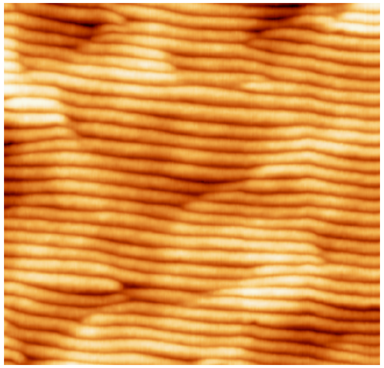
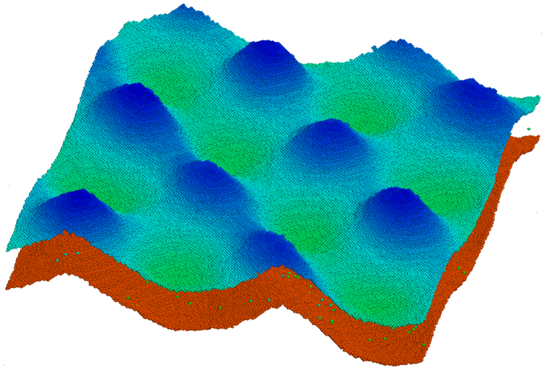
Ioneninduzierte Nanostrukturen
Damage and Sputtering

von Stefan Facsko und Prof. Wolfhard Möller

Institut für Ionenstrahlphysik und Materialforschung
Forschungszentrum Dresden-Rossendorf e.V.





Forschungszentrum Dresden Rossendorf

Overview

- Last lecture
  - Simulation of ion stopping, ion trajectories, and ranges
    a. Molecular Dynamic Simulations: MDRANGE
    b. Monte Carlo Method: TRIM, Crystal-TRIM, TRIDYN

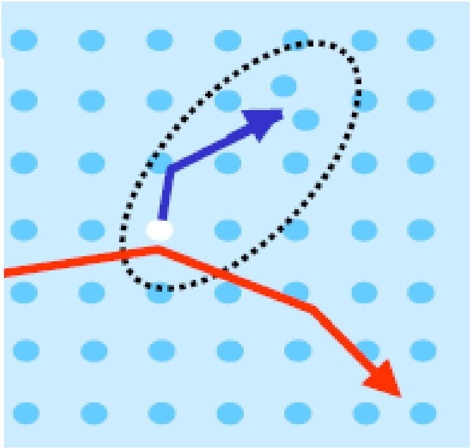
- Today:
  - Radiation Damage
  - Sputtering

Radiation damage

- irradiation of solid with energetic particles (100 eV- 10 GeV) causes all kinds of damage in the material by the deposited energy
- for low energy ions, in the nuclear collisional regime (50 eV – 100 keV), main "damage" is permanent displacements of atoms from their original position and sputtering
- by this, crystalline materials are amorphized in the depth of ion range and eroded
- In the following irradiations at low temperature and low flux are discussed: few K for metals (high diffusivity of defects) or RT up to ~400K for semiconductors

typical replacement collision sequence

"Frenkel pair" is produced when $E_i > U_d$ (displacement threshold)



Radiation damage

- The formation energy of a Frenkel pair is

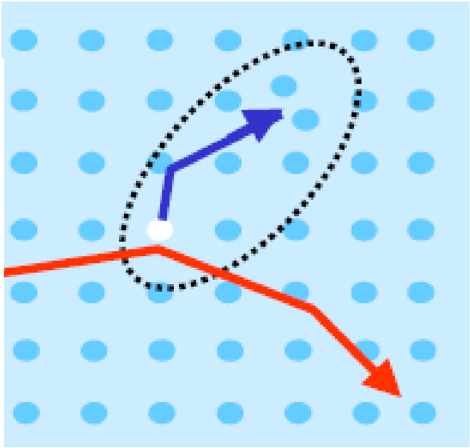
$$U_f = U_{vf} + U_{if}$$

- U_f depends on the direction of the momentum with respect to the crystal
- a range of U_f exists for a target; normally an averaged value is taken

  its value lies between the binding energy and the

  displacement threshold

$$U_b < U_f < U_d$$



U_b ~ few eV

U_f ~ 5-10 eV

U_d ~ 20-80 eV

Binding energy

- The binding energy of an elemental solid can be estimated from his sublimation energy

$$-\Delta H_s = \frac{1}{2} n_c N_A U_b$$

coordination number

Calculation of created damage

Displacement damage function: $N_d(E)$

defined as number of displaced atoms in a cascade produced by an ion of energy E

simplest treatment in the hard-sphere model by ***Kinchin and Pease*** (1955)

Calculation of created damage

Assumptions in the Kinchin Pease model:

for $M_1=M_2$
(recoil collisions)

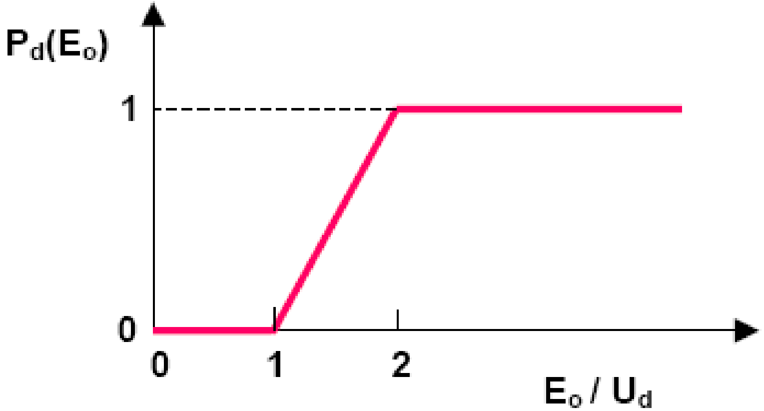
1) Hard Sphere Model: $$P(E,T)dT \cong \frac{dT}{\gamma E} = \frac{dT}{E}$$

2) cascade is created by sequence of two-body nuclear collisions

3) amorphous solid – no effects of crystalline structure

4) probability for a displacement is given by:

$$P_d(E) = \begin{cases} 0 & \text{if } E < U_d \\ \dfrac{E - U_d}{U_d} & \text{if } U_d < E < 2U_d \\ 1 & \text{if } E > 2U_d \end{cases}$$



Calculation of created damage

Total number of created Frenkel pairs by a recoil with energy T:

$$N_F(T) = \int_{U_d}^{T} P(E,T) F_E(T,E) dE$$

recoil density in the collision cascade

Calculating $F_E(T)$ from the Boltzmann transport equation for the hard sphere model one gets the Kinchin Pease formula:

$$N_F(T) = \frac{T}{2U_d}$$

However, corrections have to be made according to the screened Coulomb potential and the threshold for displaments

$$P_d(E) = \begin{cases} 0 & \text{if } E < U_d \\ 1 & \text{if } U_d < T < 2.63U_d \\ 0.38\dfrac{T}{U_d} & \text{else} \end{cases}$$

Calculation of created damage

Total number of created Frenkel pairs by the incident ion with energy E_0:

$$N_F^{tot}(E_0) = \int_{U_d}^{E_0} \frac{dE}{S_{tot}(E)} \int_{U_d}^{\gamma E} N_F(T) \frac{d\sigma_n(E,T)}{dT} dT$$

γ = energy transfer function

in a dense cascade approximation (large nuclear energy deposition):

$$N_F^{tot}(E) = \frac{E}{2U_d}$$

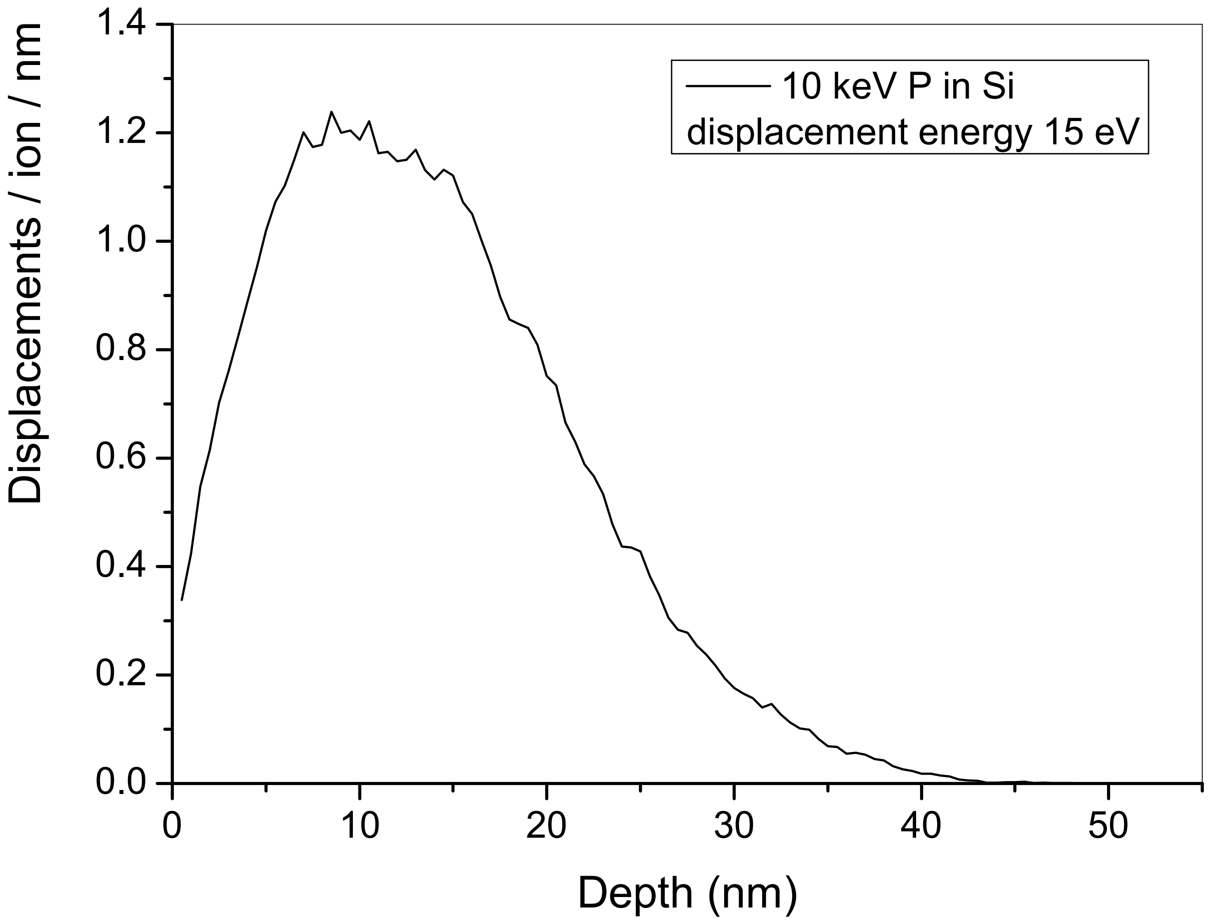
„Kinchin Pease expression“

this is an upper limit, because dynamic annealing will take place
annealing will be highr for denser cascades

$$N_F^{eff}(T) = \xi(T)\frac{T}{2U_d}$$

„cascade efficiency“: lies between 1 and ~0.3

TRIM simulations of created damage



Total number of displacements ~250

Kinchin Pease relation would give around 400 displ.

Depends on displacement energy: therefore, better to use deposited energy
Dynamic annealing effects are neglected

TRIM simulations of created damage

Important value for the created damage in solids by ion irradiation (or general by energetic particles) is the number

displacements **p**er **a**tom

dpa gives the number of displacements each atom of the solid has undergone for an ion beam with fluence *F* [cm^{-2}]

´

ion fluence

$$n_d[dpa] = \frac{N_F F}{\rho N_A / m_A}$$

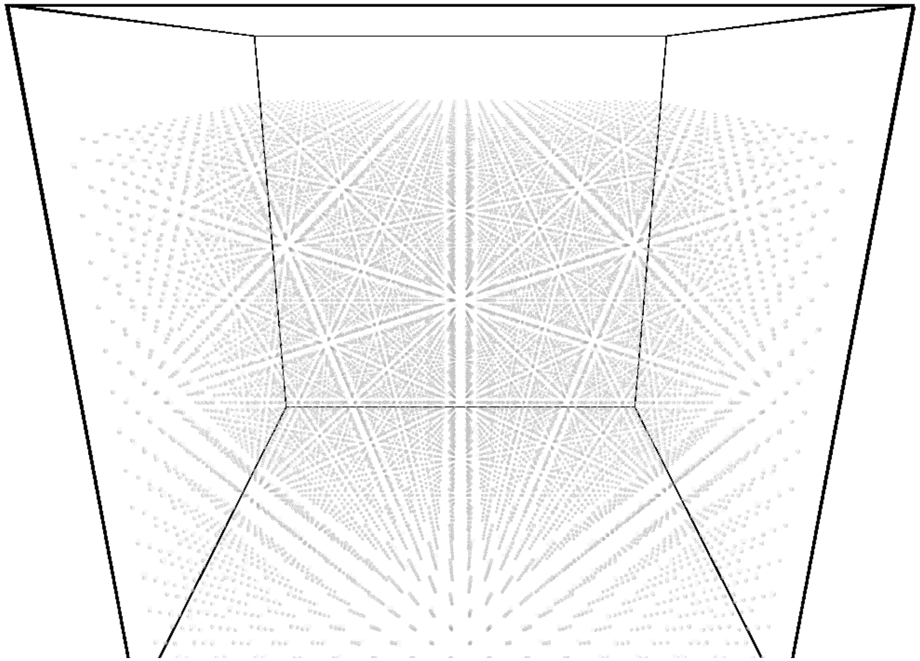
In addtion to the effect of „dynamic annealing" the recombination of Frenkel defects on a larger time scale has to be considered
For this, diffusion of interstitials and vacancies have to be treated

→ „kinetic Monte-Carlo" (kMC) simulations

Single Ion Incident Simulation – full collision cascade (Binary Collision Approximation)

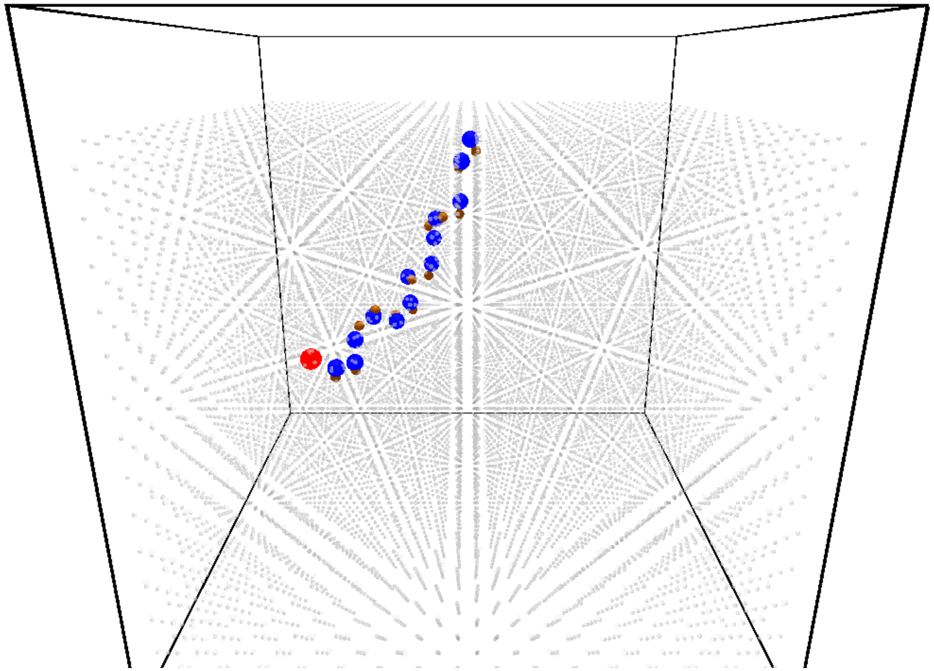
600 eV $Ar^+ \rightarrow$ Si, normal incidence

Phase 1 – Ion Displacement



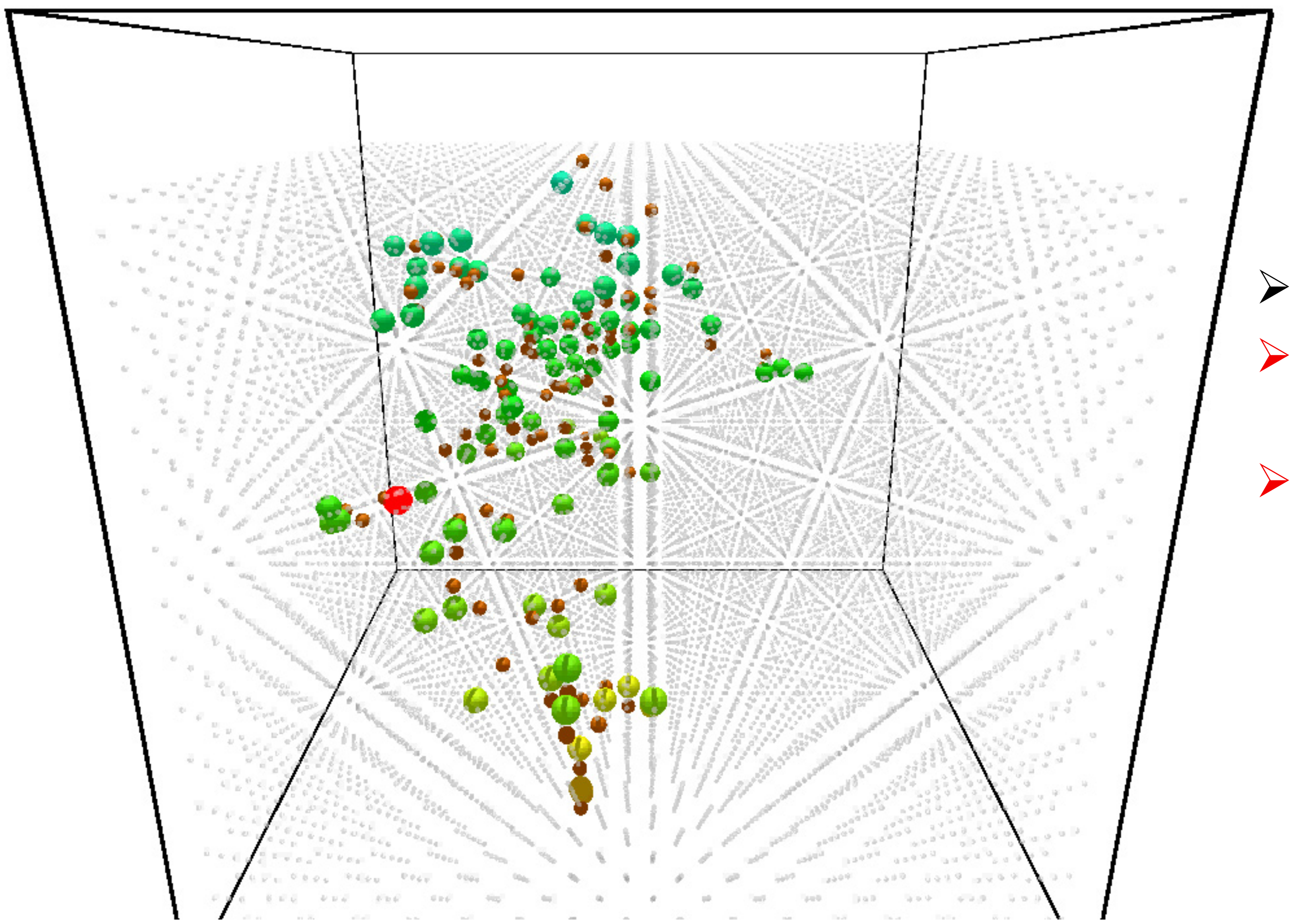
red – **ion (Ar)**
blue – **energetic recoils**
brown – **vacancies**
green – **bulk interstitials**
grey – **lattice atoms (Si)**

Phase 2 –Recoil Displacement



- Sputtering is included

Single Ion Incident Simulation: Thermally Activated Defect Movement (kMC)



red – **ion (Ar)**
brown – **vacancies**
green – **bulk interstitials**
grey – **lattice atoms (Si)**
dark grey – **ad-atoms**

- Defects **Annihilation**
- **Migration** of Interstitials and Vacancies
- **Creation and Diffusion** of Ad-atoms and Surface Vacancies

Sputtering

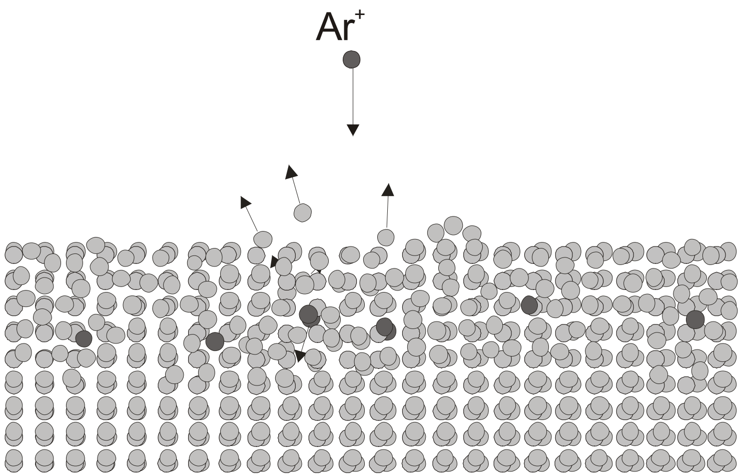
- sputtering is erosion, i.e.the removal of atoms from the surface, by ion irradiation
- dominant effect at low and medium ion energies (100 eV- 1 MeV)
- sputtering changes the implantation profile
- used extensively in industry for material removal, material deposition (ion beam sputter deposition)

sputter yield:

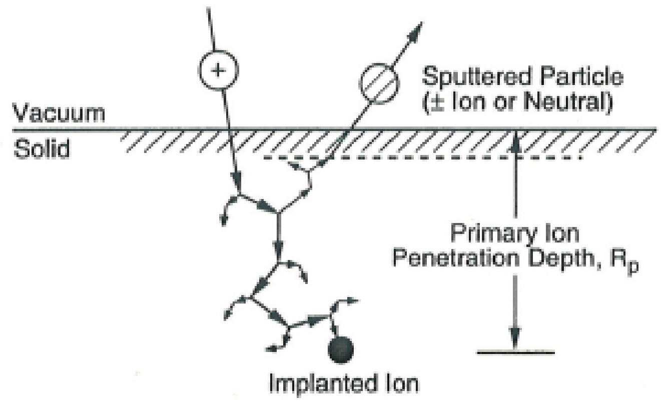
$$Y \equiv \frac{\text{mean number of emitted atoms}}{\text{number of incident particles}}$$

in the energy range of 100 eV – 1 MeV Y ~ 0.3 -20 depending on ion species, ion energy, incidence angle, and target material

Depth of sputtering

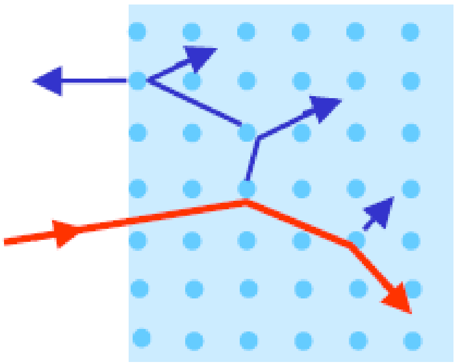


- Firstly the surface is amorphized after a fluence of ~10^{15} cm^{-2}
- around 1 monolayer (ML) is sputtered at this fluence
- ejected atoms are coming from the first atomic ML of the target



Nastasi, Ion-Solid Interactions, Cambridge Solid State Science Series

Sigmund‘s Theory of Sputtering



- for single-element material sputtering yields can be predicted in the linear cascade regime
- the sputter yield is proportional to the number of recoil atoms moving towards the surface
- Sigmund demonstrated with Boltzmann‘s transport equation that in the linear cascade regime the number of recoils is proportional to the energy deposited per unit depth in nuclear energy loss $F_D(E_0, \theta, z)$

$$Y = \Lambda F_D(E_0, \theta, 0) \qquad \text{with} \qquad \Lambda \text{ a material factor}$$

□ Λ contains all material parameters including surface binding energy

$$F_D(E_0, \theta, 0) = \alpha N S_n(E_0)$$

correction factor

atomic density

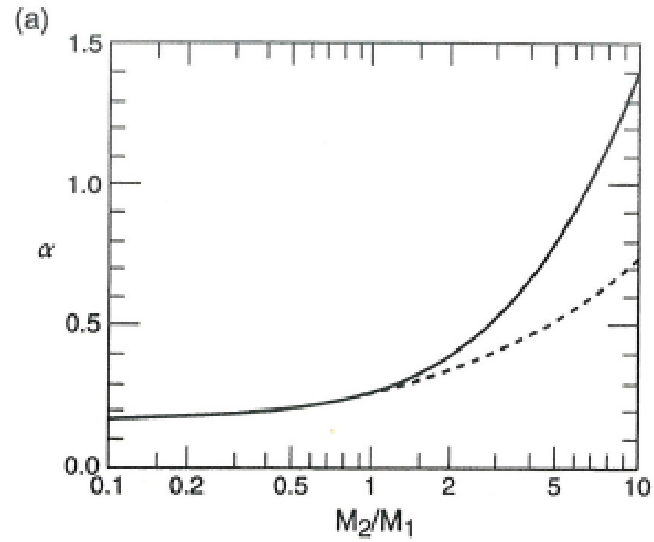
nuclear stopping power

Sigmund's Theory of Sputtering

- correction factor α is a dimensionless function of incidence angle θ and mass ratio M_2/M_1

- for $M_2/M_1<0.5$, α is constant and ~0.2
  rises strongly for $M_2/M_1>0.5$
  approximation for the regime: $0.5 < M_2/M_1 < 10$

$$\alpha = 0.3(M_2 / M_1)^{2/3}$$



- increase of α with M_2/M_1 is due to rising importance of large-angle scattering events

- α also increases strongly with incidence angle θ

Sigmund's Theory of Sputtering

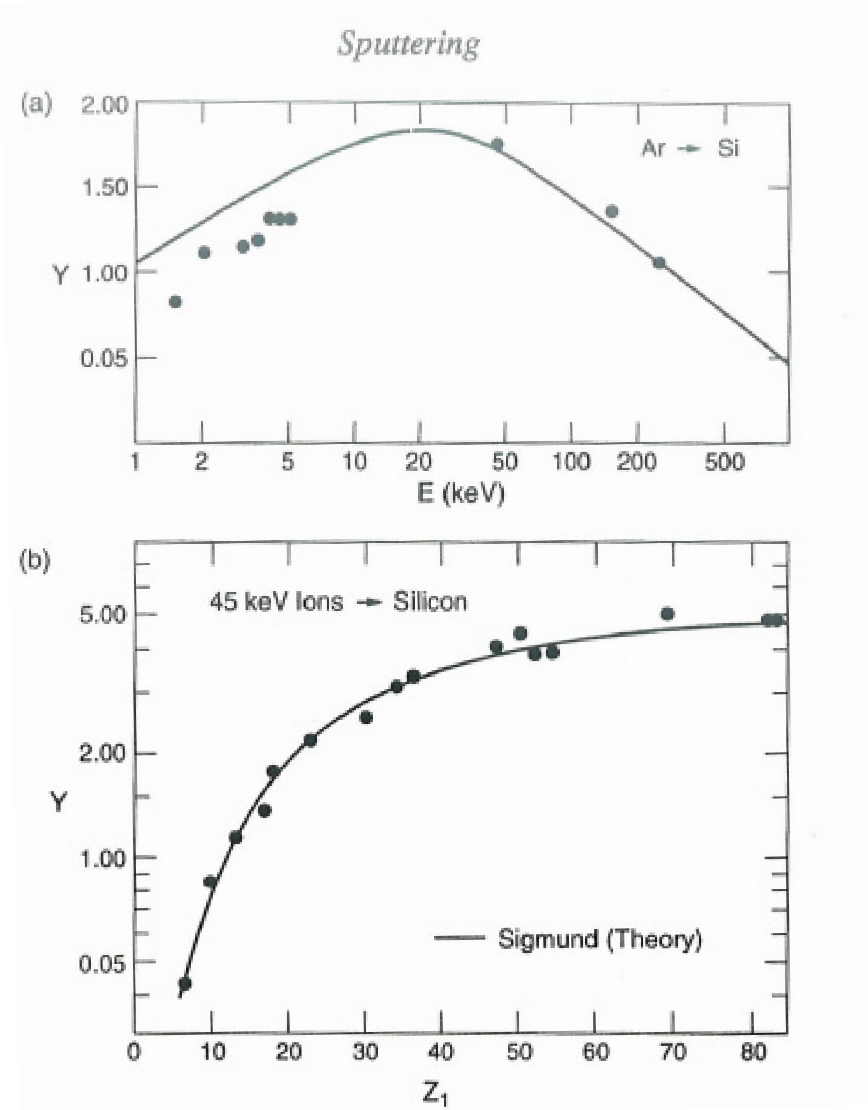
• recoils can only be ejected when they have an energy higher than the surface binding energy
• one can assume a planar surface barrier U:

$$P(E_r,\theta_r) = \begin{cases} 1, & E_r \cos^2\theta_r \geq U \\ 0, & E_r \cos^2\theta_r < U \end{cases}$$

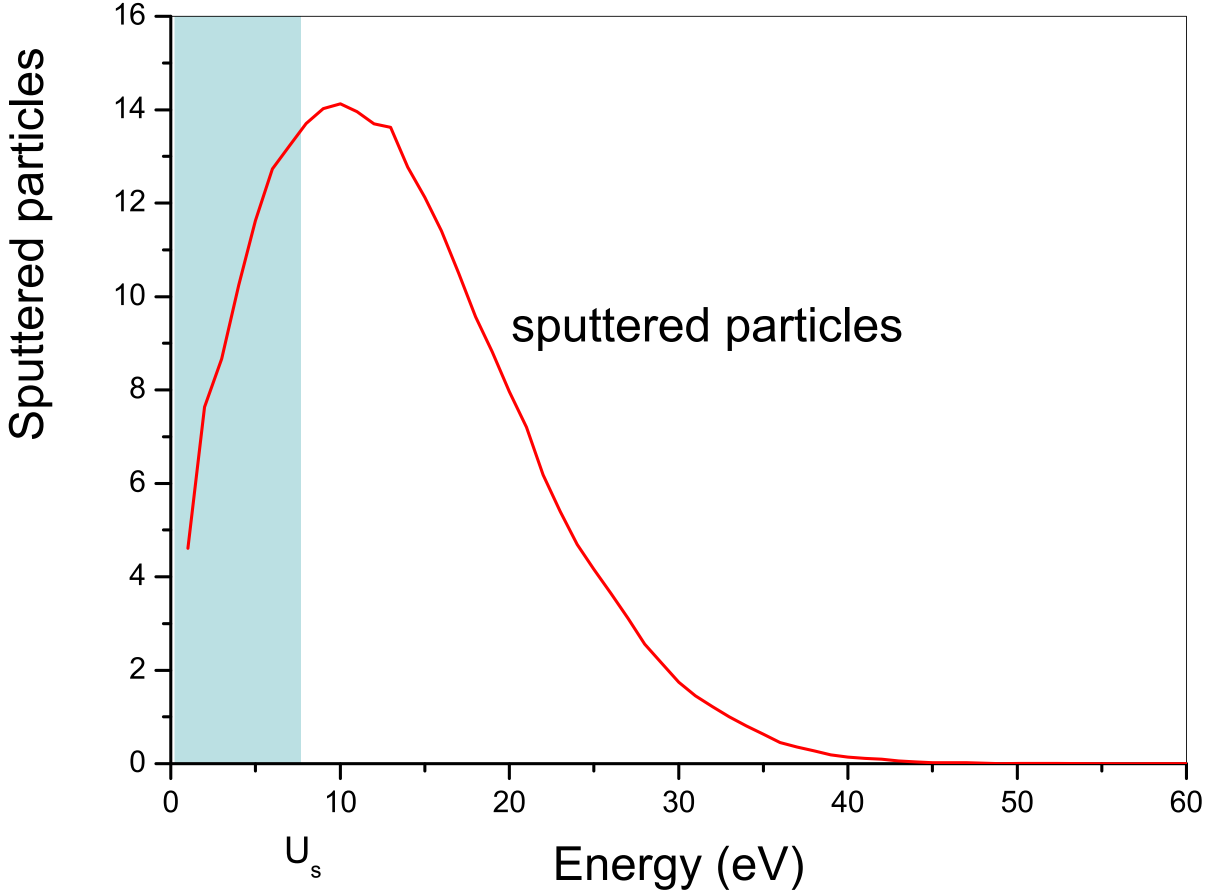
• taking the nuclear stopping with the potential function V(r)~r$^{-1/m}$ (e.g. m=1/2)

$$\Lambda = \frac{\Gamma_m}{8(1-2m)} \frac{1}{NC_m U^{1-2m}}$$

$$Y = \frac{\Gamma_m}{8(1-2m)} \frac{\alpha N S_n(E_0,\theta,0)}{NC_m U^{1-2m}}$$



Sputtering



Only those particles are sputtered which escape the barrier U_s

Sigmund's Theory of Sputtering

- for low energy recoils E_r~U, Sigmund proposed m=0

$$\Lambda = \frac{3}{4\pi^2}\frac{1}{NC_0U} \qquad \text{with} \qquad C_0 = 0.0181\,\mathrm{nm}^2$$

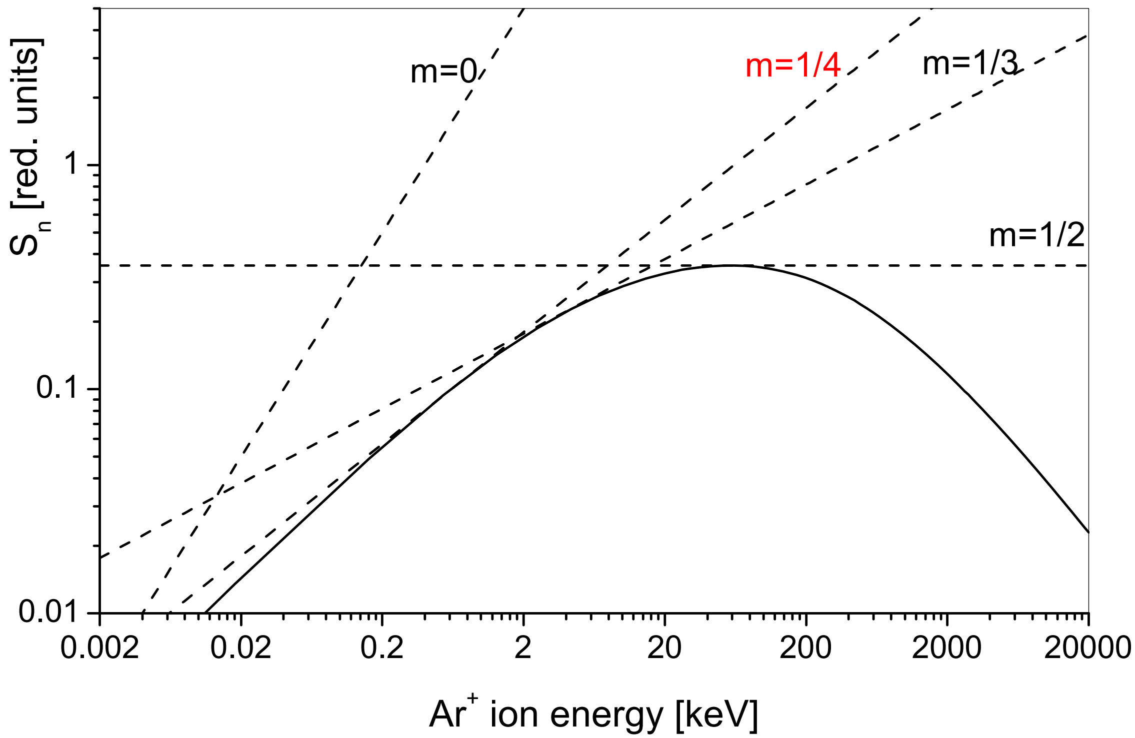
Total sputtering yield:

$$Y(E,\theta) = 0.042\frac{\alpha S_n(E)}{U}$$

Differential yield of sputtered atoms of energy E_0 into the solid angle Ω_0 around the emission angle θ_0

$$\frac{d^3Y}{dE_0 d^2\Omega_0} = F_D(E,\theta,0)\frac{\Gamma_m}{4\pi}\frac{1-m}{NC_m}\frac{E_0}{(E_0+U)^{3-2m}}\cos\theta_0$$

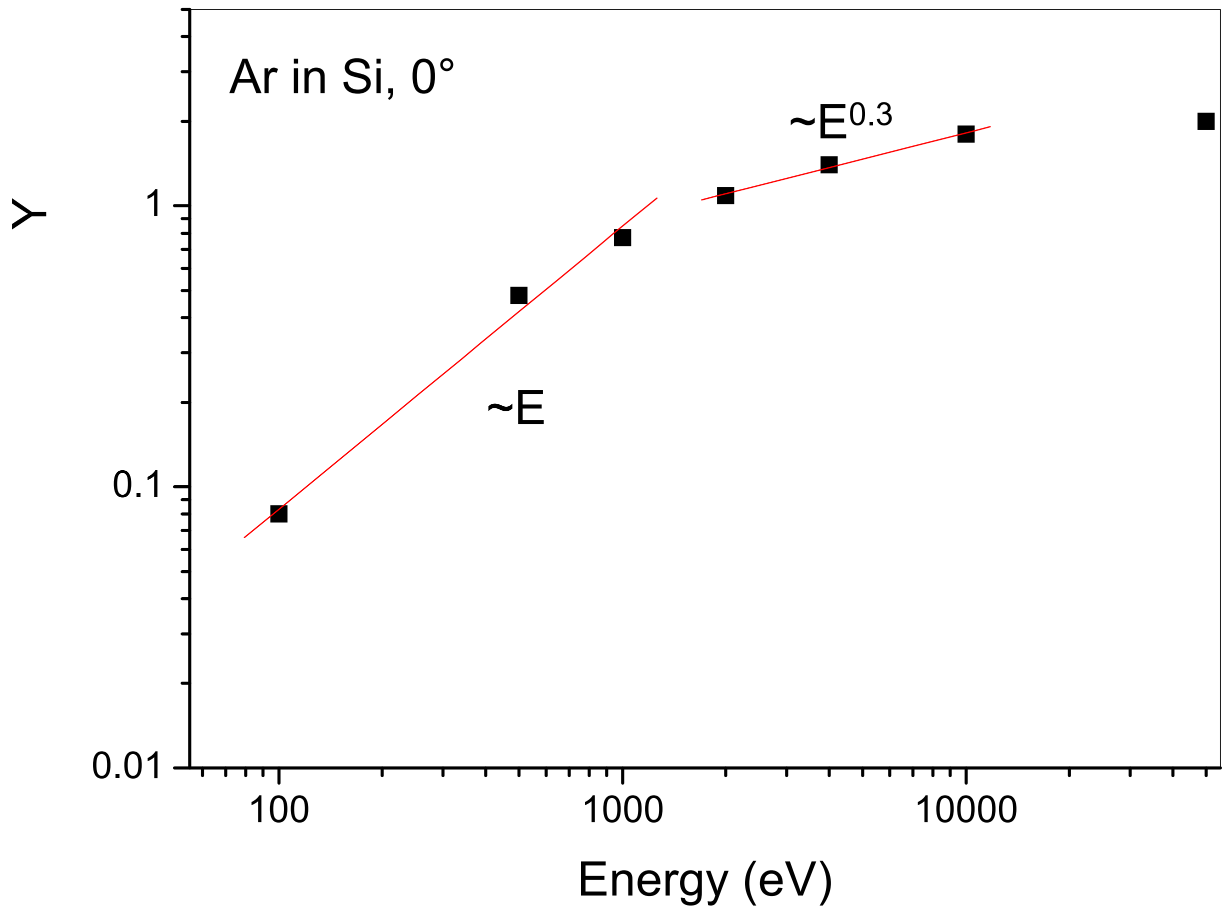
Energy dependence of sputter yield



$$S_n(E) \sim E^{1-2m}$$

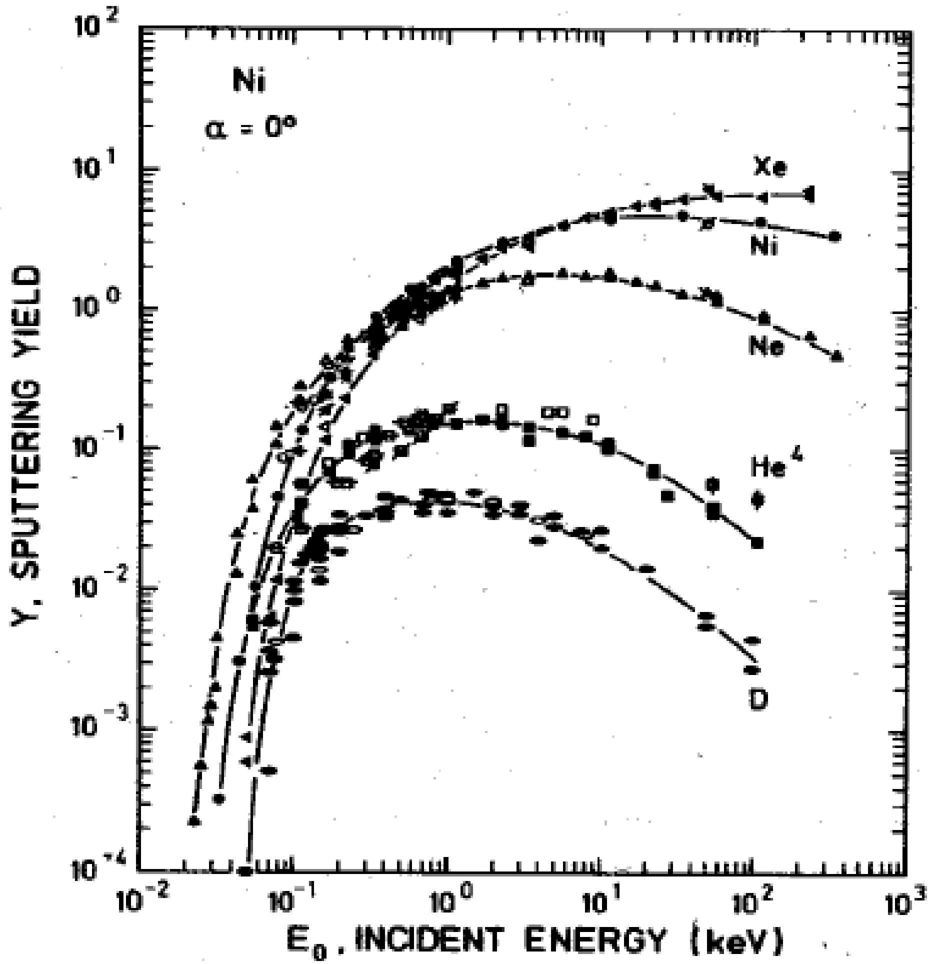
- Nuclear stopping power: Ar^+ in GaSb
- Regime of 200 – 2000 eV is approximated by a power law with m=1/4

Energy dependence of sputter yield: TRIM



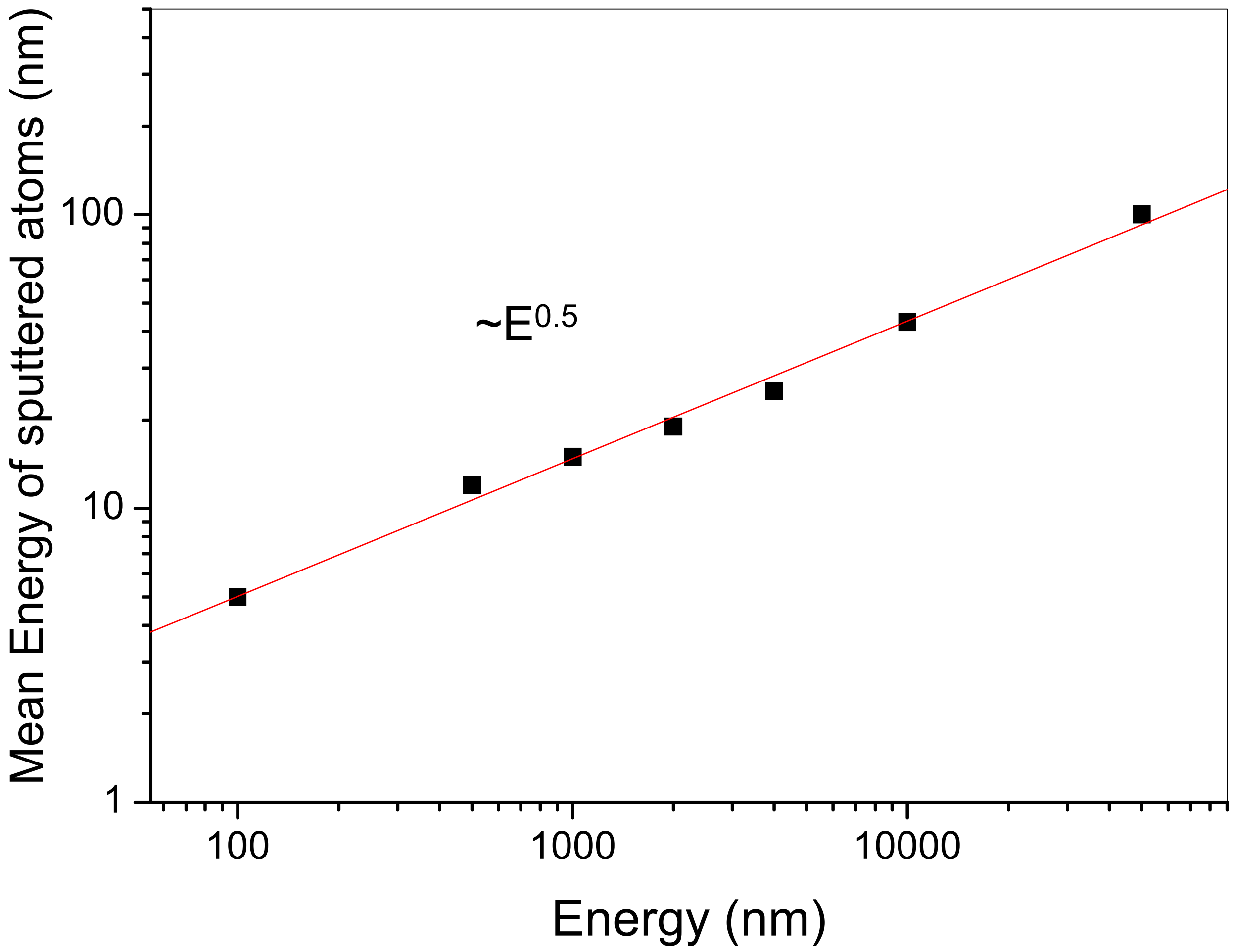
Sputter yield shows same power law dependence than $S_n(E)$

Energy dependence of sputter yield: TRIM

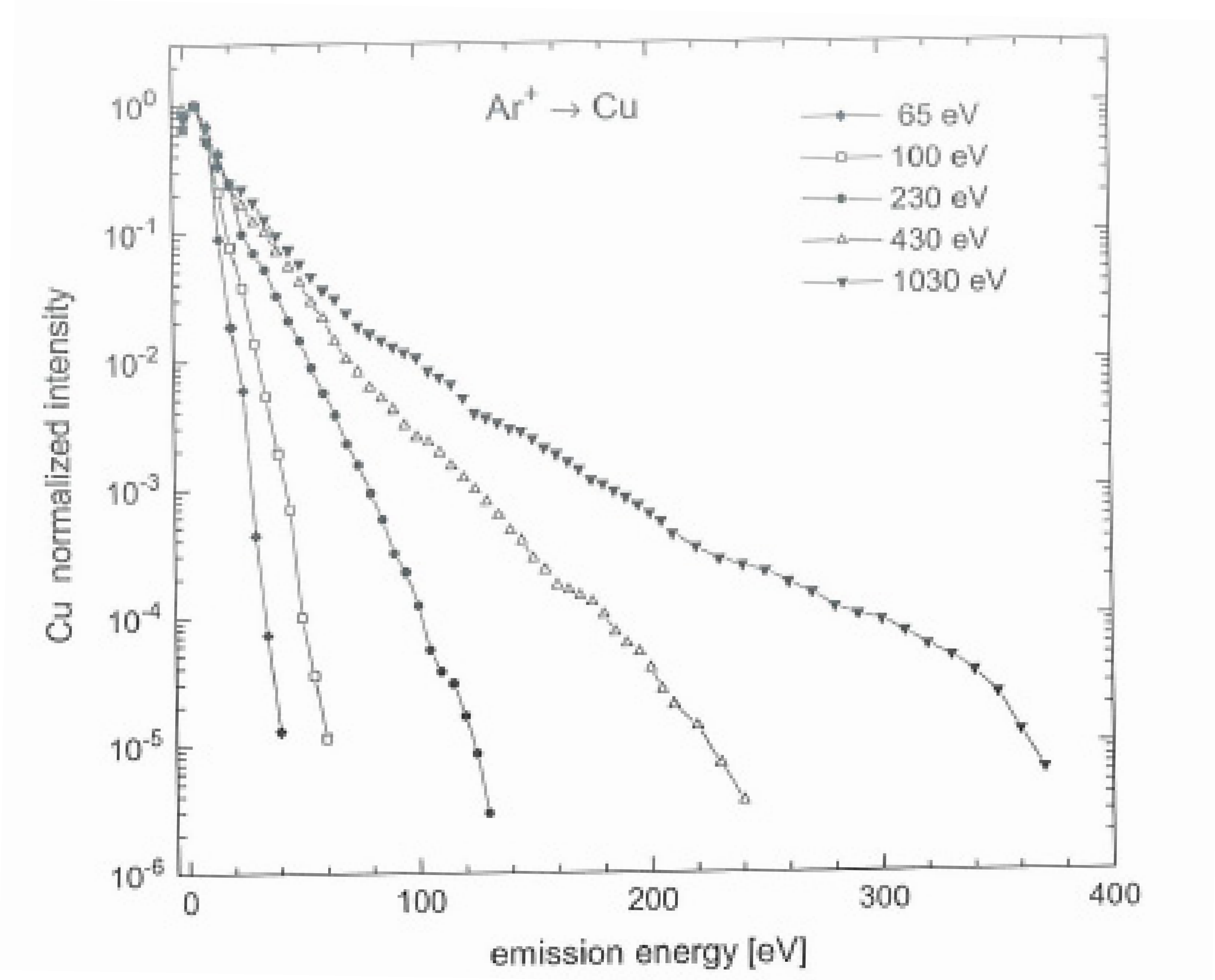


TRIM results for sputter yields are good from 50 eV – 1 MeV

Energy of sputtered particles: TRIM



Energy spectrum of sputtered particles

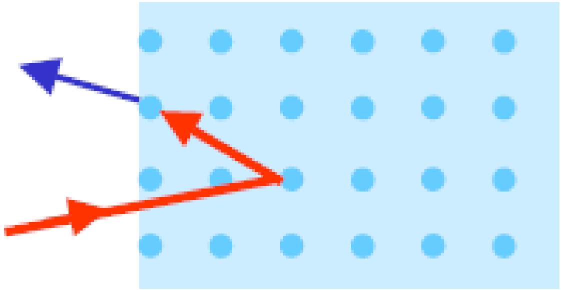


Sputtering: energy dependence

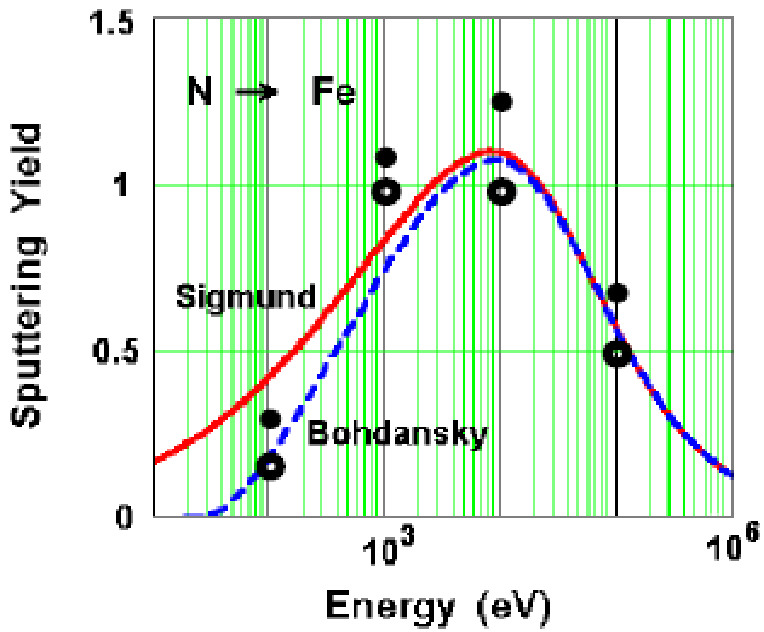
- at low energy the maximum energy transfer T to the target recoils can be smaller then U
- also single-collision regime is possible for light ions
- in this case the maximum energy received by the surface atom

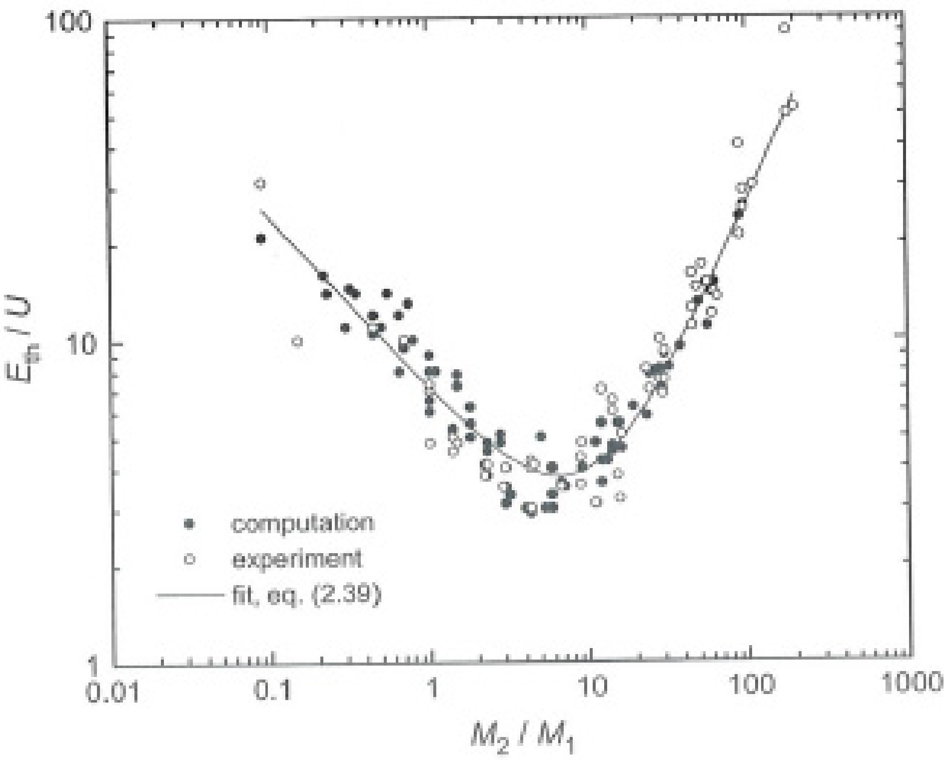
$$E_0^{\max} = \gamma(1-\gamma)E$$

- sputtering threshold can be derived from this $$E_{thr} = \frac{U_s}{\gamma(1-\gamma)}$$



Sputtering threshold

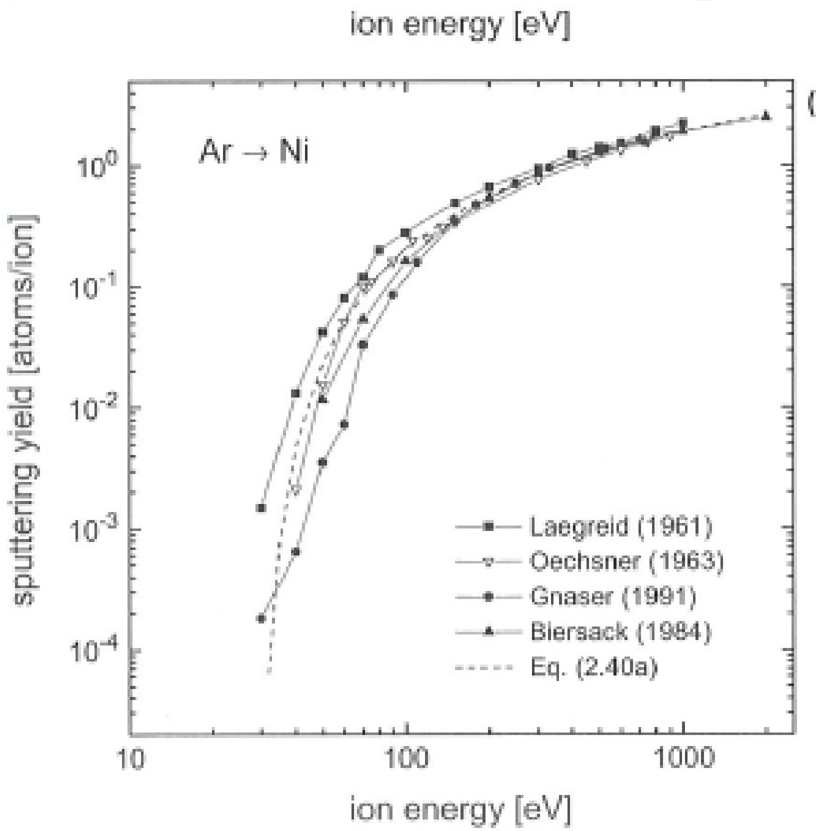


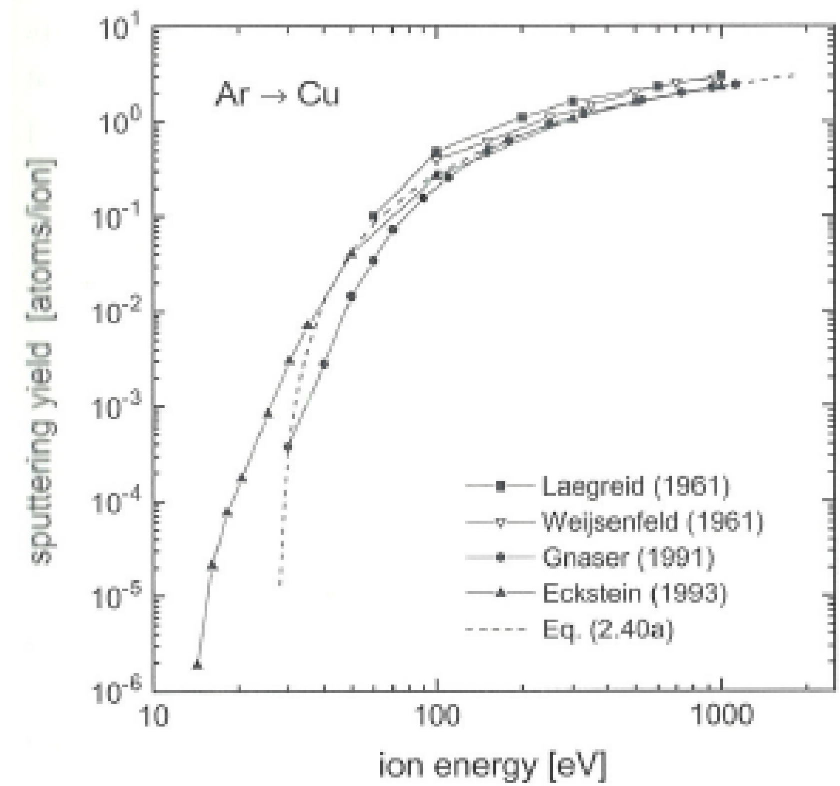


threshold energy for sputtering depends on U_s and M_2/M_1

Sputtering threshold

$$Y(E) = QS_n(E_0)\left[1-\left(\frac{E_{th}}{E}\right)^{2/3}\right]\left(1-\frac{E_{th}}{E}\right)^2$$





Q and E_{th} are fitted to experimental data

Sigmund's Theory of Sputtering

- A cosine law is predicted for the angular emission of the sputtered particles (amorphous or polycrystalline materials) for normal incident ions
- This results from an isotropic flux of recoils in the target
- However, often deviation from the cosine law are observed
  1. under-cosine at low energies (collision cascade is not fully developed)
  2. over-cosine law at higher energies

$$\frac{dY(E,\theta)}{d^2\Omega} \sim \cos^{\beta}\theta$$

  Normally, $1 < \beta < 2$, however, it can also have much larger values
- For off-normal angles of incidence cosine laws are not observed
- emission distribution is peaked at or near the specular direction

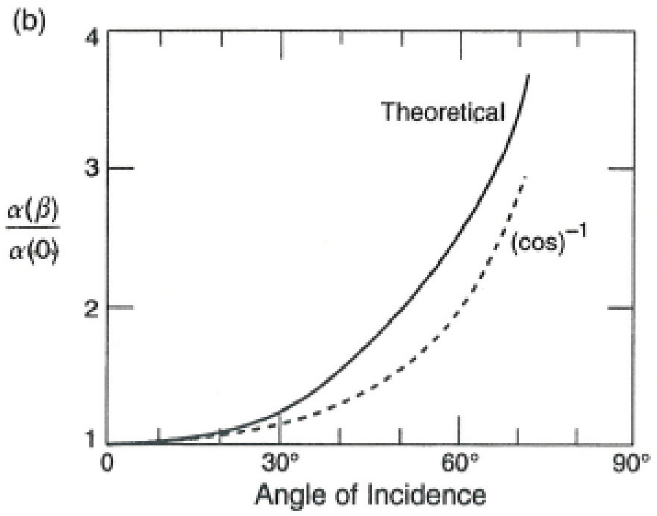
Sigmund‘s Theory of Sputtering: angle dependence

- theoretical prediction: $$\frac{Y(E,\theta)}{Y(E,0)} = (\cos\theta)^{-b}$$

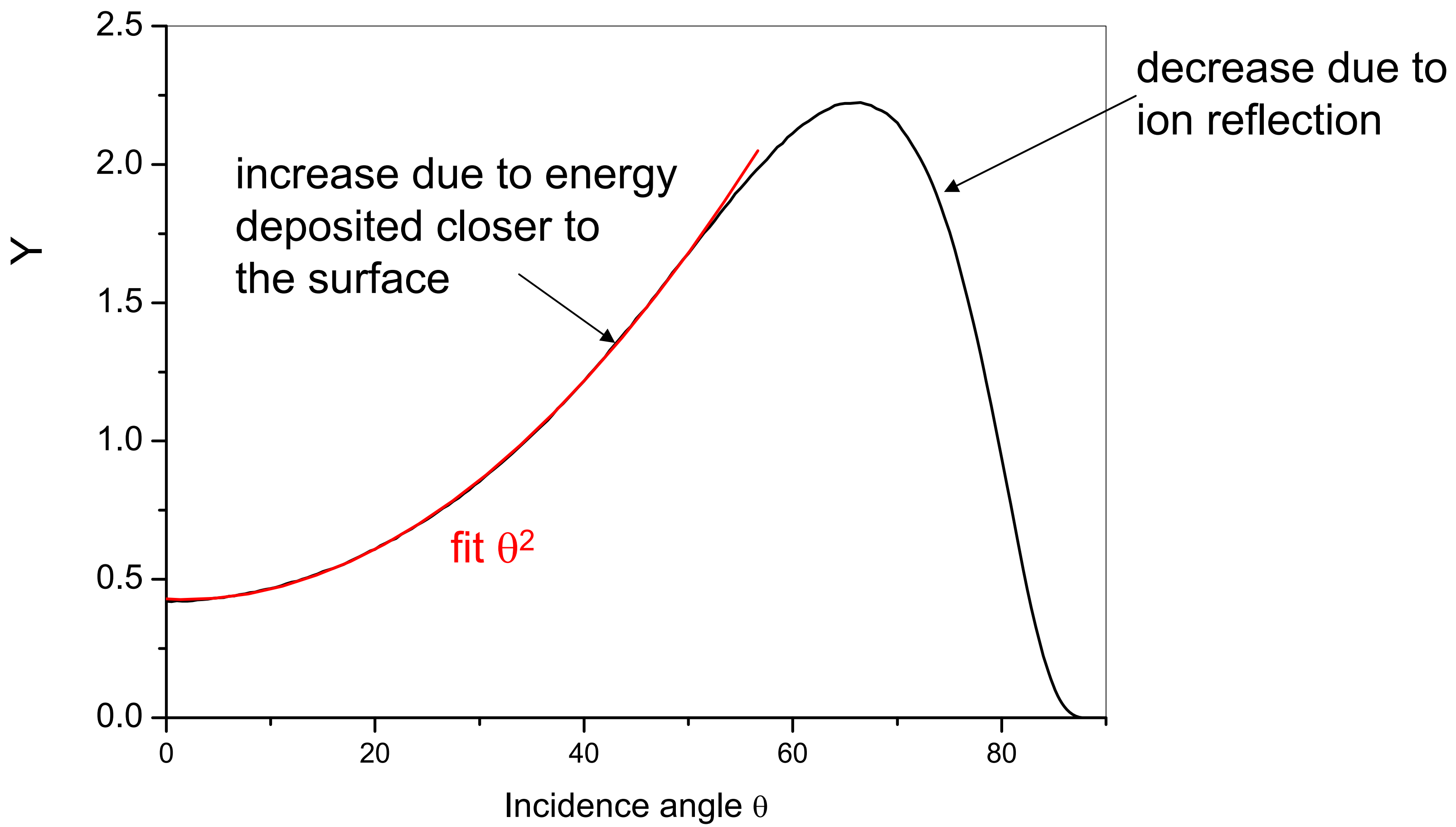
with $$b \sim \begin{cases} 1 & for\ M_2/M_1 > 5 \\ 5/3 & for\ M_2/M_1 < 3 \end{cases}$$

for high angles of incidence reflection of ions is important

Y(θ) decrease for *θ >~ 60°*



Sputter yield: angle dependence

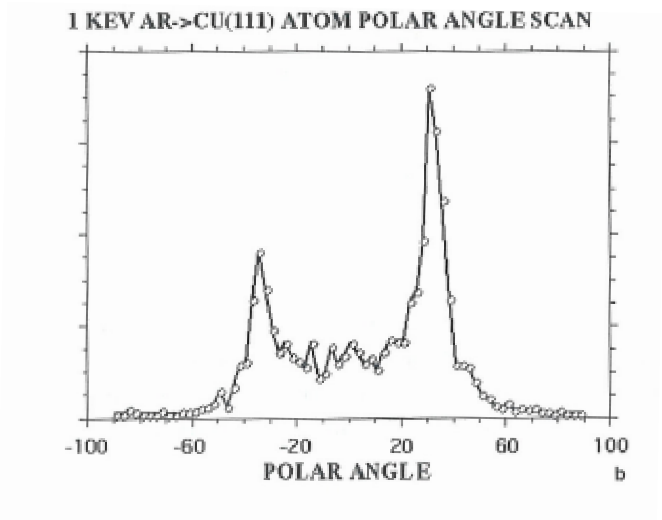


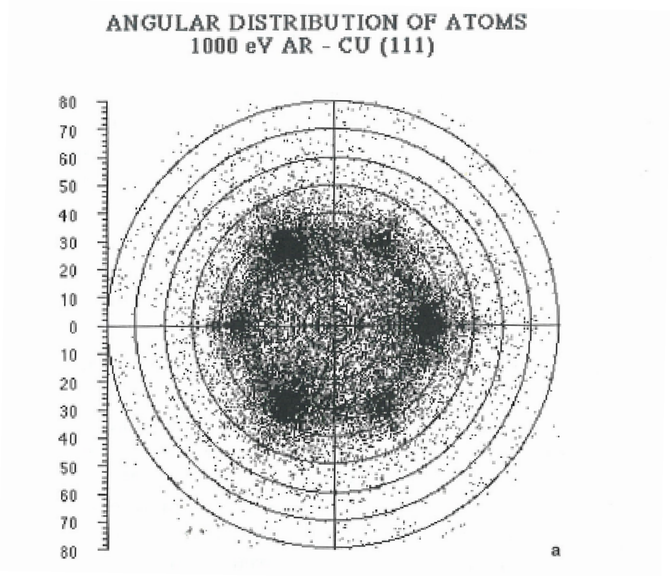
Yield increses with θ^2 until a maximum angle of ~65°

Sputtering from single crystals

- sputtering from single crystals are influenced by the crystallographic orientation of the target relative to the beam direction
- the sputter yield $Y_{(uvw)}$ from a surface (uvw) increases with increasing interatomic distance d_{uvw} along the [uvw] direction
- for normal incidence on fcc targets:

$$Y_{(111)} > Y_{(100)} > Y_{(110)}$$





the reason for this observation is the channeling effect

Sputtering of alloys and compounds

- sputtering is only from the first two three atomic layers
- sputtering yield is proportional to the nuclear stopping power of the incident ion in the near-surface region
- in a compound material two species A and B are present
  → „preferential sputtering“ and surface segregation will be observed

- start of sputtering:
- partial sputter yield:

$$\frac{N_A^s}{N_B^s} = \frac{N_A^b}{N_B^b}$$

- ratio of sputter yields:

$$Y_{A,B} = \frac{\text{number of ejected atoms } A, B}{\text{number of incident ions}}$$

$$\frac{Y_A}{Y_B} = r\,\frac{N_A^s}{N_B^s}$$

r includes the effects of different binding energy, sputter escape depth, and energy transfer

r~ 0.5 - 2

Sputtering of alloys and compounds

in steady state:

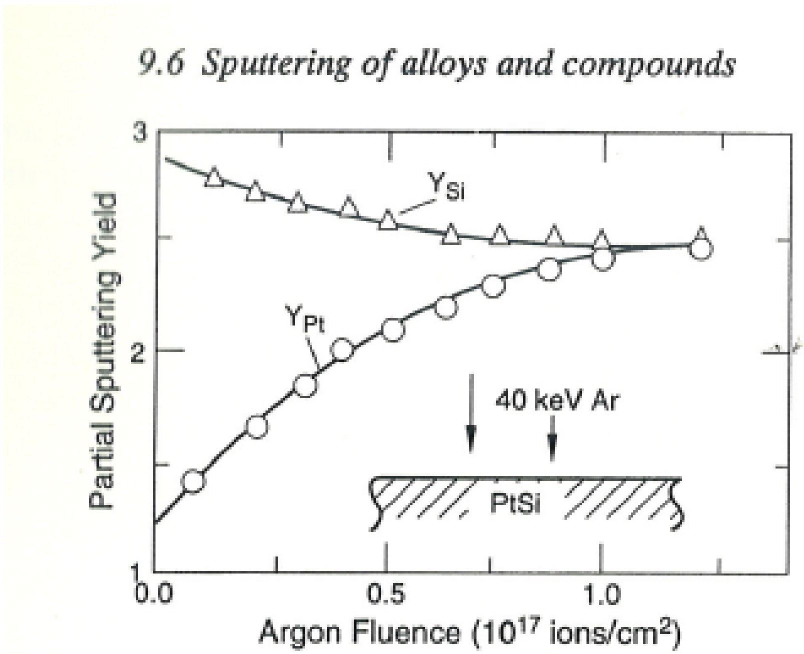
$$\frac{Y_A(\infty)}{Y_B(\infty)} = \frac{N_A^b}{N_B^b}$$

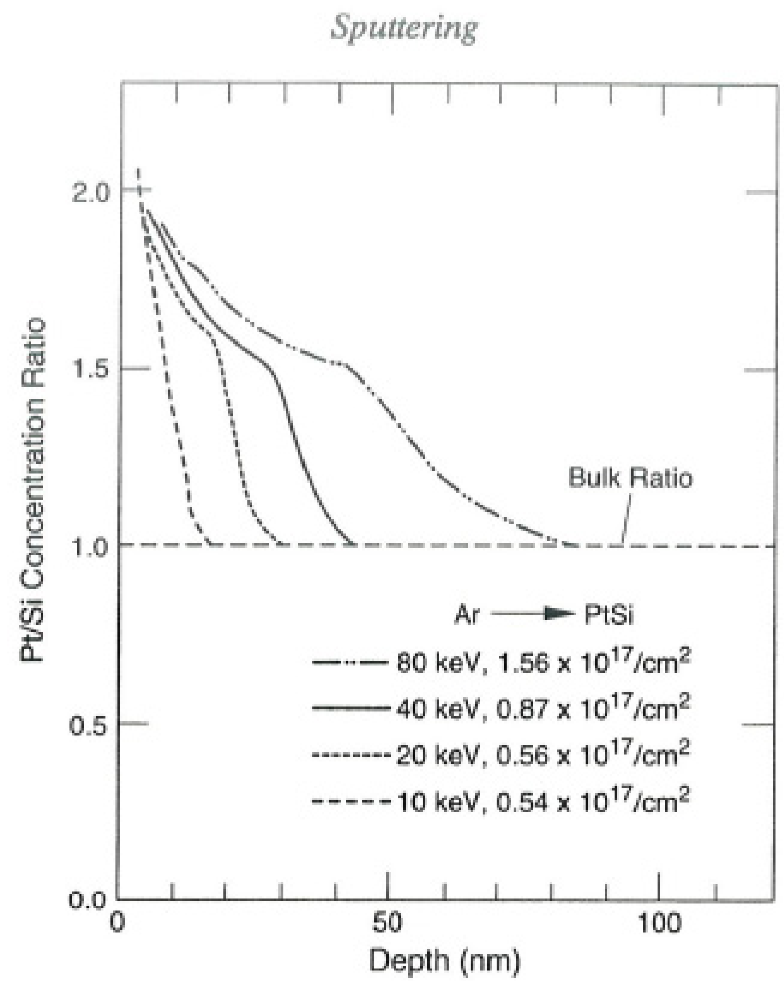
and the surface concentration changes accordingly:

$$\frac{N_A^s(\infty)}{N_B^s(\infty)} = \frac{1}{r}\frac{N_A^b}{N_B^b}$$

if r>1, sputter yield of A is greater than sputter yield of B
→ B is enriched on the surface

Sputtering of alloys and compounds





Preferential sputtering