Joint DESY and University of Hamburg Accelerator Physics Seminar
Tuesday, 16.02.2021 at 16:00 via ZOOM.

Plasma-based Coatings for Accelerators

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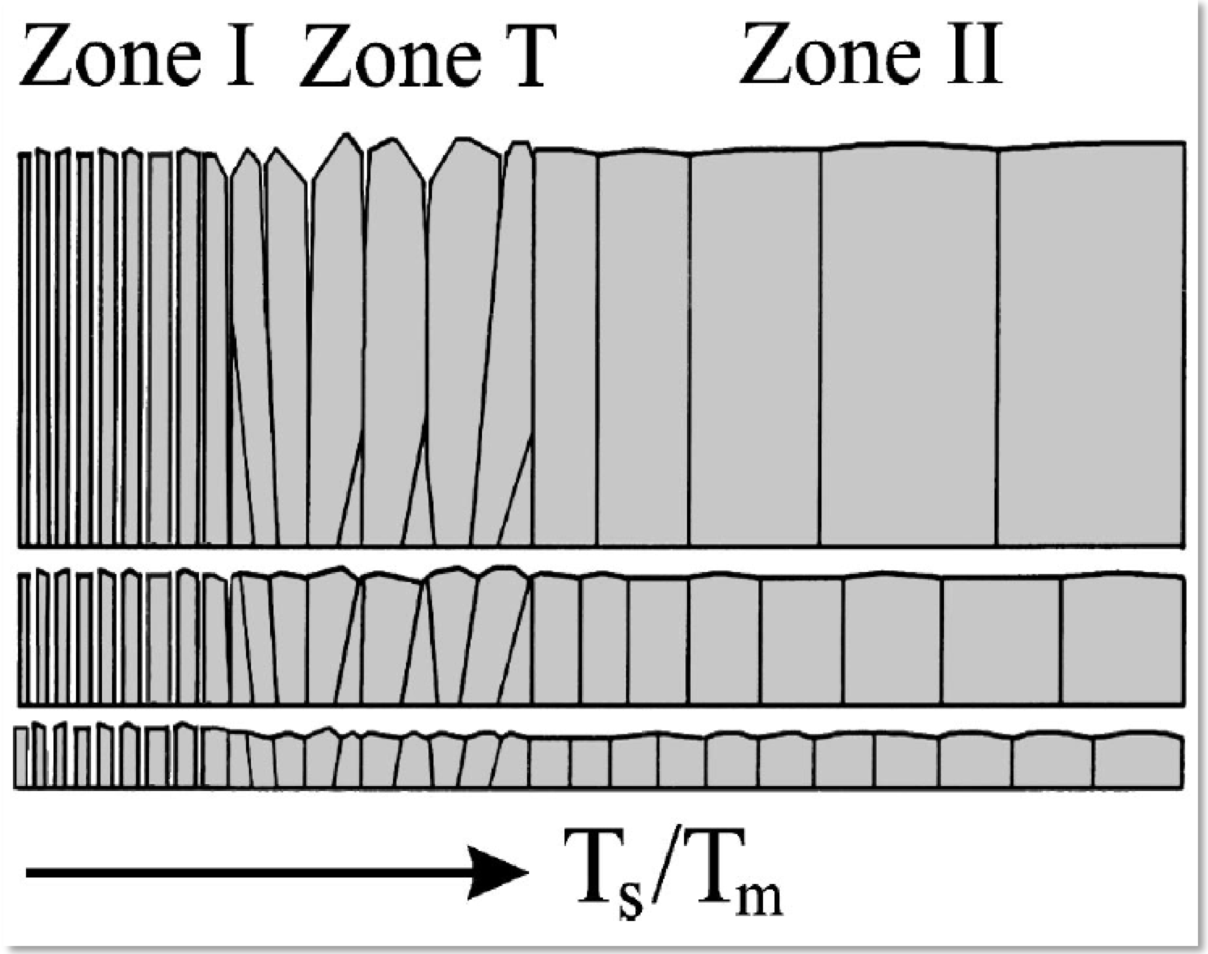
where much of this work was done

Special Thanks go to Joe Wallig and many former colleagues and guest of the Plasma Applications Group, Lawrence Berkeley National Laboratory, Berkeley, CA.

Outline

- (Plasma-based) deposition techniques (Introduction)
  - by evaporation
  - by ion-beam assisted evaporation
  - by magnetron sputtering
  - by cathodic arcs
  - by filtered cathodic arcs
- non-evaporative getter (NEG) coatings
- Cu and CuO coatings – high emissivity coatings
- Coatings for RF windows
- some other curious points…

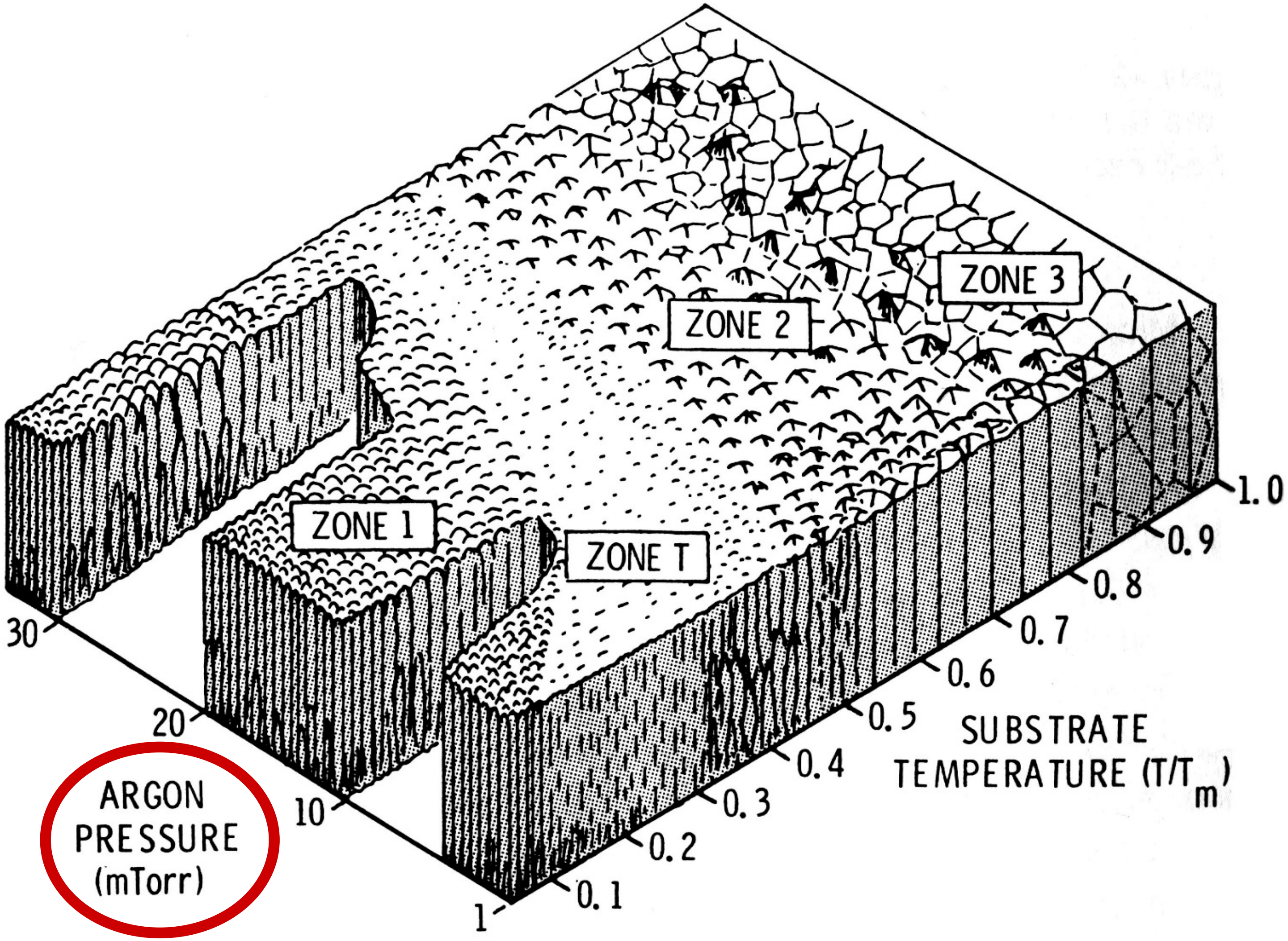
Structure Zone Diagram for Deposition by Evaporation



- Movchan-Demchishin: Film morphology as a function of Temperature
- Define homologous temperature T_s / T_m:
  - T_s – substrate temperature
  - T_m – melting point

B.A. Movchan, A.V. Demchishin, Fizika Metallov i Metallovedenie (Physics of Metals and Metallography) 28 (1969) 653.
I. Petrov, et al., J. Vac. Sci. Technol. A 21 (2003) S117.

Thornton's Structure Zone Diagram for Sputtering



Contains the effects of energetic particle bombardment

J. A. Thornton, *J. Vac. Sci. Technol.* **11** (1974) 666

IOM

Ion Beam Assisted Deposition (IBAD)

- 1960s: Space propulsion ion sources available
- Use of such sources to accomplish densification effects, as already known by ion plating

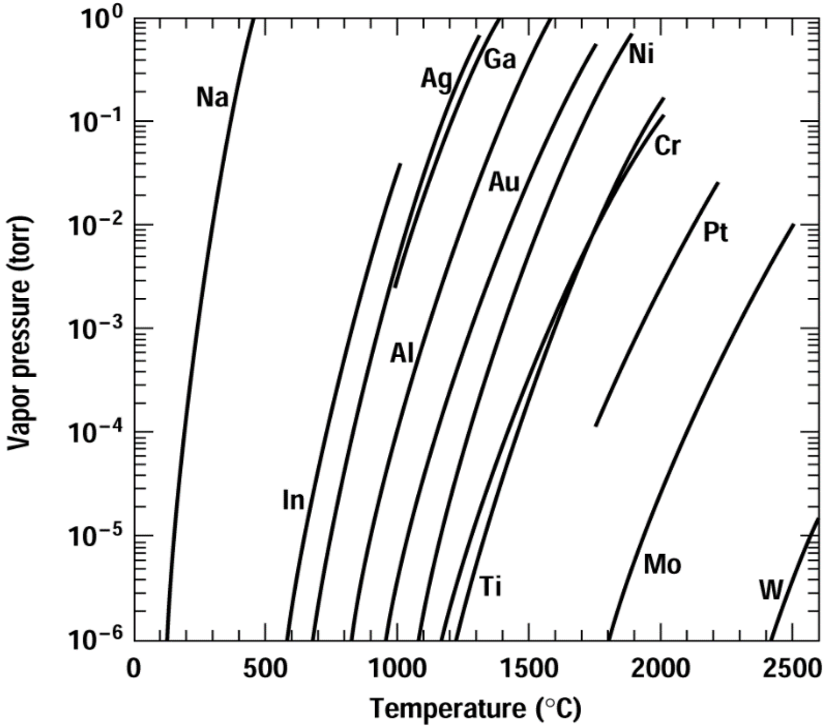
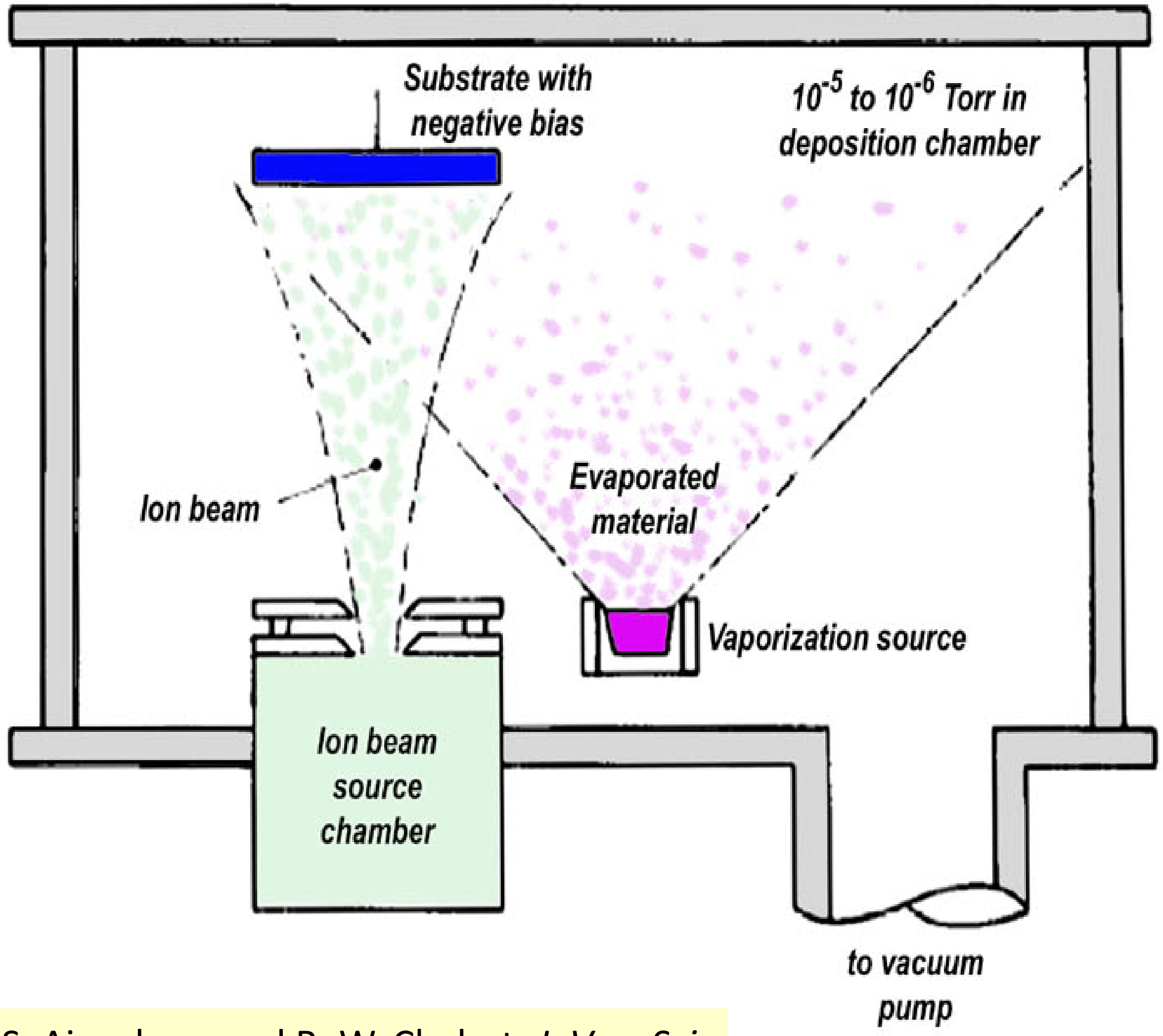


Figure 12.2 Vapor pressure curves for some commonly evaporated materials *(data adapted from Alcock et al.)*.



S. Aisenberg and R. W. Chabot, *J. Vac. Sci. Technol.* 10 (1973) 104.

Biasing: Controlling the Kinetic Energy of Ions upon Arrival on the Substrate Surface

Final kinetic energy is enhanced by acceleration in sheath adjacent to the substrate surface

$$E_i = E_0 + Qe\underbrace{\left(V_{plasma} - V_{surface}\right)}_{V_{sheath}}$$

kinetic energy in plasma before acceleration

ion charge state number

V_{sheath} is usually determined by bias

A more complete consideration includes all kinds of potential energies:

$$E_i = E_0 + Qe\left(V_{plasma} - V_{surface}\right) + E_{coh} + E_{exe} + \sum_{Q'=1}^{Q} E_{Q'}$$

A. Anders, Appl. Phys. Lett. **80** (2002) 1100.

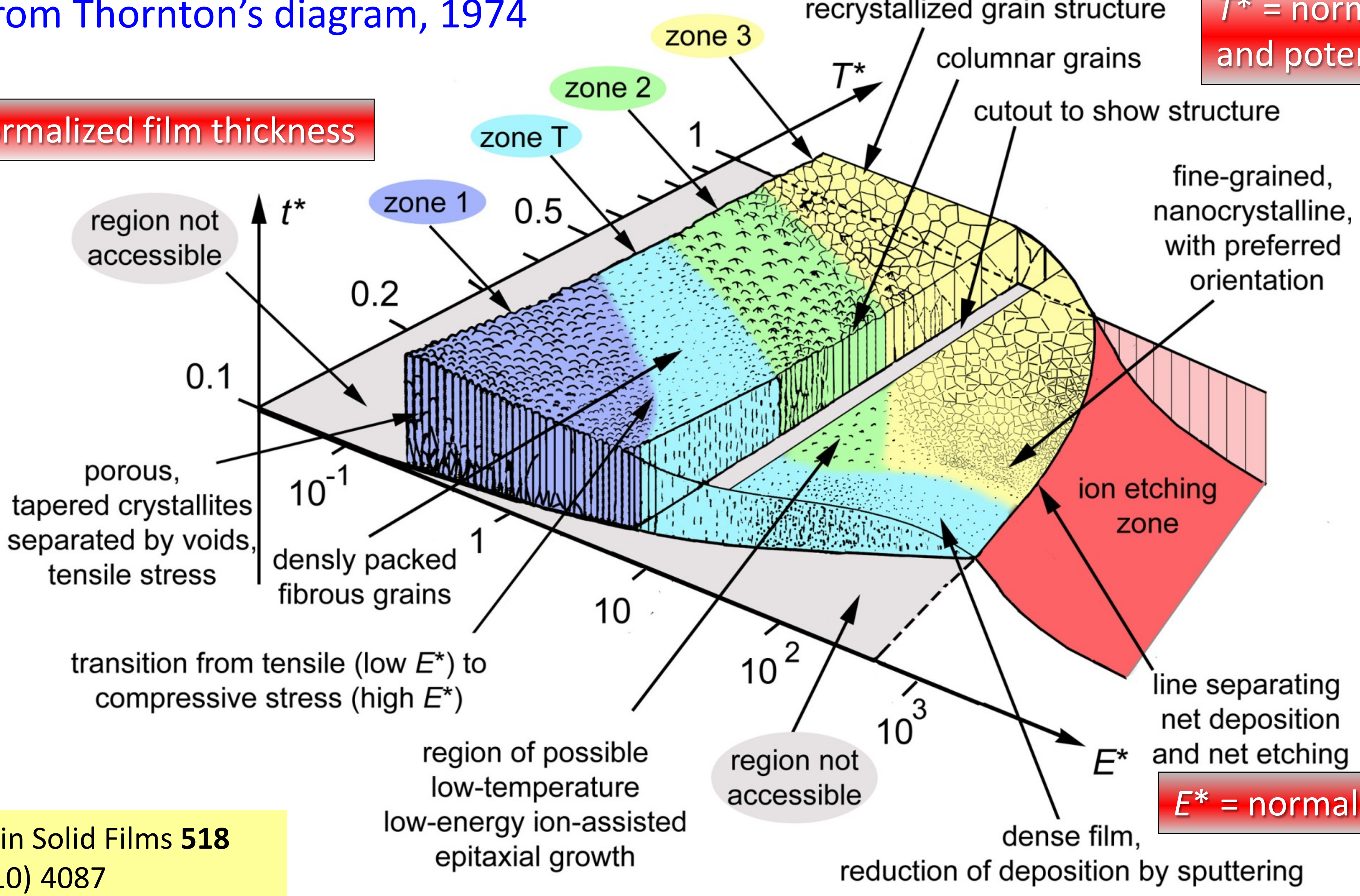
IOM

Generalized Structure Zone Diagram including the Effects of Plasma Assistance on Films

derived from Thornton's diagram, 1974

T^* = normalized temperature and potential energy

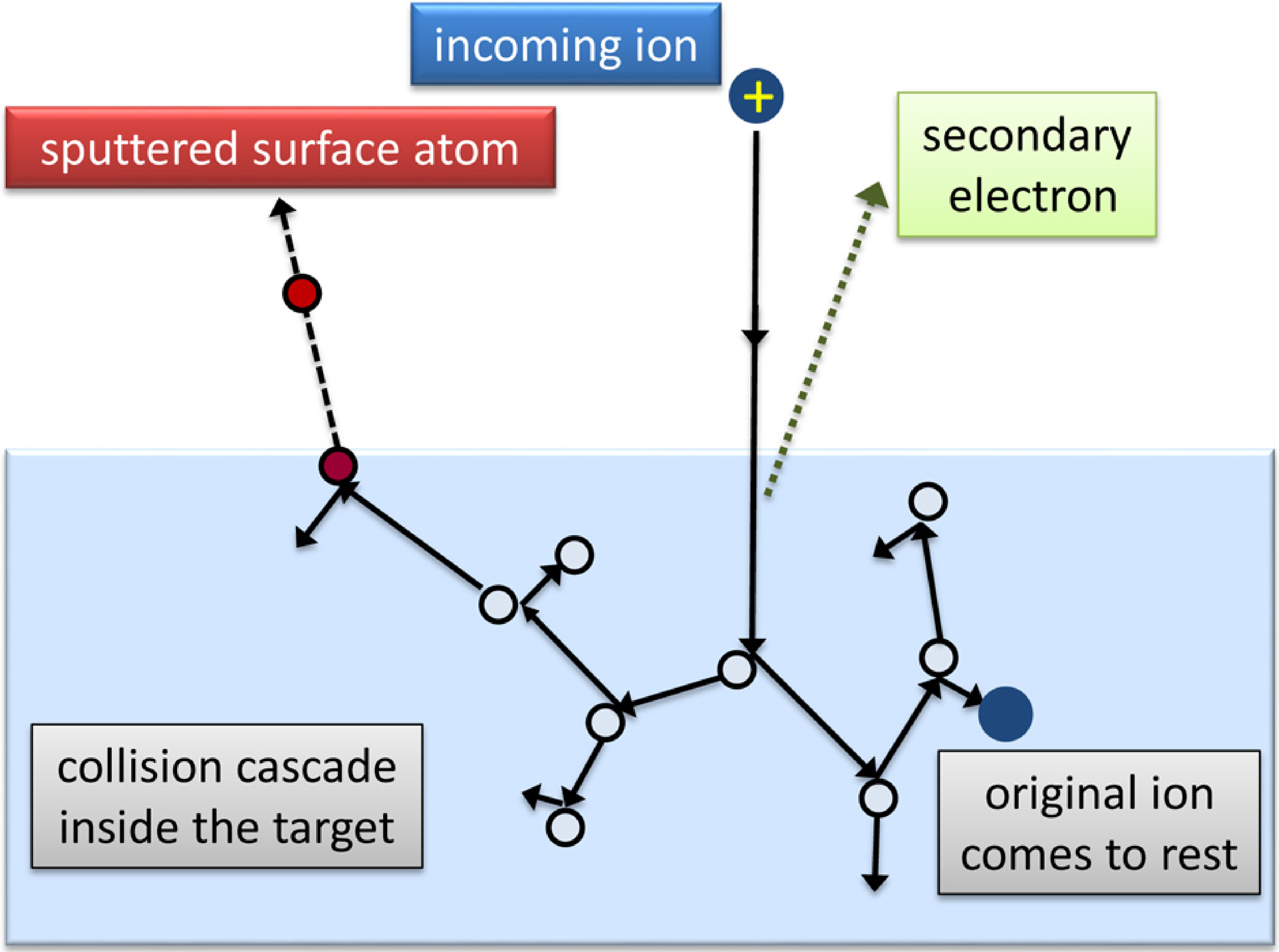
t^* = normalized film thickness



E^* = normalized kinetic energy

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

The Sputtering Process

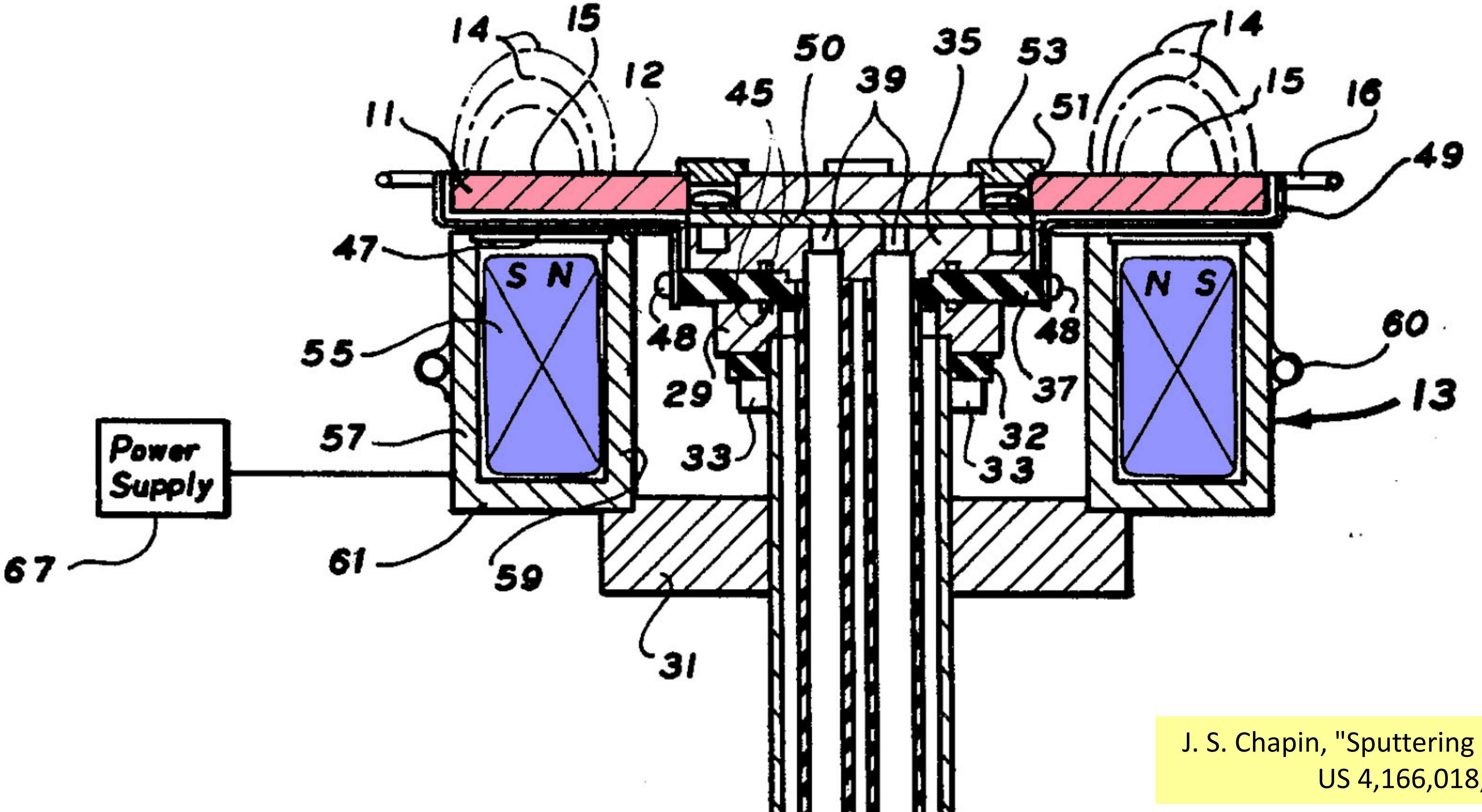


R. Behrisch, W. Eckstein (Eds.), Sputtering by Particle Bombardment, Springer, Berlin, 2007.

D. Depla, S. Mahieu (Eds.), Reactive Sputter Deposition, Springer, Heidelberg, 2008.

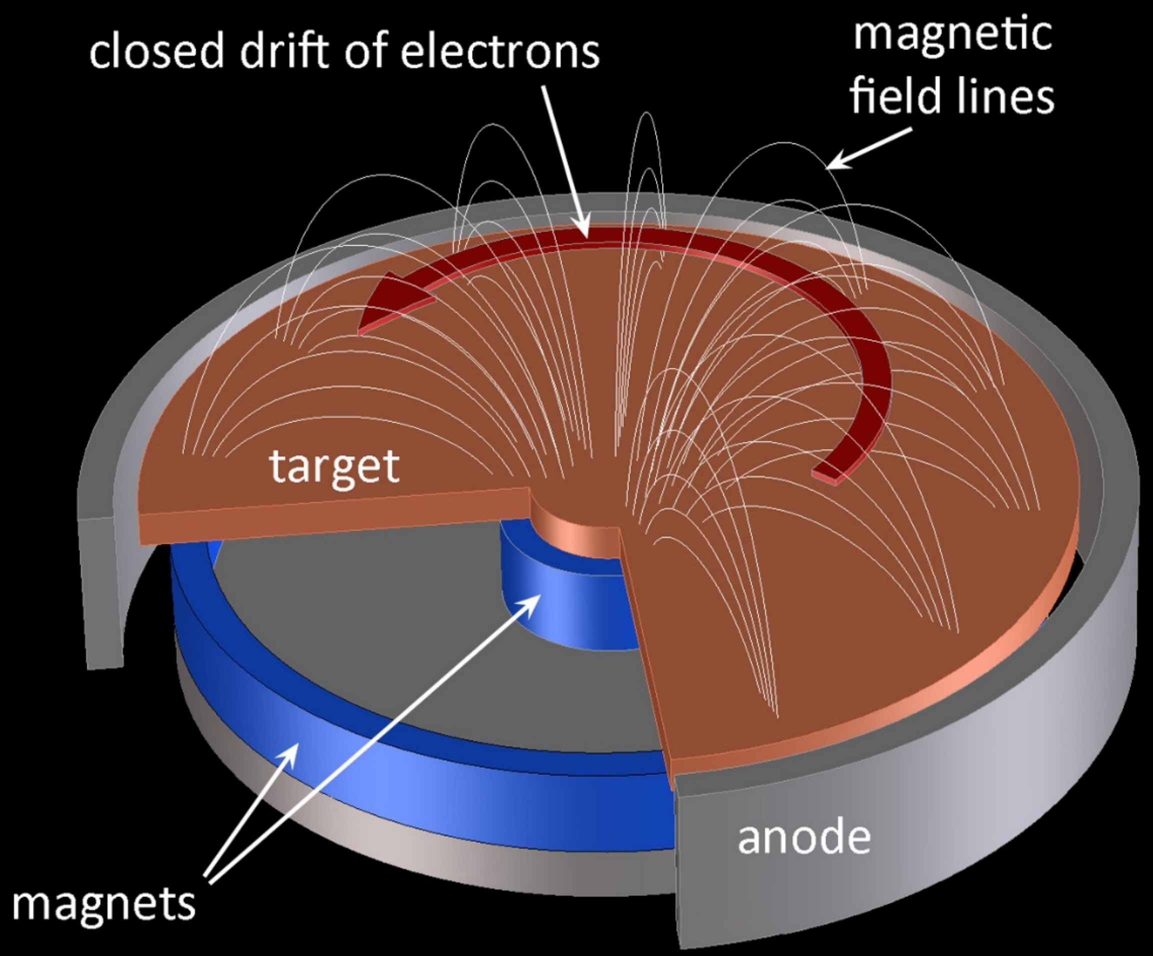
A. Anders, J. Appl. Phys. 121 (2017) 171101 (Tutorial).

early 1970s: Planar Magnetron



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

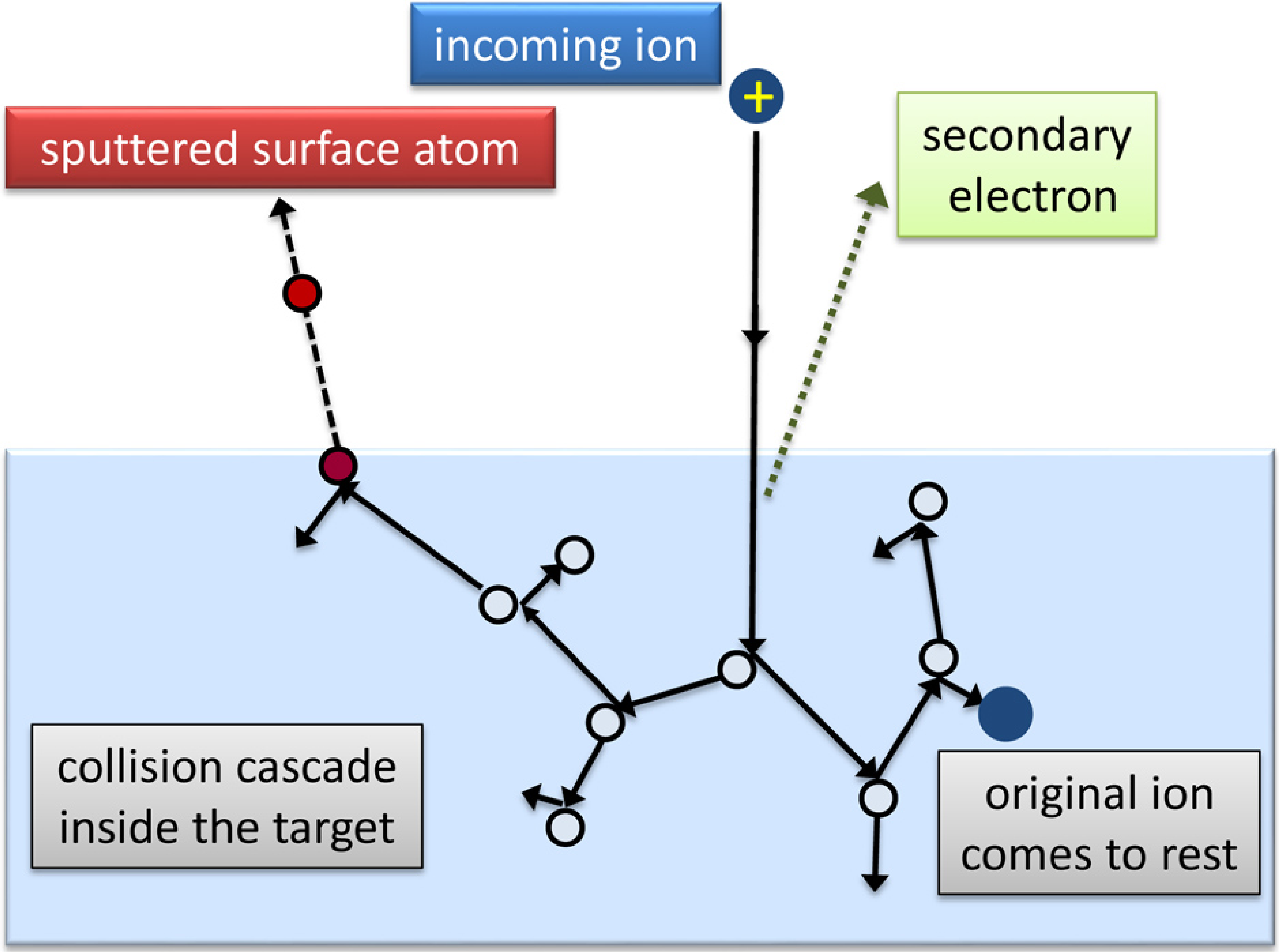
Magnetron as an electron trap and a source of target atoms



- target is a magnetic mirror as well as an electrostatic reflector for electrons
- electron *cyclotron motion* around field lines, resulting in closed azimuthal drift, the *magnetron motion*
- electrons cause ionization, and ions sputter the "race track" under the drift zone

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

The Sputtering Process



R. Behrisch, W. Eckstein (Eds.), Sputtering by Particle Bombardment, Springer, Berlin, 2007.

D. Depla, S. Mahieu (Eds.), Reactive Sputter Deposition, Springer, Heidelberg, 2008.

A. Anders, J. Appl. Phys. 121 (2017) 171101 (Tutorial).

1980s: The Unbalanced Magnetron

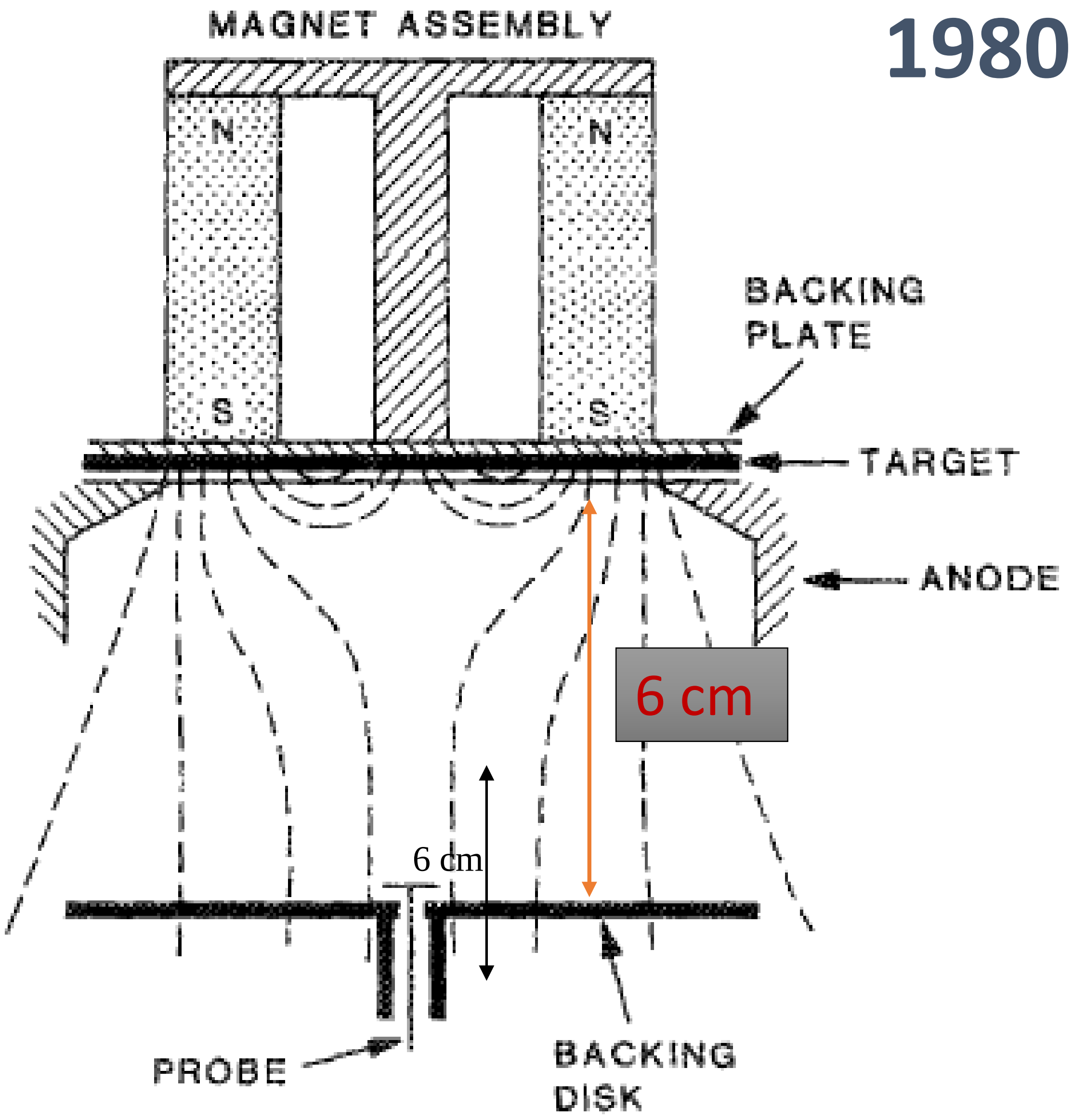


FIG. 1. Magnetron and probe assembly are shown schematically. For the measurements reported here the target to probe distance was maintained at 60 mm.

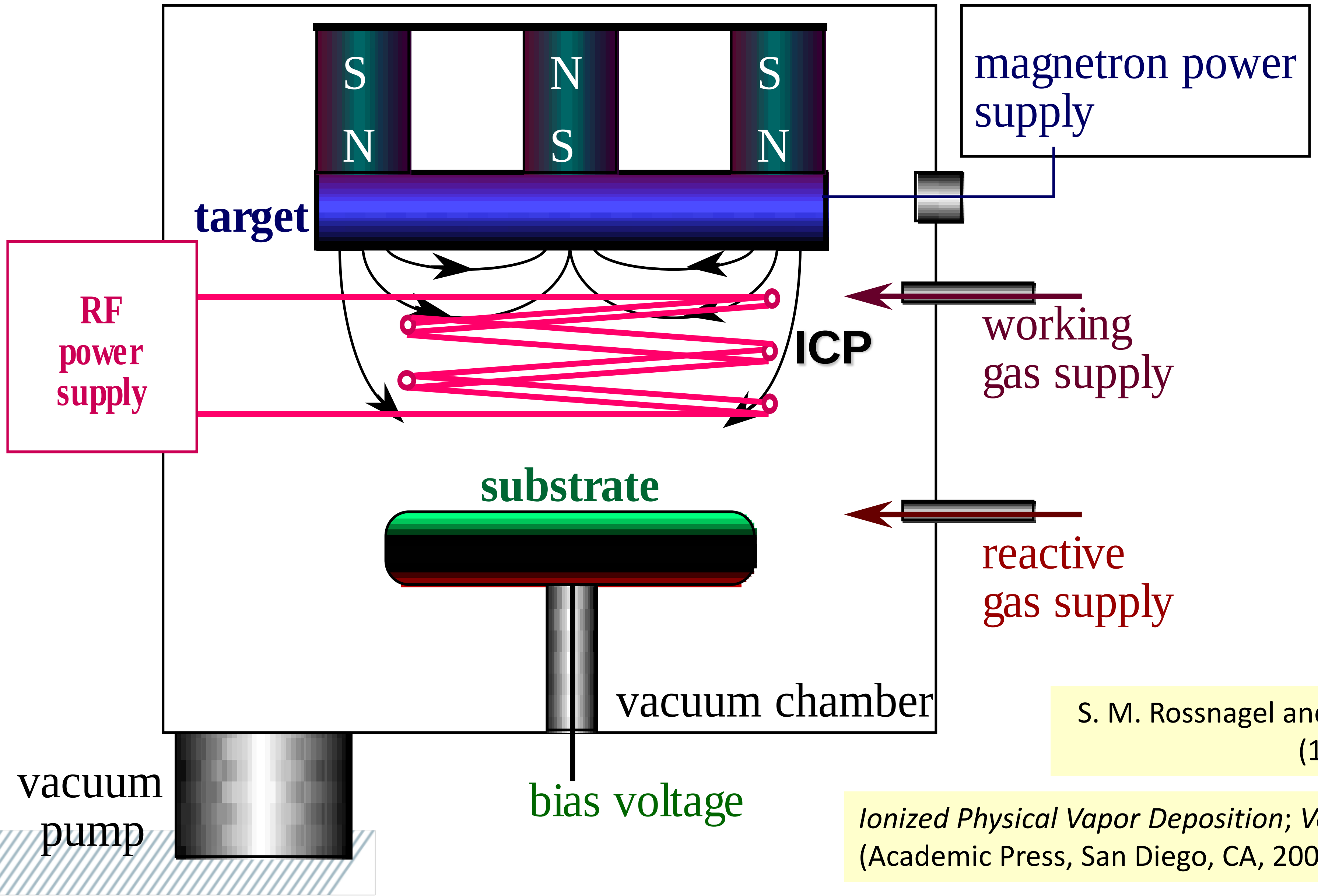
- A first step to using the plasma of the magnetron to assist film growth
- Unbalanced magnetic field allows electrons and ions to escape from target, providing a means of ion assistance
- n_e ~ 10^{12} cm^{-3}, for up to a distance of 10 cm.

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

Co-Sputtering, here with unbalanced magnetrons

Beam-like excitation (light) is indicative for an unbalanced magnetron

1990s: i-PVD = Magnetron Discharge with Ionization



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

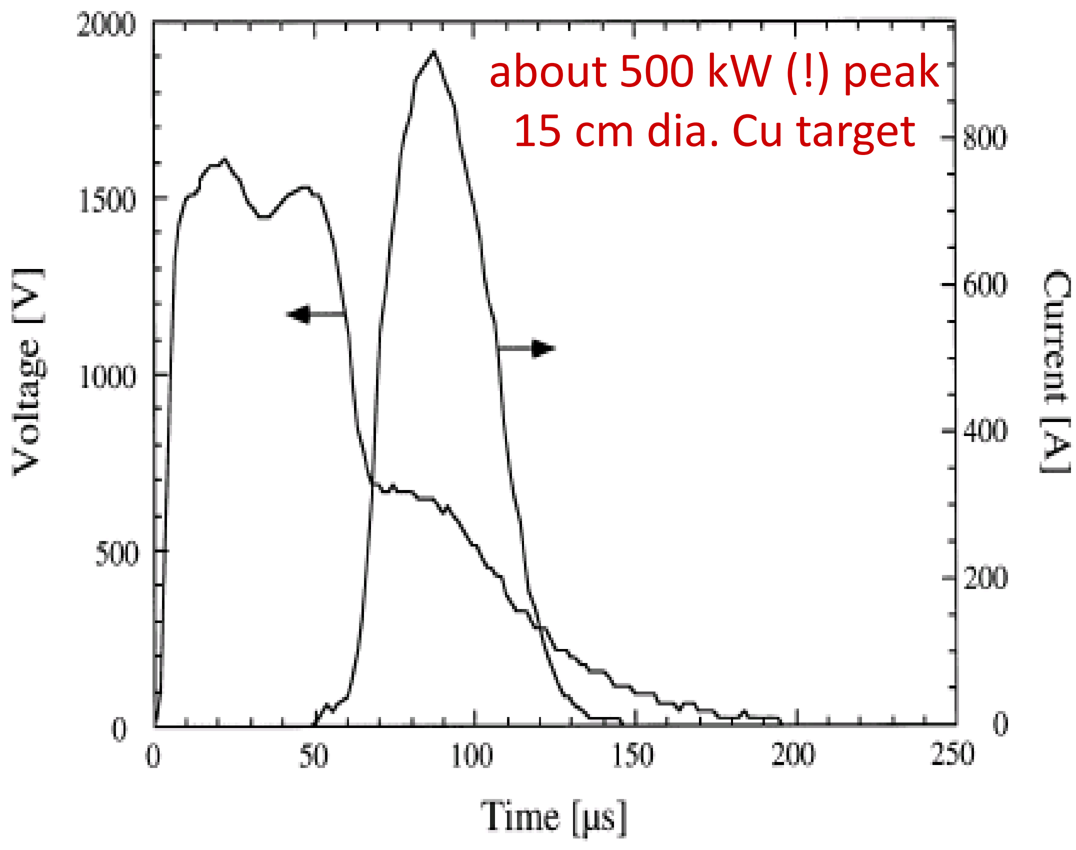
Ionized Physical Vapor Deposition; *Vol.*, edited by J. A. Hopwood (Academic Press, San Diego, CA, 2000).

HiPIMS: A Form of "Ionized Sputtering."

"What distinguishes HIPIMS from the long-practiced pulsed sputtering?"

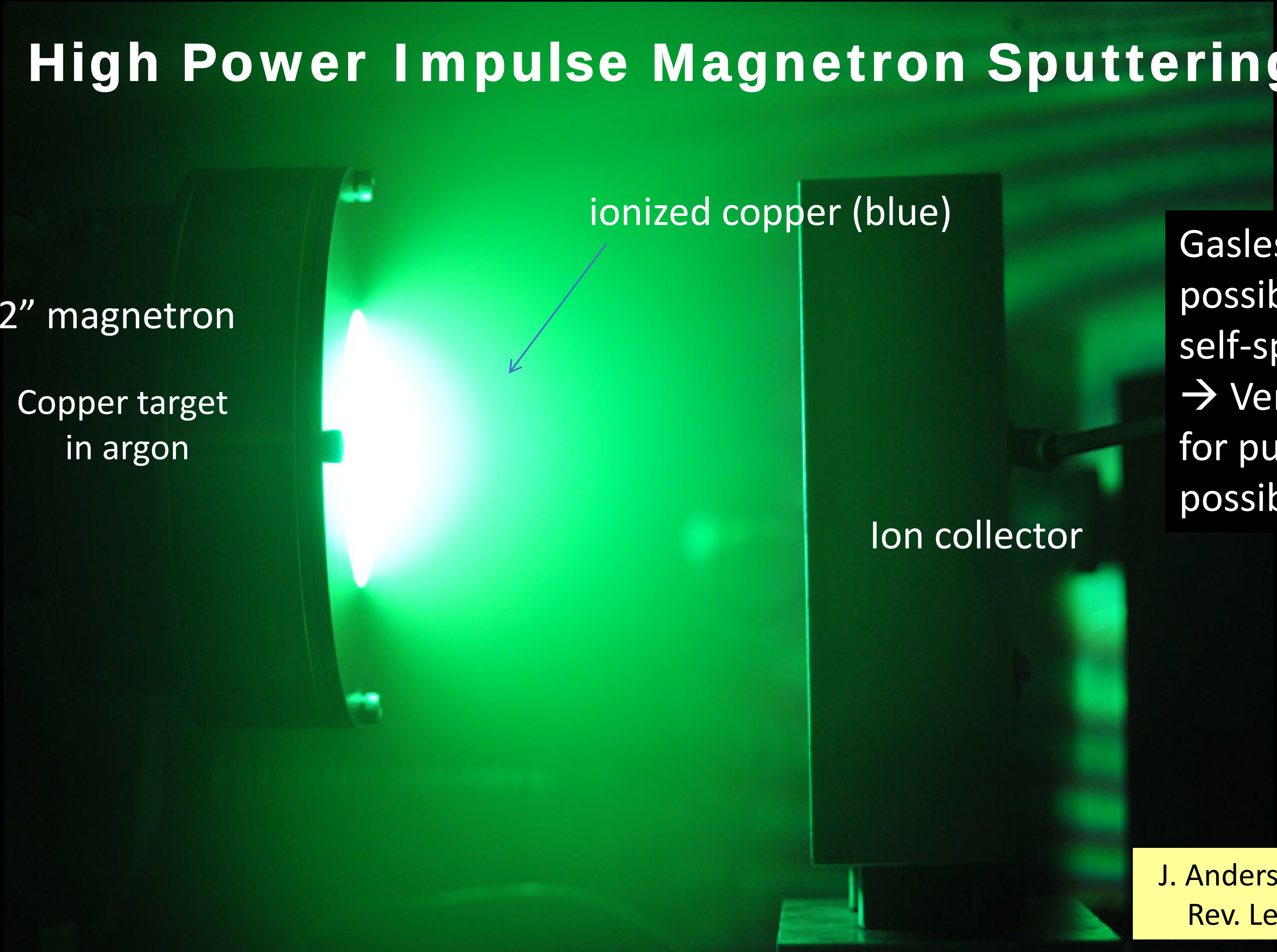
Technical Definition:
HiPIMS is pulsed sputtering where the peak power exceeds the average power by typically two orders of magnitude.
(implies a long pause between pulses, hence the term "impulse")

Physical Definition:
HiPIMS is pulsed sputtering where a very significant fraction of the sputtered atoms becomes ionized.
(implies that self-sputtering occurs, which may or may not be sustained by target ions)



seminal (but not first) HIPIMS paper:
V. Kouznetsov, *et al.*, Surf. Coat. Technol. **122** (1999) 290

High Power Impulse Magnetron Sputtering (HiPIMS)

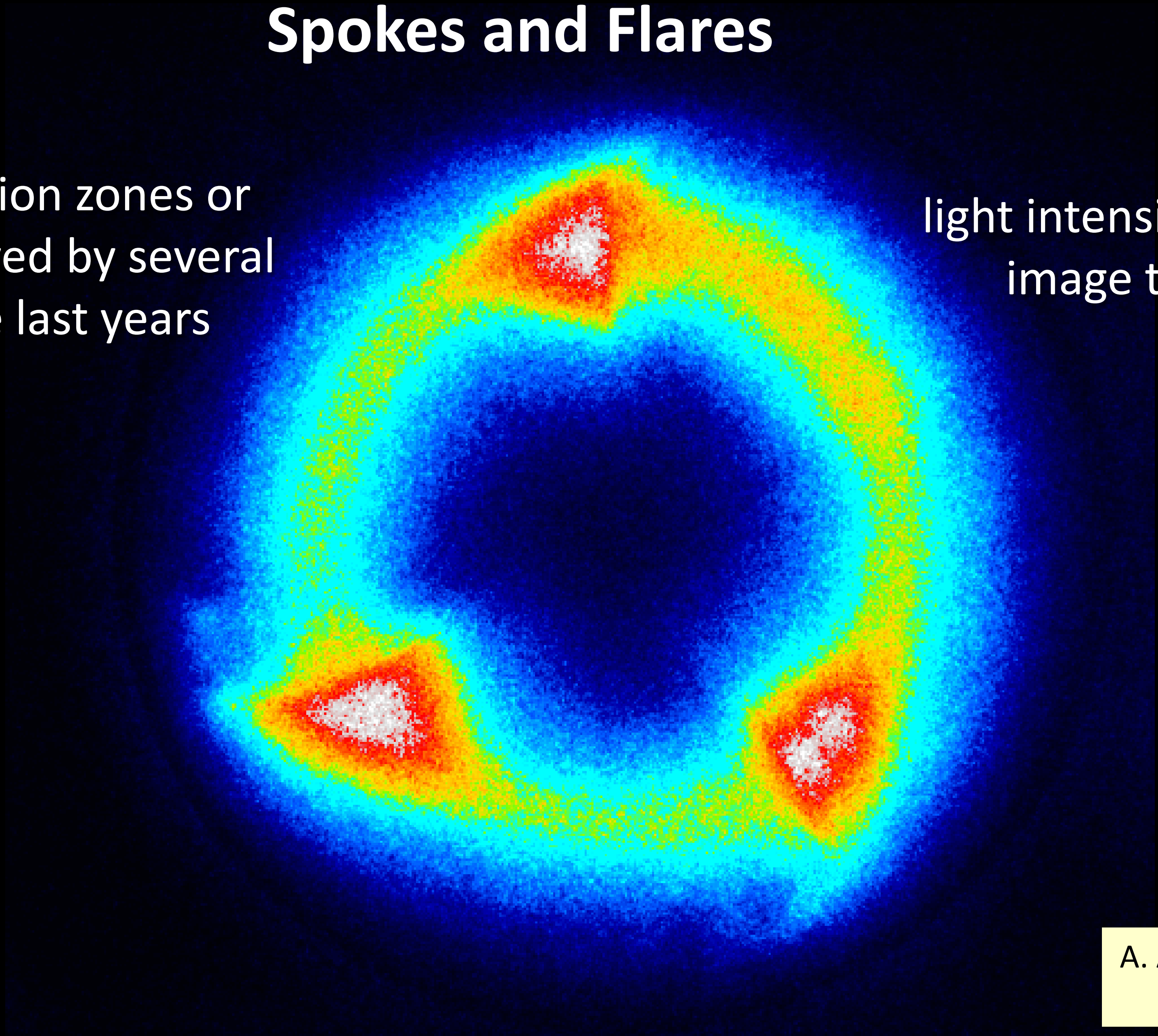


Gasless sputtering is possible for Cu (has high self-sputter yield)
→ Very efficient system for pure Cu-coatings possible

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

Localization of Ionization and Plasma Self-Organization in Spokes and Flares

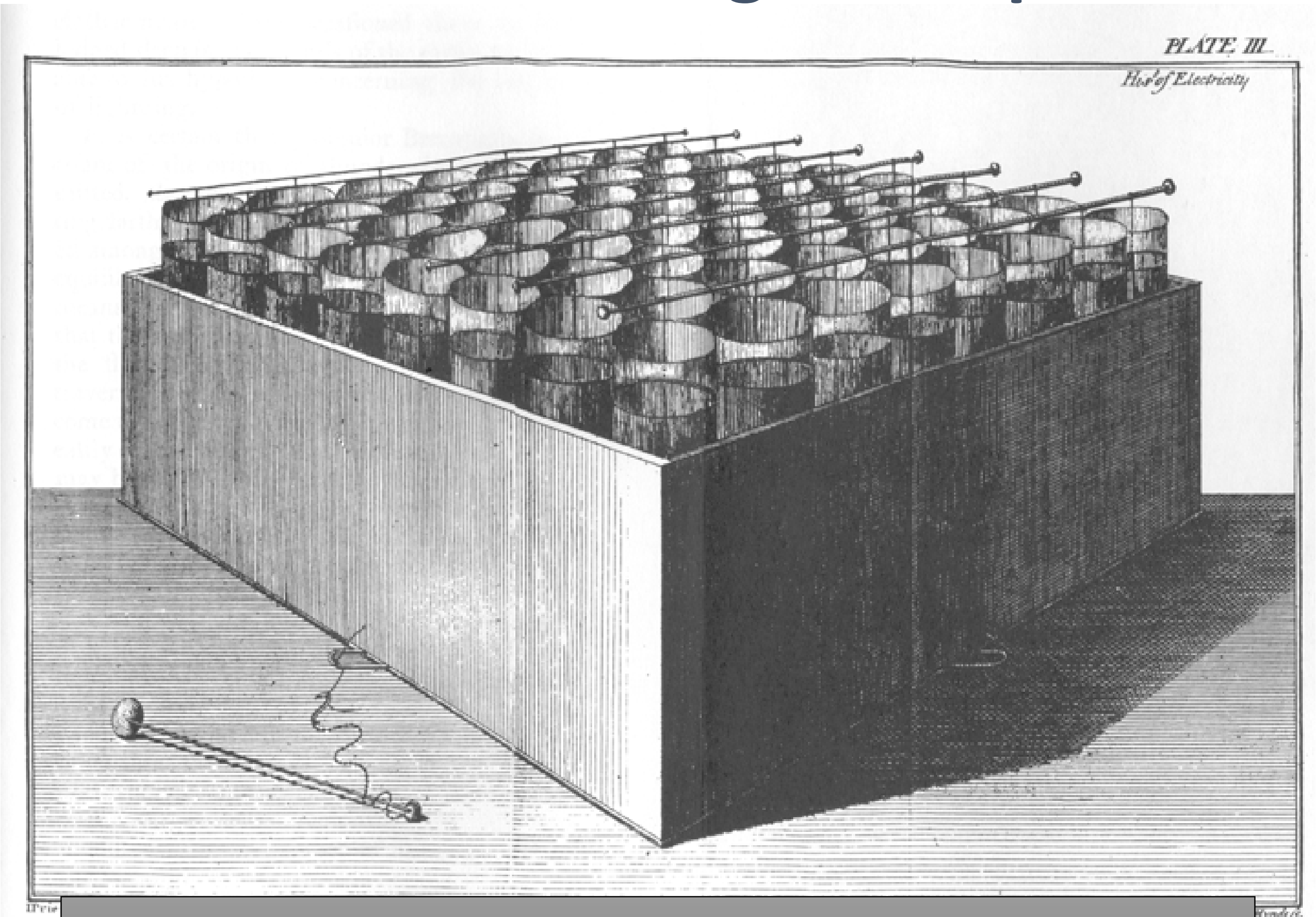
Moving ionization zones or "spokes" observed by several groups in the last years



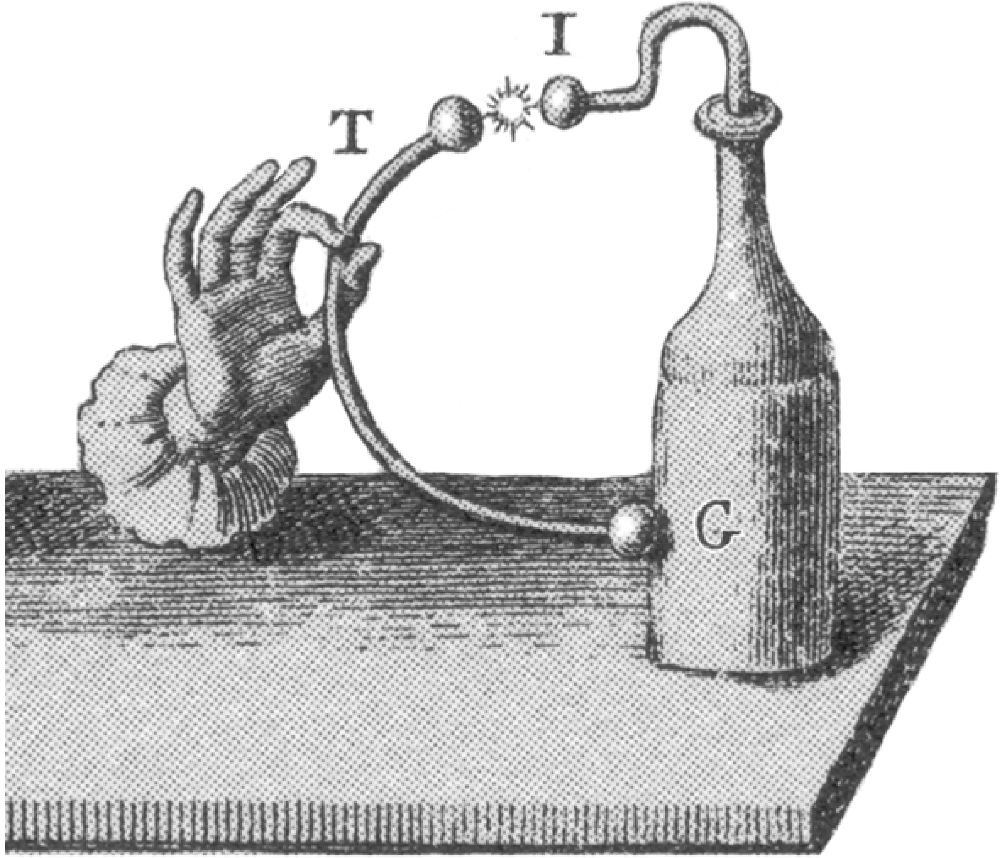
light intensity in false color, image taken in 5 ns

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

1766 - Joseph Priestley:
First Energetic Deposition by Pulsed Arcs in Air



Battery of Leyden Jars (capacitors), ca. 1760

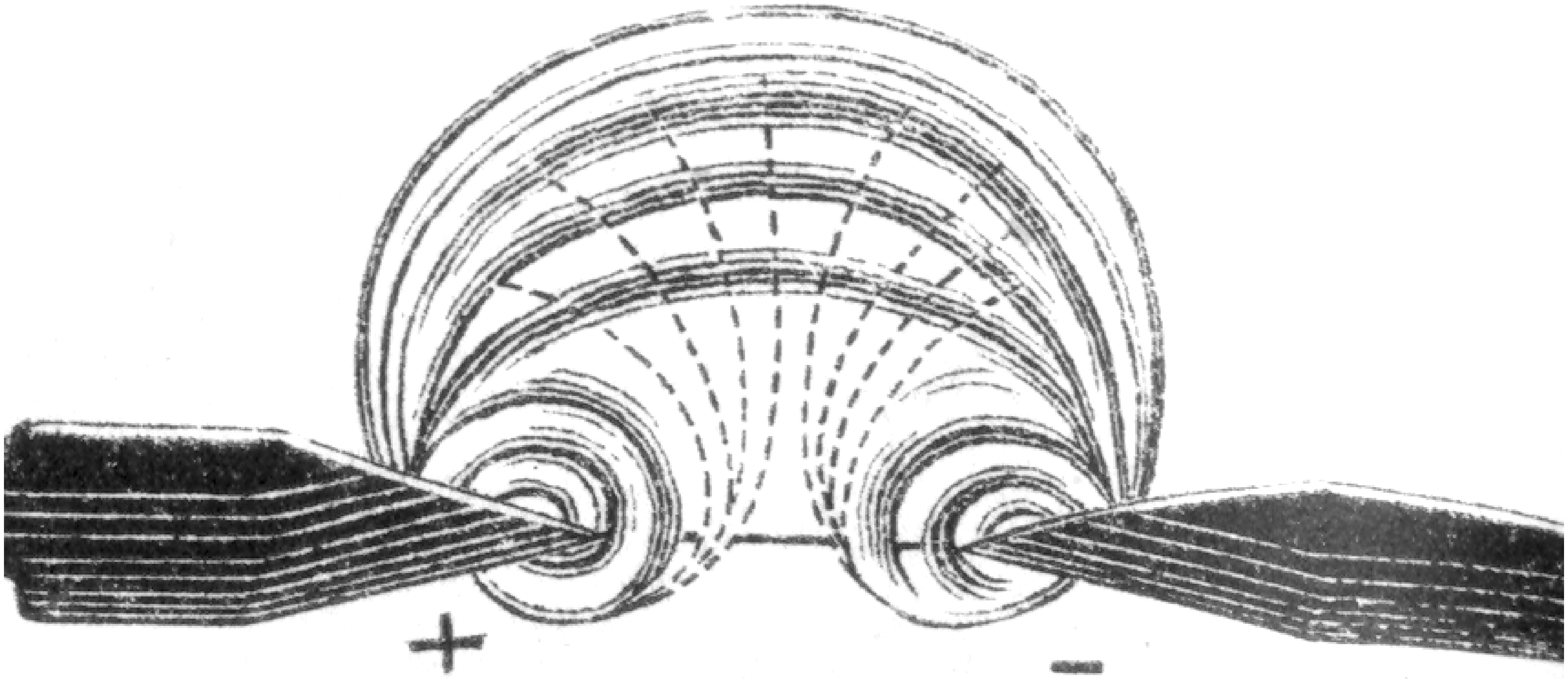


Alessandro Volta, ca. 1765

J. Priestley, The History and Present State of Electricity, London 1766

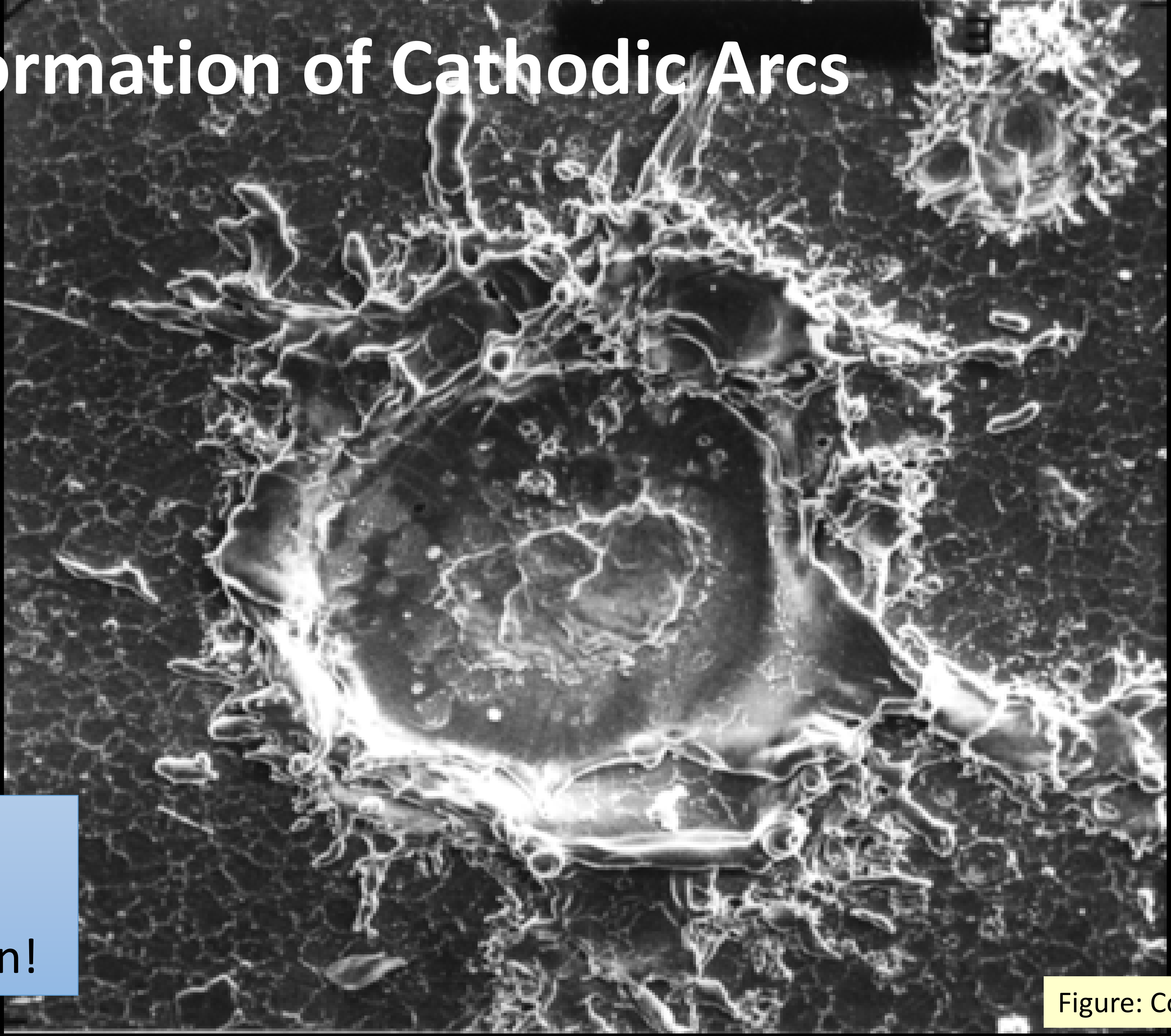
A. Anders, *IEEE Trans. Plasma Sci*. 31, 1052 (2003), and “Cathodic Arcs”, Springer, NY 2008.

Arc Discharge



G. Wiedemann, Die Lehre von der Elektricität, Braunschweig 1885

Plasma Formation of Cathodic Arcs

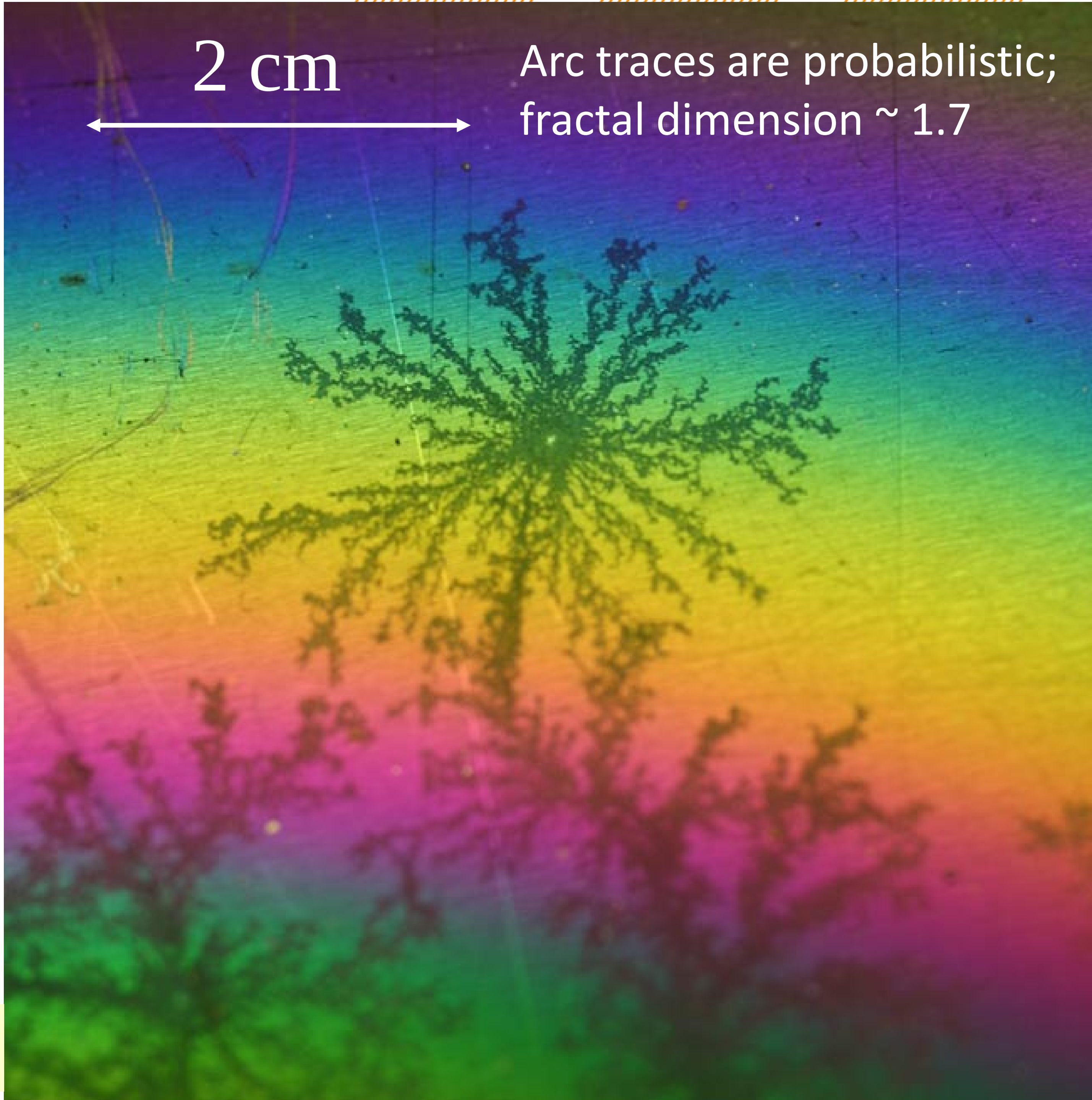


This is
- not sputtering!
- not evaporation!

Figure: Courtesy of B. Jüttner

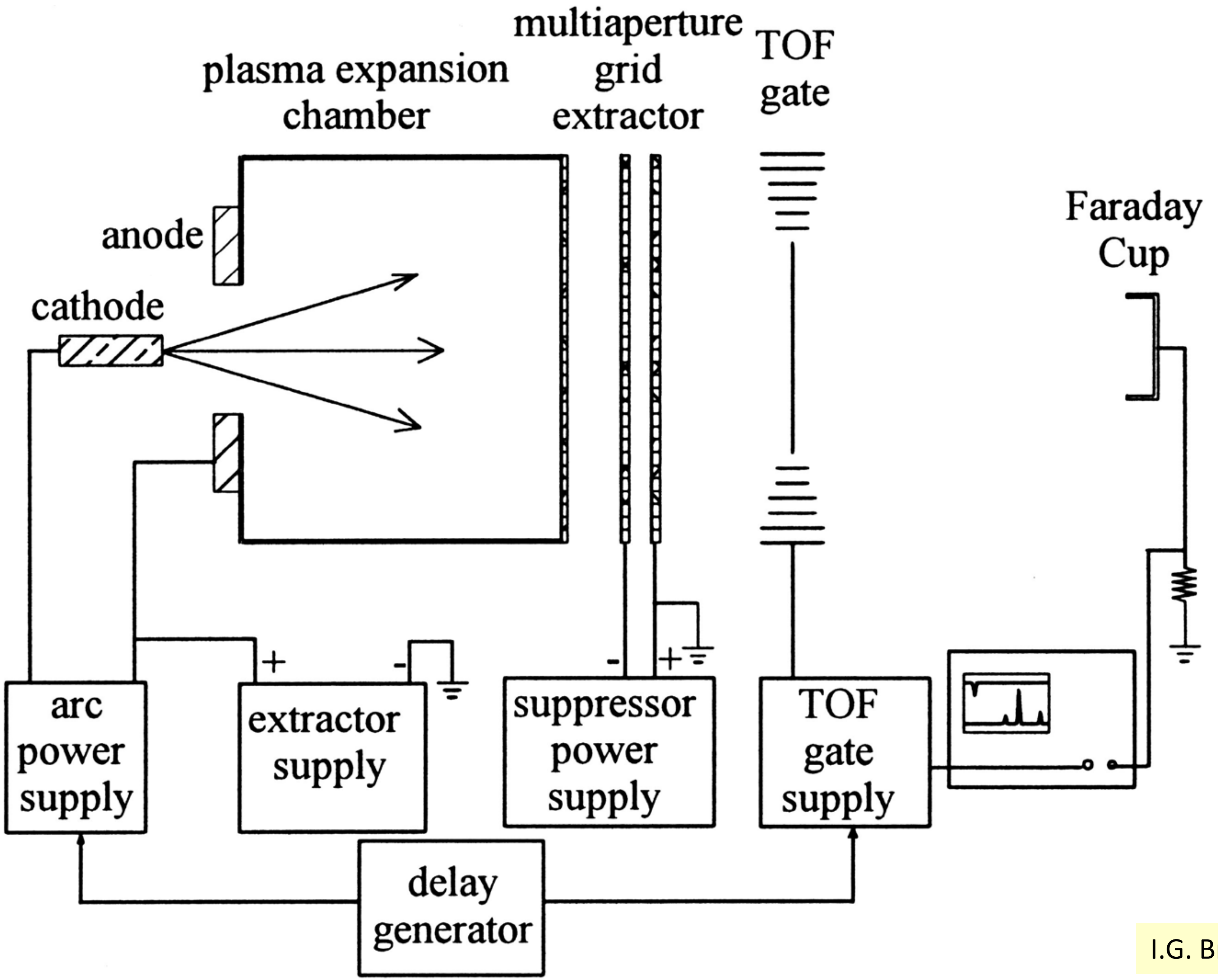
The Fractal Nature of Cathode Spots

- An object ("fractal") is self-similar (= invariant with scaling) if it is reproduced by magnifying some portion of it.
- Self-similarity may be discrete or continuous, deterministic or probabilistic.
- Self-similarity can be mathematically exact or only approximate and asymptotical.
- Physical fractals have scaling limits

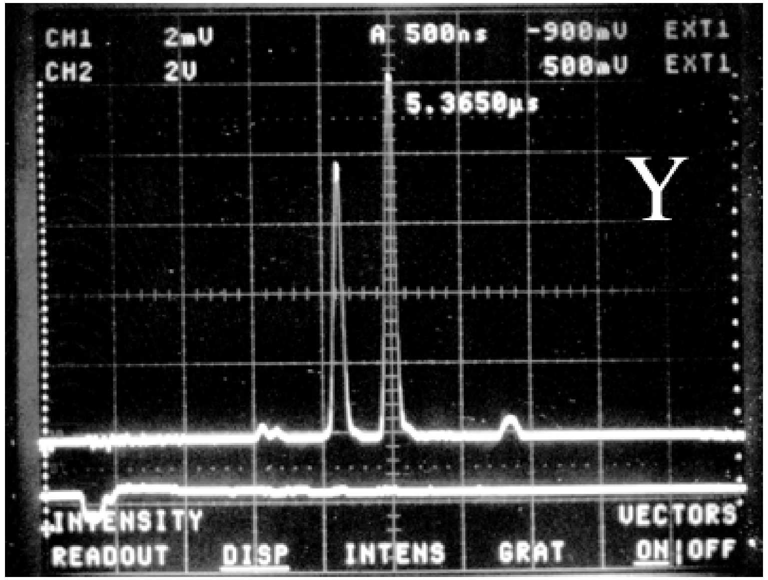


M. Schroeder, Fractals, Chaos, Power Laws, Freeman, N.Y., 2000
A. Anders, IEEE Trans. Plasma Sci. **33** (2005) 1456.

Ion Charge-State Spectrometry



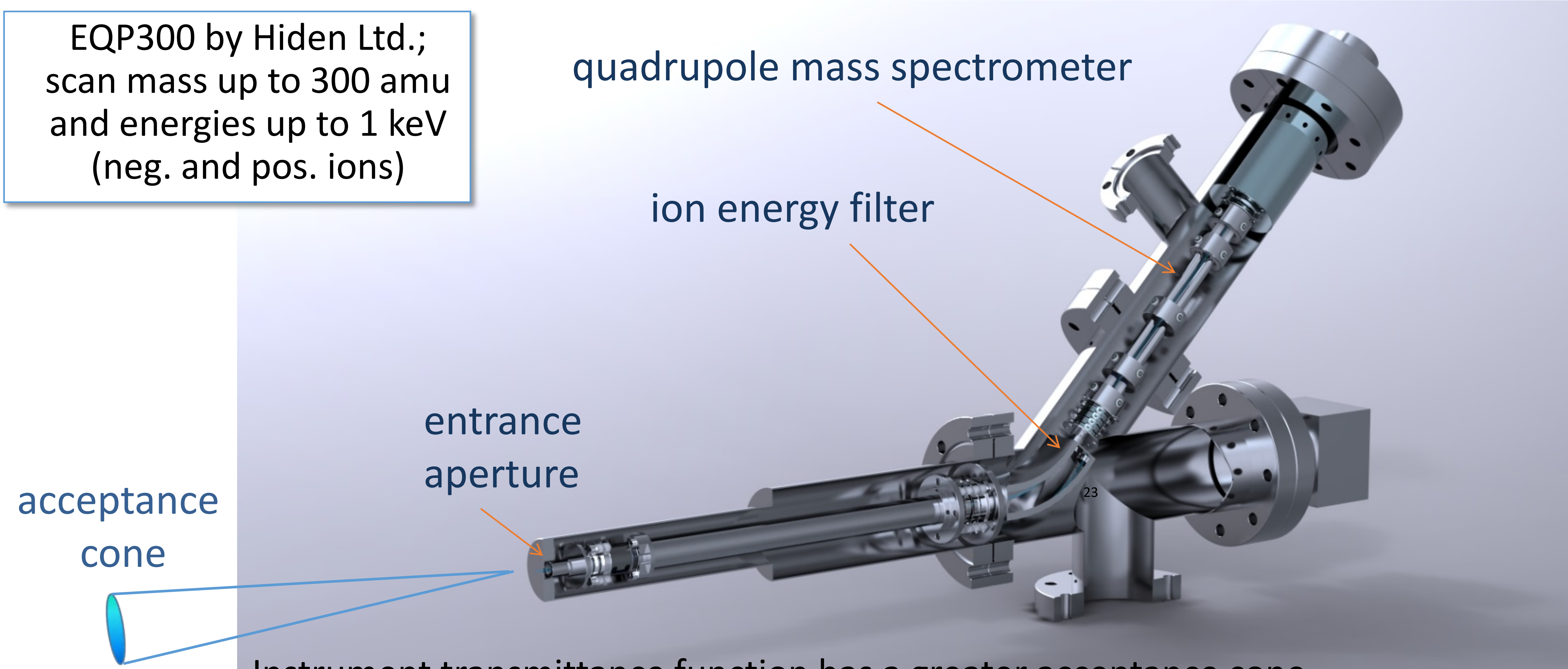
time-of-flight (TOF) method



I.G. Brown, et al., Rev. Sci. Instrum. 58 (1987) 1589.

Measurements of Ion Energy Distributions

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

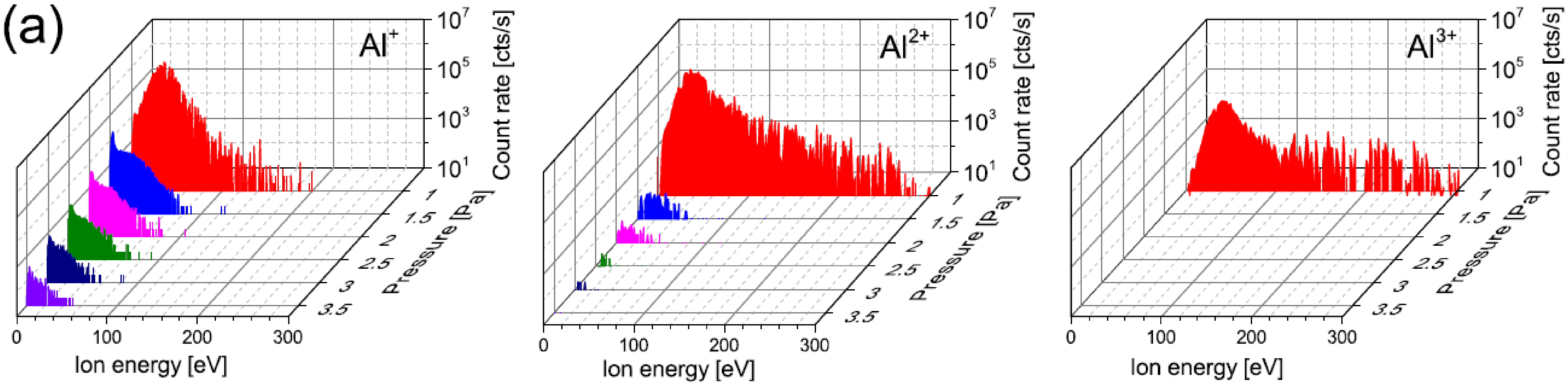


Instrument transmittance function has a greater acceptance cone angle for small (especially < 10 eV) ion energies

Effect of reactive gas on ion charge and energy distributions

Example here: Al cathode in O_2 atmosphere

- effects include collisions, mostly charge exchange collisions, and
- changes of plasma production due to changes of the chemical composition of the cathode itself ("poisoning")



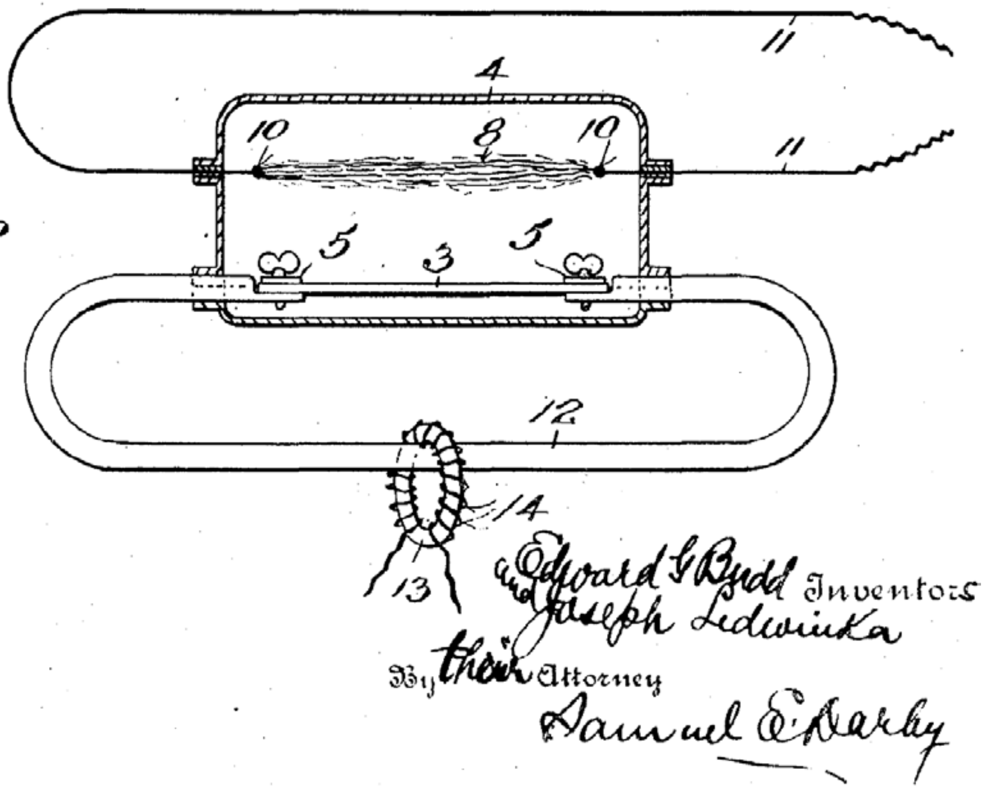
- Coatings by arc are dense (free of voids)!
- contain particulates ("macroparticle") unless plasma is filtered.

R. Franz, et al., Surf. Coat. Technol. 272 (2015) 309.

Getter materials: evaporative versus non-evaporative

Exploiting discharges producing gettering effects is long known

Fig. 2.



E. G. BUDD AND J. LEDWINKA.

METHOD OF ANNEALING METAL.

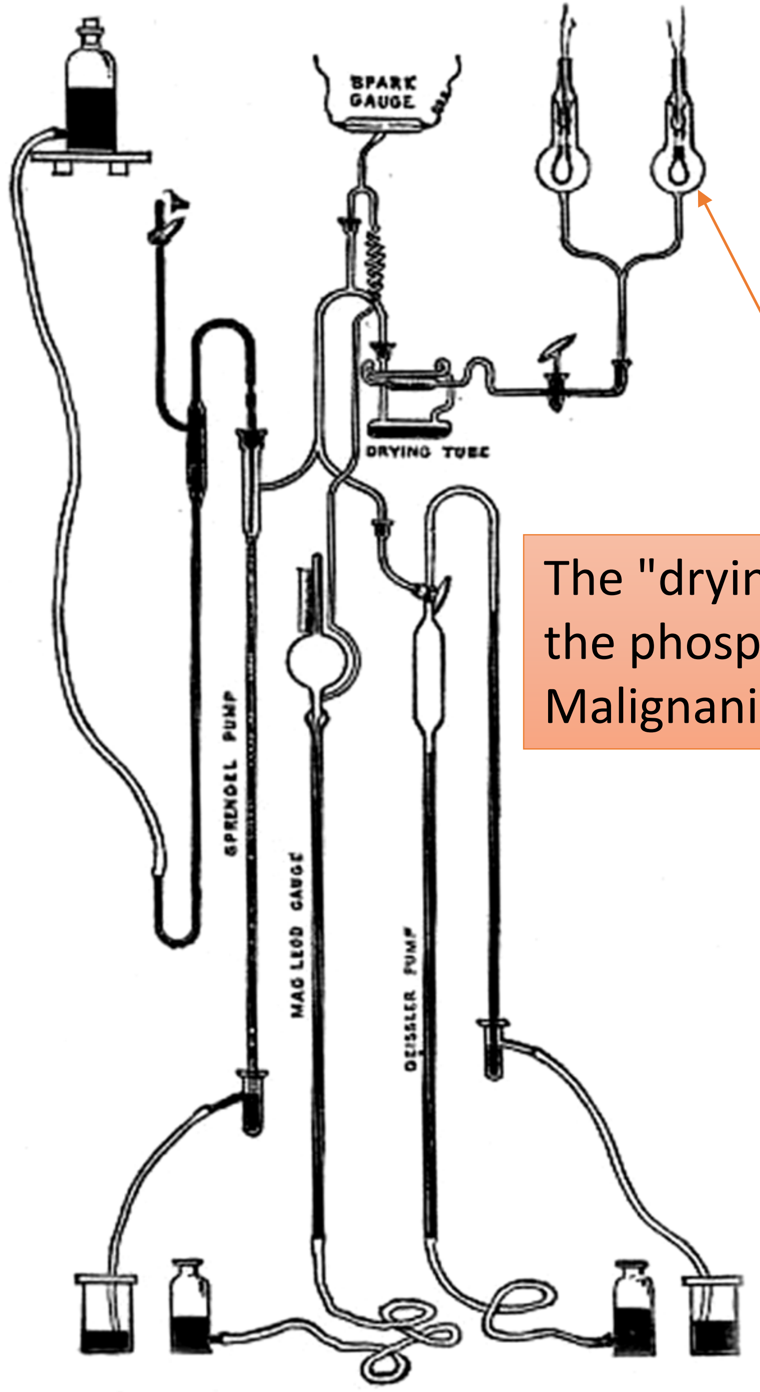
APPLICATION FILED SEPT. 6, 1916.

1,427,753. Patented Aug. 29, 1922.

In Fig. 2 we have shown means for producing a high tension electric spark or discharge, indicated at 8, within the chamber 4, as a means for exhausting said chamber of its oxidizing air, the spark terminals 10, 10, being included in circuit connections 11, 11, supplied with high tension current from any convenient source.

After the removal of the oxidizing agent, air or gas, or the influence thereof, from

Edison’s light bulb fabrication used getters



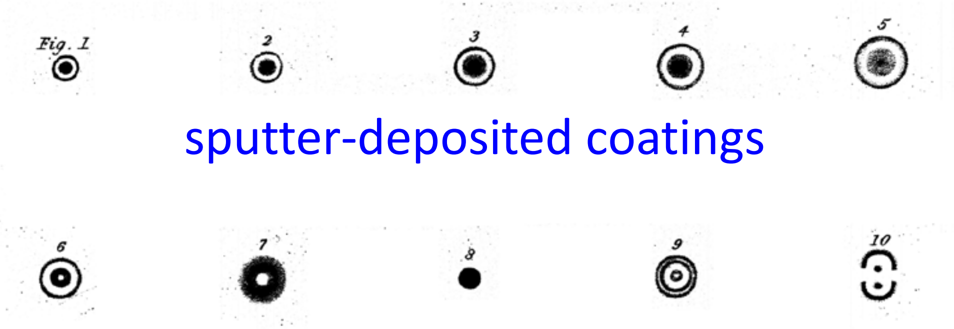
The "drying" tube contained the phosphoric anhydride, Malignani US 537,693 (1885)

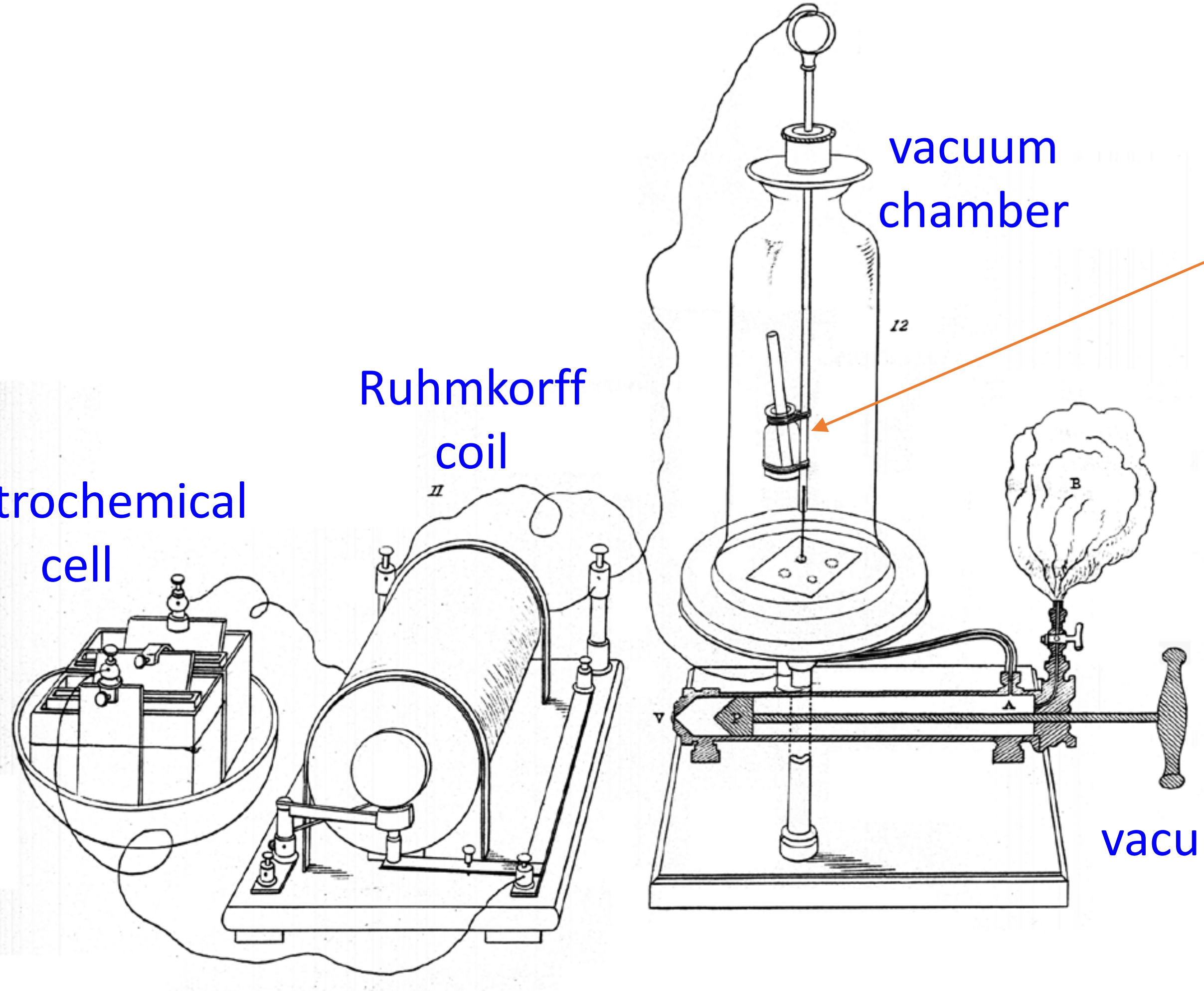
DR. LANGMUIR AND MR. EDISON, 1922

When Mr. Edison visited the Research Laboratories at Schenectady in 1922, Dr. Langmuir showed him a 30,000-watt lamp he had made for experimental purposes. This is the largest lamp ever made, giving 100,000 candle power.

http://home.frognet.net/~ejcov/P3N5.html

We can find a getter with the first sputtering experiments (Grove 1852)

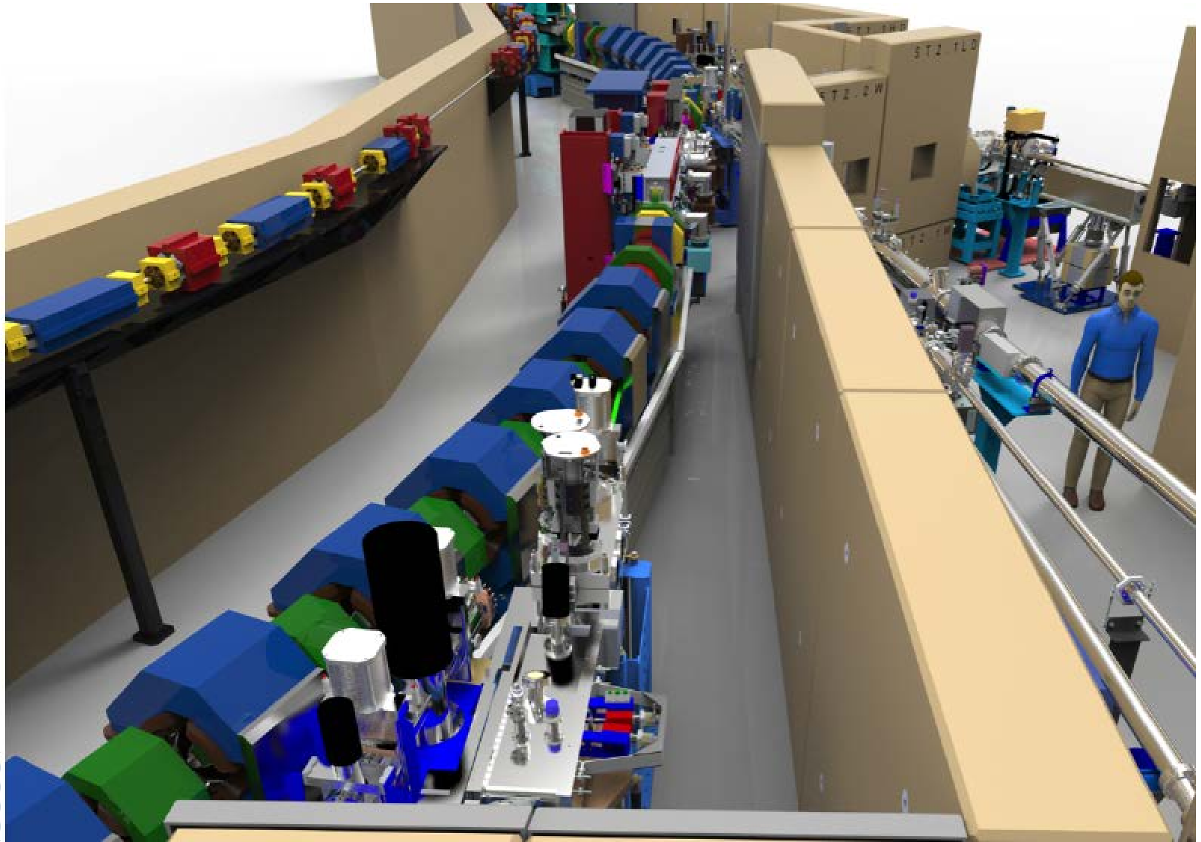


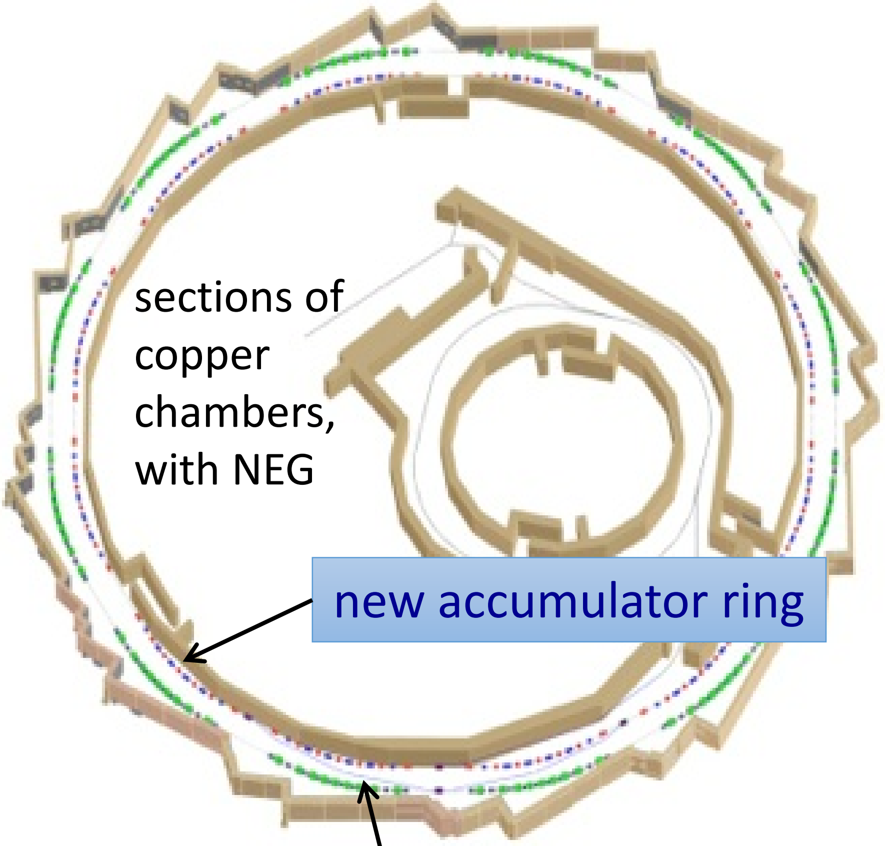


W. R. Grove, Phil. Mag. vol. **4** Ser. 4 (1852) 498

Application to NEG Coatings for Berkeley's Synchrotron (ALS) Upgrade

- Diffraction-Limited Storage Ring yields 2-3 orders of magnitude improvements in coherent photon flux
- Enables advanced imaging techniques to address essential new science and technology

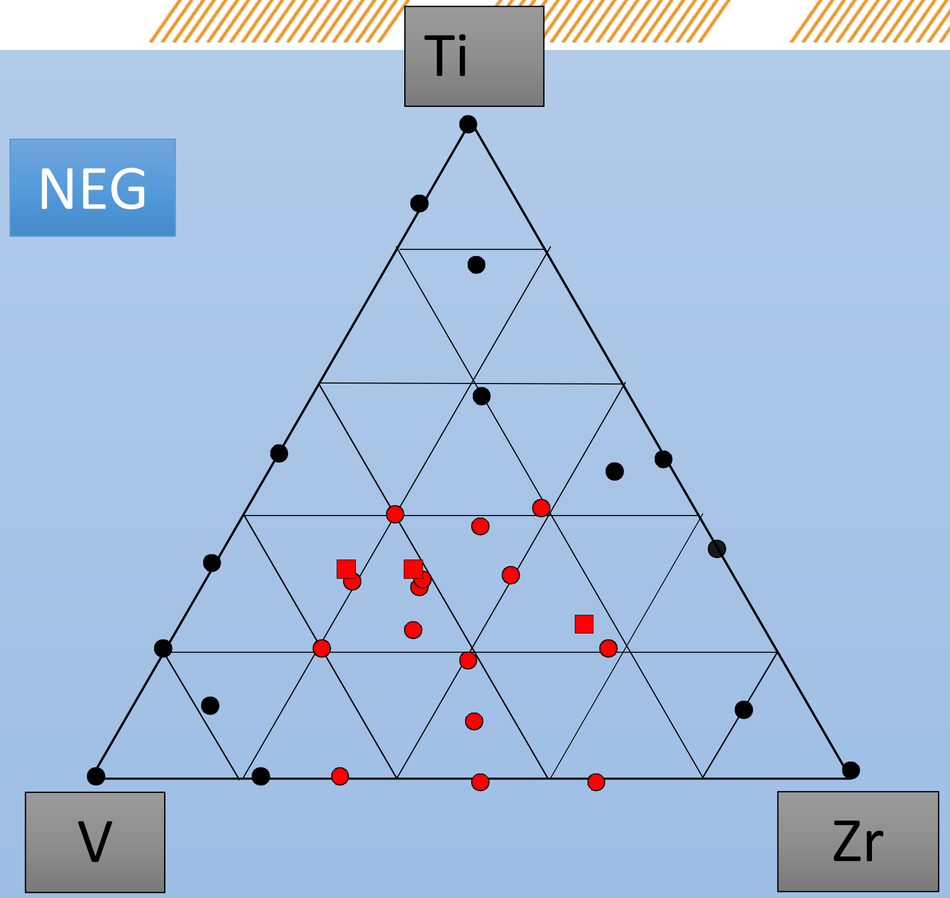




Using the same (historic) building: Lawrence's Cyclotron

Deposit NEG coatings in very narrow chambers for ALS-U

- NEG: advanced Ti-Zr-V getter coatings pioneered by CERN, commercially available for large (> 10 mm) beam vacuum chambers.
- **Challenge**: for ALS-U and other accelerators, very narrow beam chambers are required, ID = 6 mm or even 4 mm for some components, if possible.



composition and microstructure affects activation energy and pumping performance

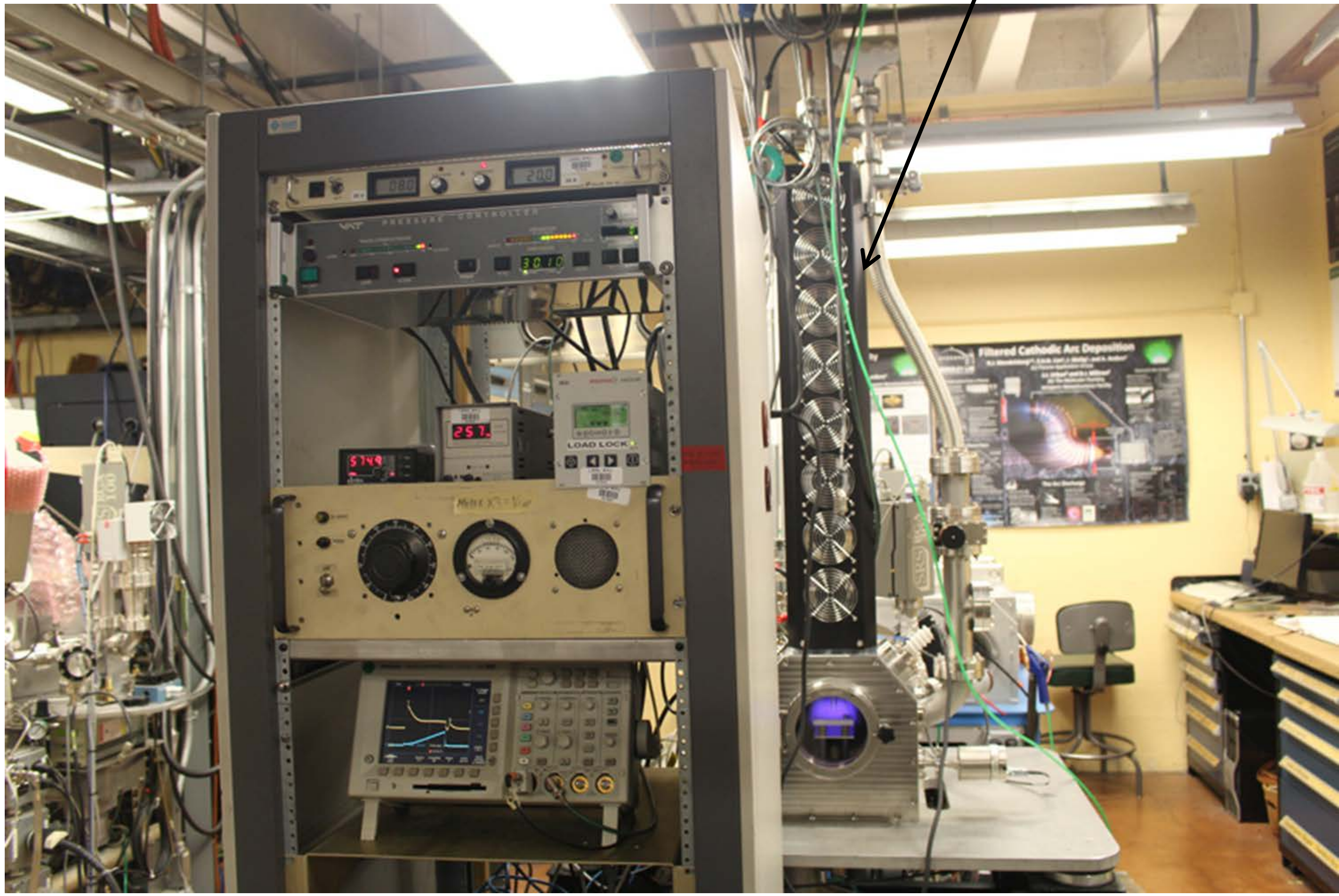
C. Benvenuti, et al, J. Vac. Sci. Technol. A 19 (2001) 2925.

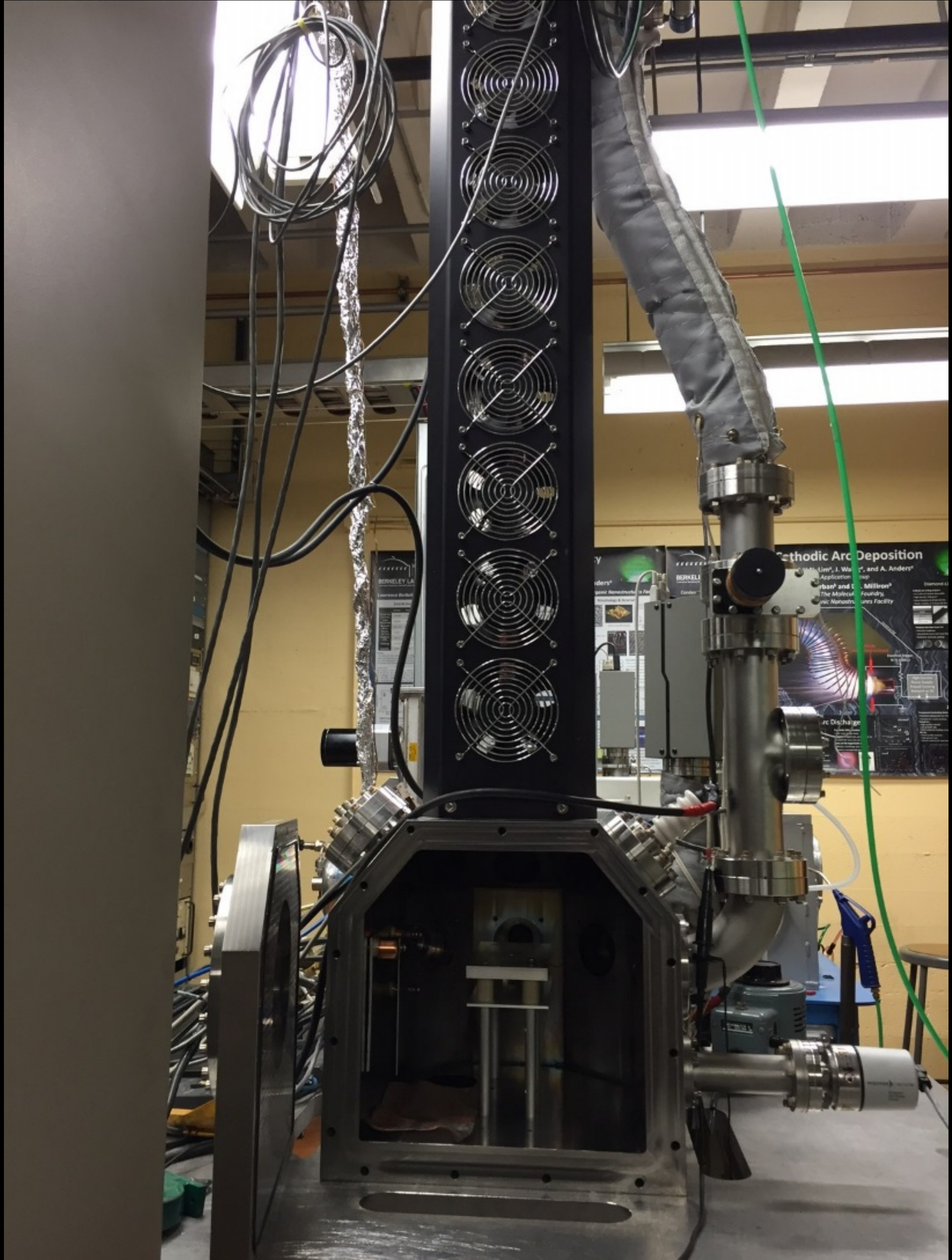
IOM

NEG Coatings: Progress at LBNL toward coating or small diameter chambers

- Developing in-house expertise in NEG wire sputtering for ***small* diameter chambers** at relatively high pressure
- up to now: twisted wire elemental metals (we also consider alloy wire)
- Using pulsed sputtering → higher currents, more complete length coverage
- RBS compositional analysis at many inner tube locations

Vertical wire sputtering system



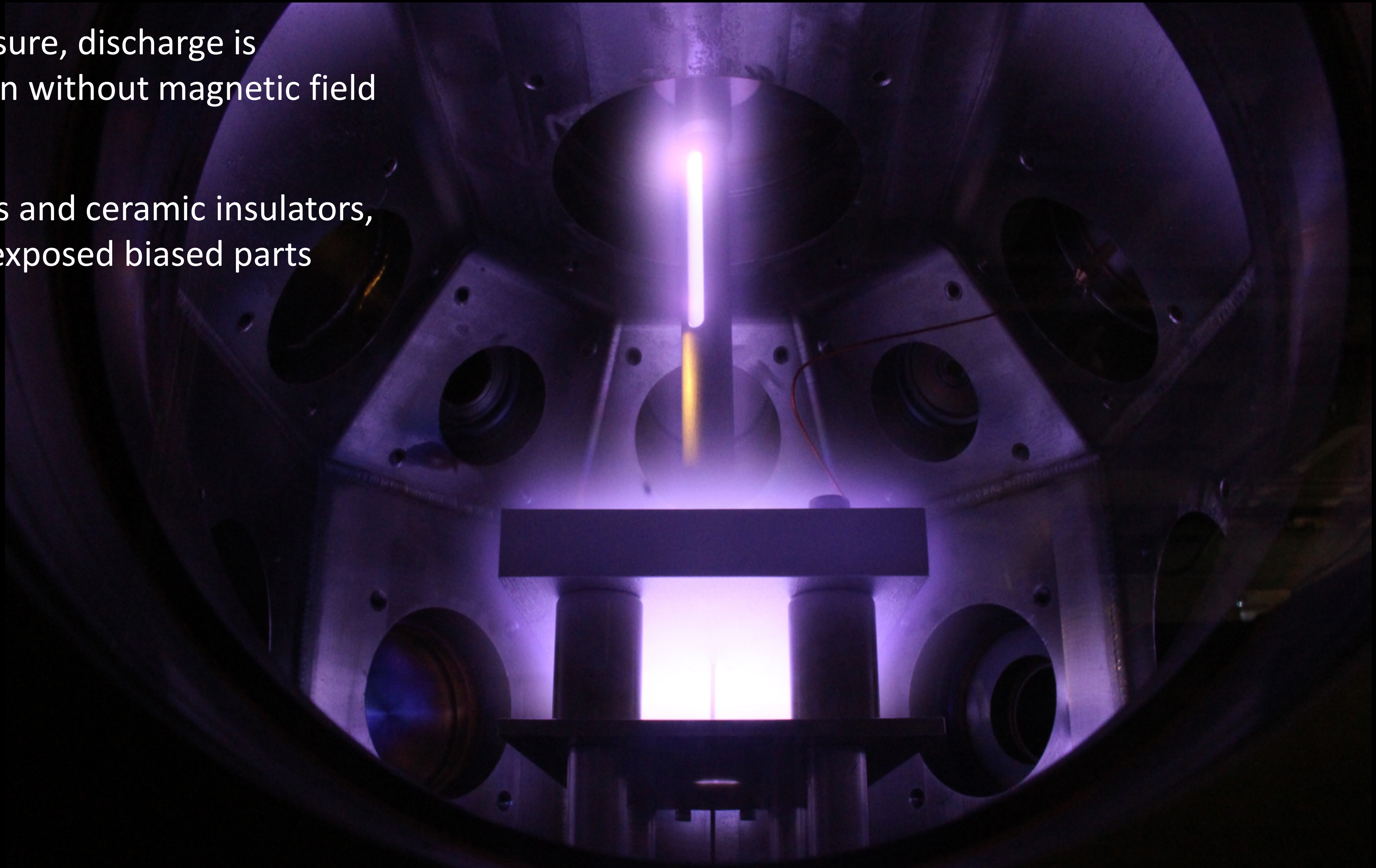

Arc Deposition

Parasitic discharges in the lower chamber

at high pressure, discharge is
enabled even without magnetic field

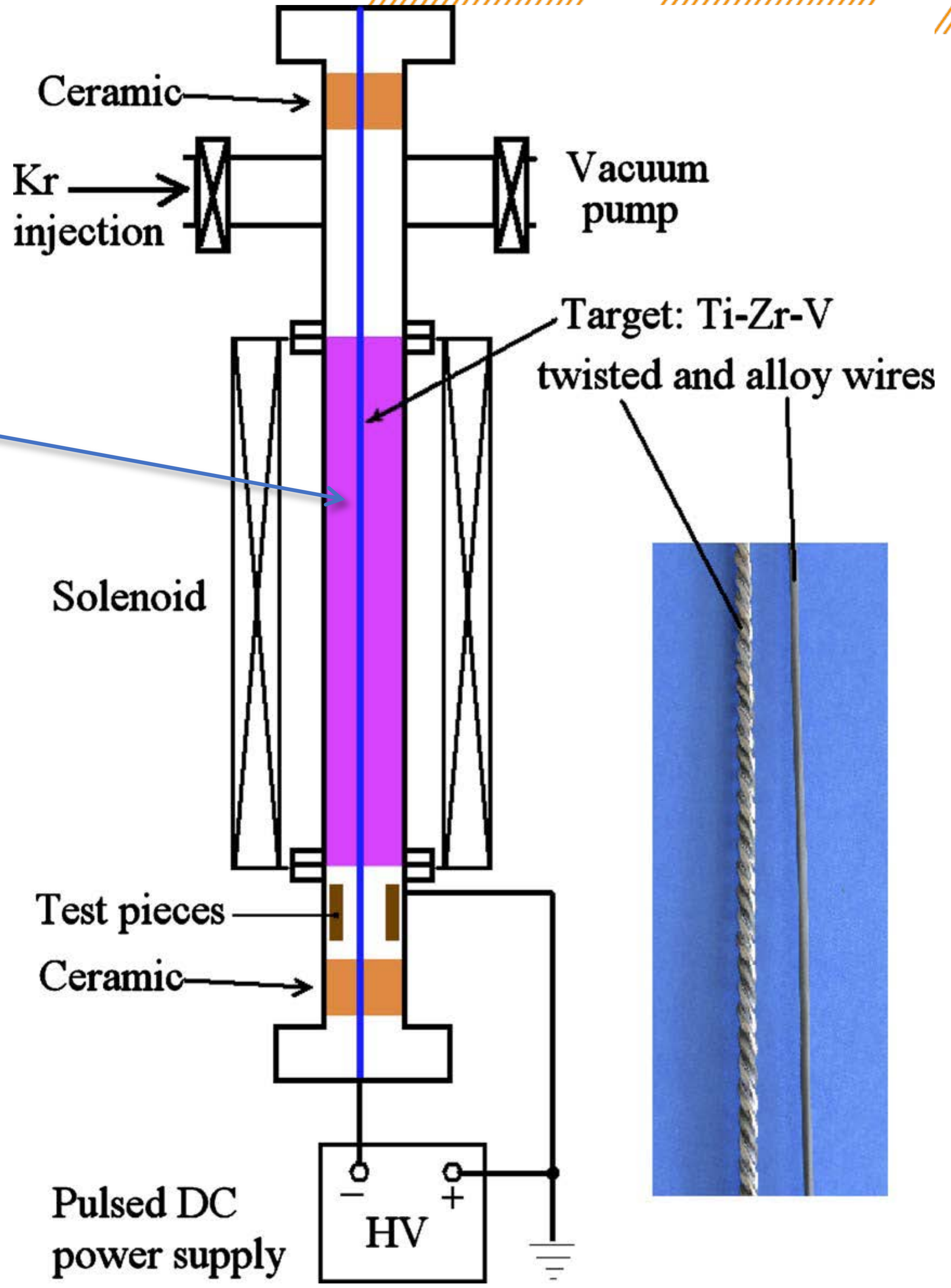
↓

using breaks and ceramic insulators,
minimized exposed biased parts



Deposition by Wire Sputtering

space between wire and inner wall needs to accommodate:
- sheath
- presheath & plasma



R. Valizadeh, et al., J. Vac. Sci. Technol. A **28** (2010) 1404.

Characteristic Lengths Considerations in Sputtering

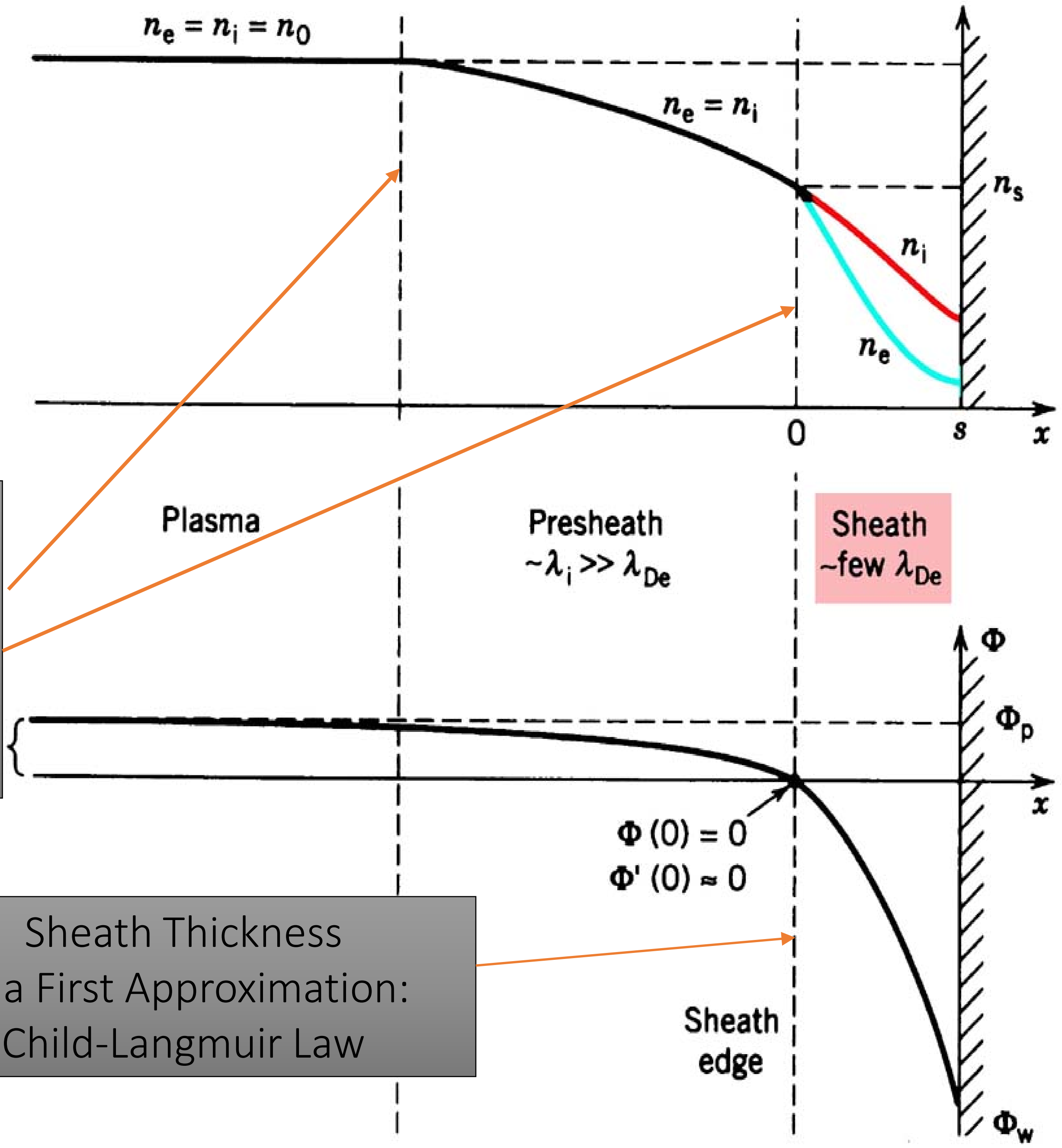
symbol	quantity	for "typical" magnetron sputtering (m)	for sputtering in narrow chambers (m)
L	characteristic distance between target and substrate	10^{-1}	10^{-3}
λ_{fe}	mean free path of electrons	10^{-2}	10^{-4}
λ_{fa}	mean free path of sputtered atoms	10^{-1}	10^{-3}
λ_{De}	Debye length	10^{-4}	10^{-4}
l_s	sheath thickness	10^{-4}	10^{-4}
l_{ps}	presheath thickness	10^{-2}	10^{-2}
r_{Le}	electron gyration radius (Larmor radius)	10^{-3}	10^{-3}

We have at least two huge issues when going to high pressure and small diameter!

1. no space for plasma, all is presheath, at best: $L < l_{ps}$
2. electrons are no longer magnetized: $\lambda_{fe} < r_{Le}$ and $L \leq r_{Le}$

Sheaths and Presheath

- there must be space for sheath, presheath, and plasma
- boundaries are dynamic for pulsed discharges

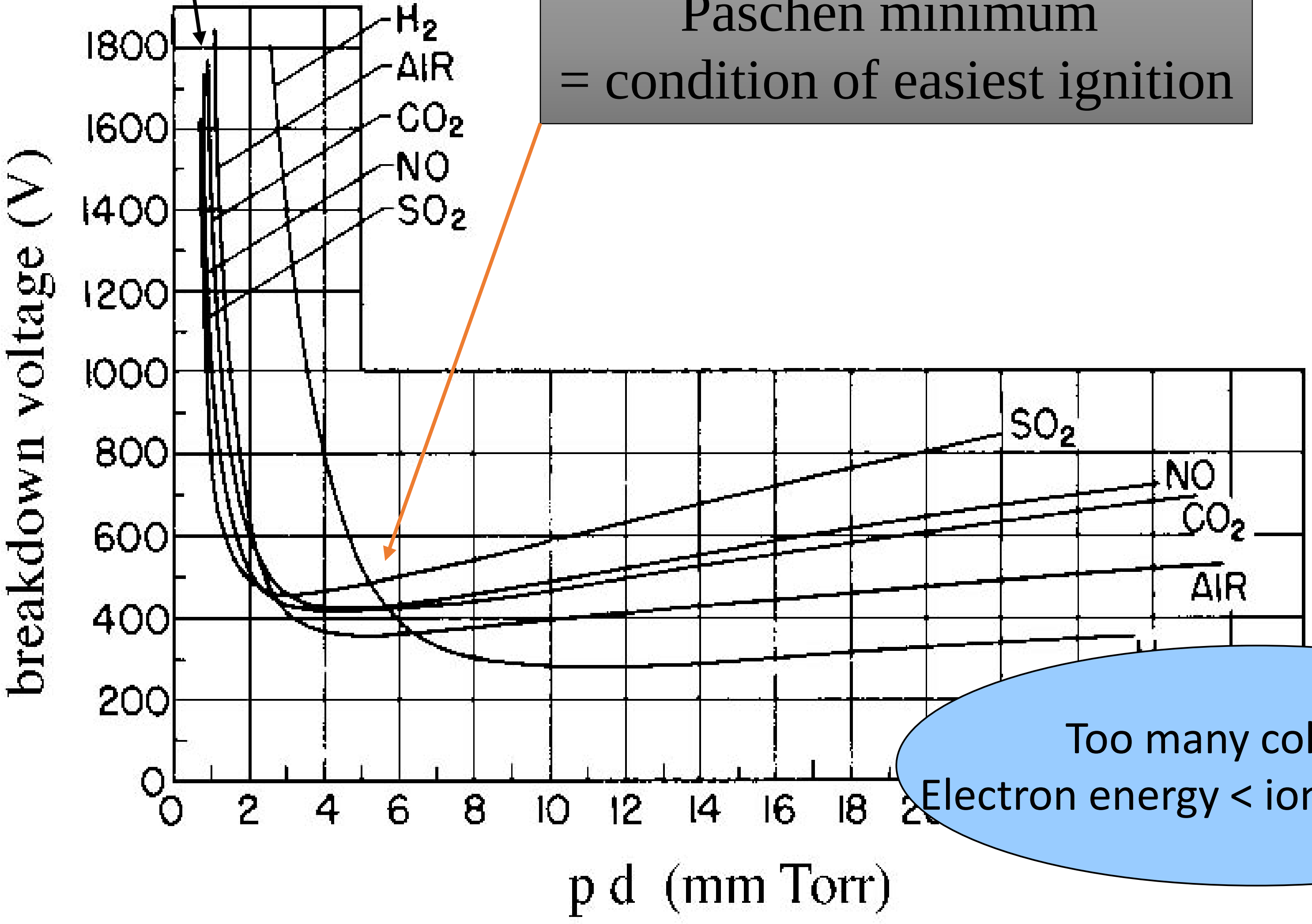


Sheath Thickness
In a First Approximation:
Child-Langmuir Law

Paschen: *pd*-scaling

Too few ionizing collisions: l > d

Paschen minimum
= condition of easiest ignition

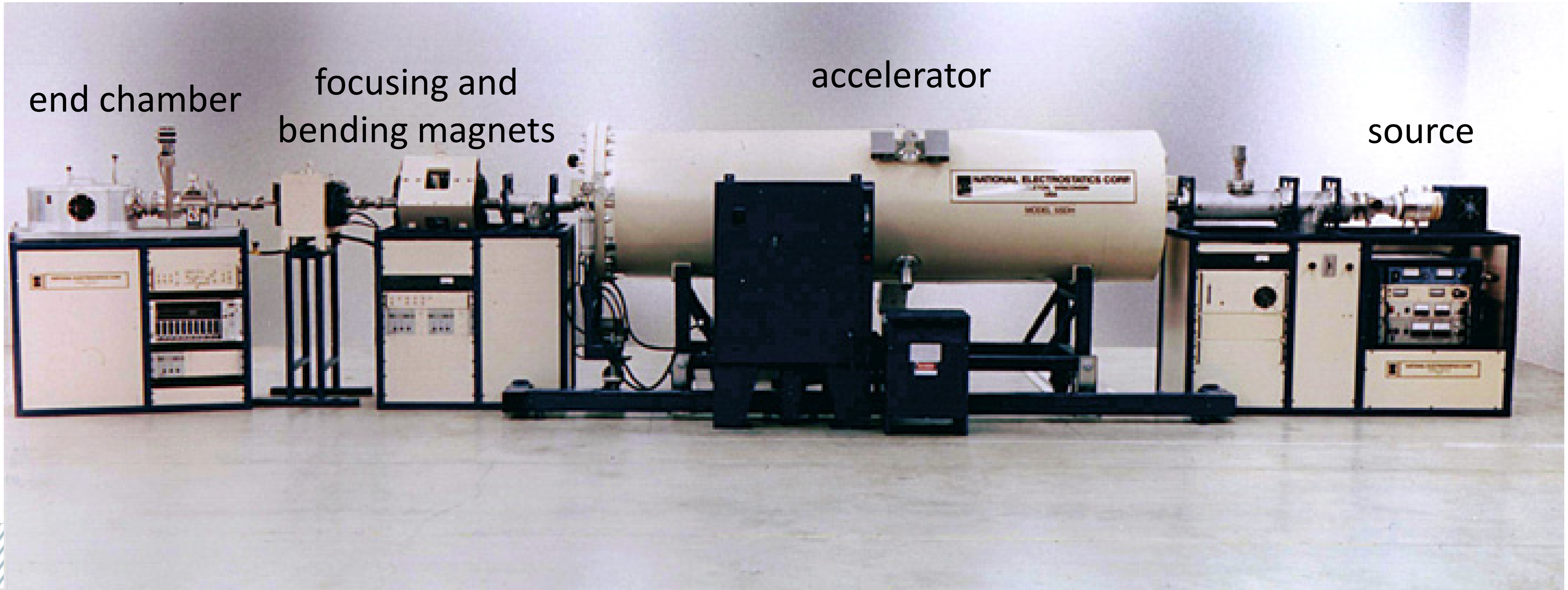


Too many collisions:
Electron energy < ionization energy

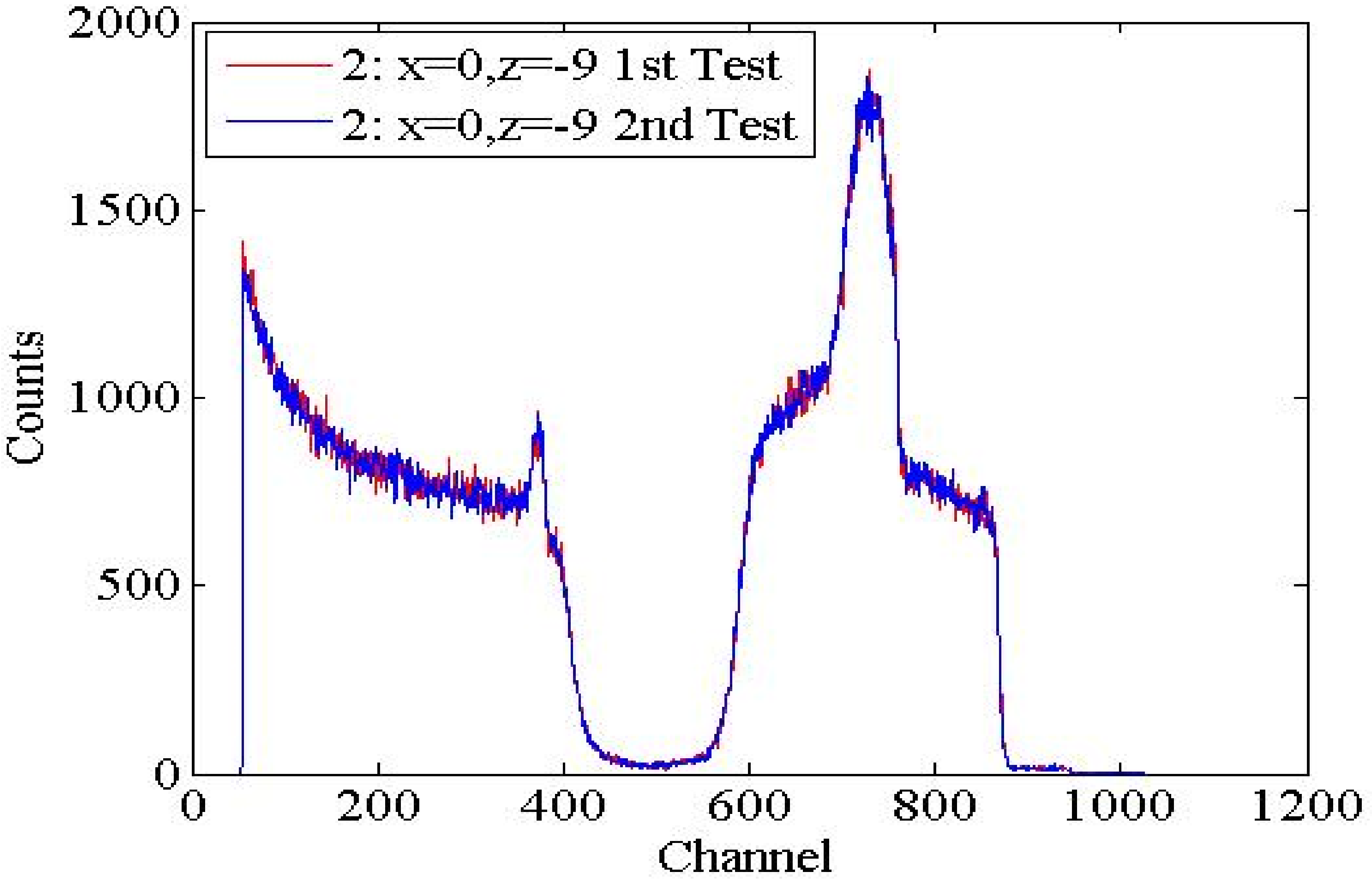
Friedrich Paschen
1865-1947

Ion Beam Materials Characterization Facility

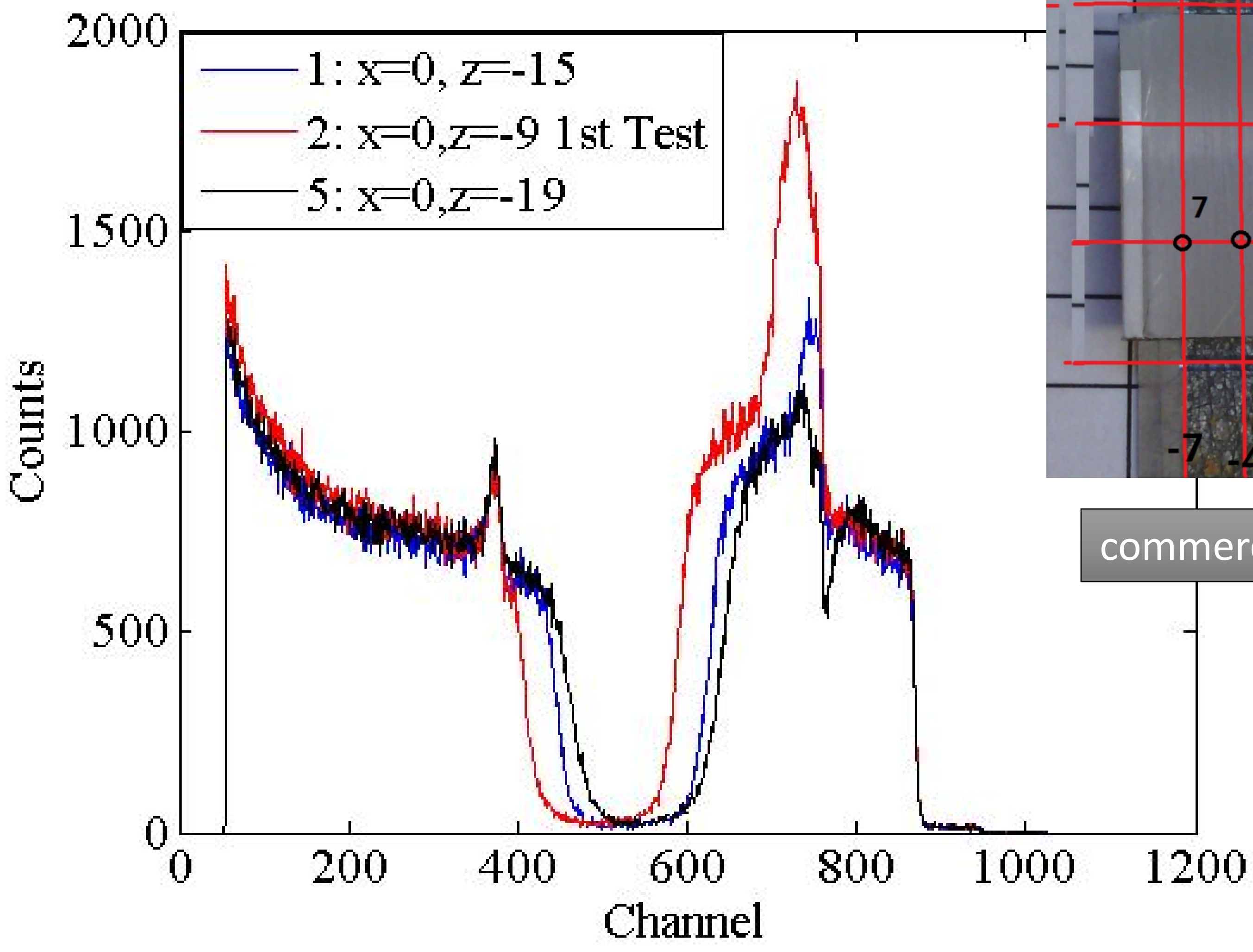
- 1.7 MV Pelletron, up to 5.1 MeV for helium ion beam
- quantitative **depth profiling of elemental composition**
- Use RBS for heavy ion measurements, and forward scattering for hydrogen;
  - o also have PIXE, channeling, and NRA techniques available

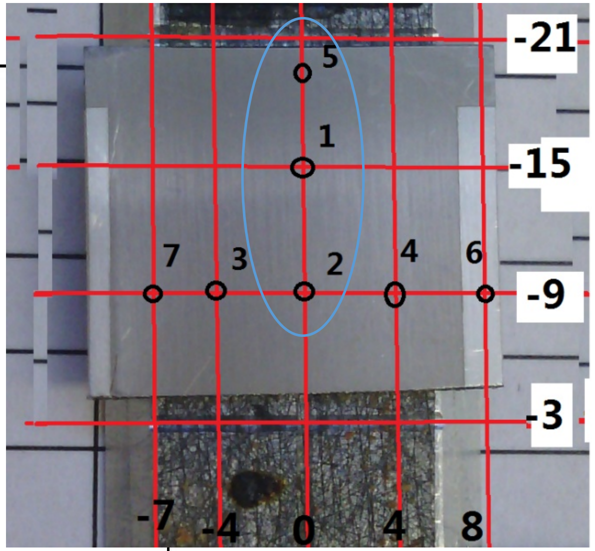


Reproducibility of Rutherford Backscattering is excellent



Composition variations can be significant when using twisted wires

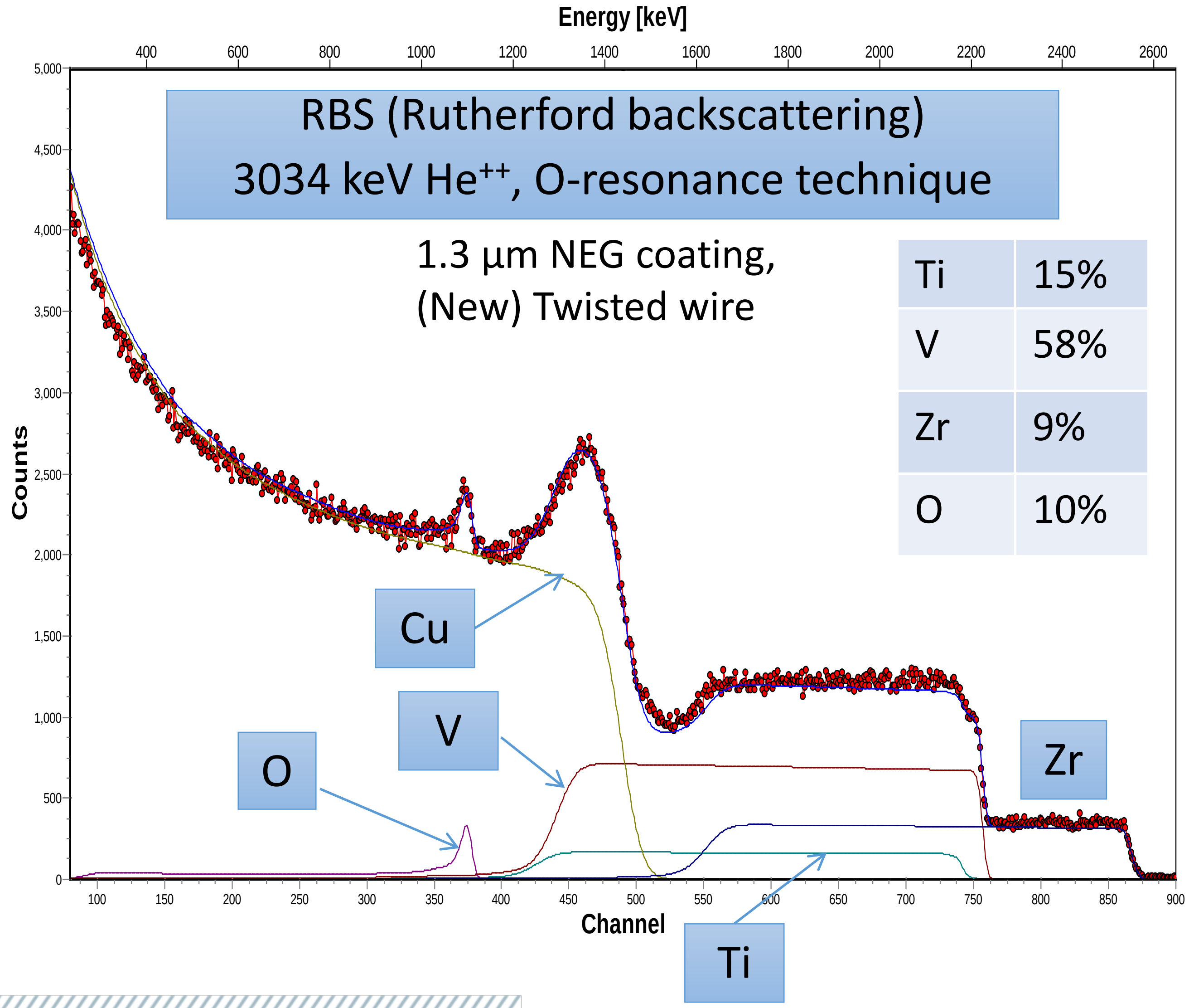




commercial NEG sample

Thickness : Point 5 < Point 1 < Point 2

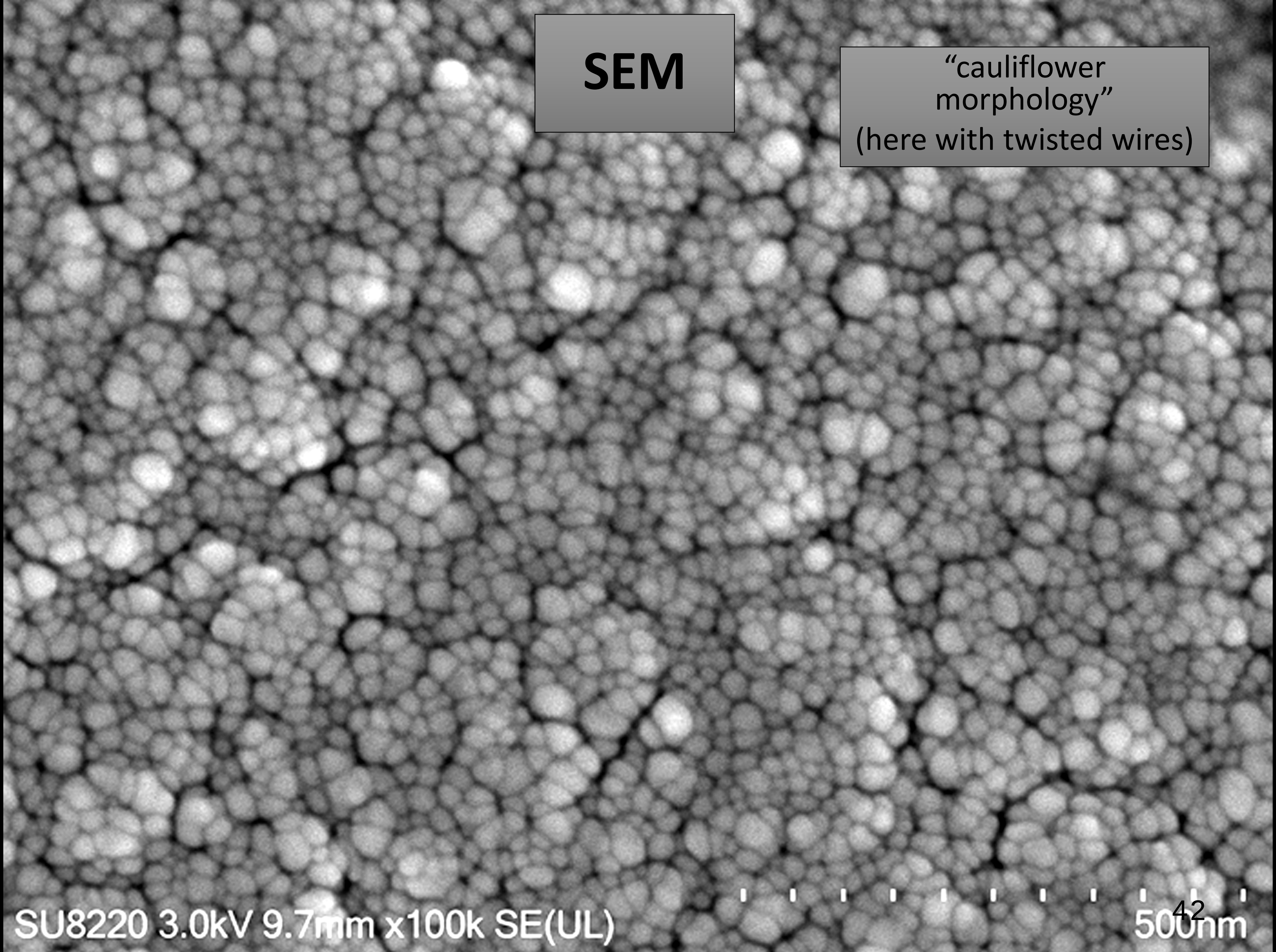
Quantify NEG Coatings by Ion Beam Analysis



Ti	15%
V	58%
Zr	9%
O	10%

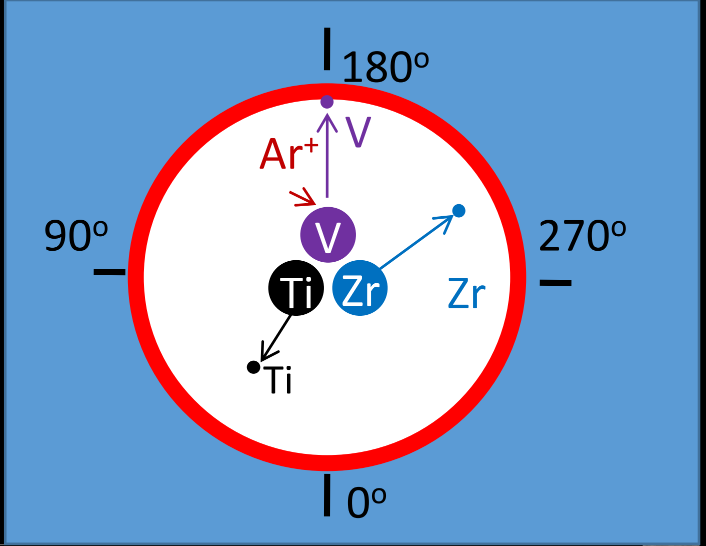
Findings

- wire has different twist pitch → film composition varies by several percent within millimeters
- thickness is uniform at negligible argon flow but has a gradient > 50% when operating under flow conditions due to different local partial pressures
- Surface oxide forms as surface was exposed to air

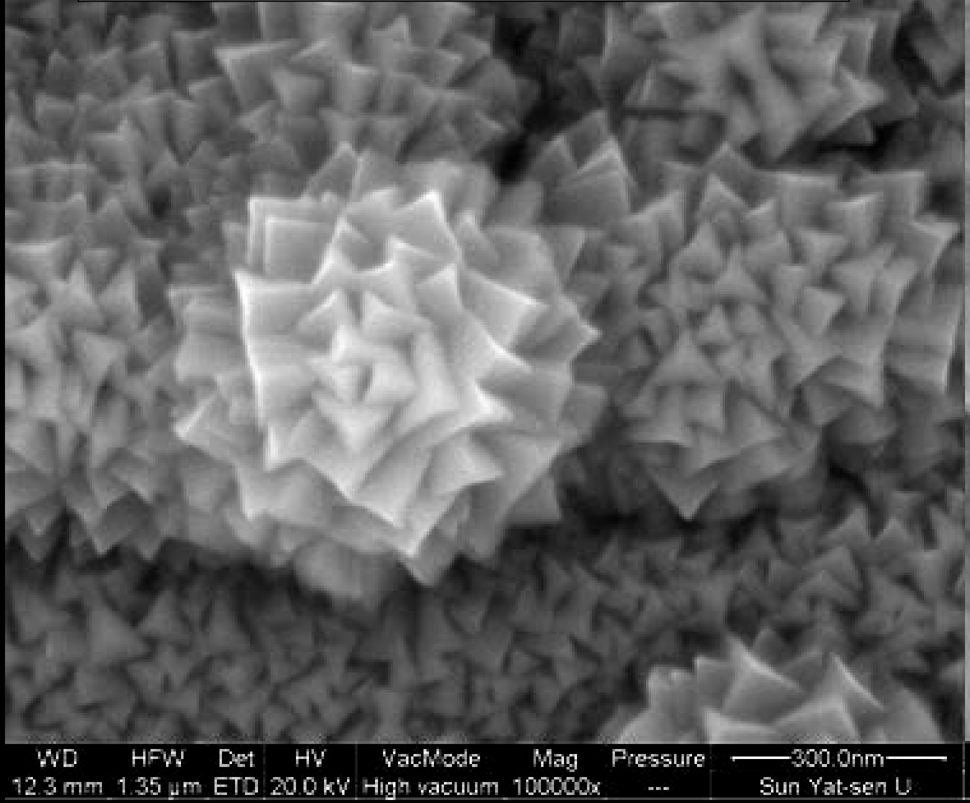

SEM
"cauliflower morphology"
(here with twisted wires)
SU8220 3.0kV 9.7mm x100k SE(UL)
500nm

SEM micrographs

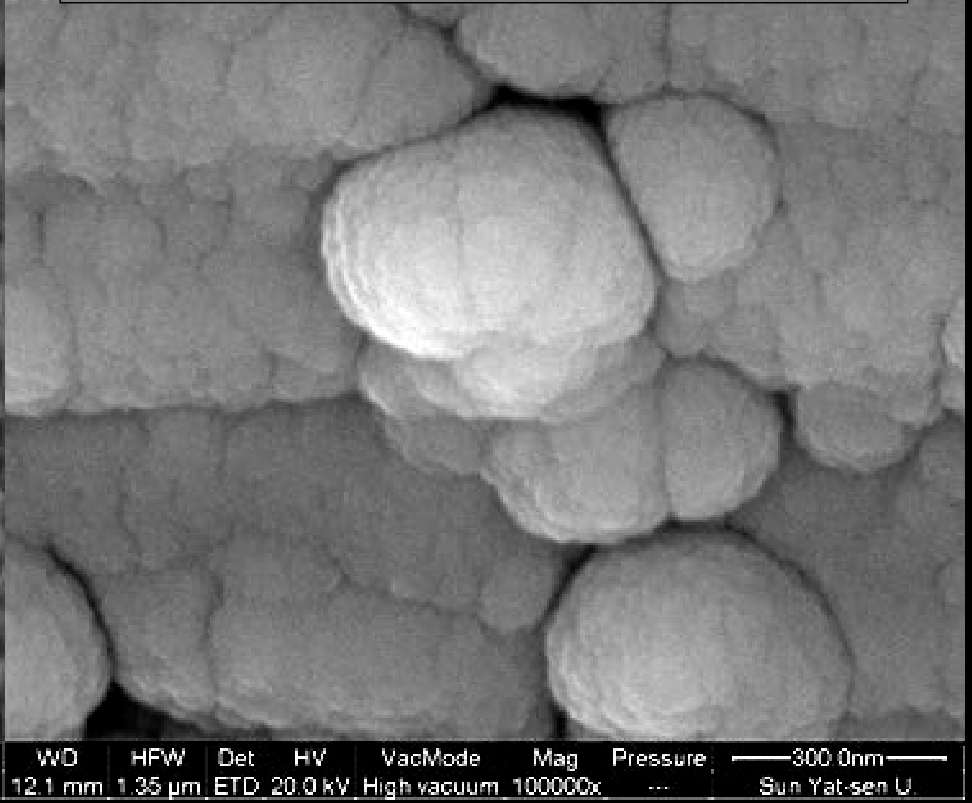
same sample, different regions, mm apart



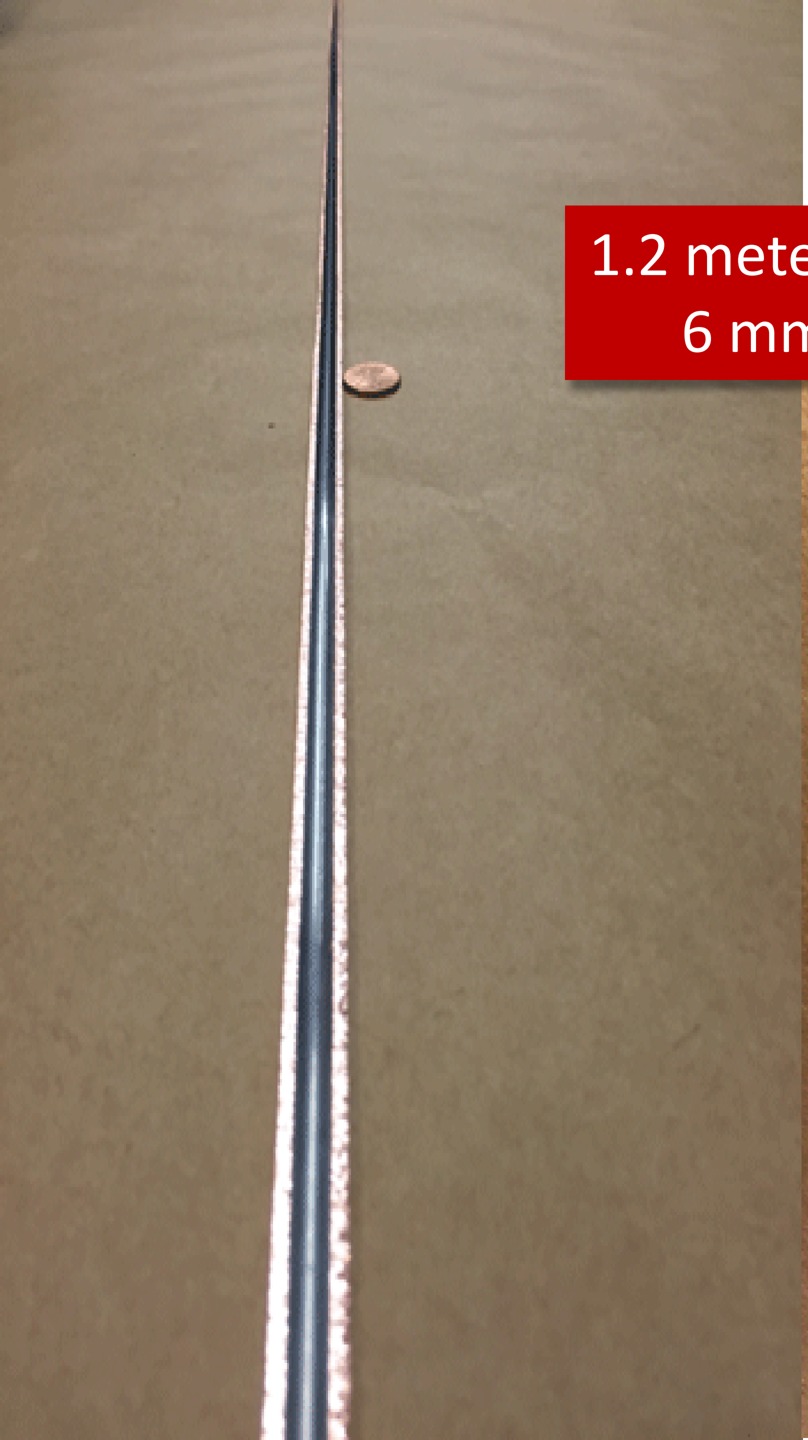
inside dark region, V-rich, Ti-poor

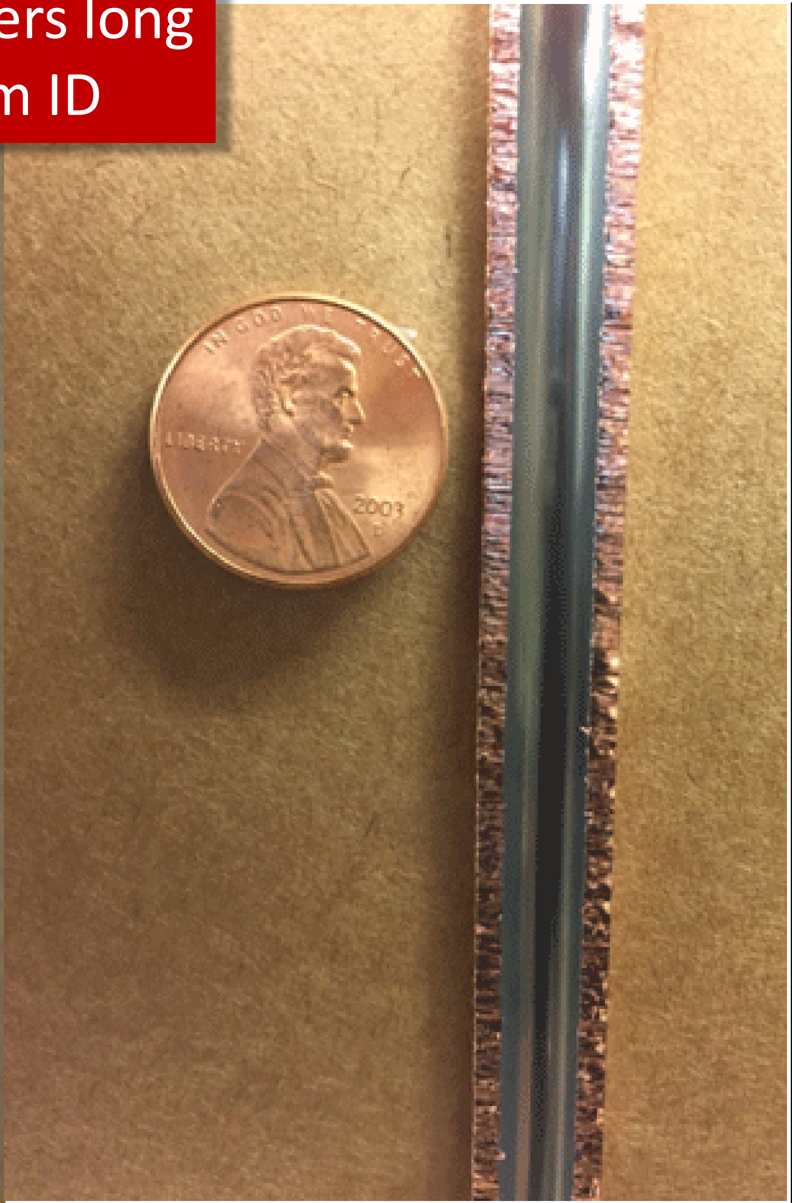


outside dark region, "stoichiometric"



NEG Coatings in Very Narrow Chambers at LBNL: Results and Challenges (2017)





- Use twisted wires
- coating up to 1 µm thick
- no adhesion issues on Al and Cu chambers
- we find some local composition variations

Optimal parameter set:

- 1000 V, 50 mA
- pulsed (10 µs on/ 50 µs off)
- mag. coil current 20 A dc
- original base pressure in low 10^{-8} Torr range
- 0.54 Torr (72 Pa) pure Ar, no flow to get uniformity

Obvious solution is using alloy wire but…

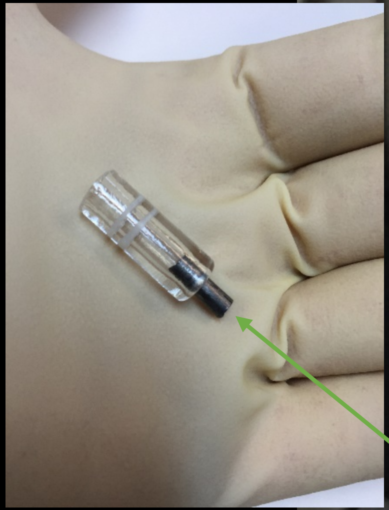
Vendors have great difficulties to manufacture suitable alloy wire because it takes up oxygen and becomes brittle.

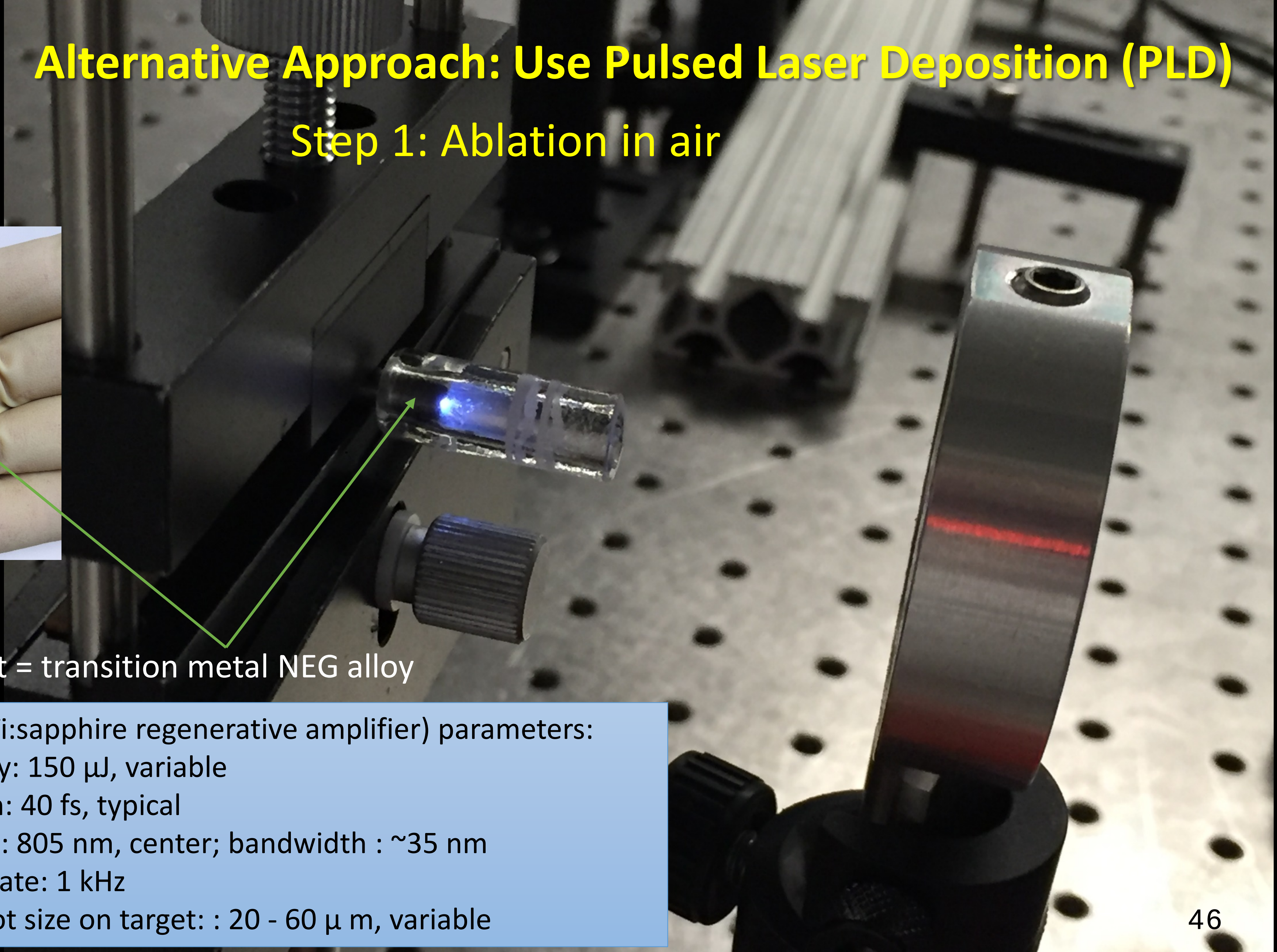
1. “We were not able to roll your material, as I indicated, so we sent it off to a specialty wire mill, and they were only able to get it to about 0.155” diameter before their machine stopped working on it….”
2. “We have prepared a new alloy rod and fabricated it. I am developing a small matrix of processing to determine where the oxygen is getting into the alloy in the processing…. “
3. “Leider müssen wir Ihnen eine negative Antwort geben. In unserer Sprühkompaktieranlage arbeiten wir mit Tongrafit-Tiegel deren max. Anwendungstemperatur bei 1600 °C liegt... Daher sind wir nicht in der Lage solche Legierungen herzustellen.“

HOWEVER, it has been shown: R. Valizadeh, et al., "Comparison of Ti-Zr-V nonevaporable getter films deposited using alloy or twisted wire sputter-targets," J. Vac. Sci. Technol. A, vol. 28, pp. 1404-1412, 2010.

Alternative Approach: Use Pulsed Laser Deposition (PLD)

Step 1: Ablation in air



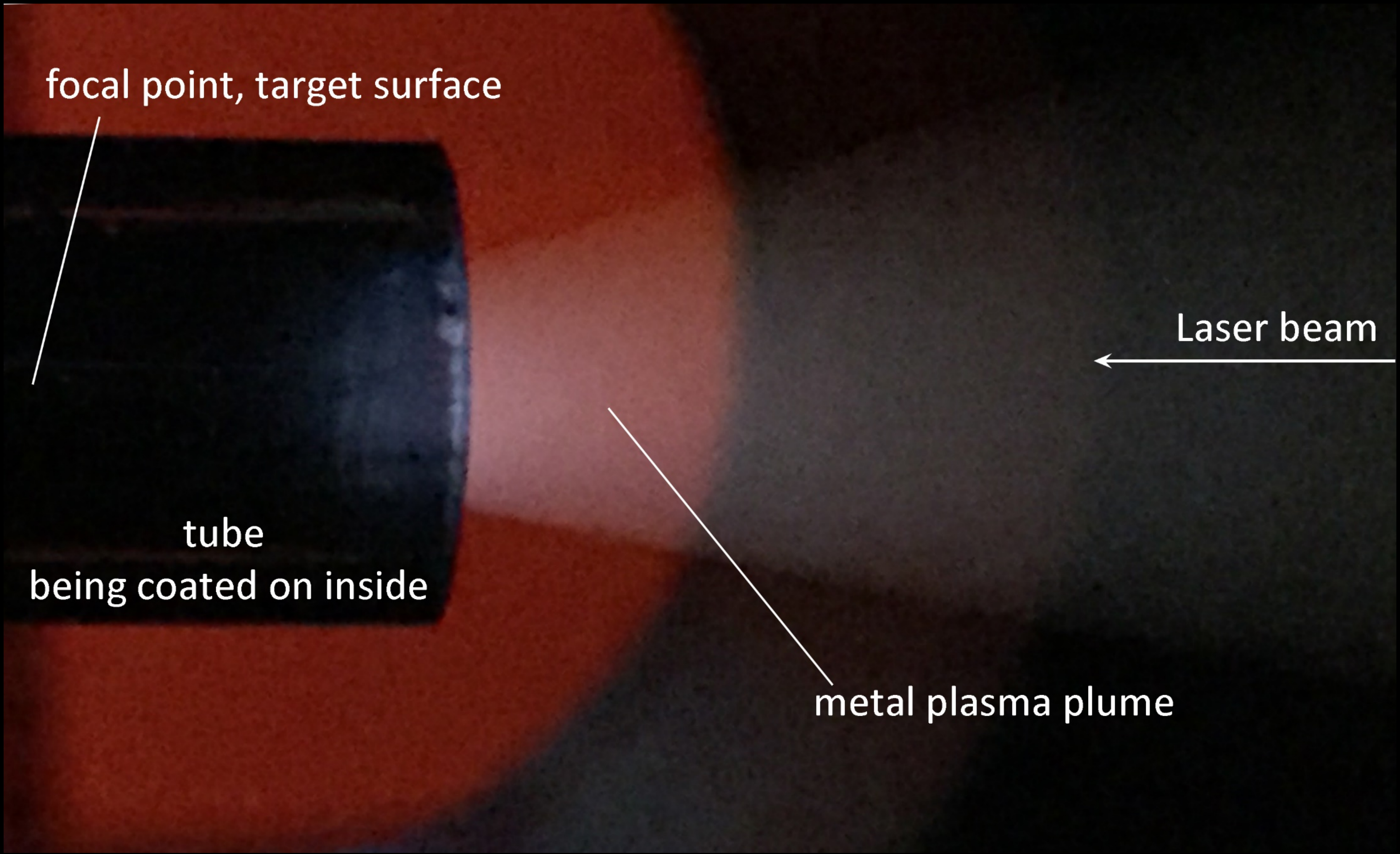


Laser target = transition metal NEG alloy

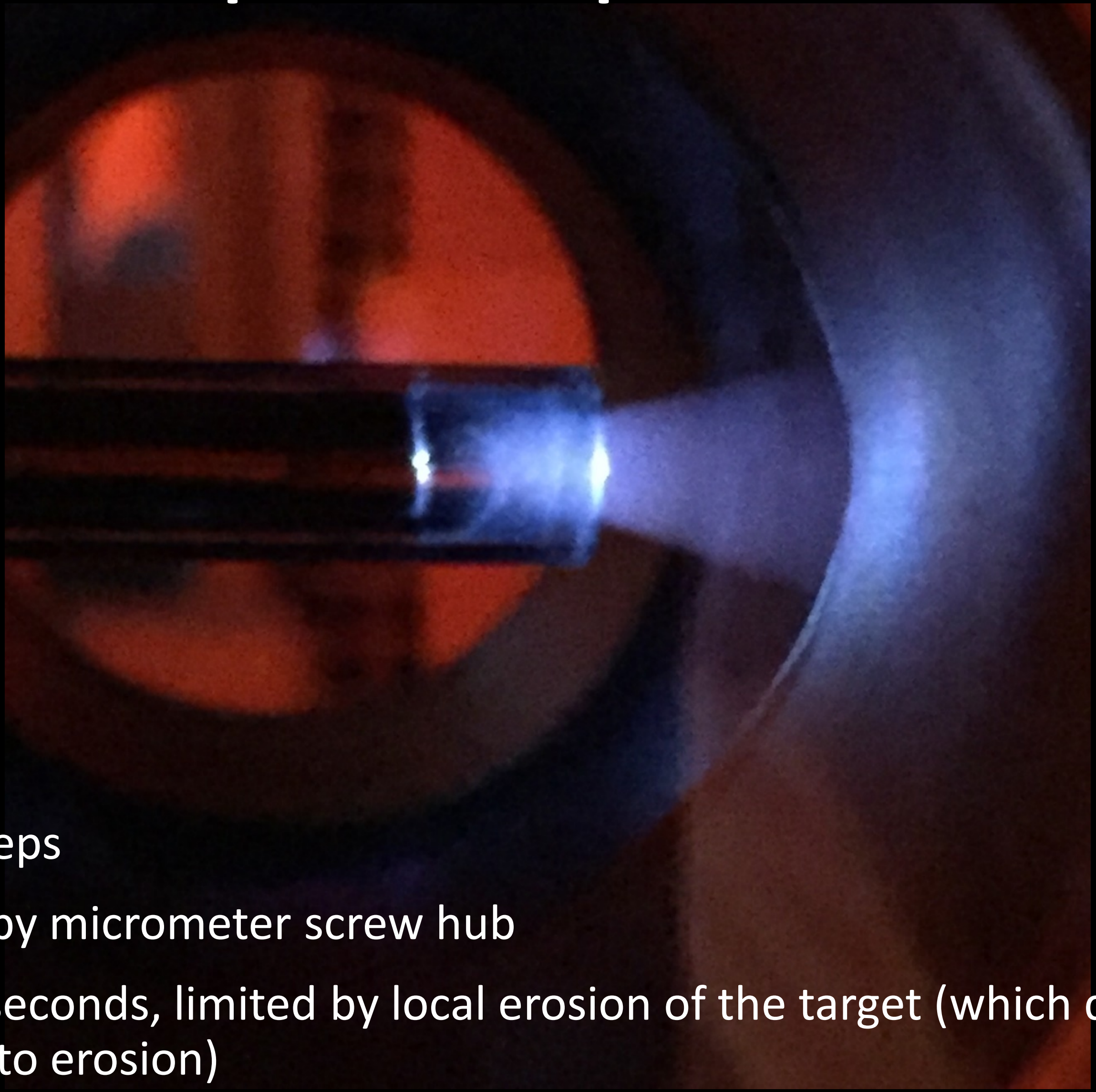
Laser source (Ti:sapphire regenerative amplifier) parameters:

- Pulse energy: 150 μJ, variable
- Pulse length: 40 fs, typical
- Wavelength: 805 nm, center; bandwidth : ~35 nm
- Repetition rate: 1 kHz
- Focused spot size on target: : 20 - 60 μ m, variable

2. Step: Deposition in vacuum

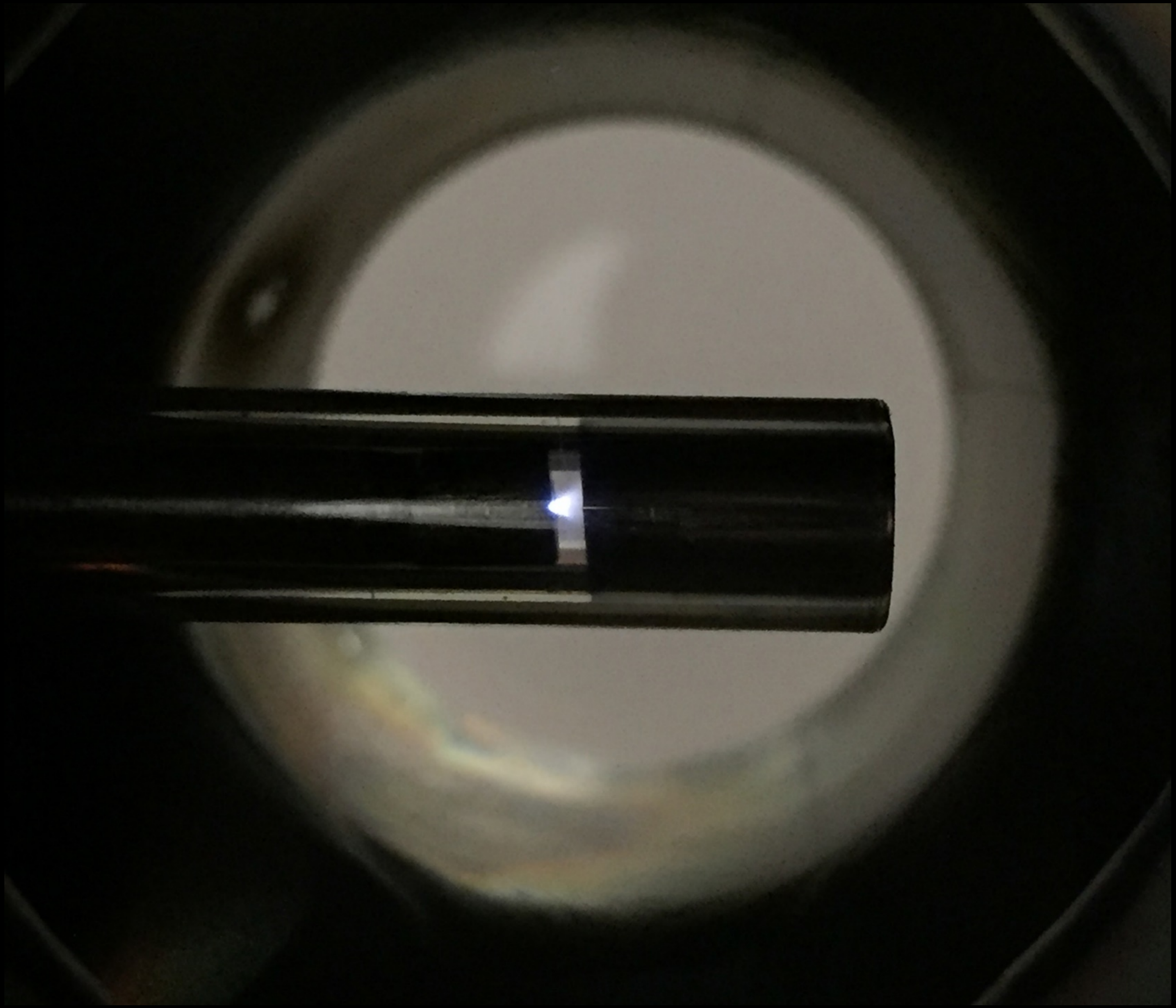


Begin of Deposition Experiment in Vacuum



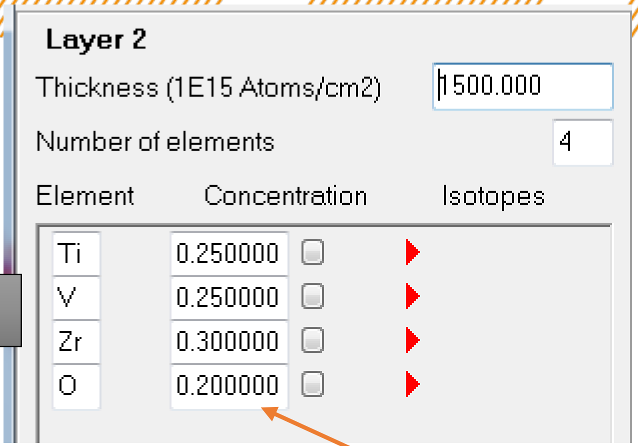
- Deposition in 2 mm steps
- total length is limited by micrometer screw hub
- Each deposition 5-10 seconds, limited by local erosion of the target (which quickly goes out of focal point due to erosion)

Near End of Deposition Experiment in Vacuum



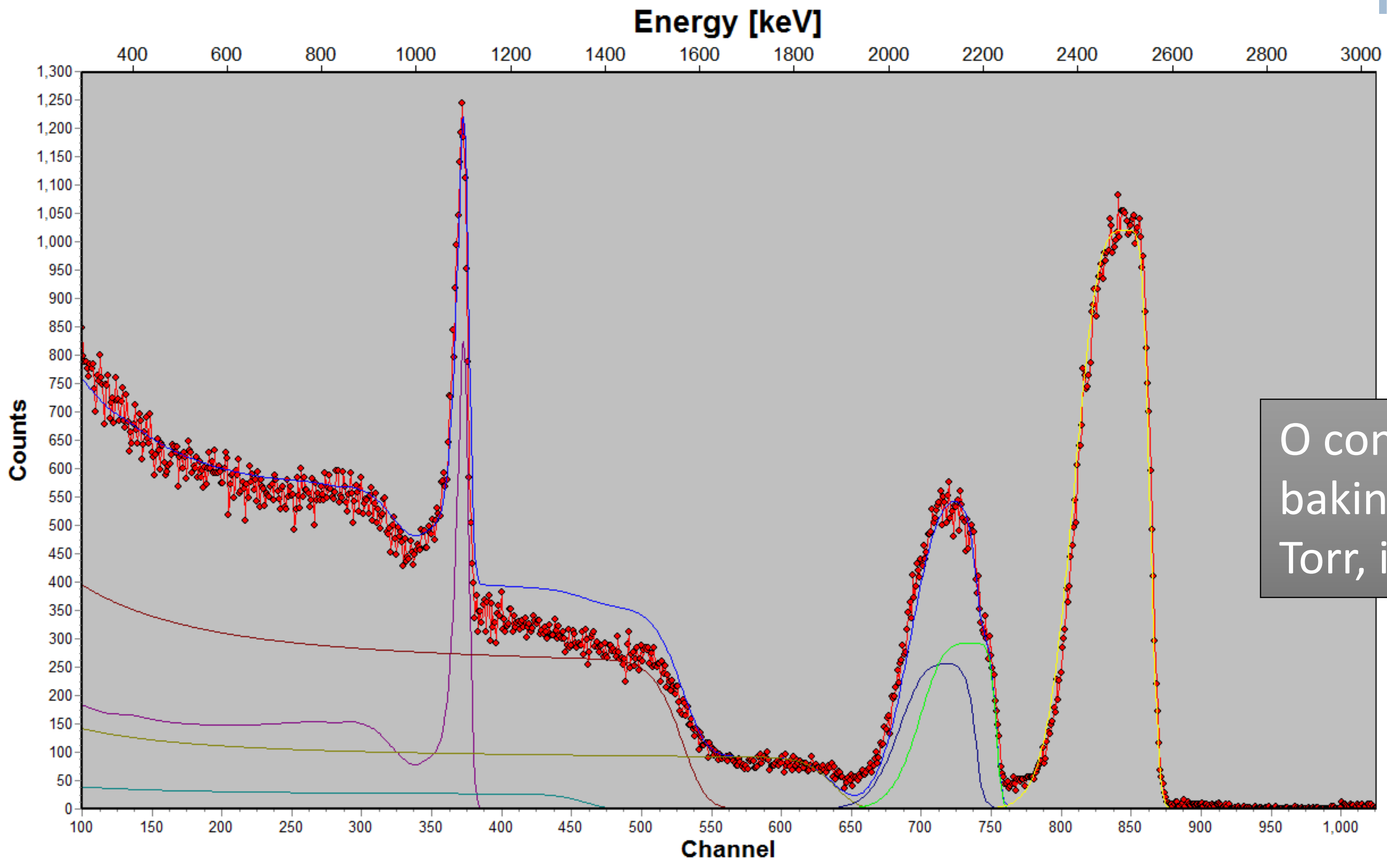
RBS of PLD coating,

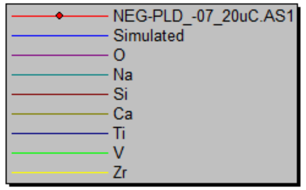
NEG on inside of glass tube, movable target



Main layer

!!



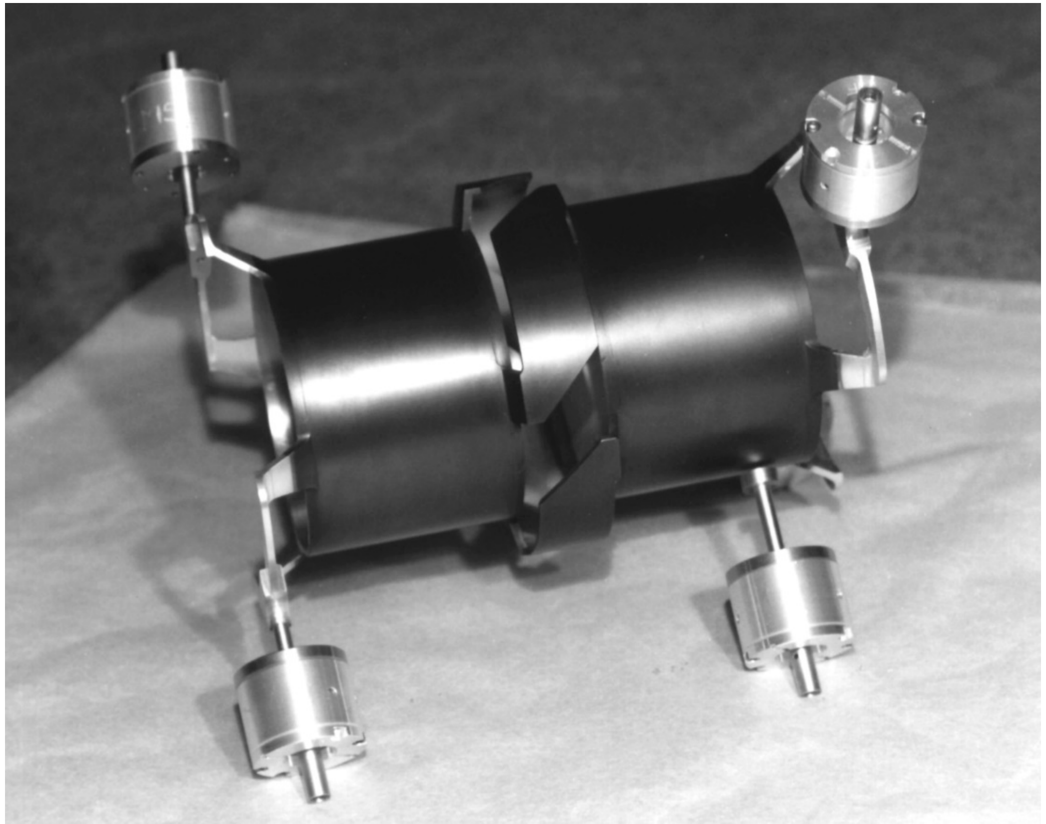


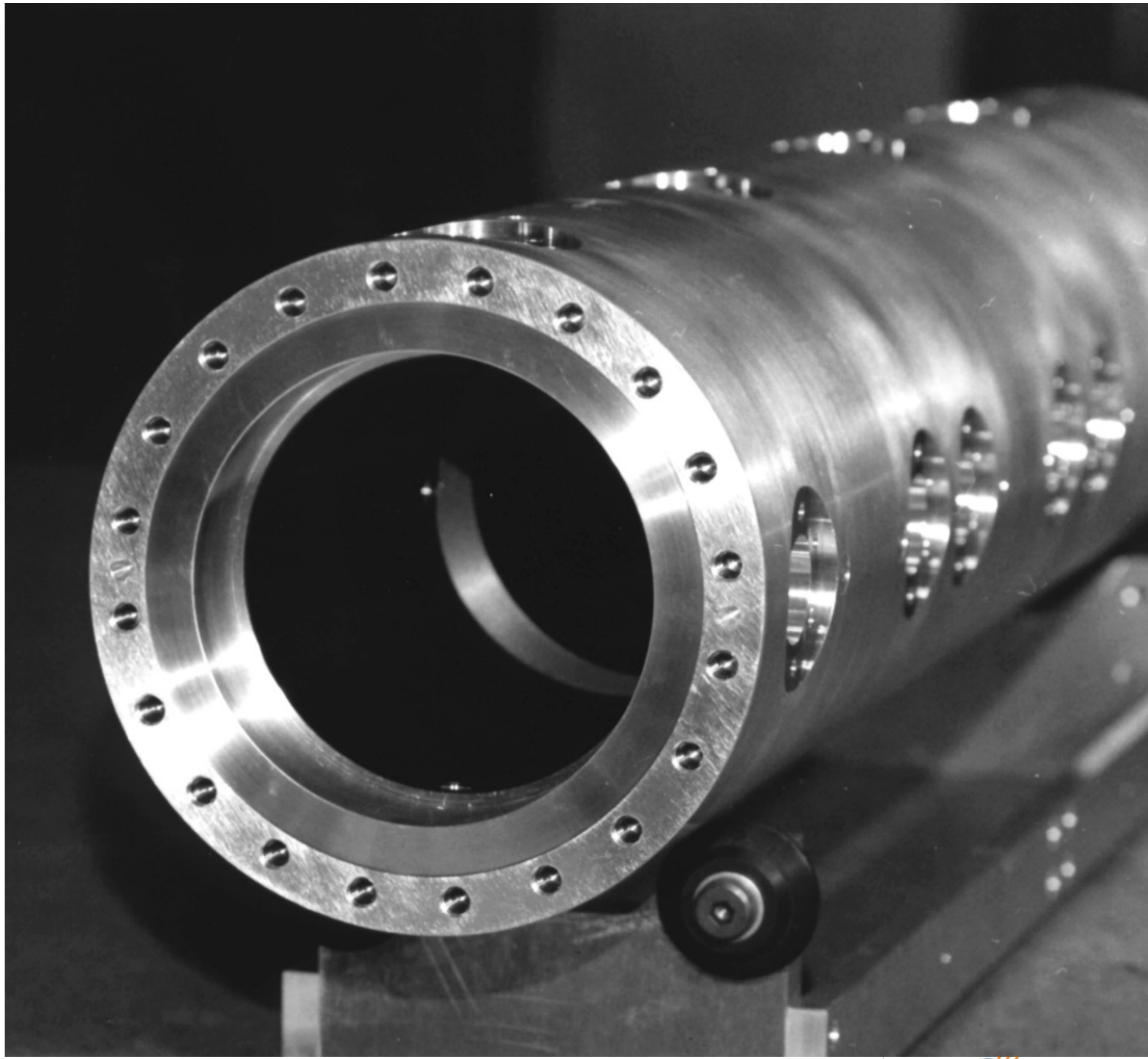
O content is high as the vacuum (without baking and only short pumping) is ~ 10^{-6} Torr, i.e., not sufficient for NEG coating

IOM

High Emissivity CuO Coatings on Synchrotron Kickers

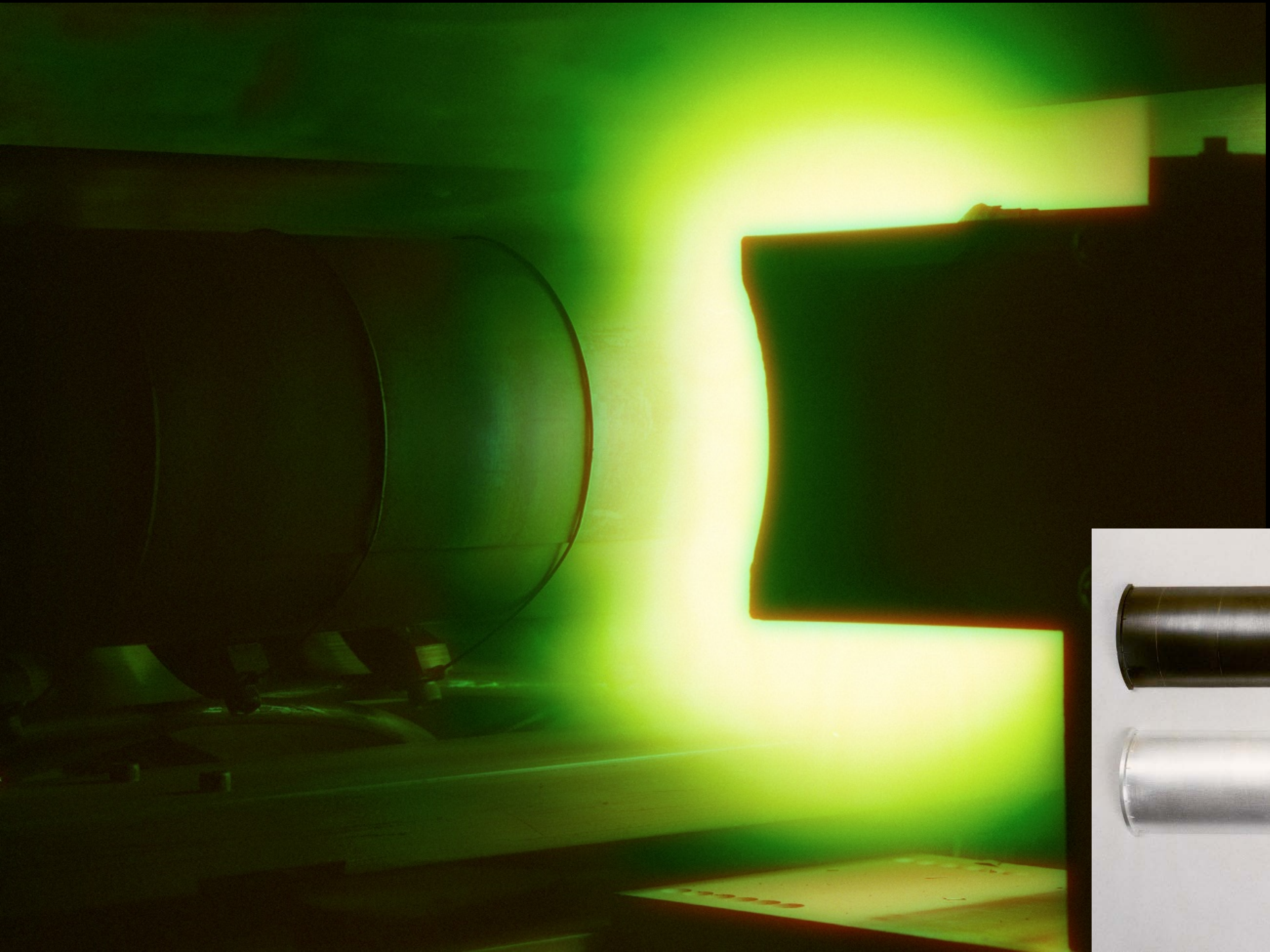
- UHV compatible
- high emissivity
- good adhesion (pull strength 50 MPa) even after repeated cycling to 150 °C
- RF transparent (tested at 500 MHz – 26 GHz)





S. Anders, et al., Surf. Coat. Technol. 76 (1995) 167.

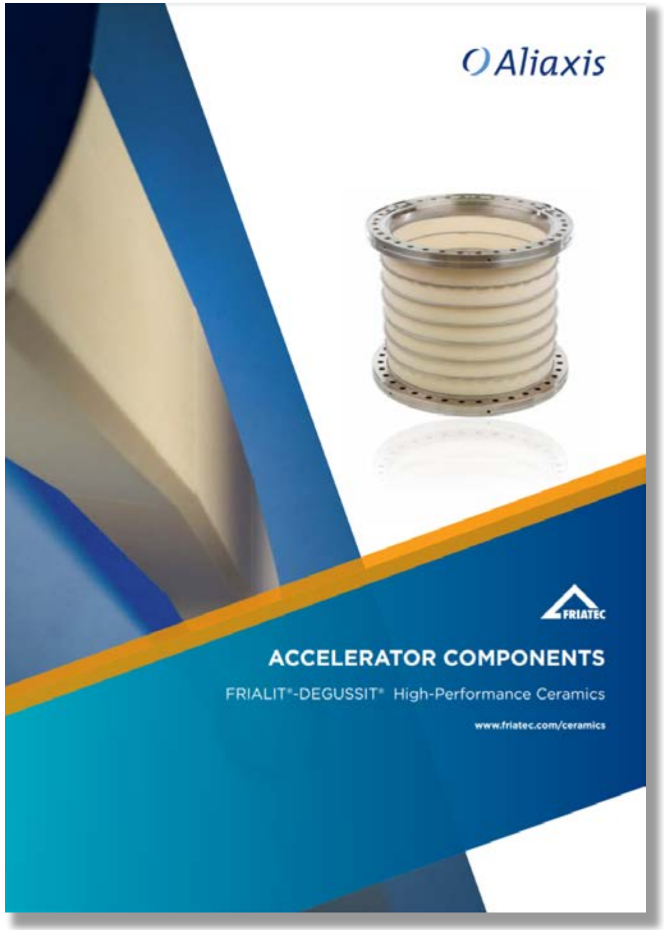
High Emissivity CuO Coatings on accelerator insert components



Cu dc-arc discharge in low pressure oxygen background

Modifying the surface resistivity of high voltage insulators by metal ion implantation

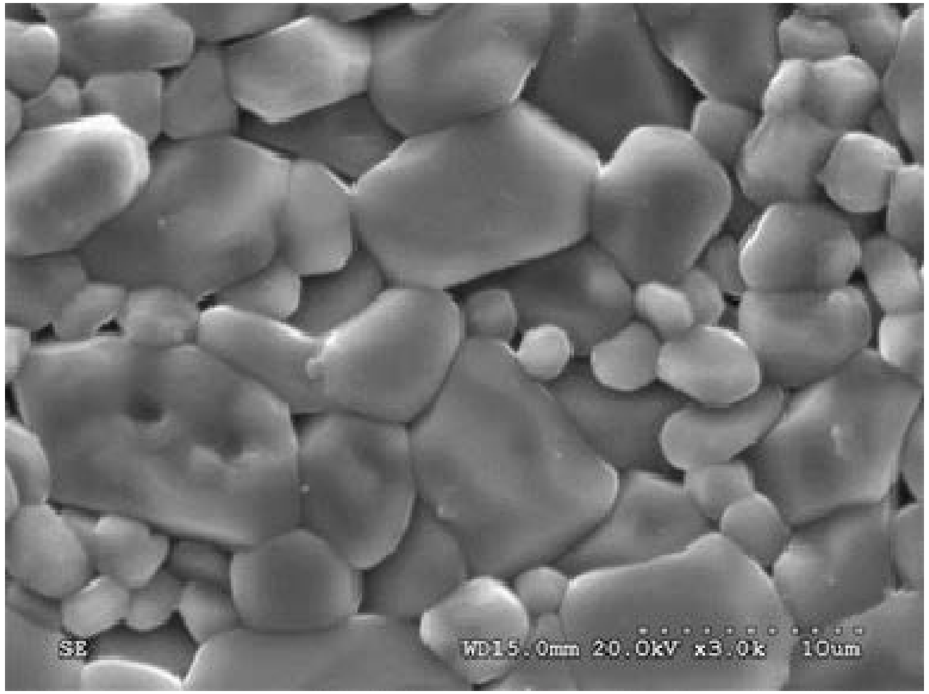
- idea: reduce charge-up by a controlled leakage current
- 100 kV CEBAF high voltage insulator
  - Ti or Pt ions, 135 keV, 5 x 10^{16} cm^{-2}
  - the insulator was rotated in vacuum
  - in situ monitoring of leakage current between electrodes at both ends, surface sheet resistance ~ 10^{10} Ω/sq.



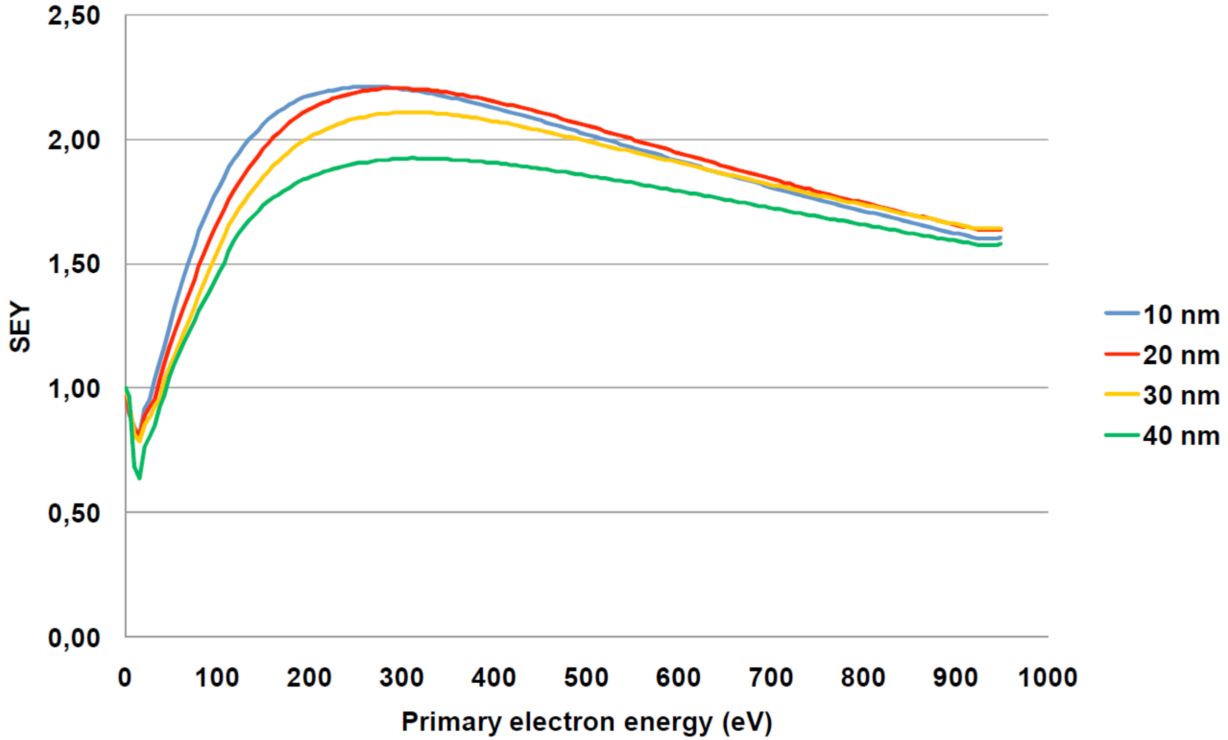
- S. Anders, et al., Surface resistivity tailoring of ceramic accelerator components, IEEE 1993 Particle Accelerator Conf., Washington, D.C., 1993.
- F. Liu, et al., "A method of producing very high resistivity surface conduction on ceramic accelerator components using metal ion implantation," Proc. 1997 PAC, Vancouver.

Coatings on RF Windows, Reducing Multipacting

- Alumina window
- common coating by magnetron sputtering
- TiN, < 50 nm



Al_2O_3, uncoated has yield as high as 7



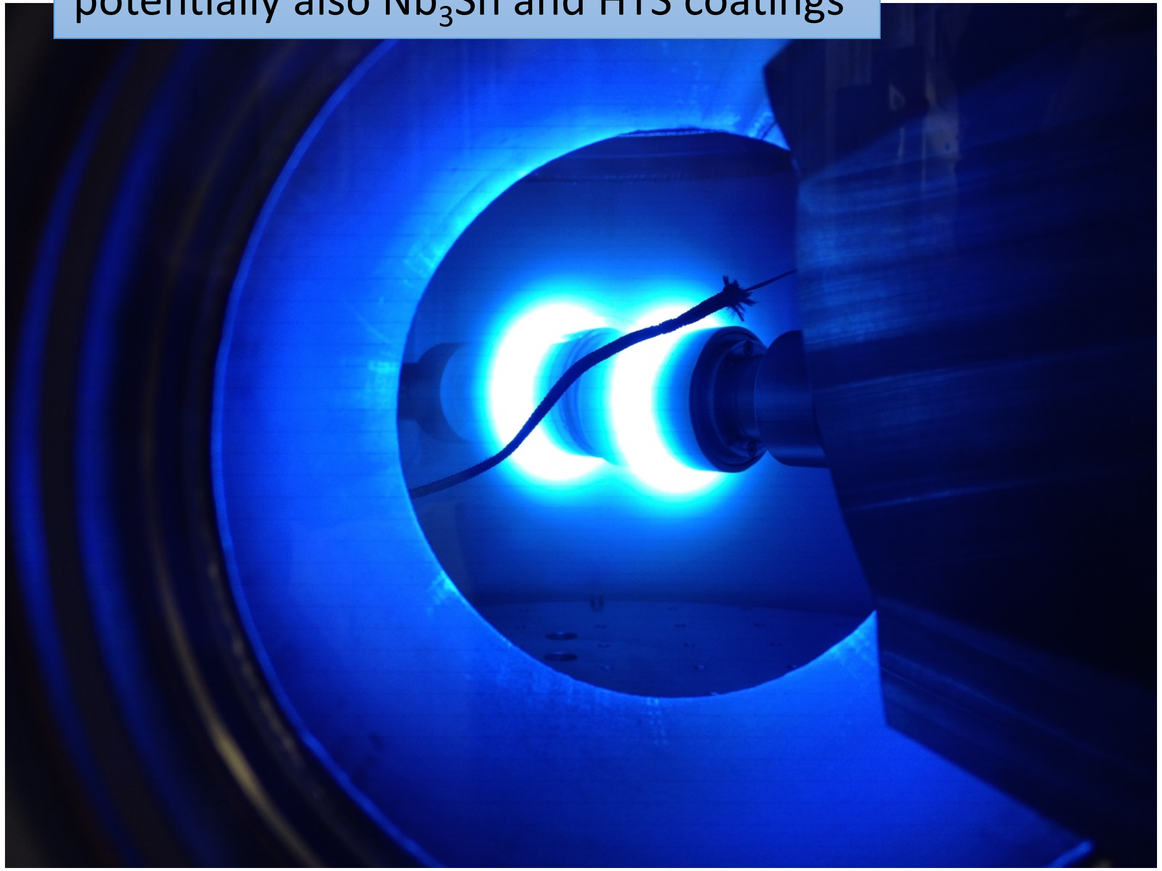
W. Kaabi, et al., IPAC'10, Kyoto, Japan (2007)2887-2889.

Superconducting Coatings on inner surface of SRF Cavities

bulk Nb cavities

H. Padamsee, et al., RF Superconductivity for Accelerators, 2nd ed., New York: Wiley-Interscience, 2008.

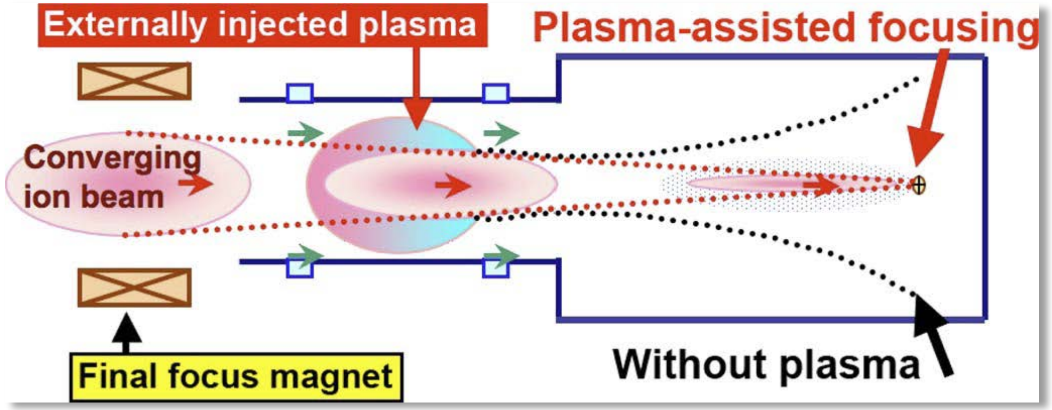
Nb coating on Cu or Al cavities
potentially also Nb_3Sn and HTS coatings

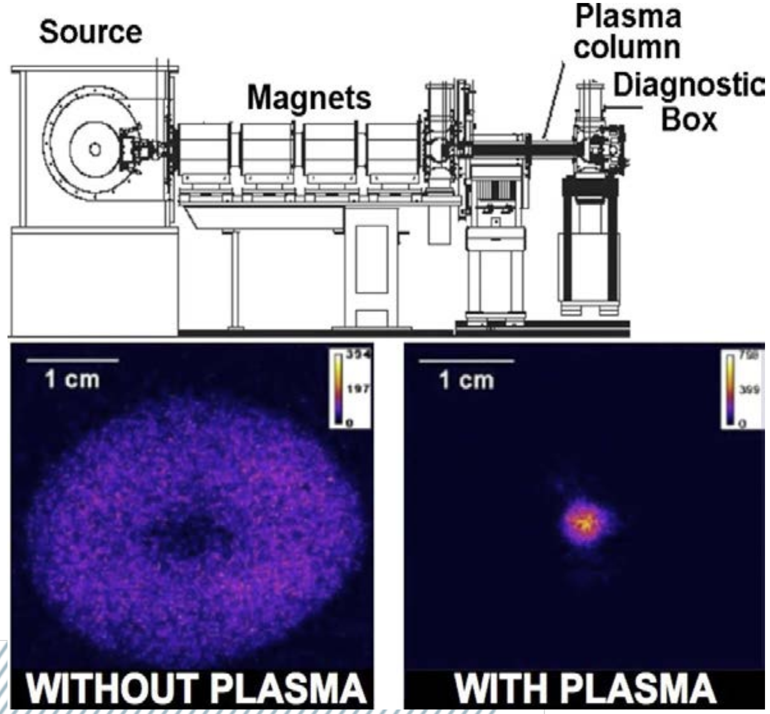


A. Anders, et al., "Deposition of niobium and other superconducting materials with high power impulse magnetron sputtering" 15th Int. Conf. SRF, Chicago, 2011.

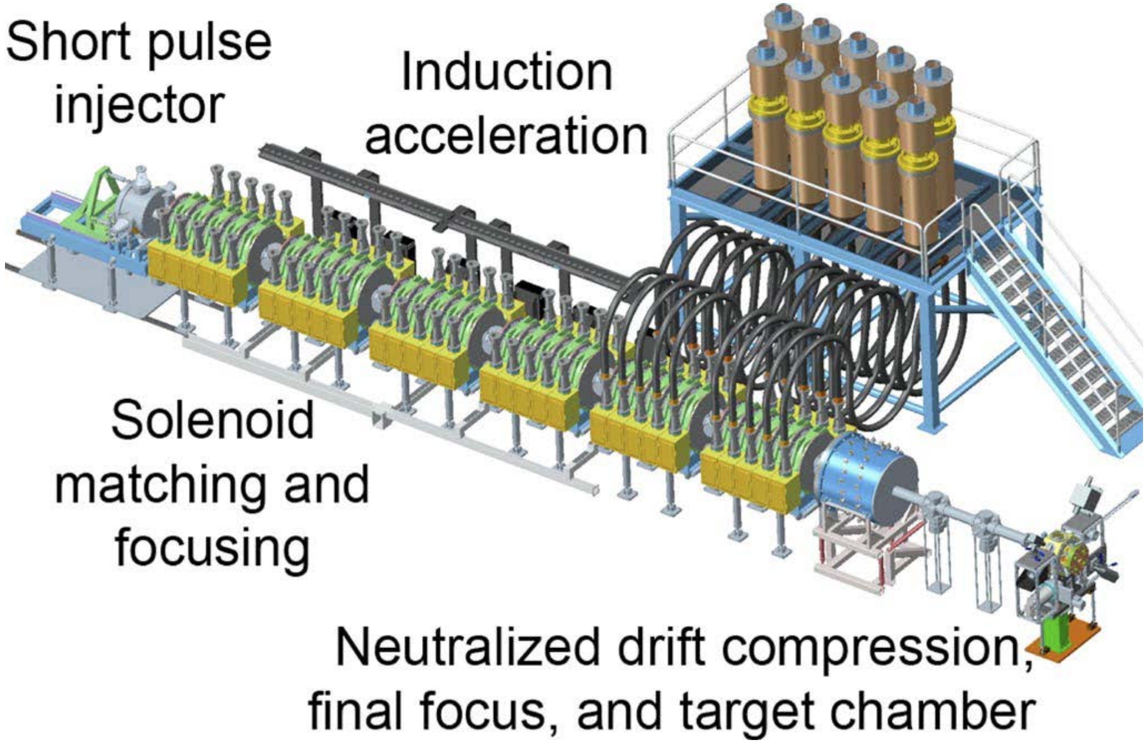
Self-Pumping Plasma in an Accelerator

- Plasma-based ion beam neutralization to enable ion beam compression



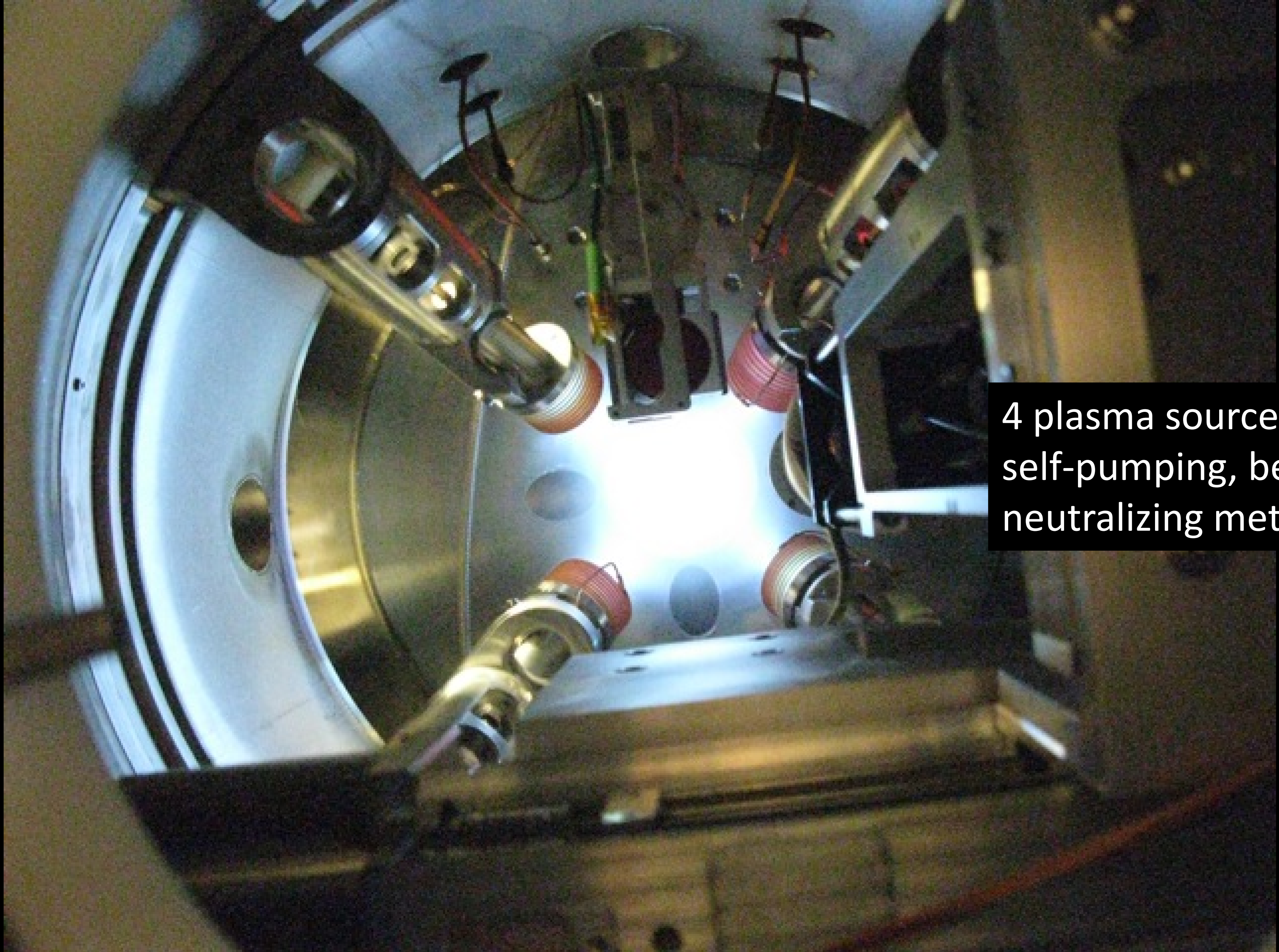


K^+ ion source 200–400 keV beams, 10–80 mA



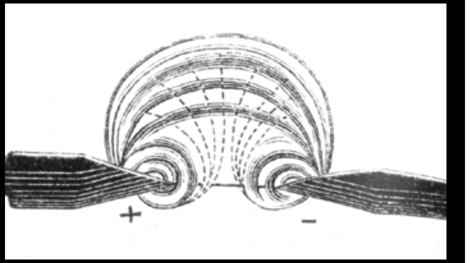
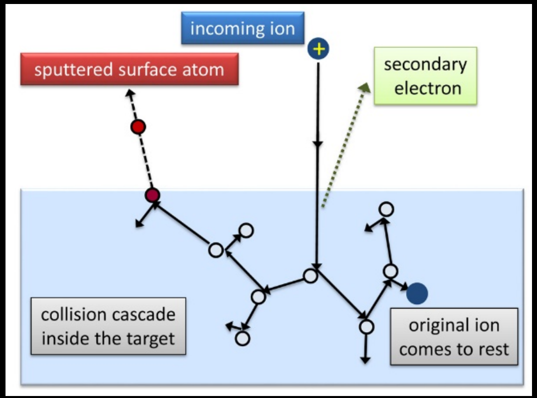
A. B. Sefkow, et al., Phys. Plasmas 16 (2009) 056701.

final focus ~ > 1 A of ion beam for ~ 1 ns, spot size ~ 1mm



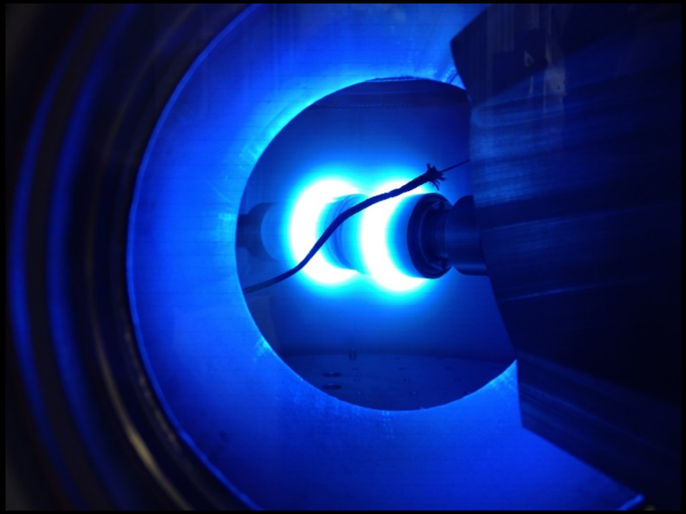
4 plasma sources to provide self-pumping, beam-neutralizing metal plasma

Summary

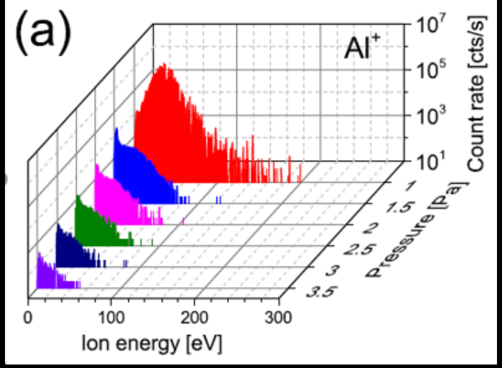



arcs and sputtering techniques

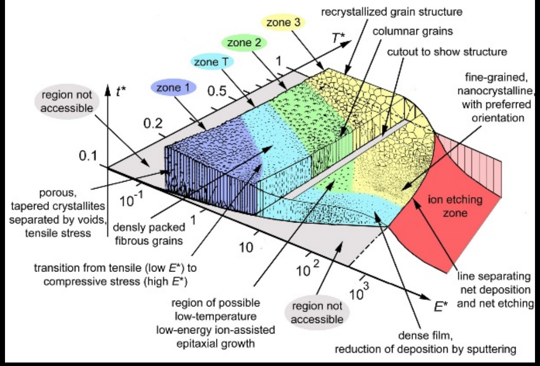
CuO high emissivity



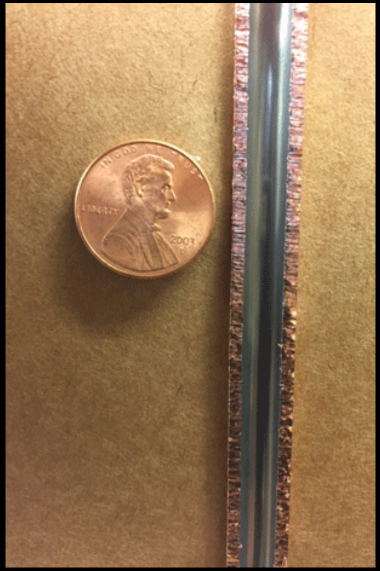
SRF cavity coatings



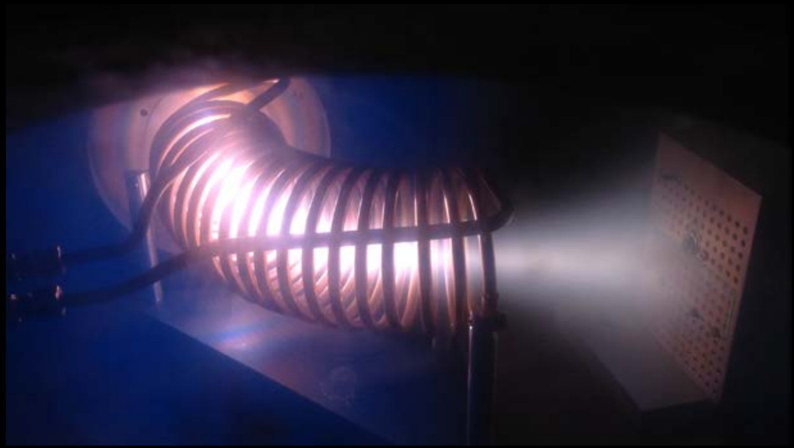
ion charge state and energy distribution functions



coating microstructure



NEG coatings



plasma macroparticle filtering