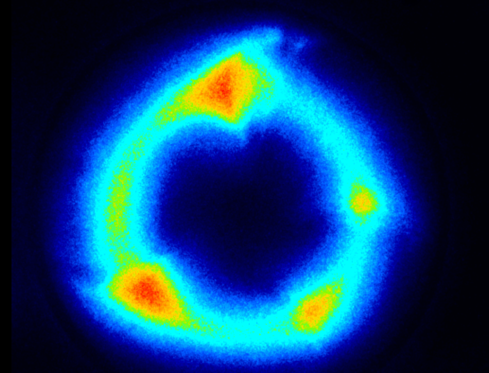
Inclination of Columns is reduced at high target current densities due to high ion-to-neutral ratio

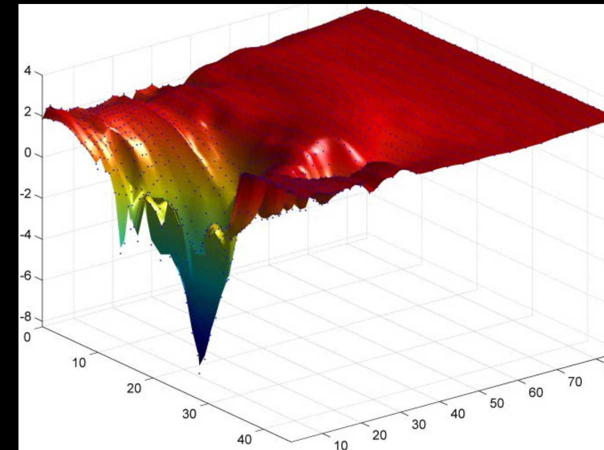


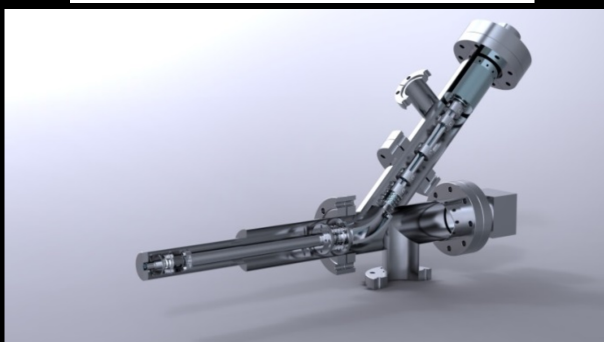
G. Greczynski, *et al.*, Thin Solid Films **519** (2011) 6354.

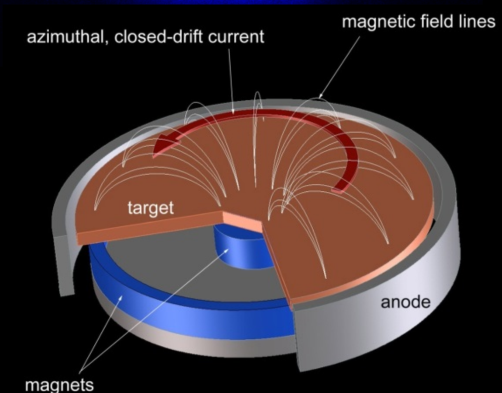
Summary

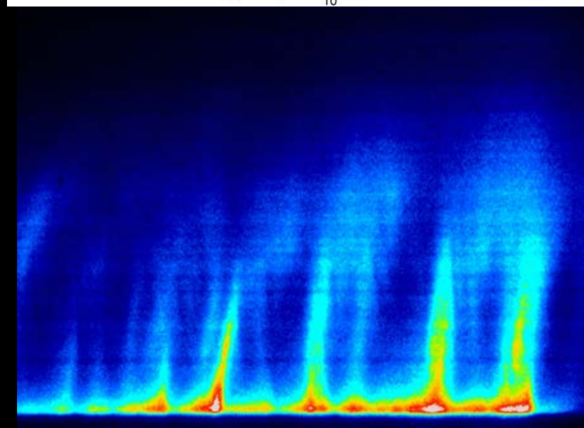


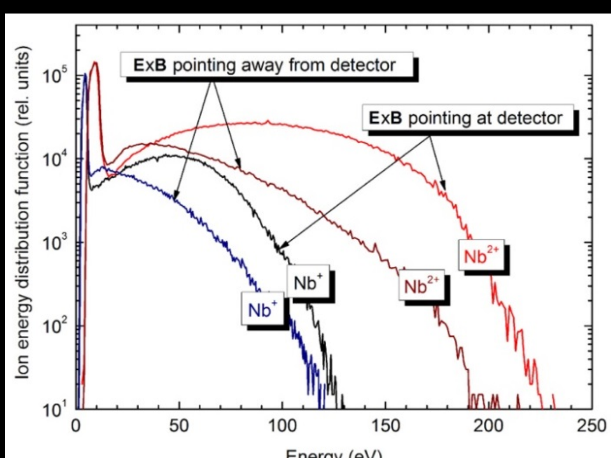


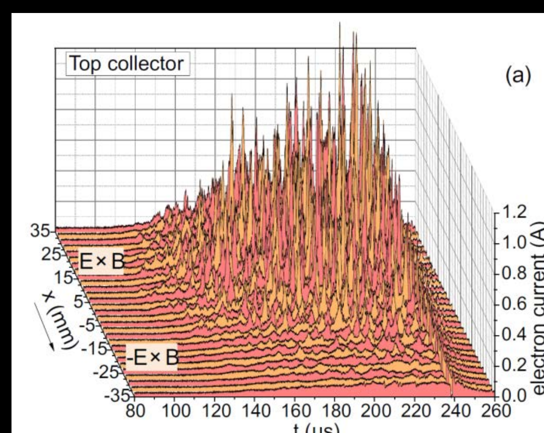


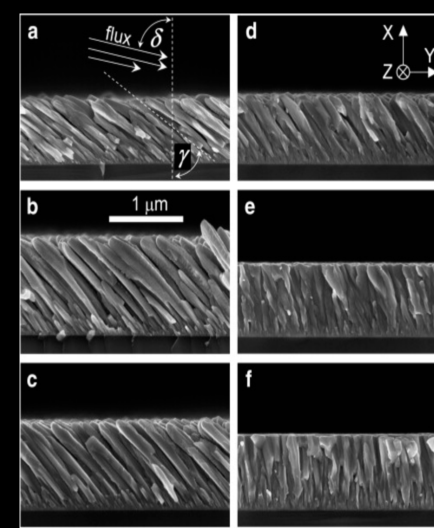



azimuthal, closed-drift current
magnetic field lines
target
anode
magnets




ExB pointing away from detector
ExB pointing at detector
Ion energy distribution function (rel. units)
Energy (eV)
Nb^+
Nb^+
Nb^{2+}
Nb^{2+}


Top collector
(a)
E × B
-E × B
x (mm)
t (μs)
electron current (A)


a
flux
δ
γ
d
X
Y
Z
b
1 μm
e
c
f