Microstructure and Purity of Plasma-Deposited Coatings and Thin Films

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What to expect

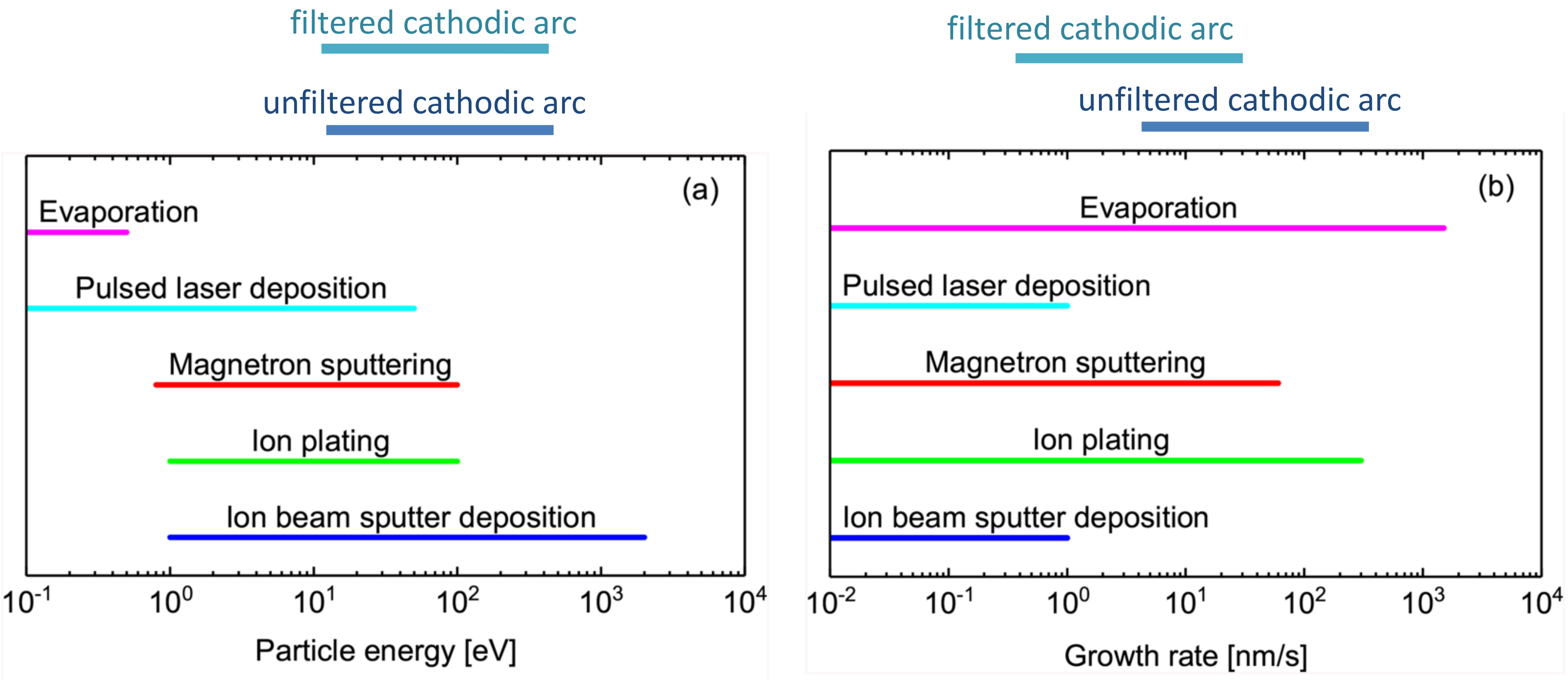
- equilibrium versus non-equilibrium (atom-scale, transient) heating
- contributions to non-equilibrium heating by arriving particles
  - kinetic energy → the special role of the plasma potential and substrate potential relative to the plasma
  - potential energy → the special role of the ionization energy
- some extra slides about sheath and their role on adjusting the ion energy
- structure zone diagrams for deposition by evaporation, sputtering, HiPIMS, arc plasma
  - ion energy effects: densification, microstructure changes, ion etching, subplantation growth
- deposition in vacuum and gases
  - ultraclean
  - gasless
  - residual water effects
  - noble gas inclusion
- examples of films made by plasma-based deposition: cathodic arc, HiPIMS, low-rate, high-rate

Vapor deposition affected by kinetic and potential energy of film-forming particles

- starting with low energy (< 0.5 eV) → neutral vapor deposition
- going to intermediate energies (several eV) → sputter deposition
- going to even higher energy (10s of eV) → PLD and cathodic arc deposition
- adding plasma (or ion) assistance (up to 100s eV)→ plasma deposition with bias / ion beam assisted deposition (IBAD)
- subplantation film growth (several 100 eV)
- ion implantation, formation of buried layers (often > 100 keV)

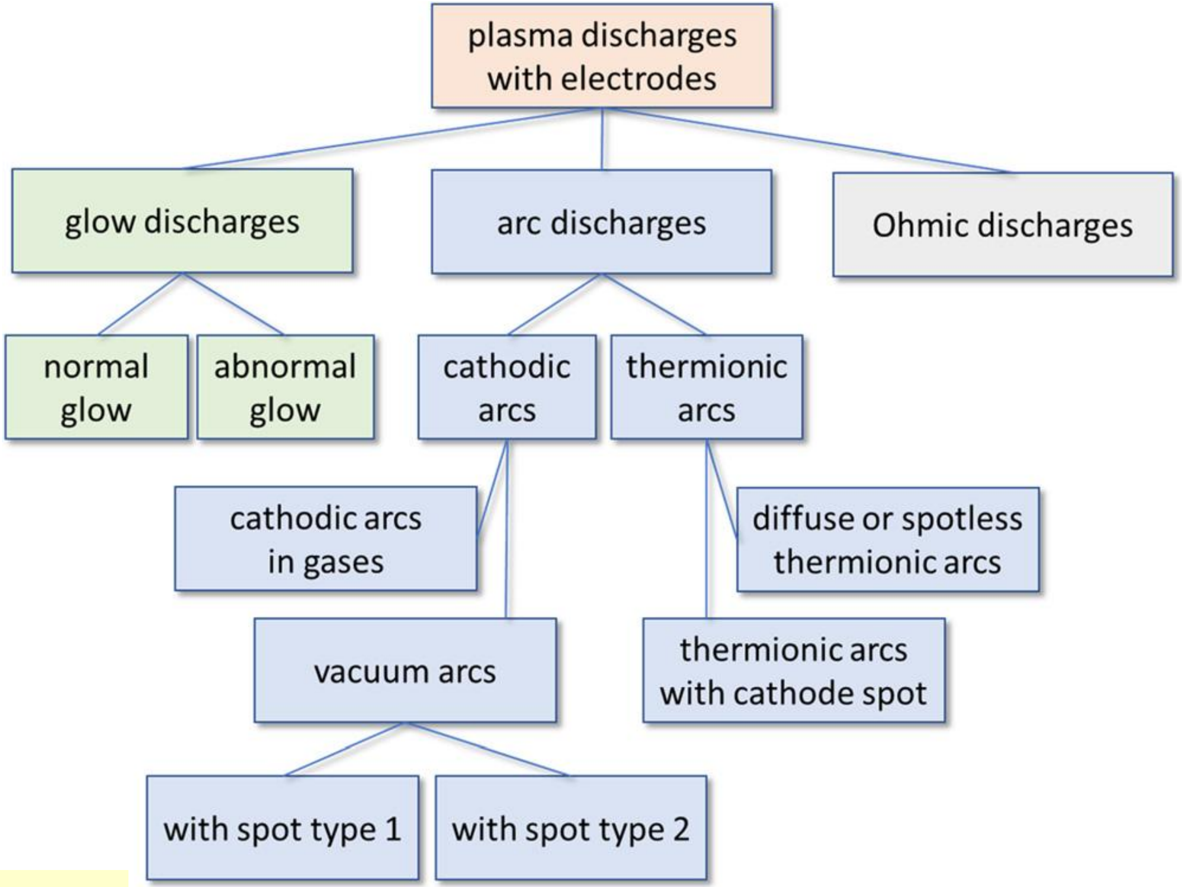
increasing energy

Plasmas in Deposition Techniques



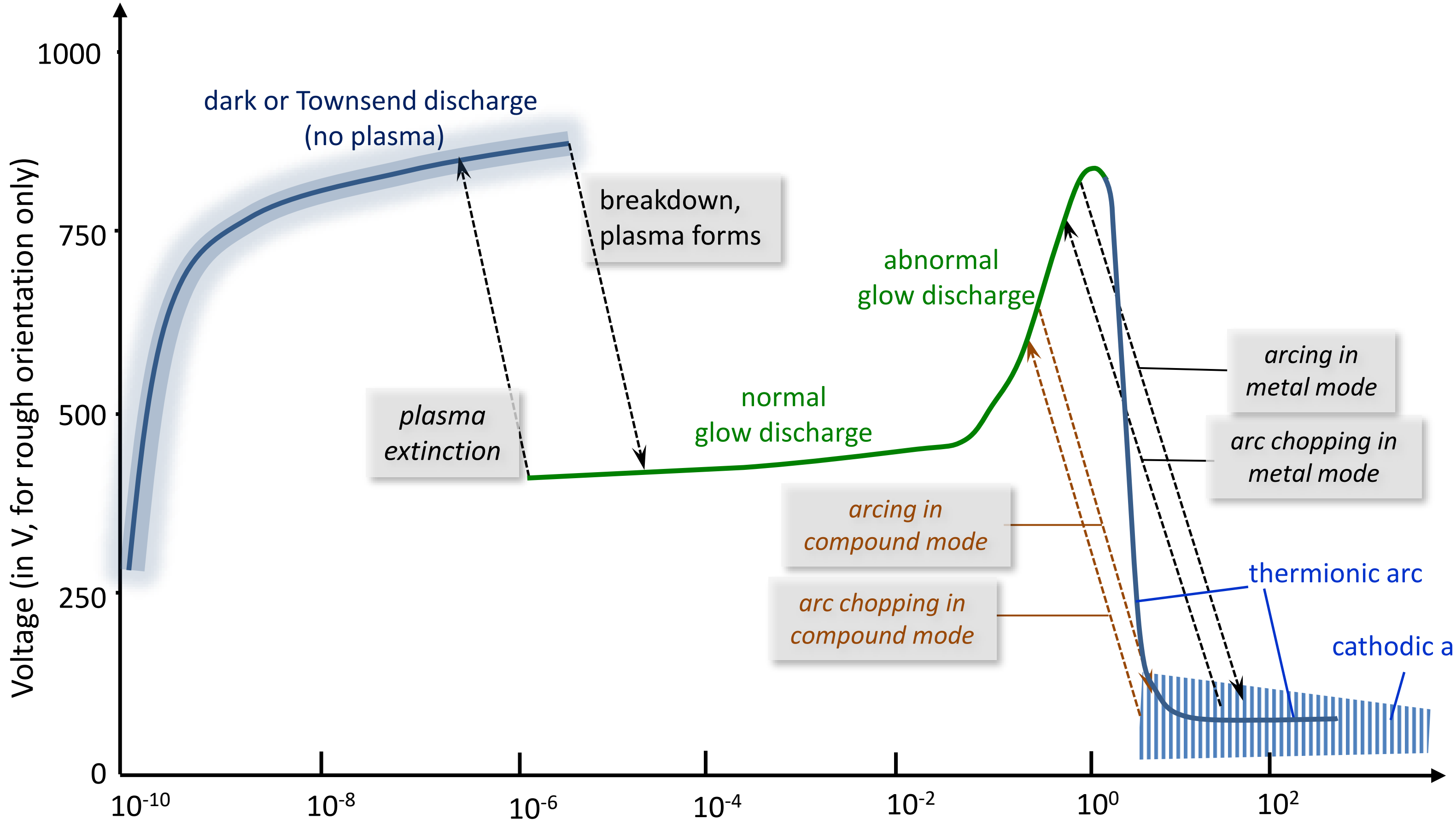
adapted from: C. Bundesmann and H. Neumann, J. Appl. Phys. 124 (2018) 231102

Summarizing the Mode Nomenclature



A. Anders, Appl. Phys. Rev. 11 (2024) 031310.

Extended Current-Voltage Characteristics



A. Anders, Appl. Phys. Rev. 11 (2024) 031310.

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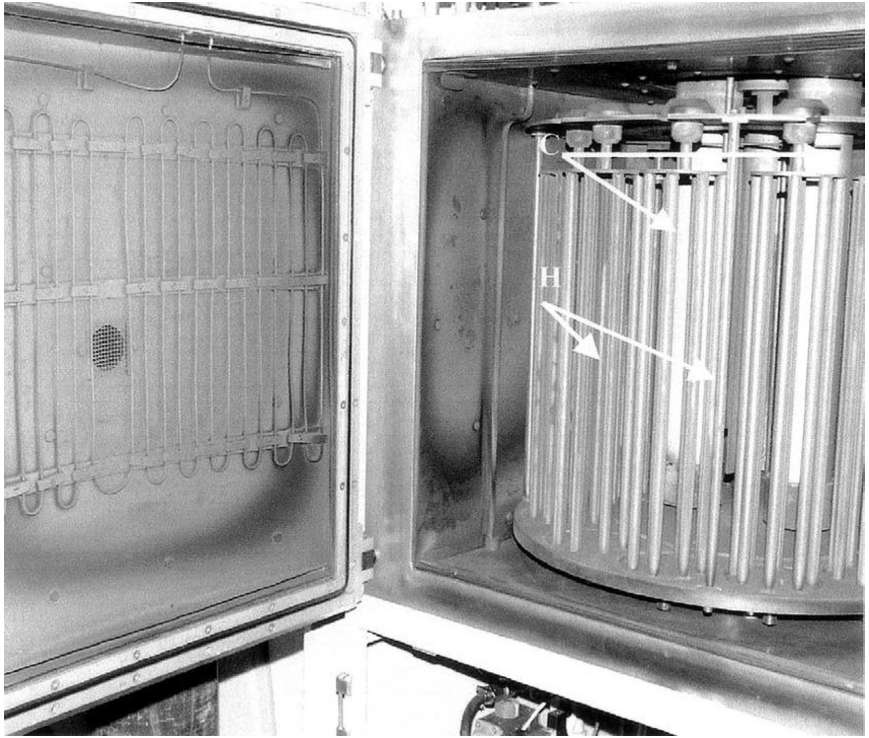
Conventional (equilibrium) heating

substrate heater

Kurt J. Lesker Company



M. Jilek, et al., Plasma Chemistry and Plasma Processing 24 (2004) 493.

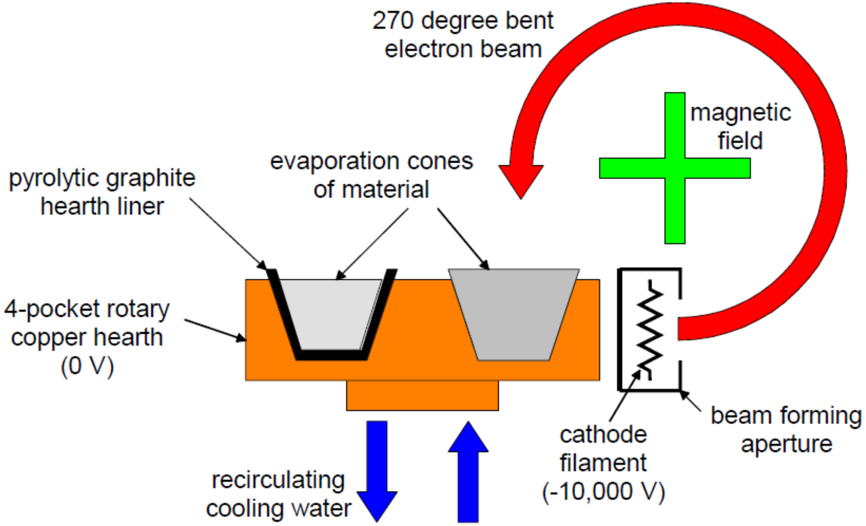
When it is *not* desirable to have conventional heating to high temperature:

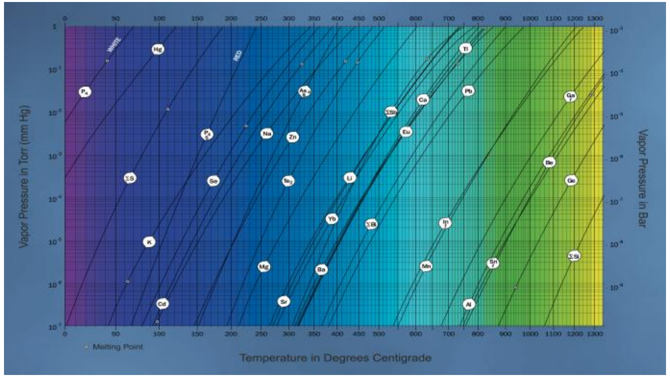
1. coatings on tool steel (the base material may soften)
2. crystalline phases on temperature-sensitive substrate, such as rutile TiO_2 or thermochromic VO_2 on plastic web
3. when high process temperature has negative effects on previously deposited materials, interfaces or structures, e.g. unwanted diffusion in semiconductor processing
4. actually, almost always, as conventional heating costs process time, energy and $$$

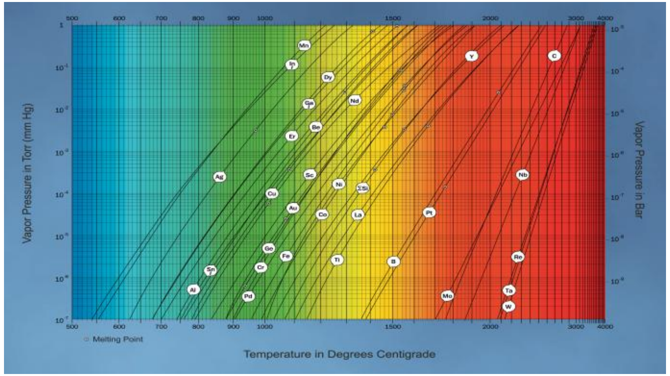
Deposition by Evaporation

- rel. easily scaled, often for inline processes
- vapor pressure scales appr. exponentially with temperature
- porous films
- challenging in reactive mode
- for high-end application combined with ion source (IBAD)

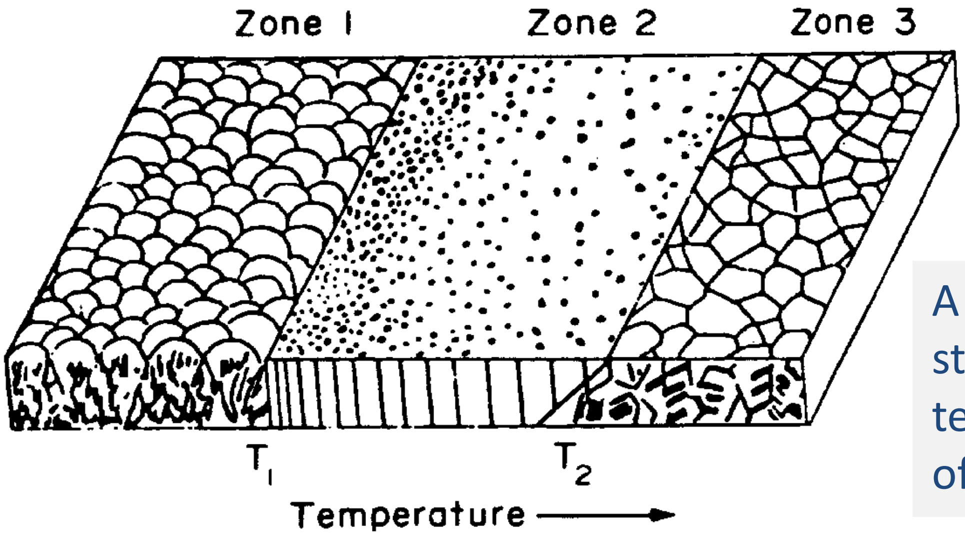
Electron Beam Heated Evaporation Source







Structure-Zone Diagram for Deposition from Vapor



A "***Structure-Zone Diagram***" relates film structure to deposition conditions, here to the temperature of substrate / melting temperature of film material, T_m

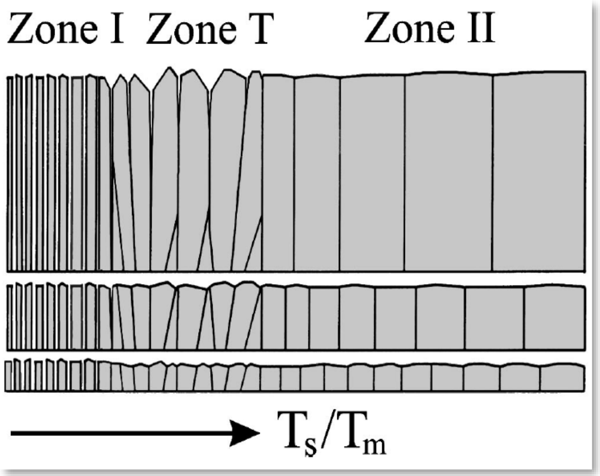
	Zone 1	Zone 2	Zone 3
Metals	<0.3 T_m	0.3-0.45 T_m	>0.45 T_m
Oxides	<0.26 T_m	0.26-0.45 T_m	>0.45 T_m

Zone 1 - tapered columns with domed tops
Zone 2 - smooth-topped granular structure
Zone 3 – equiaxed grains with polyhedral structure

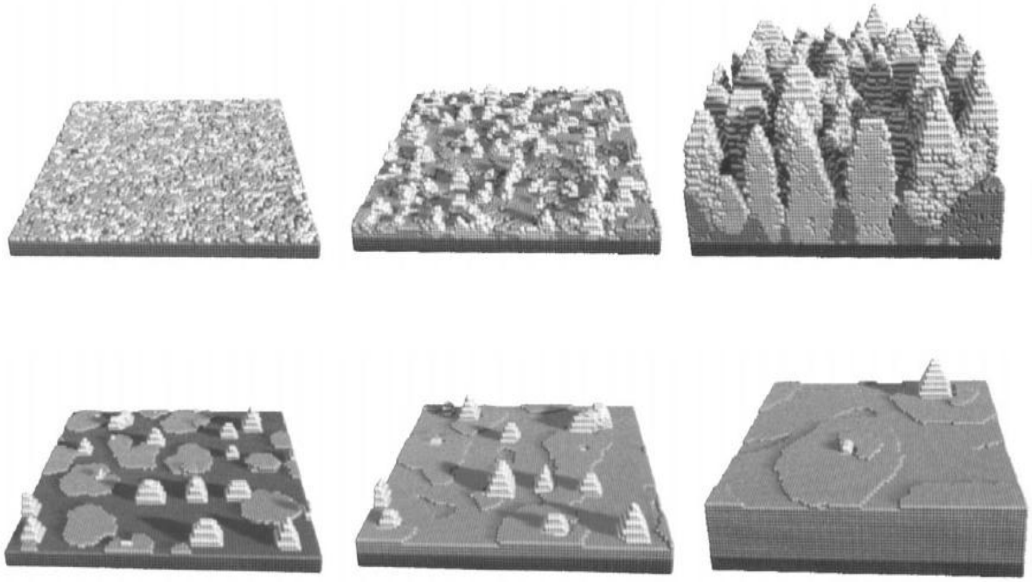
B. A. Movchan and A. V. Demchishin, Fizika Metallov i Metallovedenie **28** (1969) 653.

Deposition from vapor:

Film microstructure is affected by temperature due to mobility of surface atoms



Monte Carlo (MC) simulation of deposition of Al (T_m = 933 K)



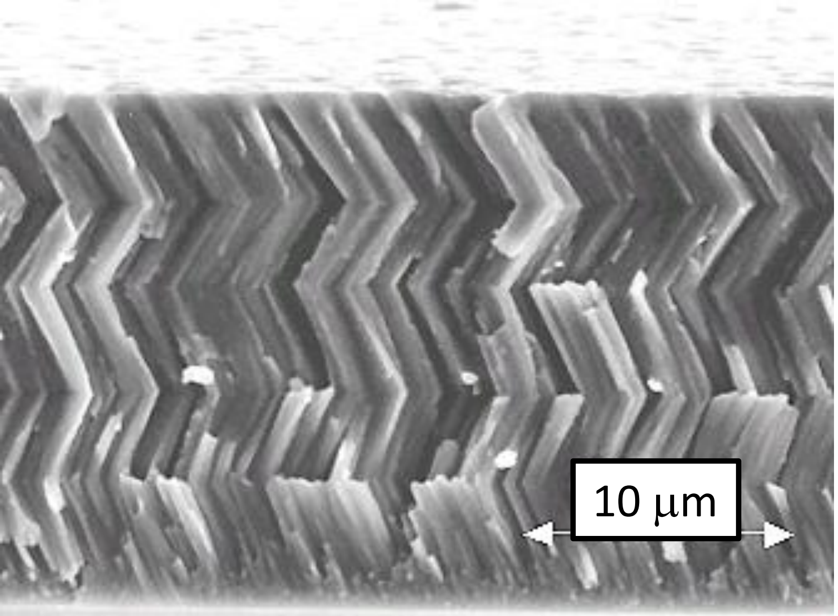
T = 100 K

T = 300 K

I. Petrov et al., J. Vac. Sci. Technol. A **21** (2003) S117

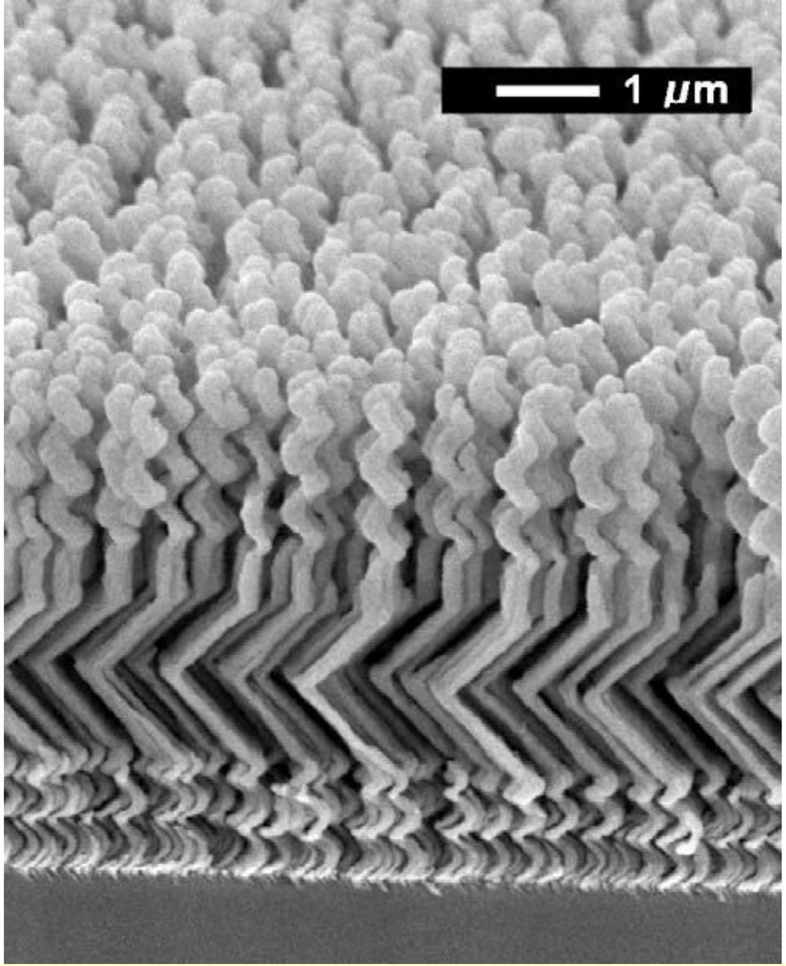
G.H. Gilmer et al. , Thin Solid Films **365** (2000) 189

Columnar structure can be used to make "sculptured films" by GLAD



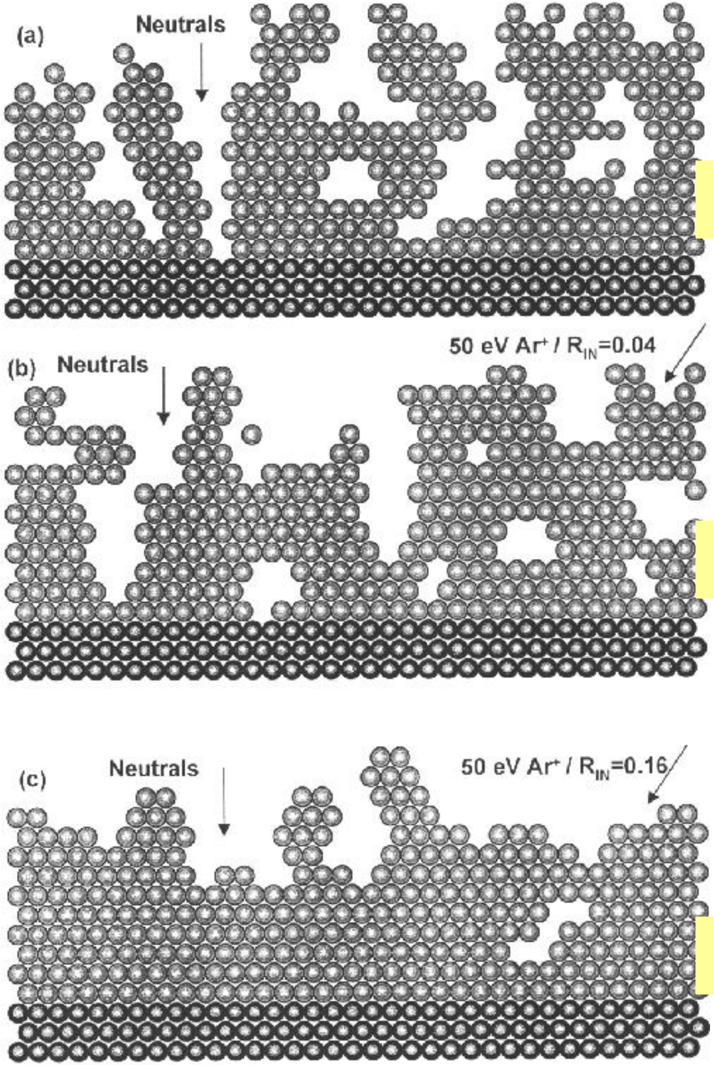
"Chevrons" are obtained by periodically flipping the flux incidence angle

O. R. Monteiro, *et al.*, J. Phys. D: Appl. Phys. **31** (1998) 3188



M.T. Taschuk, et al., in: Handbook of Deposition Technologies, P.M. Martin (Ed.), 2010, p. 621.

Kinetic energy of ions can be used to densify films



0% ions

Parameter: Ion/Neutral Arrival Ratio

4% ions

16% ions

The main idea behind using ions:

- the kinetic energy of heavy particles (atoms or ions) enables **high ad-atom mobility**
- surface atoms move until they find an energetically preferred place

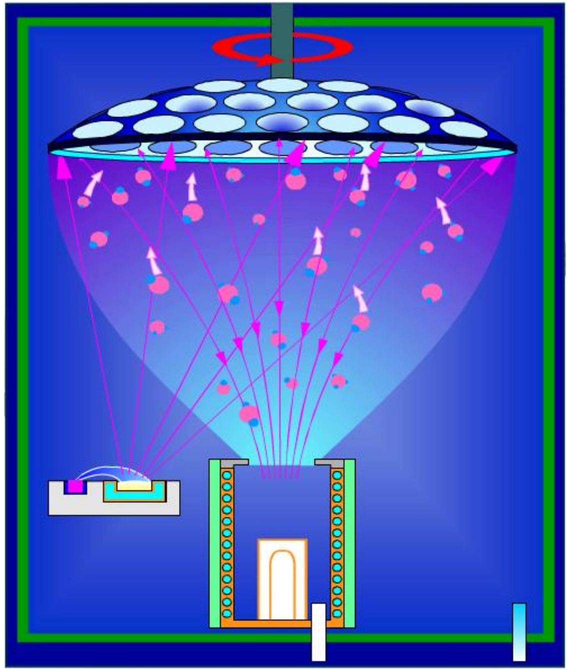
→ densification

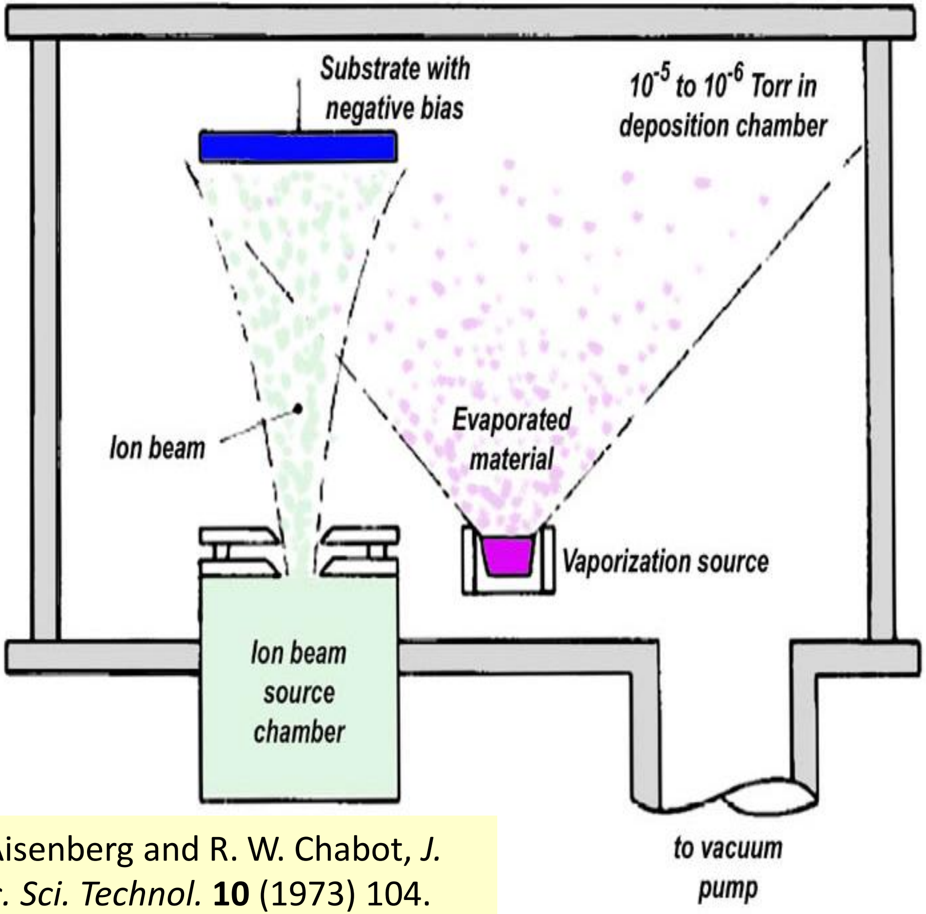
→ shift from amorphous to crystalline microstructure

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

Use of Ion Sources in "Ion Beam Assisted Deposition" (IBAD)

- 1960s: Space propulsion sources available
- Use of such sources to accomplish densification effects, e.g. for optical coatings





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

Temperature versus Energy

- Temperature is a parameter for a Maxwellian energy distribution
- Caution: we do not always have a Maxwellian energy distribution (equilibrium)
- Suppose we have equilibrium: **What is the temperature equivalent of 1 eV?**

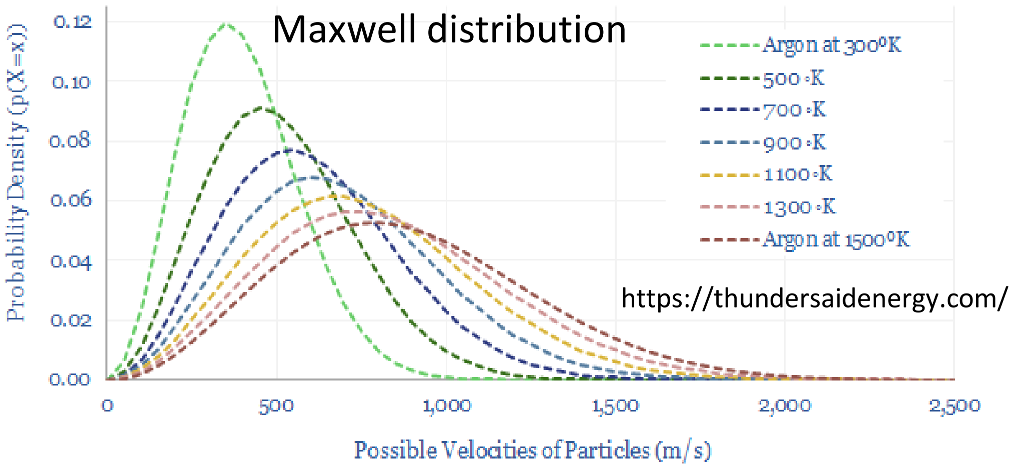
$$eV \rightarrow kT \; [\text{with } T \text{ in K}]$$

$$T \; [\text{Kelvin}] = \frac{eV \; [\text{electron Volt}]}{k}$$

$$1\,\text{eV} = 1.602 \times 10^{-19} \; \text{J}$$

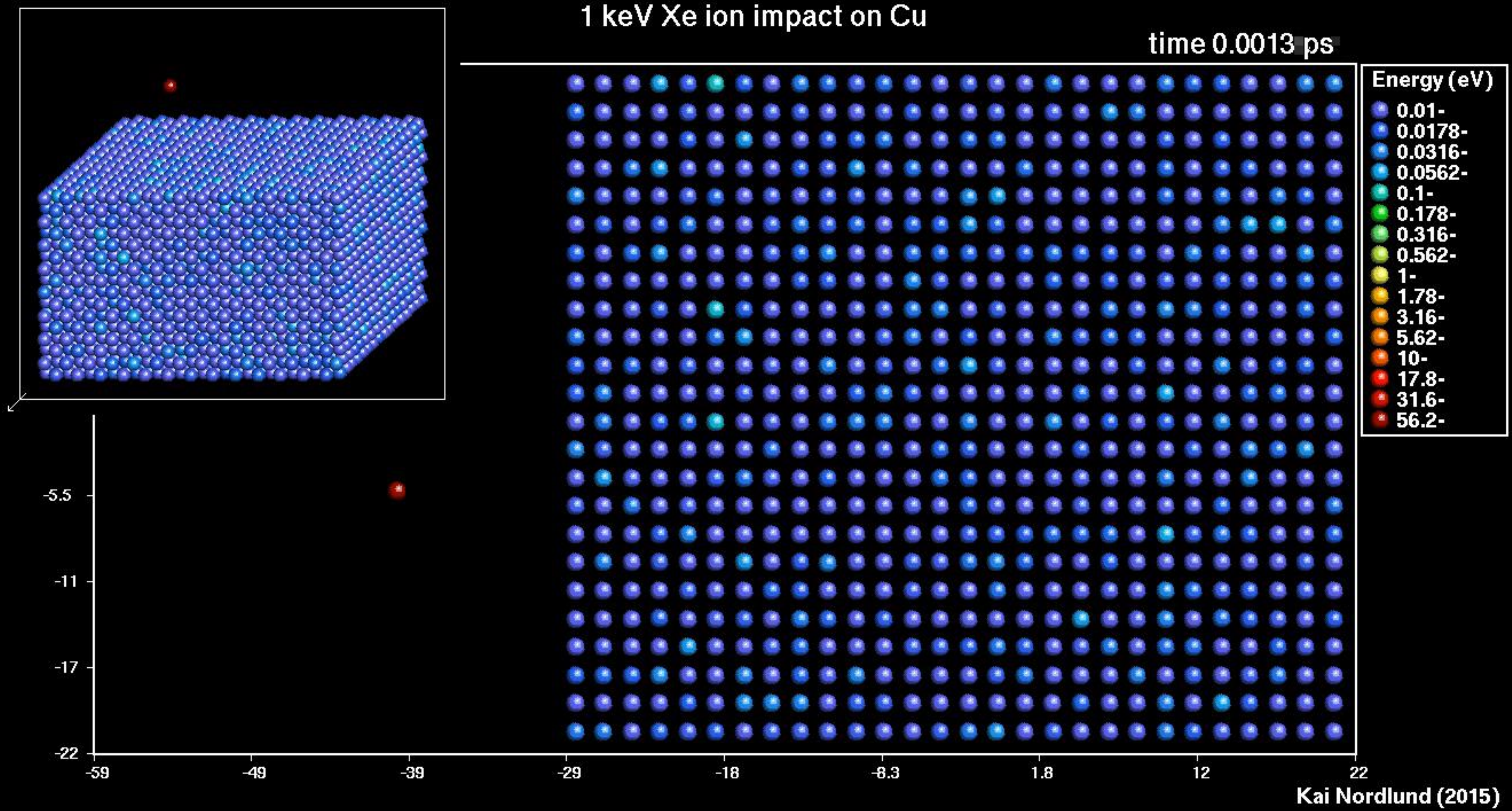
elementary charge $e = 1.602 \times 10^{-19}\,\text{As}$

Boltzmann constant $k = 3.1806 \times 10^{-23}\; \text{J/K}$



Wow! in equilibrium: $1\text{ eV} \triangleq 11605\text{ K}$ **Wow!**

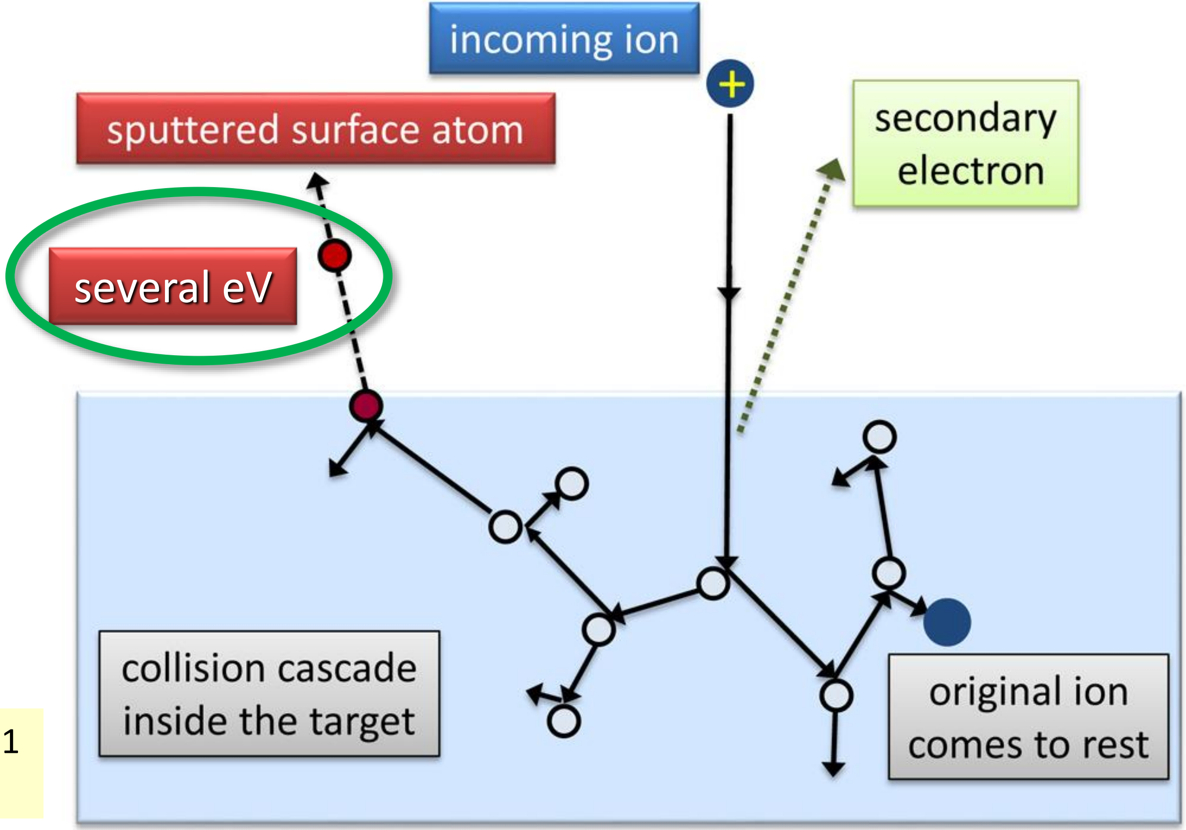
Collision cascade inside the target: energy vs. temperature



From evaporation to sputtering

(magnetron or ion beam sputtering)

(in other words: from ~100 meV to several eV per atom!)



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

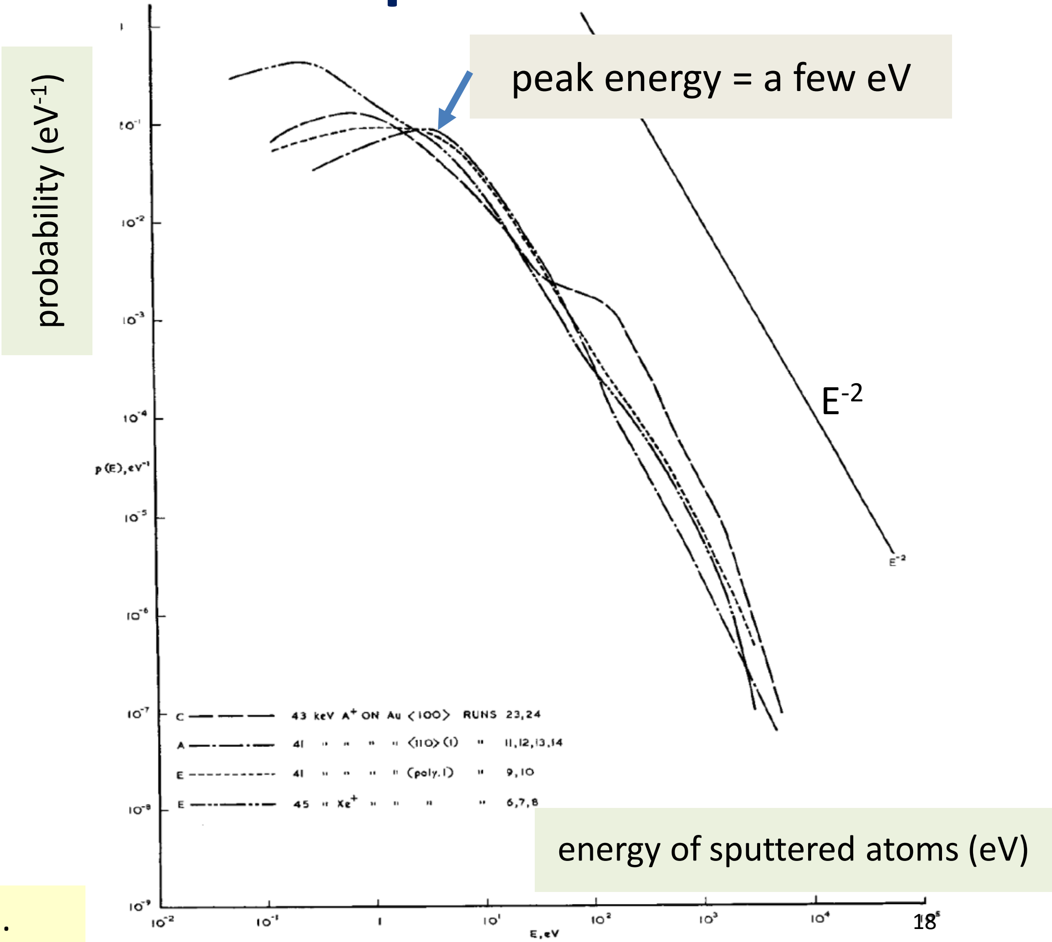
Thompson energy distribution of sputtered atoms

$$f_{\text{Thompson}}(E) \propto \frac{E}{(E + E_{SB})^3}$$

surface binding energy

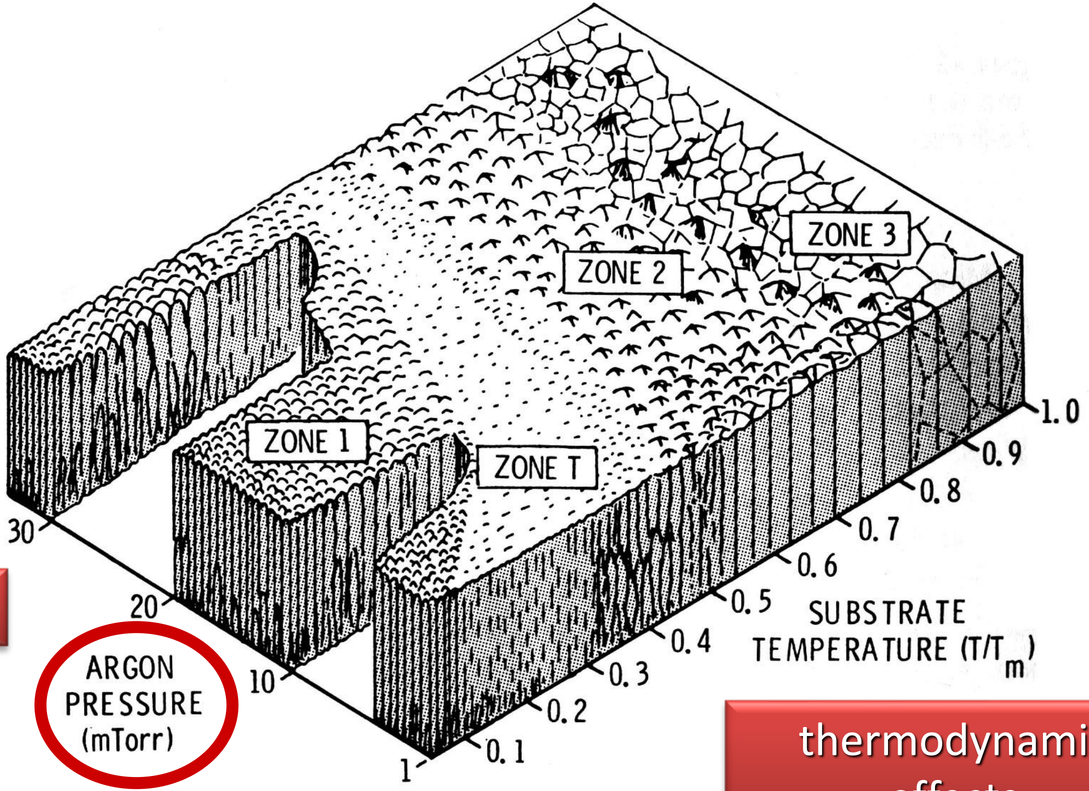
- describes the kinetic energy of sputtered atoms (without ionization effects)
- caution: atoms in high energy tail can cause defects in crystalline films

M. W. Thompson, Phil. Mag. 18 (1968) 377.



Thornton's Structure Zone Diagram for Magnetron Sputtering:

Thermodynamic (temperature) and kinetic energy effects



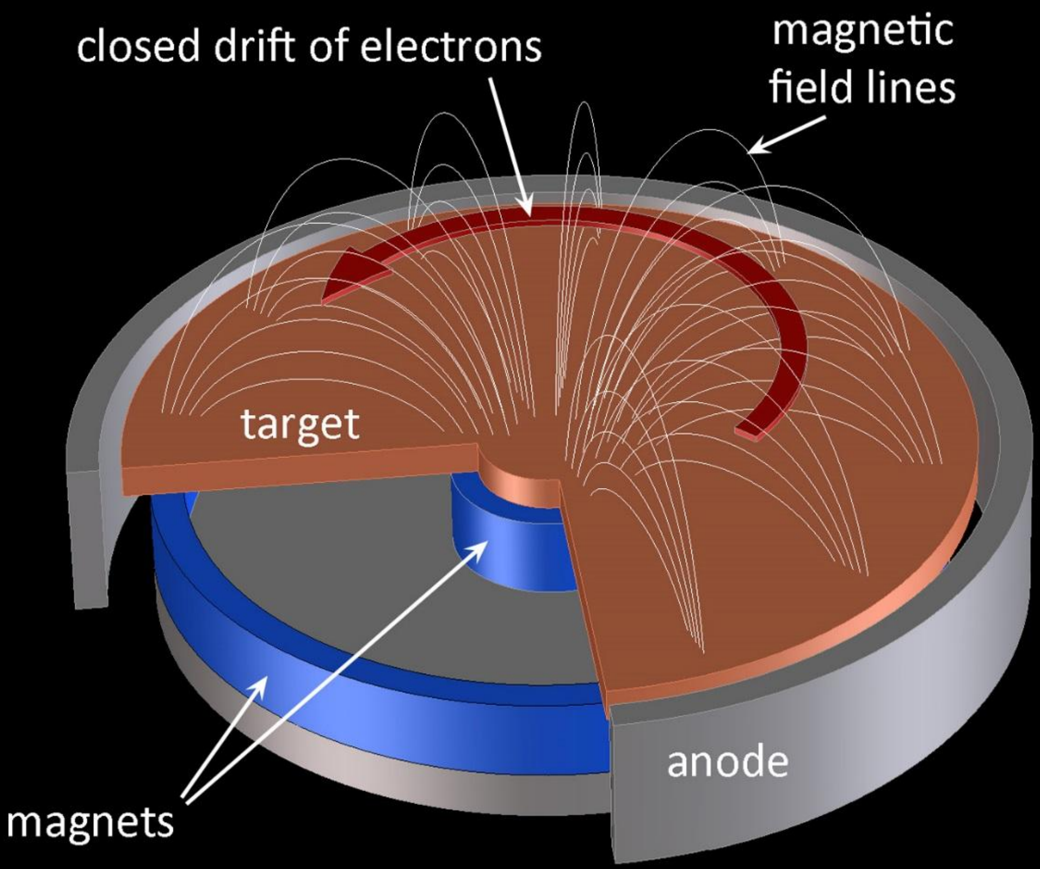
kinetic energy effects

thermodynamic effects

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

Magnetrons:

Sputtered atoms have
“a few eV” kinetic energy,
affecting film structure



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

Illustration of ExB Drift

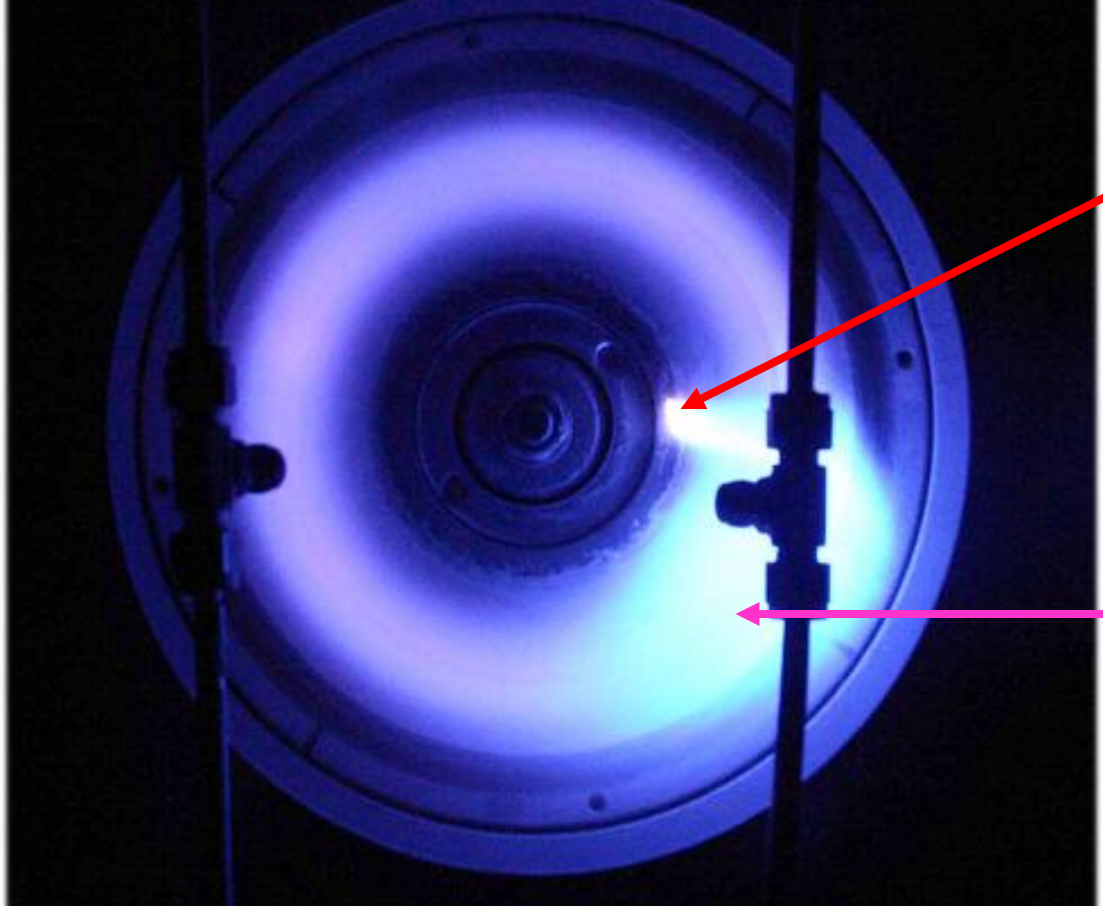
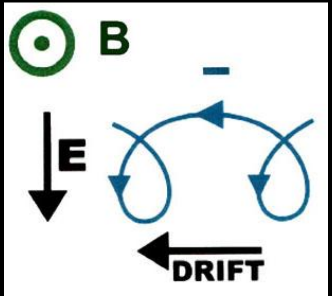


Photo courtesy of Bill Sproul

(unwanted) arc spot



Plasma plume drifts in **ExB** direction

Unbalanced Magnetron

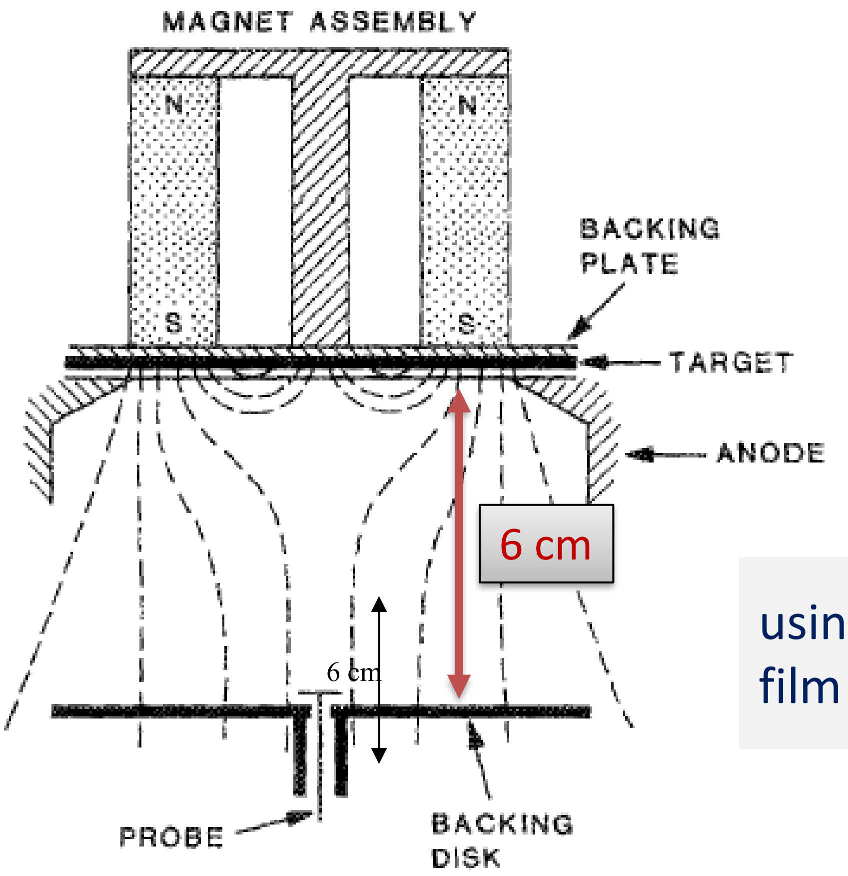
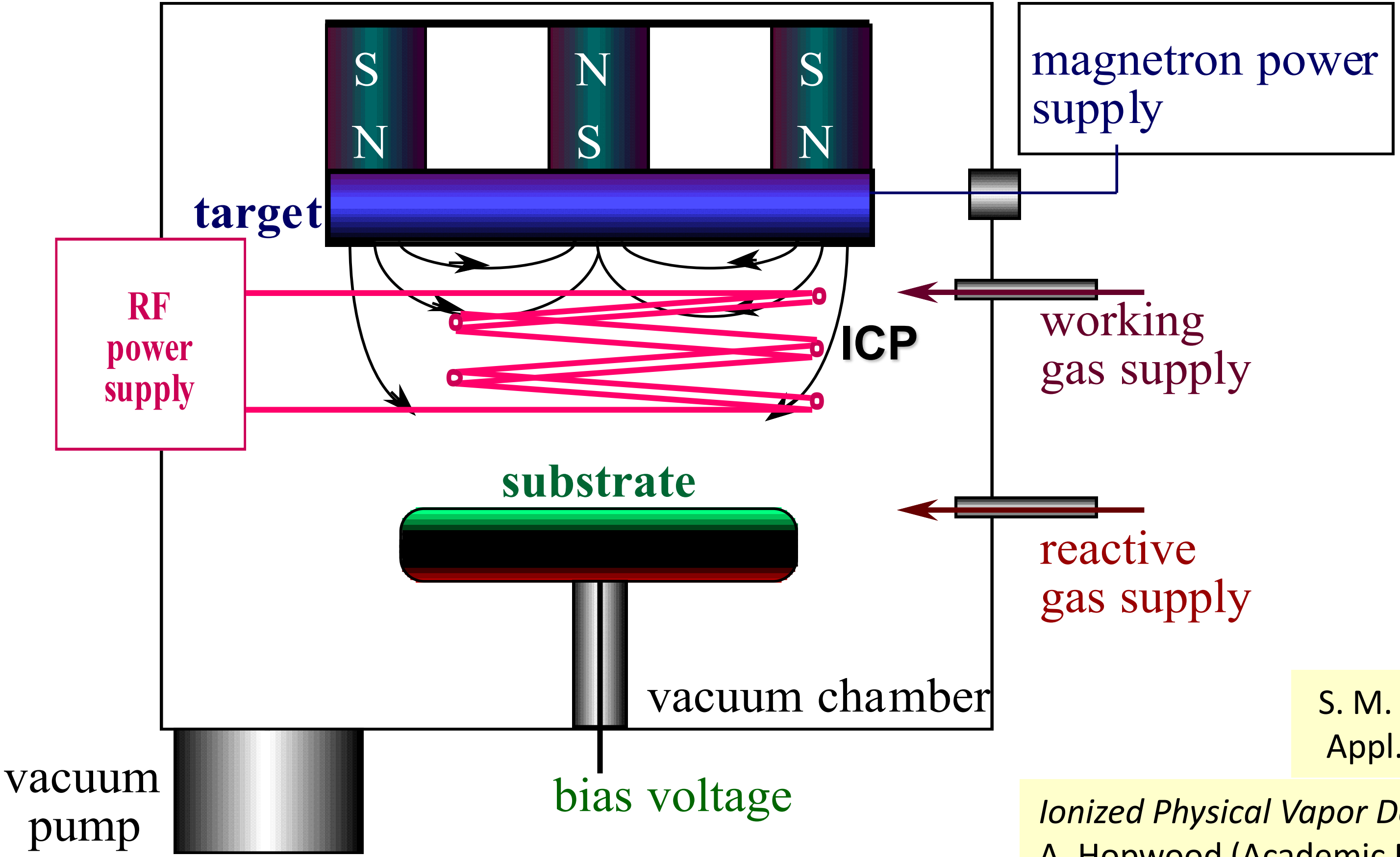


FIG. 1. Magnetron and probe assembly are shown schematically. For the measurements reported here the target to probe distance was maintained at 60 mm.

using the plasma of the magnetron to assist film growth, affecting microstructure

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

i-PVD = Magnetron Discharge with Ionization (1990s)



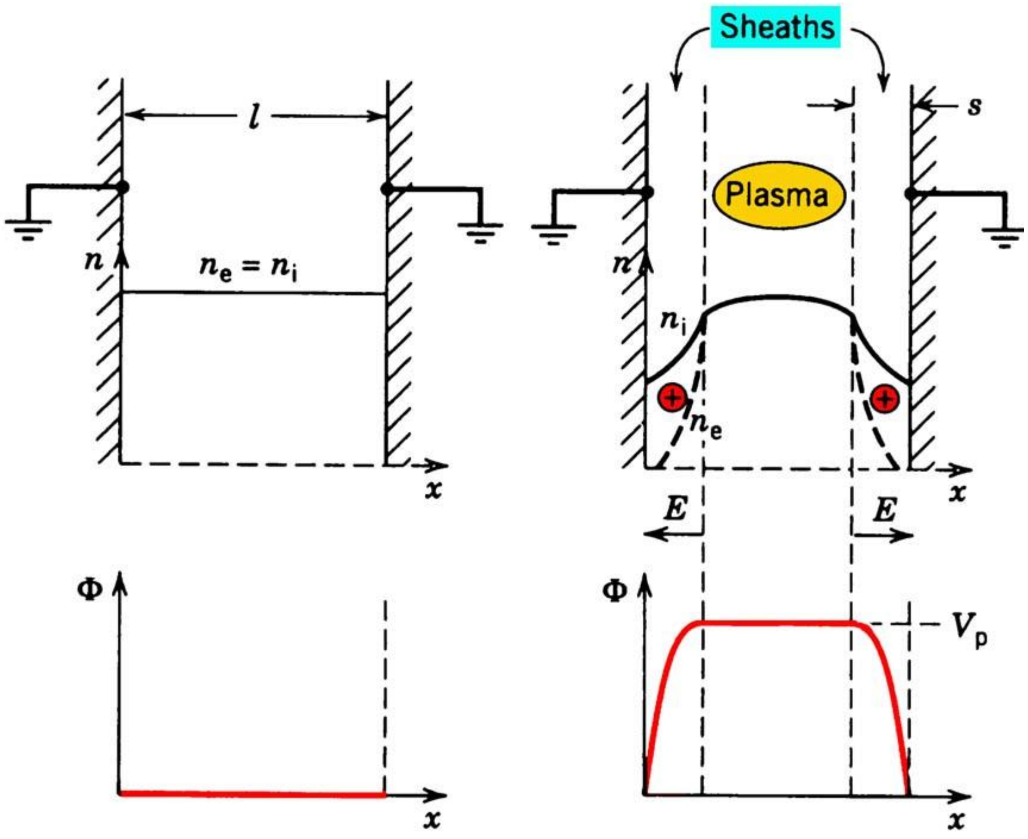
S. M. Rossnagel and J. Hopwood, Appl. Phys. Lett. 63 (1993) 3285

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

Interlude:

The **sheath** and its decisive role in tuning ion energy

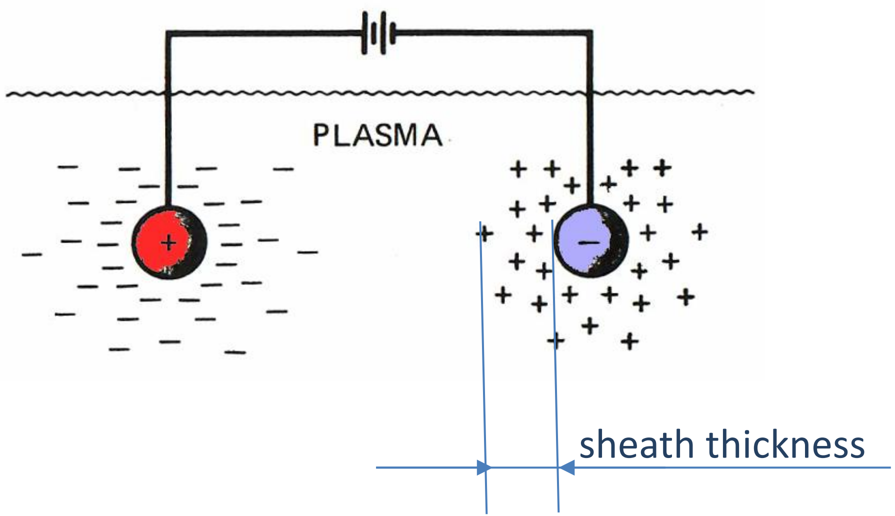
Plasma and Sheaths



M. A. Lieberman and A.J. Lichtenberg, Principles of Plasma Discharges and Materials Processing, 1994, 2005, Wiley, N.Y.

Debye Shielding → Child Langmuir Law

Debye Shielding: A charge cloud around a charge shields the long-range force of that charge.



We are generally interested in

- the thickness of the sheath,
- current density through the sheath as a function of potential difference.

- Clement D. **Child** (1911): current through vacuum is space-charge limited:
- Irving **Langmuir** (1913): electron current to a plasma probe is space charge limited.

Reminder: Maxwell's Equations

James Clerk Maxwell
(1831–1879)

Siméon Denis Poisson
(1781–1840)

current density j and net charge ρ are the sources of fields!

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

$$\nabla \times \mathbf{B} = \mu_0 \left(\varepsilon_0 \frac{\partial \mathbf{E}}{\partial t} + \mathbf{j} \right)$$

Poisson equation relates the net charge and electric potential (thus E-field) in plasma boundary

$$\nabla \cdot \mathbf{E} = \rho / \varepsilon_0$$

$$\nabla \cdot \mathbf{B} = 0$$

These sources of fields are not independent but related by the charge continuity equation

$$\frac{\partial \rho}{\partial t} + \nabla \cdot \mathbf{j} = 0$$

permeability of free space $\mu_0 = 4\pi \times 10^{-7}\ \mathrm{H/m}$

permittivity of free space $\varepsilon_0 = 8.854 \times 10^{-12}\ \mathrm{F/m}$

Deriving the Sheath Equation

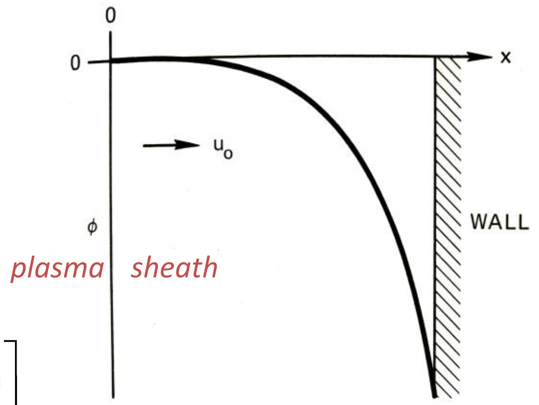
- energy conservation: $\frac{1}{2}m_i u^2 = \frac{1}{2}m_i u_0^2 - e\phi(x)$ $\rightarrow$ $u(x) = \left(u_0^2 - \frac{2e\phi(x)}{m_i}\right)^{1/2}$

- equation of continuity: $n_0 u_0 = n_i(x)u(x)$ $\rightarrow$ $n_i(x) = n_0\left(1 - \frac{2e\phi(x)}{m_i u_0^2}\right)^{-1/2}$

- steady-state: electrons are Boltzmann-distributed: $n_e(x) = n_0 \exp\left(\frac{e\phi(x)}{kT_e}\right)$

- Poisson equation:

$$\frac{d^2\phi}{dx^2} = -\frac{e}{\varepsilon_0}(n_i - n_e) = -\frac{e}{\varepsilon_0}n_0\left[\left(1 - \frac{2e\phi(x)}{m_i u_0^2}\right)^{-1/2} - \exp\left(\frac{e\phi(x)}{kT_e}\right)\right]$$



Deriving the Sheath Equation

- Introduction of three dimensionless variables

$$\chi \equiv \frac{e\phi}{kT_e} \qquad \xi \equiv \frac{x}{\lambda_D} = x\left(\frac{n_0 e^2}{\varepsilon_0 kT_e}\right)^{1/2} \qquad M \equiv \frac{u_0}{(kT_e/m_i)^{1/2}}$$

- inserted in Poisson equation leads to

$$\chi'' = \left(1 - \frac{2\chi}{M^2}\right)^{-1/2} - e^{-\chi}$$

the dimensionless sheath equation

prime means $d/d\xi$

A non-linear differential equation for the planar sheath, having a solution only for $M \geq 1$

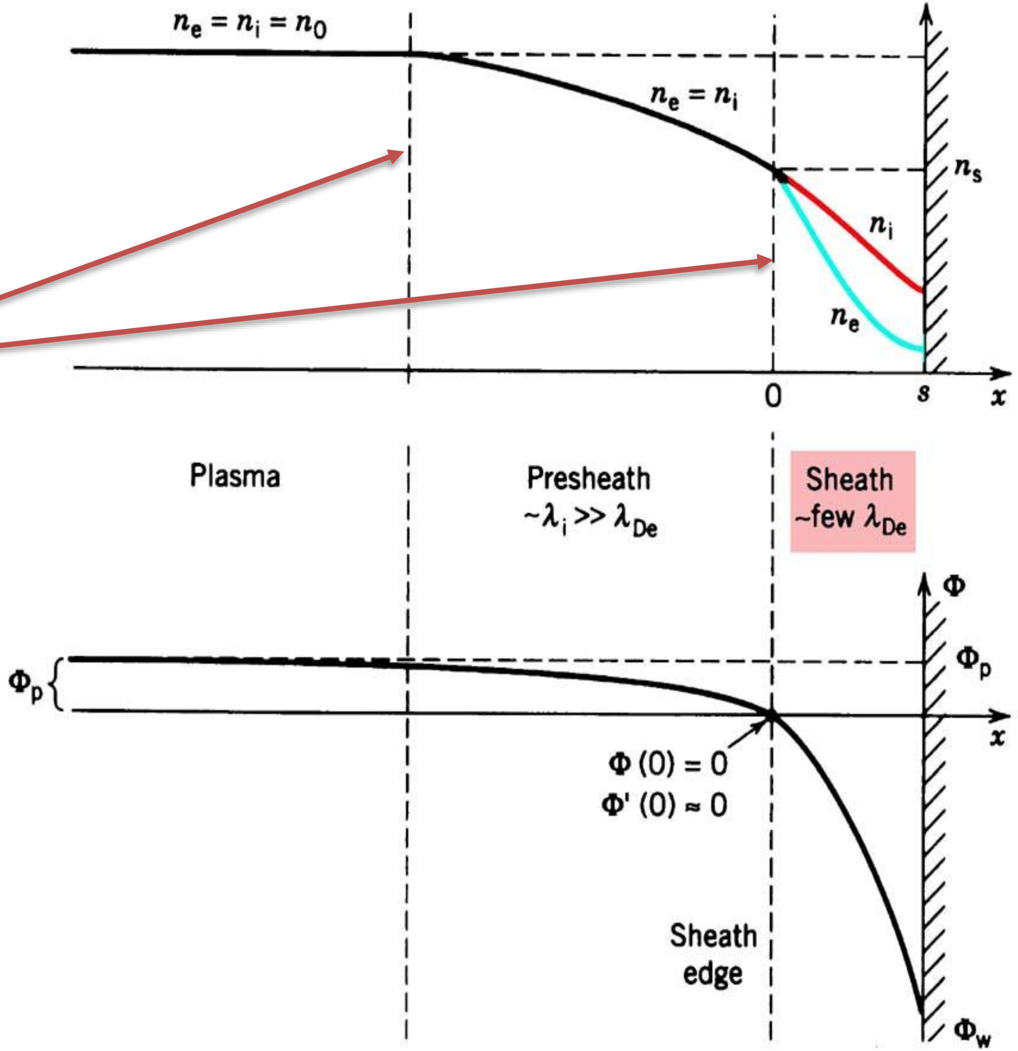
$$u_0 > \left(\frac{kT_e}{m_i}\right)^{1/2}$$

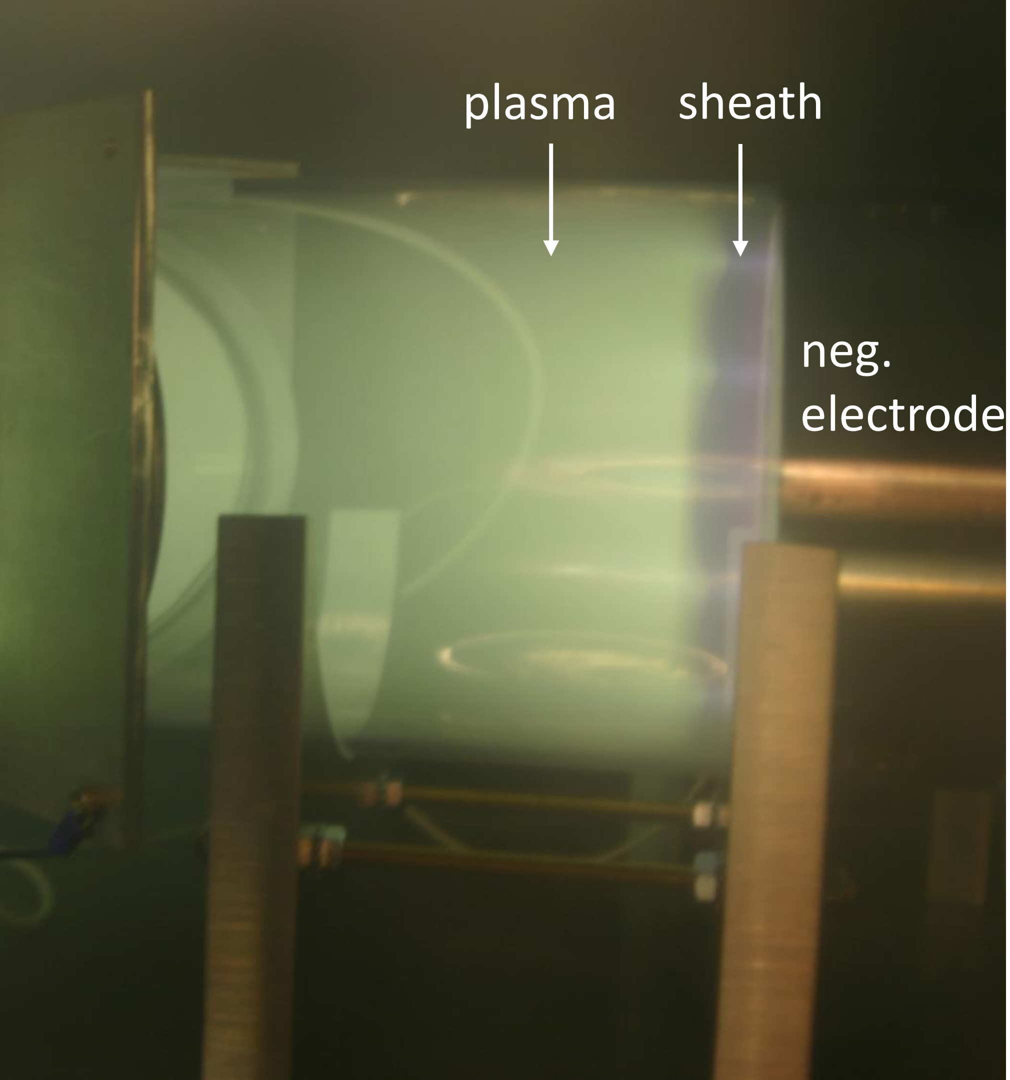
This is Bohm's sheath criterion.

→ Ions enter the sheath with at least the ion sound velocity.
→ The necessary energy is gained in the pre-sheath.

Sheaths and Presheaths

- ❑ Presheath: ion acceleration up to the ion sound velocity (Bohm)
- ❑ boundaries can be dynamic, e.g. when discharge is pulsed.





Tuning kinetic ion energy by the voltage drop in sheath

ion energy upon impact on surface

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

V_{sheath} is determined by **biasing**

ion charge state number

kinetic ion energy in plasma

Child-Langmuir Law (space-charge-limited current through a sheath)

- We start again with the **sheath equation**

$$\chi'' = \left(1 - \frac{2\chi}{M^2}\right)^{-1/2} - e^{-\chi}$$

- For a negatively biased wall → electrons are repelled and their density decays exponentially → one can neglect their contribution to the space charge, especially for large χ and the sheath equation simplifies to

$$\chi'' \approx \left(1 - \frac{2\chi}{M^2}\right)^{-1/2} \approx \frac{M}{(2\chi)^{1/2}}$$

- this can be integrated to arrive at $\chi'^2 = 2^{3/2} M \chi^{1/2}$

- We go back to non-normalized variables

Child-Langmuir Law

$$j = \frac{4}{9}\left(\frac{2e}{m_i}\right)^{1/2} \varepsilon_0 \frac{V_{sheath}^{3/2}}{s^2}$$

a relation of three variables:

1. current density
2. sheath voltage
3. sheath thickness

Child-Langmuir law and self-adjusting sheaths

Space charge limited current

$$j_i = \frac{4}{9}\varepsilon_0 \left(\frac{2e}{m_i}\right)^{1/2} \frac{V_{sheath}^{3/2}}{s^2}$$

self-adjusting sheath
(Child Sheath) given

$$s = \frac{\sqrt{2}}{3}\lambda_{De}\left(\frac{2eV_{sheath}}{kT_e}\right)^{3/4}$$

A variable bias voltage *V*(*t*) will lead to variable sheath thickness, *s*(*t*).

Sheath Dynamics

Negative voltage pulse applied:

- ❑ *electrons are repelled*

  → ion matrix sheath

- ❑ *ions are attracted*

  → expanding sheath

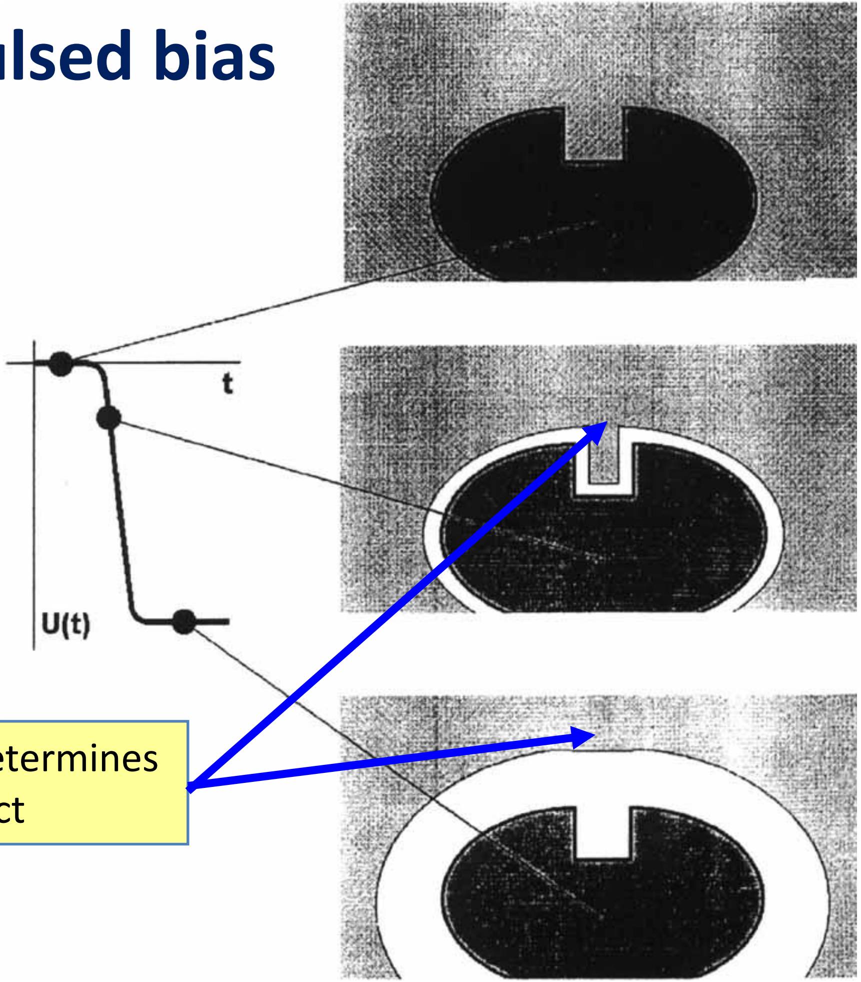
- ❑ energetic ions arrive at substrate
- ❑ a stationary sheath position will be reached when

$$\omega_{pl,e}^{-1} = \left(\varepsilon_0\, m_e / e^2\, n_e\right)^{1/2}$$

$$\omega_{pl,i}^{-1} = \left(\varepsilon_0\, m_i / e^2\, n_i\right)^{1/2}$$

ion current from plasma	=	space-charge limited current (Child current for a given voltage and actual sheath thickness)

Dynamic sheath with pulsed bias



trench size-to-sheath thickness is determines the conformal treatment of an object

W. Möller, *et al.*, Surf. Coat. Technol. **116-119** (1999) 1

Potential of a Floating Object in a Plasma

At an electrically floating wall surface: current cannot flow! → **Net current must be zero.**

Ion current = electron current

ion current $j_i = e\bar{Q} n_i v_{Bohm}$

density and velocity at sheath edge

electron current $j_e = \frac{1}{4} e n_{e,sheath} v_{e,th} \exp\left(\frac{eV_{sheath}}{kT_e}\right)$

with $v_{e,th} = \sqrt{\frac{8kT_e}{\pi m_e}}$

a weak function, it is ~ 4 for argon

a few eV

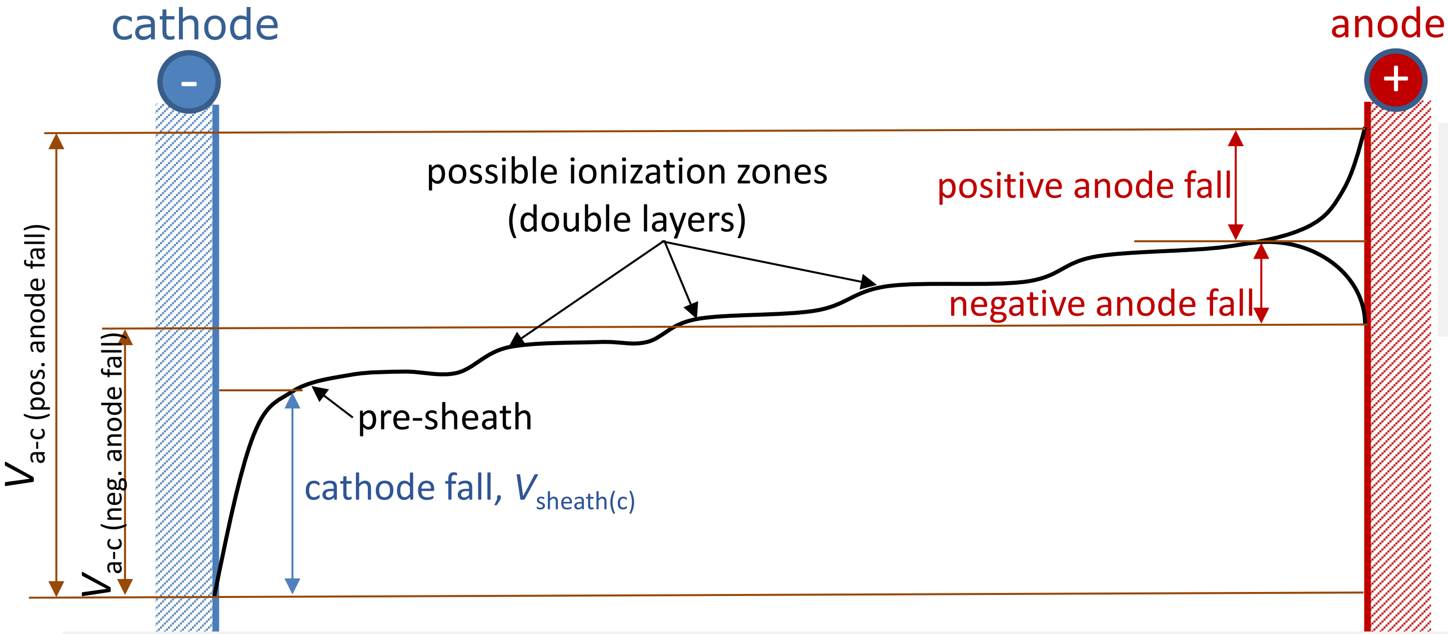
gives the **floating potential** with respect to the plasma potential $V_{sheath} = -\frac{2kT_e}{e} \ln\left(\frac{m_i}{2\pi m_e}\right)$

Plasma Potential versus *Floating Potential*

- **Plasma potential** at a certain position in the plasma is the potential that does not affect the motion of the surrounding charged particles.
- Often the **floating potential** is used as a proxy, with the cold-probe floating potential about –3 kT_e/e away from the plasma potential.
- For example, if kT_e= 3 eV, the plasma potential is about 10 V positive relative to the floating potential; this is due to the balance of electron and ion currents to the floating probe.
- The plasma potential can be directly measured with a hot, electron-emitting probe.
- Since the balance of charged particles is critical, any large area in contact with plasma determines its plasma potential → **grounded (chamber) and anode surfaces are critical!**

$$V_p - V_{surface} \approx \frac{kT}{e} \ln\left(\frac{m_i}{2\pi m_e}\right)^{1/2}$$

Anode fall can be positive or negative; plasma potential is close the anode potential



anode fall is critical to regulate the current balance

in the positive pulse for bipolar HiPIMS, the positive target affects the plasma potential, which can be positive relative to ground, depending on the size and position of grounded parts and circuit
→ ions indeed move toward the substrate, but caution: unwanted plasma may be produced, and unwanted sputtering of former anode may occur

A. Anders, Appl. Phys. Rev. 11 (2024) 031310.

Atomic-Scale Heating by Ions in a Film Deposition Process

ion energy upon impact on surface

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

kinetic ion energy in plasma

ion charge state number

V_{sheath} is determined by **biasing**

a more complete consideration gives additional contributions to ion energy delivered:

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

kin. energy in plasma

kin. energy gained in sheath

kin. energy by image charge acceleration

cohesive energy

excitation energy

ionization energy

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

Atomic-scale heating by ions

Much – but not all – of the delivered energy stays with the substrate and leads to atomic scale heating:

$$E_{heat(i)} = \underbrace{R_{kin}}_{\text{kinetic energy retention coefficient}} \underbrace{\left(E_{kin,0} + QeV_{sheath} + E_{ic}\right)}_{\text{kinetic energy}} + \underbrace{R_{pot}}_{\text{potential energy retention coefficient}} \underbrace{\left(E_c + E_{exc} + \sum_{Q'=0}^{Q-1} E_{Q'}\right)}_{\text{potential energy}}$$

kinetic energy retention coefficient

depend on substrate and other factors, ~ 0.8

potential energy retention coefficient

depend on substrate and other factors, ~ 0.6

coefficients < 1 primarily because electrons are emitted and they carry away part of this energy

A. Anders, to be submitted SCT (2025)

Cathodic arc plasma is especially suitable to study atomic scale heating during film growth

- Each ion brings **both kinetic and potential energy** to the growing film, affecting density and microstructure

- For **cathodic arc plasma**, where ions usually have multiple charge, and the plasma flows with supersonic velocity, this effect is especially pronounced:

potential ion energies up to several 10 eV
kinetic ion energies in the range 20-200 eV, and even higher due to bias

TABLE I. Atomic number Z, cohesive energy E_c,[a] ion kinetic energies $E_{kin,0}$,[a] ion charge state distributions (particle fractions),[b] and cumulative ionization energies, as defined by Eq. (2), for cathodic arc plasmas. The kinetic energies and ion charge state distributions are values averaged over many discharges. Values in *italics* are based on calculations[c] or extrapolation using the cohesive energy rule.[d]

Z		E_c (eV/atom)	$E_{kin,0}$ (eV)	$f(1+)$ (%)	$f(2+)$ (%)	$f(3+)$ (%)	$f(4+)$ (%)	$f(5+)$ (%)	E_1^{sum} (eV)	E_2^{sum} (eV)	E_3^{sum} (eV)	E_4^{sum} (eV)	E_5^{sum} (eV)
3	Li	1.63	19	100	0	0	0	0	5.39	81.0	203		
6	C	7.37	19	100	0	0	0	0	11.3	35.6	83.5	148	540
12	Mg	1.51	49	46	54	0	0	0	7.65	22.7	103	212	353
13	Al	3.39	33	38	51	11	0	0	5.99	24.8	53.3	173	327
14	Si	4.63	34	63	35	2	0	0	8.15	24.5	58.0	103	270
20	Ca	1.84	40	8	91	1	0	0	6.11	18.0	68.9	136	221
21	Sc	3.90	50	27	67	6	0	0	6.56	19.4	44.1	118	209
22	Ti	4.85	59	11	75	14	0	0	6.83	20.6	48.1	91.3	191
23	V	5.31	70	8	71	20	1	0	6.75	21.4	50.7	97.4	163
24	Cr	4.10	71	10	68	21	1	0	6.77	23.3	54.2	103	173
25	Mn	2.92	*40*	49	50	1	0	0	7.43	23.1	56.7	108	180
26	Fe	4.28	46	25	68	7	0	0	7.90	24.1	54.7	110	185
27	Co	4.39	44	34	59	7	0	0	7.88	25.0	58.5	110	189
28	Ni	4.44	41	30	64	6	0	0	7.64	25.8	61.0	116	192
29	Cu	3.49	57	16	63	20	1	0	7.73	28.0	64.9	122	202
30	Zn	1.35	36	80	20	0	0	0	9.39	27.4	67.1	126	209
32	Ge	3.85	45	60	40	0	0	0	7.90	23.8	58.1	104	197
38	Sr	1.72	80	2	98	0	0	0	5.70	16.7	59.6	117	188
39	Y	4.37	80	5	62	33	0	0	6.22	18.5	39.0	99.6	177
40	Zr	6.25	112	1	47	45	7	0	6.63	19.8	42.8	77.1	157
41	Nb	7.57	128	1	24	51	22	2	6.76	21.1	46.1	84.4	135
42	Mo	6.82	149	2	21	49	25	3	7.09	23.3	50.4	96.8	151
44	Ru	6.74	139	*2*	*17*	*70*	*10*	*1*	7.36	24.1	52.6	102	169
45	Rh	5.75	142	*2*	*21*	*68*	*8*	*1*	7.46	25.5	56.6	110	181
46	Pd	3.89	131	23	67	9	1	0	8.34	27.8	60.7	122	200
47	Ag	2.95	69	13	61	25	1	0	7.58	29.1	63.9	124	204
48	Cd	1.16	27	68	32	0	0	0	8.99	25.9	63.4	122	201
49	In	2.52	21	66	34	0	0	0	5.79	24.7	52.7	107	185
50	Sn	3.14	30	47	53	0	0	0	7.34	22.0	52.5	93.2	165
51	Sb	2.75	17	99	1	0	0	0	8.64	25.2	50.5	94.7	151
56	Ba	1.90	32	0	100	0	0	0	5.21	15.2	49.7	98.1	160
57	La	4.47	35	1	76	23	0	0	5.58	16.6	35.8	85.8	147
58	Ce	4.32	36	3	83	14	0	0	5.54	16.4	36.6	73.3	139
59	Pr	3.70	55	3	69	28	0	0	5.46	16.0	37.6	76.6	134
60	Nd	3.40	50	0	83	17	0	0	5.53	16.3	38.4	78.8	147
62	Sm	2.14	43	2	83	15	0	0	5.64	16.7	40.1	81.5	152
63	Eu	1.86	48	*2*	*86*	*12*	*0*	*0*	5.67	16.9	41.8	84.6	157
64	Gd	4.14	45	2	76	22	0	0	6.15	18.2	38.9	82.9	155
65	Tb	4.05	45	*2*	*72*	*26*	*0*	*0*	5.86	17.4	39.3	79.1	152
66	Dy	3.04	46	2	66	32	0	0	5.94	17.6	40.4	81.8	158
67	Ho	3.14	58	2	66	32	0	0	6.02	17.8	40.7	83.2	161
68	Er	3.29	59	1	63	35	1	0	6.11	18.0	40.8	83.5	162
69	Tm	2.42	61	13	78	9	0	0	6.18	18.2	41.9	84.6	165
70	Yb	1.60	*48*	3	88	8	0	0	6.25	18.4	43.5	87.0	168
72	Hf	6.44	79	3	24	51	21	1	6.82	21.7	45.0	78.4	146
73	Ta	8.10	136	2	33	38	24	3	7.89	22.4	45.8	82.2	131
74	W	8.90	117	2	23	43	26	6	7.98	23.1	48.5	87.8	141
75	Re	8.03	*115*	*2*	*17*	*57*	*21*	*3*	7.88	23.6	49.5	91.0	147
76	Os	8.17	*115*	*2*	*20*	*56*	*21*	*1*	8.70	25.0	52.8	95.4	155
77	Ir	6.94	113	5	37	46	11	1	9.10	26.0	55.5	101	162
78	Pt	5.84	67	12	69	18	1	0	9.00	28.2	63.5	115	182
79	Au	3.81	49	14	75	11	0	0	9.23	29.7	67.1	122	193
82	Pb	2.03	35	36	64	0	0	0	7.42	22.4	54.4	96.7	166
83	Bi	2.18	24	83	17	0	0	0	7.29	24.0	50.8	96.9	155
90	Th	6.20	118	0	24	64	12	0	6.08	17.6	37.6	66.4	124
92	U	5.55	160	20	40	32	8	0	6.19	17.8	35.9	66.8	117

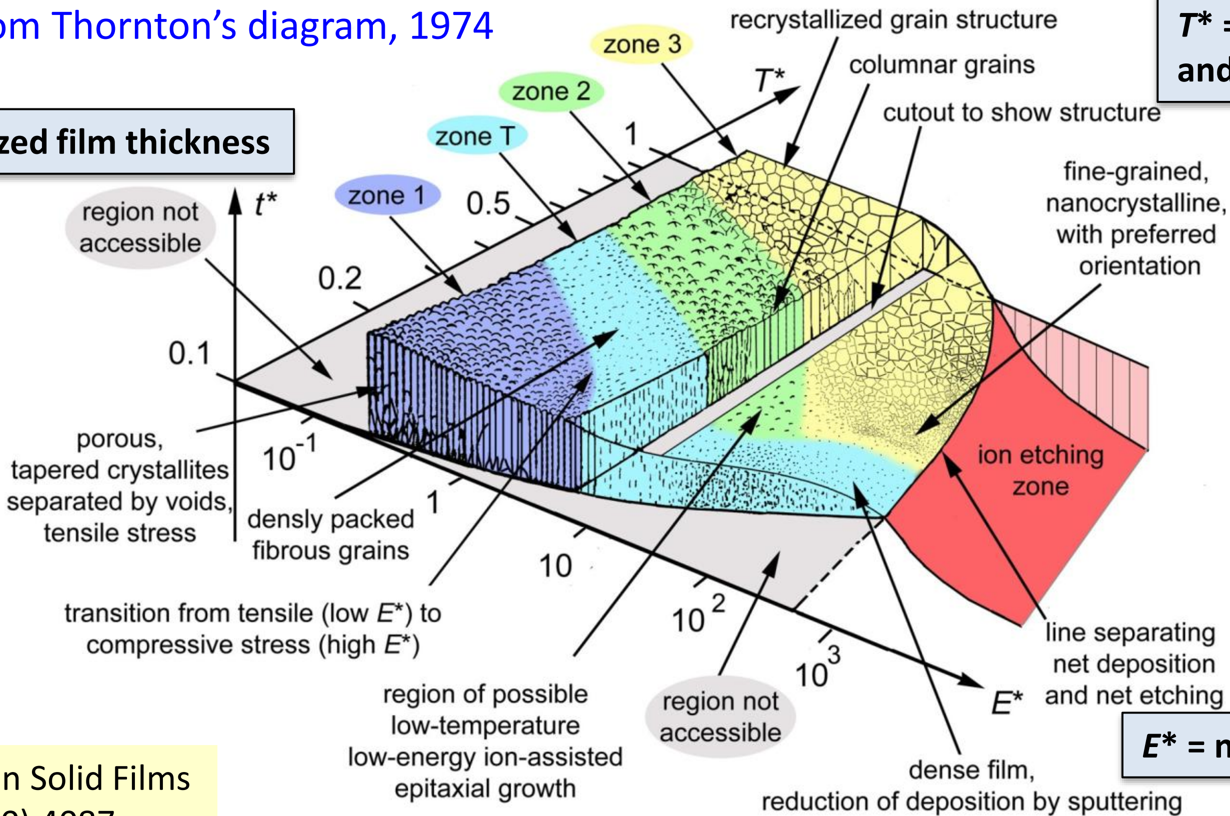
A. Anders, Appl. Phys. Lett. 80 (2002) 1100.

A generalized structure zone diagram including the effects of plasma assistance on microstructure of films

derived from Thornton's diagram, 1974

t* = normalized film thickness

T* = normalized temperature and potential energy



E* = normalized kinetic energy

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

Estimating overlaps of ion impacts

- The flux of arriving ions and atoms *J* is related to the deposition rate *R* by the expression

$$J = R\, n_{film} = R \frac{\rho}{M\ m_{amu}}$$

- Example of a VAlN, dep. rate *R* = 10 nm / min, and using material values Al, V →

$$J \sim 10^{-11} \frac{\text{ions}}{\text{nm}^2\text{ps}}$$

typical thermal quench time ~ 1 ps
typical area affected < 1 nm^2

→

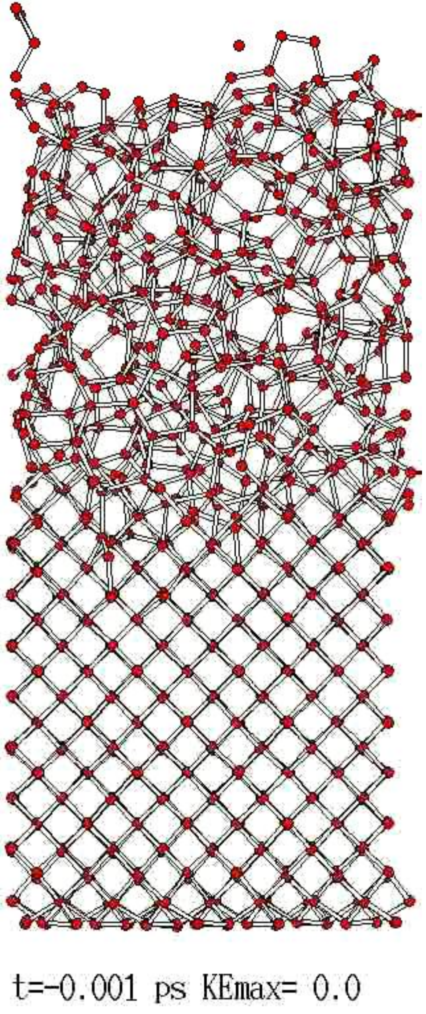
that means ion impacts are **isolated events** → *a change of flux even by 1-2 orders of magnitude does not matter, at least not directly*
but cumulative heating: average surface temperature will rise as the process continues, implies a shift to the higher global temp in the structure zone diagram

Carbon ion subplantation to grow ta-C films

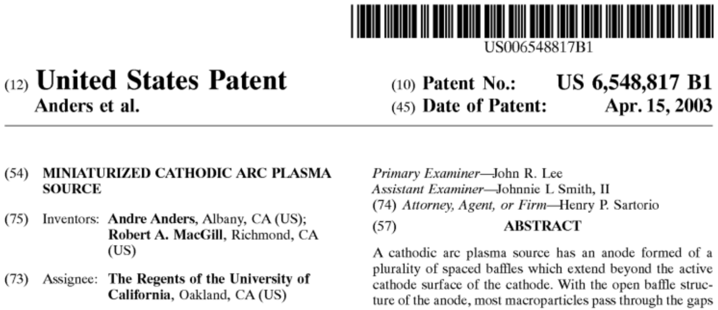
Molecular Dynamics (MD) simulation
red = sp^3-bonded C-atoms
blue = sp^2-bonded C-atoms

Interest in ta-C or DLC due to

- low friction
- corrosion protection
- diffusion barrier, even for hydrogen
- electrode application if doped



With Veeco: filtered arc system for read-write heads (2003)



US006548817B1

(12) **United States Patent**
Anders et al.

(10) **Patent No.: US 6,548,817 B1**
(45) **Date of Patent: Apr. 15, 2003**

(54) **MINIATURIZED CATHODIC ARC PLASMA SOURCE**

(75) Inventors: **Andre Anders**, Albany, CA (US); **Robert A. MacGill**, Richmond, CA (US)

(73) Assignee: **The Regents of the University of California**, Oakland, CA (US)

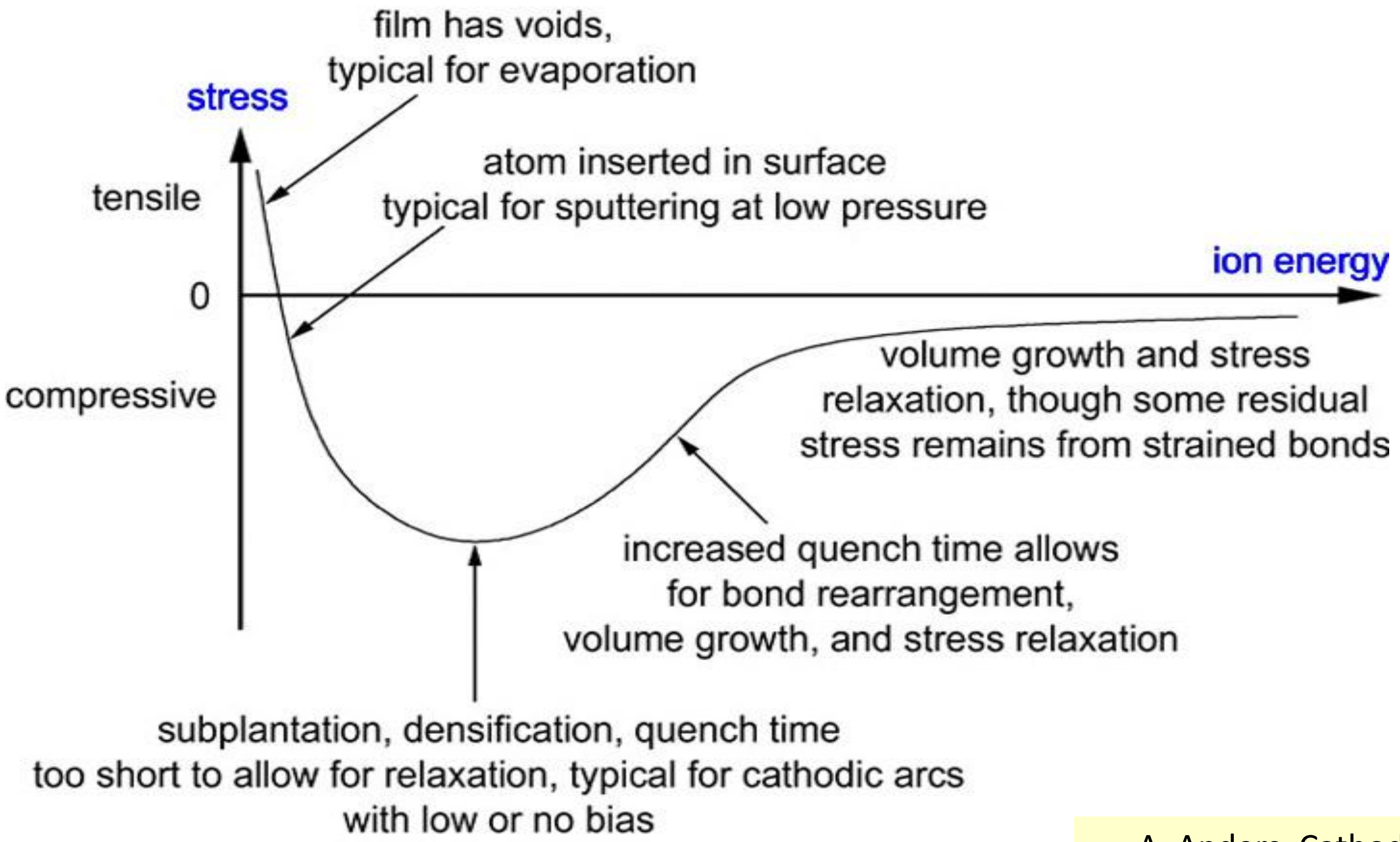
Primary Examiner—John R. Lee
Assistant Examiner—Johnnie L Smith, II
(74) *Attorney, Agent, or Firm*—Henry P. Sartorio

(57) **ABSTRACT**

A cathodic arc plasma source has an anode formed of a plurality of spaced baffles which extend beyond the active cathode surface of the cathode. With the open baffle structure of the anode, most macroparticles pass through the gaps

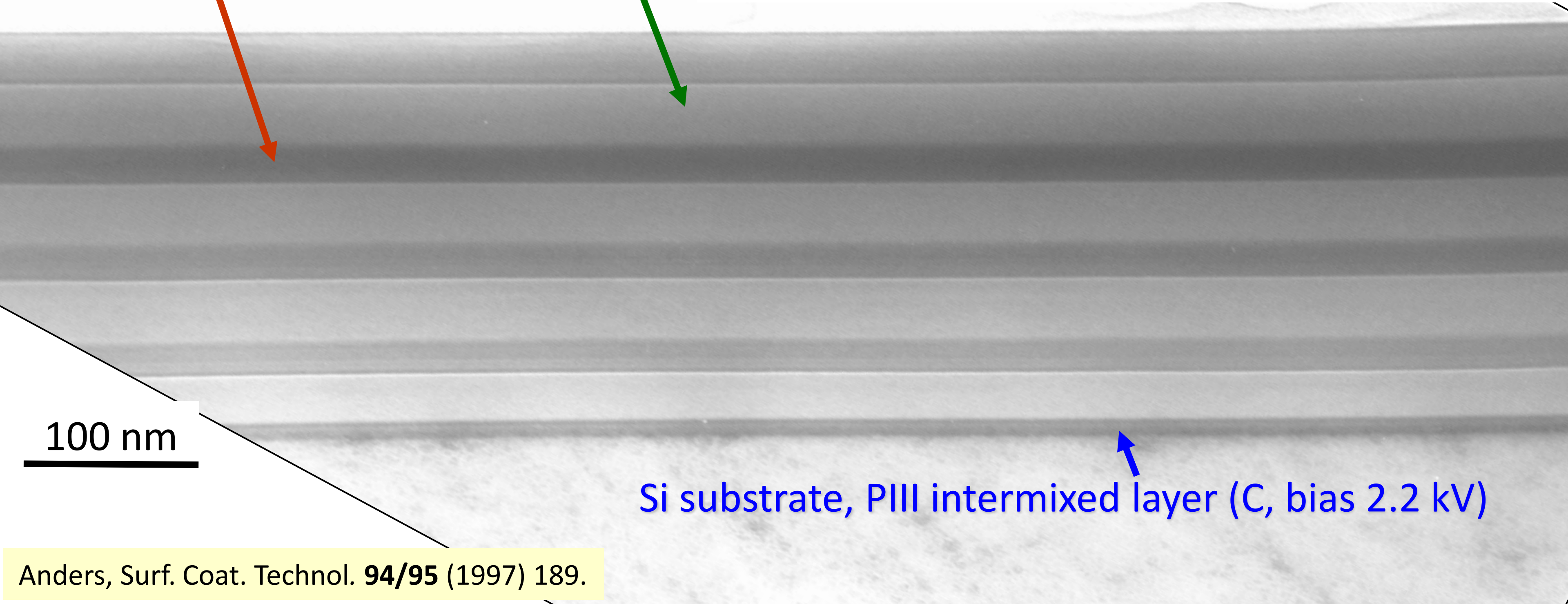
N.A. Marks, et al., Diamond and Related Materials 12 (2003) 2003.

Buildup and control of intrinsic stress in PVD-films with bias



A. Anders, Cathodic Arcs, Springer, NY 2008

Diamond-like carbon-carbon multilayer made by filtered arc plasma deposition via shallow implantation (= “subplantation”) with alternating bias periods.
Cross-section TEM:

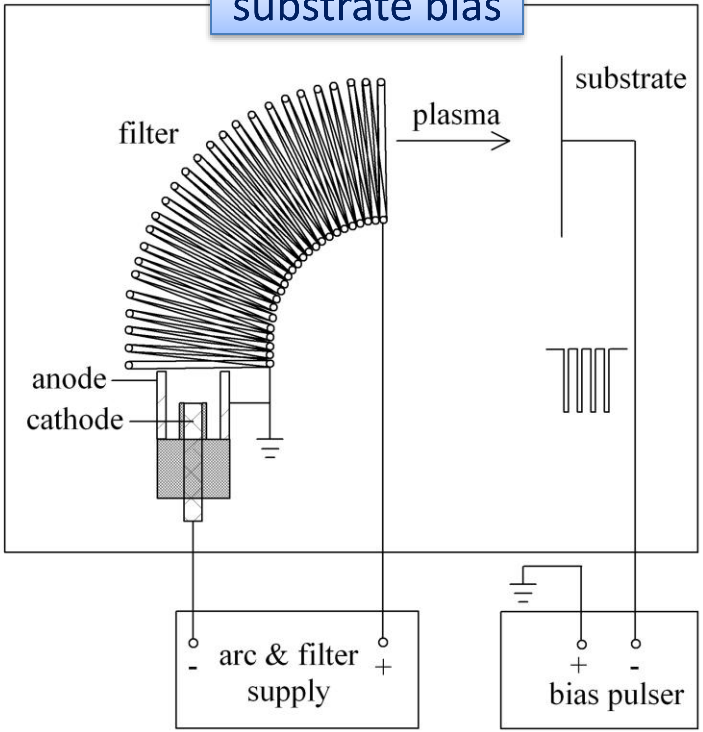


Anders, Surf. Coat. Technol. **94/95** (1997) 189.

Controlling ion energy via Substrate Bias or/and Plasma Bias

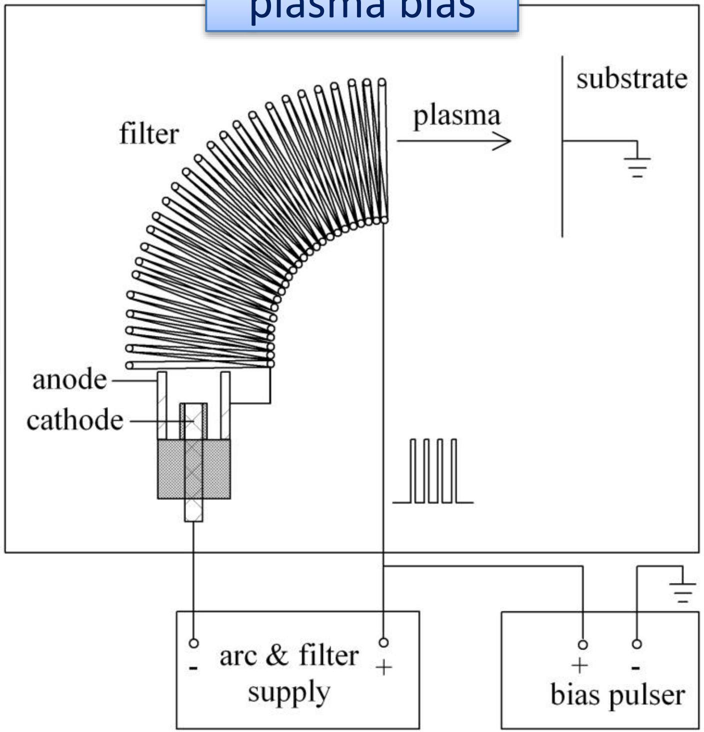
All that matters is the ***difference*** *of plasma potential and surface potential.*

substrate bias



resulting in the same microstructure of thin films

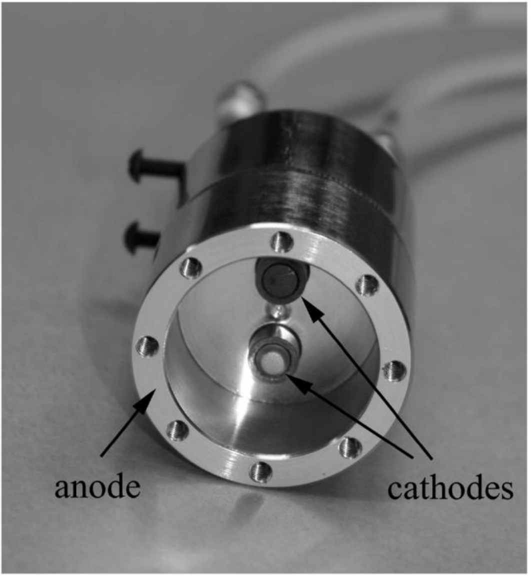
plasma bias



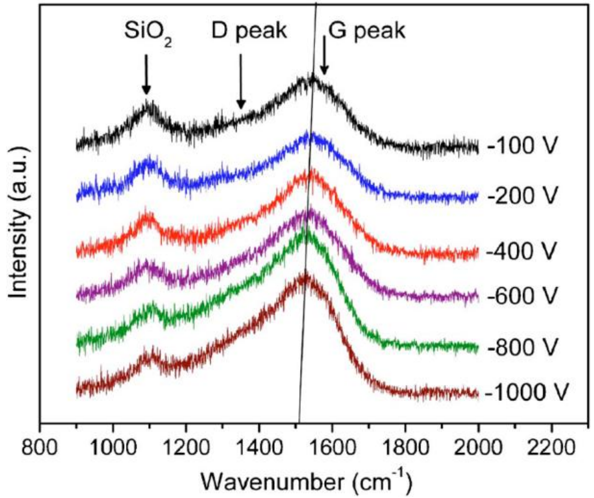
A. Anders, *et al*., Surf. Coat. Technol. **201** (2007) 4628-4632.

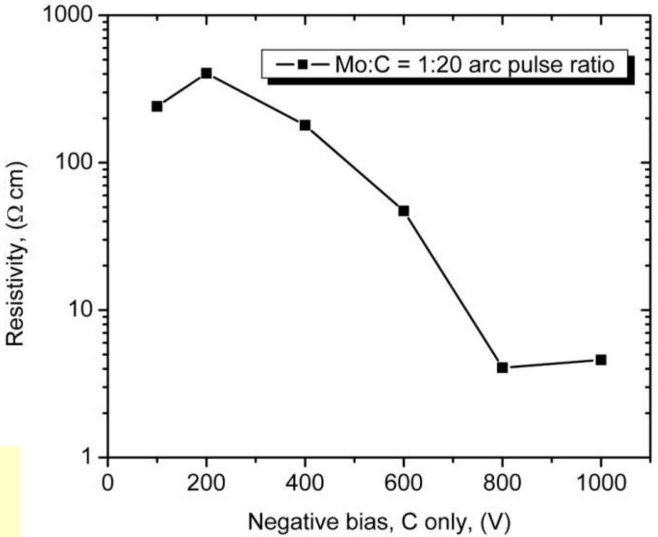
“Species-Selective Bias”

Bias amplitude depends on which plasma is present



- cathodic arc source with two cathodes, here C, Mo, to make metal-doped ta-C films
- apply bias (100 V) **only** when **C** is pulsed
  → to get ta-C
- no bias when **Mo** is pulsed
  → to not destroy ta-C but to make it conductive



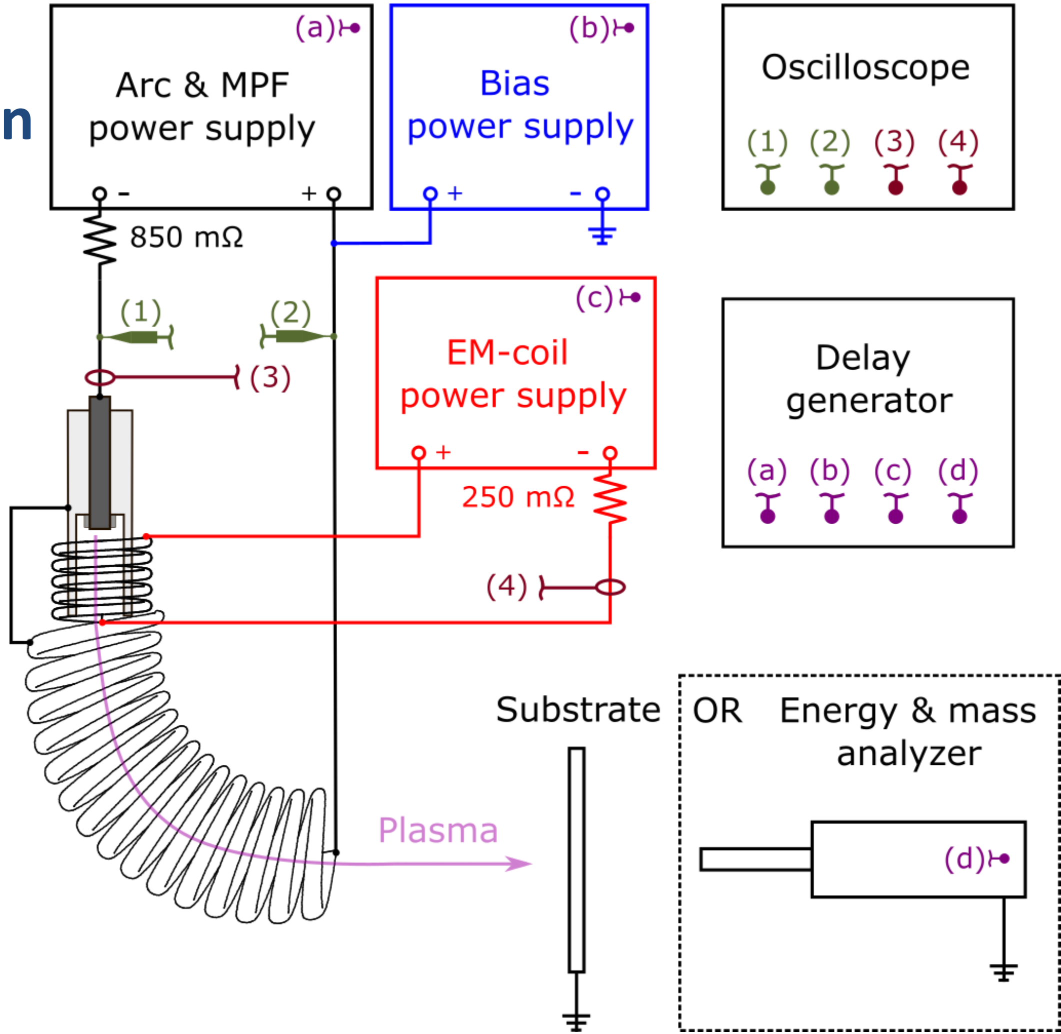


A. Anders, Rev. Sci. Instrum. **78** (2007) 063901.
J. L. Endrino, Surf. Coat. Technol. **202** (2008) 3675.

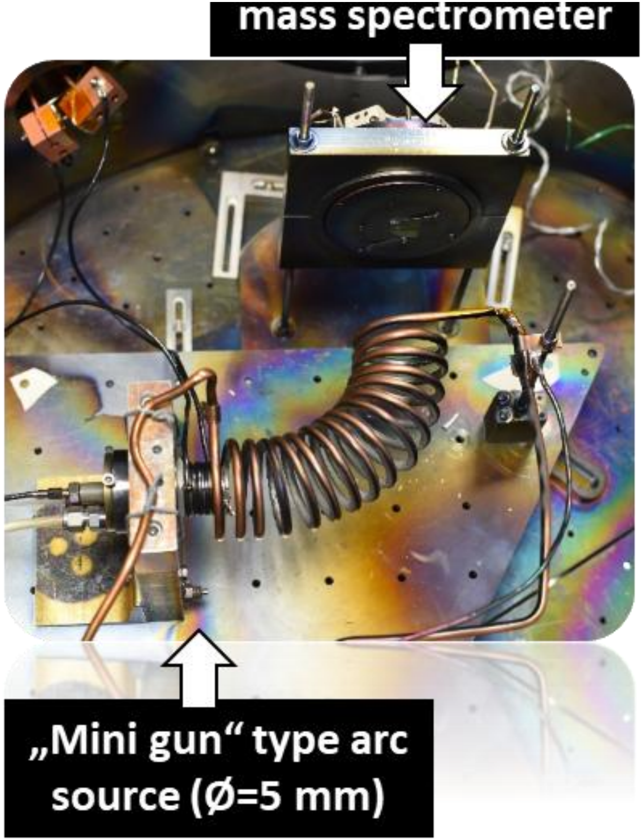
Ion Energy Tuning in Pulsed Filtered Cathodic Arc Deposition

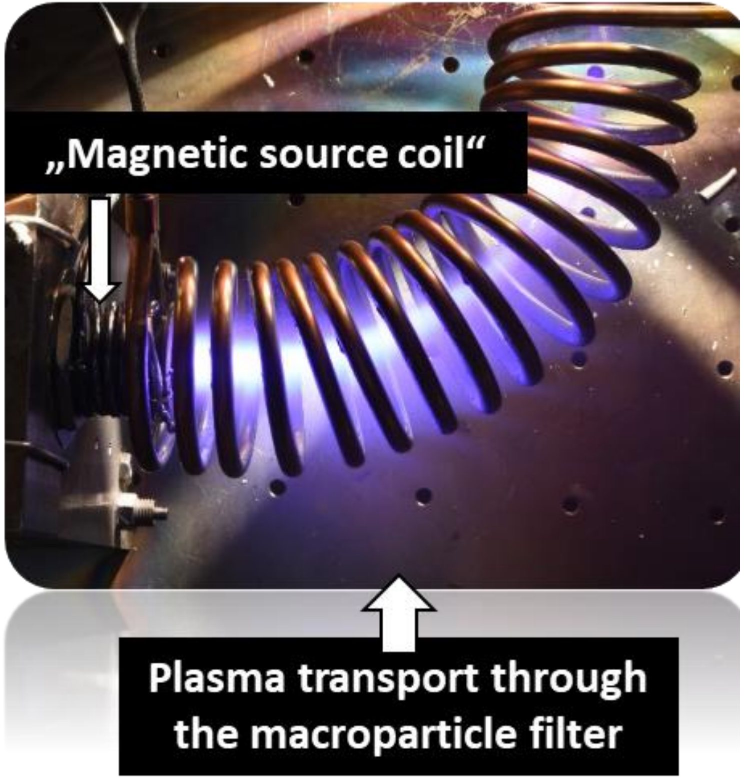
- Use plasma biasing to shift kinetic energies
- Use magnetic field coil at plasma source to shift charge states (hence affect the potential energies)

- Decoupling of the effects of kinetic versus potential energy is possible, but possible flux effects should be considered



Ion Energy Tuning in Pulsed Filtered Cathodic Arc Deposition





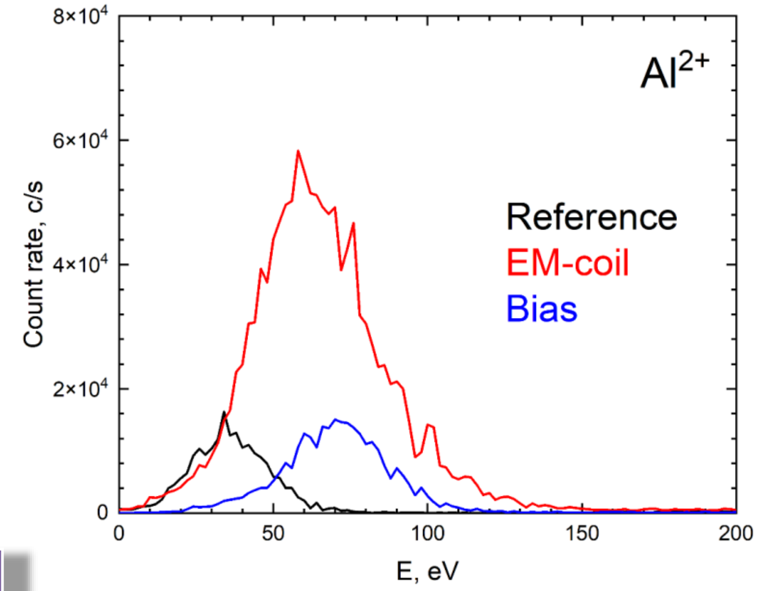
Y. Unutulmazsoy, et al., J. Vac. Sci. Technol. A 41 (2023) 063106.

Process parameters and ion energy distribution functions (IEDFs)

Process parameters:

Cathode composition	60 % V – 40 % Al (at. %)
Substrate temperature	RT, 500 °C
Base pressure	$1x10^{-5}$ Pa (RT), $2x10^{-4}$ Pa (500 °C)
Working pressure	0.2 Pa
Arc pulse length	1 ms
Repetition rate	5 Hz
Arc source current	440 A

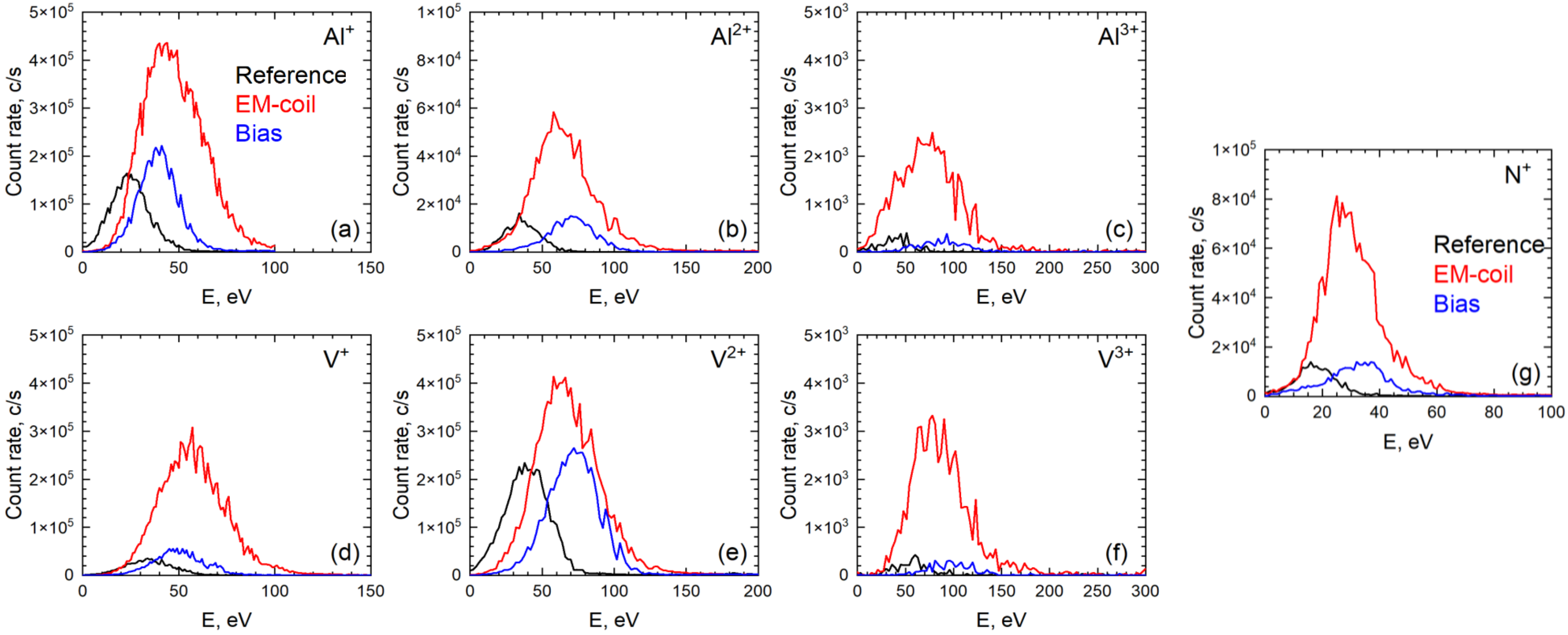
Configuration	Magnetic field (mT)	Bias voltage (V)
„Reference“	0	0
Plasma bias (affecting kin. energy)	0	30
EM-coil (affecting pot. and kin. energy as well as flux)	200	0



By changing the B-field, both charge states(potential energy) and kin. energy is shifted.
Bias voltage is selected as to compensate the difference in E_{kin} between "Reference" and EM-coil configurations.

V-Al-N arc plasma: Ion energy distribution functions

0.2 Pa (N_2), Cathode: 60% V – 40% Al (at.%)

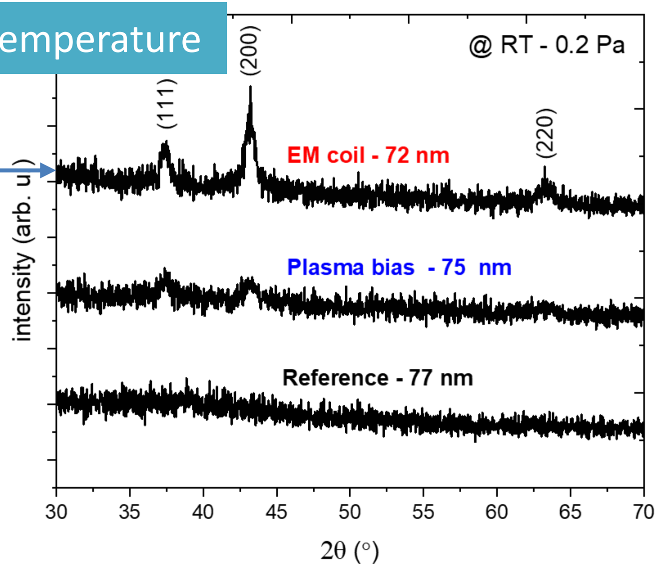


Y. Unutulmazsoy, et al., J. Vac. Sci. Technol. A 41 (2023) 063106.

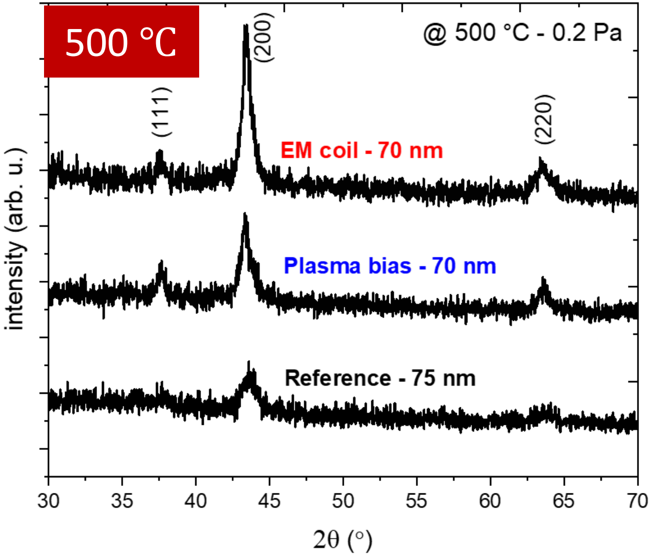
Structural properties of (V,Al)N films are affected by substrate heating and by „atomic scale heating“ → Crystallinity of AlVN is possible @ RT

at room temperature

from plasma with enhanced charge states: effect of potential energy!



500 °C



Deposition Condition	XRR density (g/cm^3)
Reference	4.25
Plasma Biasing	4.95
EM-Coil (higher charge states)	5.06

Condition	XRR density (g/cm^3)
Reference	4.25
Plasma Biasing	4.70
EM-Coil	4.85

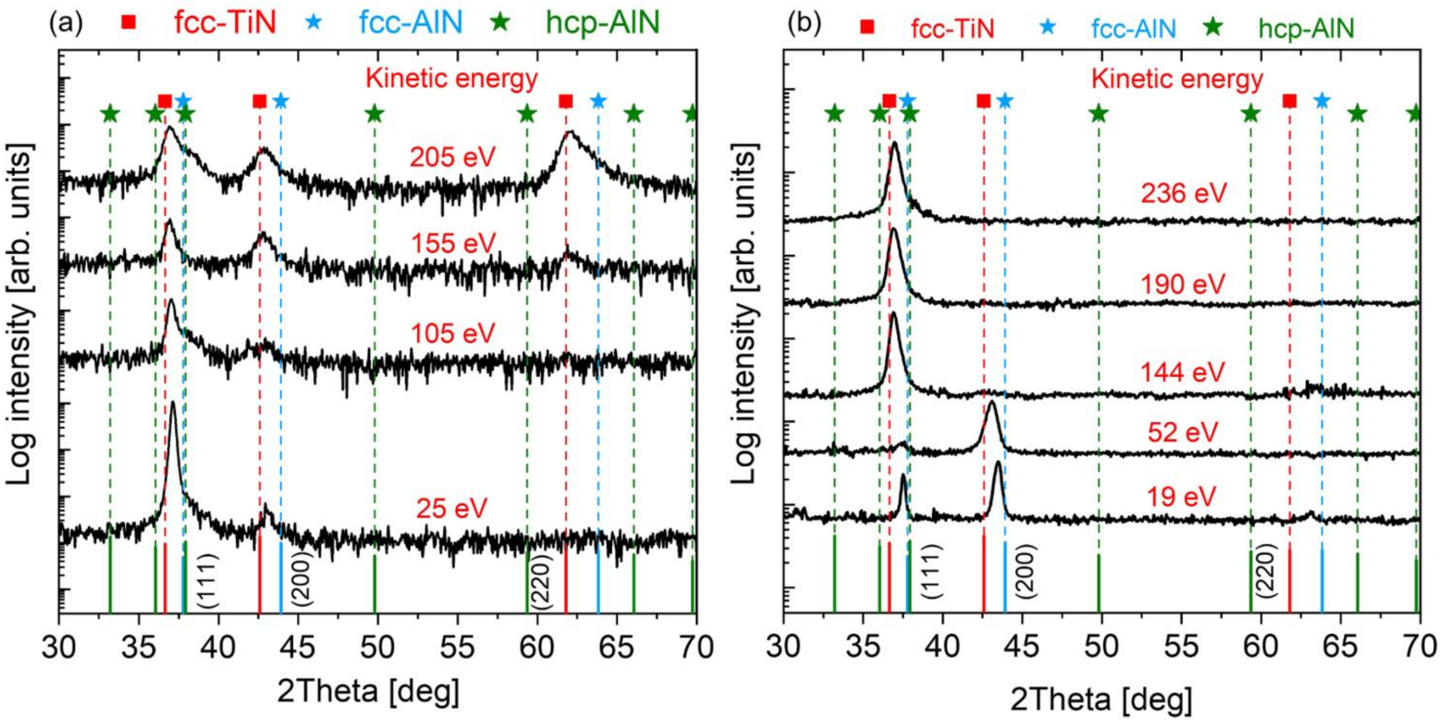
Y. Unutulmazsoy, *et al.*, J. Vac. Sci. Technol. A 41, 063106 (2023).

Effect of kinetic energy via biasing the substrate

(comparison of HiPIMS and cathodic arc)

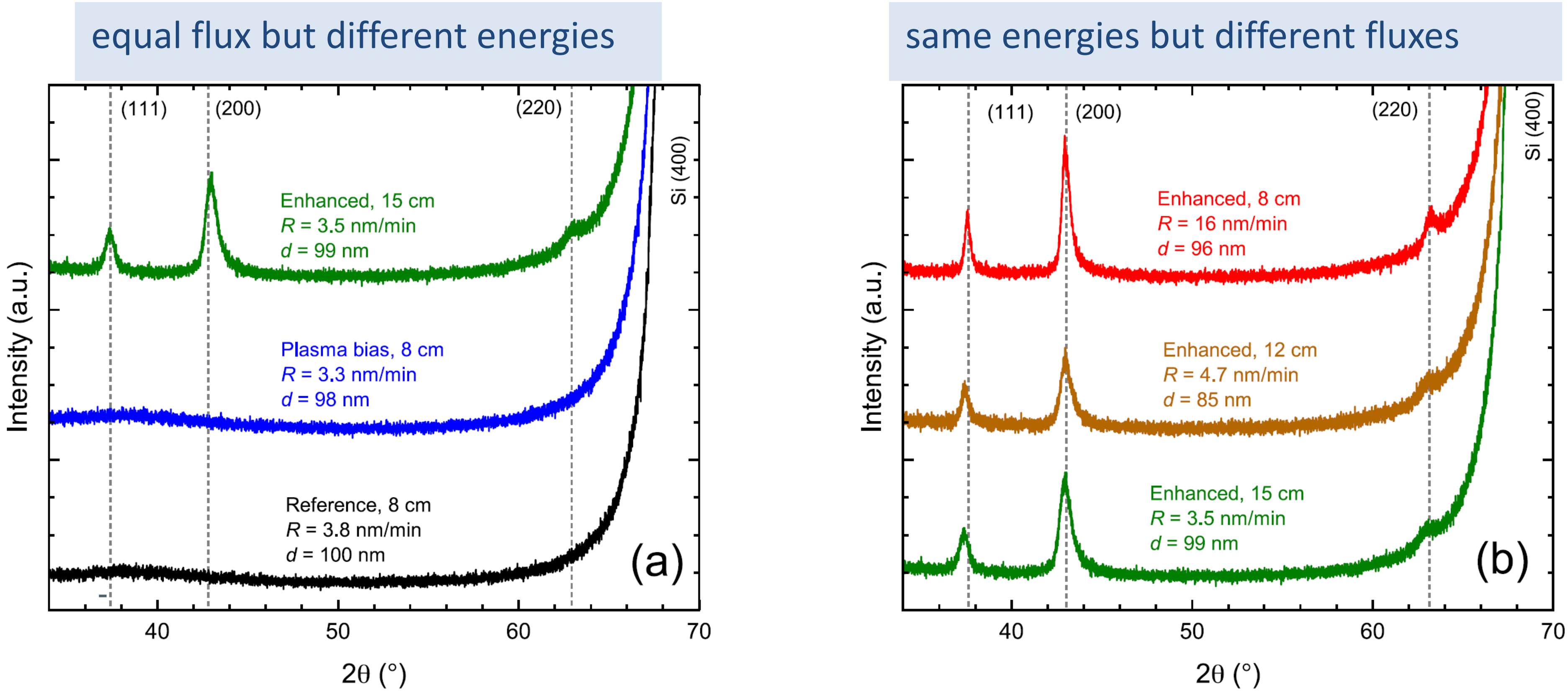
phased bias HiPIMS process

cathodic arc process



S. Karimi Aghda, *et al*., Acta Materialia 250 (2023) 118864.

Parsing the effects of energy and flux on microstructure



D. Kalanov, et al., Surf. Coat. Technol. 497, 131720 (2025).

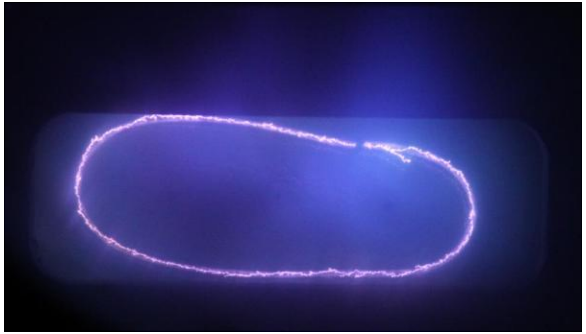
Cathodic Arc Deposition

- well established for hard, corrosion-resistant and decorative coatings since the 1980s
- usually batch coating systems
- steered arc technique, sometimes combined with sputtering systems

INVENTA by Oerlikon

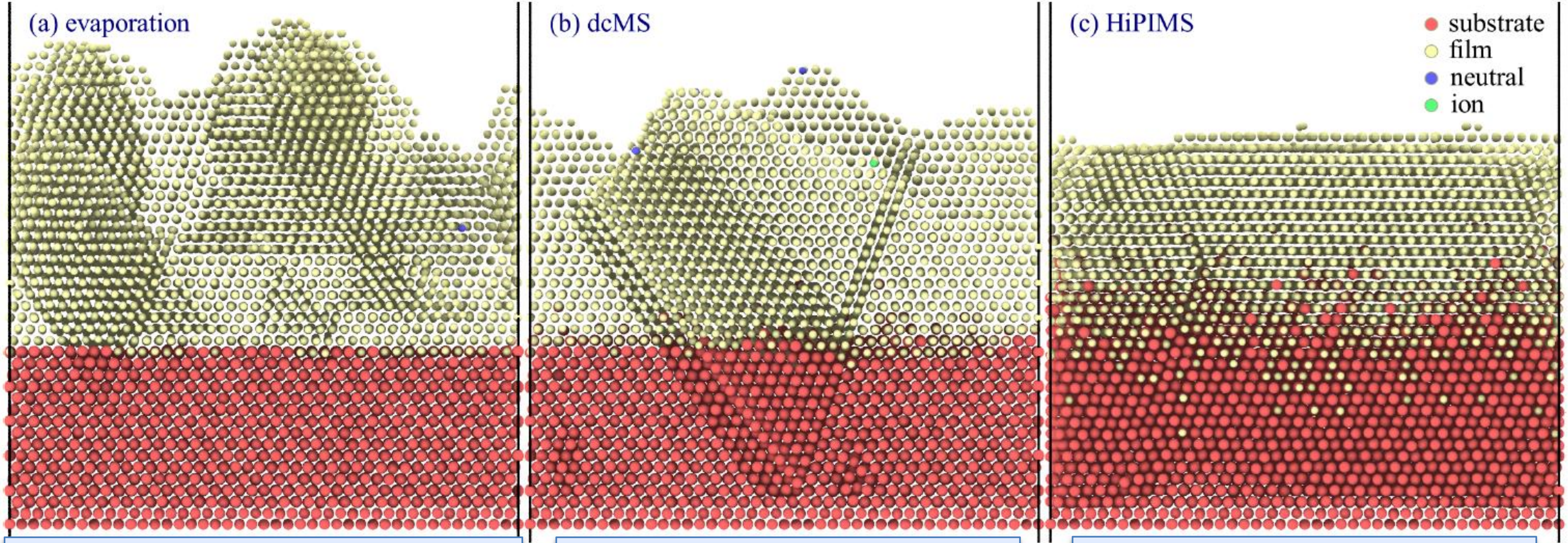
https://www.indiamart.com/

https://www.pvdamerica.com/



A. Anders, Cathodic Arcs: From Fractal Spots to Energetic Condensation, Springer, New York, 2008.

Interface mixing and film smoothing by low-emery ion-assist



MD Simulation, Assumption: only thermal energy of arriving atoms

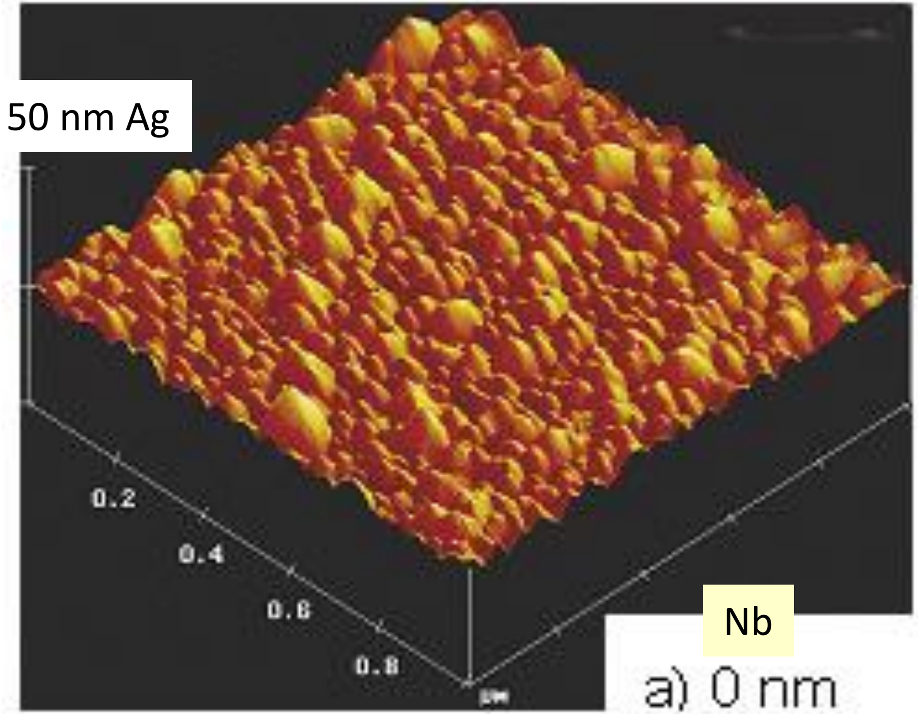
50% with energy randomly distributed between 0-100 eV

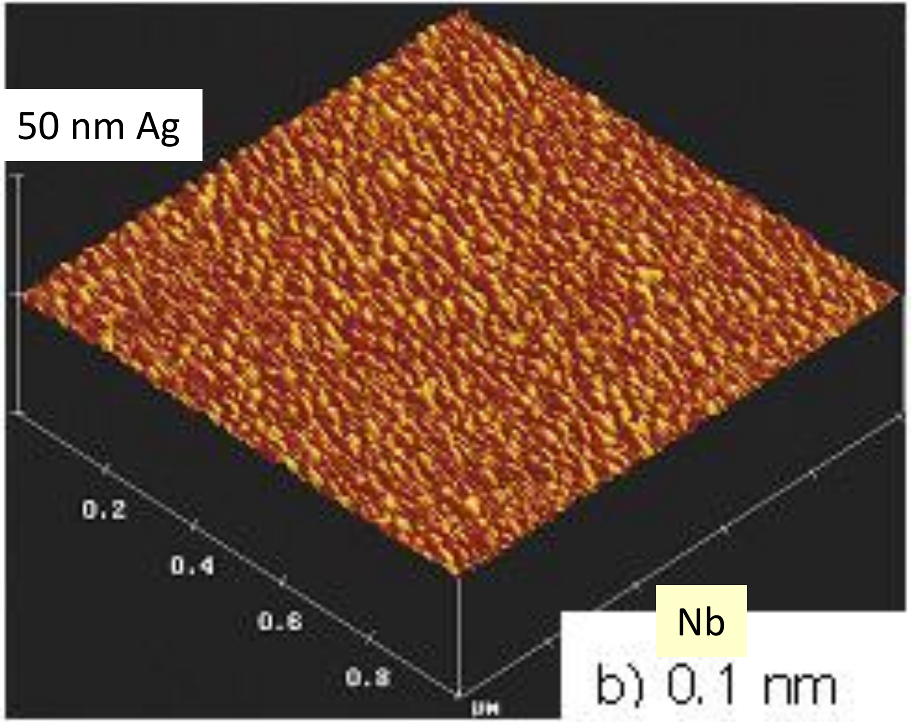
100% with energy randomly distributed between 0-100 eV

M. Kateb, et al., J. Vac. Sci. Technol. A 37 (2019) 031306.

Kinetic and thermodynamic effects: Sub-monolayer affects interface energy for subsequent film growth

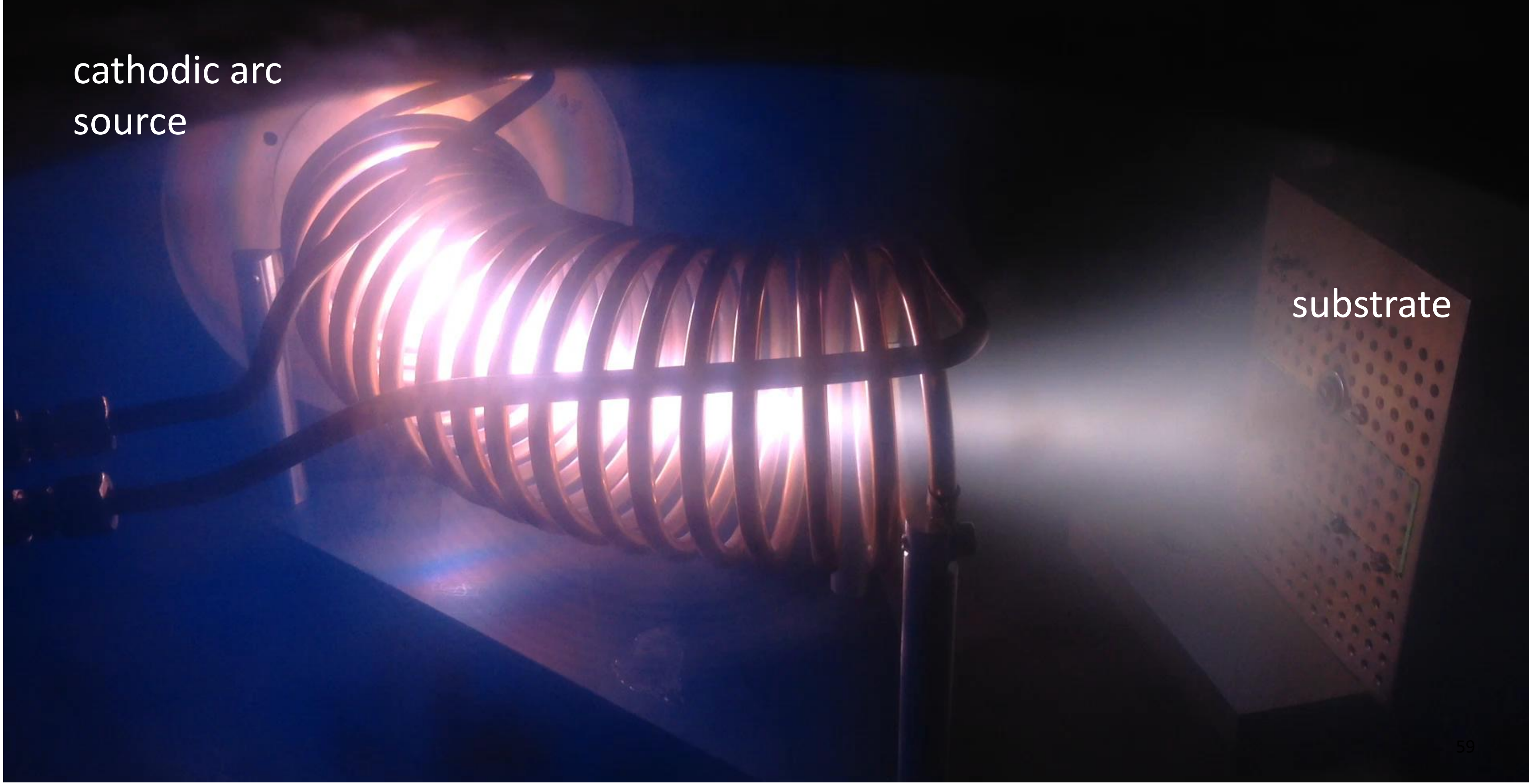
less than a monolayer of a transition metal (here Nb) changes surface energy, adatom mobility, coalescence, roughness, and optical properties





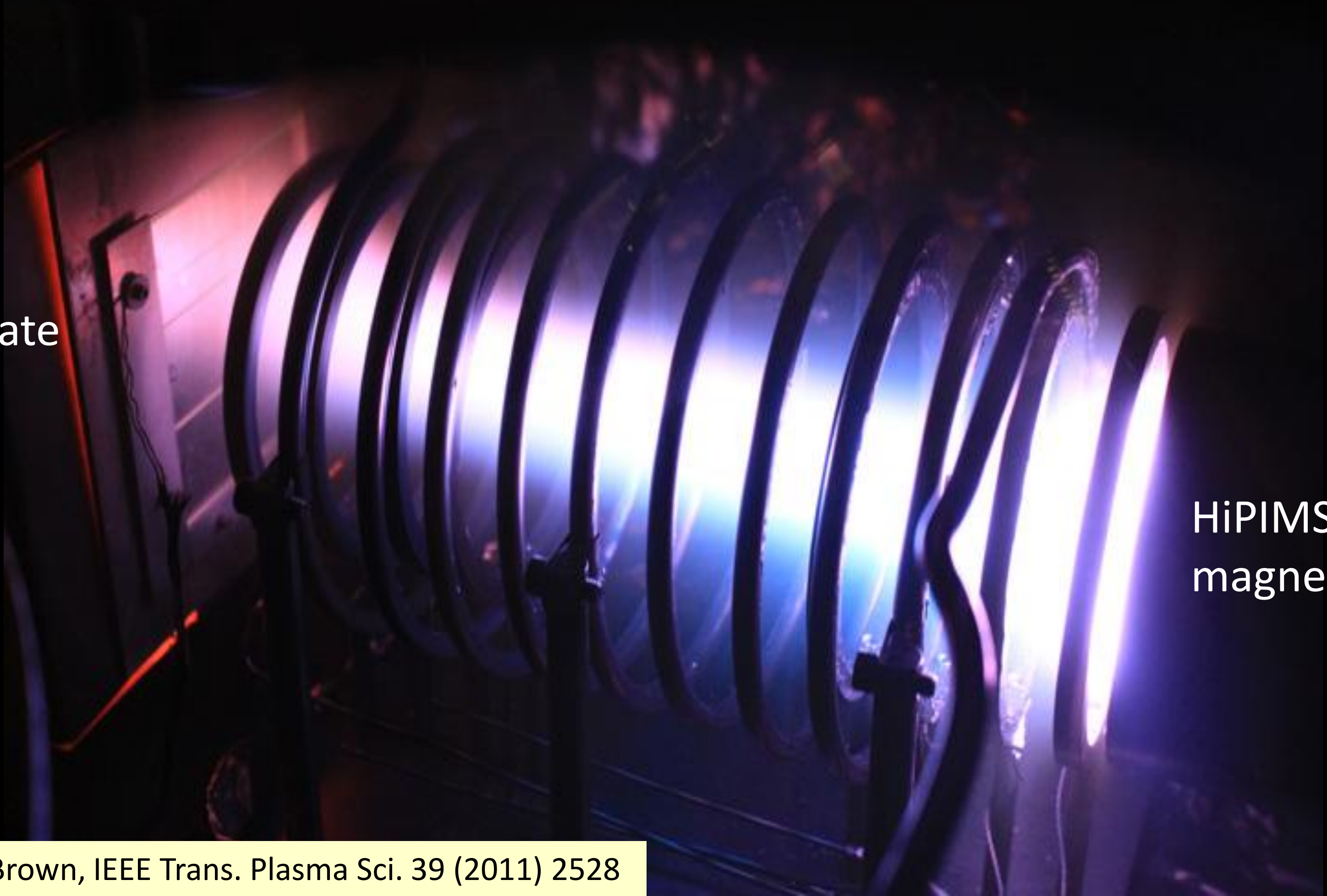
A. Anders, et al., Solid State Comm. 140 (2006) 225; K. Fukuda, et al., Thin Solid Films 516 (2008) 4546.

Filtered Cathodic Arc: here ZnO:Al deposition



HiPIMS plasma can be transported in a magnetic field

substrate



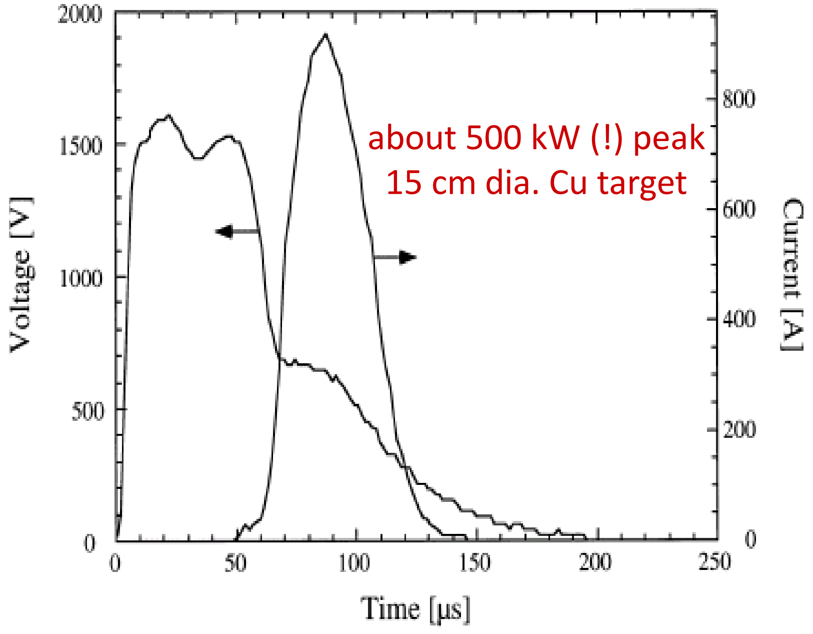
HiPIMS magnetron

A. Anders, J. Brown, IEEE Trans. Plasma Sci. 39 (2011) 2528

HiPIMS: A Form of "Ionized 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")

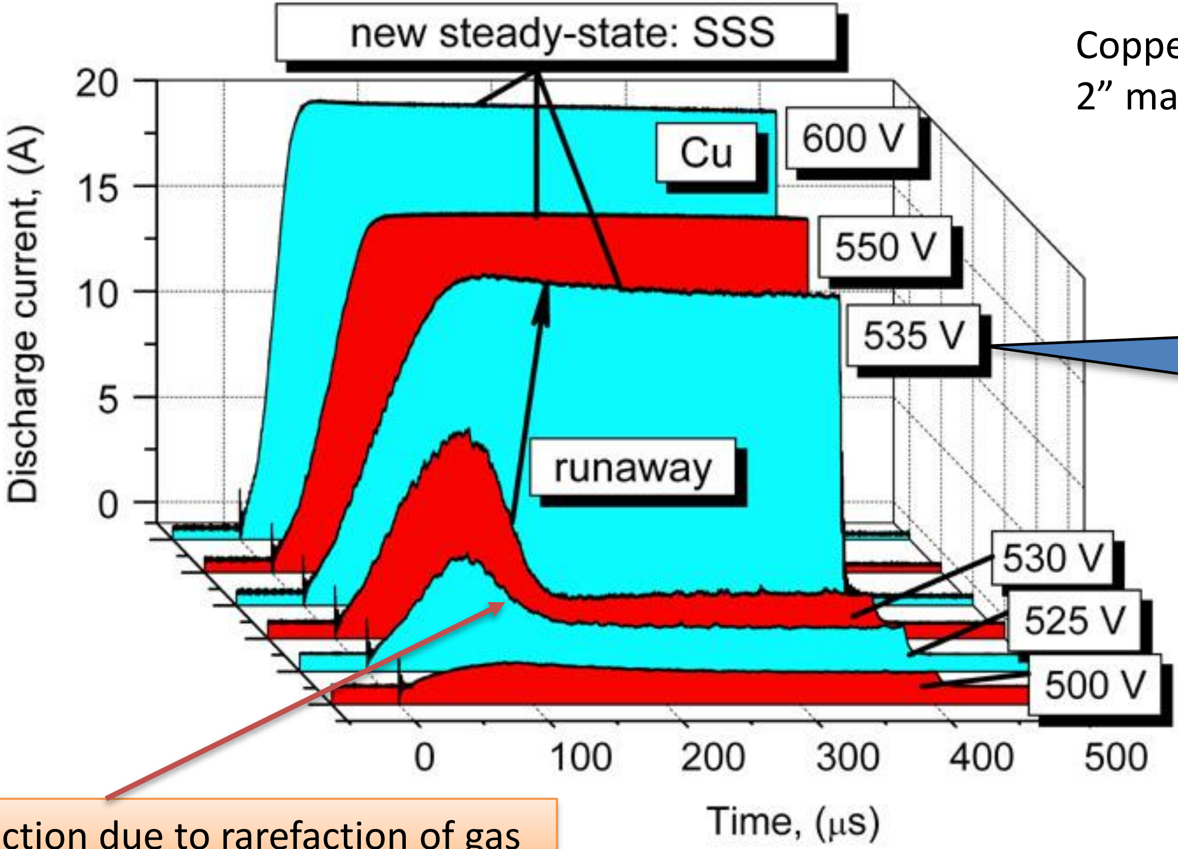
Physical Definition:
HiPIMS is pulsed sputtering where a very significant fraction of the sputtered atoms becomes ionized.
(implies that self-sputtering occurs, which may or may not be sustained by target ions)



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

HIPIMS with Copper target in Argon

Runaway of Self-Sputtering to a new, high level

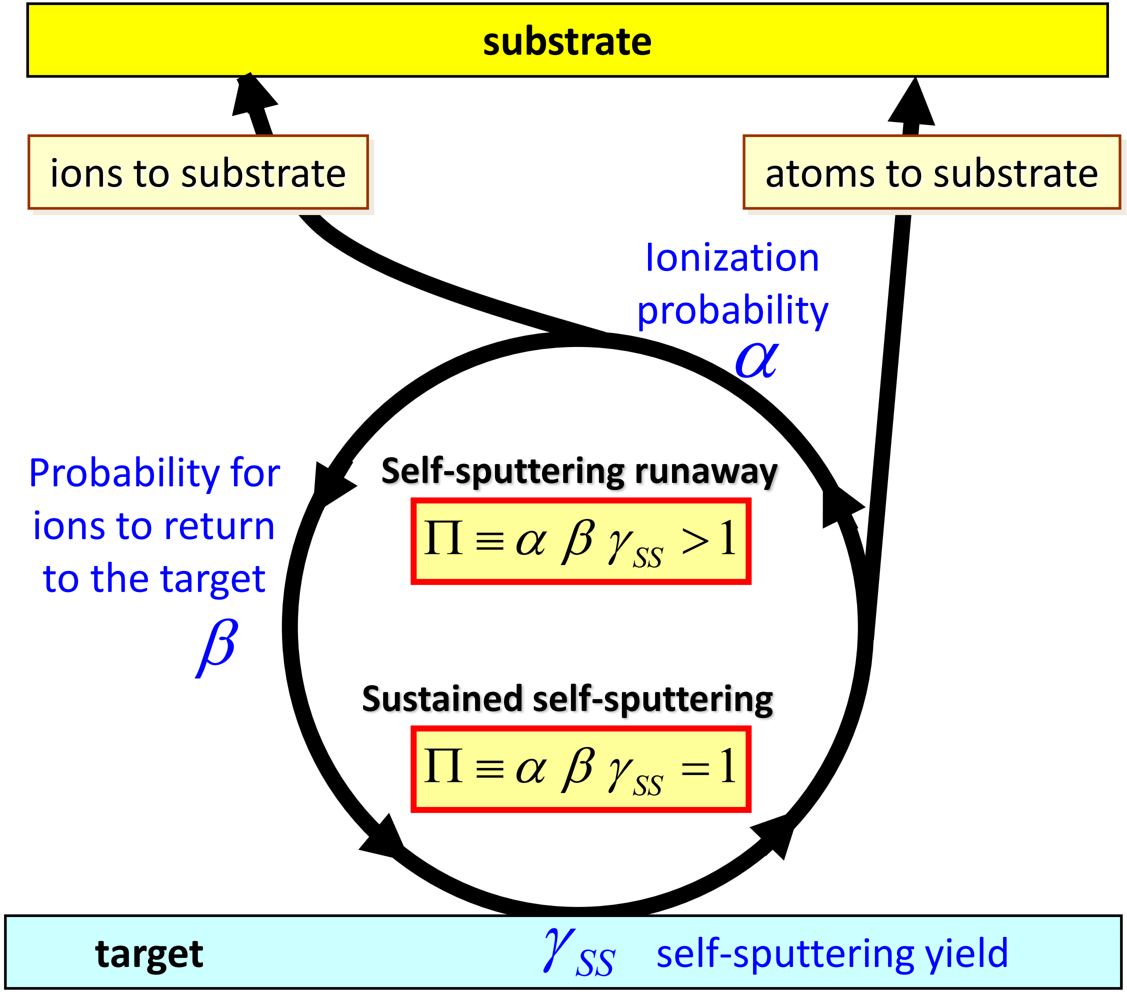


Copper target,
2” magnetron

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

reduction due to rarefaction of gas

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



N. Hosokawa et al., Proc. 8th Vac. Con., (1980) 11;

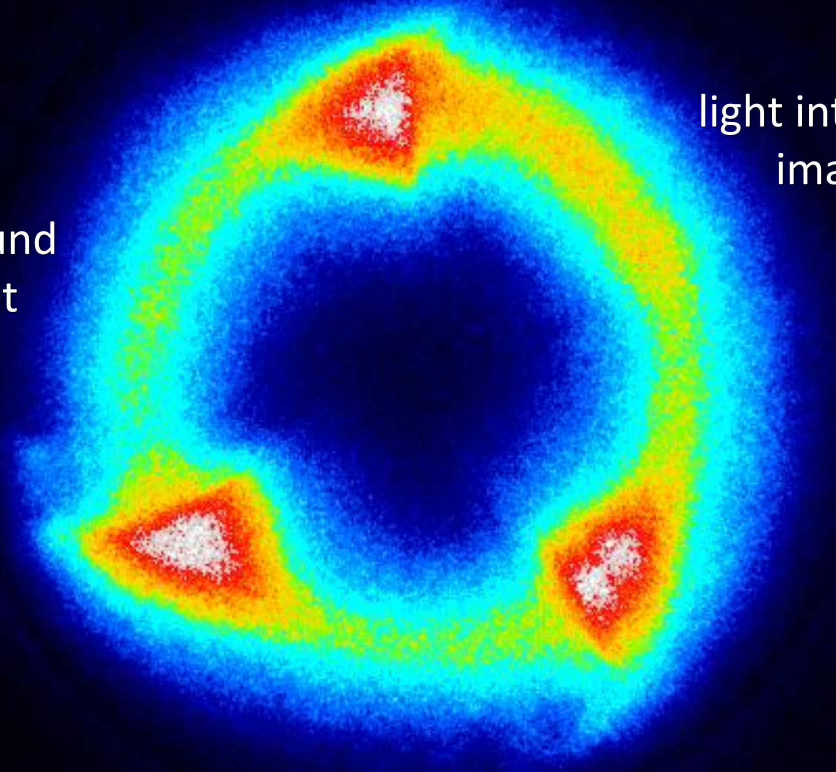
A. Anders, Appl. Phys. Lett. **92** (2008) 201501

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

Magnetron Sputtering: Ionization of the sputtered atoms occurs in moving ionization zones or “spokes”

light intensity in false color, image taken in 5 ns

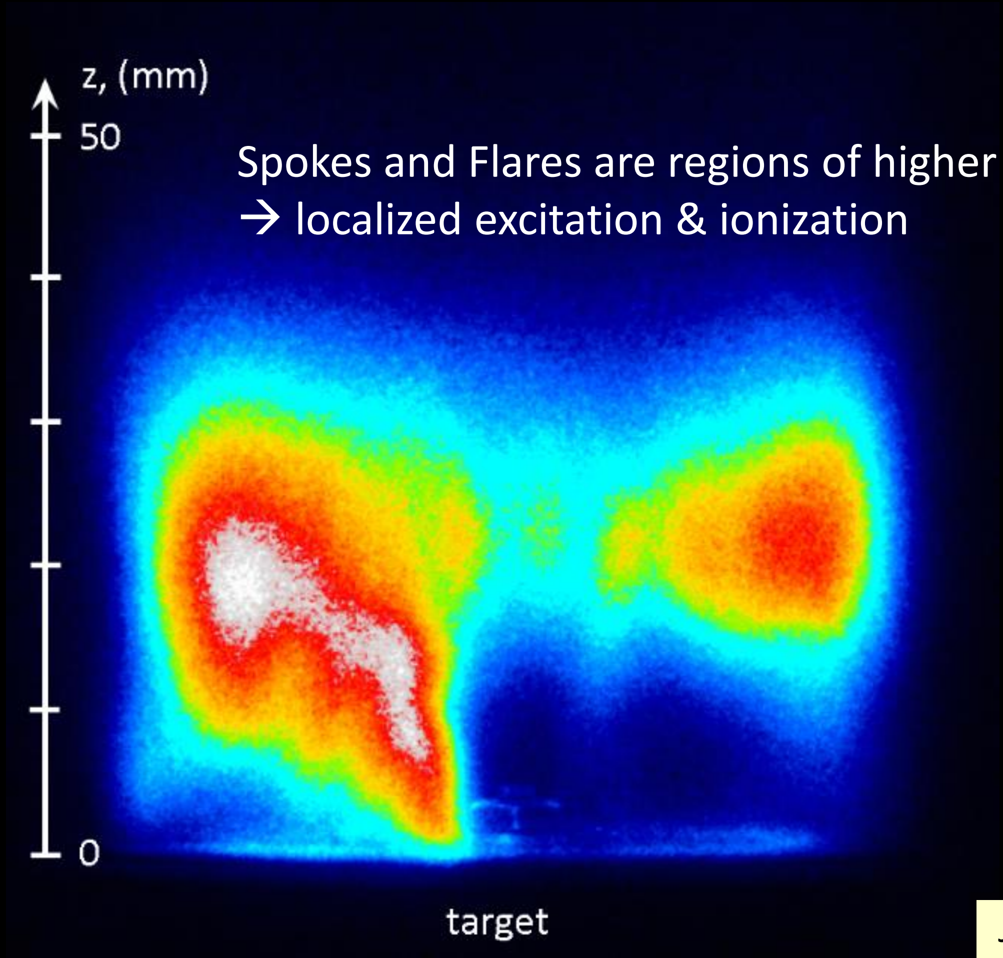
Here: HiPIMS with a small round magnetron, 75 mm Al target



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

Spokes and Flares: Transport of Plasma to the Substrate

Spokes and Flares are regions of higher potential → local electron heating
→ localized excitation & ionization



Spectroscopic imaging, side view in the light of Ar II 436 nm; 7.5 cm Al target, Ar, current at the time of this image was 100 A

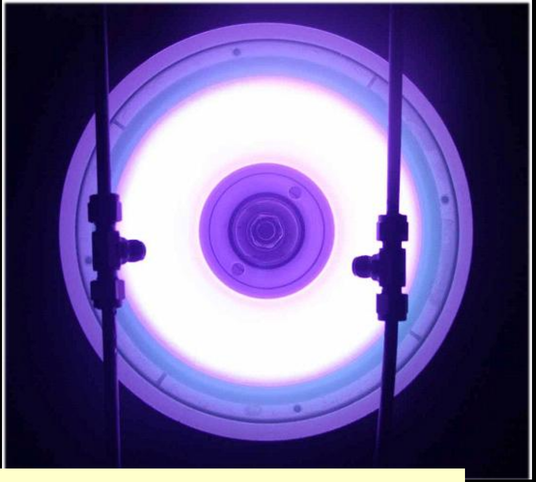
J. Andersson, *et al.*, Appl. Phys. Lett. **103** (2013) 054104.

HiPIMS: Advantages and Disadvantages

- film microstructure can be tune via energies of ions (biasing)
- many new parameters for process tuning
- deposition rate, normalized by power, is reduced, primarily due to return of ions
- unwanted arcing is prevalent, requires sophisticated arc management
- power supplies expensive

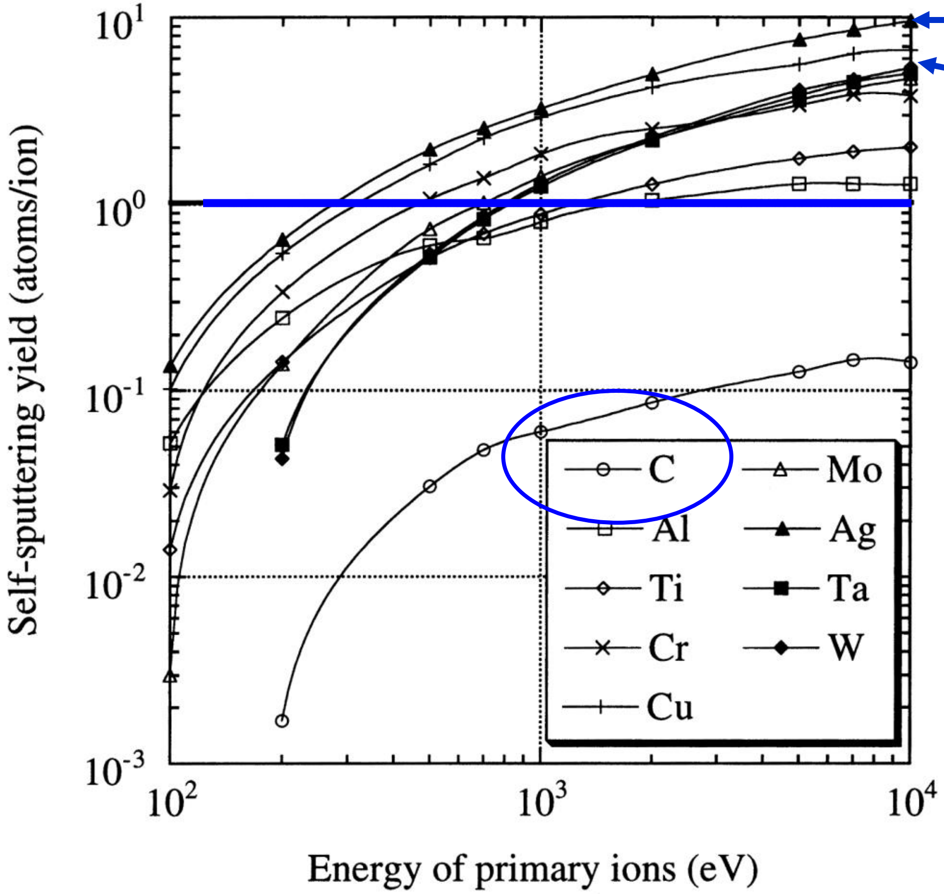
arcing

less after conditioning



Courtesy of Bill Sproul, SVC Ann. Techn. Conf., Dallas, 2004

Self-Sputter Yields



Ag

Cu

$\gamma > 1$

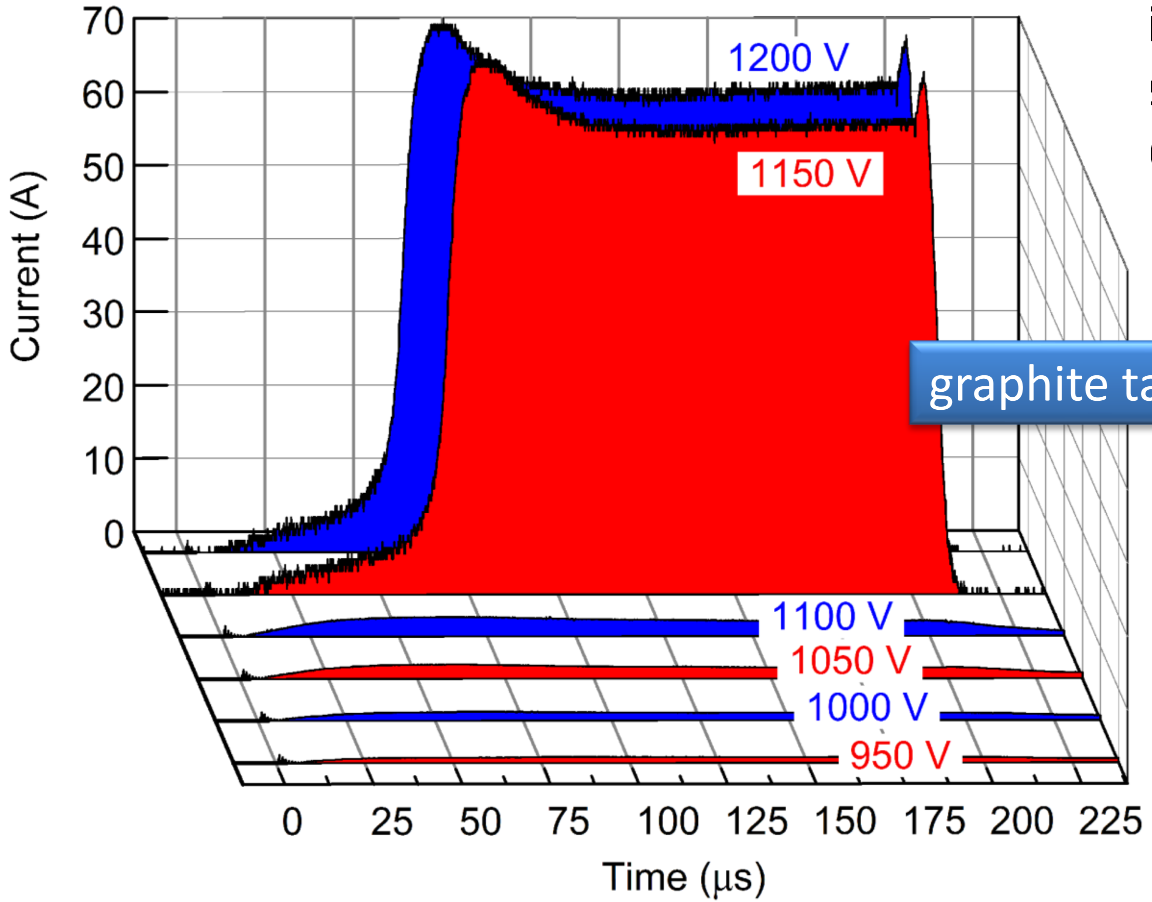
is a necessary but not sufficient condition for sustained self-sputtering

Note: $\gamma_{carbon} < 1$

carbon cannot go in sustained self-sputtering

(originally for research on Pseudosparks)
A. Anders, et al., IEEE Trans. Plasma Sci. **23** (1995) 275

Runaway to high current can be observed for *all* target materials

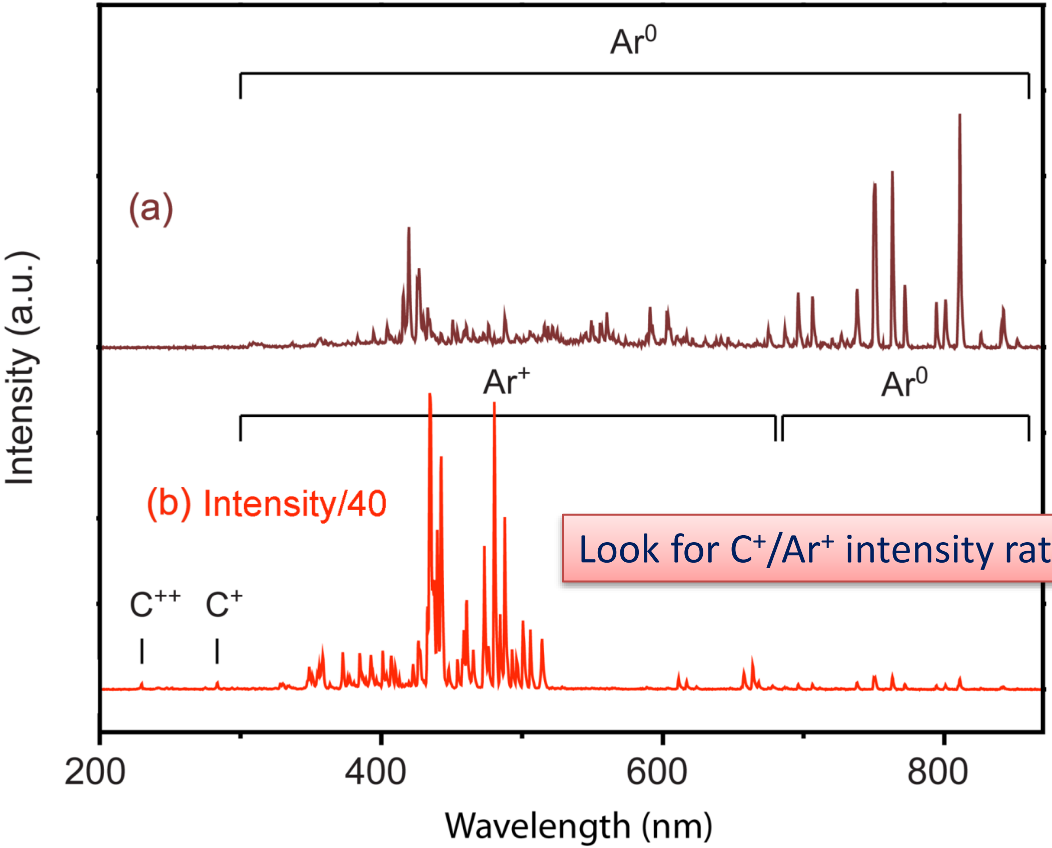


including those with extremely small self-sputtering yield, which initially was surprising

graphite target in argon

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

Evidence for “Gas-Recycling”



Look for C$^+$/Ar$^+$ intensity ratio

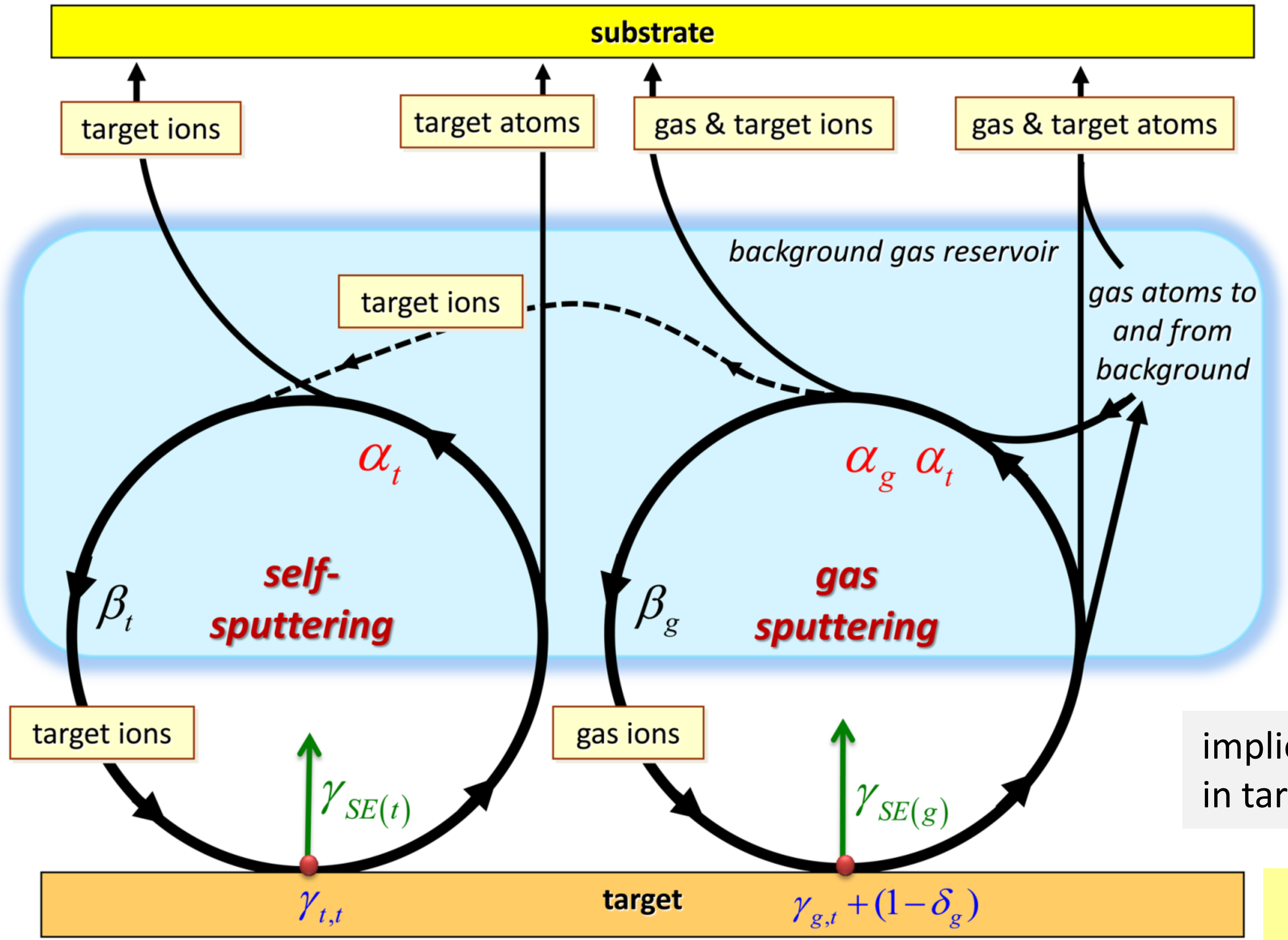
after runaway to high power, argon emission remains dominant

Below runaway, low power

above runaway, high power

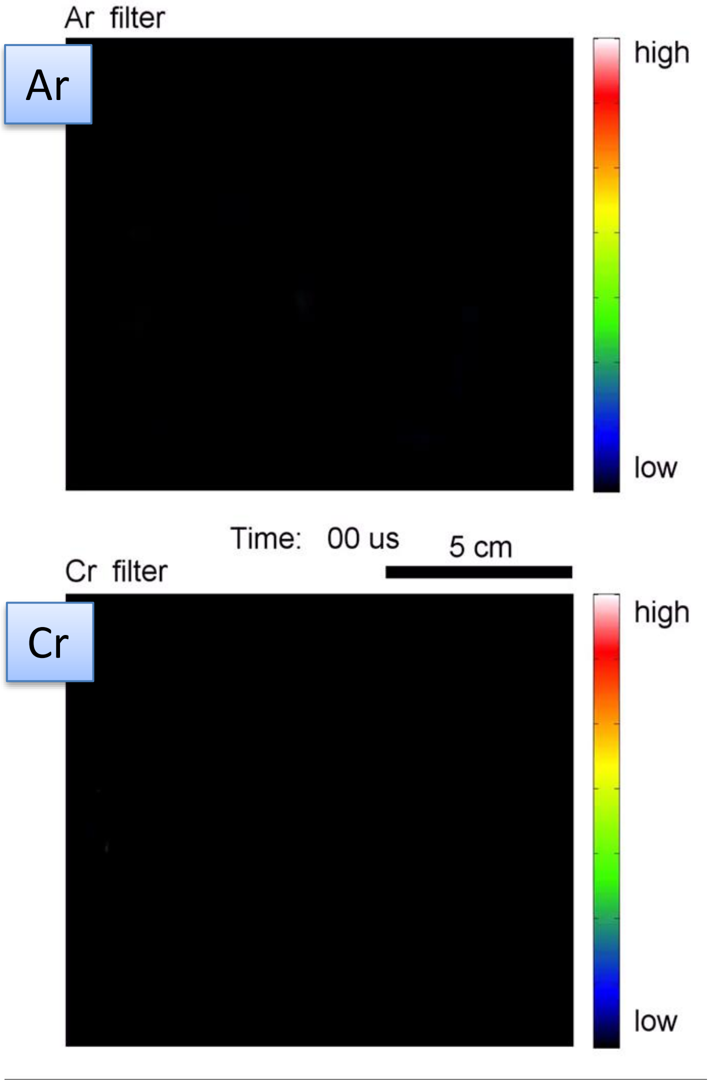
A. Anders, *et al.*, J. Phys D: Appl. Phys. **45** (2012) 012003.

Generalized Flux Model for HiPIMS includes Gas-Recycling



implies presence of gas in target surface region

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



HiPIMS: from gas-dominated to metal-dominated plasma

Cr target, 4 Pa Ar, apply 2000 V

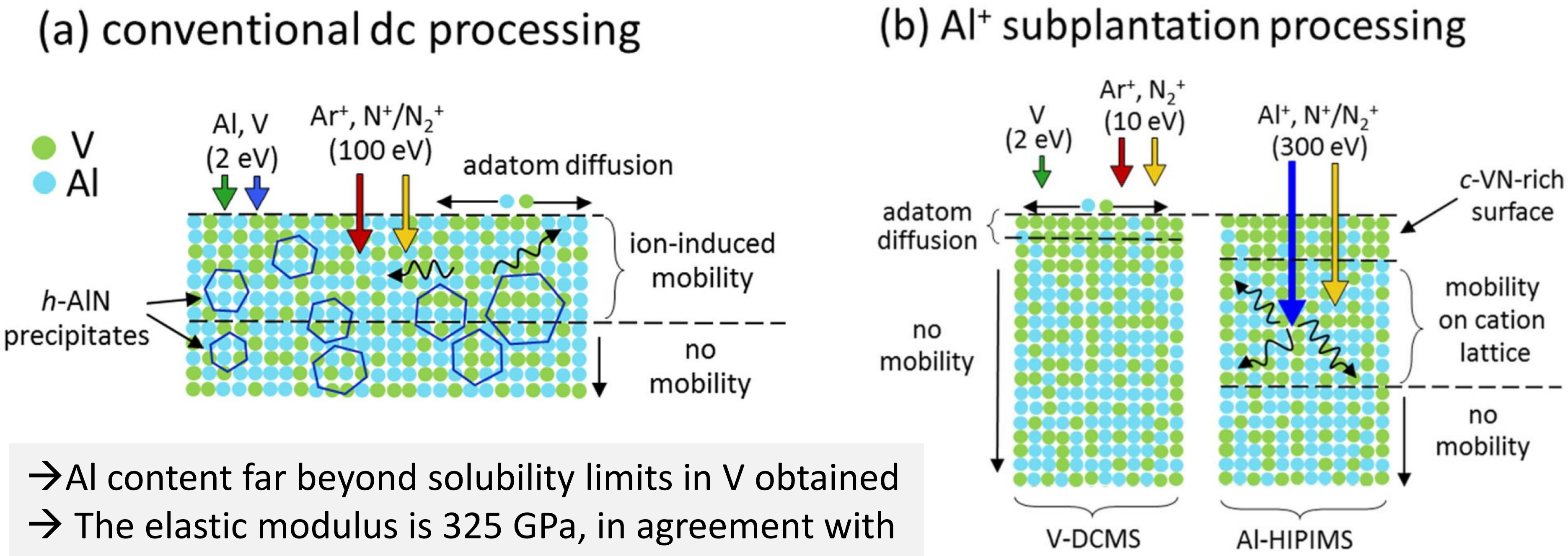
The composition of the plasma changes during each pulse: from gas-dominated to metal-dominated.

time-dependent plasma composition suggests using time-dependent bias to select the kind of ion-based modification

Video clip courtesy of Matej Hala; spokes not yet observed since time resolution still insufficient.

M. Hála, et al. , IEEE Trans. Plasma Sci. 38 (2010) 3035.

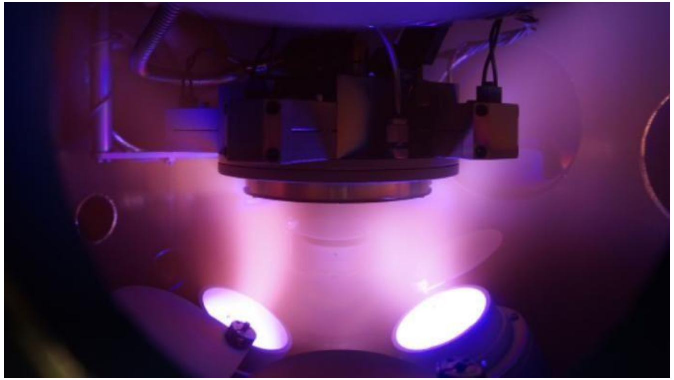
From species-selective bias to phased-bias deposition

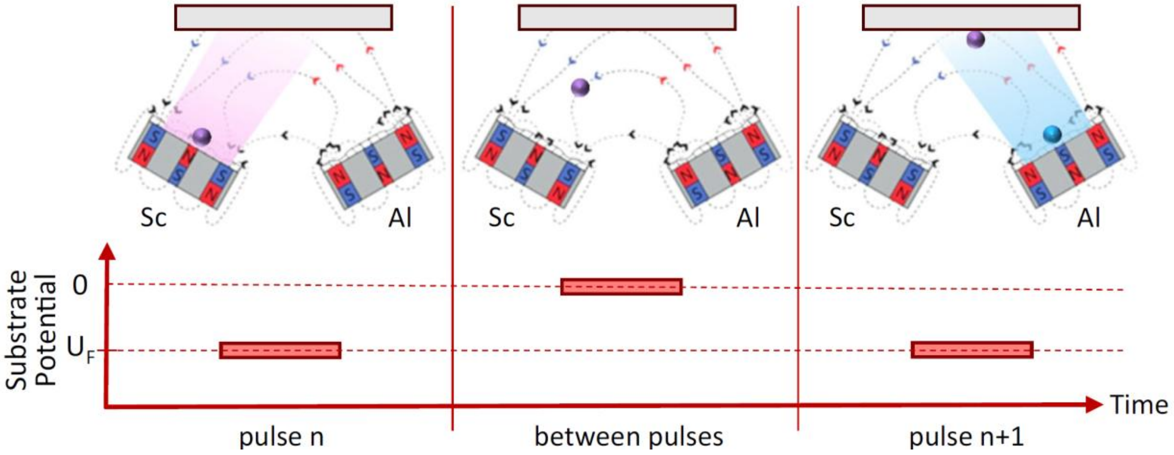


→Al content far beyond solubility limits in V obtained
→ The elastic modulus is 325 GPa, in agreement with DFT calculations, 50% higher than for films grown by dc magnetron sputtering

G. Greczynski, *et al.*, J. Appl. Phys. 121, 171907 (2017).

“Clean” is a wider sense: minimize including of noble gases





- HiPIMS-timing to avoid argon inclusions, accelerating only the desired ions onto the substrate by applying voltage right after most argon ions have passed and using magnetron pulses to speed up electrons
- → deposition on insulating materials incl piezoelectric thin films

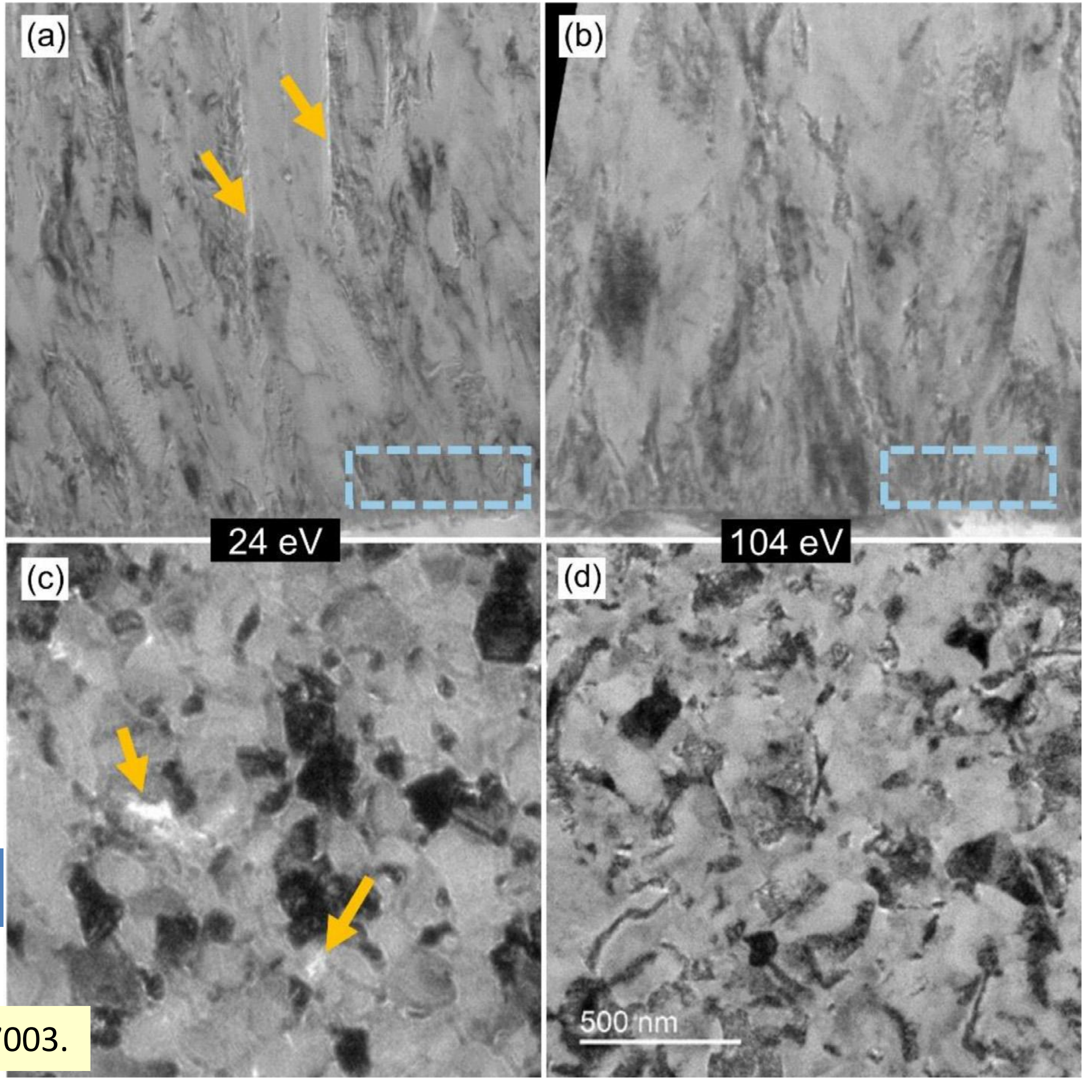
J. Patidar, Nature Communications 16 (2025) 4719.

Enhancing kinetic energy via biasing the substrate:

Here: (V,Al)N, this time by HiPIMS

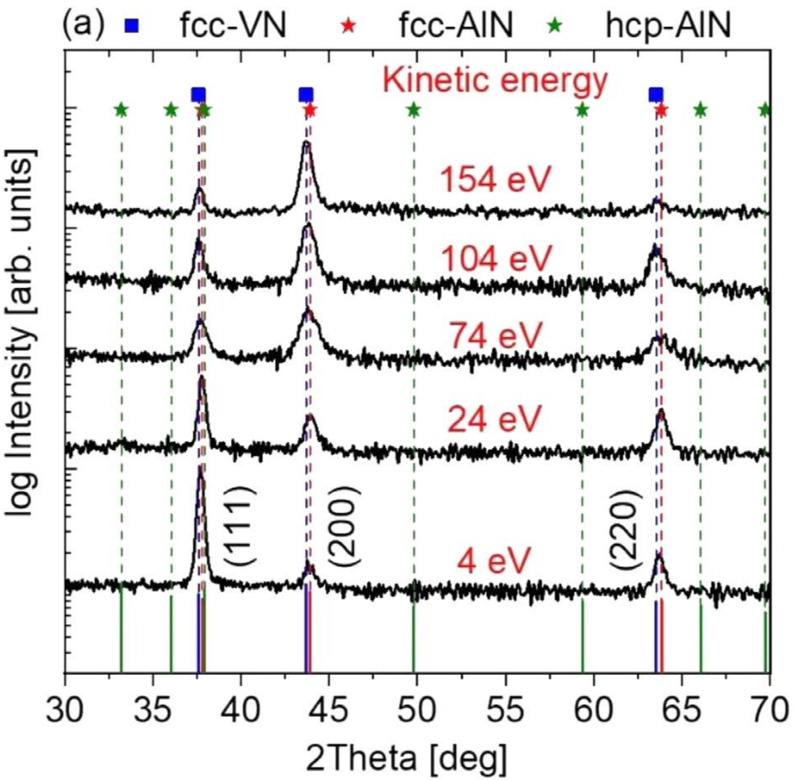
at relative low energy we detect pores and gaps between columns

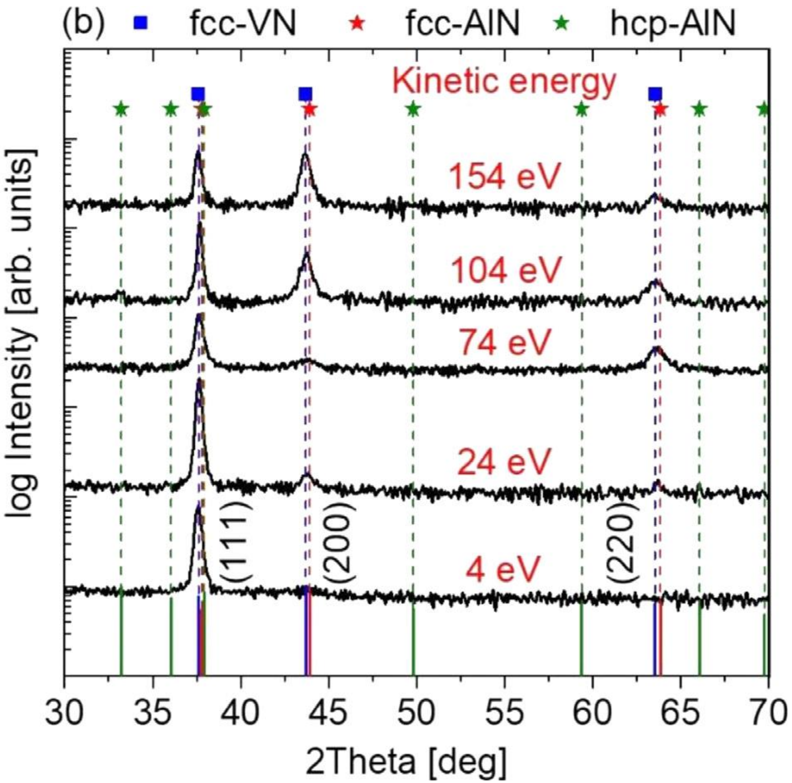
phased bias HiPIMS process



S. Karimi Aghda, *et al*., Acta Materialia 214 (2021) 117003.

Effect of kinetic energy via biasing the substrate (HiPIMS)





phased-bias HiPIMS process

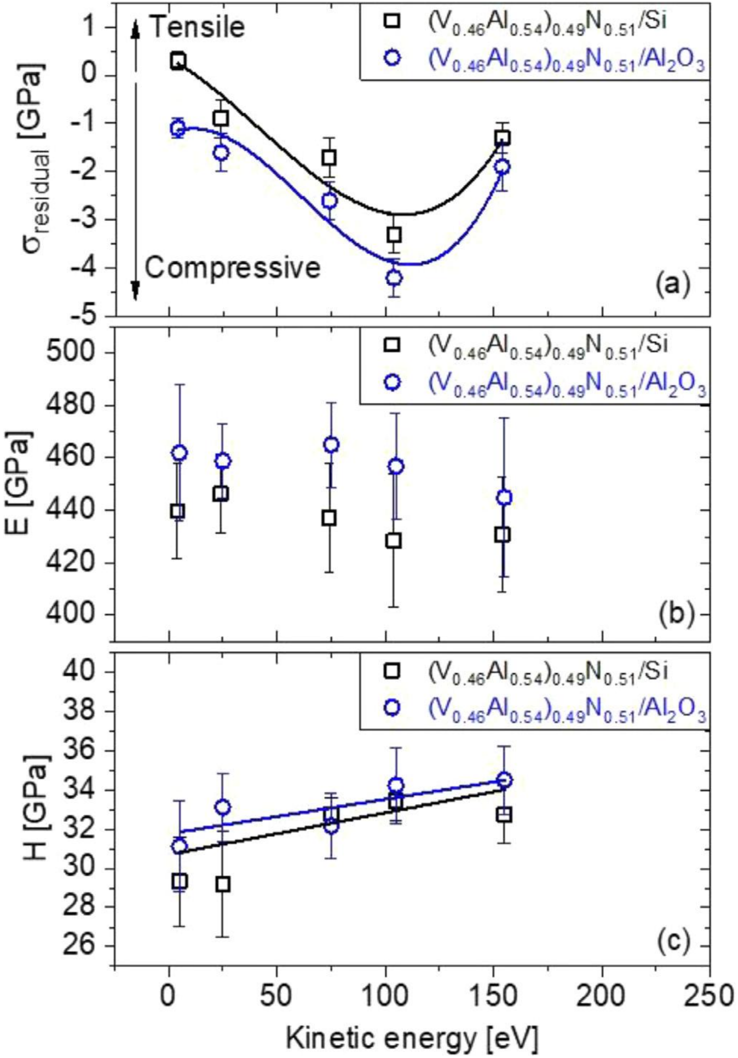
S. Karimi Aghda, *et al.*, Acta Materialia 214 (2021) 117003.

Structure evolution and elastic properties of (V,Al)N thin films by HiPIMS with bias

stress

elastic modulus

nano-indentation hardness



S. Karimi Aghda, *et al.,* Acta Materialia, 214 (2021) 117003.

Bipolar HiPIMS

Several ideas and goals when using bipolar HiPIMS:

1. “release” ions produced in negative HiPIMS pulse by switching off the electric field that “returns” ions
2. provide controlled enhanced ion energy to the substrate, affecting film microstructure
3. reduce arcing

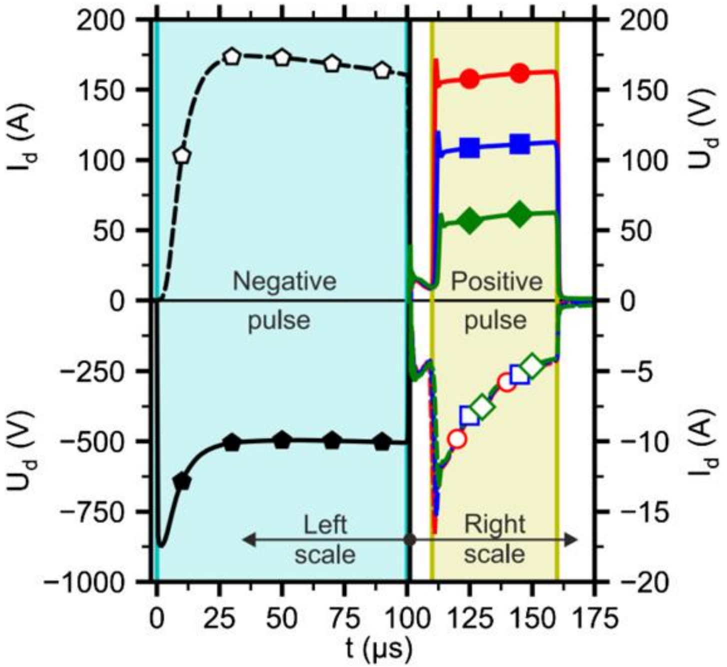
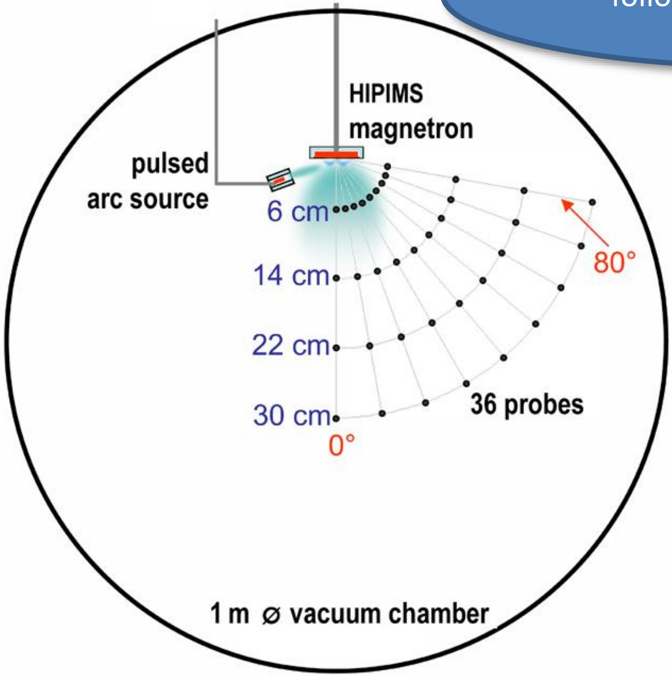


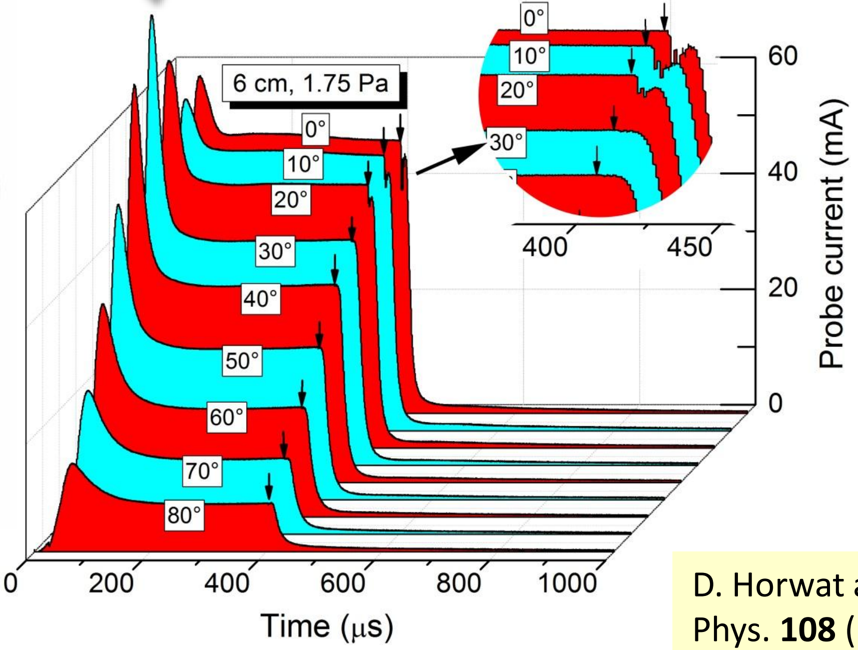
Figure 3. The waveforms of the magnetron voltage, U_{d}, (filled symbols) and the discharge current, I_{d}, (unfilled symbols) during NP and PP for the positive voltage pulse amplitudes of $U_{+} = 50$ (diamond symbols), 100 (square symbols) and 150 V (circle symbols) with $t_{\mathrm{D}} = 10\,\mu\mathrm{s}$. The vertical black line separates the validity of the left and right scales.

A.D. Pajdarová, et al., Plasma Sources Sci. Technol. 29 (2020) 085016.

Strong compression and rarefaction in HIPIMS: Collisions affecting transport of atoms and ions

peak due to strong compression followed by rarefaction of process gas



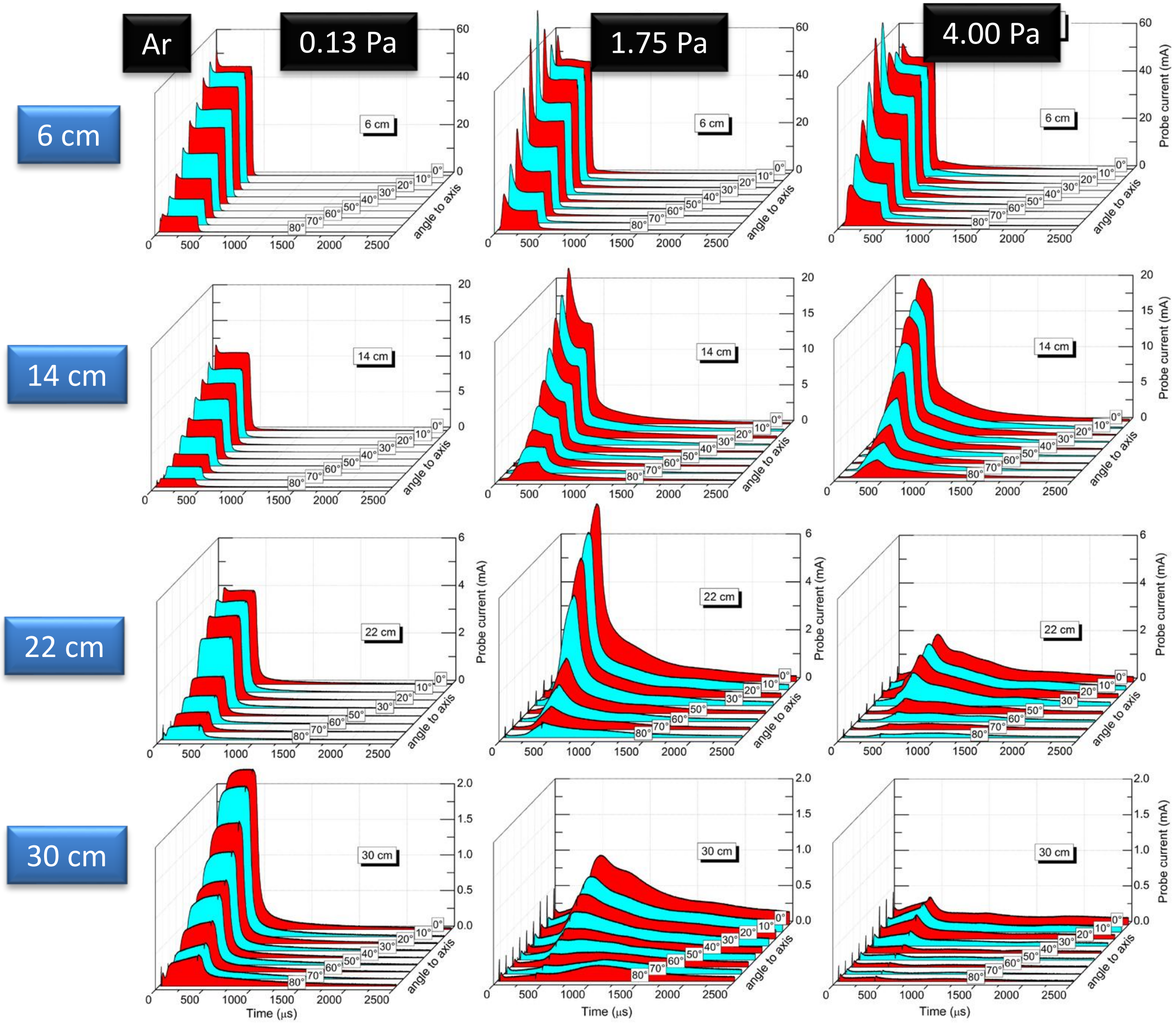


Cu, 5 cm diam. target, 1000 V, 400 µs, 34 A in stead-state

D. Horwat and A. Anders, J. Appl. Phys. **108** (2010) 123306.

Ion collector measurements of 400 μs HiPIMS pulses

(Cu in Ar)

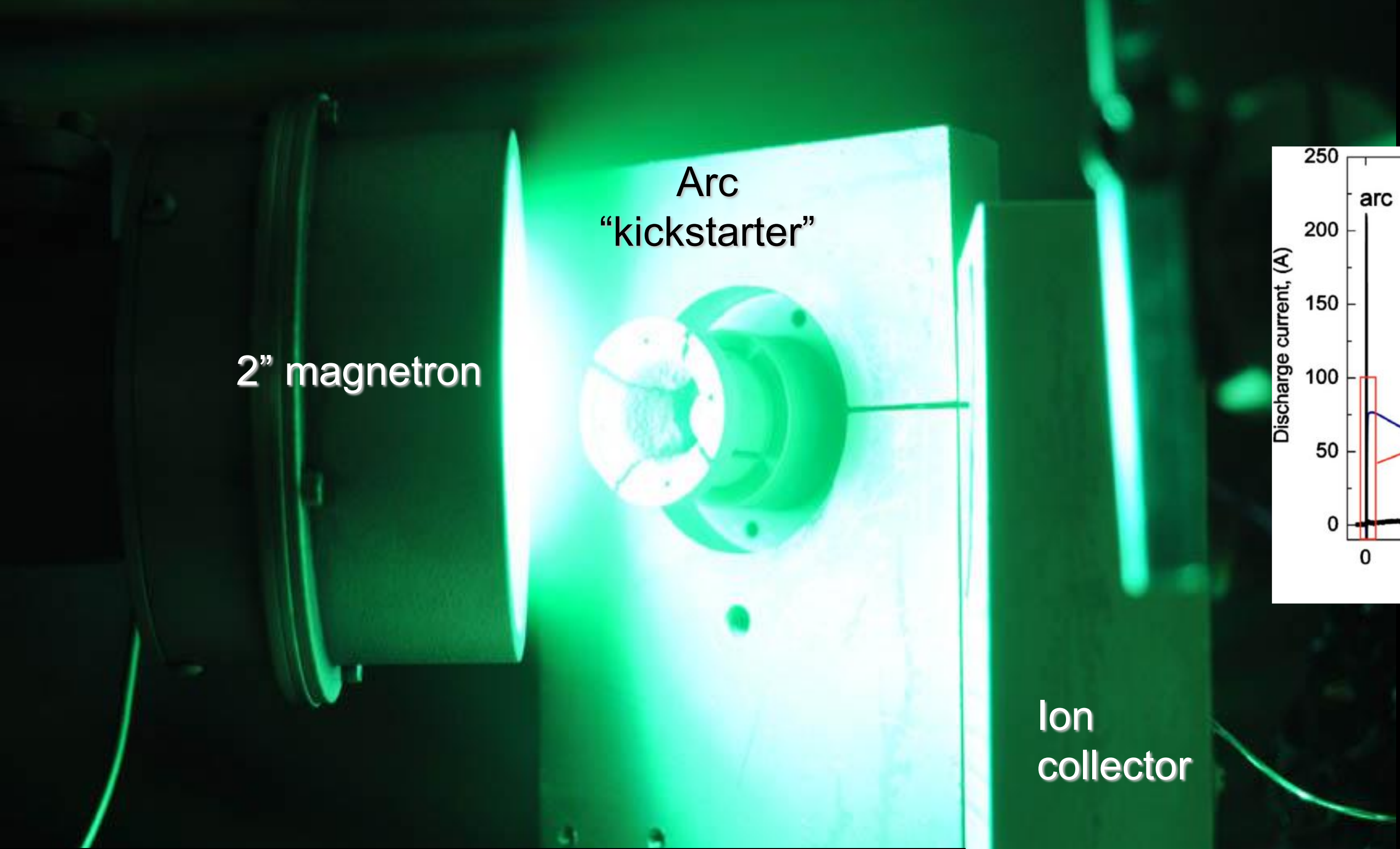


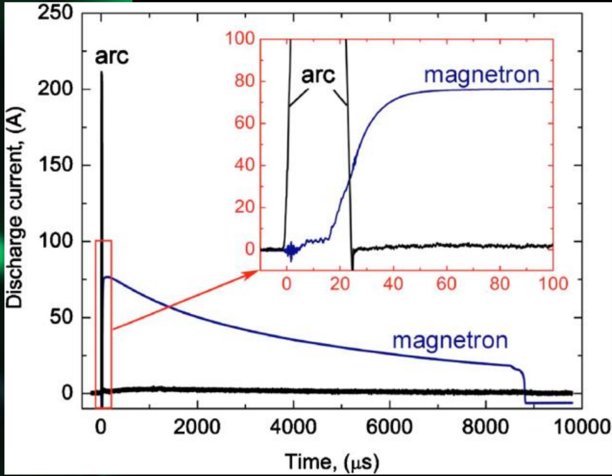
at low pressure, little compression and rarefaction

at large distances, significant differences in ion speed and plasma arrival

D. Horwat and A. Anders, J. Appl. Phys. **108** (2010) 123306.

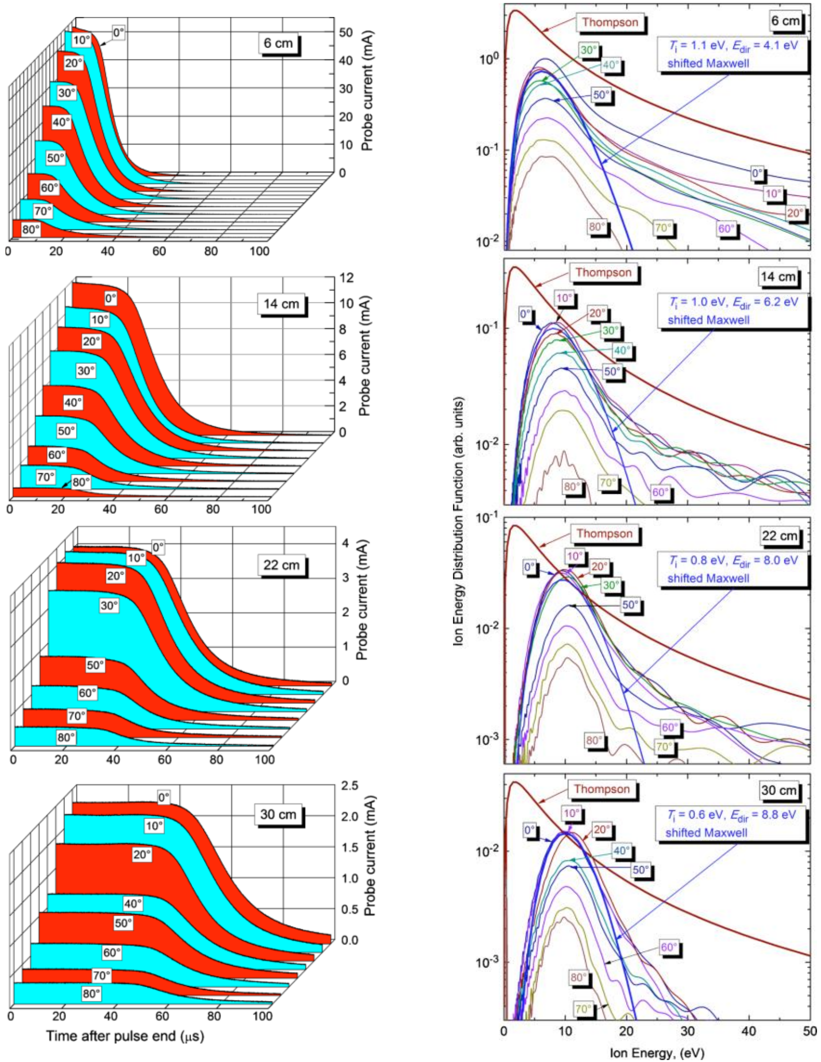
HIPIMS without any gas: Pure Self-Sputtering in Vacuum





J. Andersson and A. Anders, Appl. Phys. Lett. **92** (2008) 221503
J. Andersson and A. Anders, Phys. Rev. Lett. **102** (2009) 045003

Ion cooling but acceleration in gasless HiPIMS

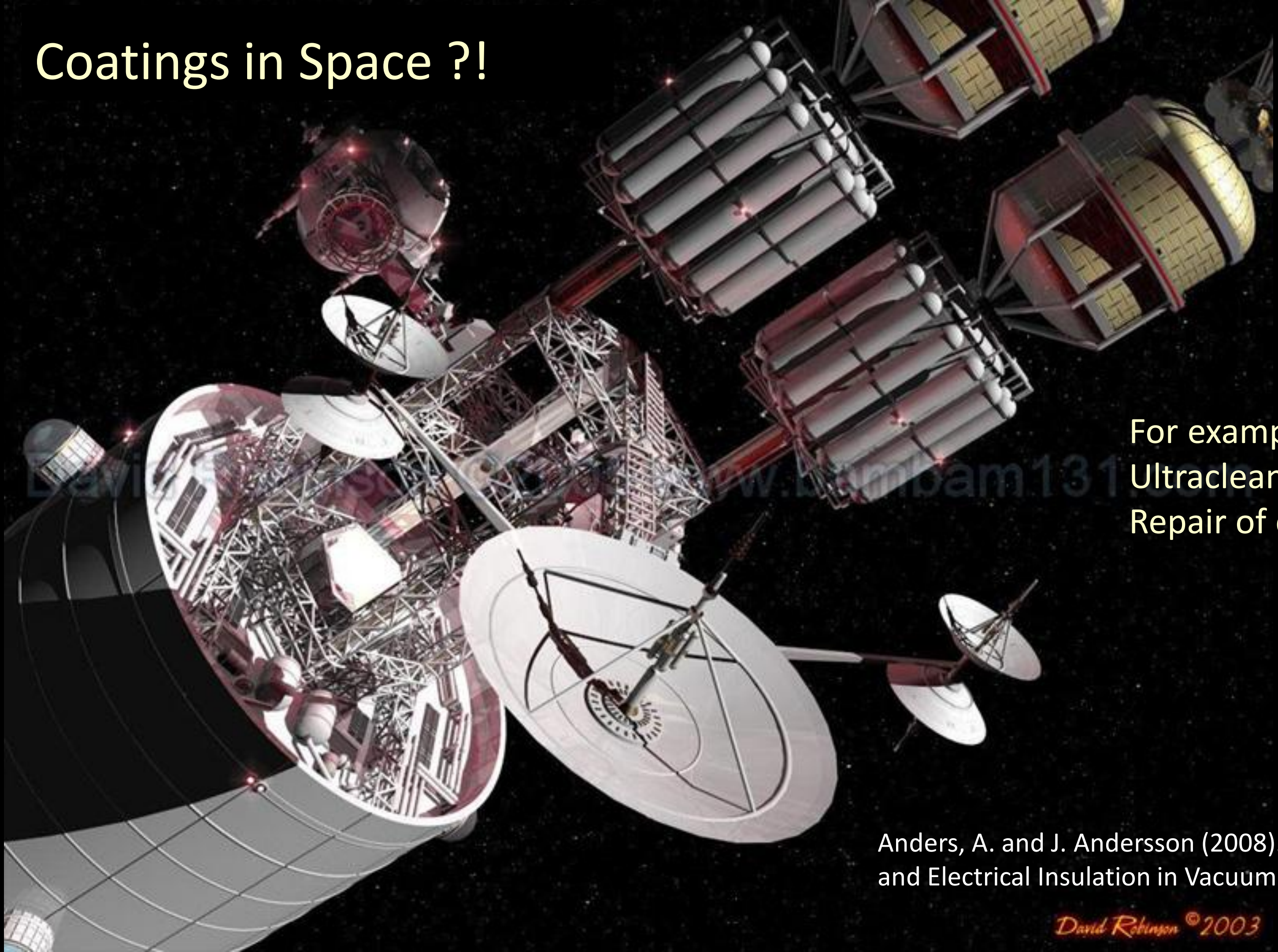


As the HiPIMS plasma expands from the target, no collisions with background gas but acceleration driven by pressure gradient and/or field of a charge double layer

→ Increase of ion energy even before reaching the sheath of the substrate

D. Horwat and A. Anders, Appl. Phys. Lett. 97 (2010) 221501.

Coatings in Space ?!

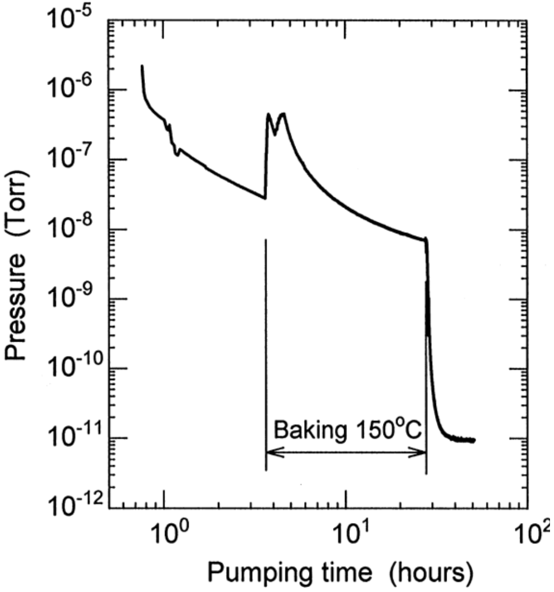


For example:
Ultraclean coatings!
Repair of coating on reflectors

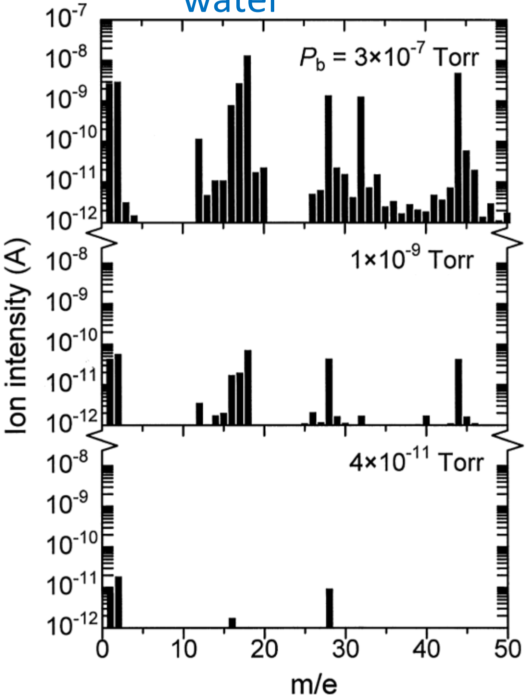
Anders, A. and J. Andersson (2008). XXIIIrd Int. Symp. Discharges and Electrical Insulation in Vacuum. Bucharest, Romania**: 561–566.**

Ultraclean sputtering: Pathway to desired materials

XHV sputtering system for magnetic thin films

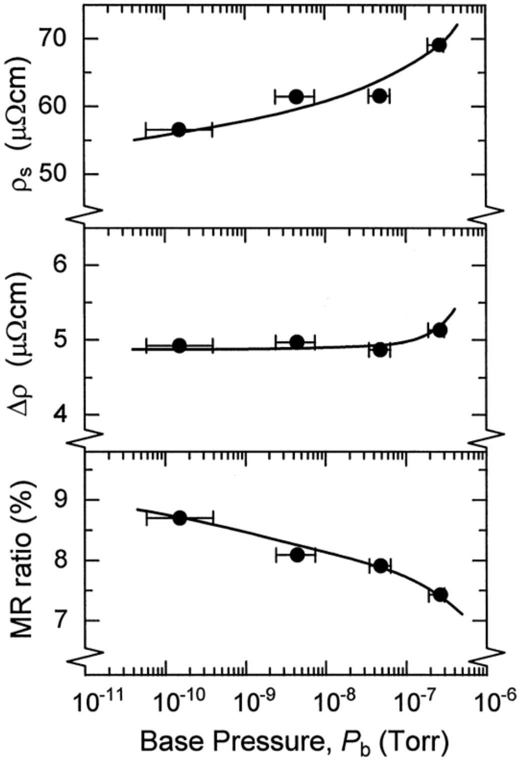


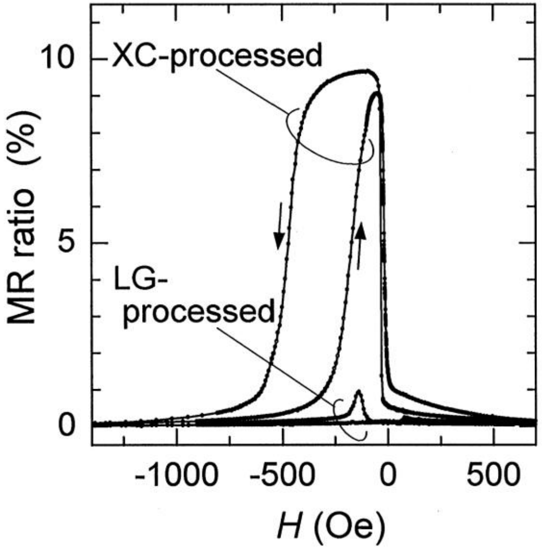
water



M. Takahashi, et al.,
Vacuum 59 (2000) 814.

Ultraclean sputtering: Pathway to desired material properties like a high magnetoresistance (MR) ratio





XC – extremely clean

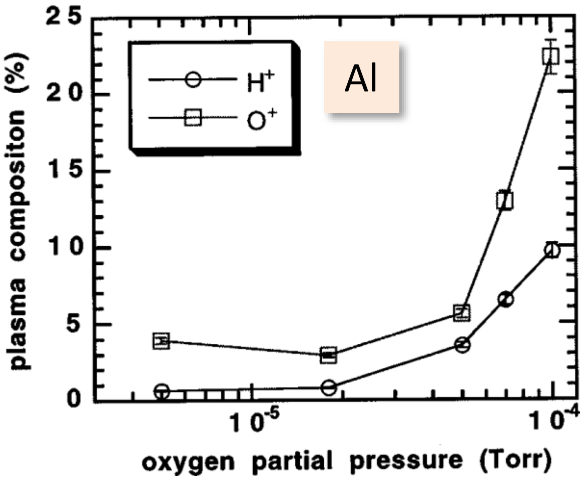
LG – lower grade vacuum

Magnetoresistance ratio of ultra-thin spin valve: substrate/Ta 35 Å /Ni-Fe 20 Å /Co 5 Å /Cu 18 Å /Co 20 Å /$Mn_{0.59}Ir_{0.41}$ 50 Å /Ta 50 Å

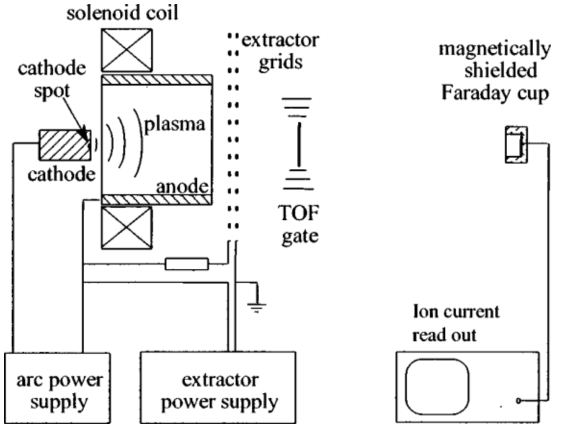
M. Takahashi, et al., Vacuum 59 (2000) 814.

Magnetoresistance (MR) is the change in the electrical resistance of a material when an external magnetic field is applied

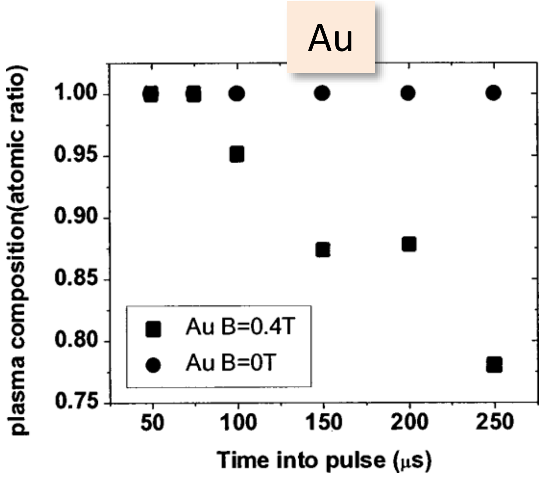
Residual gas es particularly important (disturbing) in pulsed systems: “The pause makes the music!”



pulsed arc,
no mag. field



TOF spectrometer



pulsed arc,
with pulsed mag. field

J.M. Schneider, et al. , Appl. Phys. Lett. 74 (1999) 200.

J. M. Schneider, et al., Appl. Phys. Lett. 76 (2000) 1531.

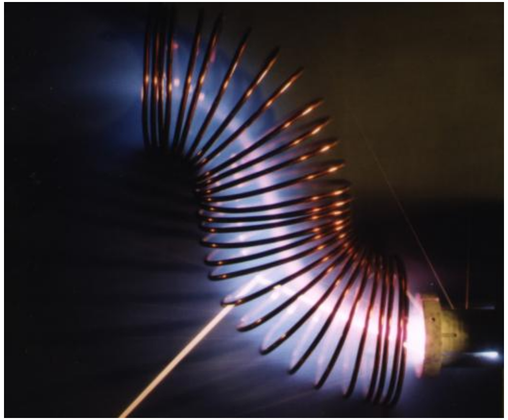
Low-rate deposition processes

General concepts to deposit ultra-thin films:

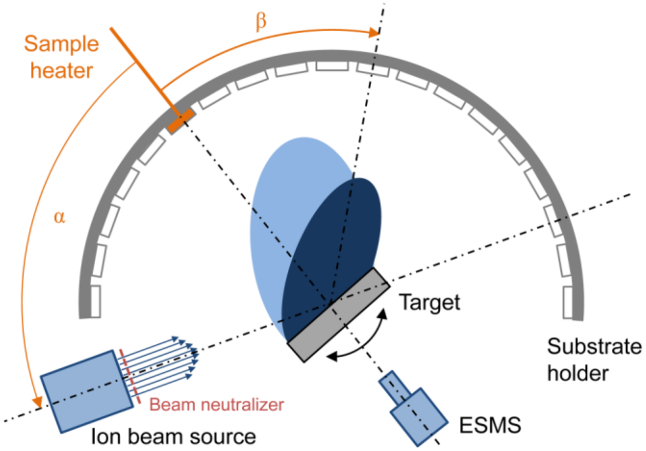
1. reduce power of process
2. increase distance between source and substrate
3. use pulsing techniques: it is still possible to control film microstructure; examples: pulsed arc, PLD, pulsed ion beam deposition
4. use self-limitation (ALD)

Caution: consider flux of wanted species versus residual gas species, especially for reactive metals.

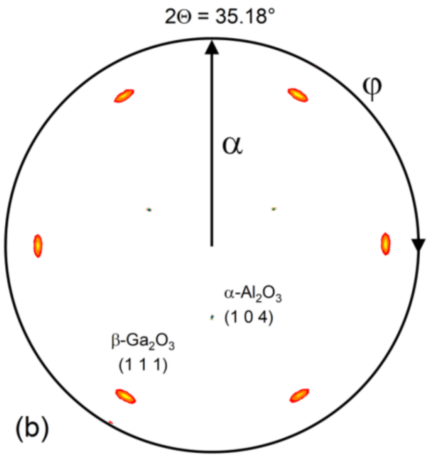
example: ultrathin ta-C on heads by filtered arc: sub-monolayer per pulse; use pulse-counting and/or in situ ellipsometry



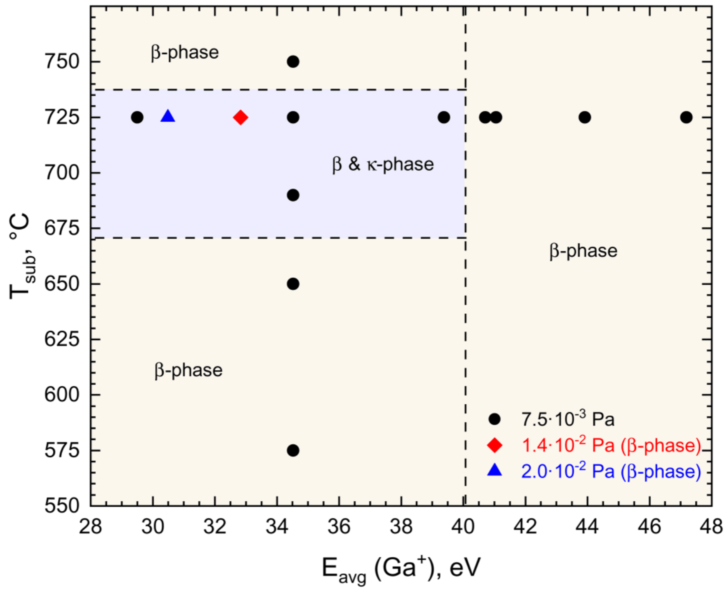
Another example of a low rate deposition process: Ion beam deposition of oxides



setup



XRD pole figure



film phase diagram

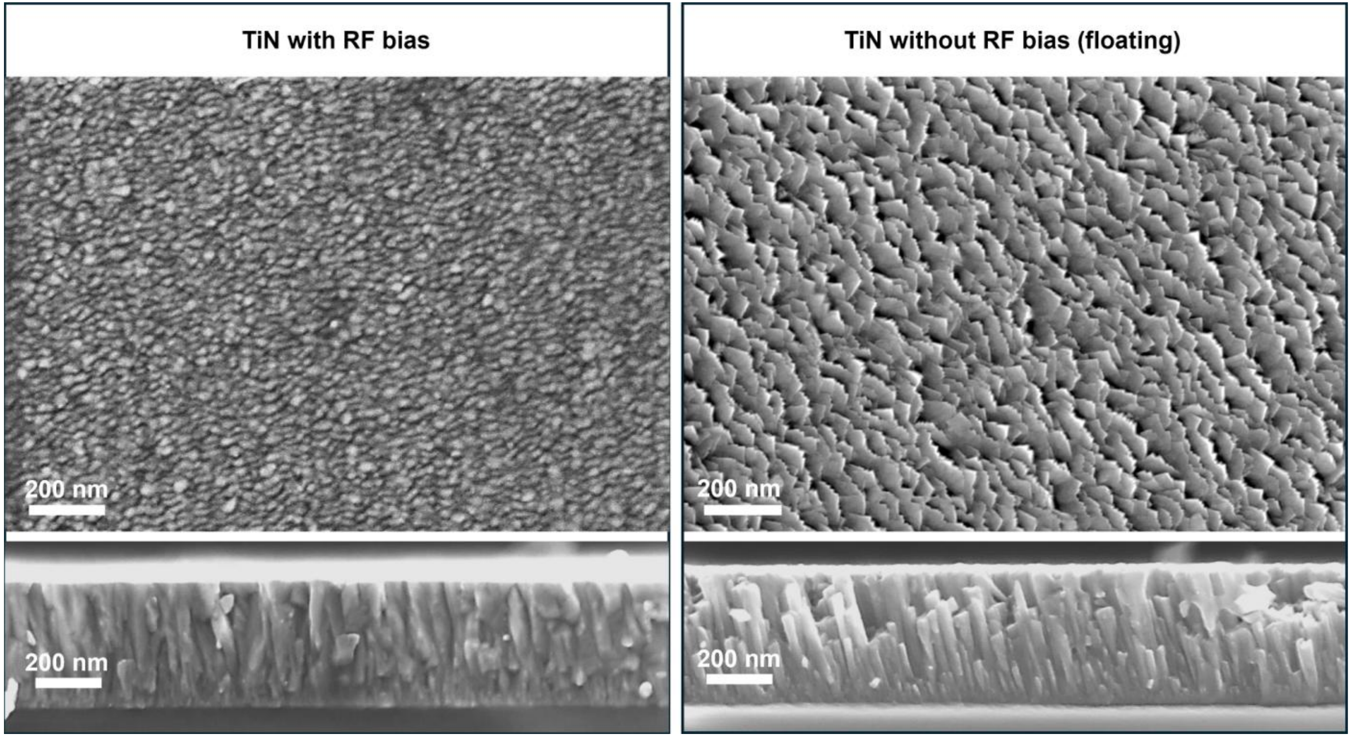
- Ga_2O_3 on sapphire, dep rate < 1 nm/min
- oxygen from background is ok, but what about hydrogen?

D. Kalanov, et al., J. Appl. Phys., 136 (2024) 015302.

A recent paper studying bias, microstructure, and oxygen incorporation

Combinatorial reactive Ti-Zr co-sputtering: The compositional gradients are complemented by orthogonal deposition temperature gradients and RF-bias under the glass substrate

→ look at densification and column size and tilt changes



K. Thorwarth, et al., Surf Coat Technol. 512 (2025) 132326.

A recent paper studying bias, microstructure, and oxygen incorporation

XPS-derived composition of TiN and ZrN films grown without and with RF substrate bias, where Me stands for Ti or Zr.

Sample		Me, at. %	N, at. %	O, at. %	C, at. %
TiN- no bias, ambient transfer	Native surface	24	22	27	27
	Ar^+ sputter-etched	44	39	8	9
TiN- no bias, UHV transfer	Native surface	39	52	7	2
	Ar^+ sputter-etched	47	49	4	0
TiN-RF bias, ambient transfer	Native surface	27	30	19	24
	Ar^+ sputter-etched	49	50	0	1
ZrN- no bias, ambient transfer	Native surface	28	15	35	22
	Ar^+ sputter-etched	55	39	7	0
ZrN- RF bias, ambient transfer	Native surface	18	7	28	47
	Ar^+ sputter-etched	58	40	2	0

K. Thorwarth, et al., Surf Coat Technol. 512 (2025) 132326.

High-rate deposition processes

very wide range,
depends a lot on context

1. evaporation
2. thermionic arc ion plating
3. cathodic arc deposition
4. PE CVD

PVD

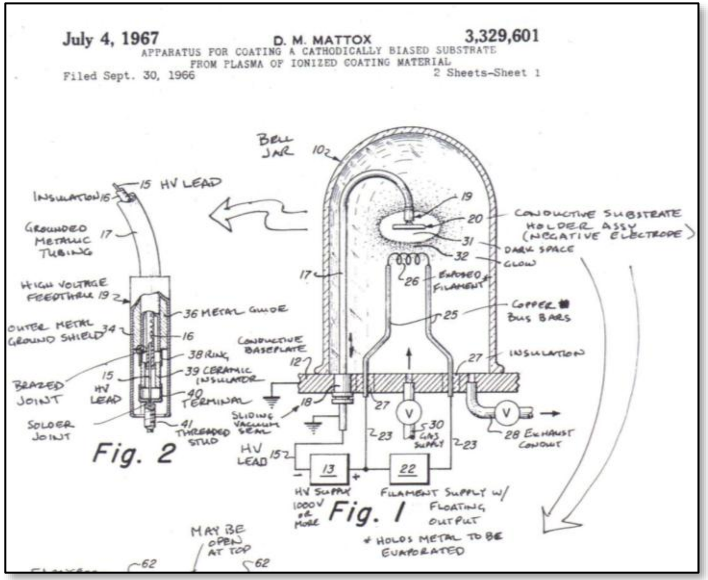
•**Thermal Evaporation**: **1–50 nm/min** (faster for metals)
•**Electron Beam Evaporation**: **10–100 nm/min**
•**thermionic arc ion plating → see evaporation**
•**Sputtering (DC or RF)**: **1–100 nm/min**, much lower for reactive sputtering when in poisoned mode
•**High-Rate Magnetron Sputtering**: Up to **several hundred nm/min, but reduced for HiPIMS**

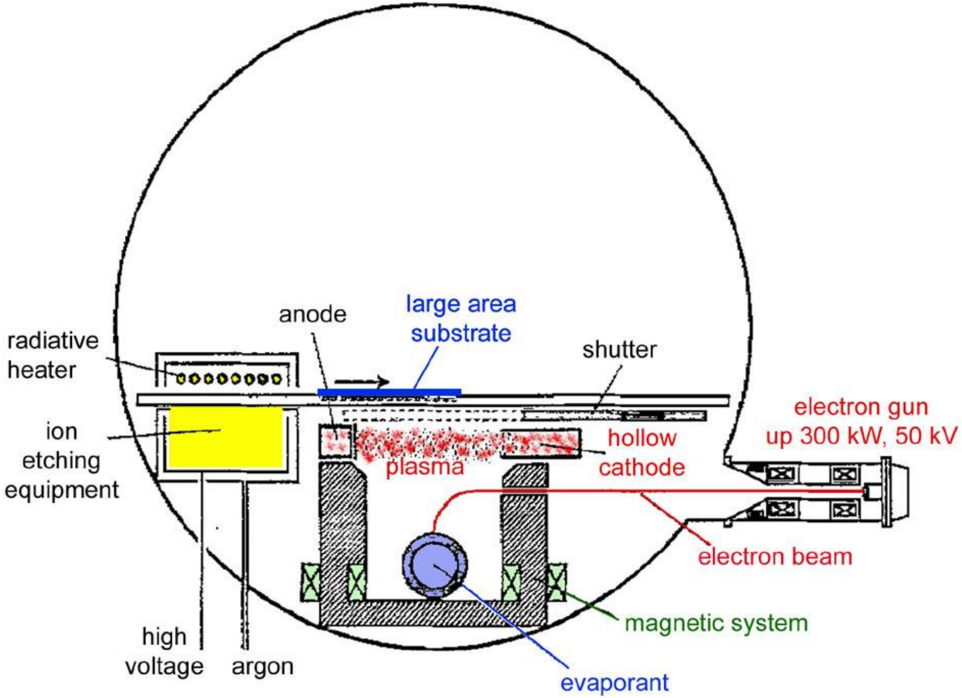
CVD

•**Thermal CVD**: **100–1000 nm/min**
•**Low Pressure CVD (LPCVD)**: **10–100 nm/min**
•**Plasma Enhanced CVD (PECVD)**: **10–500 nm/min,** depending on precursor and plasma power
•**Metal Organic CVD (MOCVD)**: **100–1000 nm/min,** commonly used in compound semiconductors

Examples of high-rate process plus film densification by biasing: Thermionic arc, hollow cathode ion plating

- combing evaporation with a thermionic arc discharge though that vapor
- substrate biased to control ion energy upon arrival on substrate
  - early patents 1939
  - Don Mattox 1964…1967
  - FEP in Dresden, Germany, scaled up

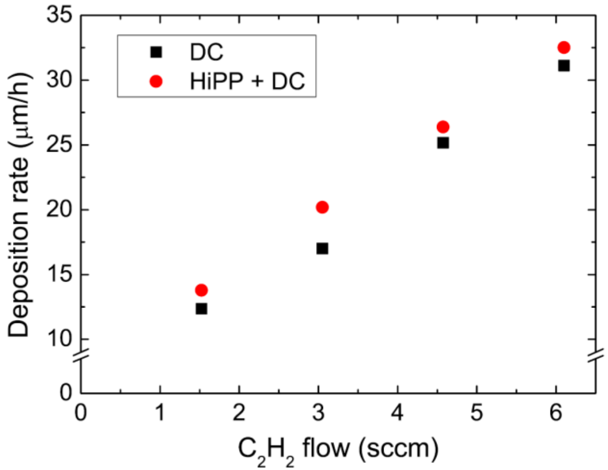


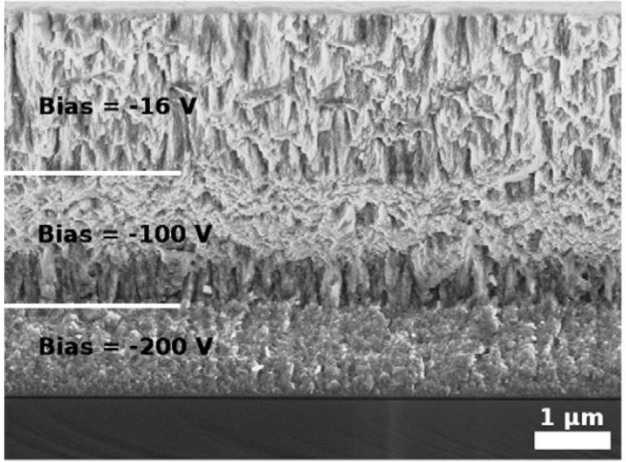


C. Metzner et al., Surf. Coat. Technol. **94-95** (1997) 663-668

Plasma-Enhanced CVD

- we have a wide range what “high-rate” means
- higher pressure make more species available for deposition → use higher pressure, flow rates
- here: example of DLC deposition, presence of plasma allows us to use bias effectively
- as with all plasma processes, pulsing or combining a process with pulsing is possible and often advantageous
- Caution: some CVD processes require hazardous precursors



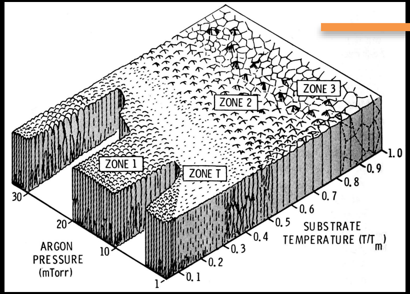


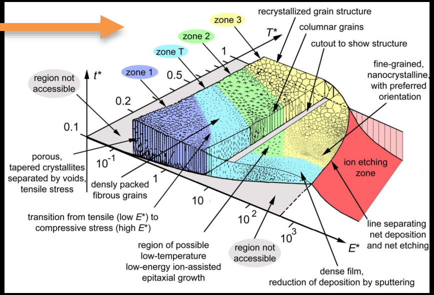
H. Pedersen, Surf. Coat. Technol., 206 (2012) 4562.

Some summarizing points for non-equilibrium heating and processes related to effects by kinetic and potential ion energies

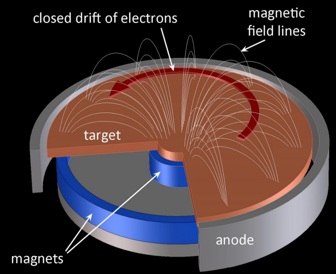
$$E_i = E_0 + Qe\left(V_{plasma} - V_{surface}\right)$$

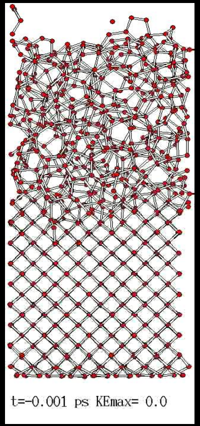
overly simplified: plasma fluxes bring potential and kinetic energy to a surface, equilibrium versus non-equilibrium heating



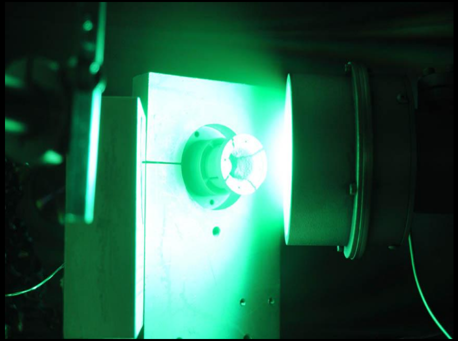


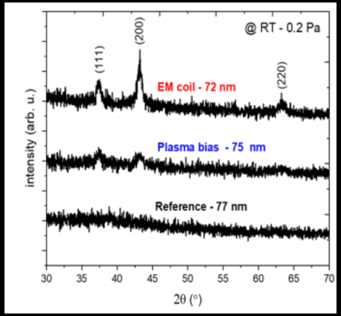
- Structure zone diagrams illustrate heating and ion energy effects
- examples: ta-C, AlVN, …





energetic deposition (e.g. HiPIMS, cathodic arcs, PLD) are key to some film materials and applications





gasless-sputtering, high rate, UHV are key approaches

Suggestions for Further Reading

Open Access:

JOURNAL OF APPLIED PHYSICS **121**, 171101 (2017)

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Tutorial: Reactive high power impulse magnetron sputtering (R-HiPIMS)

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(Received 17 November 2016; accepted 18 February 2017; published online 21 March 2017)

High Power Impulse Magnetron Sputtering (HiPIMS) is a coating technology that combines magnetron sputtering with pulsed power concepts. By applying power in pulses of high amplitude and a relatively low duty cycle, large fractions of sputtered atoms and near-target gases are ionized. In contrast to conventional magnetron sputtering, HiPIMS is characterized by self-sputtering or

https://doi.org/10.1063/1.4978350

Applied Physics Reviews REVIEW pubs.aip.org/aip/are

Glows, arcs, ohmic discharges: An electrode-centered review on discharge modes and the transitions between them

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Submitted: 25 February 2024 · Accepted: 6 June 2024 ·
Published Online: 19 July 2024

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André Anders[1,2,a)]

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ABSTRACT

Ever since they have been studied, gas discharges have been classified by their visual appearance as well as by their current and voltage levels. Glow and arc discharges are the most prominent and well-known modes of discharges involving electrodes. In a first approximation, they are

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