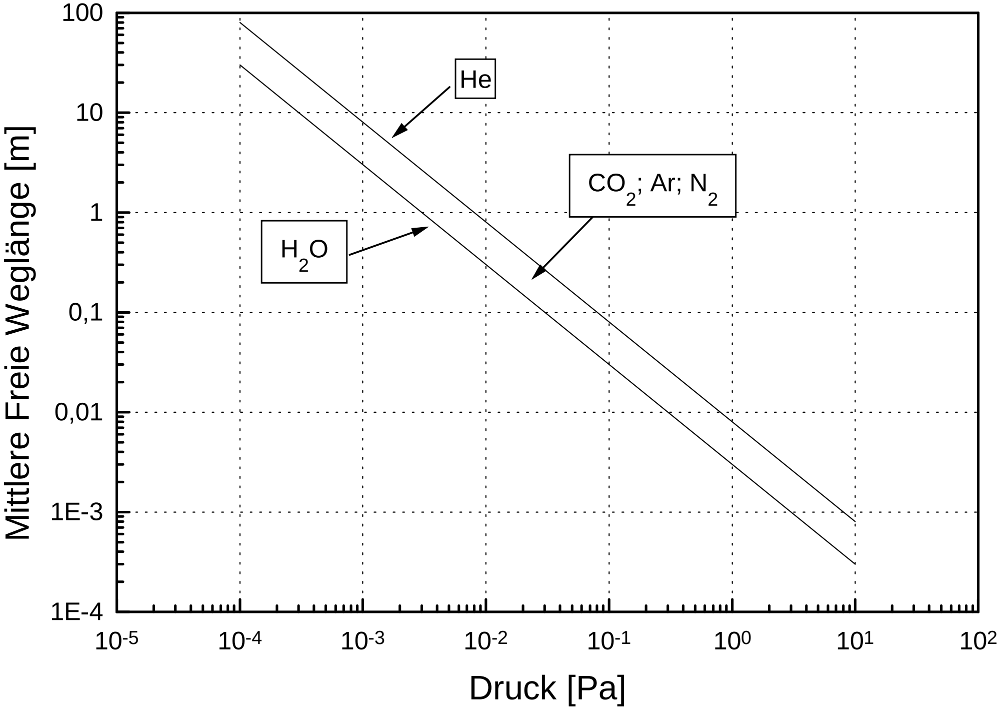
Repetition: Mean Free Path

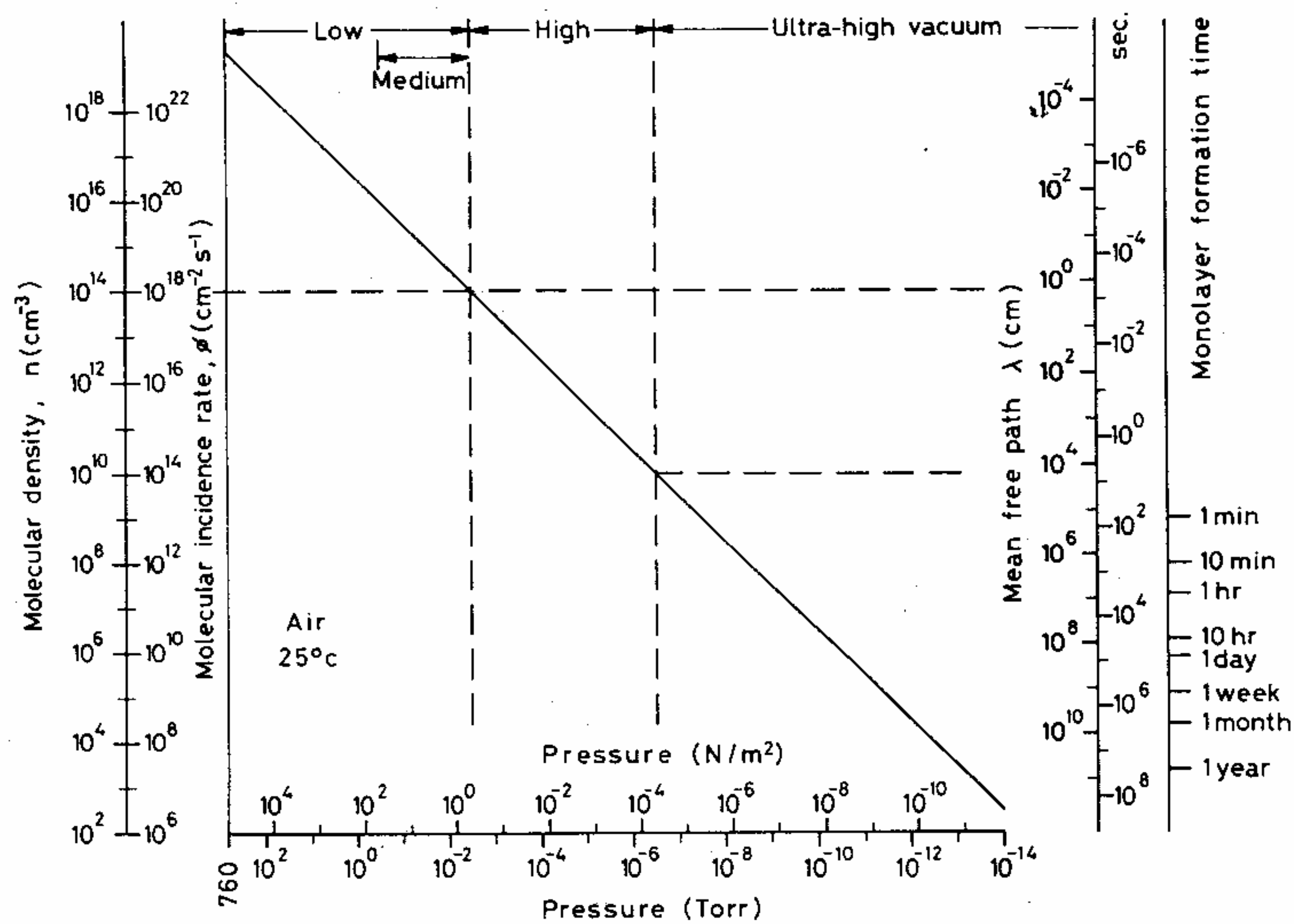
$$\lambda p = 5 \text{mmPa}$$

p = 1 Pa → λ = 5 mm

p = 10^{-4} Pa → λ = 50 m



Repetition: Areal Impingement Rate



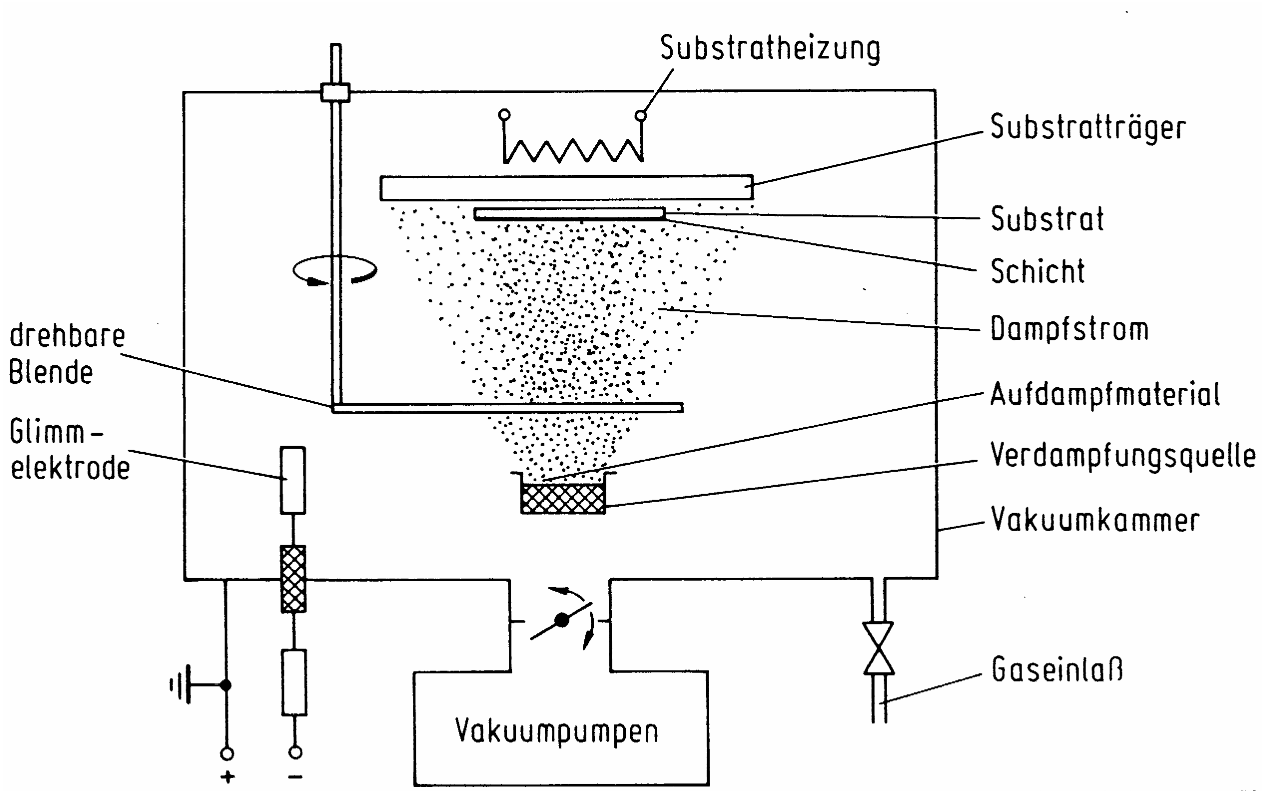
Repetition: Design Criteria

- **Mean free path λ:**
  Influences gas dynamics. Even at rather high pressures (10^{-2} Pa) the mean free path reaches the dimensions of average deposition chambers .

- **Areal impingement rate Z:**
  Crucial for coating purity. The pressure of the background gas has to be at least in the medium high vacuum to guarantee sufficient film purity.

Evaporation

Schematic:



Evaporation Rate: Temperature Dependence

Z = Z(p,T,m)=

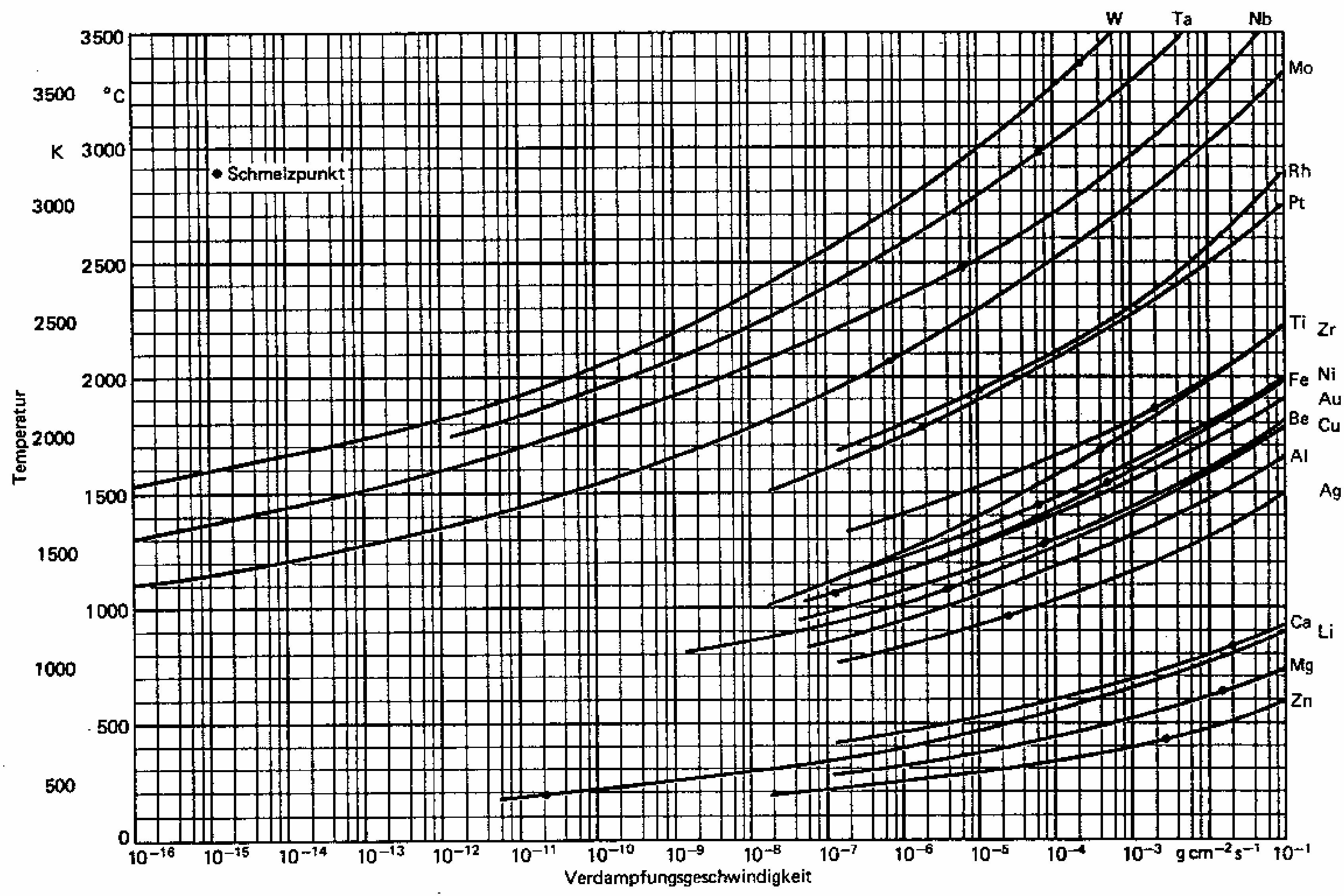
$$= a_V \frac{p^* - p}{m} \sqrt{\frac{m}{2\pi k_B T}}$$

p^* = Temperature dependent vapor pressure of the source material
a_V = Evaporation coefficient

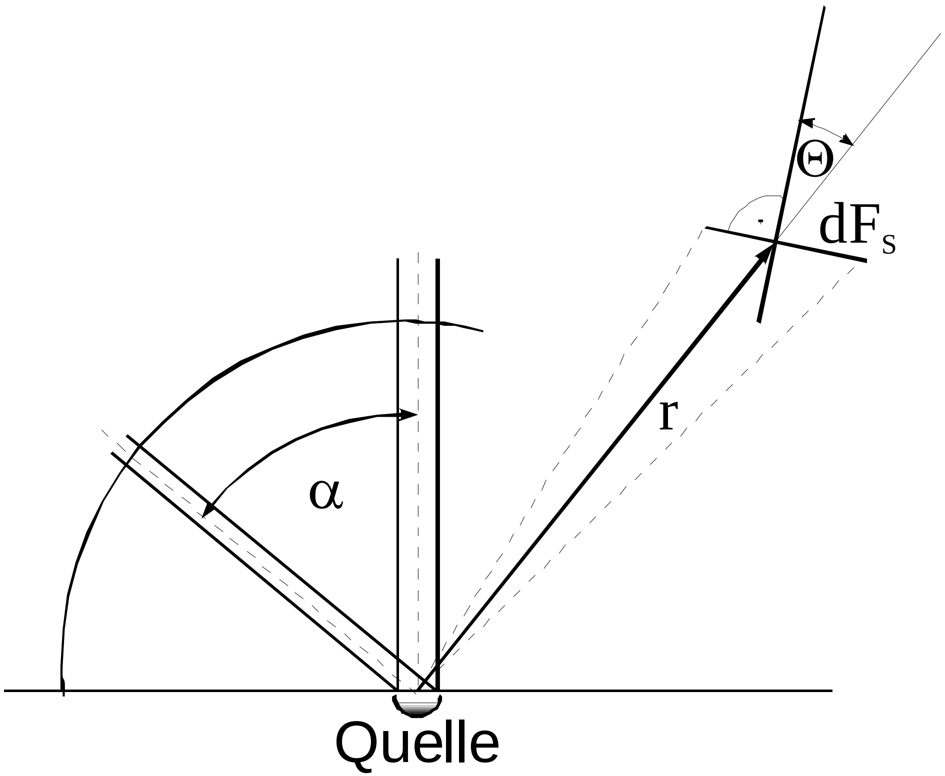
$$p^* = p_0 \exp[-(E_V/(k_B T_Q))]$$

T_Q = Source temperature
p_0 = Reference vapor pressure, e. g. at room temperature (RT)

Evaporation Velocity Curves



Spatial Distribution of Vapor Streams



$$\Phi(\alpha) = \frac{dm}{d\Omega} = \frac{m_1}{\pi} \cdot \cos\alpha$$

Substrate tilt:

$$R(\alpha, \theta, r) = \Phi(\alpha) \cdot \cos\Theta \cdot \frac{1}{r^2}$$

Infinitesimal mass dm emitted into the solid angle:

$$dm = \frac{m_1}{\pi} \cdot \cos\alpha \cdot d\Omega$$

$$d\Omega = \frac{dA}{r^2} = \sin\alpha \cdot d\alpha \cdot d\varphi$$

Normalization:

$$\int_0^{2\cdot\pi} d\varphi \int_0^{\frac{\pi}{2}} \sin\alpha \cdot \cos\alpha \cdot d\alpha =$$

$$= 2 \cdot \pi \cdot \int_0^1 u \cdot du = 2 \cdot \pi \cdot \frac{1}{2} = \pi$$

$$\Rightarrow \int_{d\Omega} dm = m_1$$

Hertz-Knudsen Equation

$$R(\alpha, \theta, r) = \frac{m_1}{\pi} \cdot \cos\alpha \cdot \frac{\cos\Theta}{r^2}$$

Special geometries:

Plane substrate:

$$R(\alpha, \theta, r) = \frac{m_1}{a^2 \cdot \pi} \cdot \cos^4 \alpha$$

Half sphere:

$$R(\alpha, \theta, r) = \frac{m_1}{\pi \cdot a^2} \cdot \cos\alpha$$

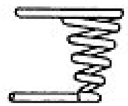
Source in pole (Knudsen-sphere):

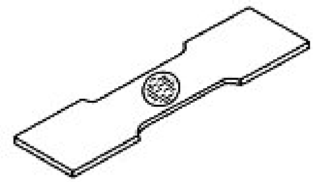
$$R(\alpha, \theta, r) = \frac{m_1}{\pi} \cdot \frac{1}{4 \cdot a^2} = \text{const}$$

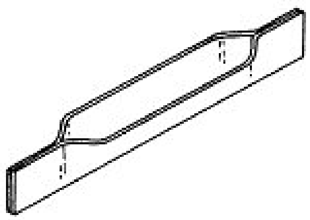
a ... Distance or radius of the respective spheres

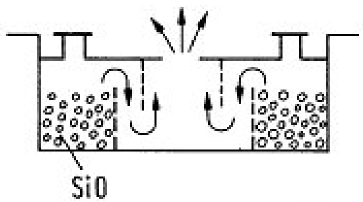
Evaporation Sources

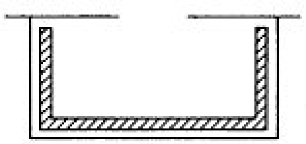
Resistivity heated sources:

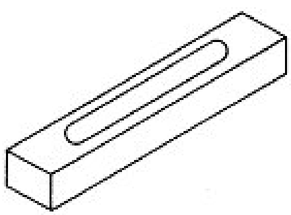


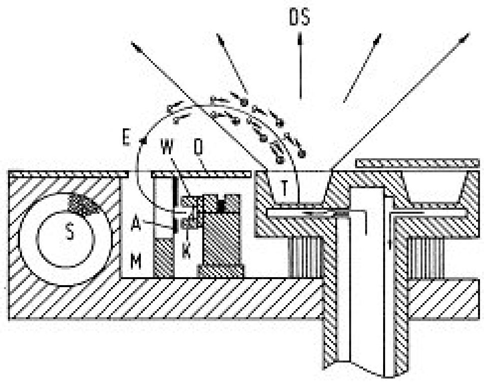












Electron gun

Vapor Pressure in Alloys I

Raoult's law:

Assumption: alloy A/B is ideal solution:

$$W_{AA} = W_{BB} = W_{AB}$$

Statement: vapor pressure of the materials in solution is smaller than in the pure state:

$$p_A^* < p_A$$

*** ... in solution**

Vapor Pressure in Alloys II

Proof of Raoult's law:

$$p_A^* = \int \underbrace{m_A \cdot u_A}_{\text{momentum}} \cdot \underbrace{n_A \cdot u_A \cdot \Phi(u_A) \cdot du_A}_{\text{differential collision rate}}$$

$$p_A = \int n \cdot m_A \cdot u_A \cdot u_A \cdot \Phi(u_A) \cdot du_A$$

$$p_A^* = \frac{n}{n} \int n_A \cdot m_A \cdot u_A^2 \cdot \Phi(u_A) \cdot du_A$$

$$p_A^* = \frac{n_A}{n} \underbrace{\int n \cdot m_A \cdot u_A^2 \cdot \Phi(u_A) \cdot du_A}_{p_A}$$

$$p_A^* = \frac{n_A}{n} \cdot p_A$$

Raoul's law of vapor pressure reduction in solutions

Vapor Pressure in Alloys III

Raoult's law of vapor pressure reduction in ideal solutions:

$$p_A^* = \frac{n_A}{n} \cdot p_A$$

Raoult's law of vapor pressure reduction in non-ideal solutions:

$$p_A^* = f_A \cdot \frac{n_A}{n} \cdot p_A$$

f_A ... coefficient of activity

Evaporation of Alloys - Prerequisites

- **Prerequisite 1:**
  Raoult's law of vapor pressure reduction in solutions is valid. The alloy is assumed to be an ideal solution.

- **Prerequisite 2:**
  The solution is homogenous during the whole duration of the evaporation process. This means that the consitituents are homogenously distributed within the melt. There is no difference in the composition between surface and volume of the melt.

Evaporation of Alloys I

$$\frac{dN}{dA \cdot dt} = \frac{p}{\sqrt{2 \cdot \pi \cdot m \cdot k_B \cdot T}} = R_{evap}[m^{-2} \cdot s^{-1}]$$

$$\frac{dN}{dA} = dn$$

Particles evaporate from the surface only

$$\frac{dn_A}{dt} = \frac{p_A^*}{\sqrt{2 \cdot \pi \cdot m_A \cdot k_B \cdot T}} \qquad p_A^* = \frac{n_A}{n} \cdot p_A$$

$$\frac{dn_B}{dt} = \frac{p_{\mathbf{B}}^*}{\sqrt{2 \cdot \pi \cdot m_B \cdot k_B \cdot T}} \qquad p_B^* = \frac{n_B}{n} \cdot p_B$$

Evaporation of Alloys II

Ratio of the changes of particle numbers in the melt

$$\frac{dn_A}{dn_B} = \underbrace{\frac{p_A}{p_B}\sqrt{\frac{m_B}{m_A}}}_{\kappa} \cdot \frac{n_A}{n_B} = \kappa \cdot \frac{n_A}{n_B}$$

n_A, n_B = Material content of material A, B

p_A, p_B = Vapor pressure of A, B

m_A, m_B = Mass of A, B

κ = Evaporation coefficient

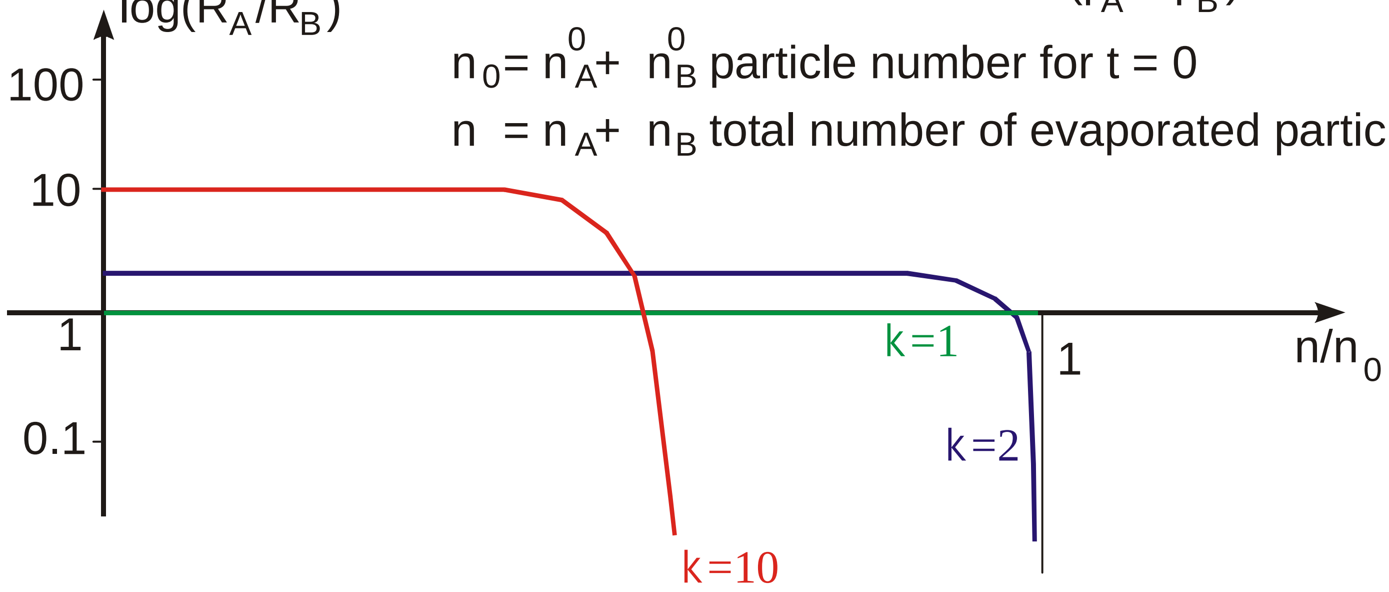
Evaporation of Alloys III

Alloy composition: A:B=1:1

A is the more volatile material ($p_A > p_B$)

$n_0 = n_A^0 + n_B^0$ particle number for t = 0

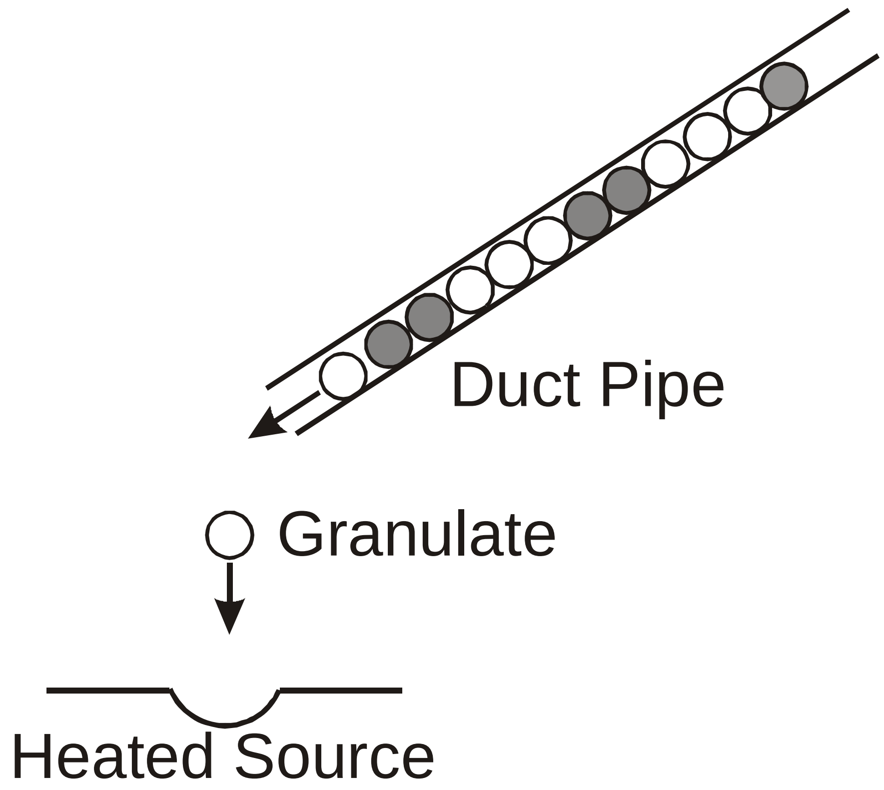
$n = n_A + n_B$ total number of evaporated particles



Evaporation of an alloy corresponds to a fractional destillation. The reason for this is the unhindered material transport within the source.

Special Evaporation Processes

Flash-evaporation



Multi-source-evaporation

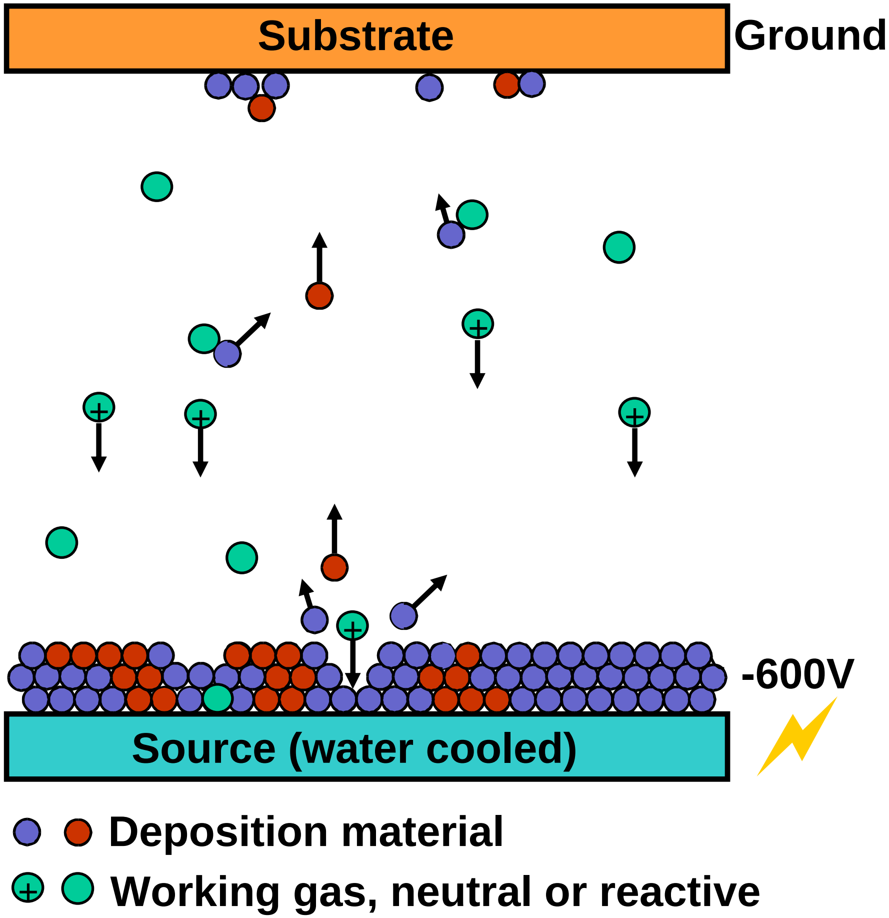
Evaporation Materials

Powders
Granulates
Wires
Pellets
Shape parts

It is important, that the source material and the evaporation material do not chemically react with each other!

Sputtering

Elementary Processes:



Characteristics:

- *Solid source, i. e. arbitrary source geometry*
- *Low deposition temperature*
- *High deposition rates can be reached*
- *Wide parameter field*
- *Coating composition = source composition*
- *Good coating adhesion*
- *Interesting film properties*

Sputtering - Particle Ejection

Projectiles:

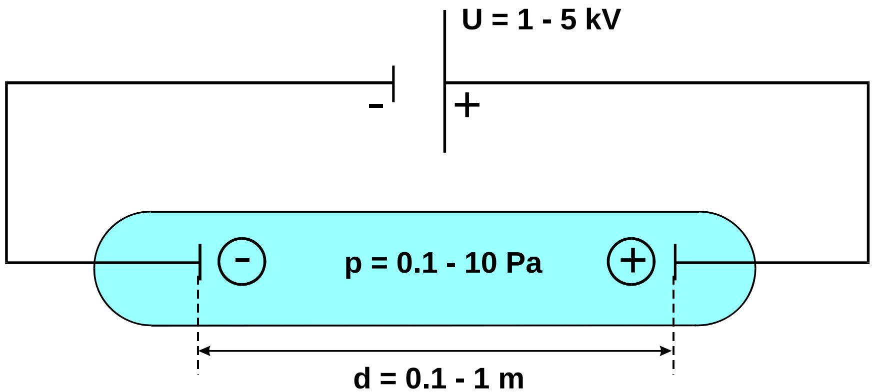
- Gas discharge
- Ion gun

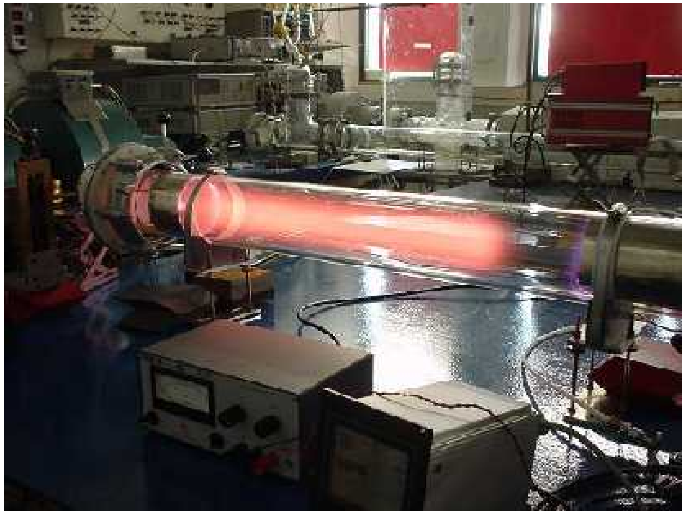
Nature of ejected particles:

- Atoms
- Ions
- Cluster
- Molecules
- Secondary electrons

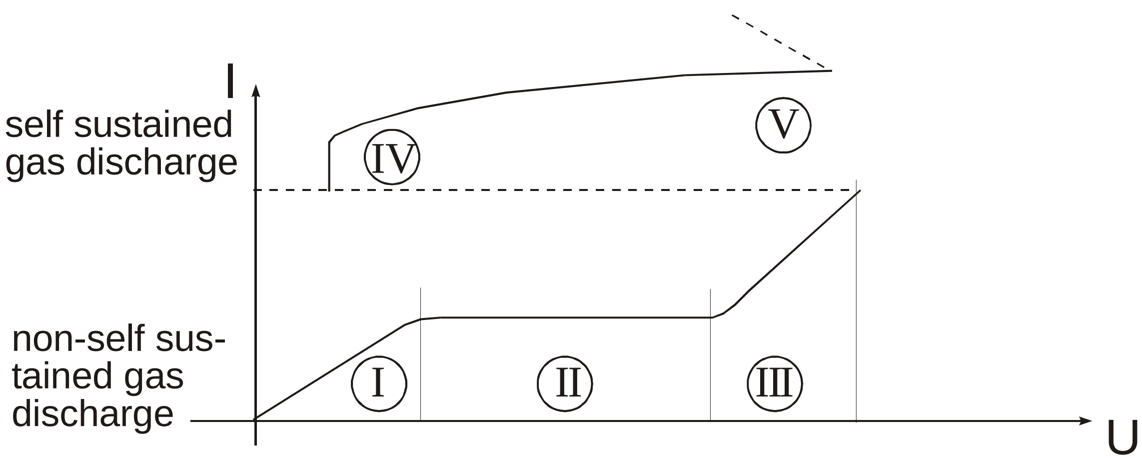
Gas Discharge - Basics

Experimental set-up:





I/V characteristic:



I: Ohmic behavior
II: Saturation region
III: collisional ionization/ Townsend-discharge
IV: normal glow
V: anormal glow secondary electron emission

Gas Discharge (Diode Discharge) - Estimate

Basic mechanism of a gas discharge: electrons in a diluted gas (p = 0.1 – 10 Pa) gain enough energy for collisional ionization of the gas atoms within their mean free path λ by applying a voltage in the kV-region.

Estimate:

p = 1 Pa
E_{ion} = 10 eV = W_{el}
Electrode distance d = 1m

Wanted:
Potential U

$$\lambda_{1Pa} = 5\,\text{mm}$$

$$W_{el} = E \cdot e \cdot \lambda = \frac{U}{d} \cdot e \cdot \lambda$$

$$U = \frac{d \cdot W_{el}}{e \cdot \lambda} = 2\,\text{kV}$$

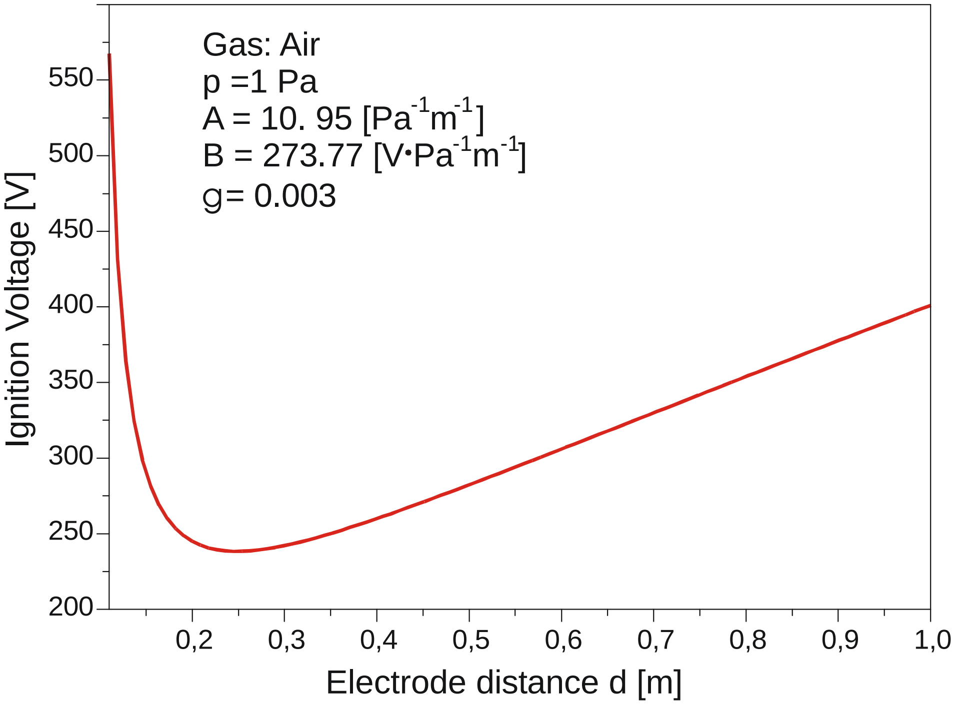
Paschen - Law

The relation between the minimal electrode distance d, the ignition voltage U and the gas pressure p to ignite a gas discharge is given by the Paschen-law:

$$U = \frac{B \cdot p \cdot d}{\ln\left[\frac{A \cdot p \cdot d}{\ln(1/\gamma)}\right]}$$

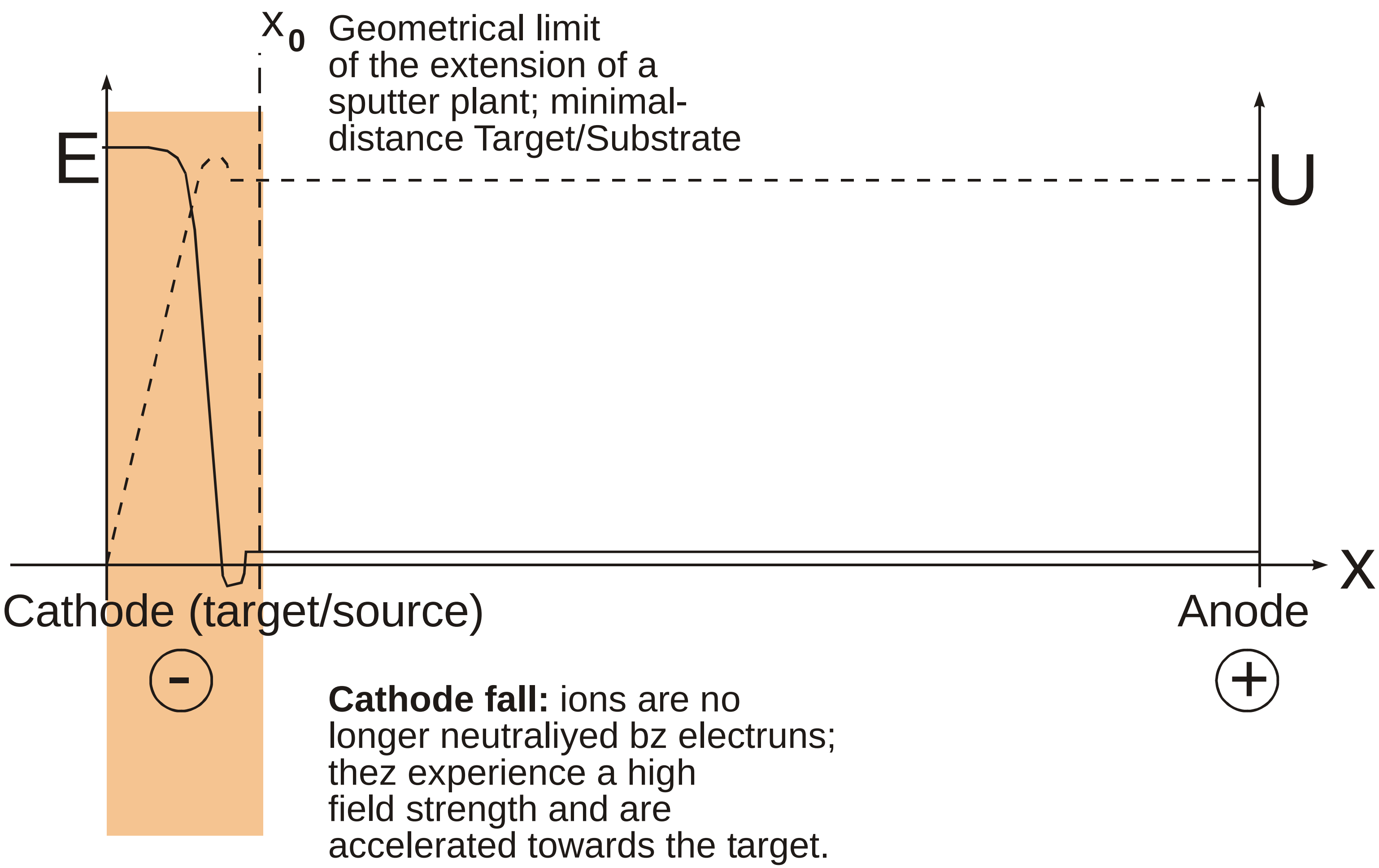
A, B: empirical constants, depending on the gas

γ: Secondary electron emission coefficient



Gas Discharge – Dark Space

Field and potential within the gas column:



Modifications of the Diode Discharge

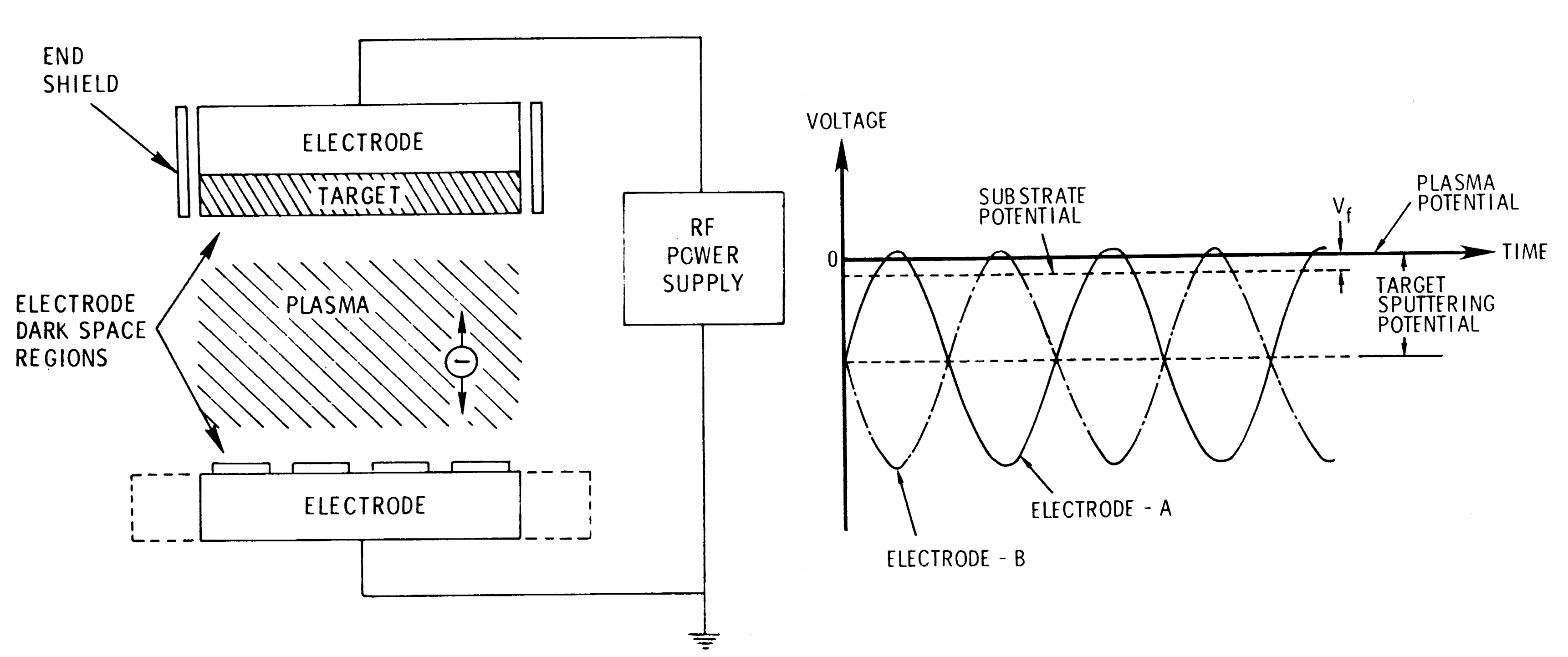
Aims:

a) Minimize the extension of the dark space
b) Increase of the ion current to maximize erosion rate
c) Decrease of the working gas pressure (purity)
d) Extension of the material class (semiconductor/insulator)

Modifications:

- **RF-sputtering:** **c/d**
- **Triode sputtering:** **a-c**
- **Magnetron sputtering:** **a-c**
- **RF-magnetron:** **a-d**
- **Ionen beam sputtering:** **c; possibility to choose ion energy and direction**

Radio Frequency Sputtering (RF-Sputtering) I



f = 13,56 MHz (open industry frequency)

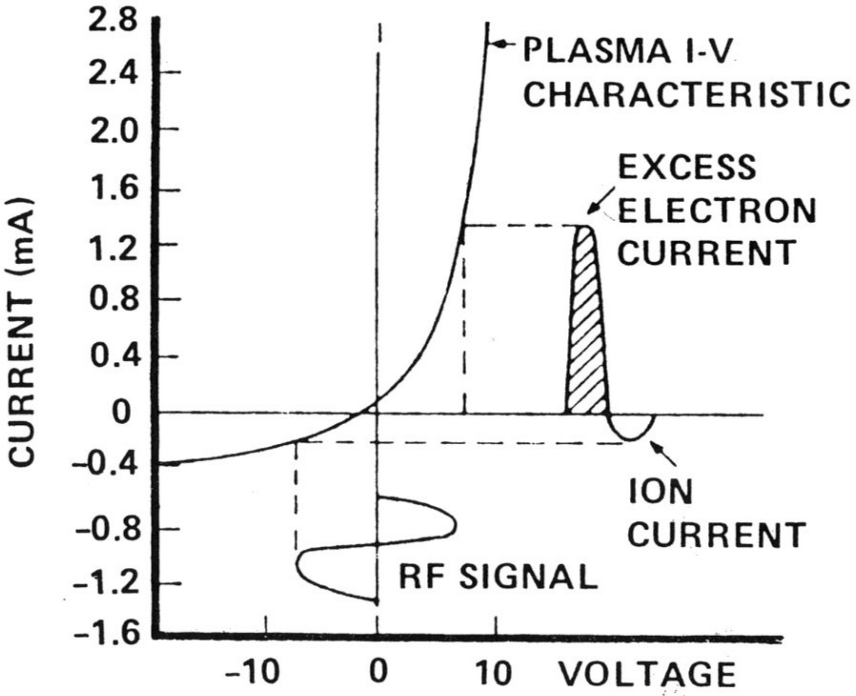
*** Higher electron density**

*** Insulators can be sputtered**

*** Gas pressure can be reduced**

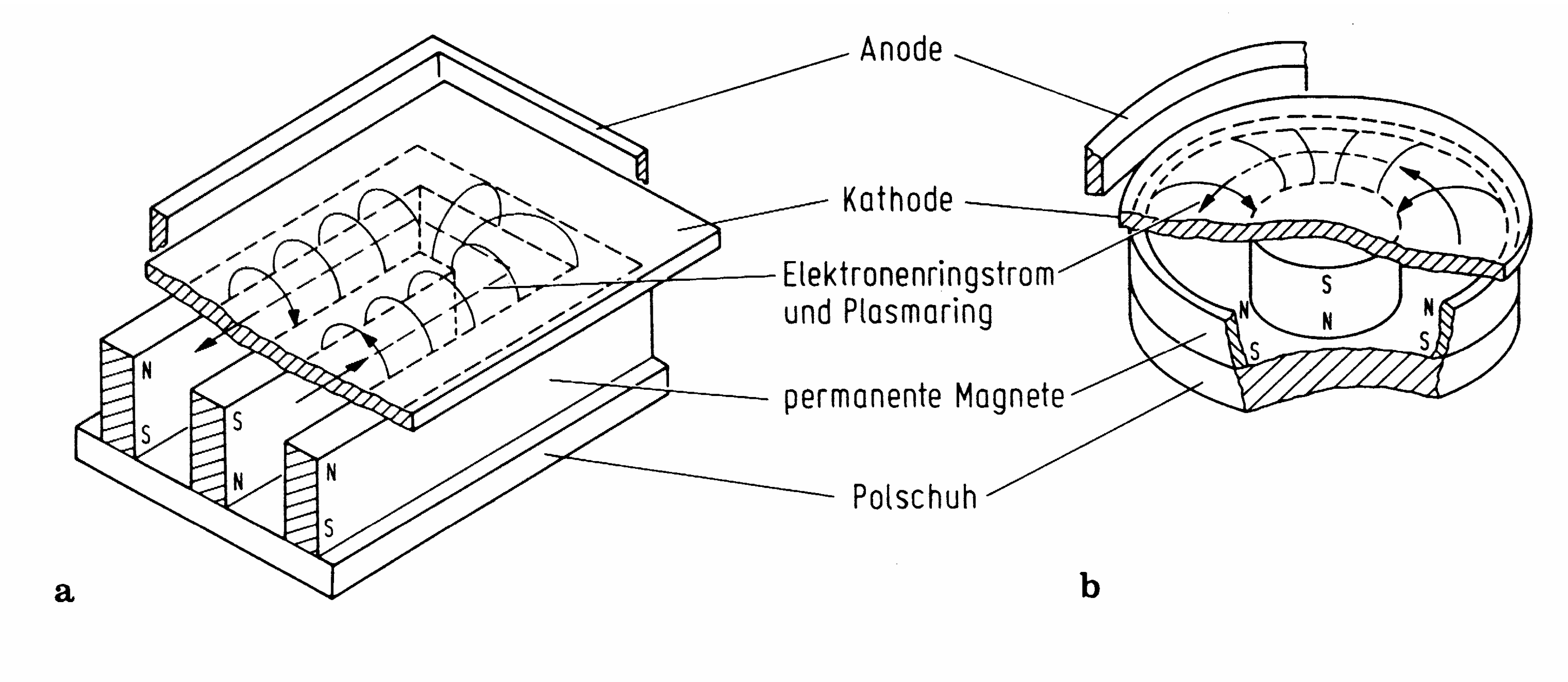
*** Different plasma characteristics (EEDF, Plasma potential)**

Radio Frequency Sputtering (RF-Sputtering) II



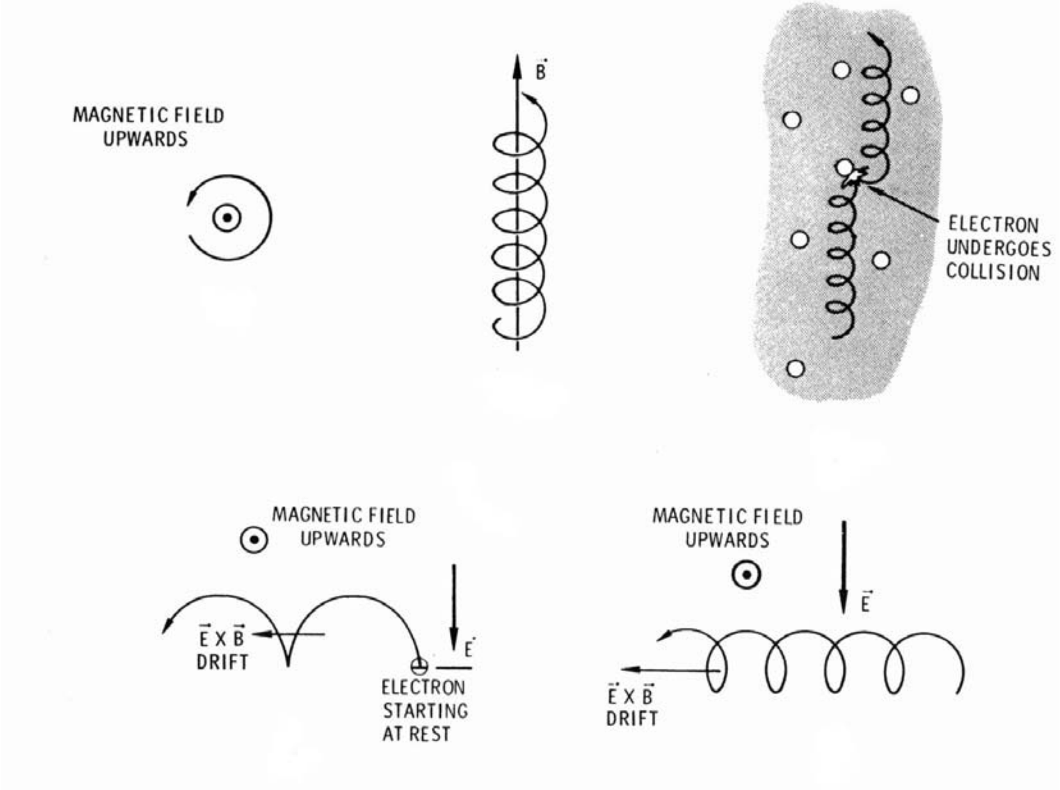
An excess electron current is generated by the higher electron mobility. It leads to a negative net voltage at the target, idependent wether the target is conductive or not.

Magnetron-Sputtering, Basics I



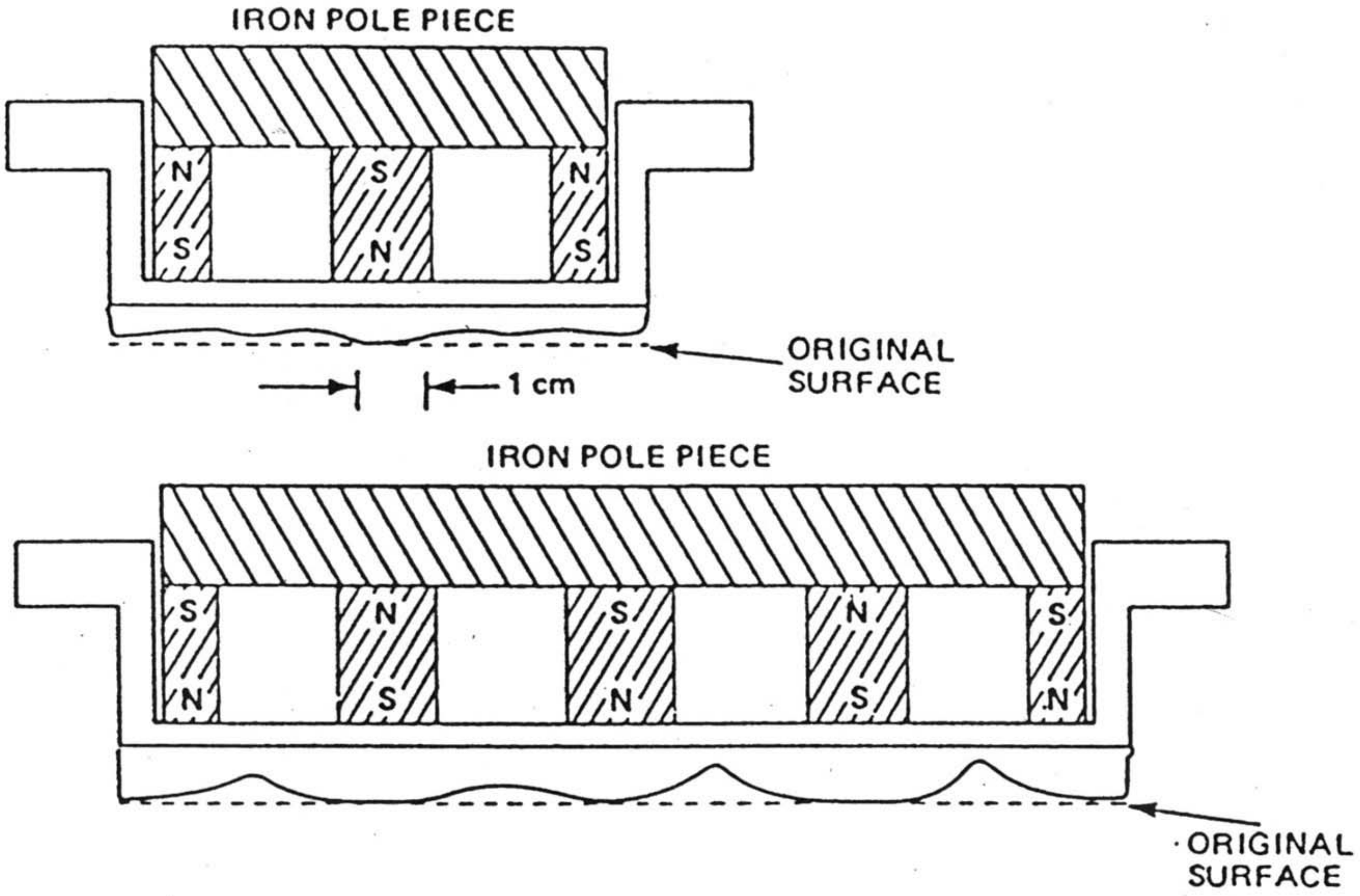
Permanent magnets behind the target concentrate the plasma in the vicinity of the target.
*** Extension of dark space is reduced**
*** Ion density is increased**
*** Gas pressure can be reduced**

Magnetron-Sputtering, Basics II

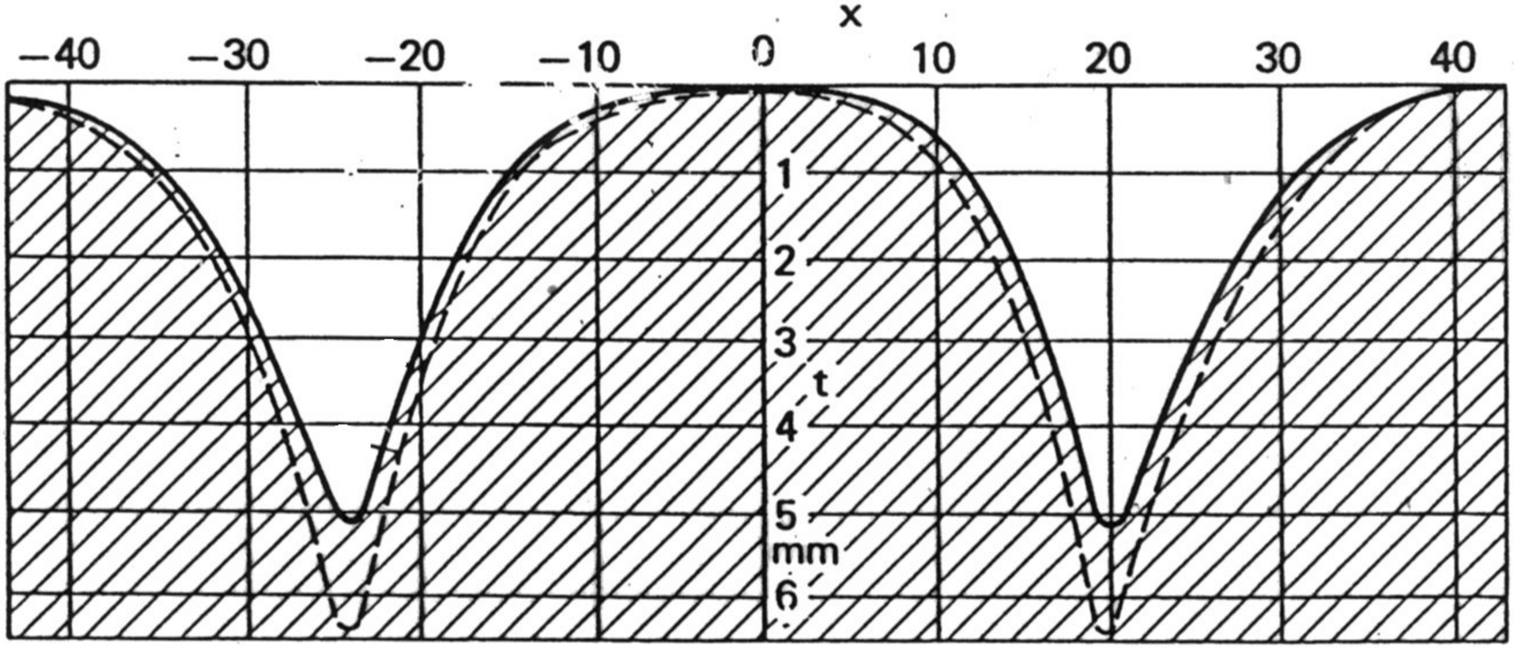


The magnetic field keeps the light electrons on spiral tracks (Lorentz-force) in the vicinity of the cathode. Therefore en electron can trigger a higher number of ionization events near the target.

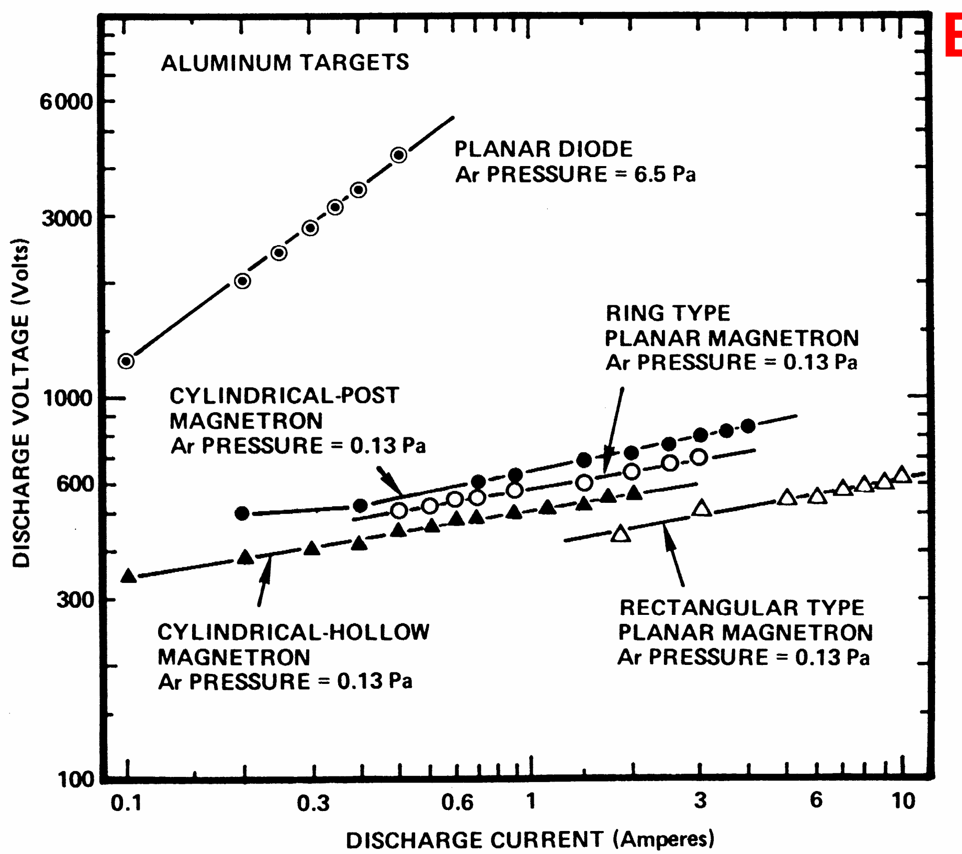
Magnetron-Sputtering: Magnetic Systems



Magnetron-Sputtering: Target Erosion



Magnetron-Sputtering: I/V Characteristics



Empirical correlation:

$$R \propto I(k \cdot \ln U)$$

R = Erosion rate

I = Discharge current

U = Discharge voltage

Magnetron discharges work at significantly lower gas pressures!