Basic Phenomena of Sputter-Deposition

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Part I
- Introduction, History and Aim
- Generation of Atoms
- Energy Transport
  - (low pressure case)

Part II
- Transport of Atoms
- Throw Distance
- Gas Rarefaction
  - (low - high pressure transition)

History

A personal view: sputtering of amorphous semiconductors

(Or: How the transistor switched my life)

1947	Bardeen, Brattain and Shockley invented the transistor (1956 Nobel Prize awarded)
1960s	Deposition of amorphous semiconductors (a-Ge, a-Si) by evaporation and sputtering aiming at thin-film electronics: Electronic defects are unsolved problem.
1971	William Paul (Harvard) proposed hydrogenation of a-Ge for defect passivation (namely dangling bonds) : a-Ge:H prepared by sputtering
1975	Spear and LeComber (Dundee) demonstrated n- and p-type doping of amorphous hydrogenated silicon (a-Si:H) by PECVD
1980s	Intense research on a-Si:H - fundamentals of preparation and characterization, application to thin film transistors, solar cells and electro-photography (Xerography)
1990s	Preparation of a-Si / metal (SiMal) layered structures

Aim

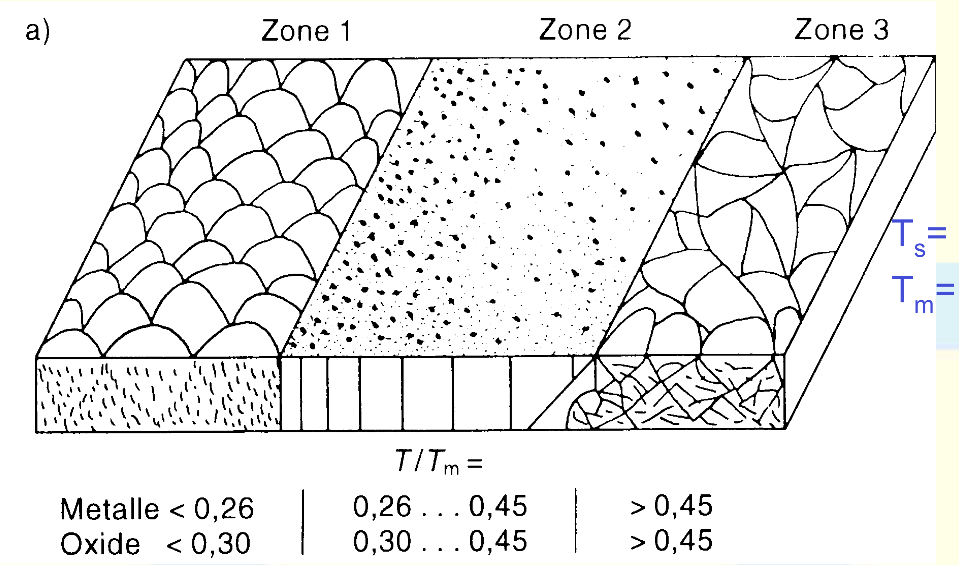
Why investigating energy fluxes connected to sputter-deposition?

Knowledge about the energy of sputtered atoms (and other species) is useful:

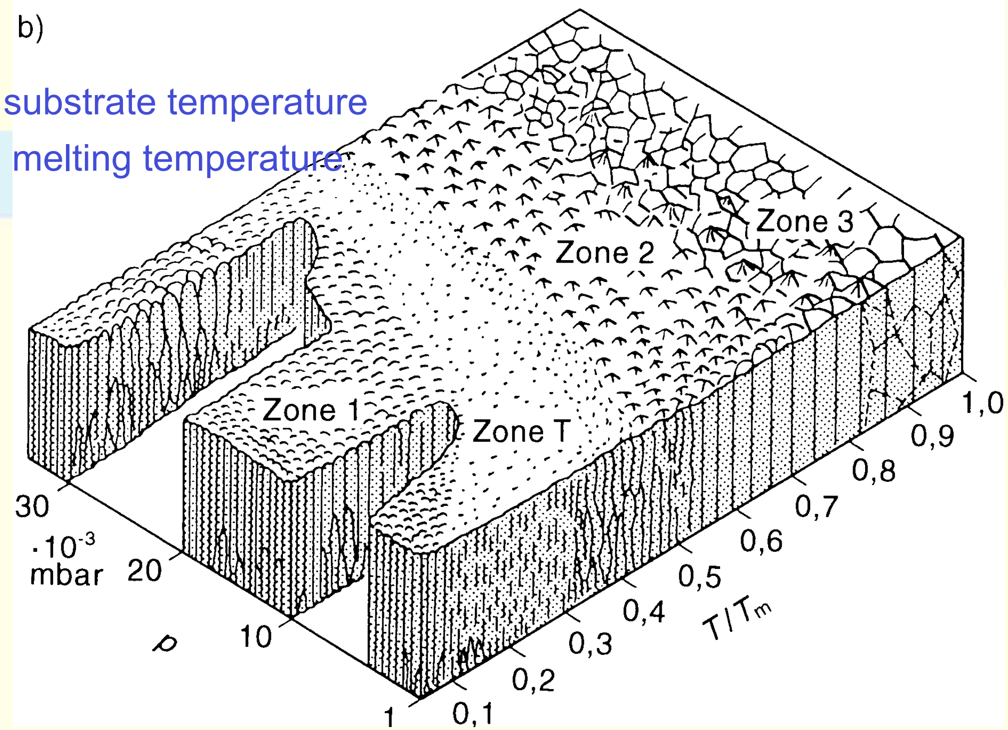
- Deposition of “zero stress” films of refractory metals , which are used as conductor lines in highly integrated electronics.
- Preparation of smooth surfaces and interfaces for examples in multi-layer films for x-ray mirrors.
- Ability to prepare dense or nano-porous metal films (fractal dimension of D_m=2.4), which can act as field emitters or catalysts.
- Enhancement or suppression of crystallite growth and the formation of specific type of texture (for example, c-axis orientation of large AlN grains).

Structure-zone model for sputtered films

a) Evaporated films (Movchan and Demchishin)
b) Sputtered films (Thornton)



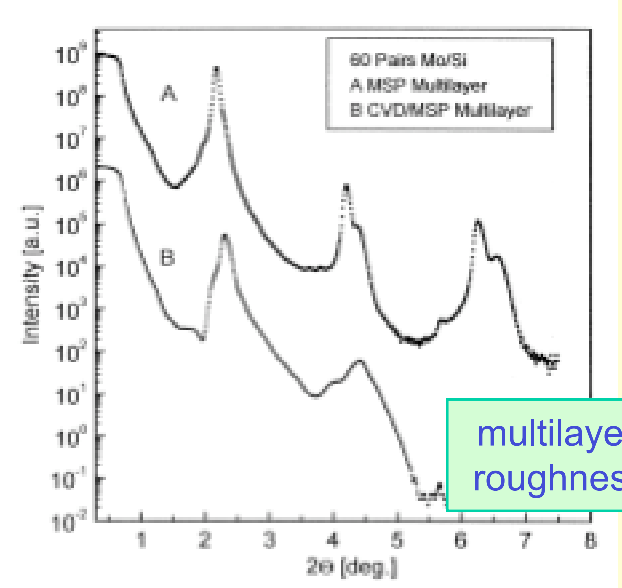
T_s= substrate temperature
T_m= melting temperature



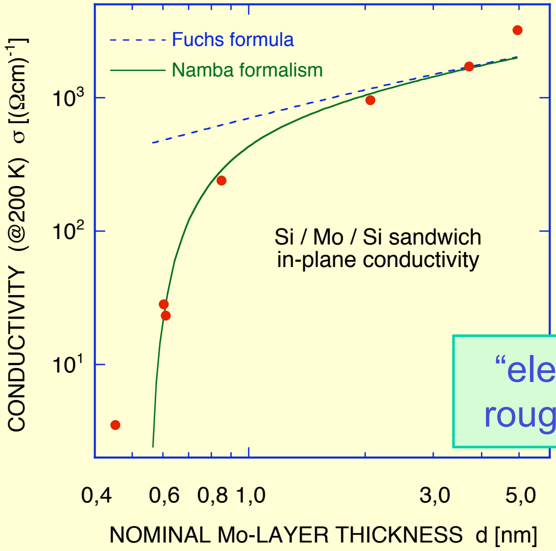
Z1: T_s/T_m < 0.3 no surface diffusion, initial columns of some 10 nm diam. + voids, amorphous or nano-crystalline films, columns grow to µm diam. at surface
ZT - transition zone: weak surface diffusion due to bombardment preventing microstructure
Z2: T_s/T_m>0.3 strong surface diffusion, columnar crystallites of µm diam. increasing with film thickness and temperature

Z3: T_s/T_m>0.5 larger non-columnar crystallites grow, smooth surfaces with grooves at boundaries

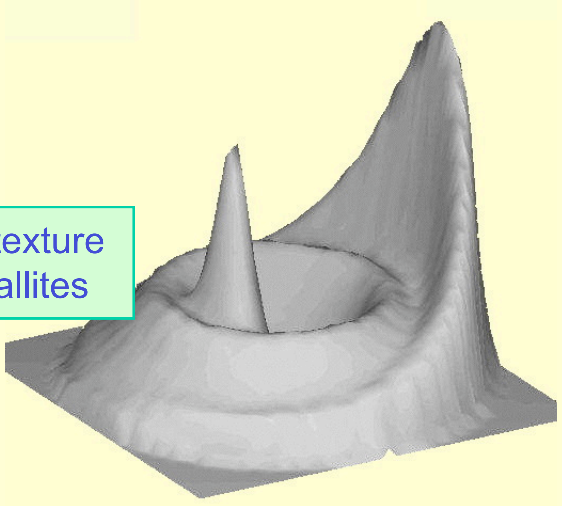
Sputtering causes novel effects on thin films !



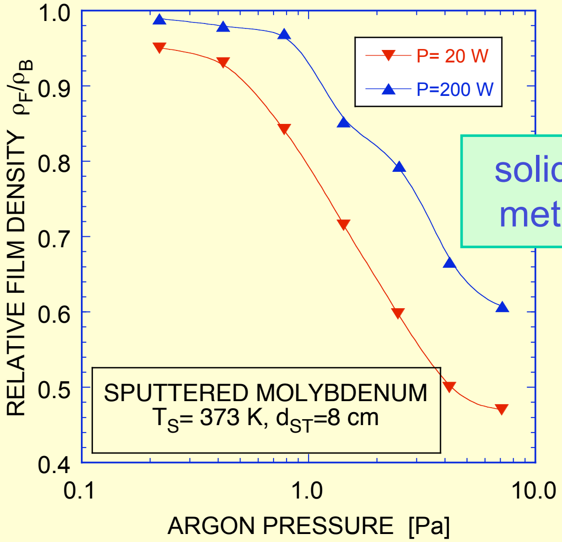
multilayer surface roughness = 1 nm



“electronic” surface roughness of 0,6 nm



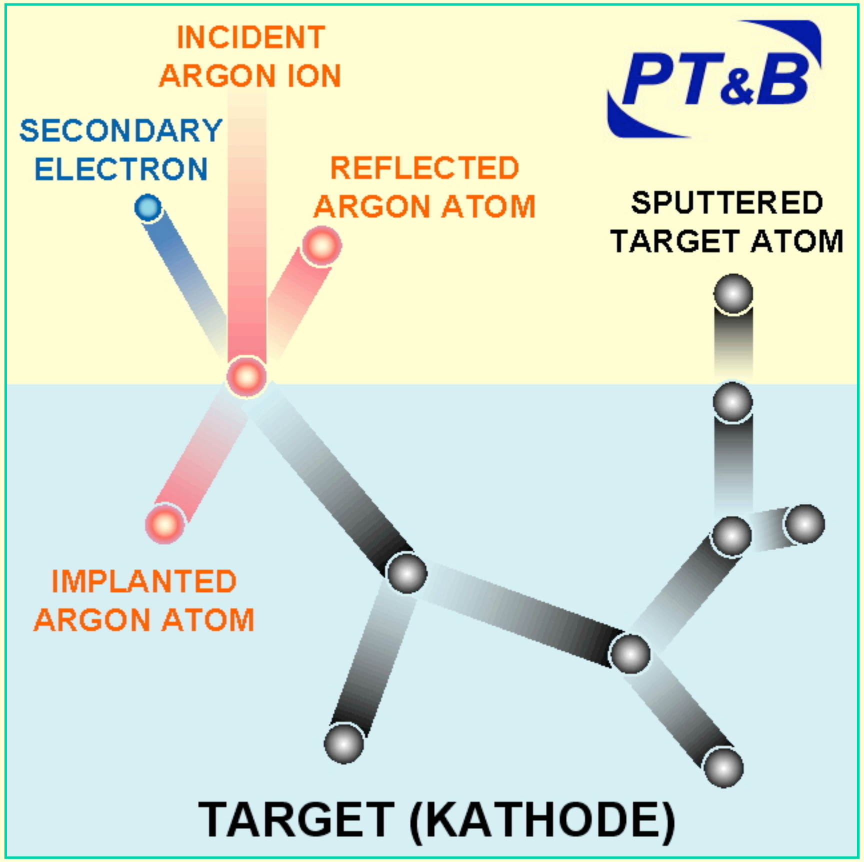
mosaic-like texture of Mo crystallites



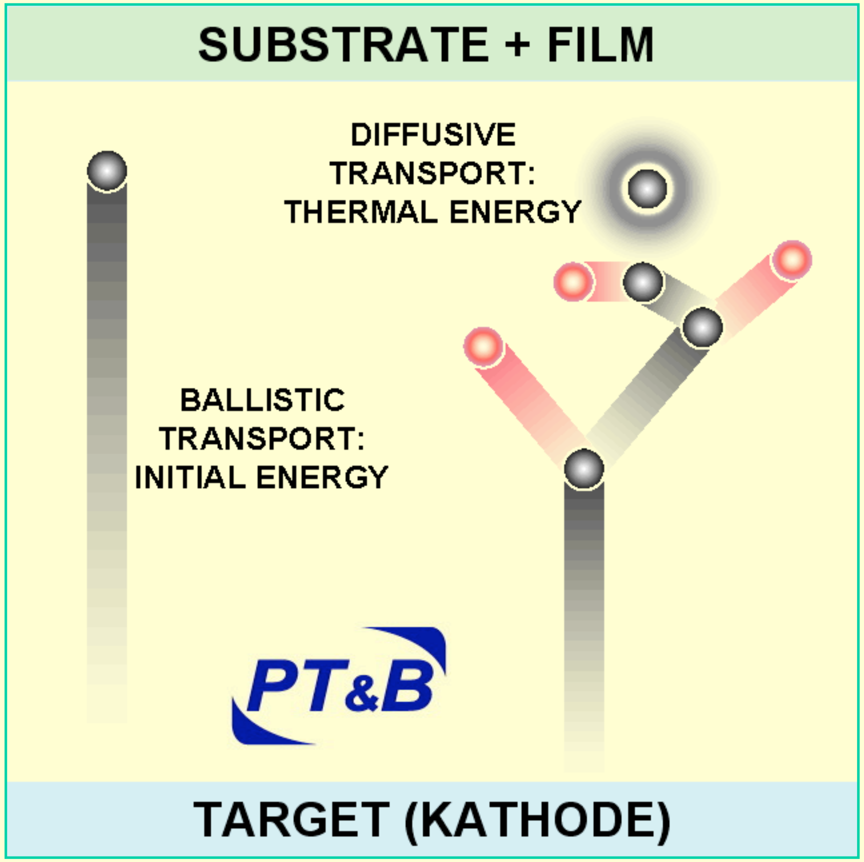
solid / porous metallic films

The two processes involved: sputtering and transport

- Ar ions recombine, emission of secondary (Auger) electrons, reflection or penetration of Ar atoms
- Evolution of collision cascade of target ions
- Momentum “reversion”, energy transferred to surface atom above surface binding energy → ejection of atom

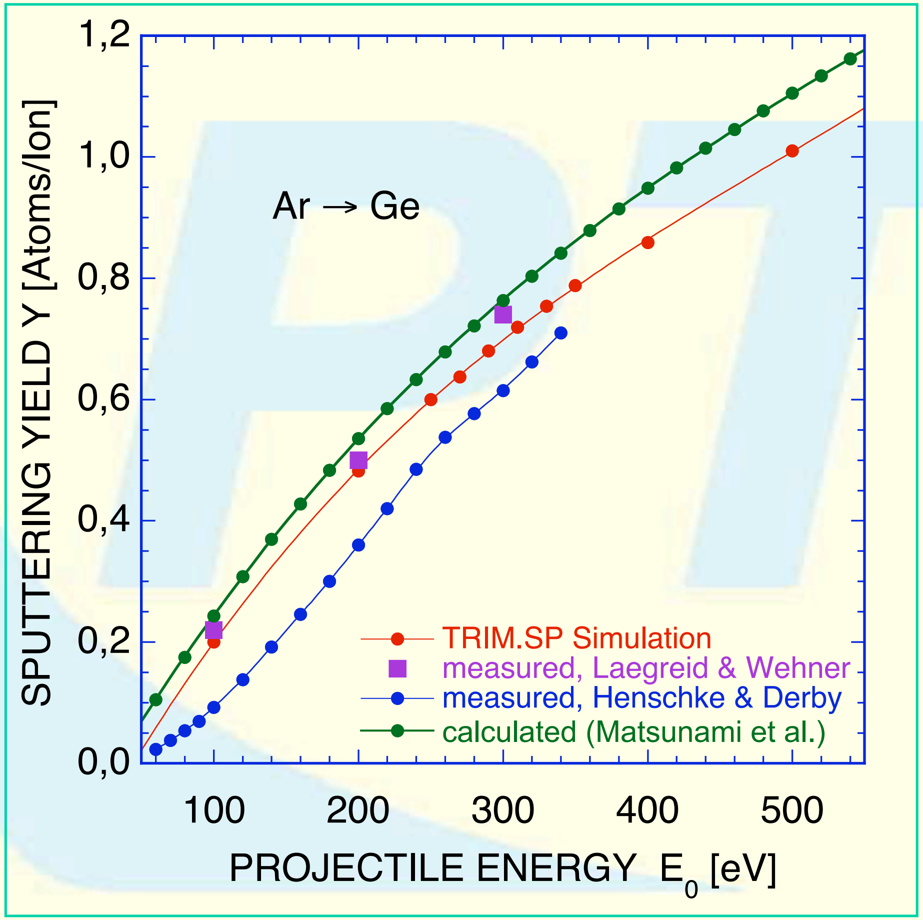


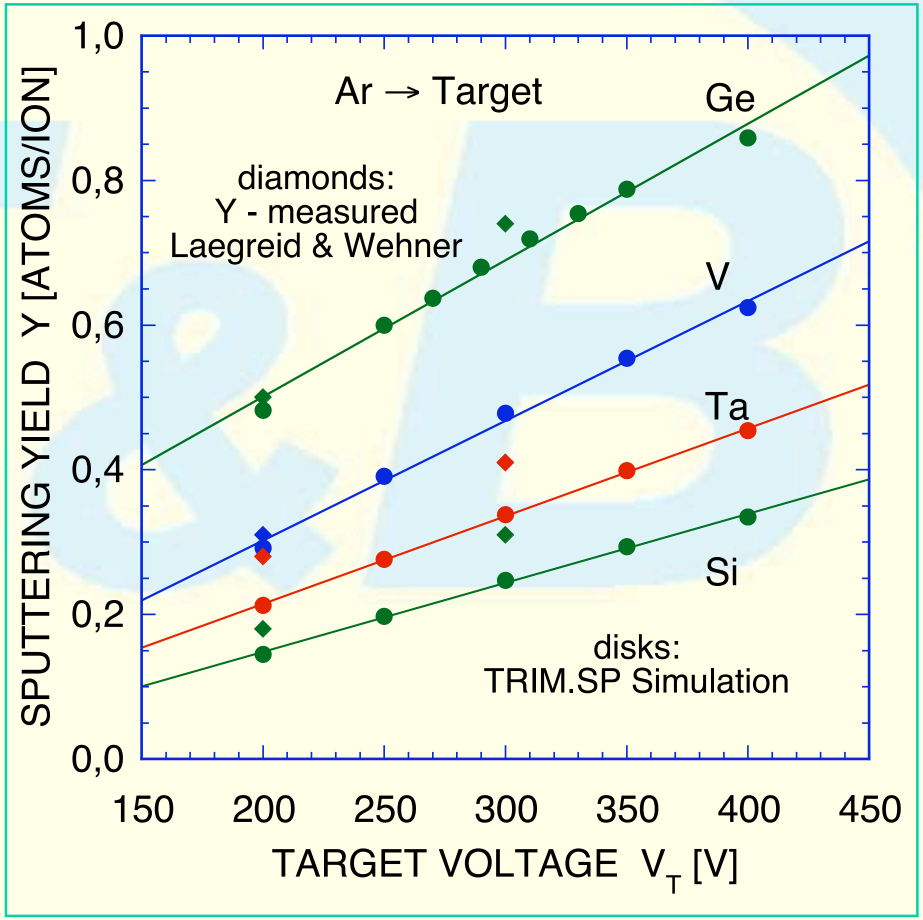
- Collisionless (ballistic) transport: target atoms conserve full initial kinetic energy (low pressure-distance product)
- Diffusive transport: multiple collisions of sputtered atoms result in complete thermalization (high pressure-distance product)



The sputtering yield Y

Most “popular” quantity of sputter deposition - Y(E) = sputter-ejected atoms per incident ion: Depends on target and projectile mass, kinetic and surface binding energy, crystallite orientation, incident angle, roughness AND ...

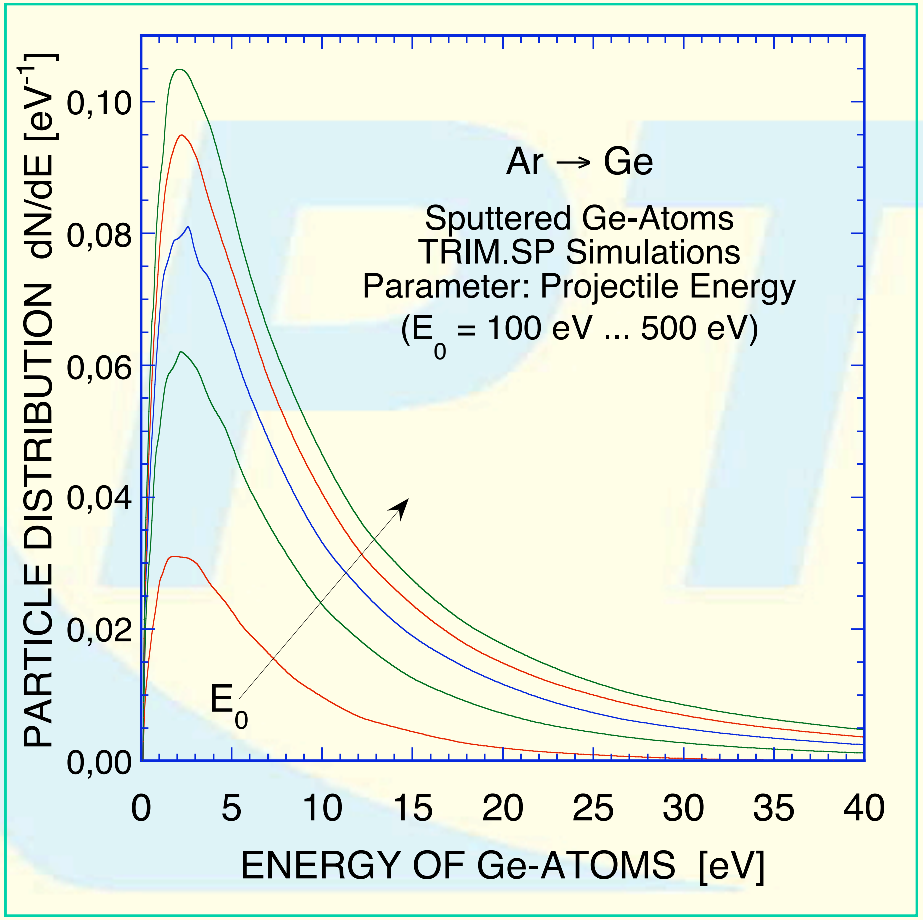


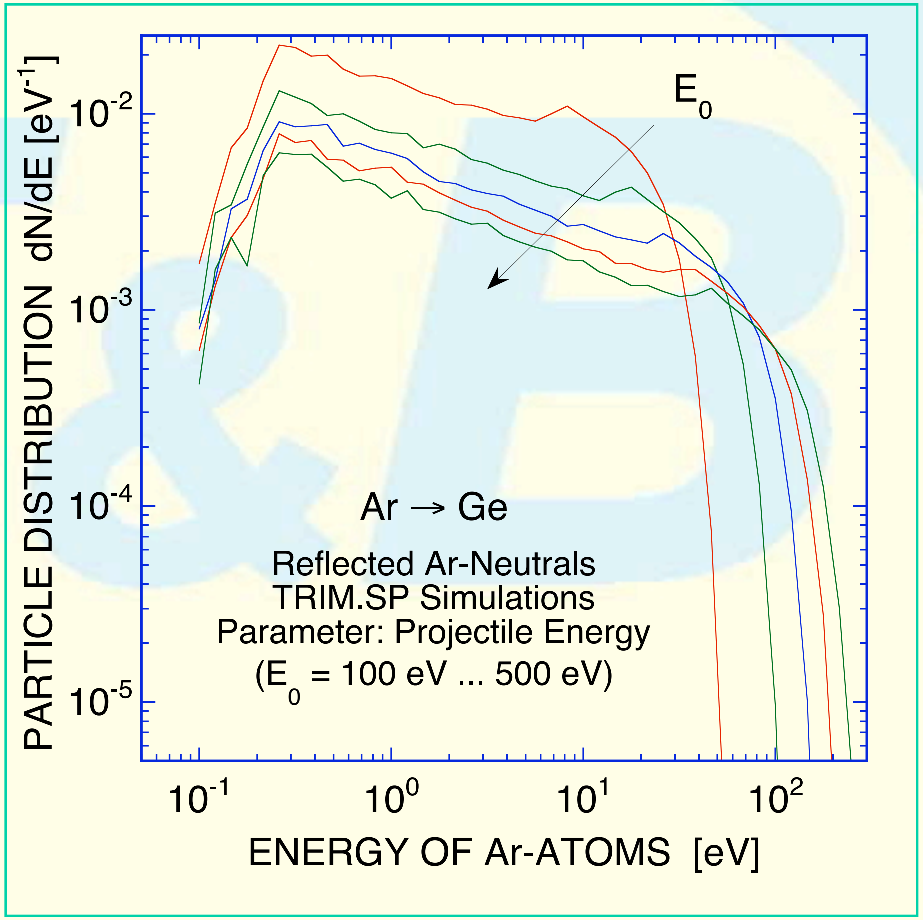


Energy of sputtered and reflected atoms

$$f(E) = \frac{E}{(E + U_0)^{3+2m}}$$

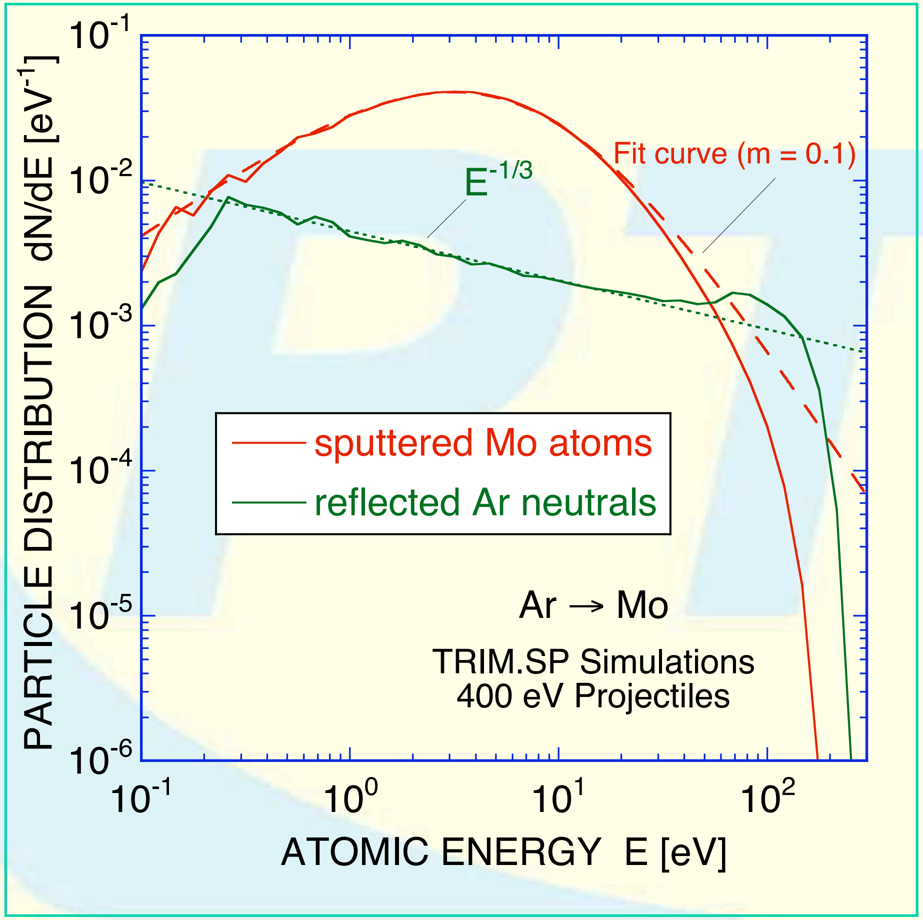
With m=0 Thompson distribution, maximum @ $U_0/2$
U_0 - surface binding energy



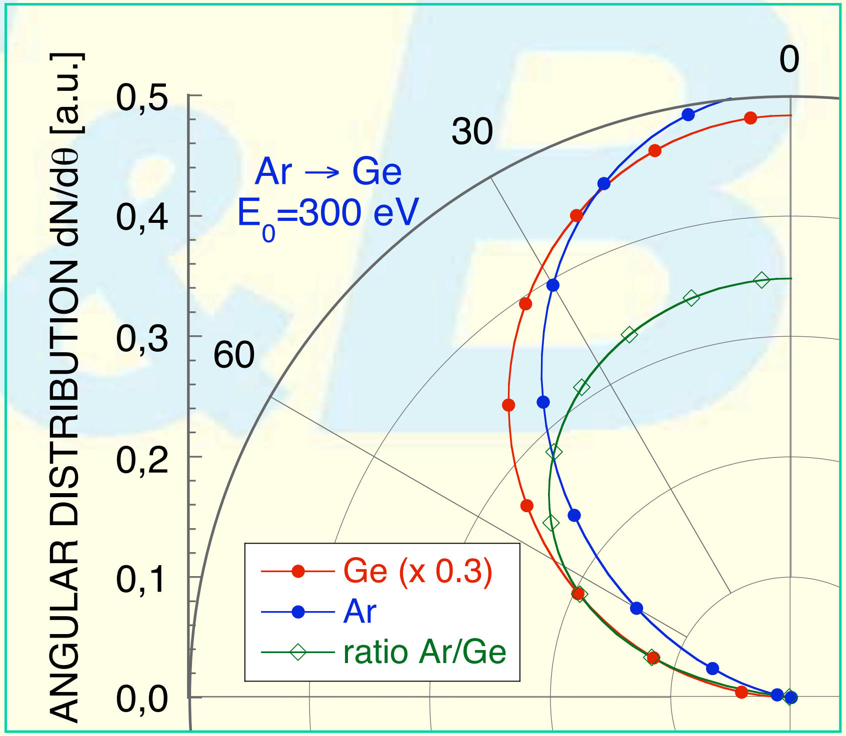


Energetic and angular distribution of sputtered and reflected atoms

Cut-off energy is about E_{max} !



$$dN / d\theta = \cos^{\nu} \theta, \quad \nu \approx 1$$



Estimate of energy input per atom by elemental sputter-deposition

$$\boxed{\langle E_t \rangle = I_{tot}/\Phi_{at}}$$

$\langle E_t \rangle$ measured by calorimetric method (power density I_{tot}) and atomic deposition rate Φ_{at}

$$\boxed{\langle E_t \rangle = U_0 + \langle E_{at} \rangle + \langle E_{Ar} \rangle / at + \langle E_{Plasma} \rangle / at}$$

$\langle E_t \rangle$ calculated from quantities resulting from TRIM.SP forward simulation

U_0 - surface binding energy

$\langle E_{at} \rangle$ - average energy of sputtered atoms

$$\boxed{\langle E_{at} \rangle = \int_0^{E_{max}} f(E) E dE \Big/ \int_0^{E_{max}} f(E) dE}$$

$$\boxed{E_{max} = k \frac{4 M_I M_T}{(M_I + M_T)^2} E_0 - U_0}$$

with E_{max} maximum transferred energy and $k = f(M) = 0.1 \ldots 0.4$

$\langle E_{at} \rangle$ - analytical approach

$$\boxed{\langle E_{at} \rangle = U_0^{2/3} E_{max}^{1/3}}$$

$\langle E_{Ar} \rangle / at$ - average energy of reflected argon per deposited atom

R_N, R_E - Particle und Energy reflection coefficient

$$\boxed{\langle E_{Ar} \rangle / at = E_0 \frac{R_E}{R_N} \frac{R_N}{Y}}$$

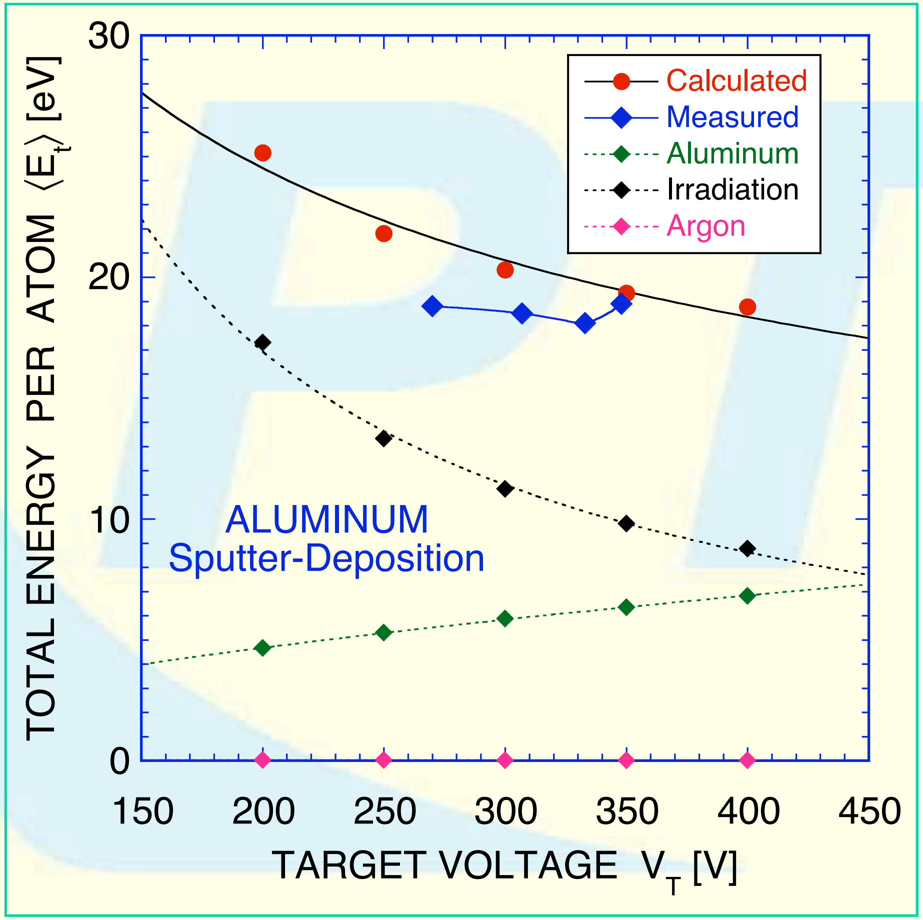
$\langle E_{Plasma} \rangle / at$ - average plasma irradiation energy per deposited atom

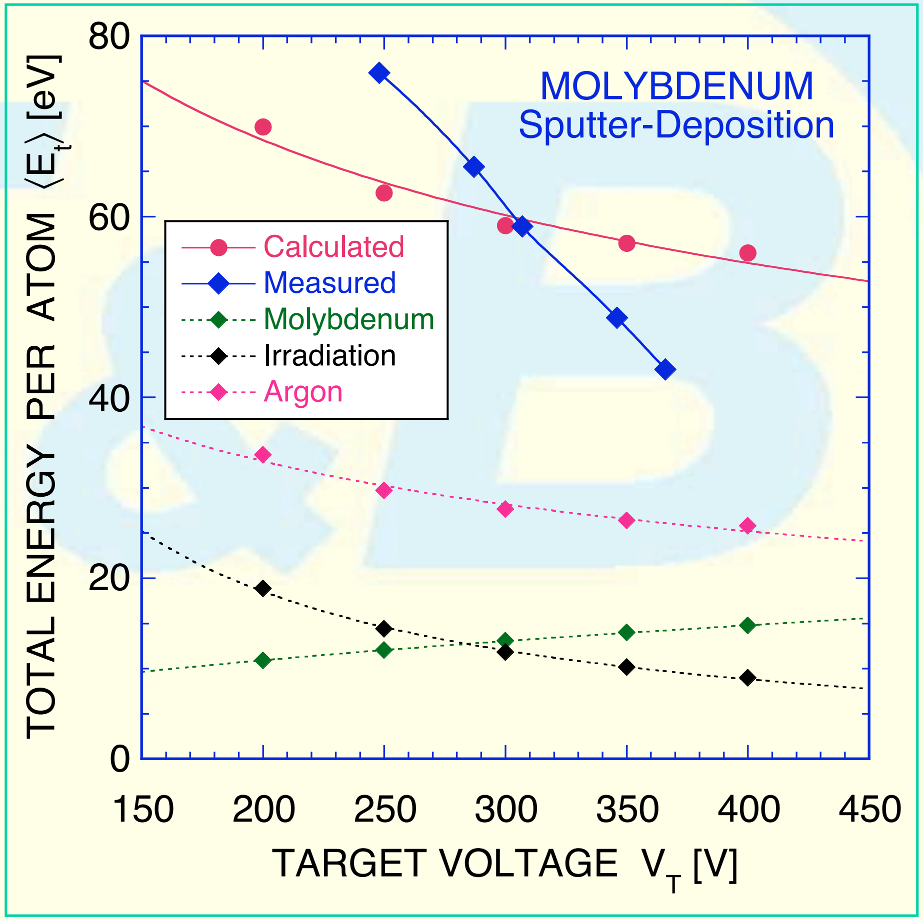
Y - sputtering yield

$$\boxed{\langle E_{Plasma} \rangle / at = \frac{5{,}33 eV}{Y}}$$

Results: Energy input by elemental sputter-deposition

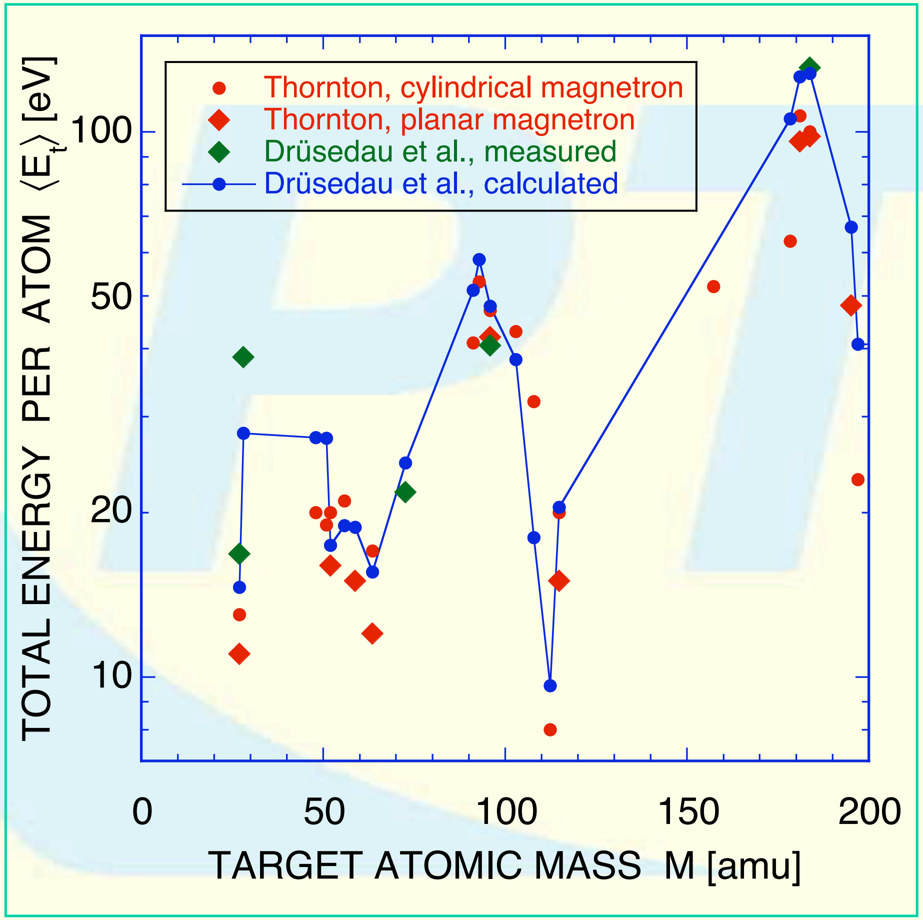
Comparison of values measured to the results of forward simulation (with the components due to kinetic energy of the sputtered atoms and reflected argon neutrals and plasma irradiation)

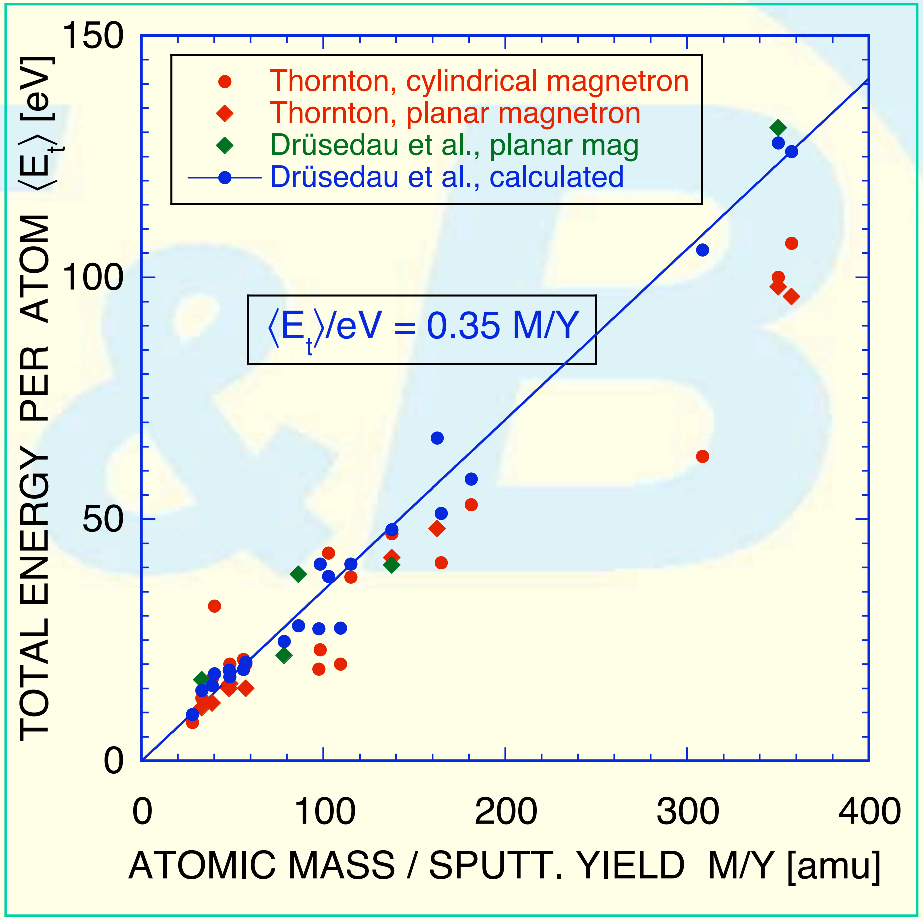




Results: Energy input by elemental sputter-deposition

Comparison of values measured to the results of forward simulation. The dependence of <E_t> on the atomic mass (left) is superimposed by the surface binding energy (sublimation enthalpy) of the elements.





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Do YOU know the meaning of the word "sputter" ?

"What is all that sputtering nonsense anyway?"

(from "Glow Discharge Processes" by Brian Chapman)

- a medical and a sputtering conference took place at Imperial College
- the well-known scientific phenomenon: conference system tends towards a condition of being in the bar
- a well-oiled medic demanded to know: "What is all that …"
- reply: "Well, we're in a branch of medical profession, too - in speech therapy actually. Sputtering is like stuttering, except, our chaps say p…p…p instead of t…t…t
- the medic warmly thanked his newly discovered colleague

"sputter" appeared in English 1598, adapted from the the words "sputteren" (Dutch) and "sputterje" (West Frisian)

English Dictionary (The Shorter OED 1957):
"To spit out in small particles and with a characteristic explosive sound … His tongue was too large for his mouth; he stuttered and sputtered (1878)"

Experimental

Sputter-deposition

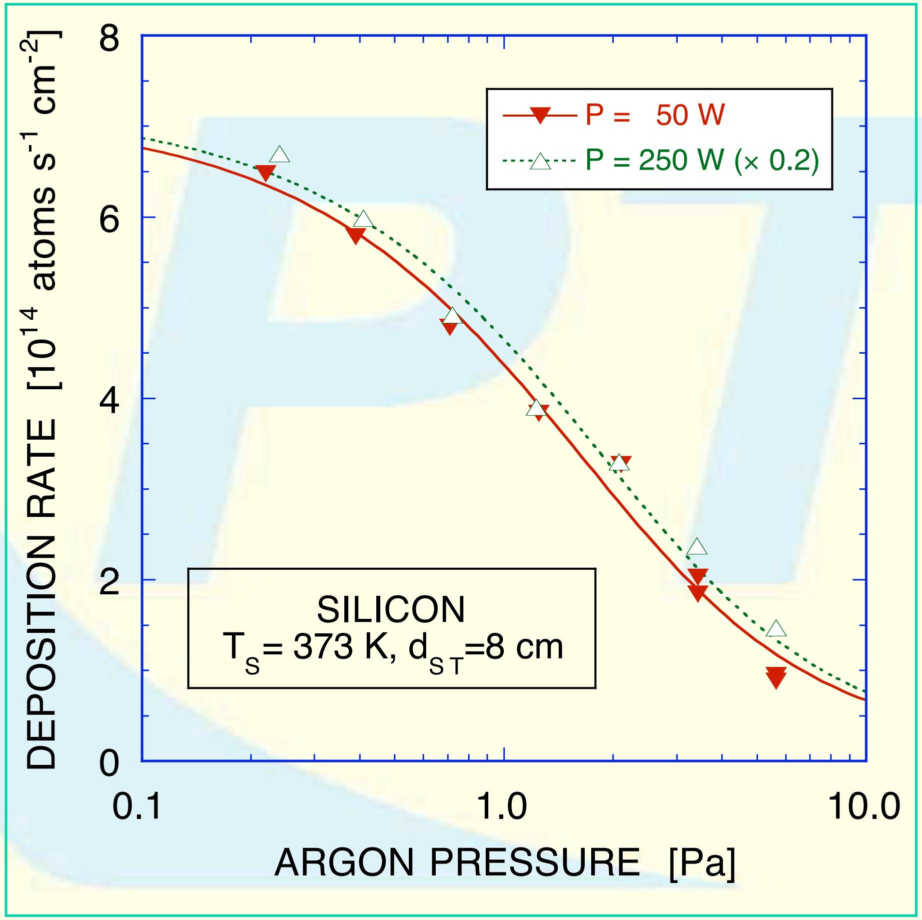
- 90 mm diameter Targets: Al, Si, Ti, V, Cr, Ge, Mo, Ta, W
- Sample sets: variation of pressure p_{Ar}=0.2 - 7.0 Pa
- Power (typical): P_{DC}=20 W (low power – 0.3 Wcm^{-2}) ***and***
  P_{DC}=200 W (high power – 3.1 Wcm^{-2})
- Substrate-to-target distance of d_{ST}=80 mm
- Substrate Temperature of T_s=373 K
- Film thickness of 100 nm and 500 nm, respectively
- Calorimetric measurements due to sample heating and cooling
- Gas density reduction measurements

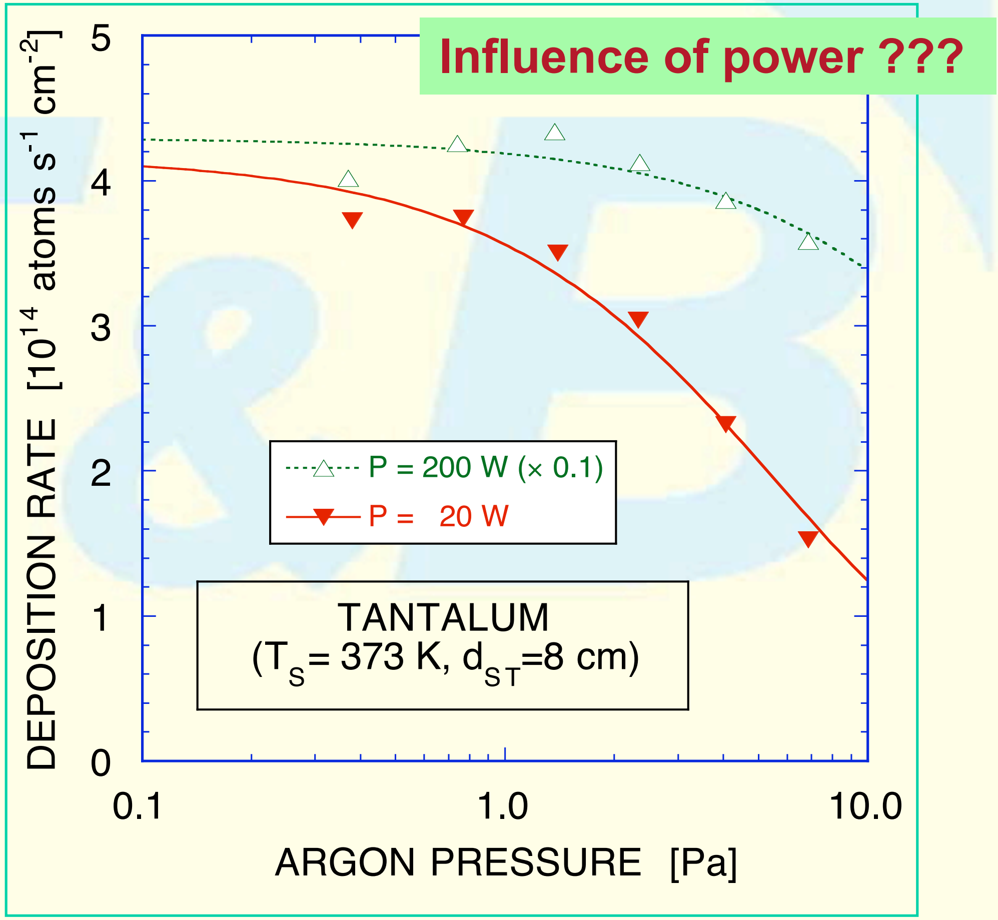
Film characterization

- Film thickness: Talystep instrument and X-ray reflectivity
- Specific gravity: X-ray reflectivity
- Determination of atomic deposition assuming unity sticking probability

Pressure-dependent atomic deposition rates

Throw distance: characteristic decay length of deposition rate as a function of distance from target at given pressure → more general: consideration of pressure - distance product !





Influence of power ???

Pressure-dependent flux of sputtered atoms

One-dimensional model by Keller and Simmons

Flux of ballistic atoms Φ_B at substrate:

$$\boxed{\Phi_B(pd_{ST}) = \Phi_0 \exp - \frac{pd_{ST}}{p_o d_o}}$$

Φ_0	"zero-pressure" flux
d_{ST}	substrate-to-target distance
$p_o d_o$	characteristic pressure-distance (throw distance)

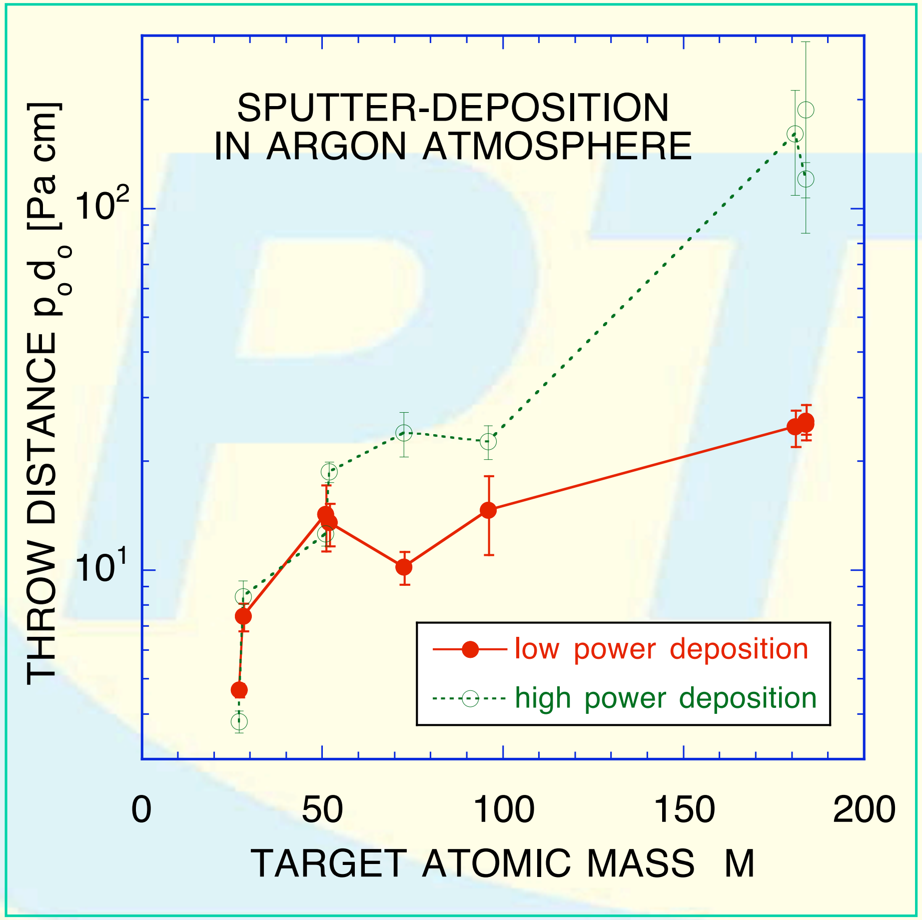
Single-step thermalization of ballistic atoms
→ source of diffusing thermal atoms of flux Φ_D at substrate:

$$\boxed{\Phi_D(pd_{ST}) = \Phi_0 \left\{ \frac{p_o d_o}{p\, d_{ST}} - \left(1 + \frac{p_o d_o}{p\, d_{ST}}\right) \times \exp - \frac{p\, d_{ST}}{p_o d_o} \right\}}$$

Total atomic flux Φ at substrate:

$$\boxed{\Phi(pd_{ST}) = \Phi_B + \Phi_D = \Phi_0 \frac{p_o d_o}{pd_{ST}} \left\{ 1 - exp - \frac{pd_{ST}}{p_o d_o} \right\}}$$

Throw distances are influenced by multiple parameters



Atomic mass:

Influence on throw distance is obviously related to fundamental atomic processes

Sputtering power:

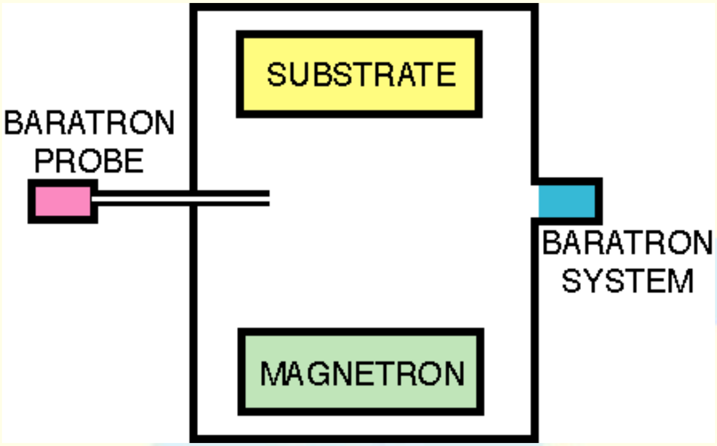
Influence on throw distance is related to process (apparatus) specific effects

The problem:

To identify and to separate the process-specific parameters from the effects measured to obtain general laws.

→ Investigation of gas rarefaction

Setup for measuring gas rarefaction (“sputtering wind“)



sputtering chamber and manometer at the tube’s end

a system of two connected vessels each characterized

by a temperature and pressure of p_S, T_S and p_P, T_P.

transition range between molecular and viscous flow: the ratio of the pressure values at both ends of the tube is described by:

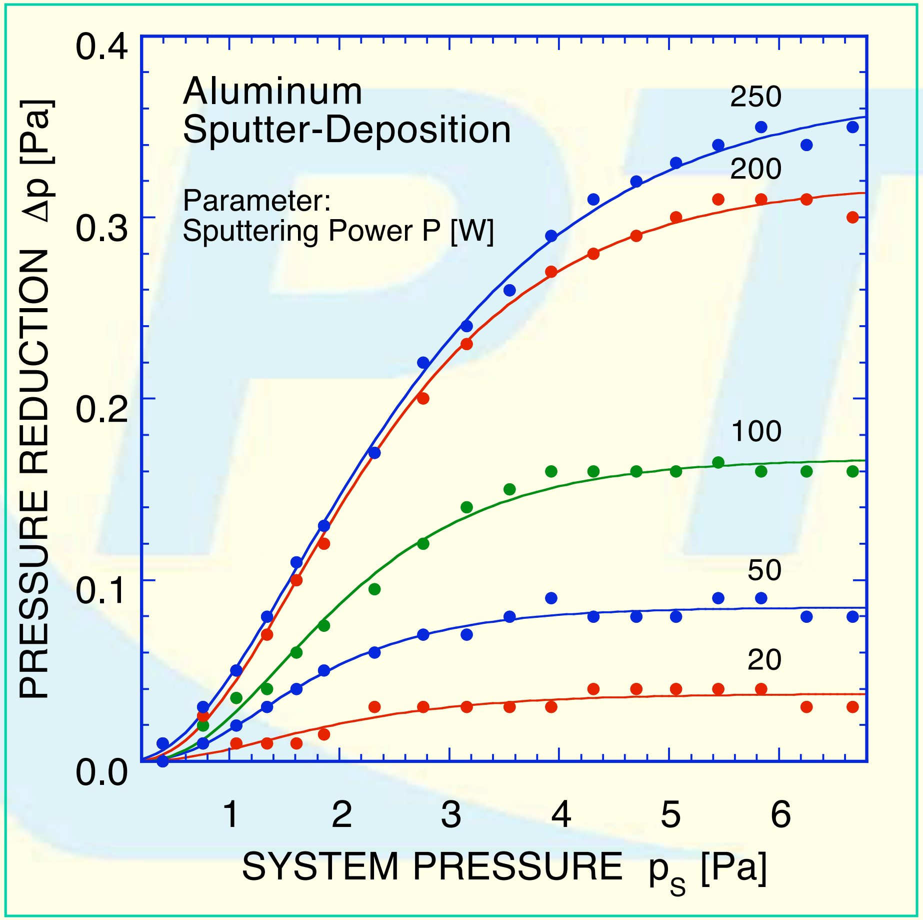
$$\frac{p_P}{p_S} = \frac{f(X) + \sqrt{T_P / T_S}}{f(X) + 1}, X = d_T p_P$$

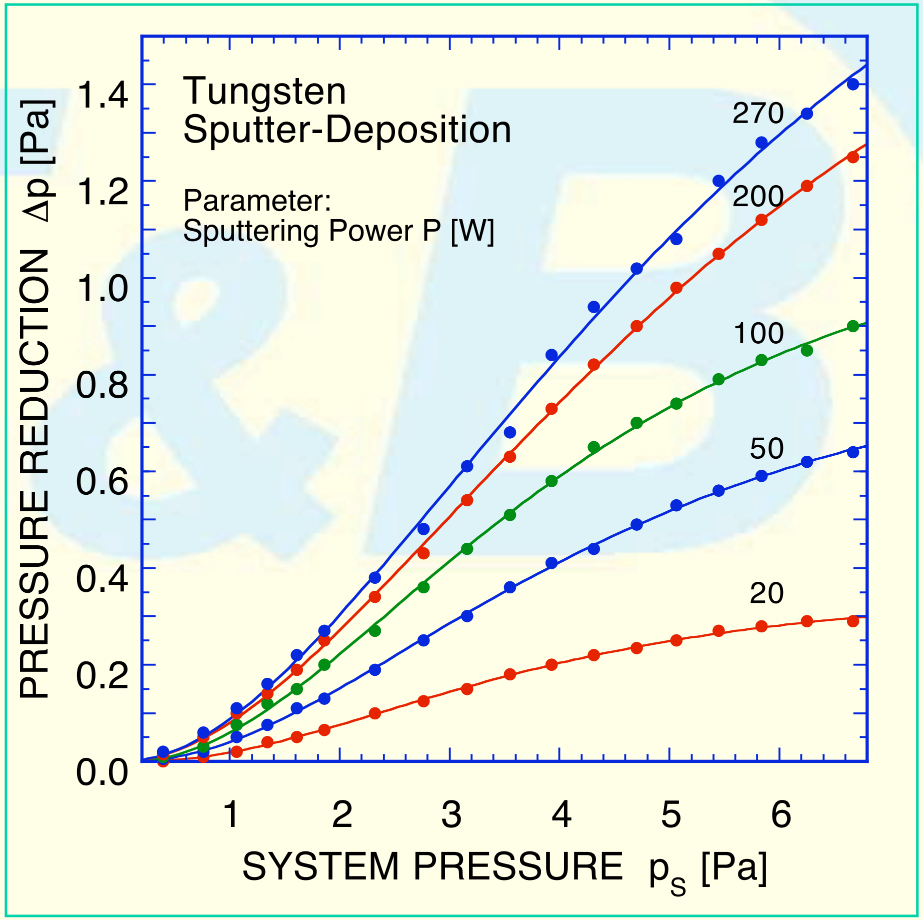
$$f(X) = A(X/T^*)^2 + B(X/T^*) + C(X/T^*)^{1/2}, T^* = (T_S + T_P)/2$$

Possible expression of f(x) with empirical constants A, B and C

Raw data: Probe pressure is reduced to system pressure

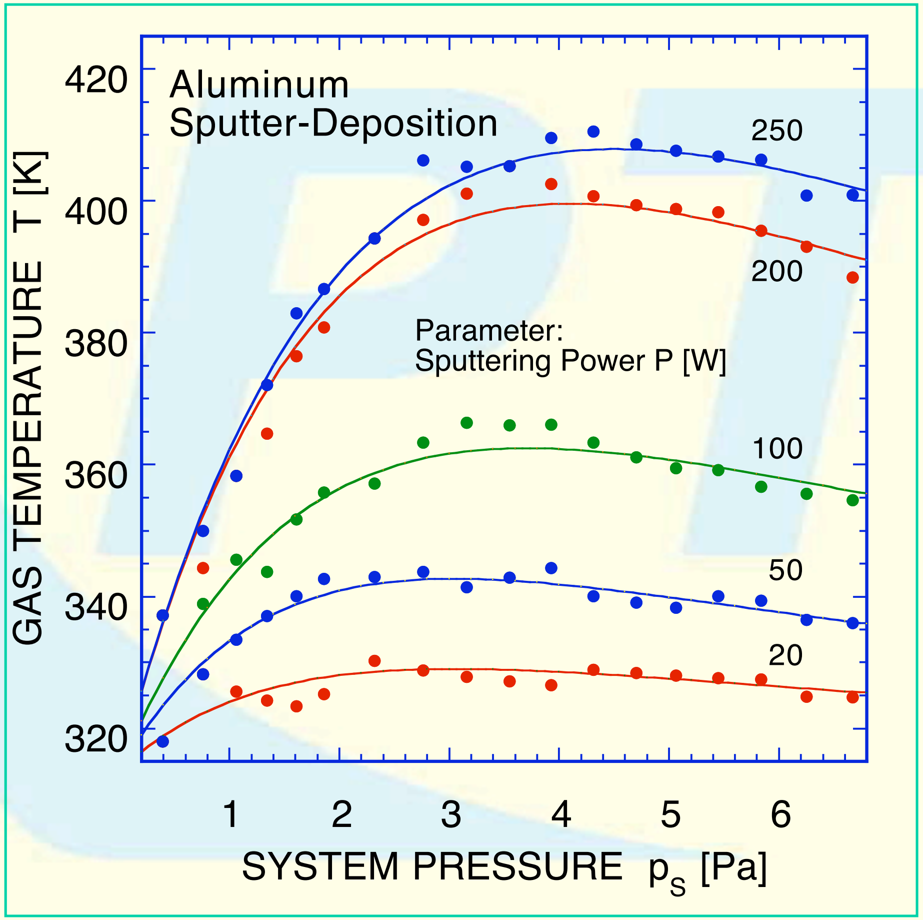
empirical fit curve: $\Delta p = p_S - p_P = m_1\{1 - \exp - (m_2 p_S)\}^{m_3}$

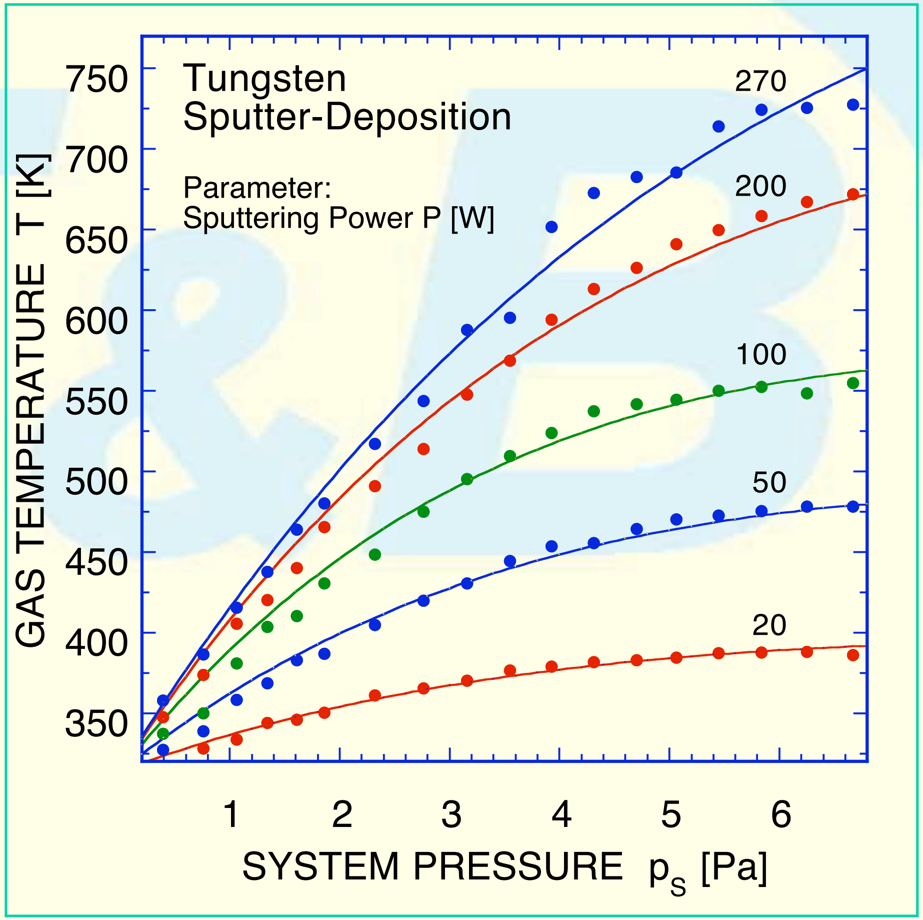




Gas temperature as a function of pressure (sputtering power)

System (gas) temperature calculated from systems pressure and temperature (p_S, T_S) and probe pressure p_P. Fit curves according to the analytical model.

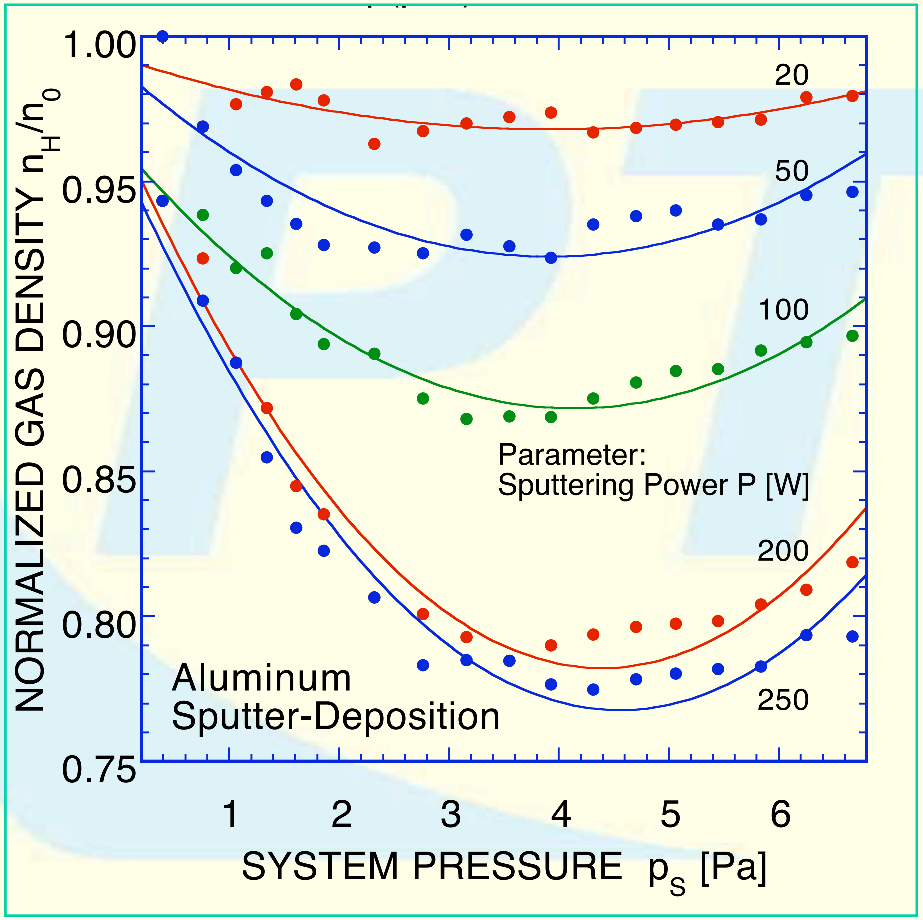


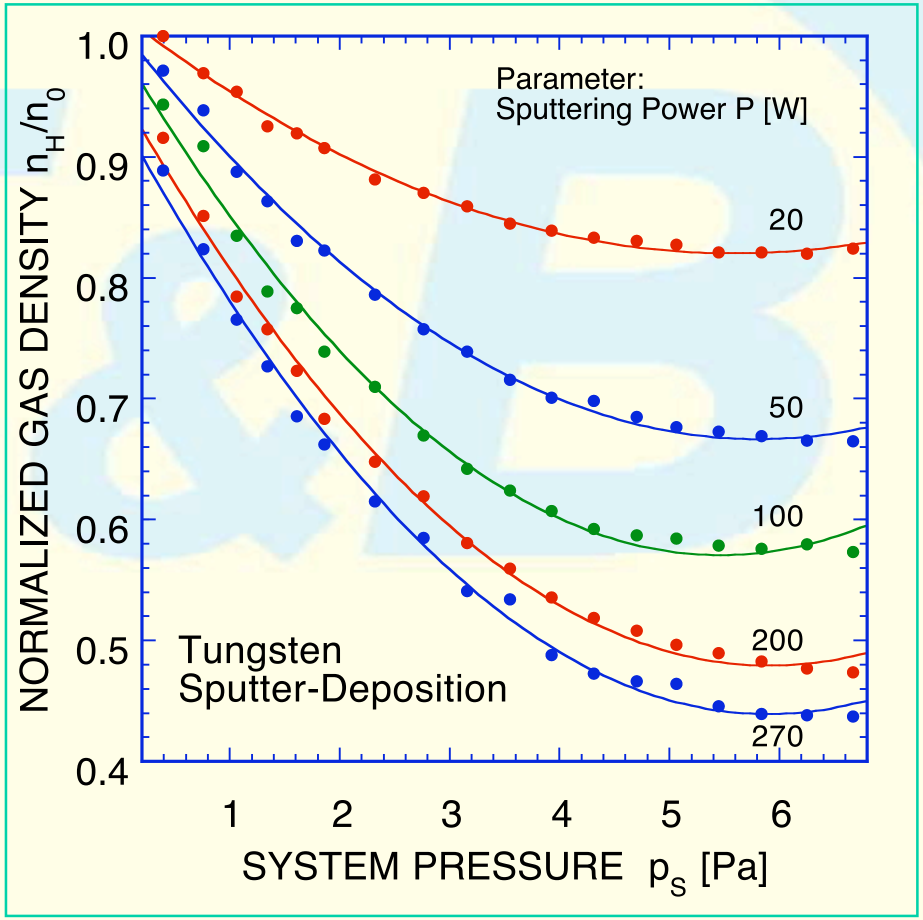


Gas density (normalized) as a function of pressure (power)

From temperature T_H measured, gas density n_H in the heated plasma region is determined (n_0 and T_0 gas density, temperature in the “cold”)

$$\boxed{\frac{n_H}{n_0} = \frac{T_0}{T_H}}$$





One-dimensional model for gas heating

In a sheath of dx around a position x a heating power P(x) is generated according to loss in ballistic atoms with average kinetic energy $\langle E_A \rangle$

$$P(x) = -\langle E_A \rangle \frac{d\Phi}{dx} dx = \langle E_A \rangle \frac{p\Phi_O}{p_o d_o} \exp - \frac{px}{p_o d_o} dx$$

Performing the integration of the differential equation of the one-dimensional steady-state heat flow:

$$T(x) = -\langle E_A \rangle \Phi_O \frac{p_o d_o}{\kappa p} exp - \frac{px}{p_o d_o} + c_1 x + c_2$$

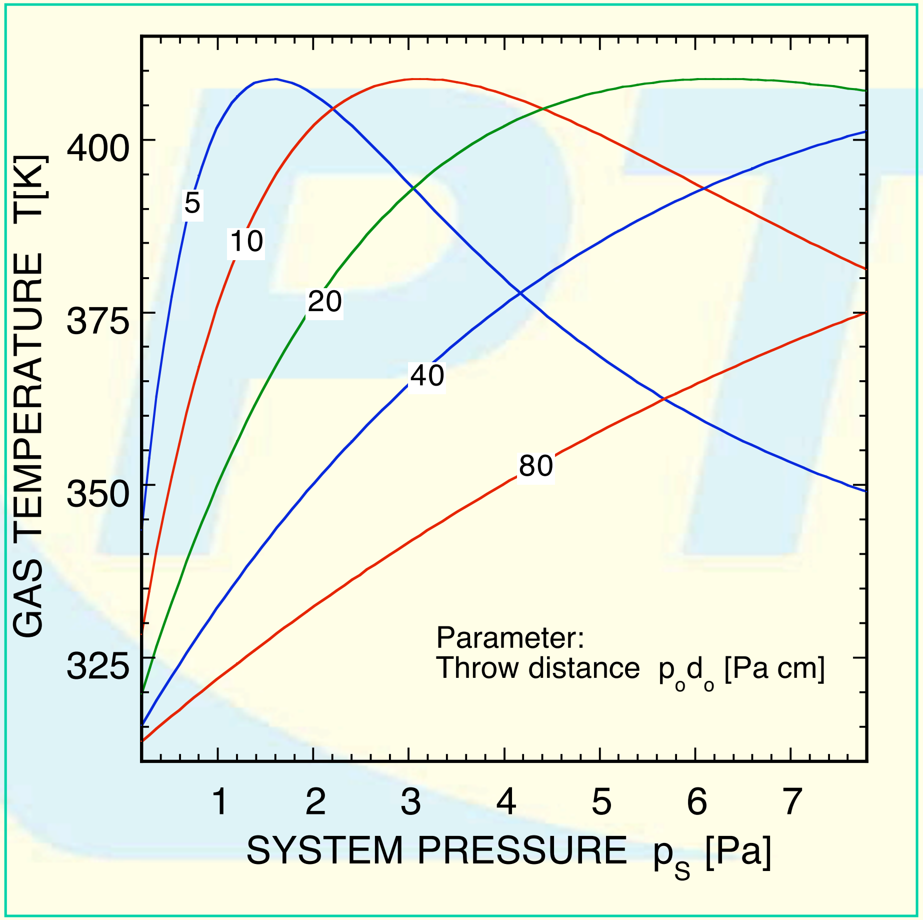
Boundary conditions:
$T=T_T$ (target position, x=0), $T=T_S$ (substrate position $x=d_{ST}$), determination of c_2 and c_1

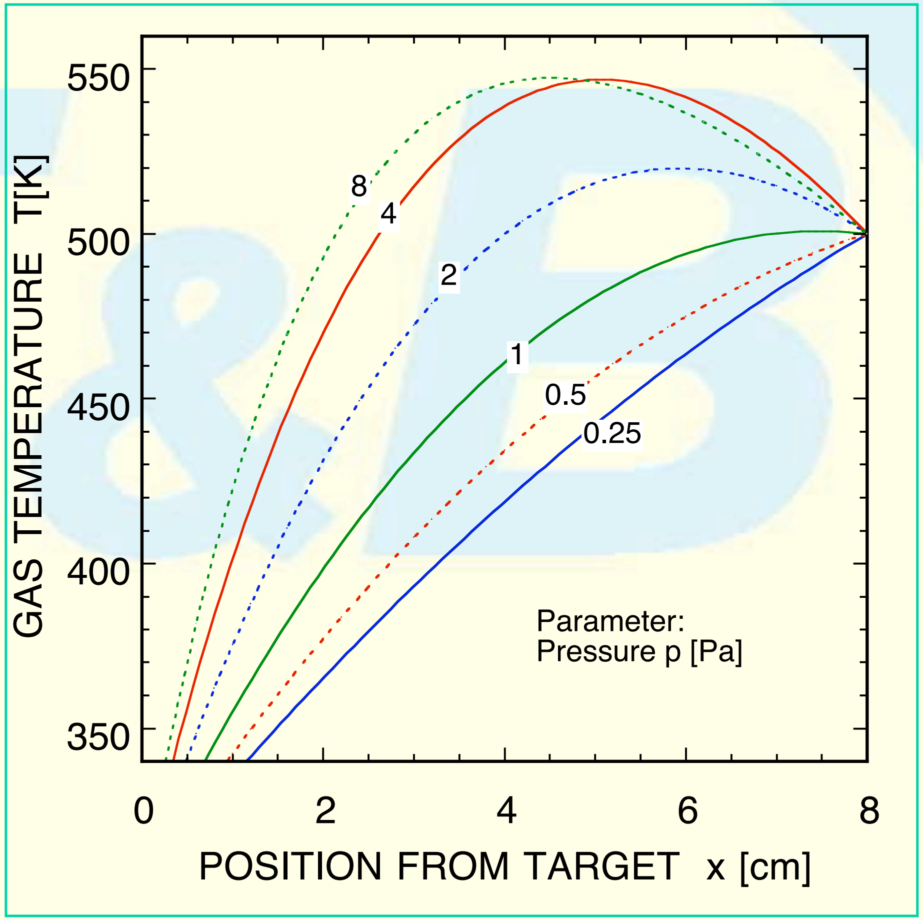
$$c_2 = T_T + \langle E_A \rangle \Phi_O \frac{p_o d_o}{\kappa p}$$

$$c_1 = \frac{1}{d_{ST}} \{ T_S + \langle E_A \rangle \Phi_O \frac{p_o d_o}{\kappa p} \exp - \frac{p d_{ST}}{p_o d_o} - c_2 \}$$

Results of model calculation

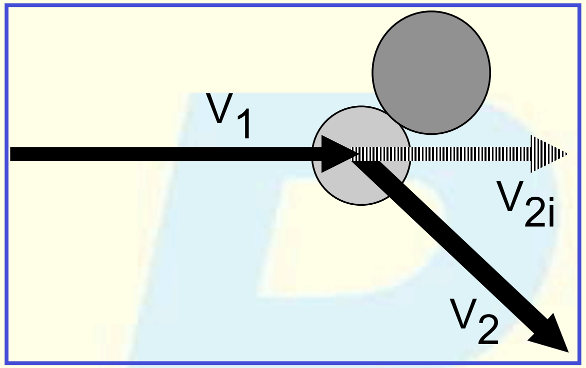
Model parameters: throw distance $p_o d_o$=20 Pa cm, average kinetic energy $\langle E_A \rangle$=10 eV, pressure p=4 Pa, position x=4 cm, atomic flux Φ_0=2 10^{15} atoms s^{-1} cm^{-2}.





The velocity persistence ν (Jeans 1954)

ν - a measure of momentum conservation in initial direction:

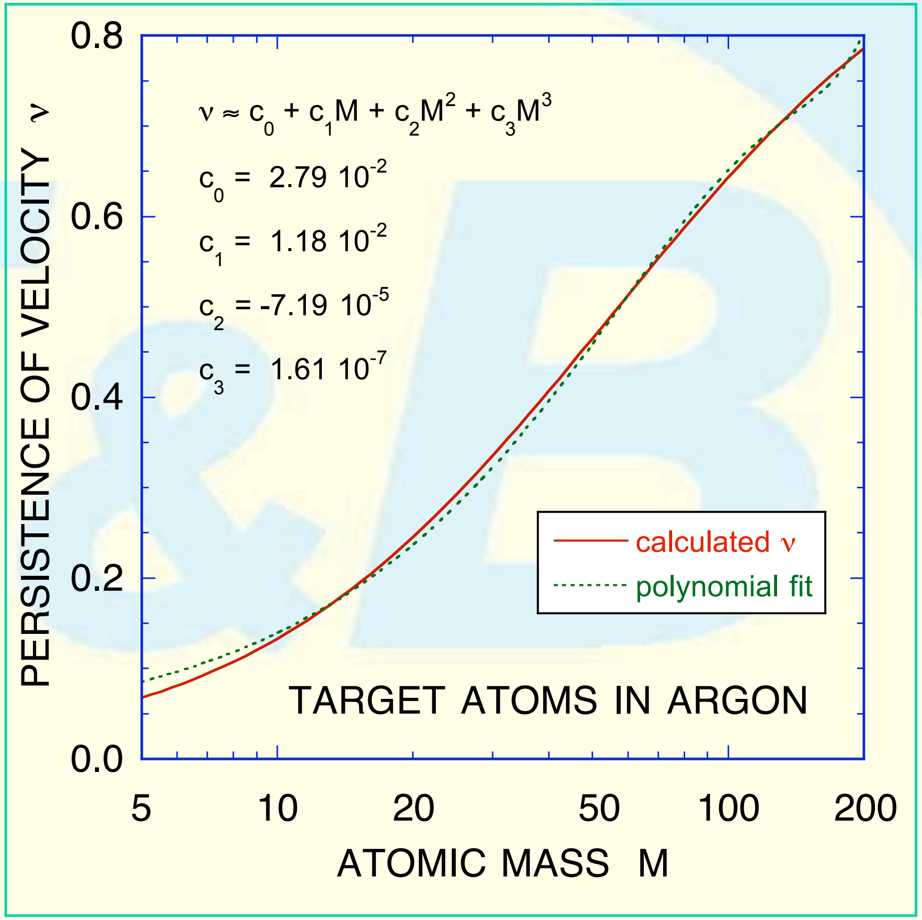


$$\nu = \frac{v_{2i}}{v_1}$$

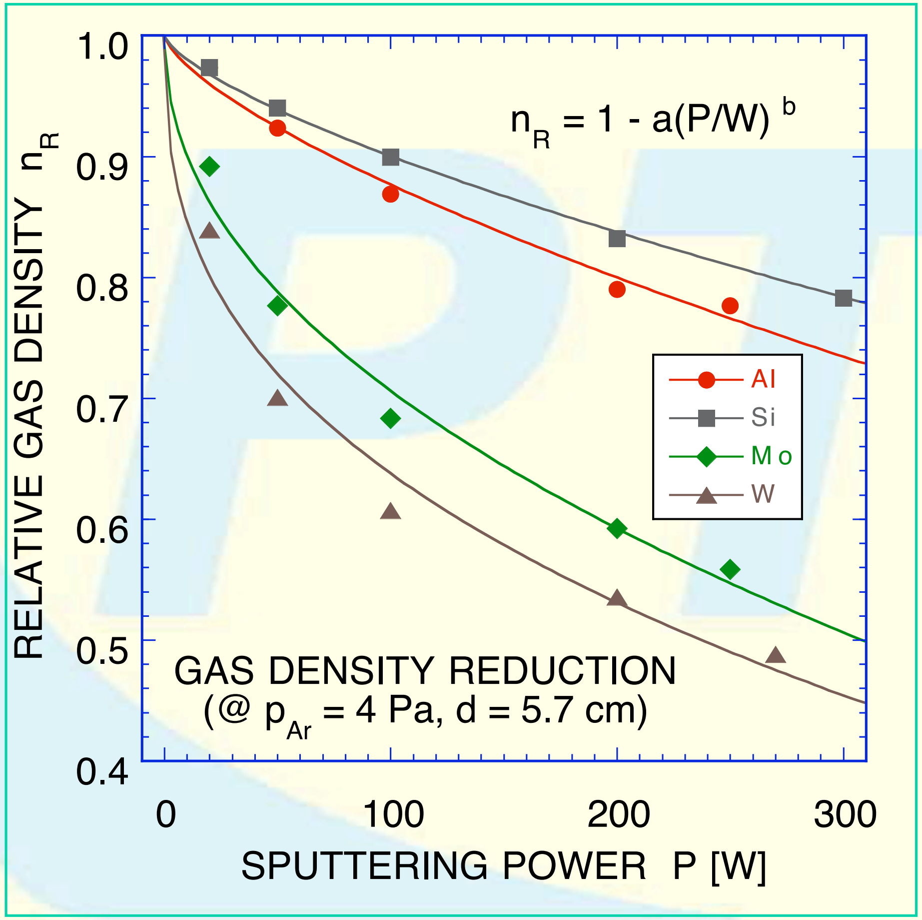
Averaging → analytical expression for ν (sputtered atoms of atomic mass M_S and gas M_G):

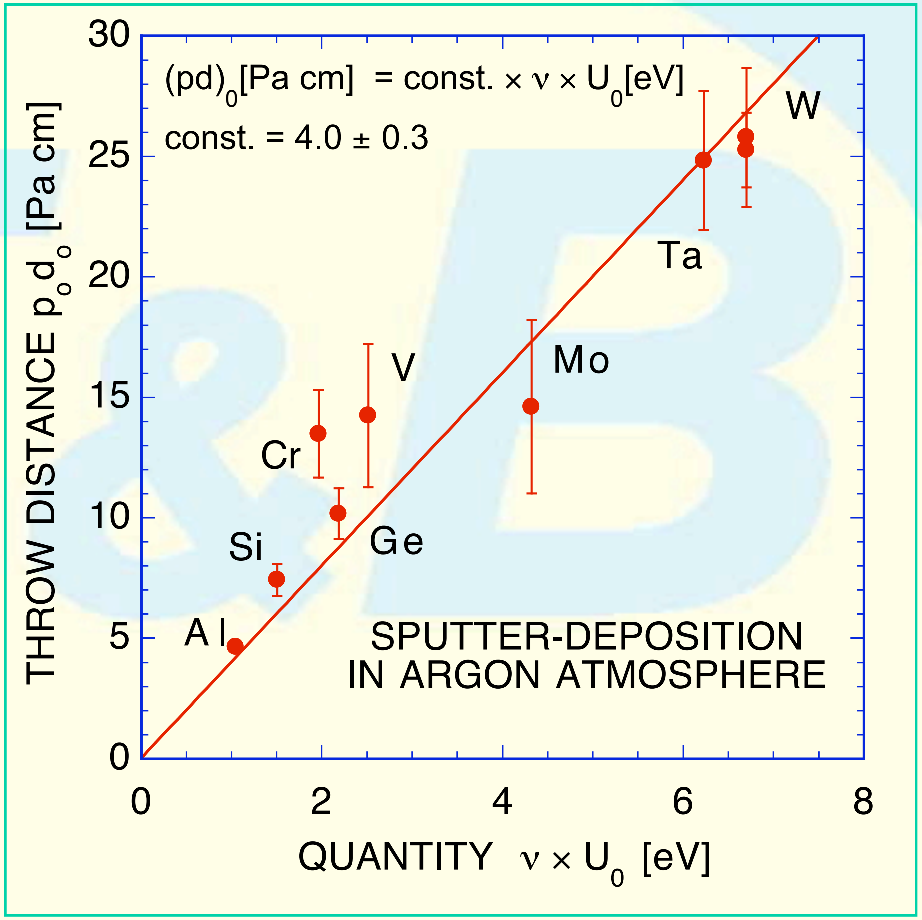
$$\nu = \frac{1-M}{1+M} + \frac{2M}{1+M}\nu_e\,, \quad \nu_e \approx 0.4\,, \quad M = \frac{M_G}{M_S}$$

$$\nu_e = \frac{\ln\left[\sqrt{1+M} + \sqrt{M}\right]}{4\sqrt{M^3(1+M)}} + \frac{2M^4 + 5M^3 + 3M^2 - M - 1}{4M(1+M)^3}$$



Avoiding gas rarefaction, there is a law for the throw distance !





A simple empirical law for the throw distance !

$$\boxed{p_o d_o \left[Pacm\right] = \left(4.0 \pm 0.3\right) \nu\, U_0\left[eV\right]}$$

fairly equivalent to:

$$p_o d_o[\mathrm{Pacm}] = \{-1.9 + 0.96 \ln(M/\mathrm{amu})\}\, U_0[\mathrm{eV}]$$

The heavier and faster sputtered atoms are, the farer they fly!

(That was, what we already felt ☺😐☹😐☺)

Thank you for your patience!