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Invited Talk for Session "Surface Engineering 5"

Pulsed Plasmas in Surface Engineering

Pulsed Metal Plasmas

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Motivation

Why do we want ions?

1. Surface Preparation ("etching") with metal ions

- The basic idea of the ABS process

2. Energetic Condensation:

- Kinetic energy can be controlled by E-field (bias!)
- Spatial distribution can be influenced by B-field
- Growth of films from hyper-thermal species
- Sub-surface insertion, and other processes

↓

3. Film properties:

- intermixed layer
- dense films, high modulus, high hardness, texture may evolve
- Trench and via filling possible
- Often good adhesion, however, stress can be excessive; need for stress control

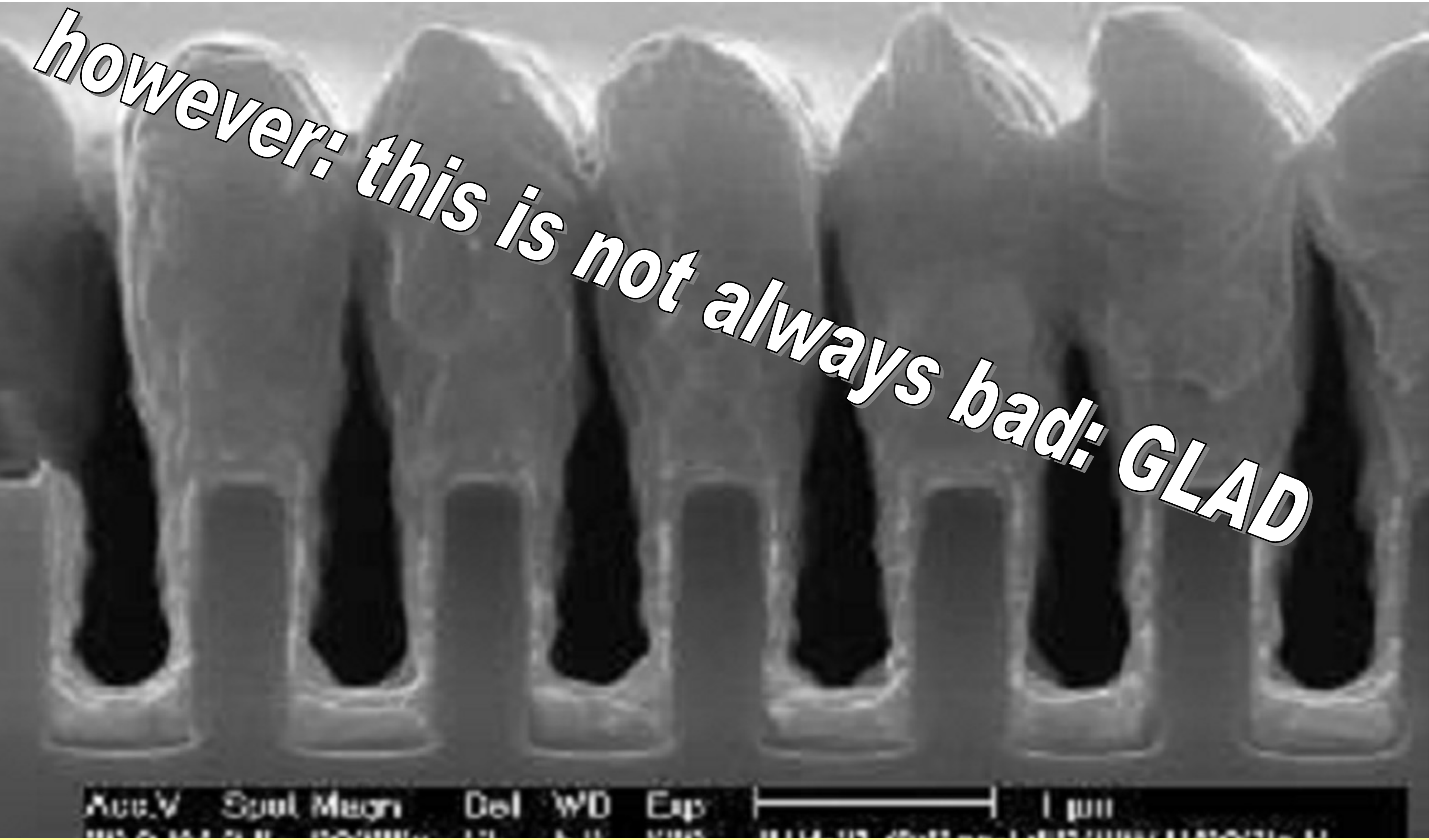
Why bothering with pulsing?

There are many reasons, some are related to each other:

PULSING is a means of…

1. **…suppress arcing in sputtering,**
2. **…enhancing the momentary power input while keeping average power unchanged, leading to**
   - **Higher degree of ionization of plasma, hence allowing us to use bias more efficiently,**
   - **Creating greater atomic excitation,**
   - **Creating greater degree of dissociation in molecular gases.**
3. **…obtaining new parameters for process control (duty cycle, pulse duration, peak amplitude, etc.)**

Why not using metal vapor, or a straight-forward sputtering technique?



Long throw sputtering [Photo courtesy P.Siemroth]

Metal Plasmas:

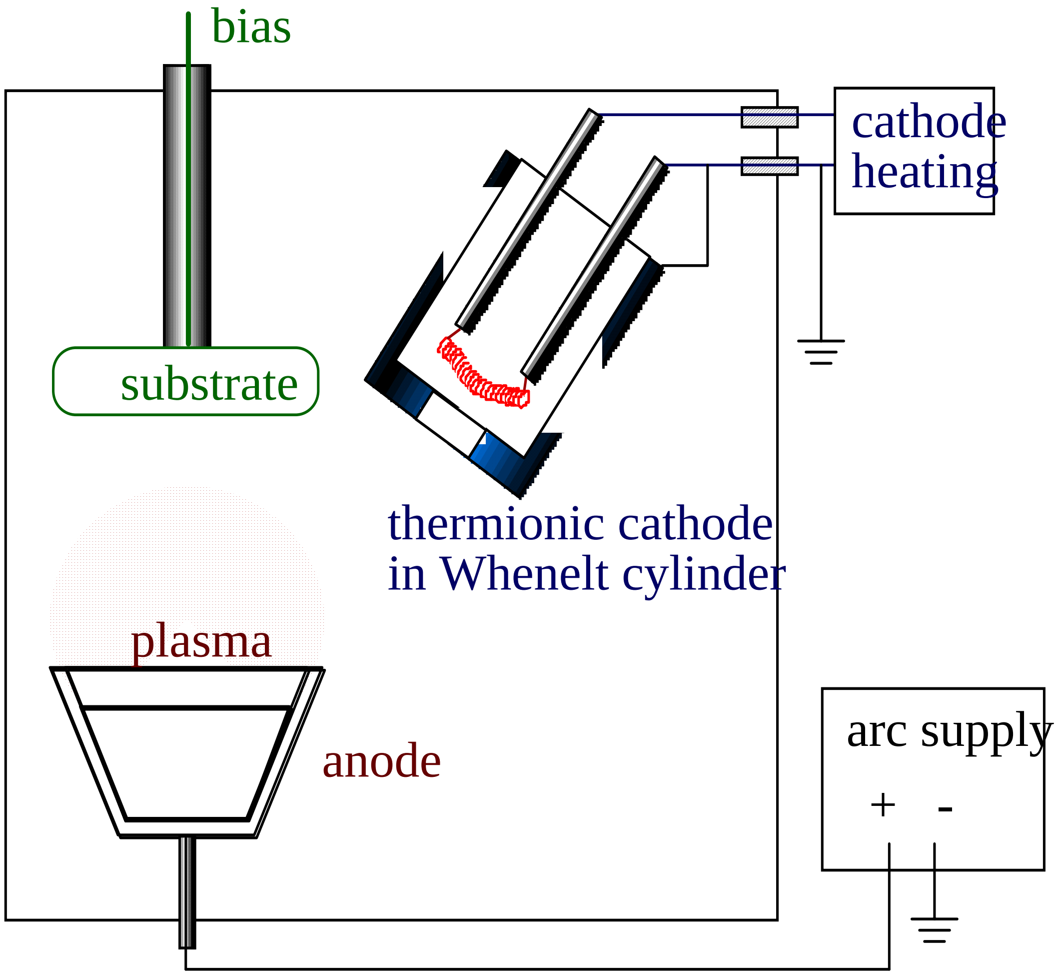
A very brief overview of how to produce it

Evaporation and Ionization: Ion Plating

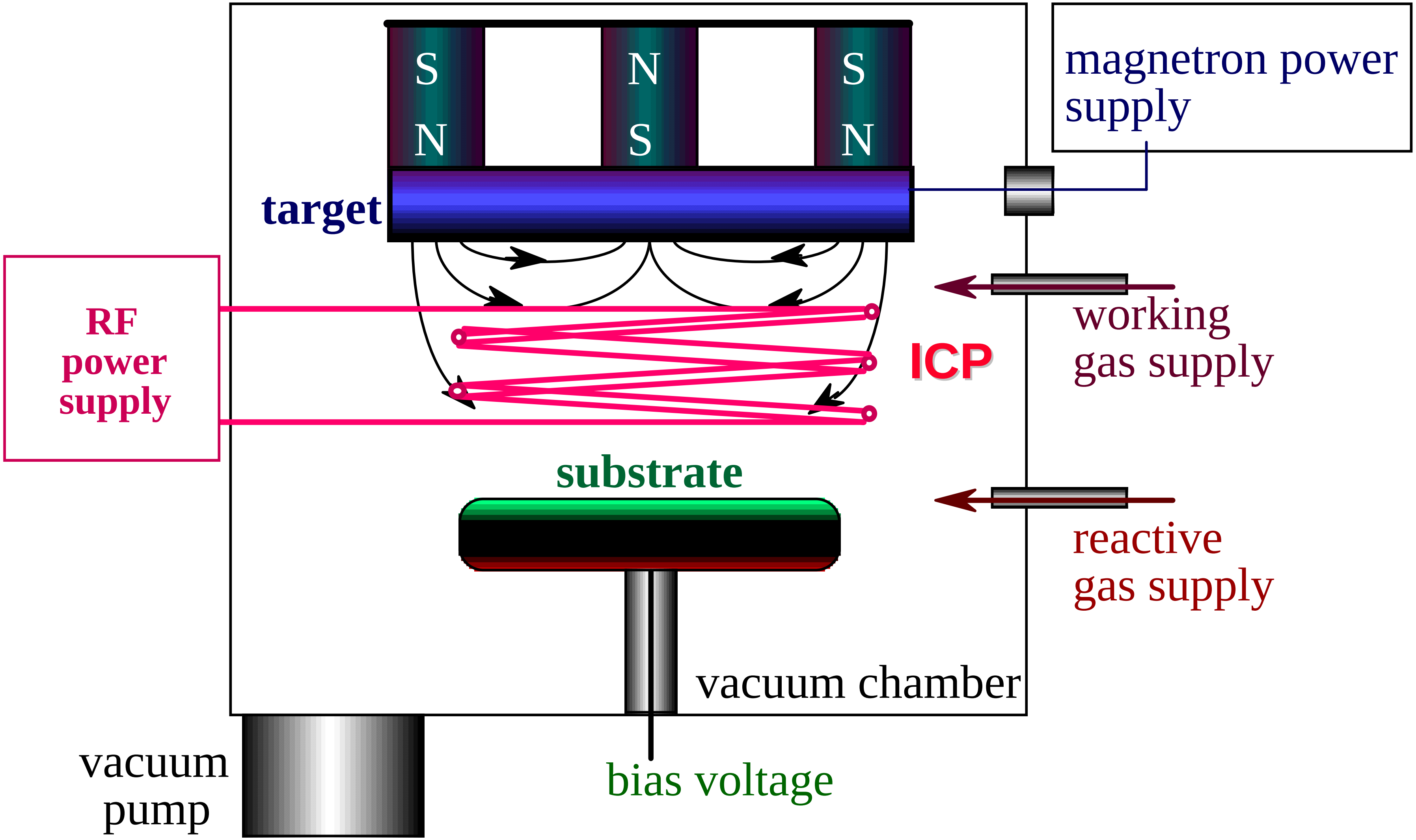
- Phase transitions, starting from solid metal
- Ionization by electron impact in discharge (Mattox,1964)

Properties

- Very high rate for low vapor pressure materials
- Low degree of ionization
- Little control in terms of energy and distribution



Magnetron Discharge with Ionization



Ion Plating with Metal Plasmas

Many incarnations:

Today a whole family of techniques.

However:

Focus here is on *PULSED* Plasmas!

- Power input provides in short pulses
- Peak power can be orders of magnitude above DC values
- pulse range may cover ms (e.g. pulsed arcs) to 100 fs (laser)

→ Plasma parameters can be significantly different, e.g.

  - ion charge and energy distributions

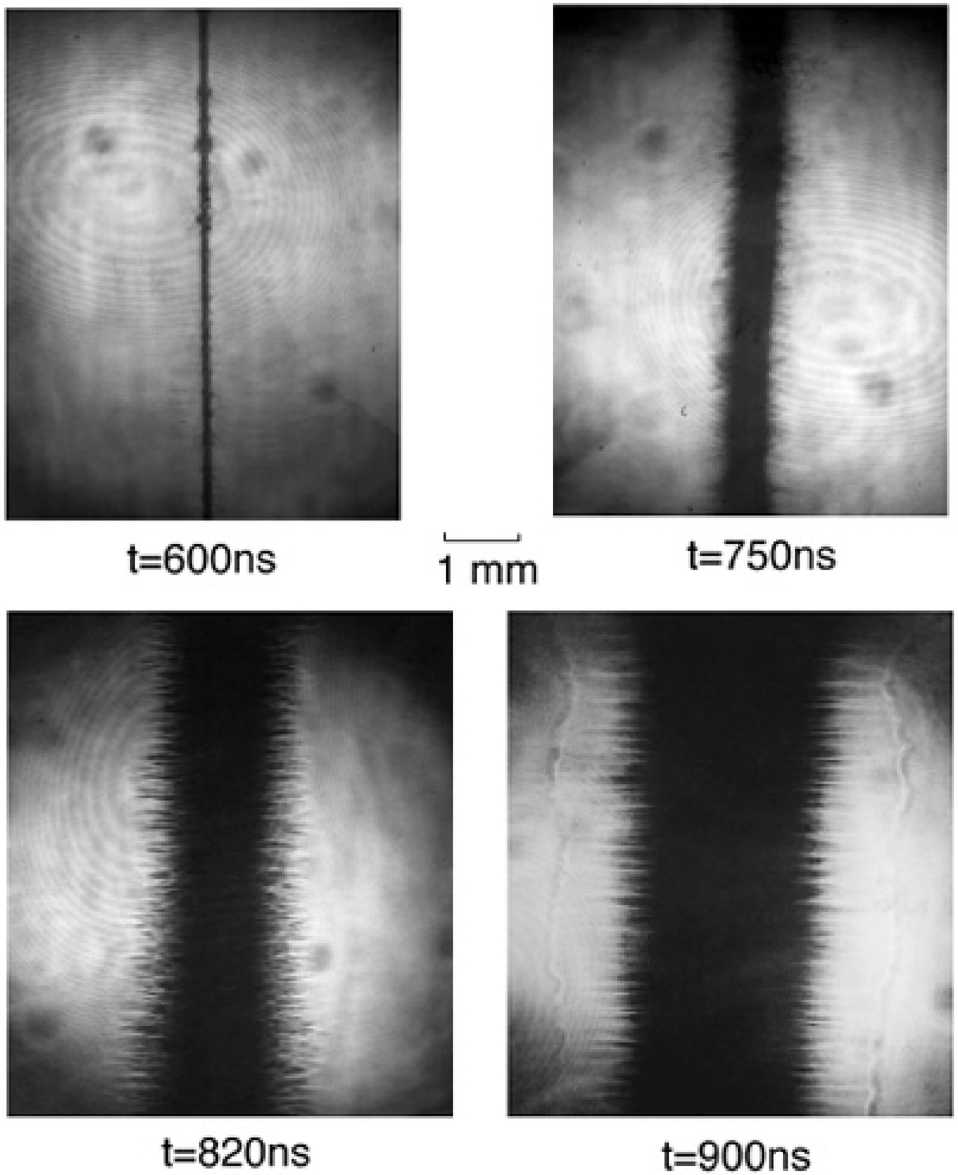
→ Film formation by energetic condensation is greatly affected

A pulsed plasma: Terawatt peak power

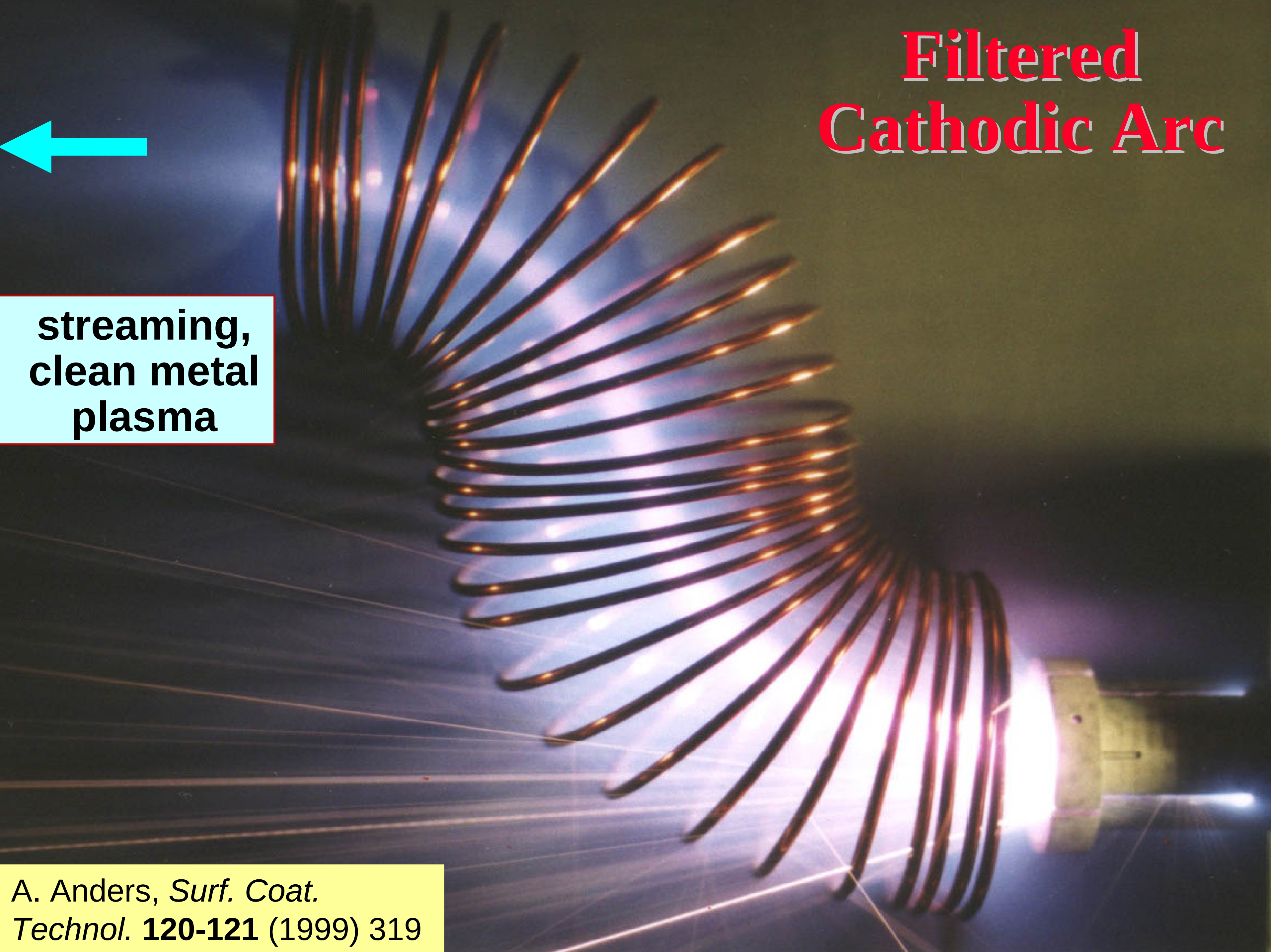
Wire Explosion

- Phase transition from solid by rapid Ohmic heating of metal
- Not well suited for coatings purposes

Shadowgrams of exploding wires
(Shift=160um, Cu, d=50um)



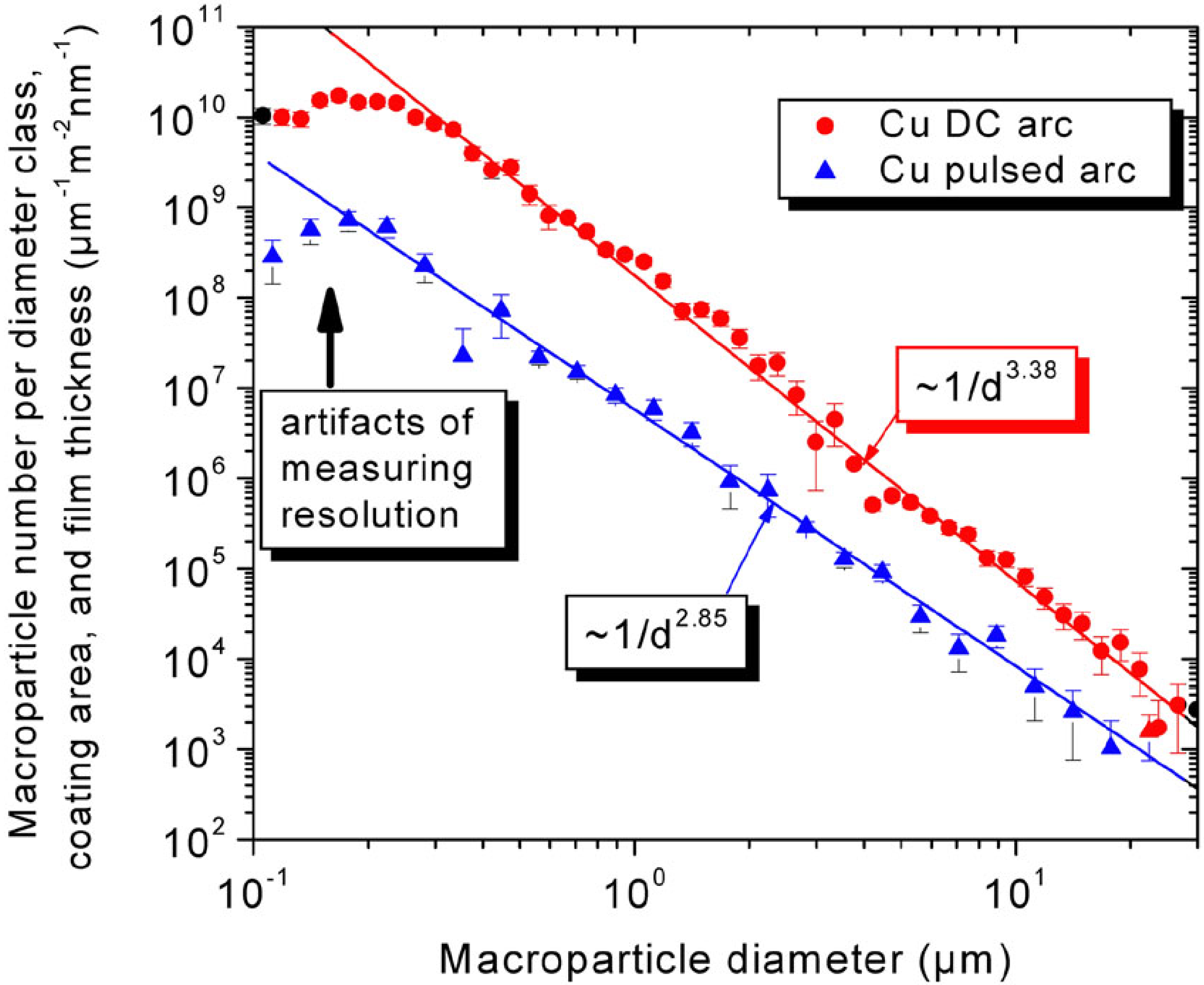
Filtered Cathodic Arc



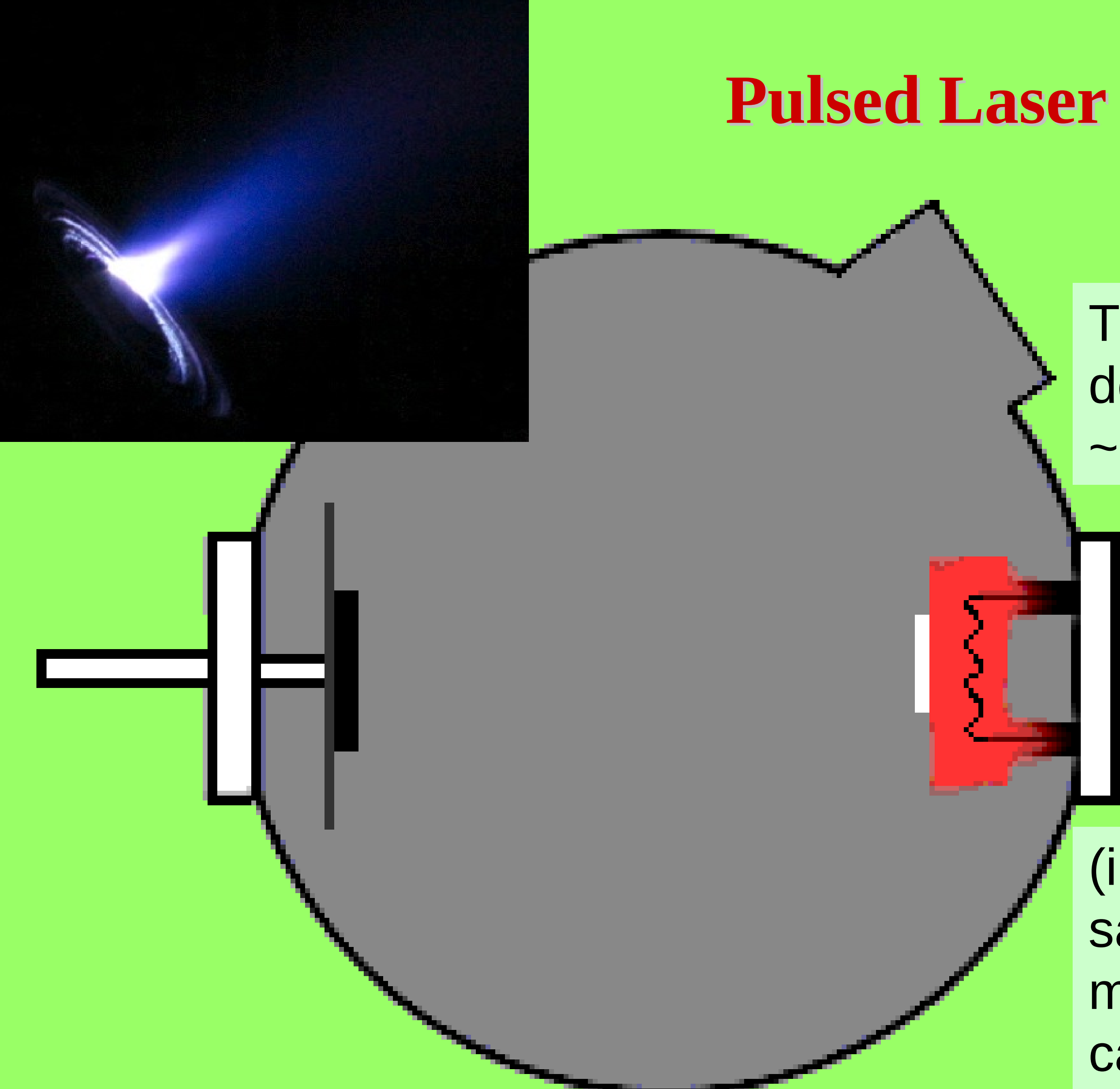
A. Anders, *Surf. Coat. Technol.* **120-121** (1999) 319

Cathodic Arc Plasmas: Macroparticles

A side benefit of pulsing: reduction of macroparticle production



Data from P. Siemroth, Dresden, Germany, see also O. Zimmer, Surf. Coat. Technol. 200 (2005) 440



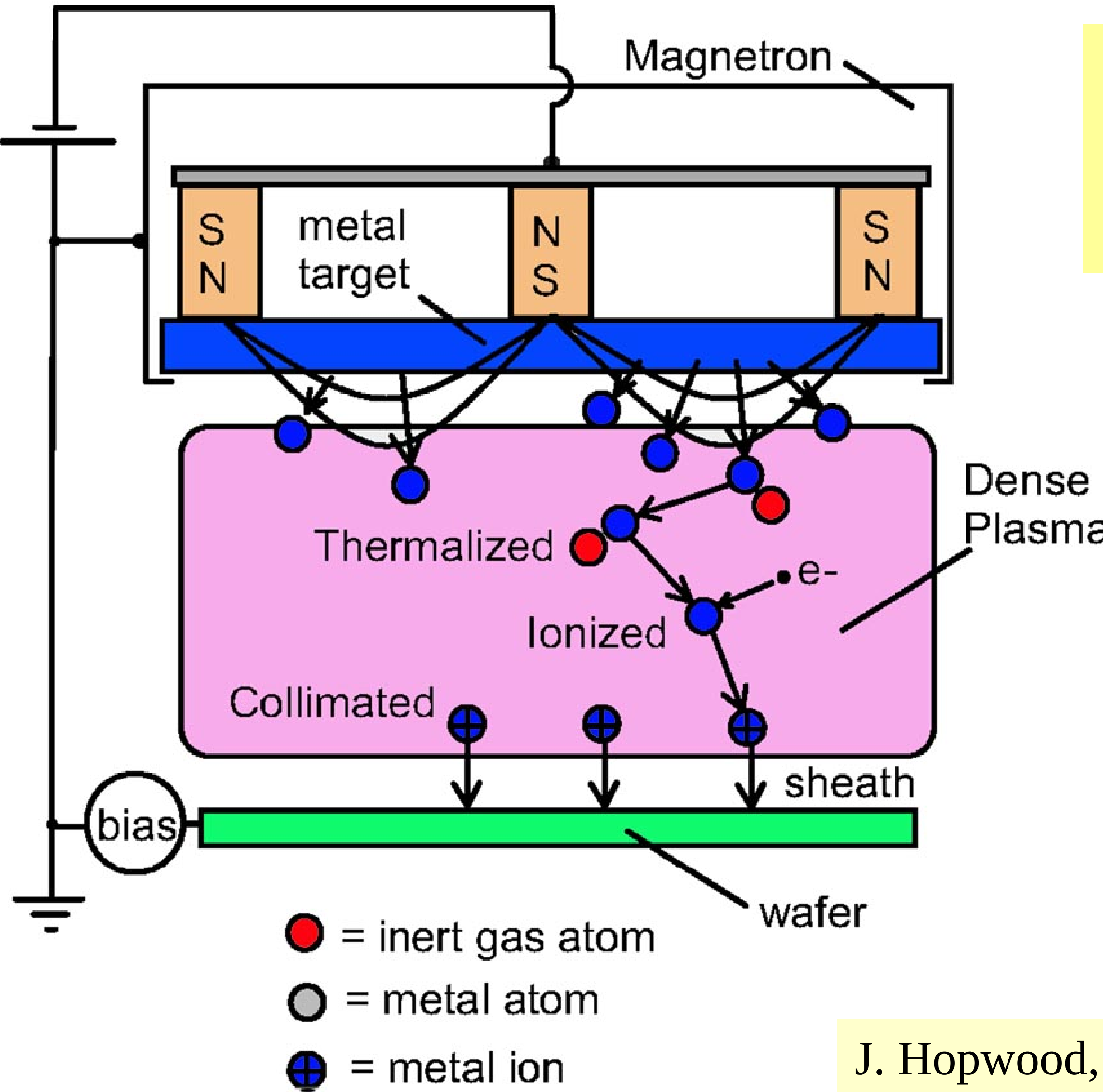
Pulsed Laser Ablation

Typical laser power density at target ~ 10^{13} W/m^2

(interestingly, the same order of magnitude as cathode spot)

Example from http://www.geocities.com/afserghei/LVE.htm

Pulsed Plasma & Ionized Sputtering: i-PVD

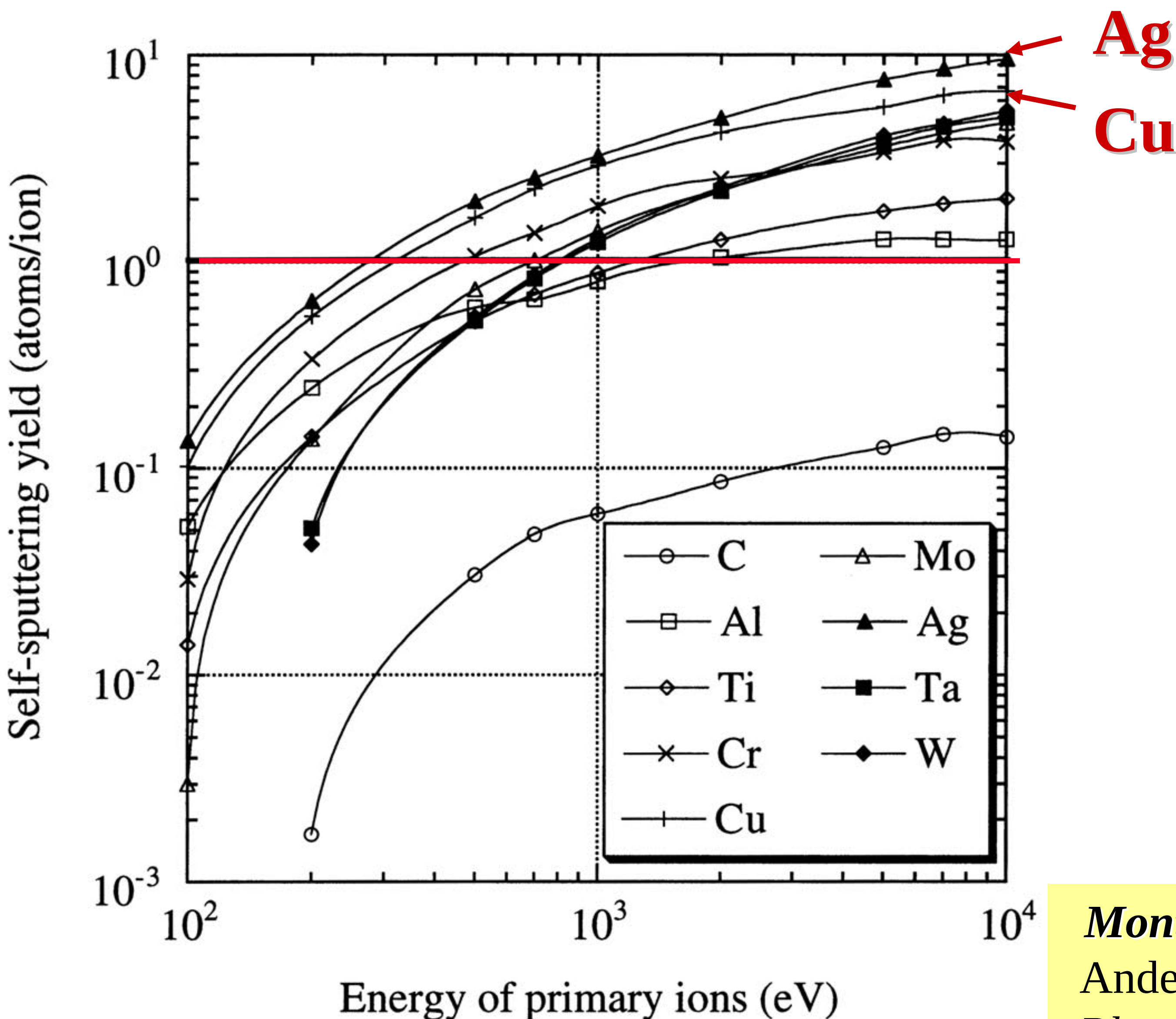


- Two developments
  - Medium Frequency sputtering
  - Ionized sputtering

- Slowing down the sputtered atoms to enhance the likelihood of ionization
- Once ionized, metal ions can contribute to sputtering:
- self-sputtering

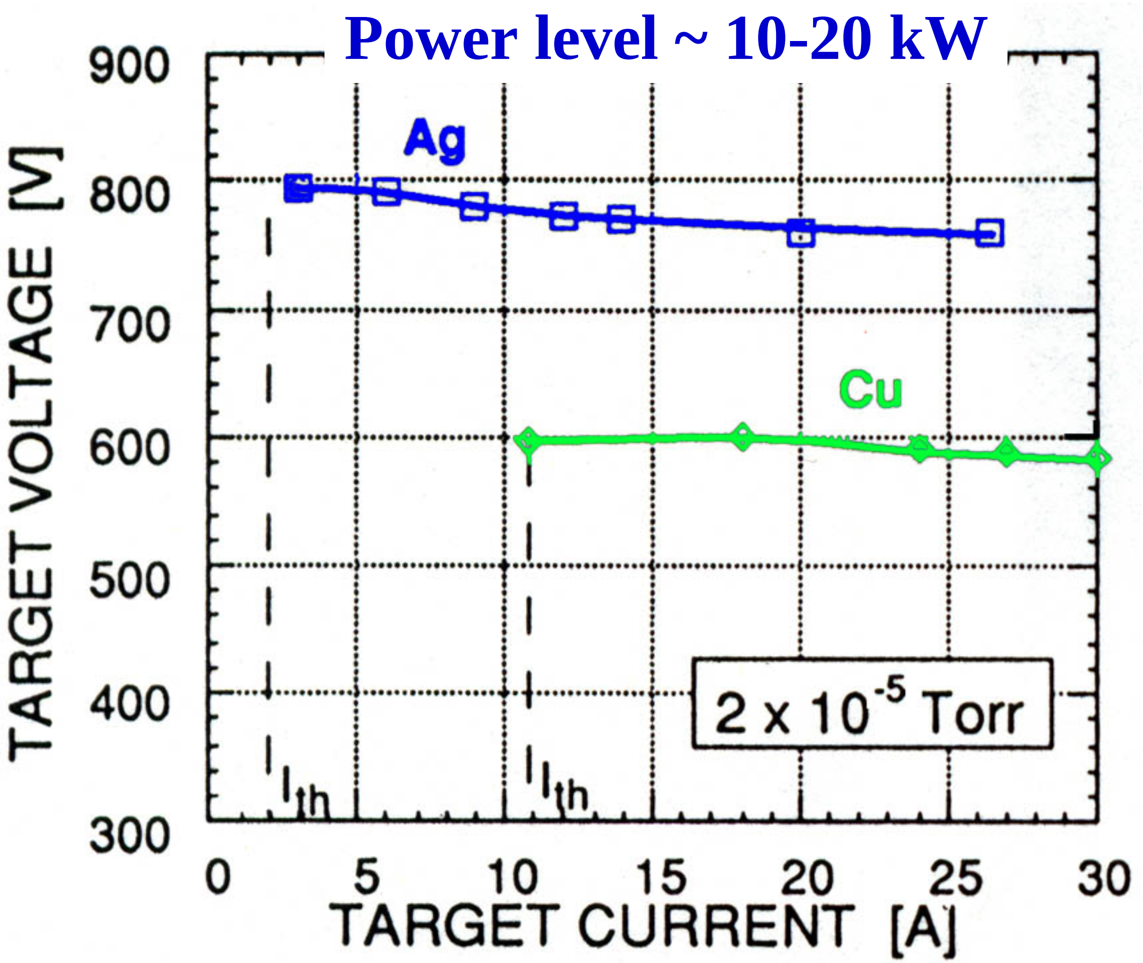
J. Hopwood, Phys. Plasmas **5** (1998) 1624

Self-Sputter Yield



Monte Carlo Simulations
Anders, *et al*, *IEEE Trans. Plasma Sci*. **23** (1995) 275

Self-Sputtering



- Ar only used at beginning.

- Works in DC mode
- To increase power density further:

How about pulsing?!

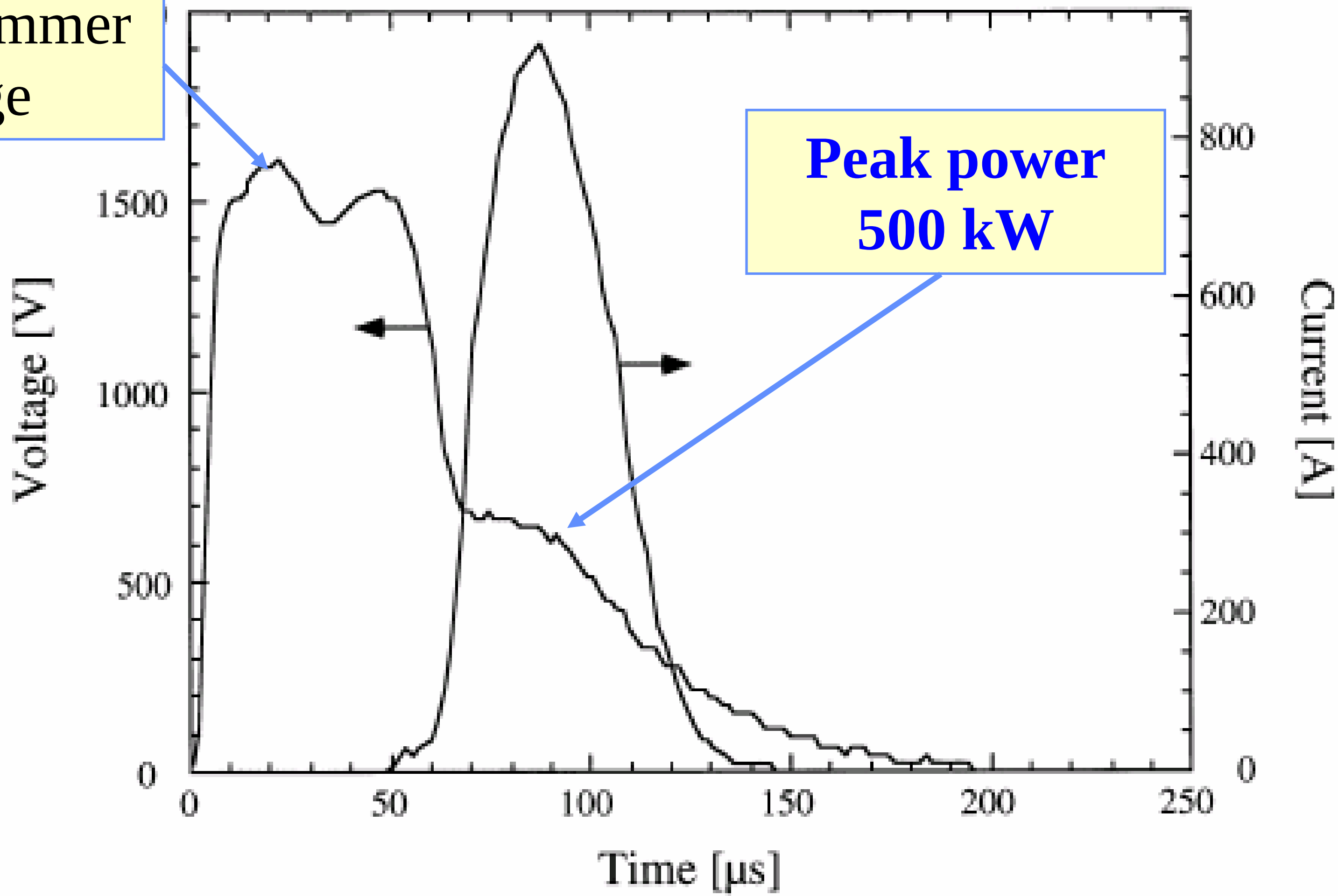
W. M. Posadowski and Z. Radzimski, *JVST A* 11 (1993) 2980

Late 1990s:
High Power Impulse Sputtering

Cu target, 65 mPa Ar

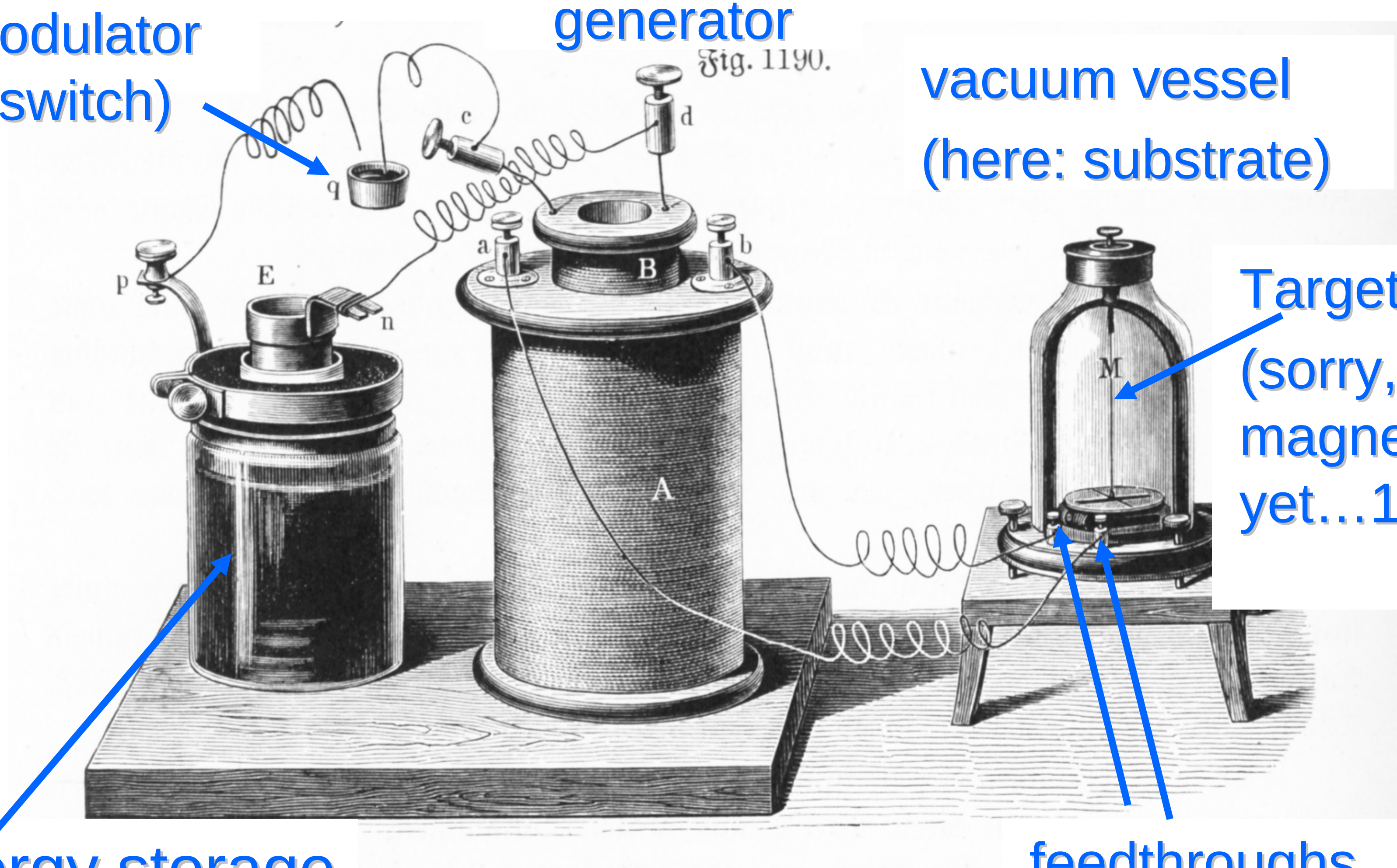
Delay: no simmer discharge

Peak power 500 kW



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

HIPIMS:
The "ingredients" to it make happen!



pulse modulator (switch)

high voltage generator

vacuum vessel (here: substrate)

Target (sorry, no magnets yet…1872)

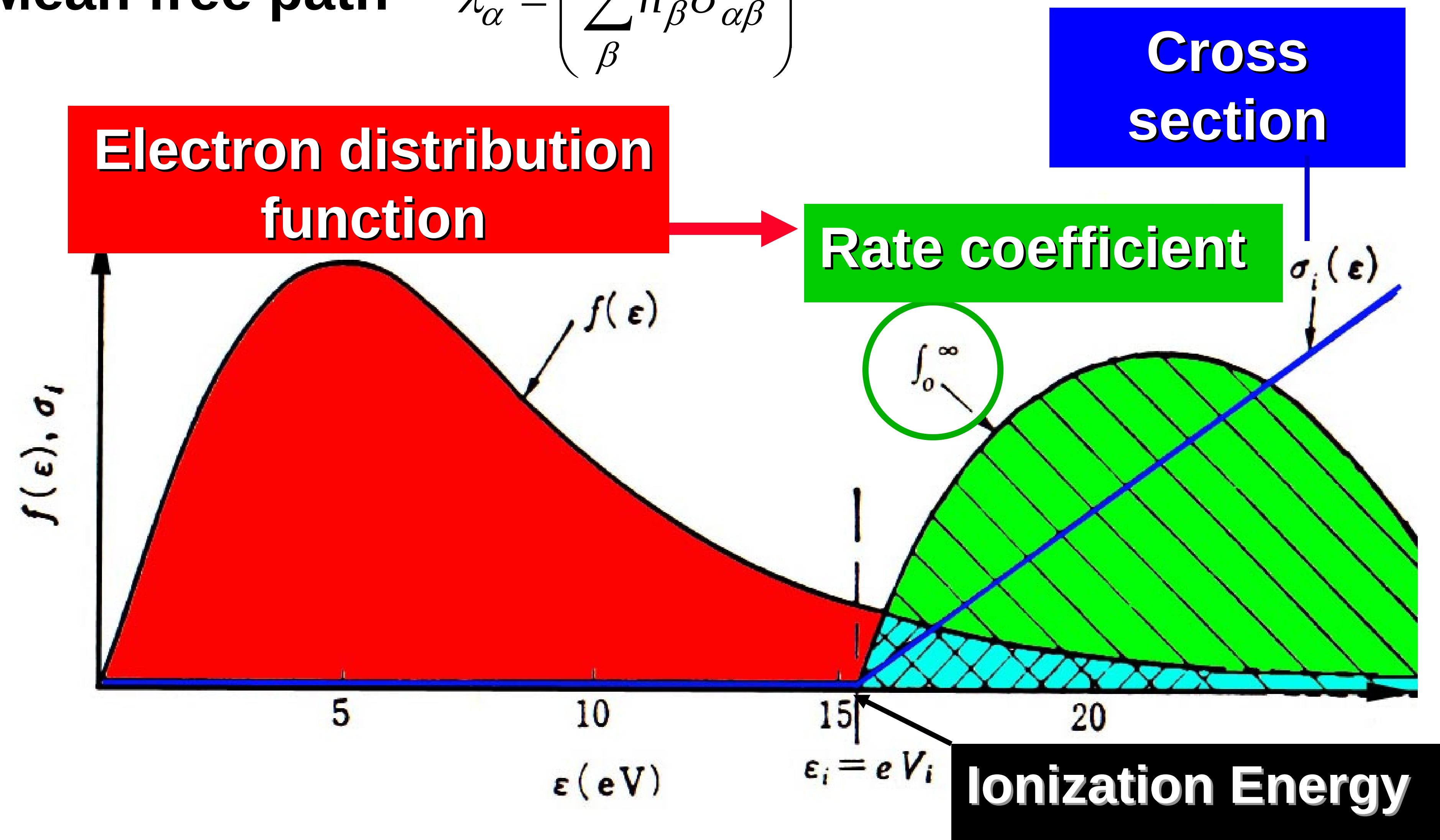
energy storage

feedthroughs

Some Ionization Physics…

Distribution Functions, Cross Sections, and Rate Coefficients

Mean free path $$\lambda_\alpha = \left(\sum_\beta n_\beta \sigma_{\alpha\beta} \right)^{-1}$$



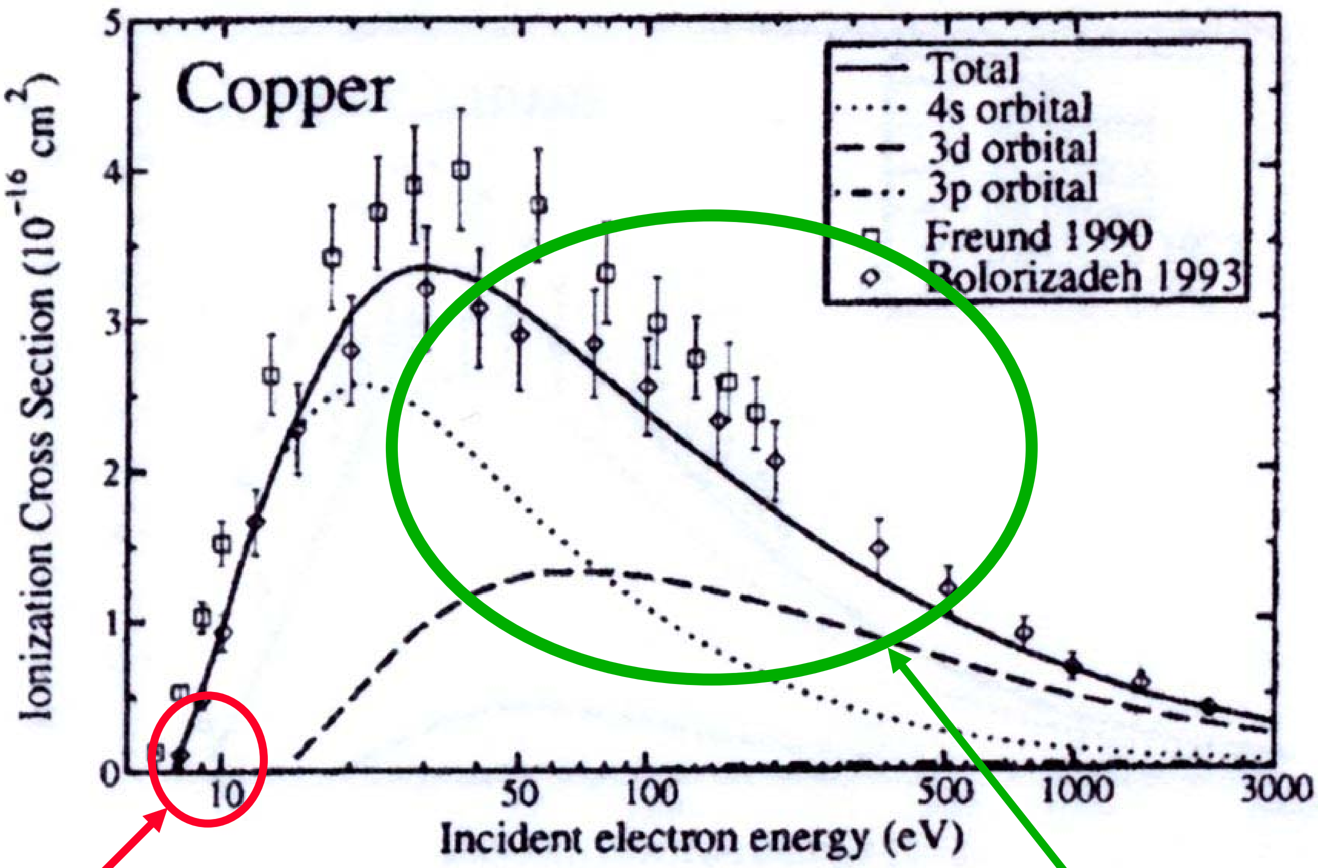
Ionization Energies: The Relative Ease of Metal Ionization

	E_{i0} (eV)	E_{i1} (eV)	E_{i2} (eV)
Al	5.99	18.83	28.45
Cu	7.73	20.29	36.84
Ti	6.82	13.58	27.49
Nb	6.88	14.32	25.0
Cr	6.77	16.50	31.0
Ni	7.64	18.17	35.3
Zr	6.84	13.13	23.1

much lower than — **comparable to** — **much higher than**

E_{io}(Ar)=15.76 eV

Ionization Cross Sections

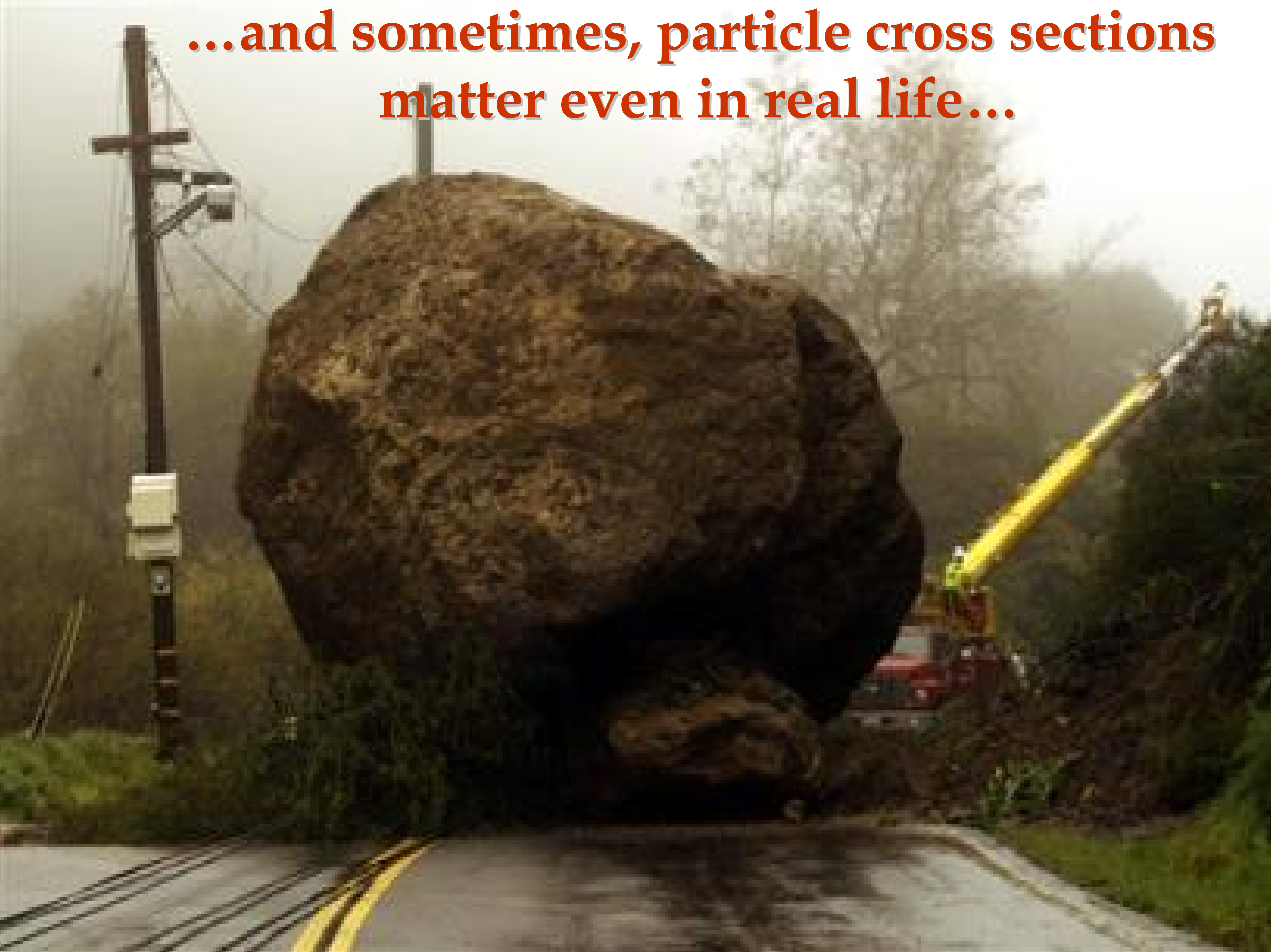


Tail of Maxwell distribution acts here

beam of sheath-accelerated electrons acts here

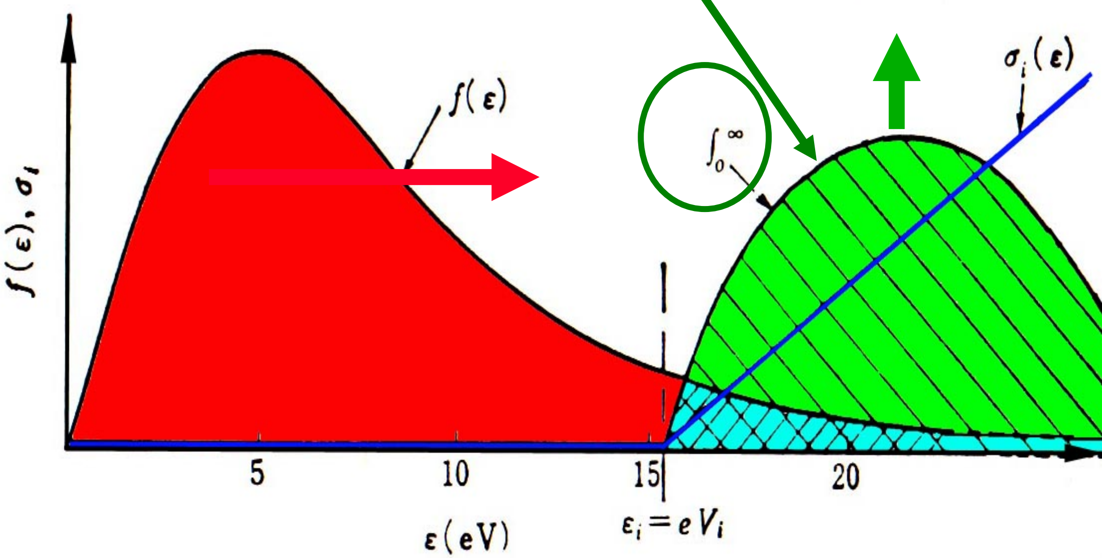
P. L. Bartlett and A. T. Stelbovics, *Phys. Rev. A* 66 (2002) 102707

…and sometimes, particle cross sections matter even in real life…



Pulsing → Sequence of Events…

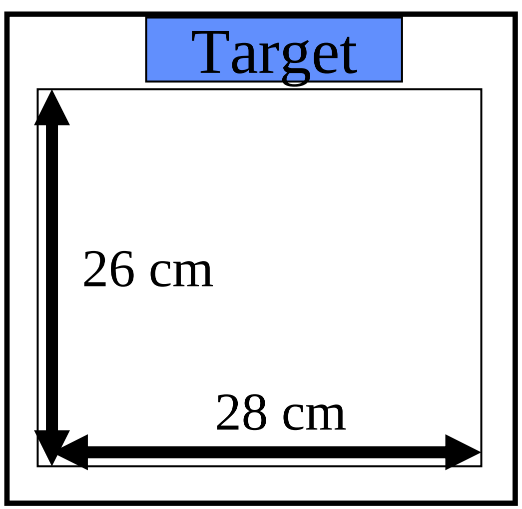
- Applied voltage increases
- Target sheath expands
- Energy of impacting Ar^+ increases
- Sputter ***yield*** and secondary electron (SE) yield increase, giving raise to increasing current
- secondary electrons gain higher energy
- rate coefficient increases
- plasma density increases
- Sheath contracts; sputter ***rate*** increases
- Density of sputtered atoms increases
- fraction becomes ionized ….



Time-Resolved Measurements of Plasma Density in High Power Pulsed Sputtering

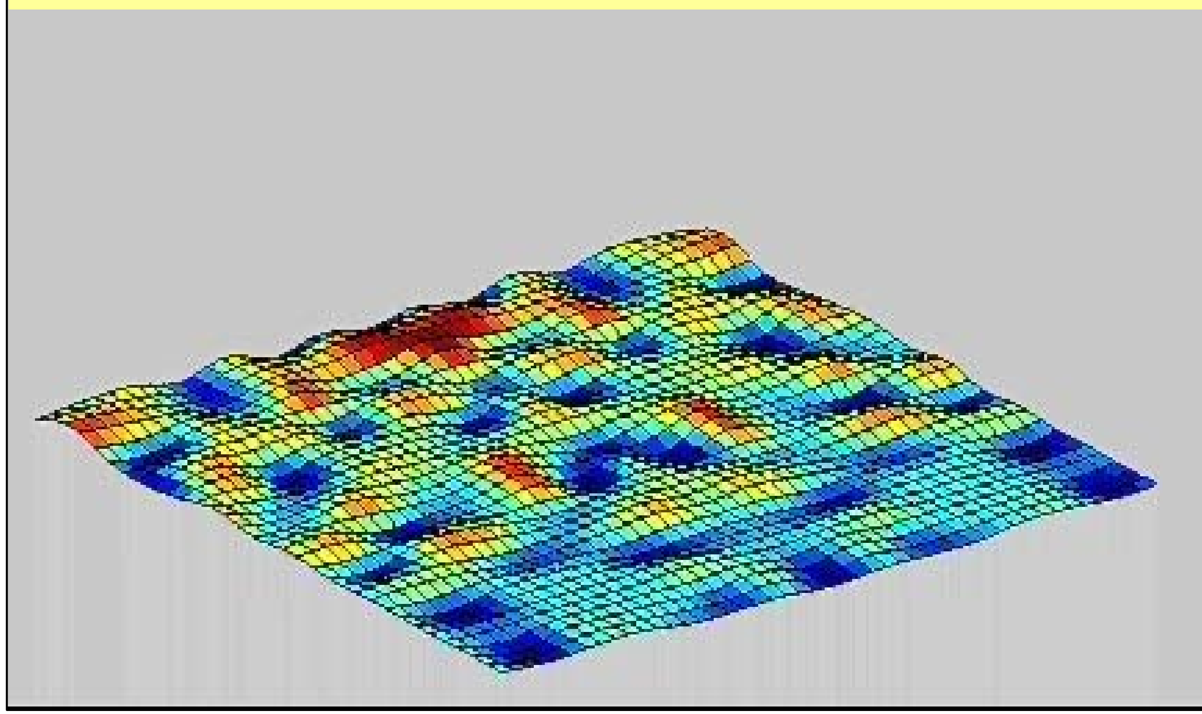
Langmuir probe data

- (Plasma density)$^{0.33}$
- Time scale: 0-1.8 ms
- 15 cm diameter target



$n^{0.33}$

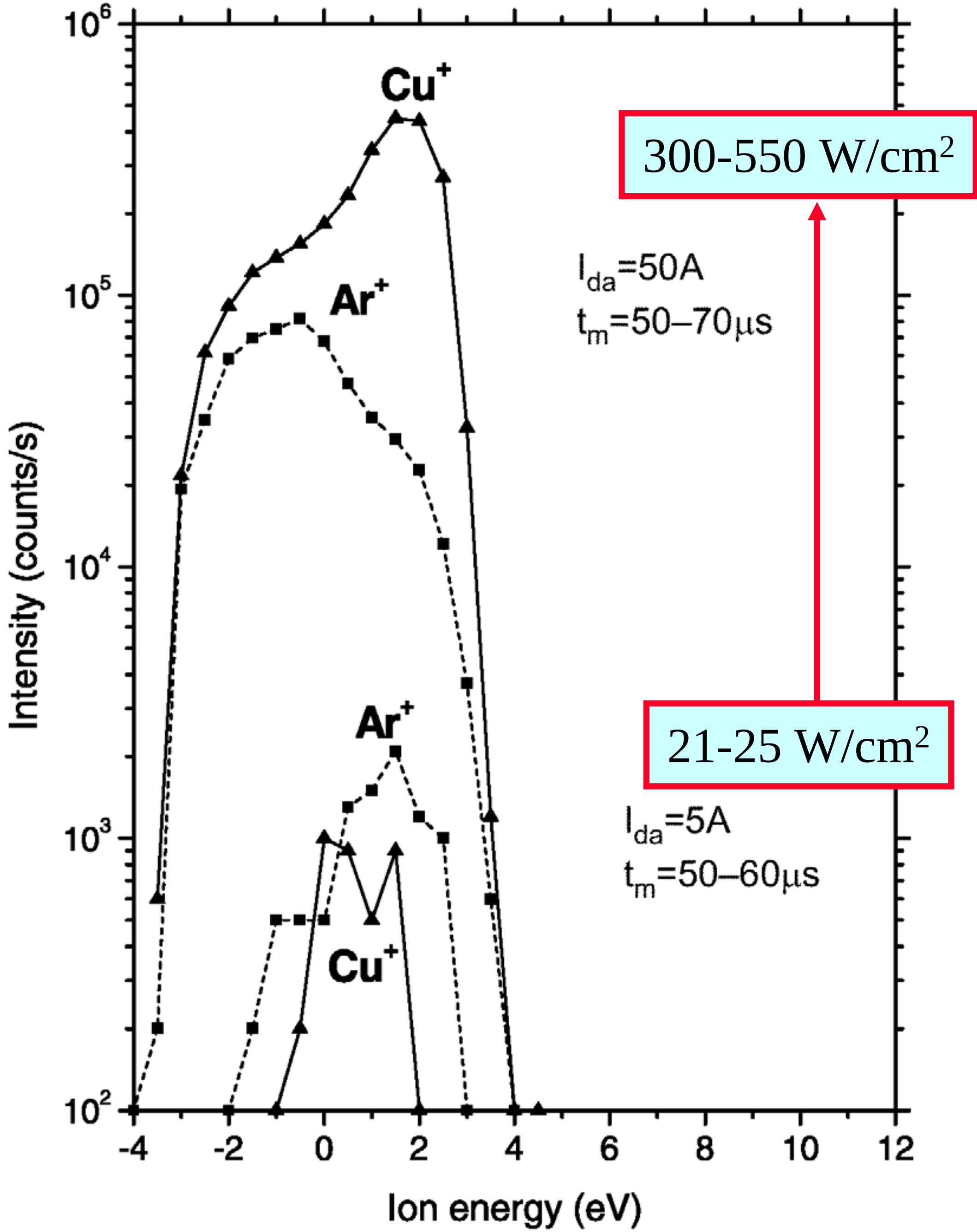
Video: Courtesy of Johan Böhlmark, Linköping, Sweden; see also J. Böhlmark, *et al.*, IEEE Trans. Plasma Sci. **33** (2005) 346 and http://ieeexplore.ieee.org for a 2 MB AVI clip visualizing the dynamics of the plasma



Time resolved OES

Ionization of sputtered material is obvious

- Ionization is observed for Cu and Ag even at moderate power density and high frequency

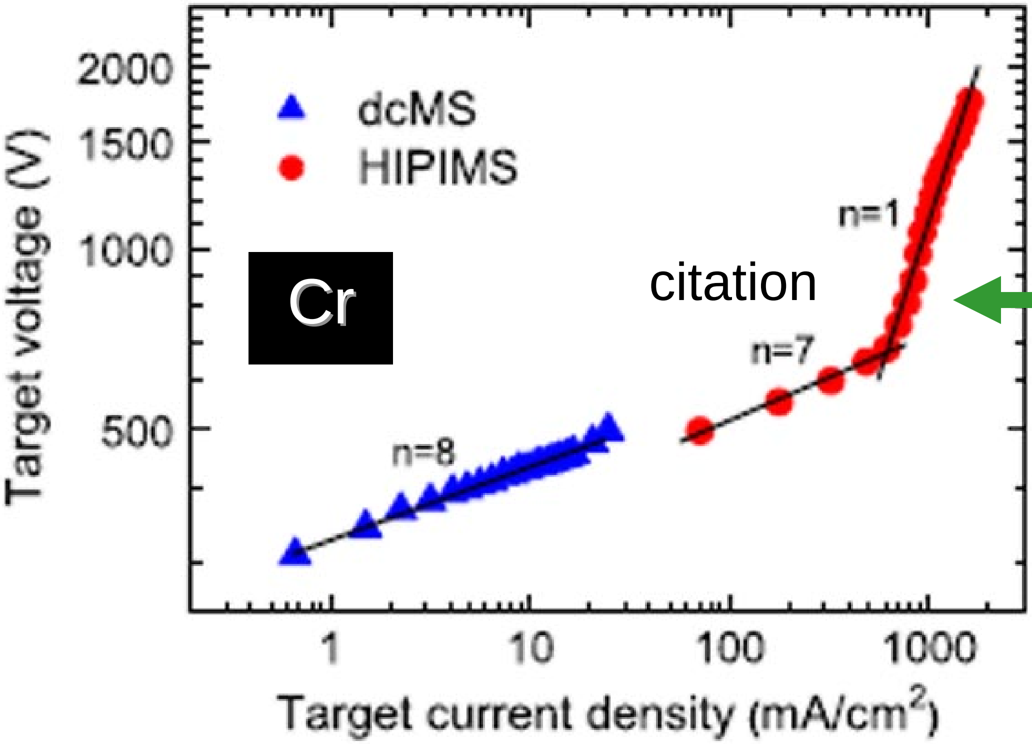


Vlcek, Pajdarova, Musil,
Contrib. Plasma Phys. **44** (2004) 426

Why is there a higher impedance at higher peak power?

Low degree of ionization: $$\sigma_1 = \frac{e^2 n_e}{m_e \sum_h \nu_{eh}}$$ ← friction term

High degree of ionization (Spitzer): $$\sigma_{Spitzer} \approx const\ T_e^{3/2}$$



- A steeper slope is indicative of the "difficulty" to transport the current between target (cathode) and the anode

A.Ehiasarian, *et al.*, *Vacuum* **65** (2002) 147

Factors affecting plasma impedance

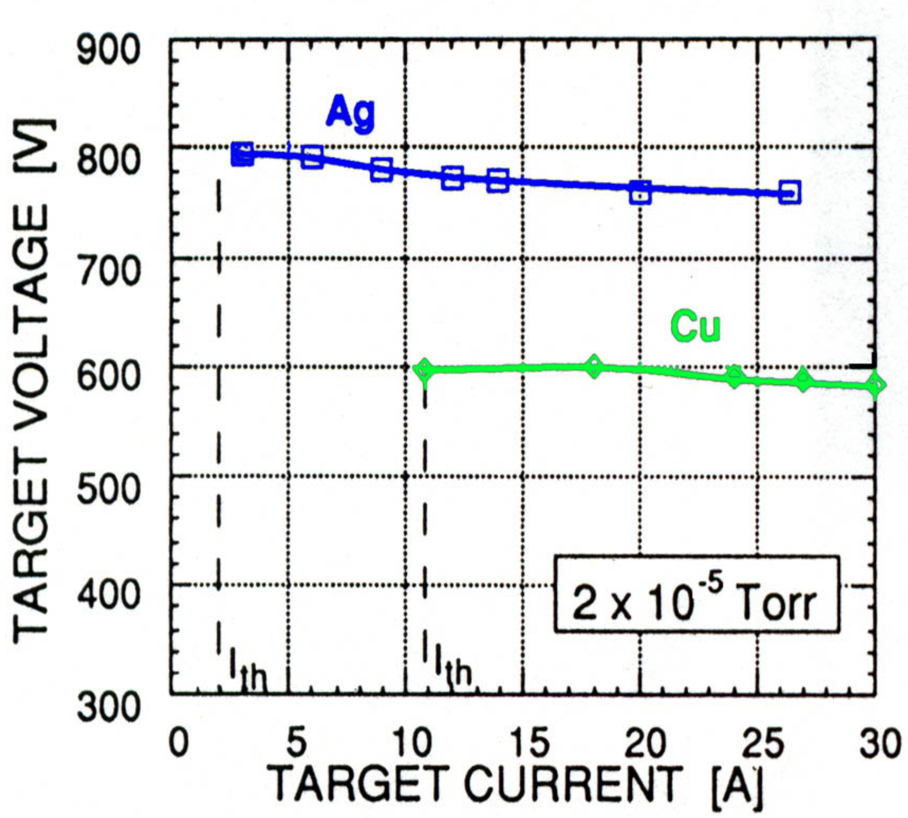
The kink in characteristic may indicate:

- A dynamic effect that the plasma is not yet in equilibrium (*the V-I relation is not in steady state*)
- A change of the character of the plasma to “fully ionized,” i.e. greater “Coulomb friction”
- Self-sputtering becomes important, creating more scattering targets for electrons
- Magnetic confinement by permanent magnets is weakened by self-field of discharge and ExB current
- Plasma creation in region with less magnetic confinement causes electron losses
- Onset of gas rarefaction due to heating of neutrals (Rossnagel 1988)

Why is there a higher impedance at higher peak power?

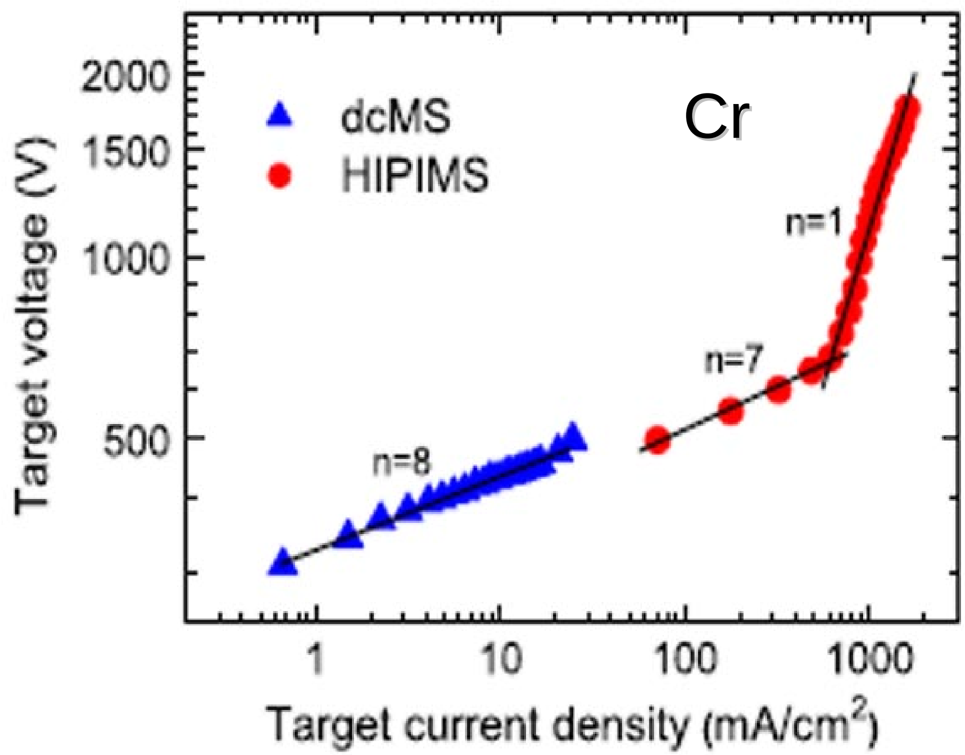
Self-sputtering cannot be the reason:

continuous



Posadowski, et al., *JVST A* 11 (1993) 2980

dynamic



Ehiasarian, *et al.*, *Vacuum* **65** (2002) 147

Energetic Condensation

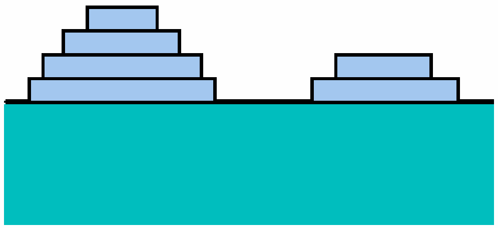
Equilibrium Film Growth Modes

(a)

V-W

Frank - van der Merve

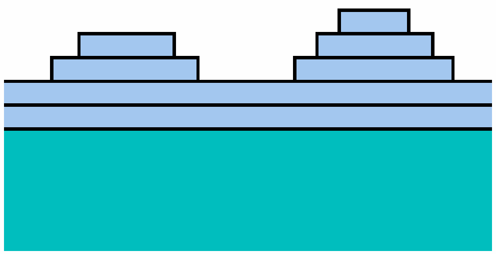
(b)



F-M

Volmer-Weber

(c)

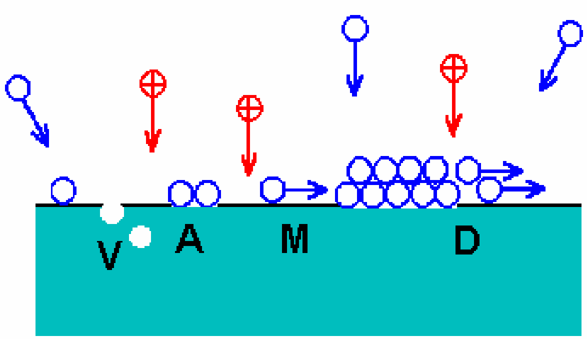


S-K

Stranski-Kastranov

→ Non-Equilibrium Film Growth Modes

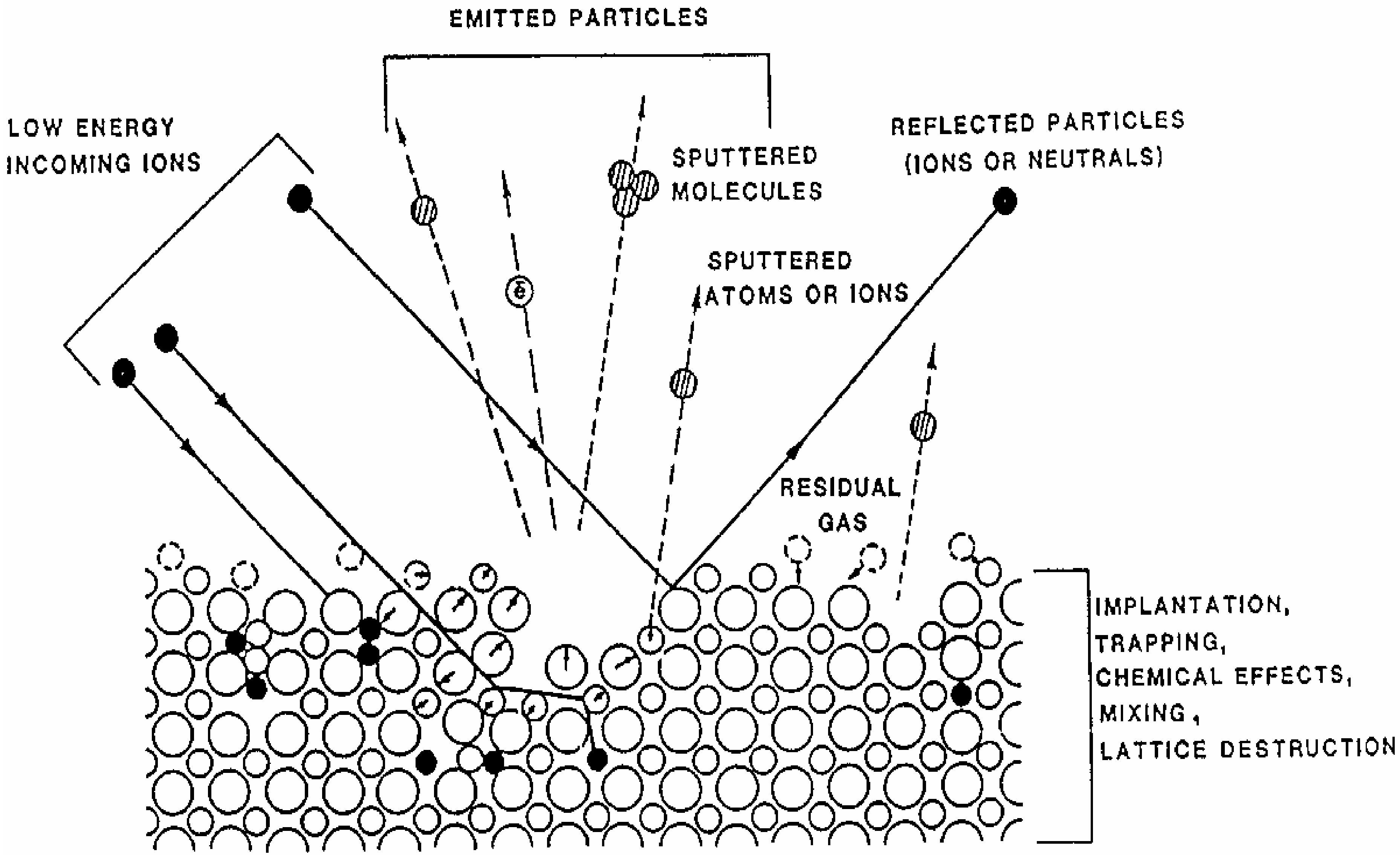
(d)



with ion bombardment:

- additional defects as nucleation sites
- sub-surface insertion of ions

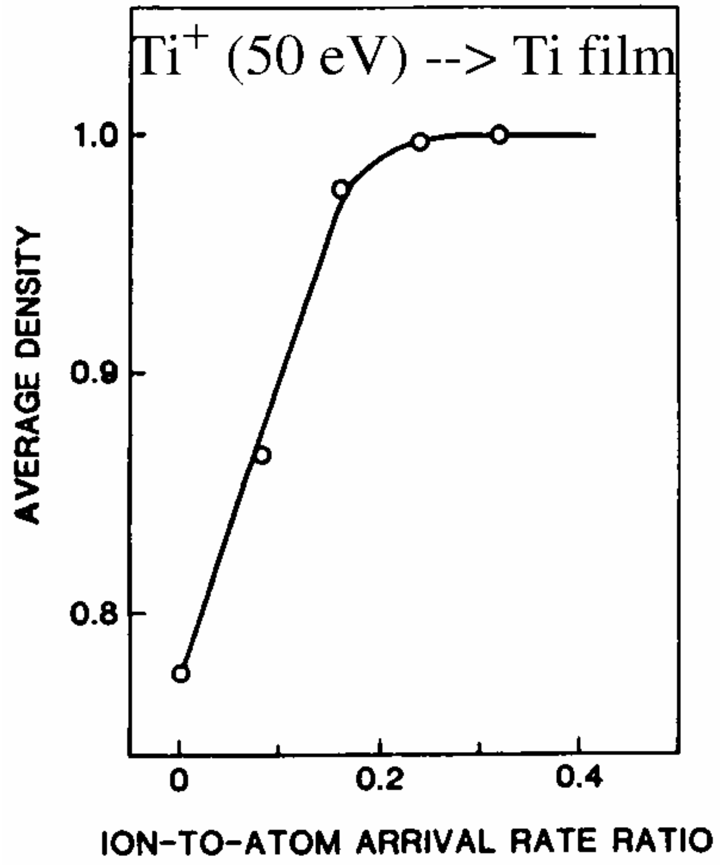
Non-Equilibrium Plasma Processing

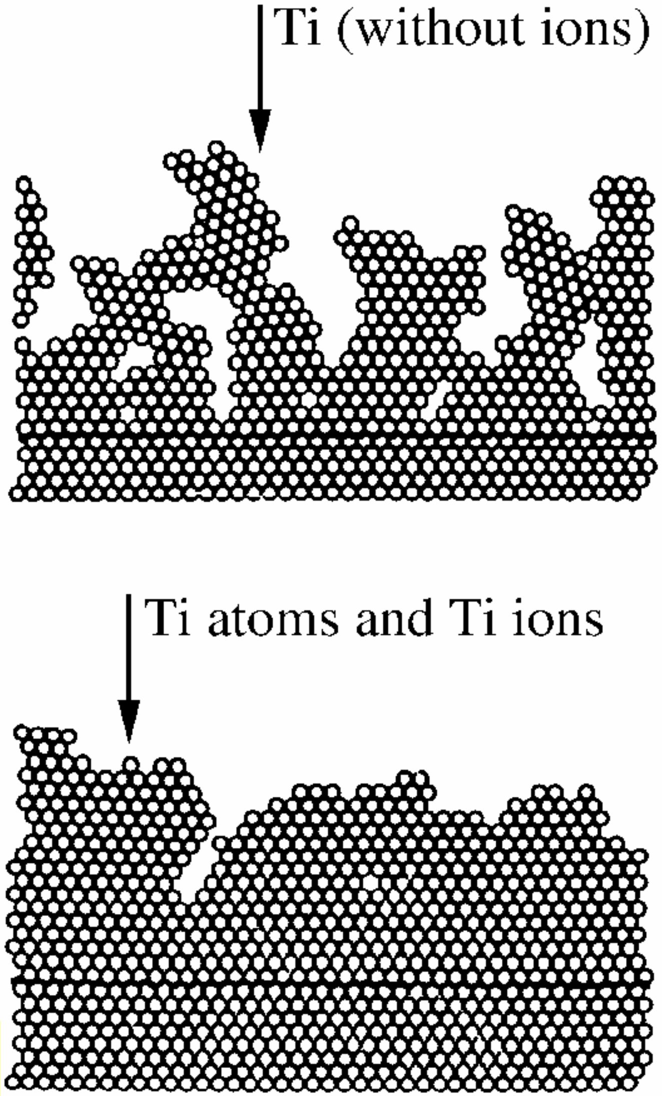


J. L. Vossen and W. Kern, *Thin Film Processes II* (Academic Press, Boston, 1991).

Effect of Ion Bombardment on Film Microstructure

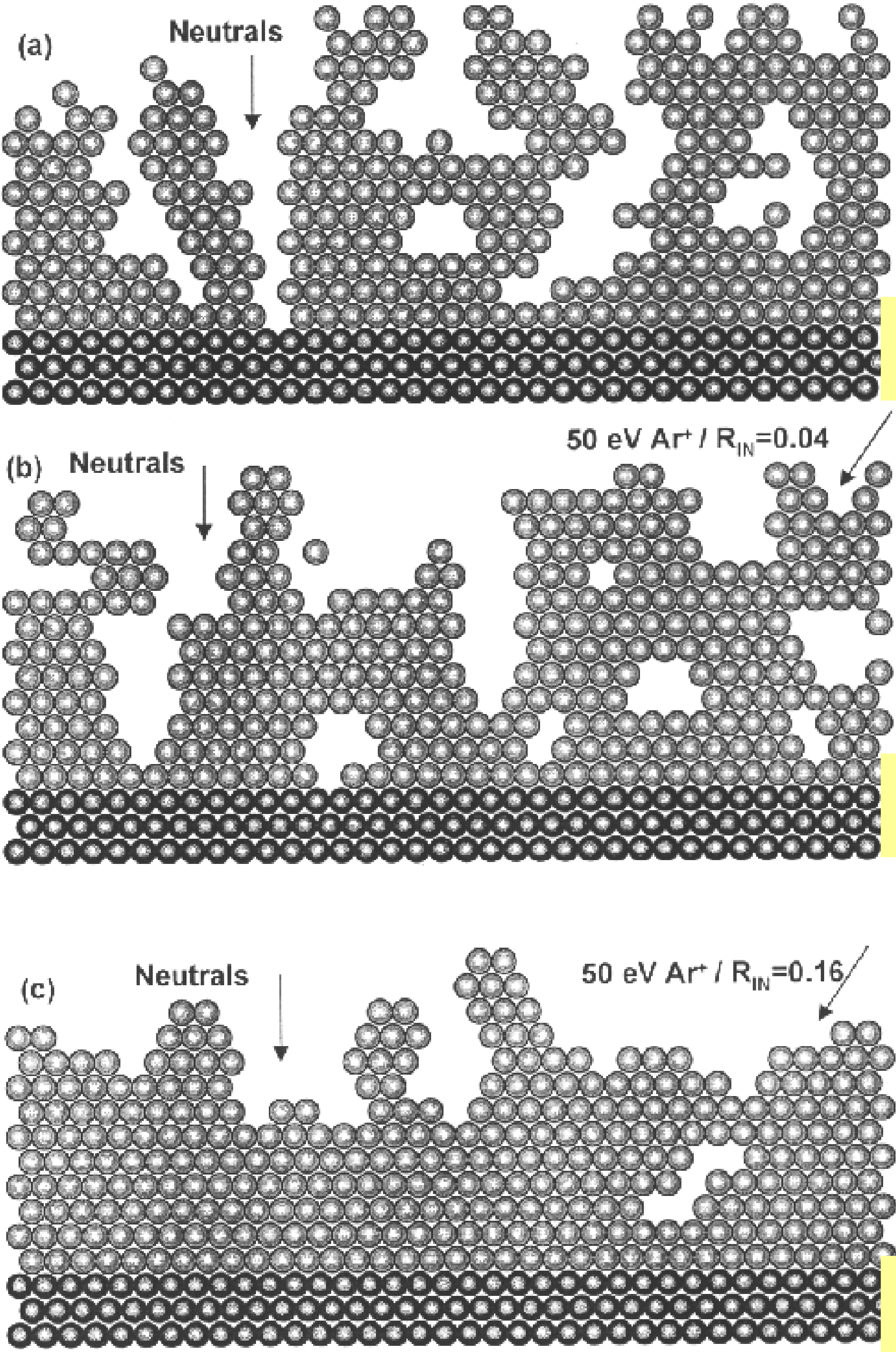
- Densification of Ti film by Ti ions (self-ion assistance)
- MC computer simulation





P. Martin et al., *JVST* **5** (1987) 22

Effect of Ion/Neutral Ratio



0

0.04

0.16

K.-H. Müller, Phys. Rev. B **35** (1987) 7606

Control Of Energy: Plasma Sheaths Driven by Biasing

Boundary between plasma volume and wall

un-driven sheath

- voltage drop ~ $k_B T_e$
- often stationary

driven (high-voltage) sheath

- voltage drop >> $k_B T_e$
- often non-stationary

used for pulsed surface engineering

In sheath, quasineutral condition does *not* apply, a very strong electric field exist.

Kinetic and Potential Energy

Energy brought to substrate / film by ions

$$E(Q) = E_{kin,0} + QeV_{sheath} + E_{ic} + E_{exc} + \sum_{Q'=0}^{Q-1} E_{Q'}$$

kinetic

potential

The greatest contributor, controlled by *bias* .

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

Largest Contribution to *Potential* Energy: Ionization Energy

- *summation* **of ionization energies for multiply charged ions**

$$E_{Q+}^{sum} = \sum_{Q'=0}^{Q-1} E_{Q'}$$

- **Example: Gold ions (in eV)**

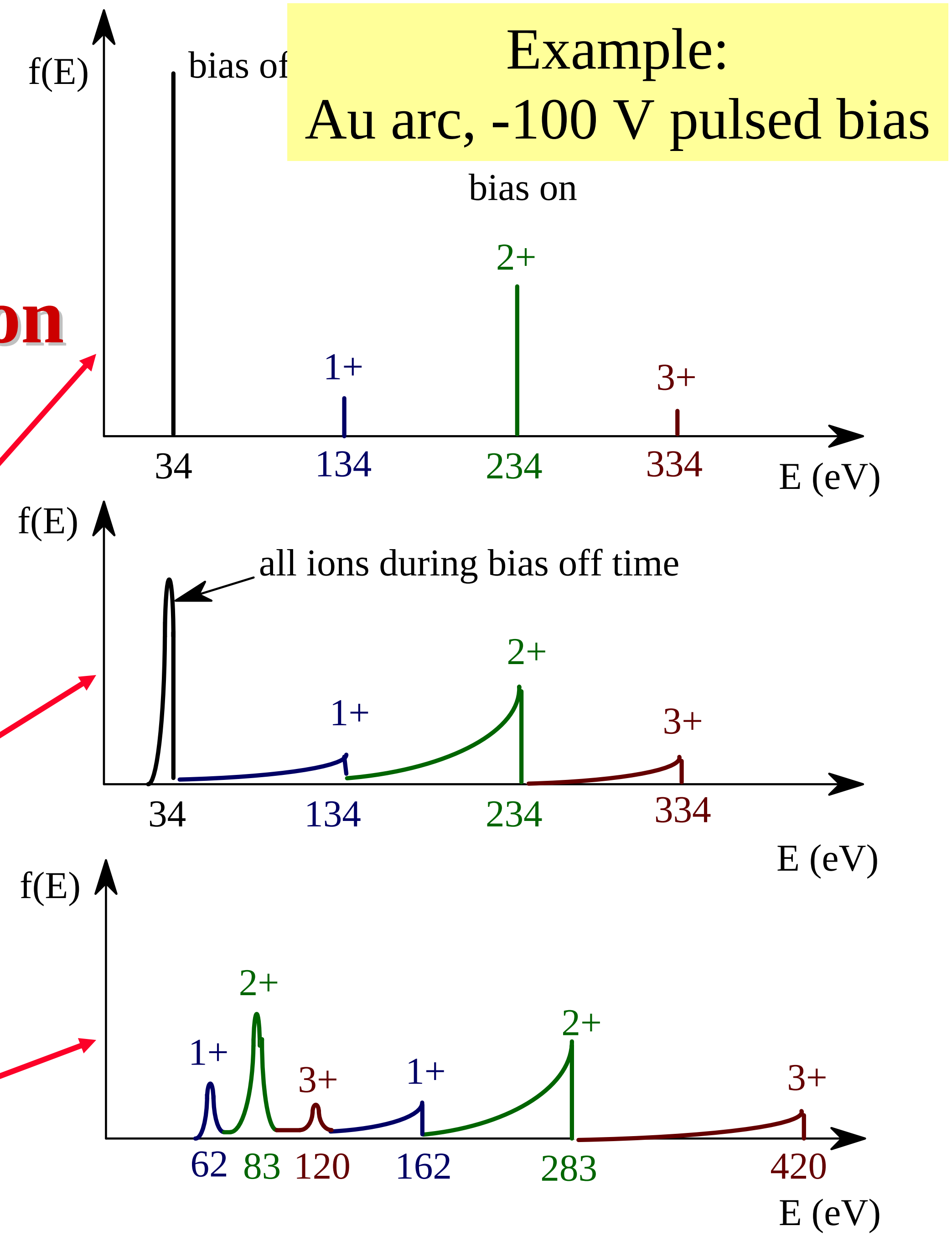
0	+1	+2	+3	+4
9.23	29.7	67.1	122	193

Ion Energy Distribution Function

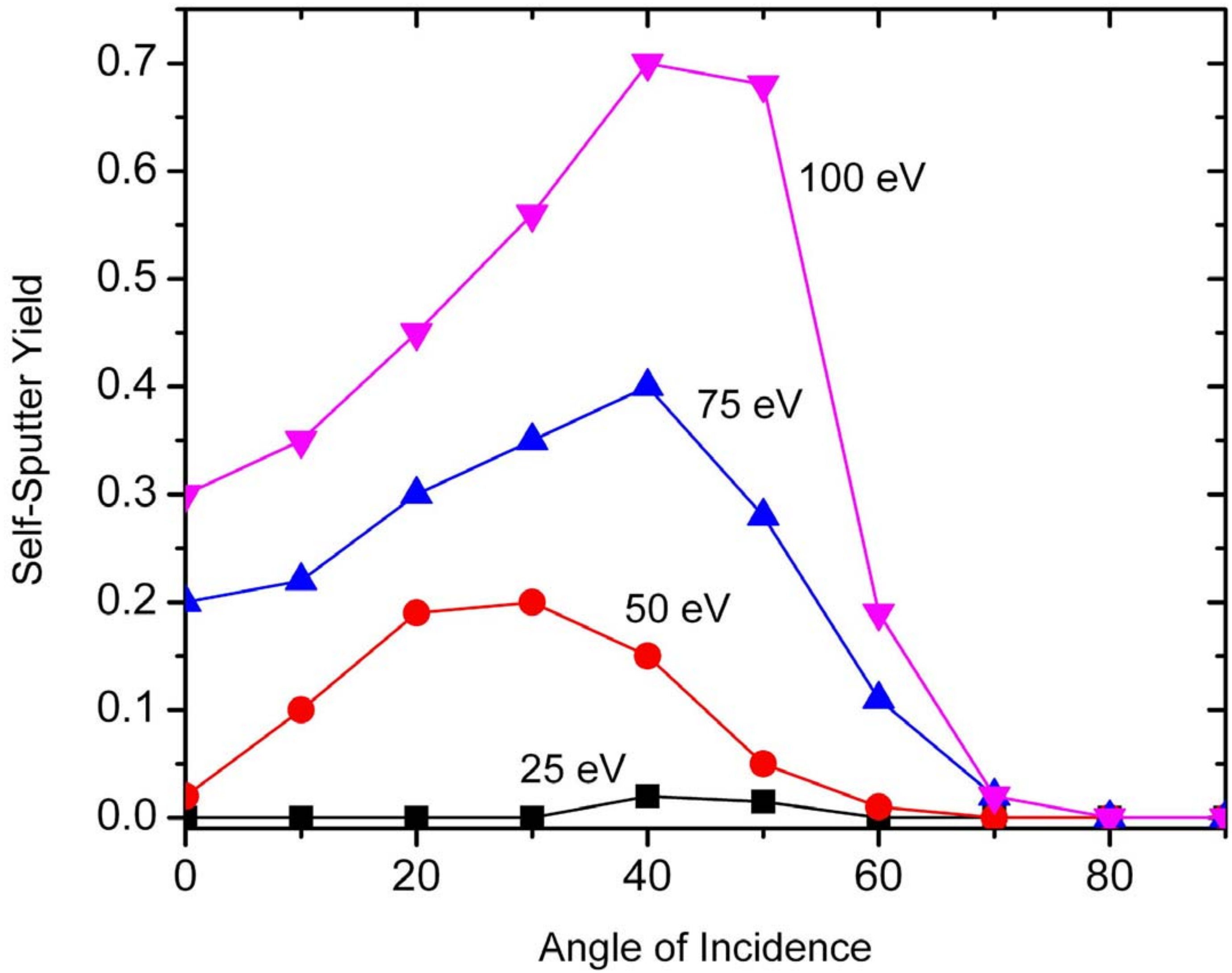
idealized distribution of the ***kinetic*** ion energy

time-averaged distribution of the ***kinetic*** energy with significant pulse rise and fall times

as above, but *with* ionization energies and cohesive energy



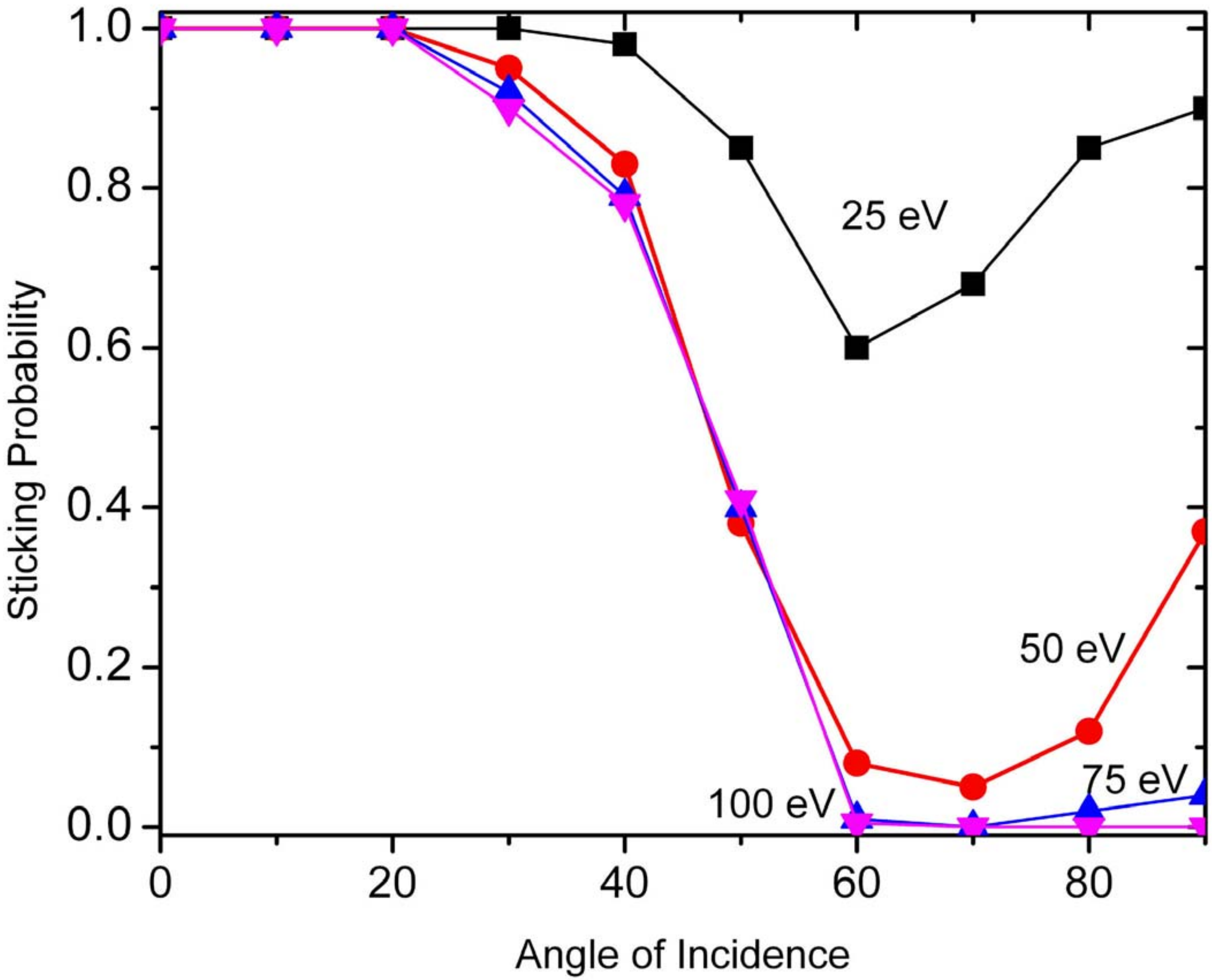
Self-Sputtering



Ni

D.E. Hanson, et al., *J. Vac. Sci. Technol. A* **19** (2001) 820

Sticking Probability



Ni

very low!

D.E. Hanson, et al., *J. Vac. Sci. Technol. A* **19** (2001) 820

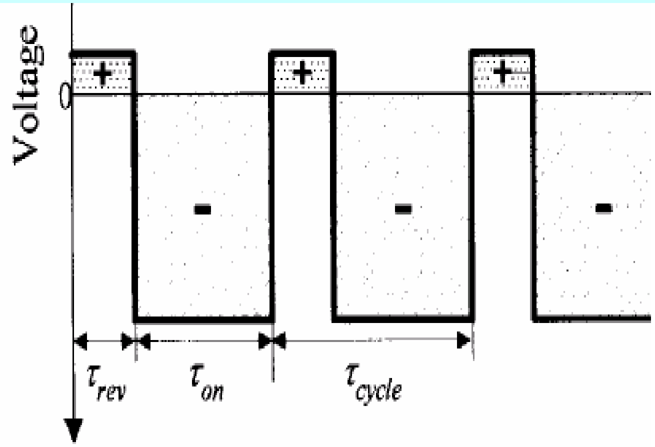
Results & Applications

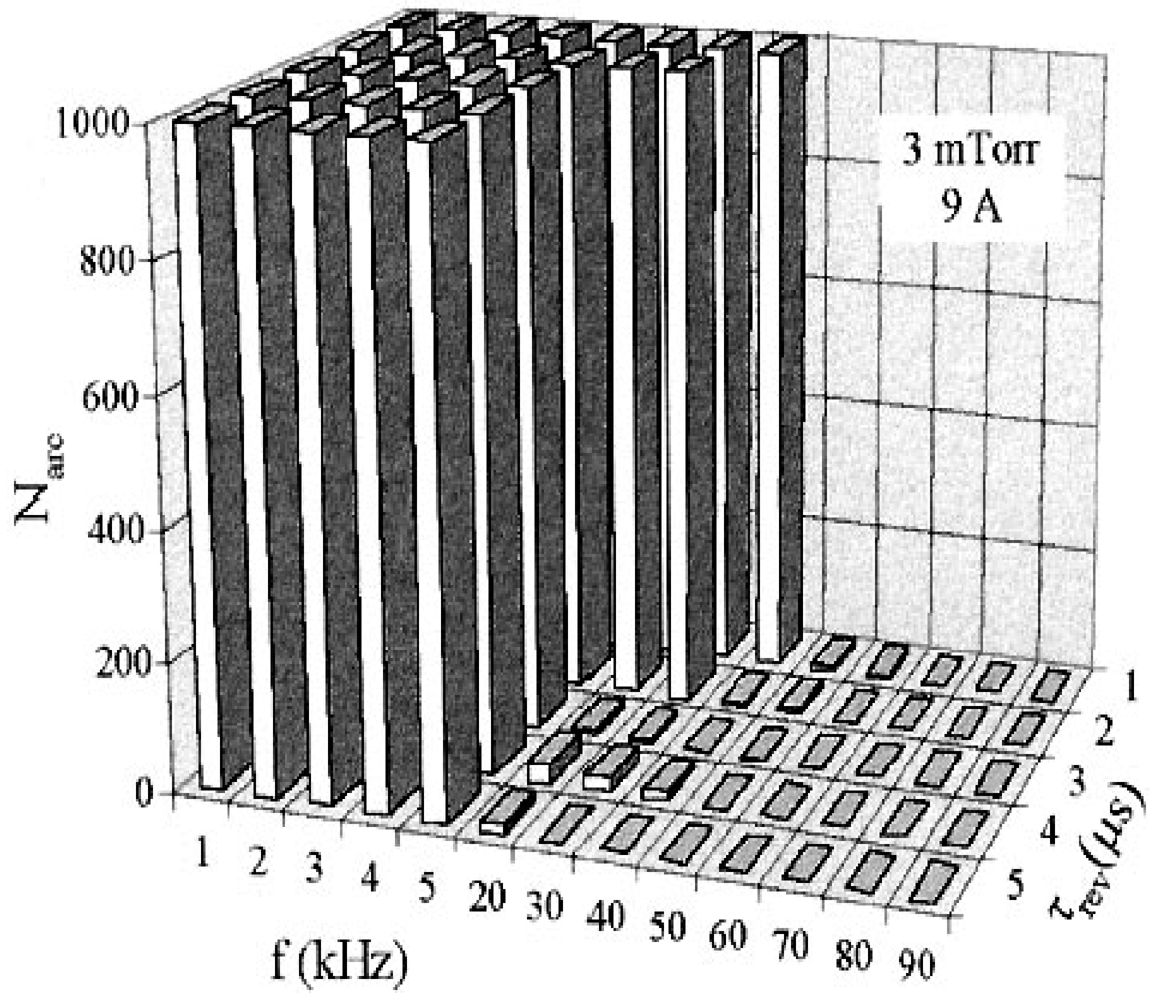
(closing the loop to Motivation)

Arc Prevention in Reactive Sputtering

- Example: Al target, Ar/O_2 mixture, bipolar pulsed
- If pulse duration long, or frequency low, arcing occurs

Conditions for explosive electron emission fulfilled





A. Belkind, et al., 41st Annual Tech. Conf. SVC, Boston, 1998.

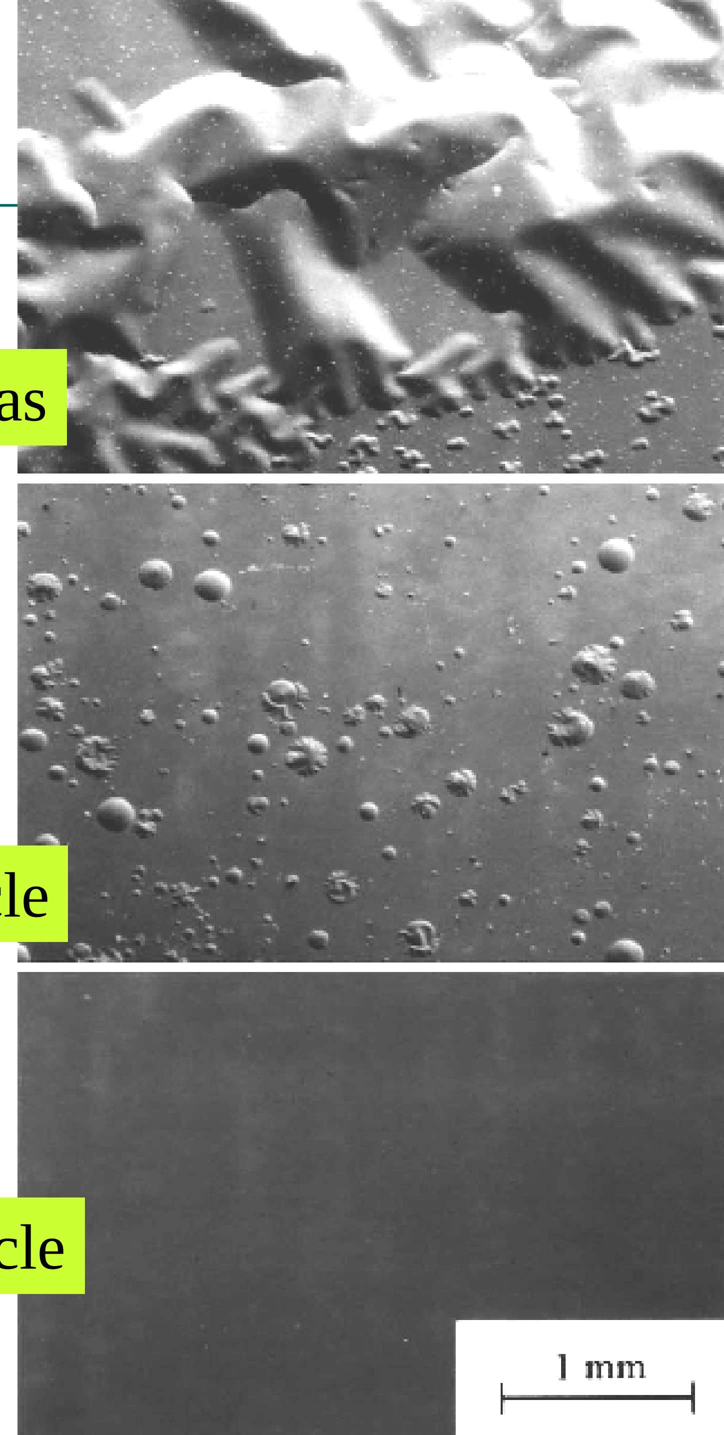
Stress Control

- Subplantation growth is associated with high compressive stress
- Effect of ion energy on *stress relaxation* and adhesion of Ag/$YBa_2Cu_3O_x$ film on Si produced by MePIIID.

no bias

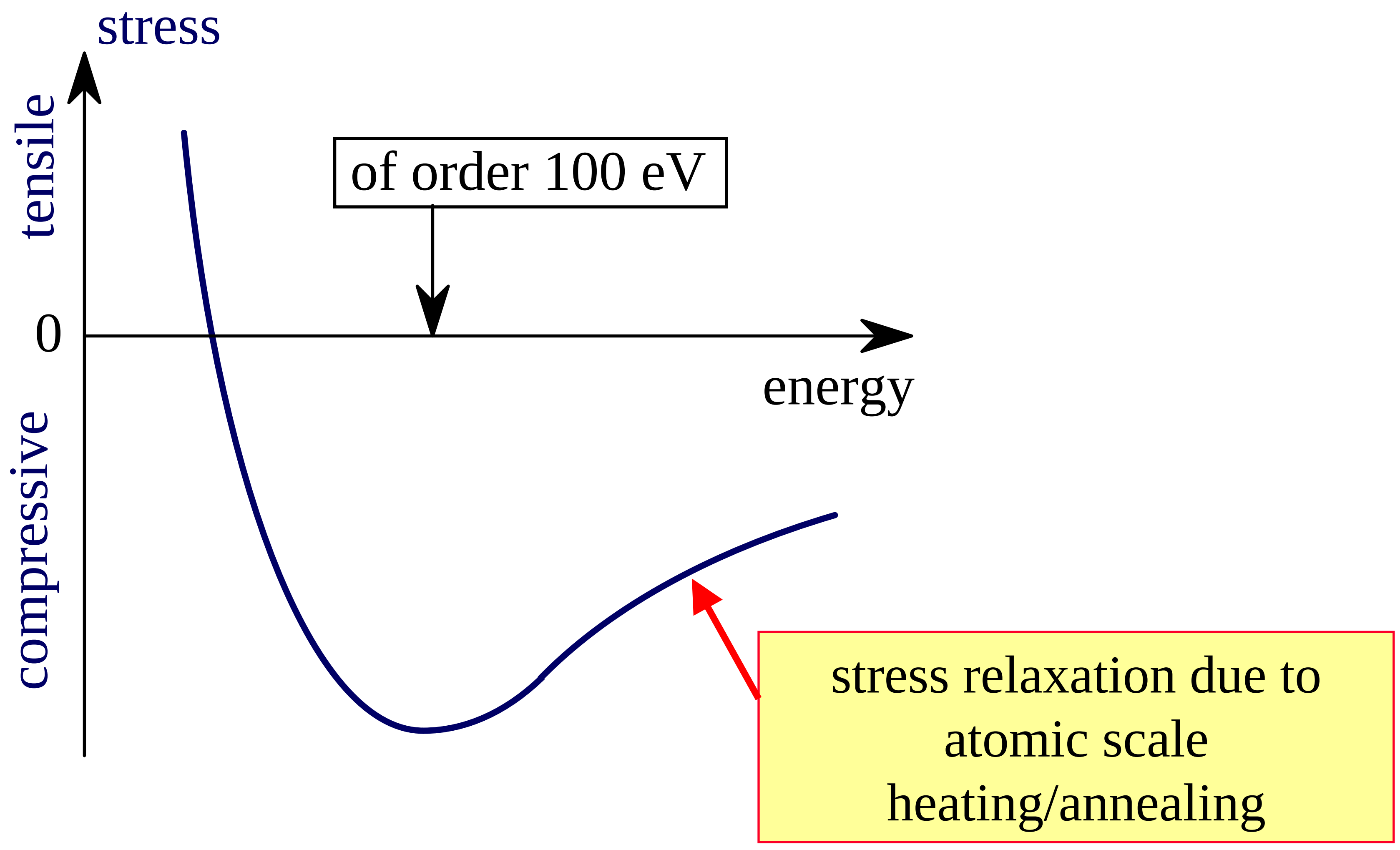
-200 V bias, 10% duty cycle

-2000 V bias, 10% duty cycle



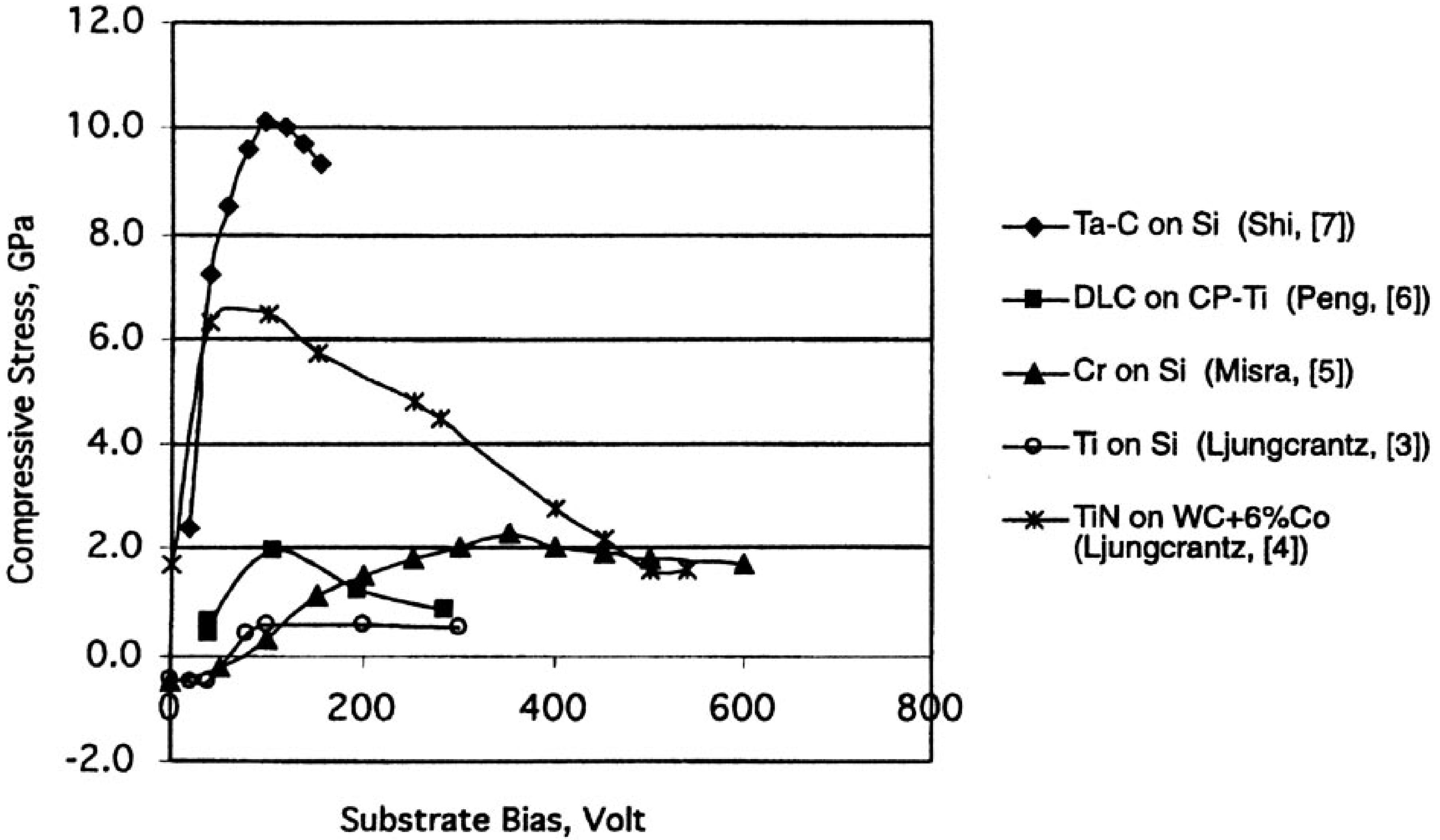
A.Anders, JVST B 12 (1994) 815

Tuning Film Density and Stress



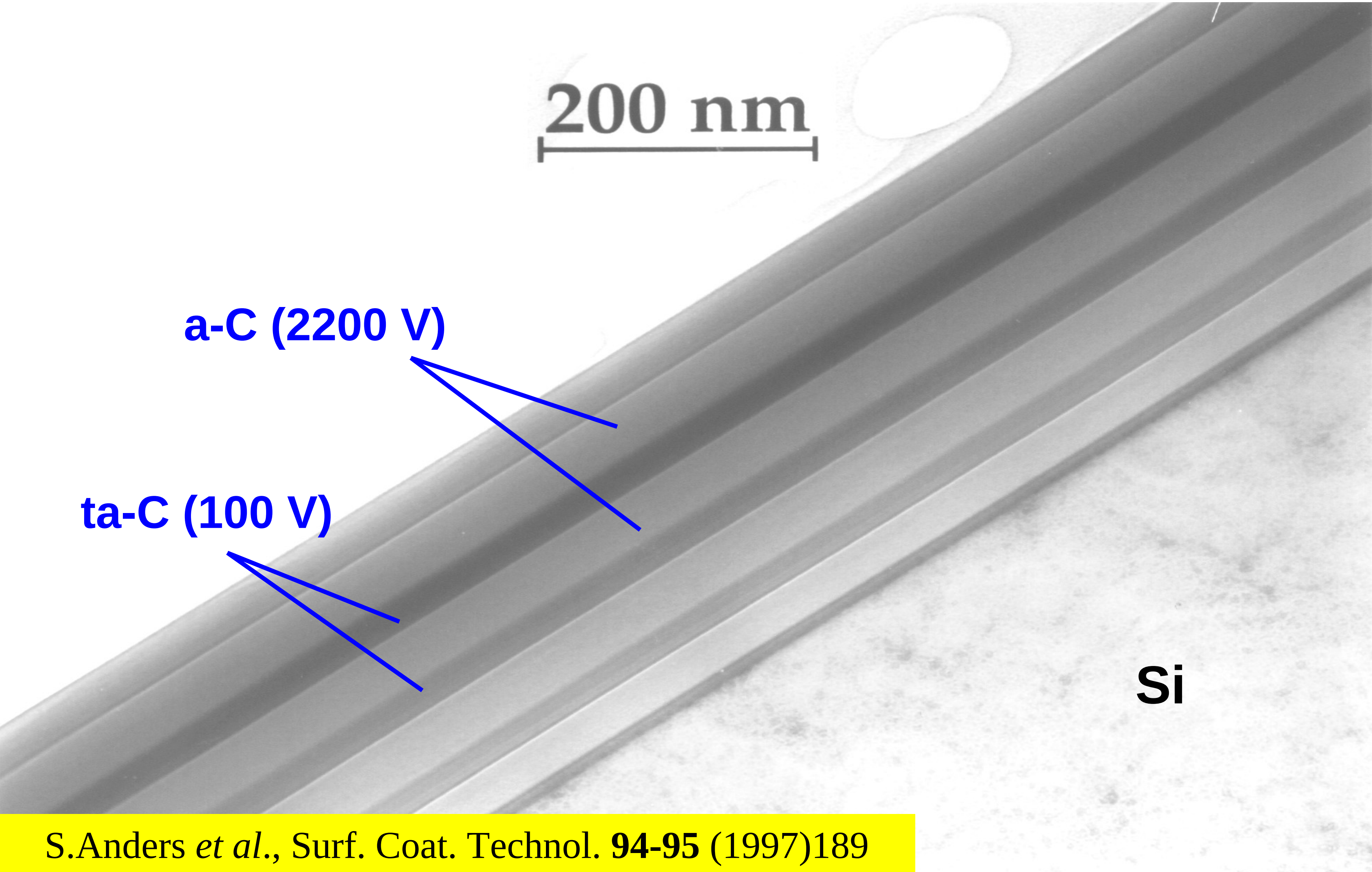
M. Bilek and D. McKenzie, *Surf. Coat. Technol.* 200 (2006) 4345

Stress Maximum and Stress Relaxation by Ion Bombardment



R.N. Tarrant et al., *Surf. Coat. Technol.* 136 (2001) 188

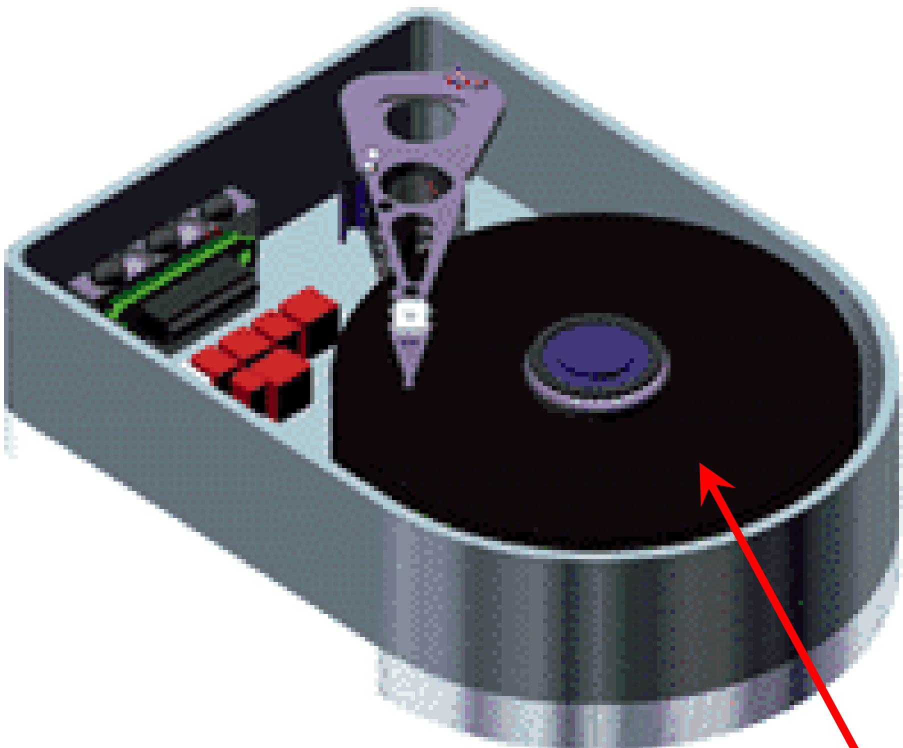
ta-C / a-C Multilayer made by Carbon PIIID



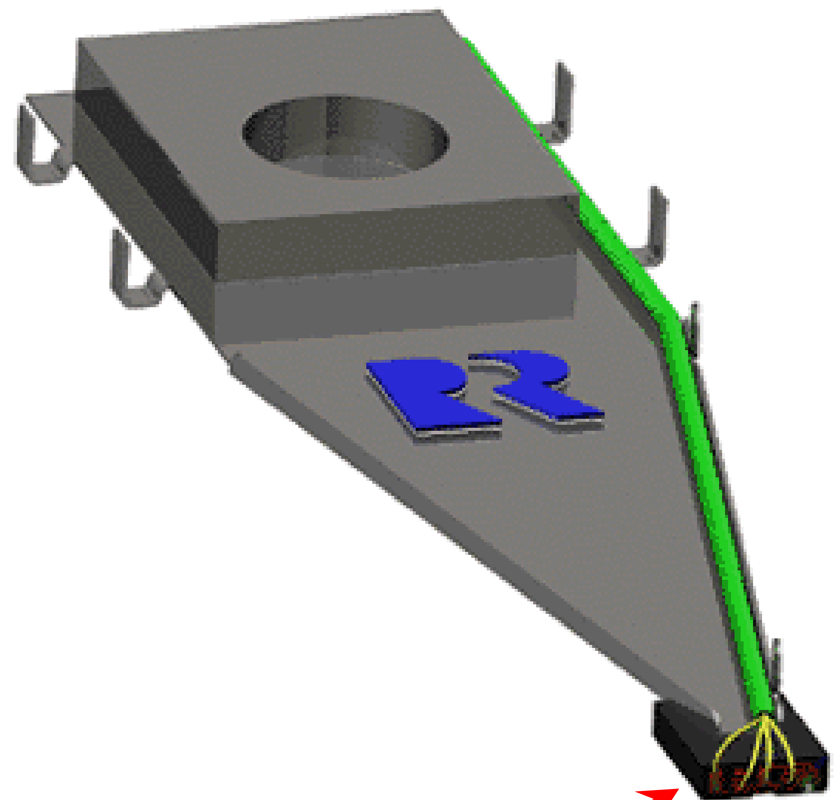
S.Anders *et al.*, Surf. Coat. Technol. **94-95** (1997)189

Dense, ultrathin ta-C films for magnetic recording applications

Hard Disk Drive



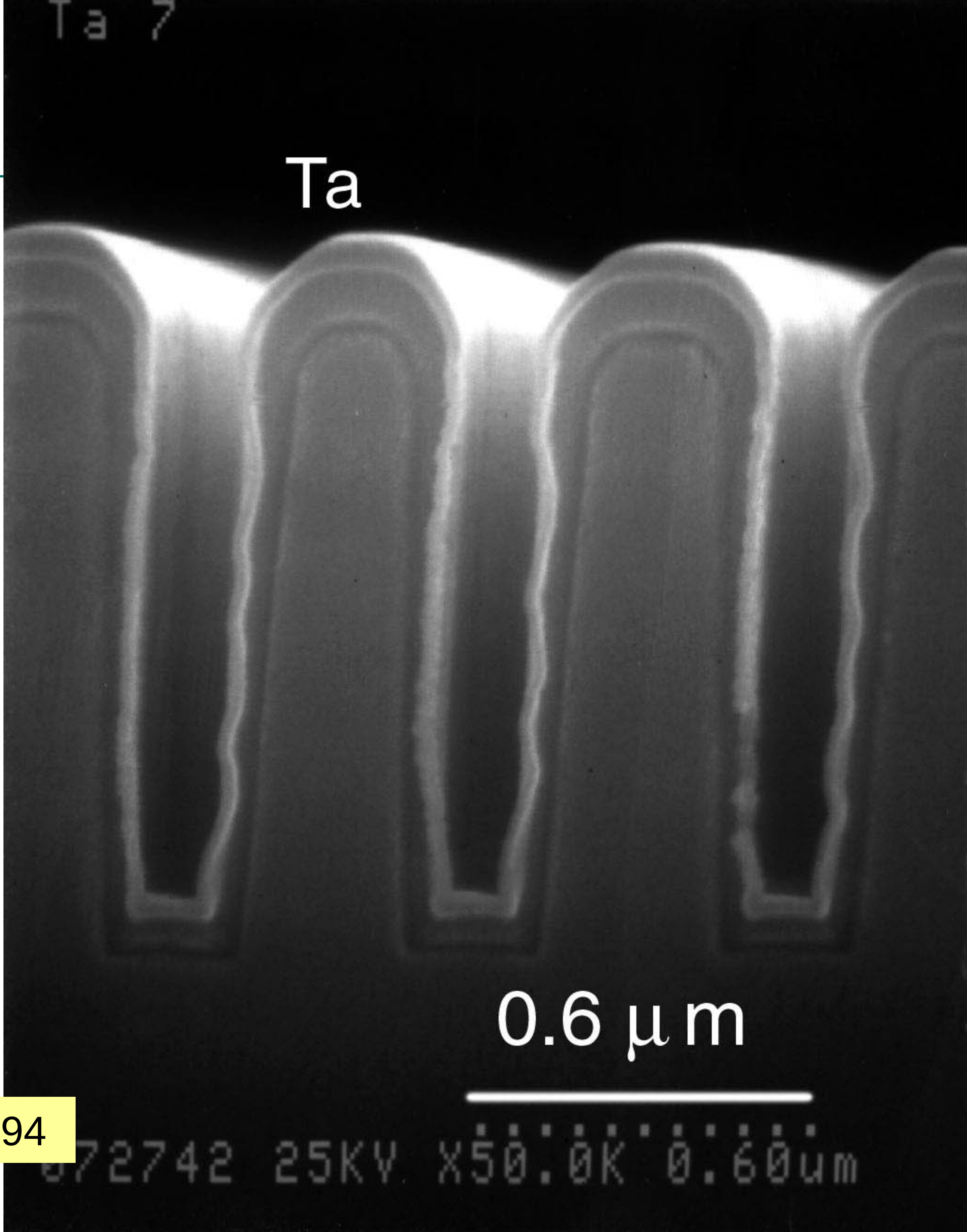
Slider with read/write head



Ultrathin (~ 2 nm) a-C protective layer

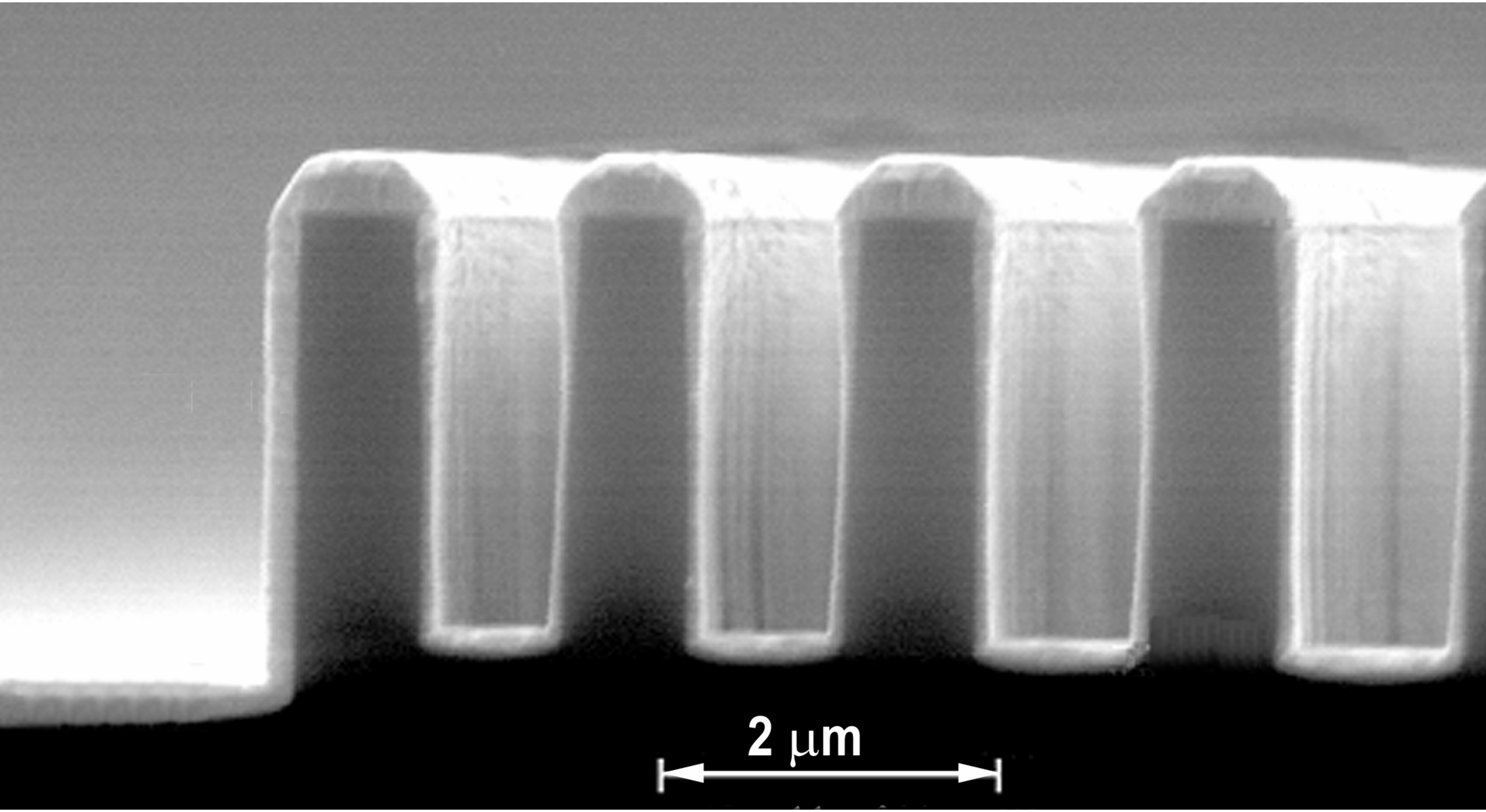
Deposition of Diffusion Barrier Layers

- Copper diffuses in silicon --> need for diffusion barrier
- Ta can be deposited conformally: nanotechnology for future ICs



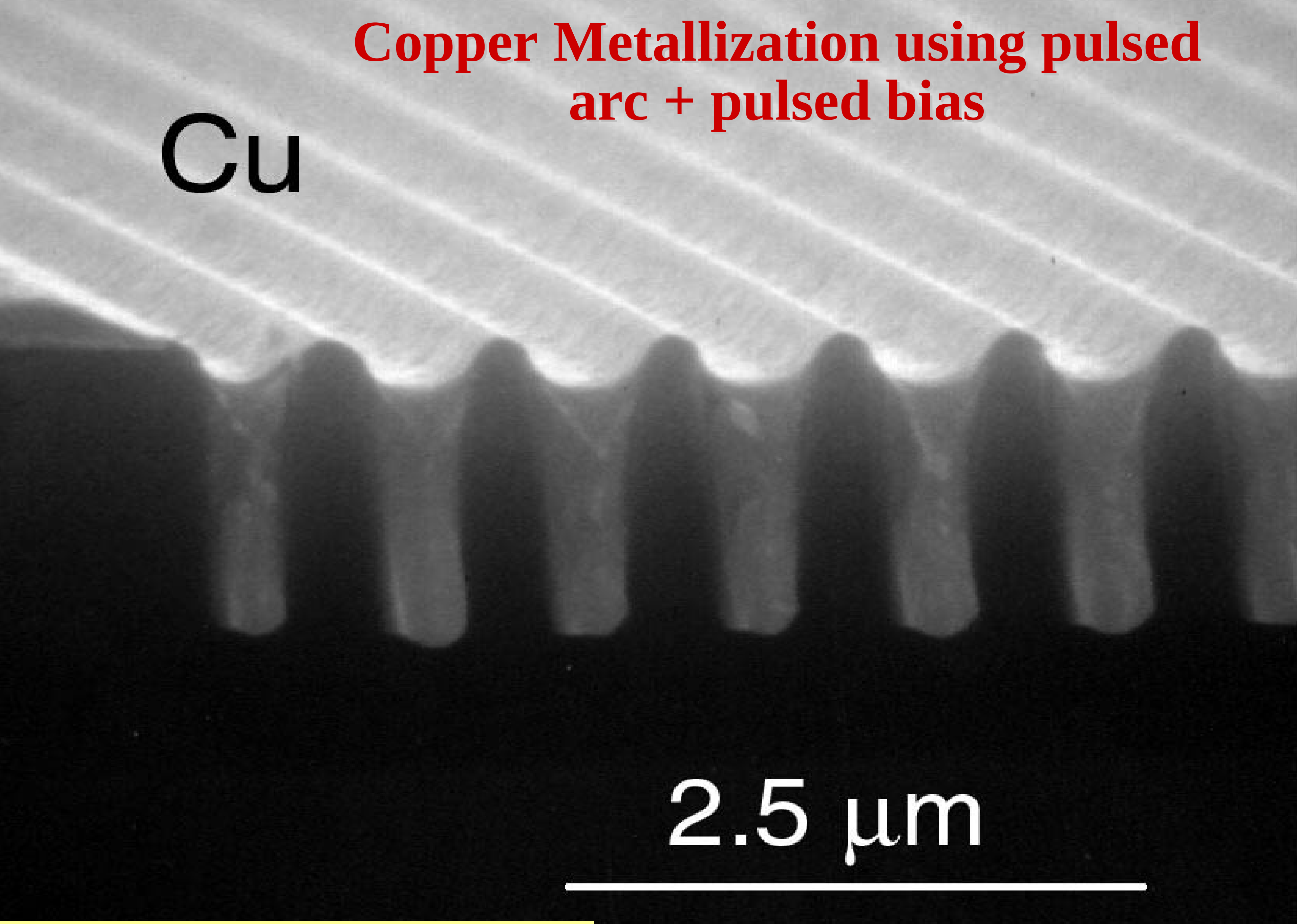
O.R. Monteiro, JVST B **17** (1999) 1094

Conformal Barrier / Seed Coatings



Courtesy of Peter Siemroth, Dresden

Copper Metallization using pulsed arc + pulsed bias



O.R. Monteiro, JVST B **17** (1999) 1094

Summary

- Plasmas, as opposed to gas and vapors, lead to energetic processes on surfaces:
  - ion etching, energetic
  - condensation,
  - subsurface insertion, etc
- Both kinetic and potential energy is brought to the surface
- The largest energy contribution comes from ion acceleration in the sheath, determined by bias voltage and charge state
- Pulsing enables very enhanced peak power, new ranges of effects are accessible
- Applications:
  - Stress reduction,
  - control of coating's microstructure
  - conformal deposition on submicron scale