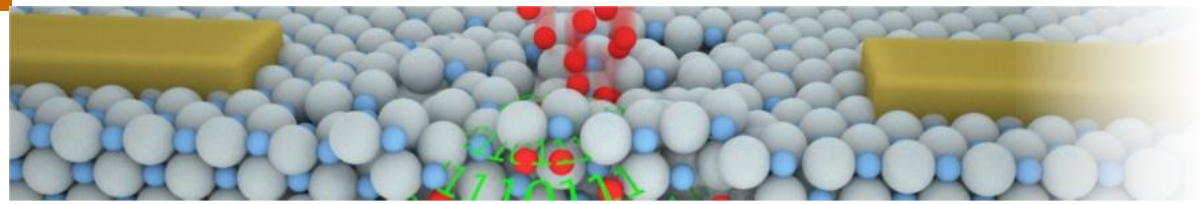

MEMRIOX
Annual Meeting
September 2012

Ion Beam Treatment of Materials

Fundamentals

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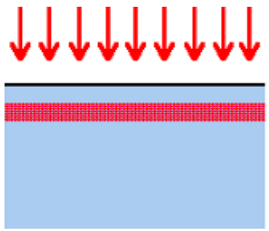
Partner von DRESDEN concept exzellenz-dresden.de

HZDR
HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF

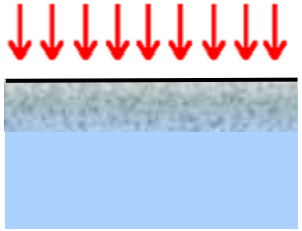
General Outline

- **Ion stopping and ranges**
  - Interaction potential
  - Nuclear and electronic stopping
  - Range and range distribution
- **Target effects**
  - Collision cascade
  - Damage
  - Sputtering
  - Ion mixing
- **Computer simulation**
  - Binary collision approximation
  - Molecular dynamics simulation
  - Kinetic Monte Carlo simulation

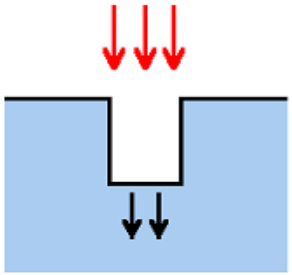
Surface Modification Using Ion Beams



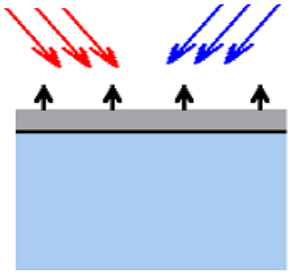
Implantation



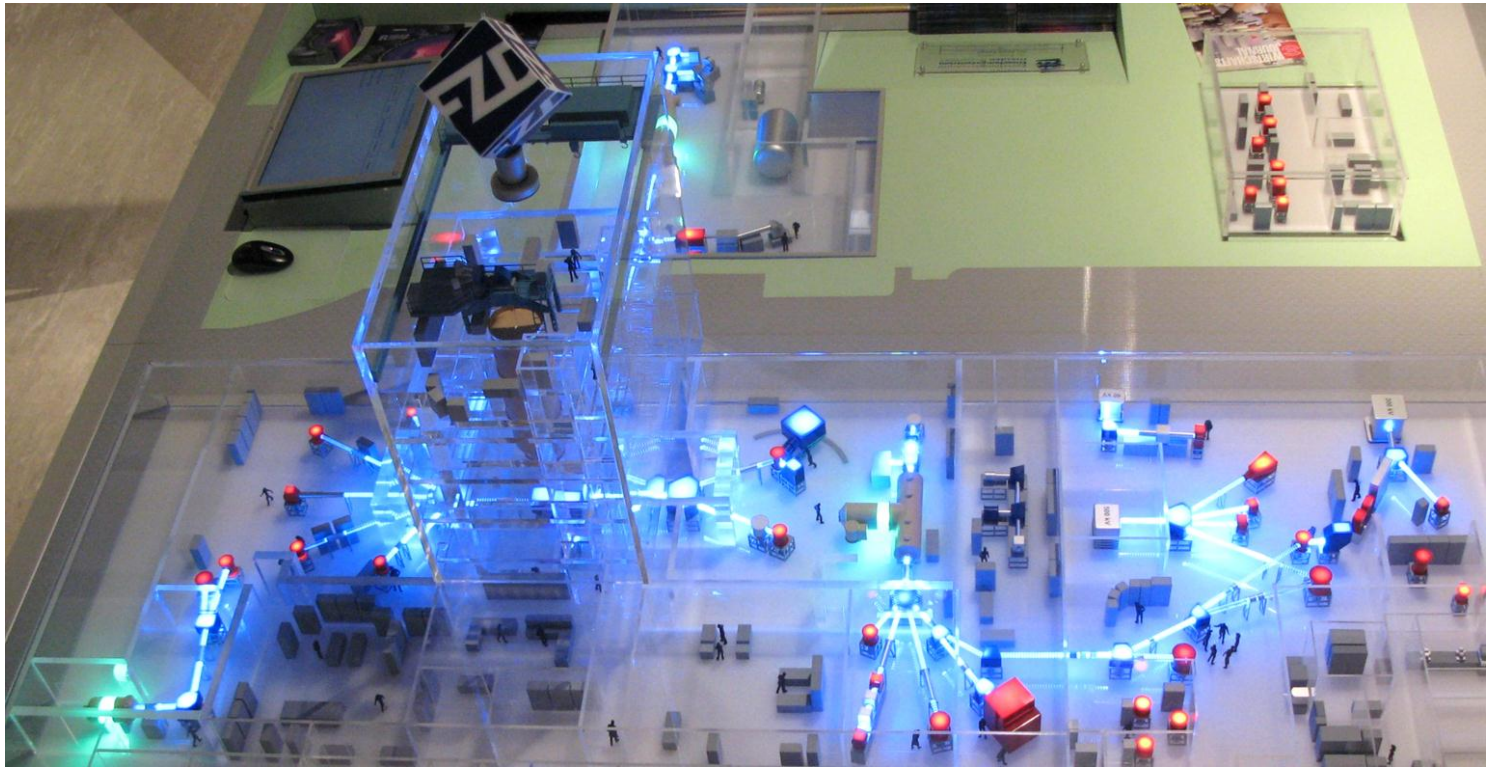
Structural and compositional modification



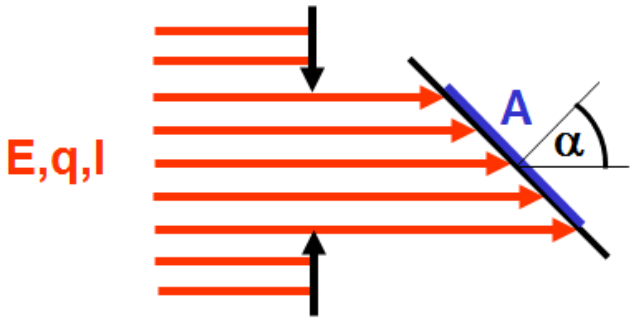
Erosion



Thin Film Deposition



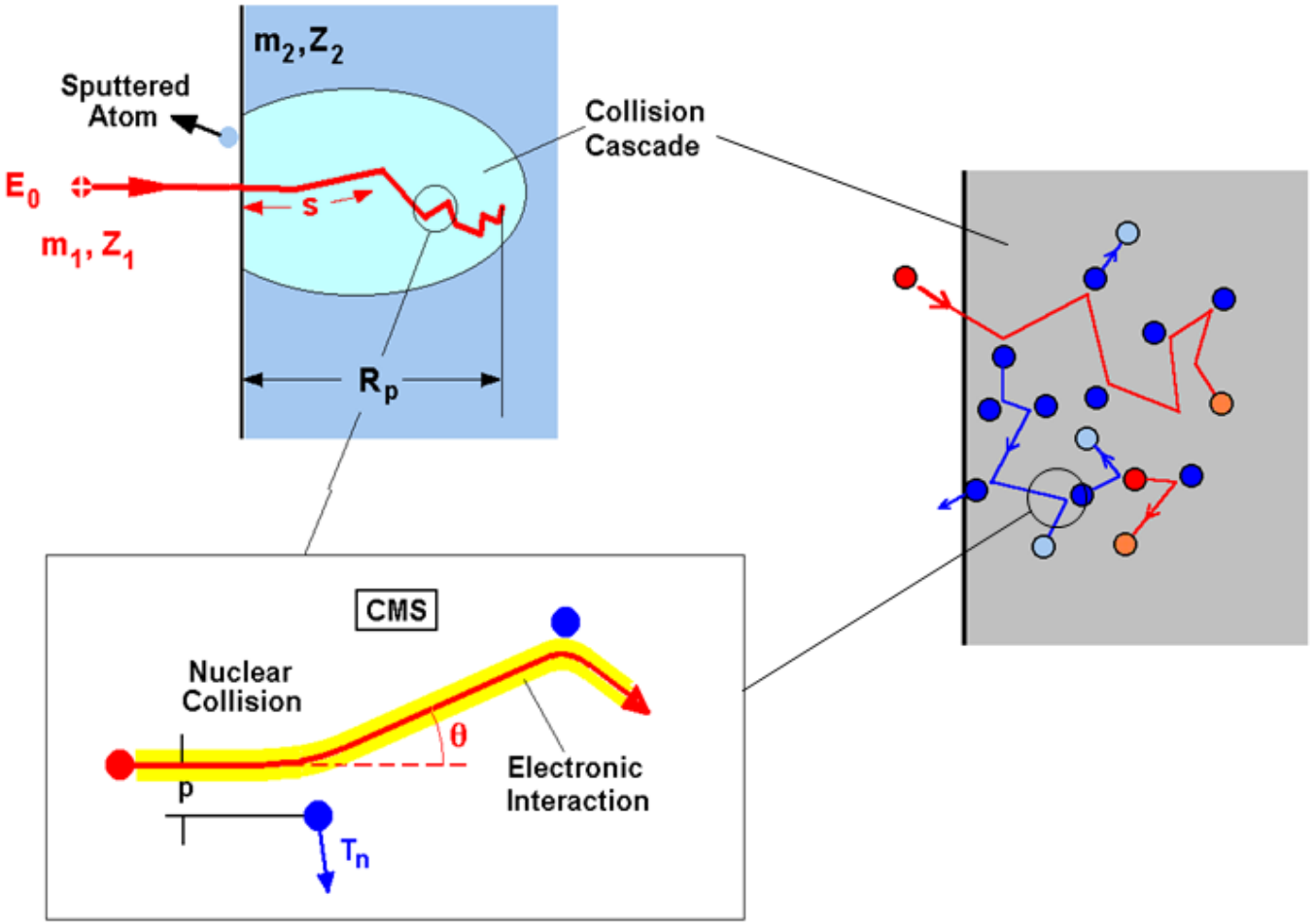
Basic definitions



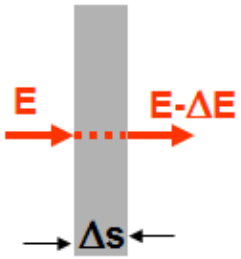
E	Ion Energy	(eV)	*typically 1...100 keV*
q	Ion Charge Number		*typically small*
I	Ion Current	(A)	*typically µA ...mA*
α	Angle of Incidence		
A	Irradiated Area	(cm^2)	
j	Ion Flux	($cm^{-2}s^{-1}$)	$j = \frac{I}{qeA}$
Φ	Ion Fluence	(cm^{-2})	$\Phi = j\,t$

Remark: "Dose" is often used rather than "Fluence"
(although "Dose" should be a volume energy density)

Ion-solid interaction



Stopping of moving atoms



Stopping Force $B = -\frac{dE}{ds}$ E Energy, s Pathlength *(also "Stopping Power")*

Stopping Cross Section $S = -\frac{1}{n}\frac{dE}{ds}$ $n = \frac{\rho L}{m_2}$ Atomic Density

Interaction with Target Atoms ("Nuclei") and Electrons $S = S_n + S_e$

Compound Materials (Bragg's Rule) $S_{A_xB_y} = xS_A + yS_B$

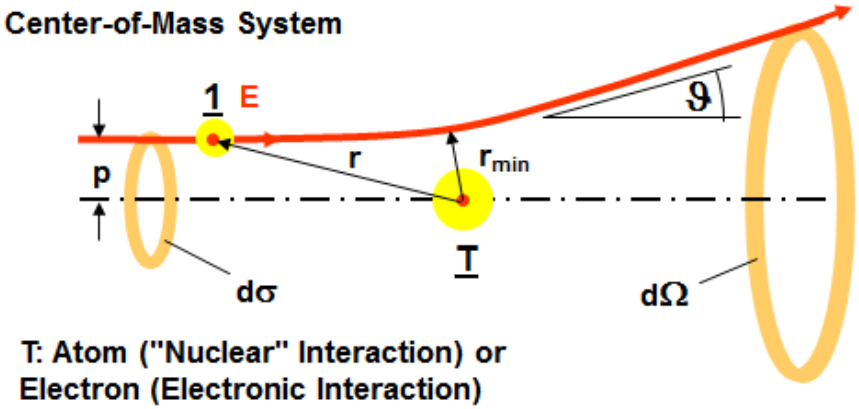
To be Calculated from Collisional Energy Transfer T and Scattering Cross Section σ $S = \int T\, d\sigma(T)$

Collisional Energy Transfer $T = \frac{4 m_1 m_T}{(m_1 + m_T)^2} E \sin^2\left(\frac{\vartheta}{2}\right)$

m_T Target Mass (atom or electron)

ϑ Deflection Angle (center-of-mass system)

Scattering cross section



T: Atom ("Nuclear" Interaction) or
Electron (Electronic Interaction)

Classical "Trajectory Integral"

$$\vartheta = \pi - 2p\int_0^{r_{min}^{-1}} \frac{d(1/r)}{\sqrt{1-\frac{V(r)}{E}-\frac{p^2}{r^2}}}$$

$$\sqrt{(r_{min})} = 0$$

V(r) Interaction Potential

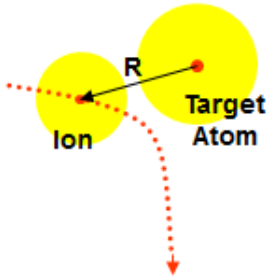
Differential Cross Section

$$\frac{d\sigma}{d\Omega} = -\frac{2\pi p\, dp}{2\pi \sin\vartheta\, d\vartheta} = -\frac{p}{\sin\vartheta}\frac{dp}{d\vartheta}$$

Rutherford Cross Section
for Coulomb Potential

$$\frac{d\sigma}{d\Omega} = \left(\frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0}\right)^2 \frac{1}{E^2}\frac{1}{\sin^4(\vartheta/2)}$$

Nuclear scattering: interatomic potential



Screened Coulomb Interaction Potential

$$V(R) = \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 R}\varphi\left(\frac{R}{a}\right)$$

Different Screening Functions and Choices of Screening Length

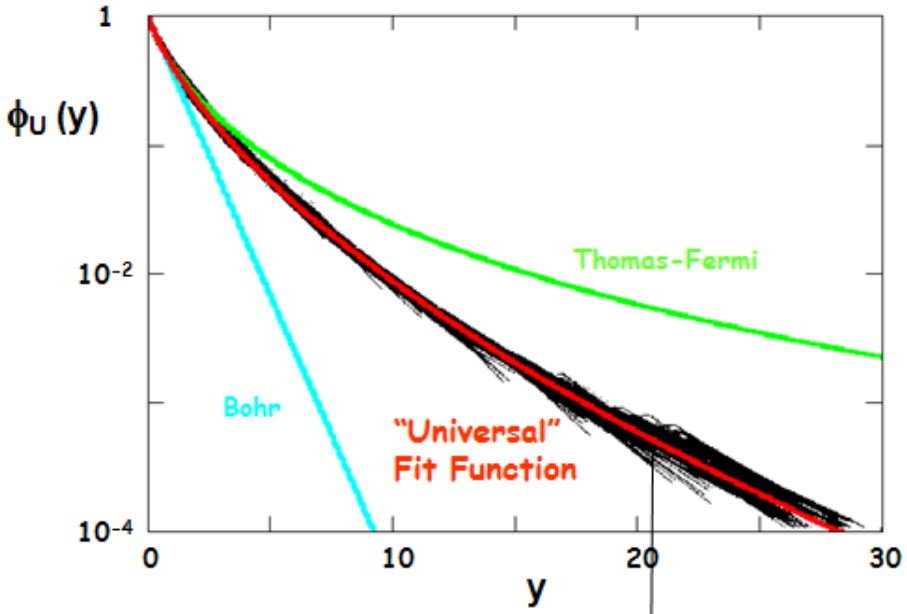
$$a_{TF} = \frac{0.8853\ a_0}{\left(Z_1^{2/3} + Z_2^{2/3}\right)^{1/2}}$$

Thomas-Fermi-Lindhard

a_0 1. Bohr Radius

$$a_F = \frac{0.8853\ a_0}{\left(Z_1^{1/2} + Z_2^{1/2}\right)^{2/3}}$$

Firsov



"Universal" Screening Function

$$\varphi_U(y) = 0.182e^{-3.2y} + 0.51e^{-0.942y} + 0.28e^{-0.403y} + 0.0282e^{-0.202y}$$

$$a_U = \frac{0.8853\ a_0}{Z_1^{0.23} + Z_2^{0.23}}$$

HFS atomic calculations with linear superposition of atomic electron densities for 522 projectile-target combinations

Lindhard universal scattering cross section

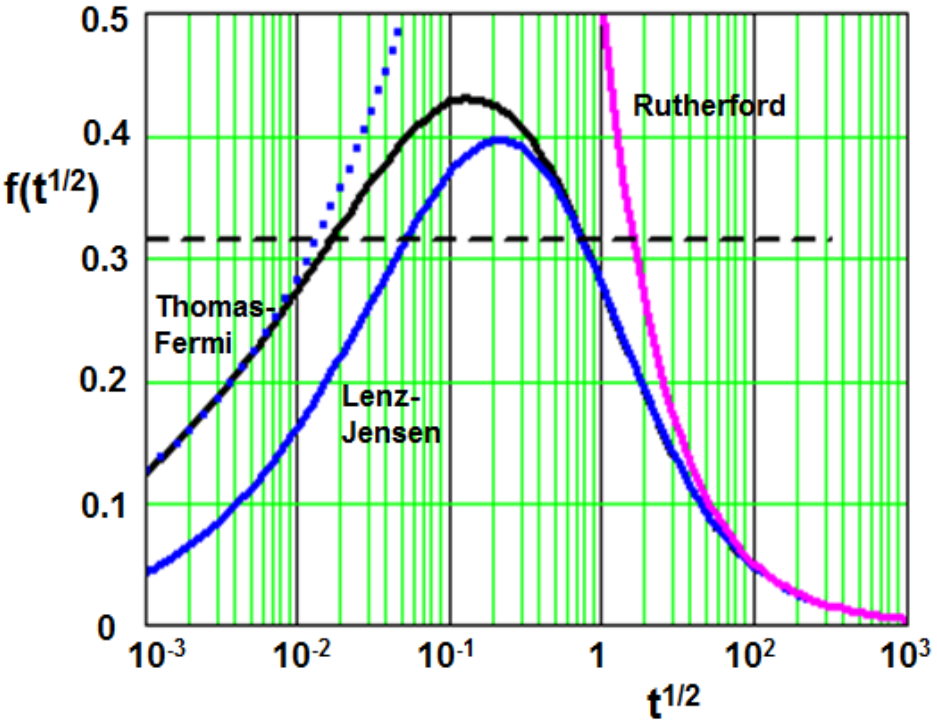
From small angle approximation

Reduced energy $$\varepsilon = \frac{4\pi\varepsilon_0 a m_2}{Z_1 Z_2 e^2 (m_1 + m_2)} E$$

Example: ε = 0.4
f. 10 keV N^+ → Fe

Reduced scattering angle $$t^{1/2} = \varepsilon \sin\frac{\vartheta}{2}$$

Scattering cross section $$\frac{d\sigma}{dt} = \pi a^2 \frac{f(t^{1/2})}{2t^{3/2}}$$



Nuclear stopping

Reduced pathlength (Lindhard)

$$\rho = \pi a^2 n \frac{4 m_1 m_2}{(m_1 + m_2)^2} s$$

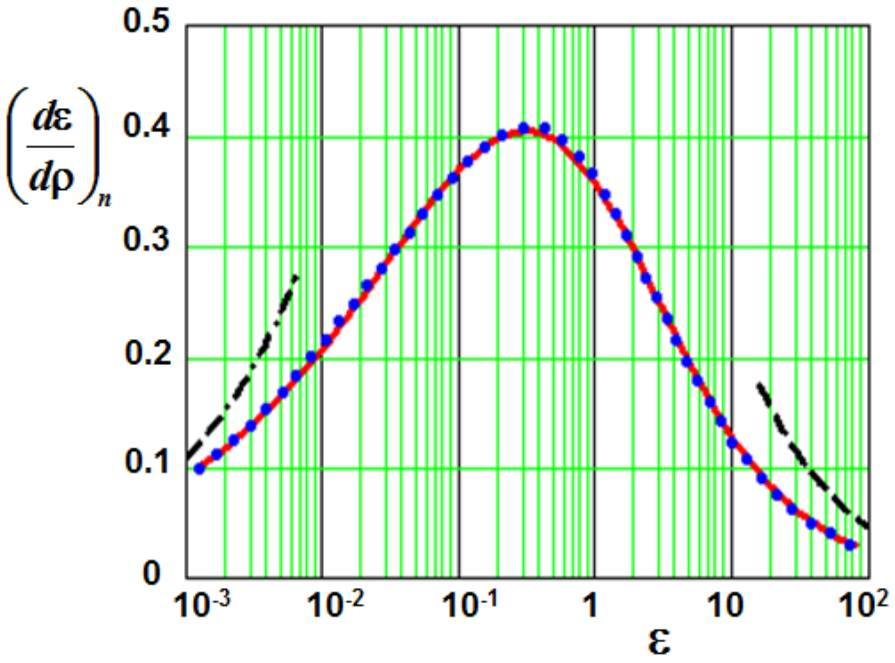
Example: ρ = 0.3 f. 10 nm N in Fe

Universal result from integration with universal scattering function

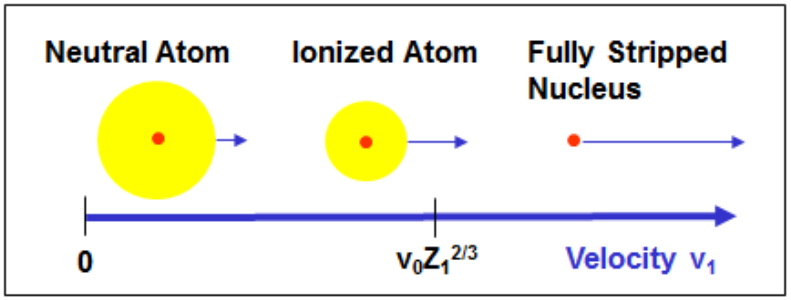
$$\left(\frac{d\varepsilon}{d\rho}\right)_n = \frac{3.44\sqrt{\varepsilon}\,\ln(\varepsilon + 2.718)}{1 + 6.35\sqrt{\varepsilon} + \varepsilon(6.882\sqrt{\varepsilon} - 1.708)}$$

Fit formula by Matsunami

$$\varepsilon << 1: \quad \left(\frac{d\varepsilon}{d\rho}\right)_n \sim \sqrt{\varepsilon}$$



Electronic interaction



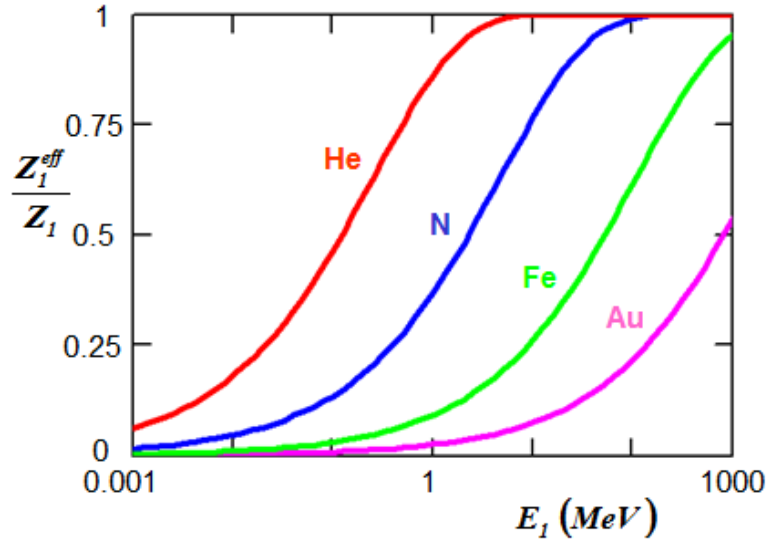
$v_1 = v_0$
$\Leftrightarrow$ E = 25 keV/amu

Actual charge of moving atom in solid results from balance of electron loss (by collisions) and electron attachment (from target electron gas)

Efficient attachment for $\upsilon_1 \le \bar{\upsilon}_{el,1} = \upsilon_0 Z_1^{2/3}$

Thomas-Fermi Model

v_1 Moving atom Velocity
$\bar{v}_{el,1}$ Mean electron velocity of moving atom
v_0 Velocity of 1. Bohr orbit



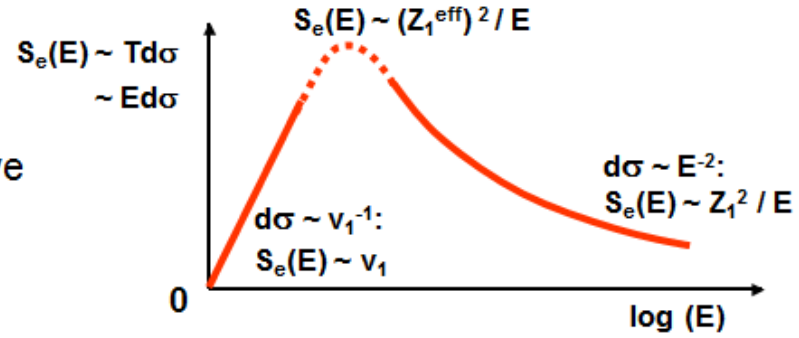
"Effective" Ion Charge (Rough Approximation)

$$Z_1^{eff} = Z_1 \frac{\upsilon_1}{\upsilon_0 Z_1^{2/3}} = Z_1^{1/3} \frac{\upsilon_1}{\upsilon_0} \Rightarrow Z_1 \left(1 - e^{-\frac{\upsilon_1}{\upsilon_0} Z_1^{-2/3}}\right)$$

High-Velocity Extrapolation

Electronic stopping

Qualitative



High Ion Velocity $\upsilon >> \upsilon_0 Z_1^{2/3}$

$$S_e^{>} = \frac{2\pi Z_1^2 Z_2 e^4}{(4\pi\varepsilon_0)^2} \frac{m_1}{m_e} \frac{1}{E} \log\left(\frac{4 m_e E}{m_1 I}\right)$$

(Bethe-Bloch)

$I \approx 10 \cdot Z_2 \; eV$

Mean Ionization Potential

Low Ion Velocity $\upsilon << \upsilon_0 Z_1^{2/3}$

$$S_e^{<} = \frac{2 e^2 a_0}{\varepsilon_0} \frac{Z_1^{7/6} Z_2}{\left(Z_1^{2/3} + Z_2^{2/3}\right)^{3/2} \upsilon_0} \sqrt{\frac{2E}{m_1}}$$

(Lindhard-Scharff)

Interpolation

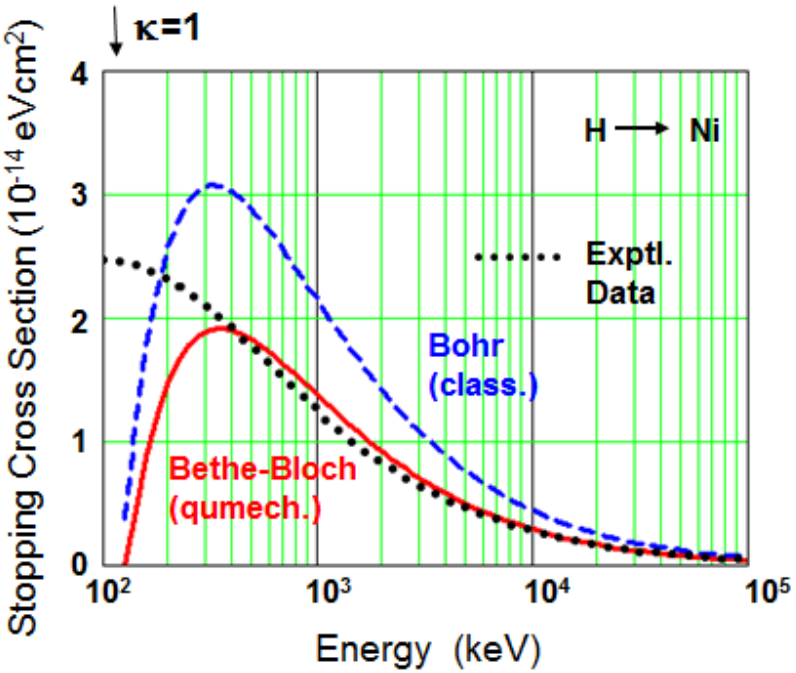
$$\frac{1}{S_e} \approx \frac{1}{S_e^{<}} + \frac{1}{S_e^{>}}$$

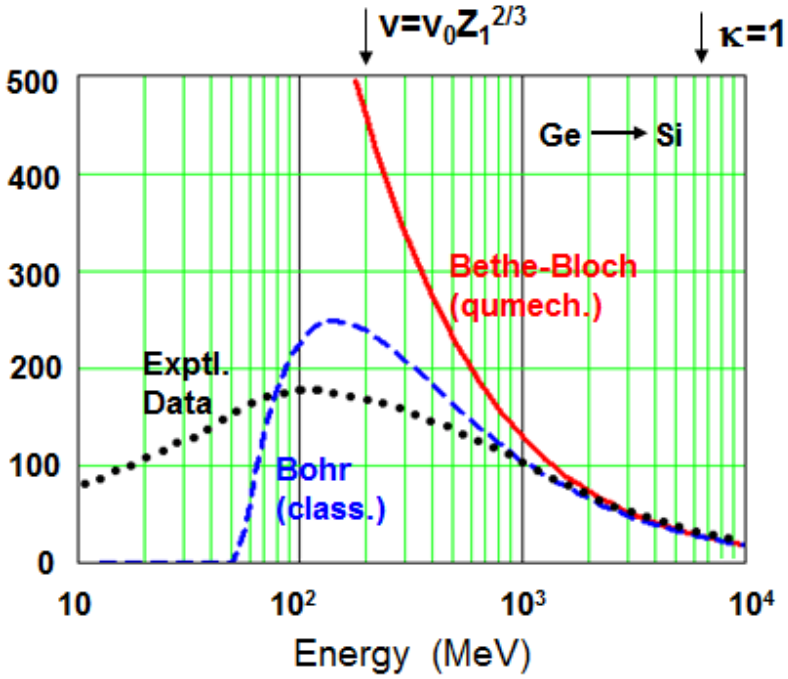
Electronic stopping – high velocity

Bohr Criterion $\kappa = 2\left|Q_1 Q_2\right| \frac{v_0}{v_1}$

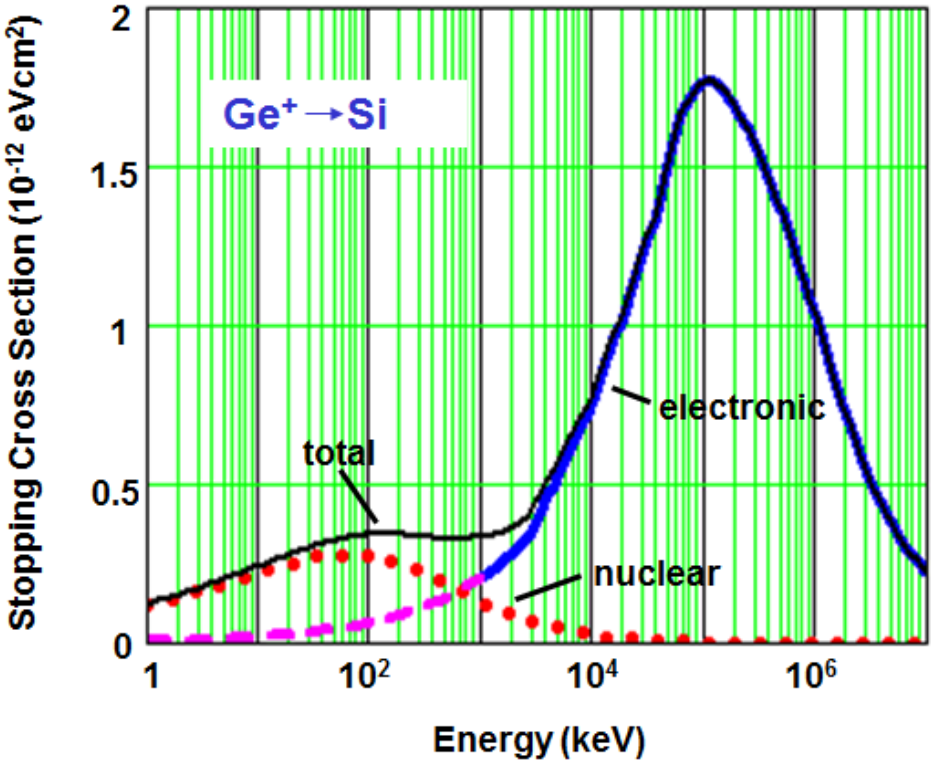
Q_1 Charge of moving atom
Q_2 Charge of collision partner (atom or electron)

$\kappa >> 1$ classical
$\kappa << 1$ quantum-mechanical

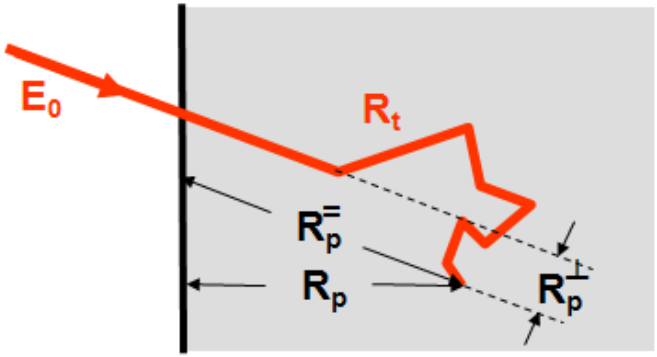




Stopping combined



Ion Ranges



R_t Total pathlength
R_p Projected range

Mean total pathlength can easily be calculated by stopping power integral

$$\overline{R}_t = \frac{1}{n}\int_0^{E_0}\frac{dE}{S(E)}$$

Analytical calculation of mean projected ranges requires elaborate transport theory.
Approximate results for special conditions are

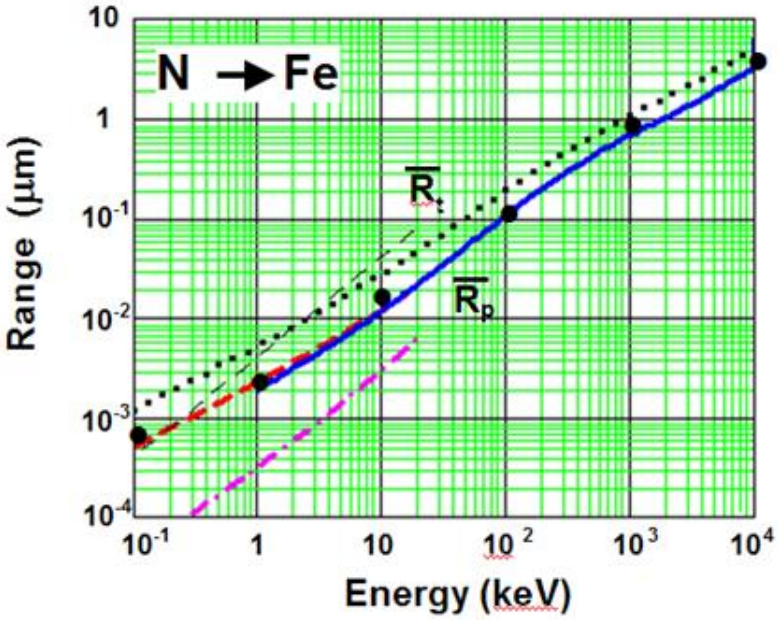
$$\overline{R}_p = \overline{R}_t\left(1+\frac{m_2}{3m_1}\right)^{-1} \qquad m_1 > m_2$$

$$\overline{R}_p = \overline{R}_t\,\lambda(1-2\lambda) \qquad \lambda = \frac{m_1}{m_2}\frac{S_e(E_0)}{S_n(E_0)} \qquad \lambda < 0.5 \quad and \quad S_e > S_n$$

Ion Ranges

Stopping and range data are available in SRIM package

www.srim.org

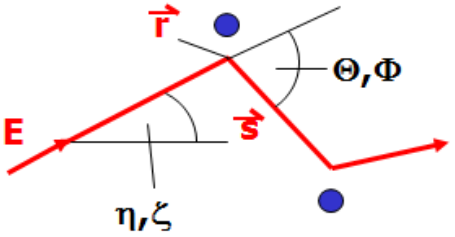


Mean Total Pathlength:
Integrated from SRIM Stopping Powers
Low-Energy Approximation
Mean Projected Range:
SRIM Transport Calculation
Heavy Ion Correction to Mean Total Pathlength
Light Ion Correction to Mean Total Pathlength
TRIM Computer Simulation (from SRIM)

Rule-of-Thumb $\frac{\overline{R}_p}{nm} \approx \frac{E}{keV}$

Computer simulation: binary collision approximation

- **Trajectories of incident ions and all recoil atoms as sequence of binary collisions**
- **"Linear" cascade regime: Only collisions with target atoms at rest**
- **Validity: above E ≈ 10..30 eV ("Collisional phase" of the cascade)**



"State" of moving atom

Energy E
Coordinates $\vec{r}$
Flight Direction η,ζ

Collisional Transformation

$$E \rightarrow E - T_n - nS_e s$$
$$\vec{r} \rightarrow \vec{r} + \vec{s}$$
$$(\eta, \zeta) \rightarrow Tr(\Theta, \Phi) \bullet (\eta, \zeta)$$

S_e Electronic Stopping Cross Section
n Atomic Density
T_n Nuclear Energy Loss (from Θ)
Tr Angular Transformation

Collisional Variables

Free Pathlength s
Polar Deflection Θ
Azimuthal Deflection Φ
Energy Loss ΔE_{el}

Most well-known code:

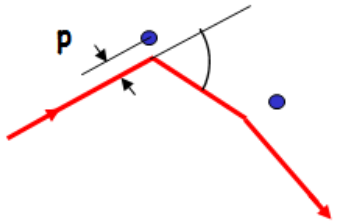
TRIM = TRansport of Ions in Matter
(www.srim.org)

Computer simulation: binary collision approximation

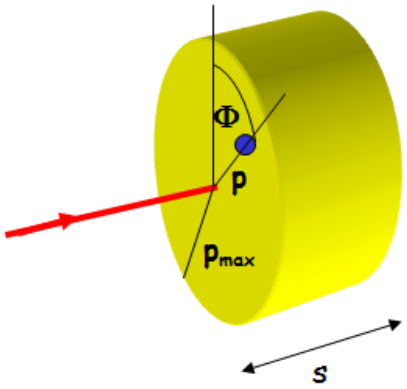
- **Amorphous Substance**

  Position of target atoms and thereby impact parameter are randomly chosen

  Path is random



- **Random Generator** $r \in [0,1]$
- **Impact Parameter** $p = p_{max} \sqrt{r_p}$
- **Azimuthal Angle** $\Phi = 2 \pi r_\Phi$



- **Conservation of atomic density, one collision per target atom** $\pi p_{max}^2 \, s = n^{-1}$
- **Constant free pathlength equal to mean atomic distance** $s = n^{-1/3}$
- **Fast algorithm for classical scattering integral Θ(p) ("Magic Formula")**
- **Multiatomic target materials**
- **Static target: No modification**

Biersack and Haggmark 1978

Eckstein and Biersack 1982 (Sputter Version)

Ziegler ~1980 ... 2010

http://www.srim.org

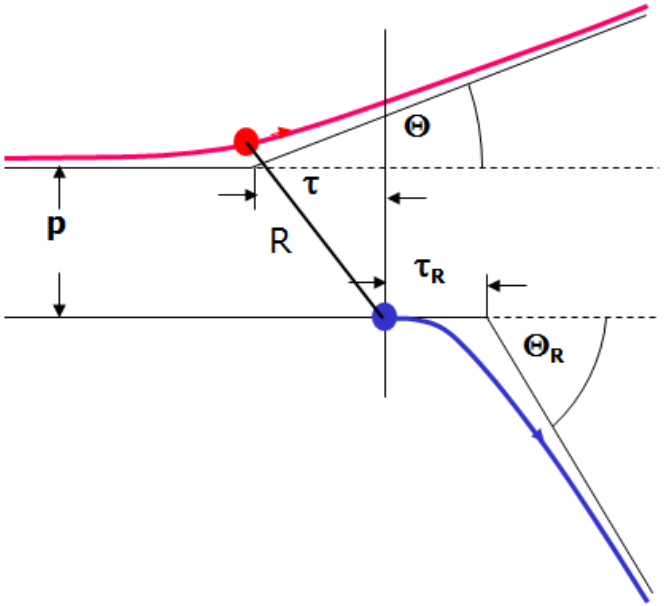
Computer simulation: binary collision approximation

- **Classical Scattering Integral (CMS System)**

$$\vartheta = \pi - 2p \int_0^{R_{min}^{-1}} \frac{d\left(\frac{1}{R}\right)}{\sqrt{1 - \frac{V(R)}{E_c} - \frac{p^2}{R^2}}}$$

- **Screened Coulomb Potential**

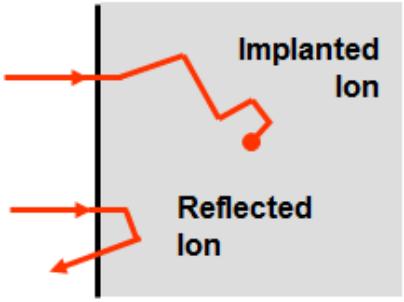
$$V(R) = \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 R} \varphi_U\left(\frac{R}{a}\right)$$



- **Asymptotic Path Approximation**
- **Approximate Time Integral**
  (Hard Sphere Approximation)

$$\tau = p \tan\frac{\vartheta}{2} \qquad \tau_R = 0$$

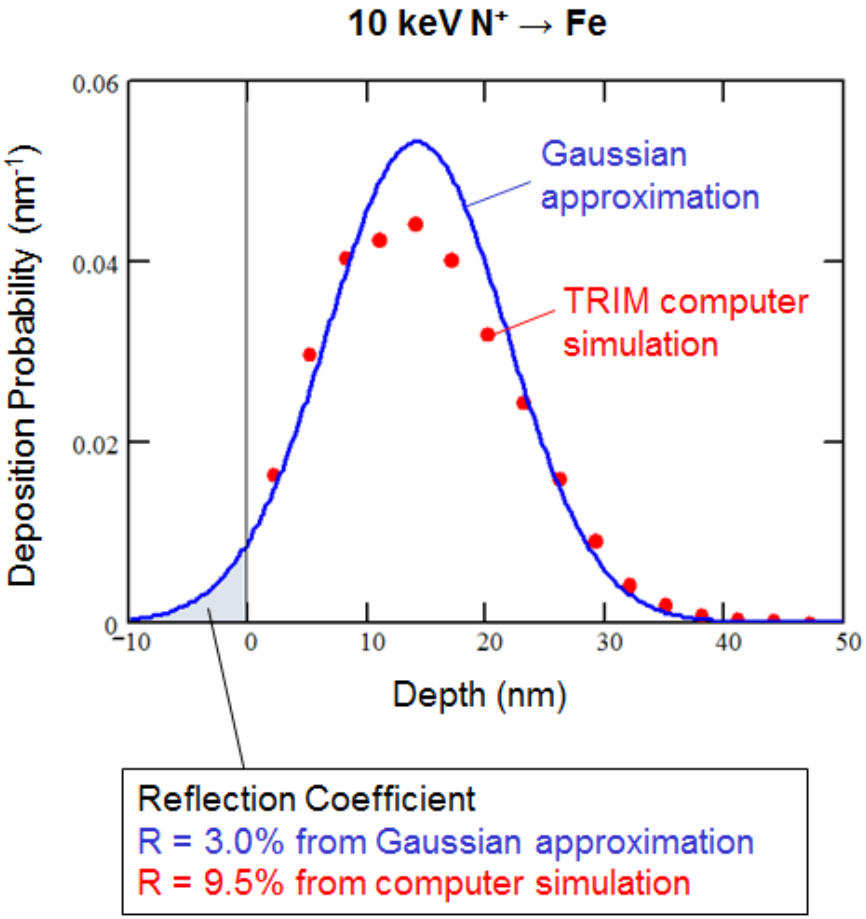
Projected range distribution



Analytical calculation of range distribution and ion reflection requires elaborate transport theory.

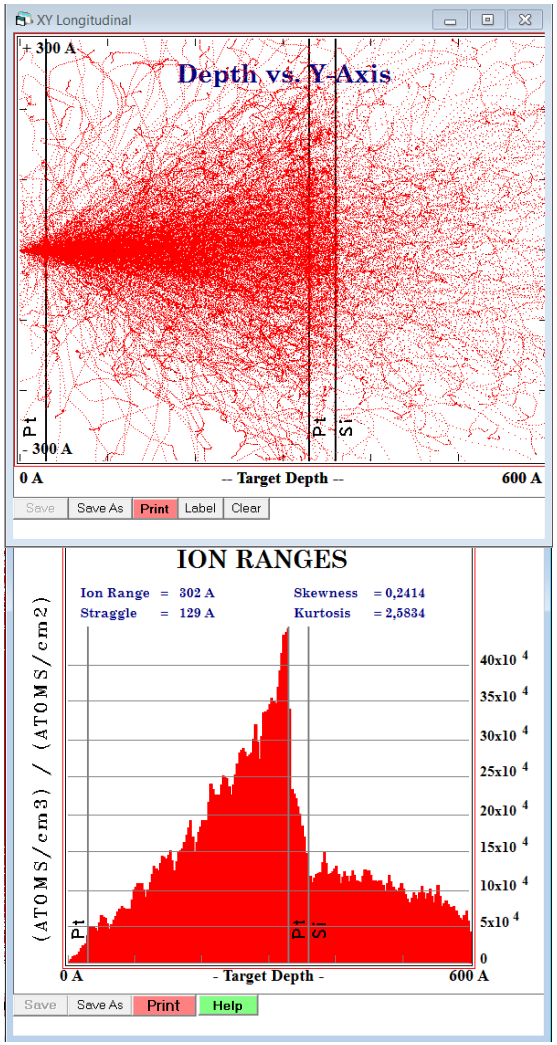
A proper tool is computer simulation in the binary collision approximation.

Range distributions can often be approximated by a Gaussian distribution.



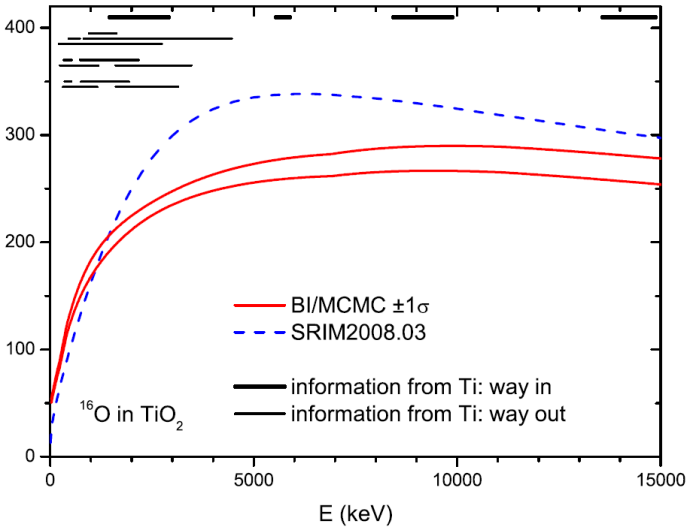
Ion range distribution in a multilayer (TRIM)

50 keV Ar^+ → 3 nm Pt / 30 nm TiO_2 / 3 nm Pt / Si

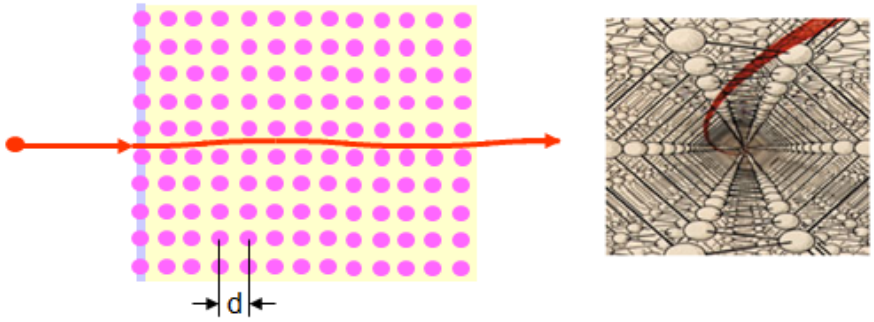


TRIM employs Bragg's rule for stopping in TiO_2: questionable!

Use specific stopping data from literature where available.



Ion channeling



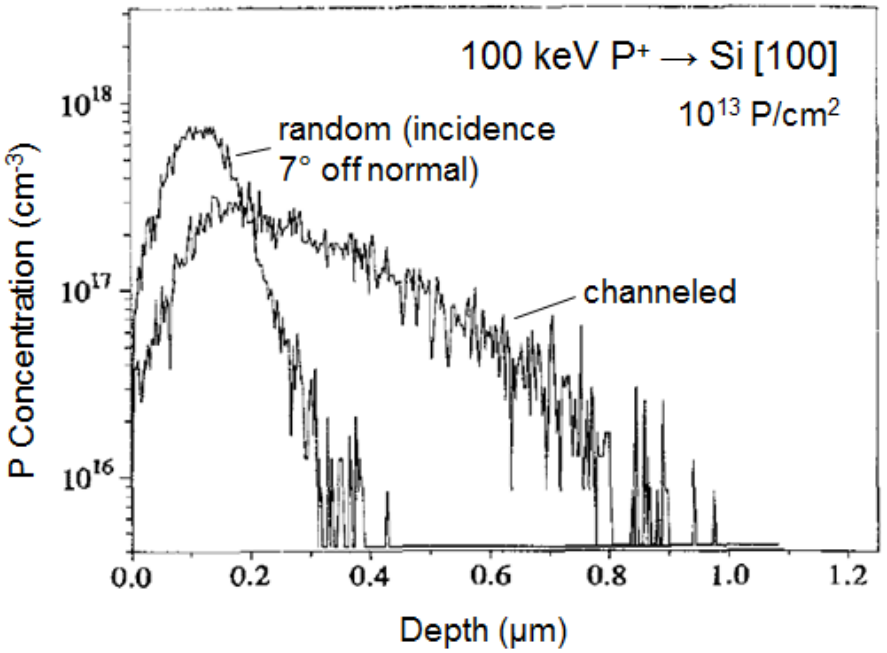
Condition for axial Channeling: Angle of incidence (with respect to channel direction) smaller than critical angle

$$\psi < \psi_c \approx \sqrt{\frac{2 Z_1 Z_2 e^2}{4 \pi \varepsilon_0 d E}}$$

d Distance of atoms along atomic strings in channel direction

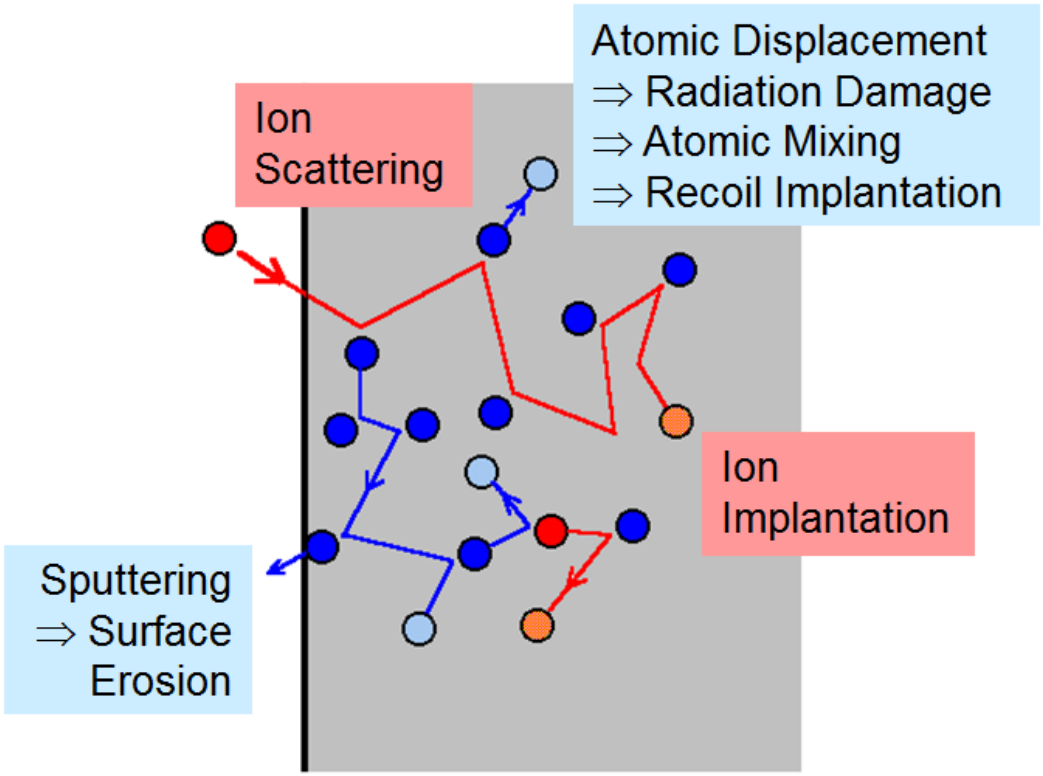
Prediction of channeling range profiles is difficult due to dependence on experimental details (beam divergence, surface quality, implantation fluence, …)

For single crystalline materials, it is often difficult to avoid channeling.



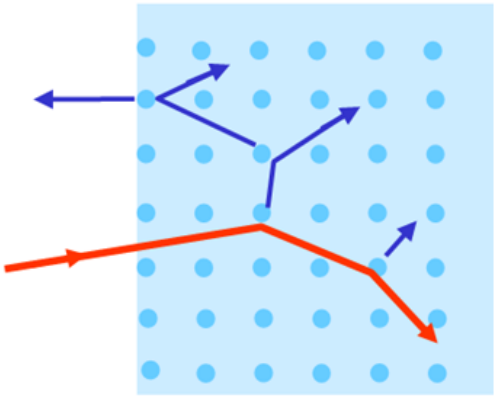
R.J. Schreutelkamp et al., Nucl. Instrum. Meth. B55(1991)615

The collision cascade



Cascade regimes

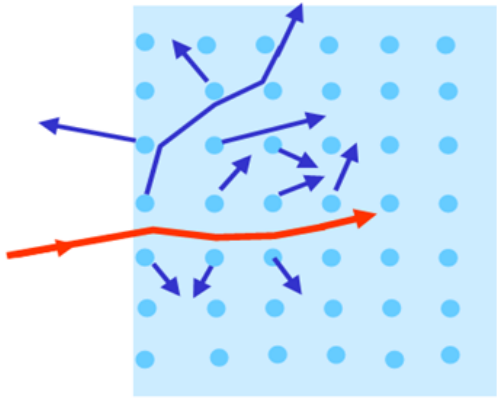
Linear Cascade



Low energy density
No interaction between moving particles
Sequence of binary collisions

BCA computer simulation

Thermal Spike



High energy density
Interaction between moving particles
Many-body interactions

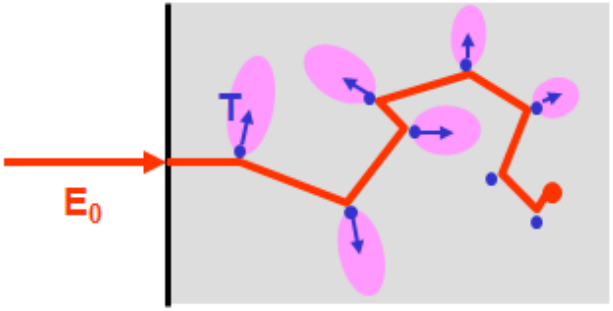
MD computer simulation

Thermal spike regime may be entered in the early phase of the cascade at sufficiently high energy density
(e.g., heavy ion incidence at energy ~100 keV)

Thermal spike regime is always entered in the thermalization phase of the cascade
(at mean energies of the cascade atoms lower than solid-state binding energies - typically a few eV)

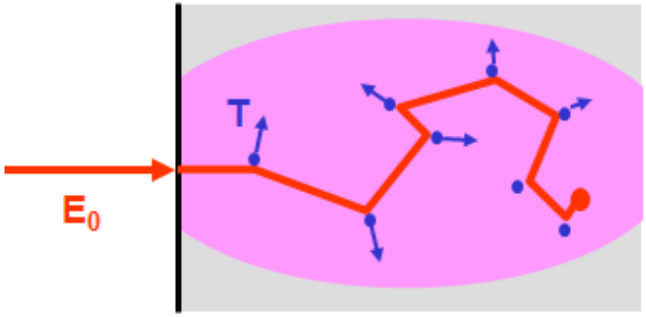
Spatial structure of the cascade

Light ions, high energies



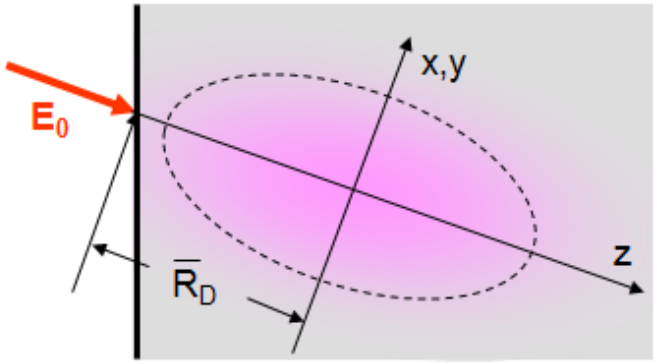
T Nuclear Energy Transfer

Heavy ions, low energies



Similar average topology for multiple ion incidence

Spatial deposition of energy in cascade is often described by a Gaussian rotational ellipsoid



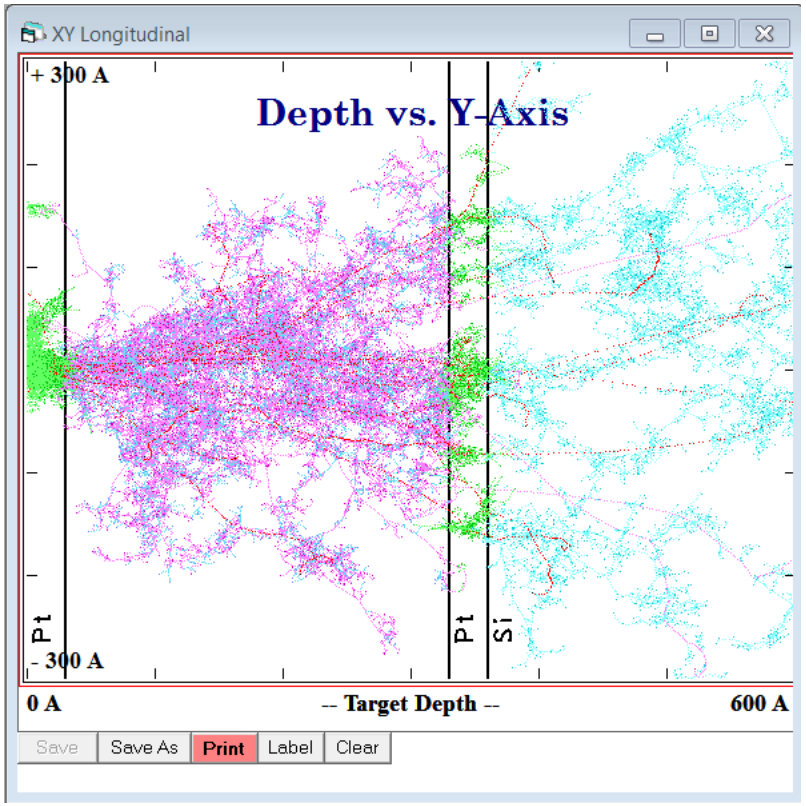
$$F_D(\vec{r}) = \frac{\nu(E_0)}{(2\pi)^{3/2}\sigma_z\sigma_x^2} exp\left(-\frac{(z-\overline{R}_D)^2}{2\sigma_z^2} - \frac{x^2+y^2}{2\sigma_x^2}\right)$$

$\nu(E_0)$ total energy deposited into nuclear collisions
$\overline{R}_D$ mean depth of nuclear energy deposition

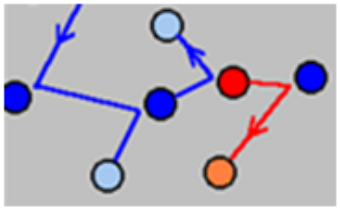
(exact values for R_D, σ_x and σ_z best from collisional computer simulation)

Collision cascade in a multilayer (TRIM)

50 keV $Ar^+ \rightarrow$ 3 nm Pt / 30 nm TiO_2 / 3 nm Pt / Si



Collisional damage



Cascade atom receives sufficient energy to become displaced

Analytical hard-sphere approximation for number of resulting I-V pairs (or Frenkel pairs) (Kinchin and Pease)

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

T initial energy of recoil atom
U_d damage threshold energy (15 ... 80 eV depending on material)

For dense cascades with <T> >> U_d, K-P formula holds for the total number of FP's generated by one incident ion

$$N_F(E_0) = \frac{E_0}{2U_d}$$

E_o incident ion energy

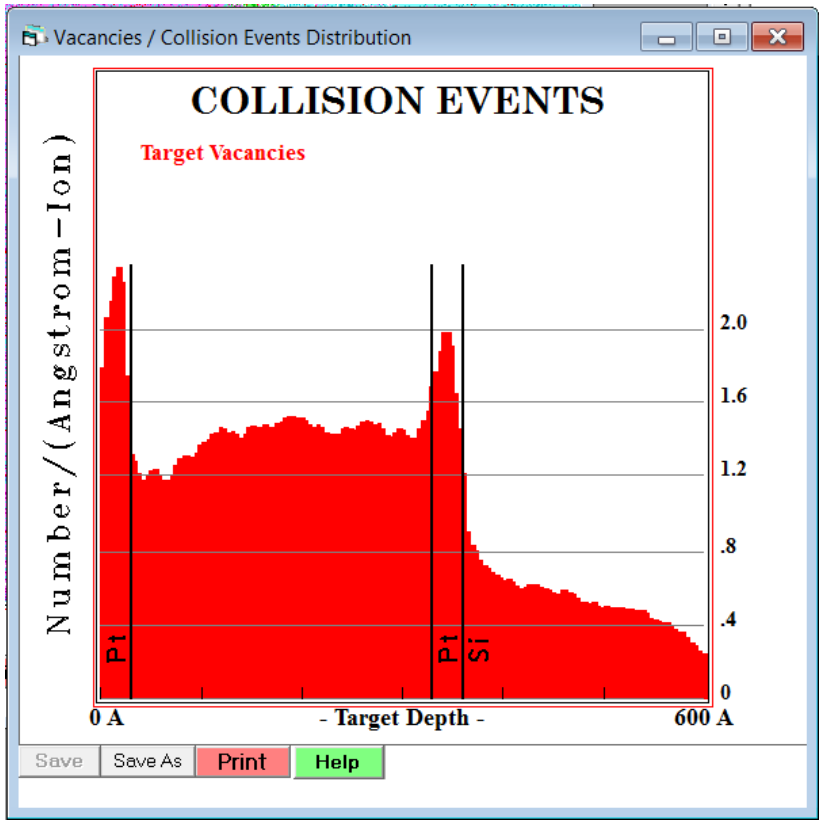
In dense cascades, I-V recombination might occur during the slowing-down phase. Further, corrections arise as part of the energy is dissipated into electronic collisions (about 10%), and from a more realistic interaction potential.

$$N_F^{eff}(E_0) \approx 0.35 \frac{E_0}{U_d} \xi(m_1, m_2, E_0)$$

ξ "cascade efficiency" (between ~0.3 – heavy ions at high energy – and 1 – light ions)

Collisional damage: TRIM computer simulation

50 keV Ar^+ → 3 nm Pt / 30 nm TiO_2 / 3 nm Pt / Si



Displacement thresholds used in TRIM:
Ti: 25 eV, O: 20 eV
questionable!

Use specific data from literature where available.

From MD computer simulation:
Ti: ~130 eV, O: ~65 eV

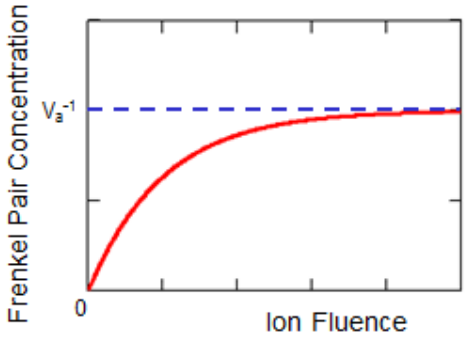
Collisional damage – high fluence

At increasing fluence, newly generated Frenkel pairs may annihilate with previously generated ones (typical for metals)

$$\frac{c_F(E_0,\Phi)}{d\Phi} \approx \frac{N_F^{eff}(E_0)}{2R_p(E_0)}\left(1-c_F V_a\right)$$

Φ ion fluence
V_a annihilation volume (for metals, typically 20...50 atomic volumes)
R_p mean projected ion range

(assuming that affected depth is ~2·R_p)



In materials with covalent binding (e.g., semiconductors), lattice damage might increase until amorphization. A simple formal estimate for the fluence required for amorphization is obtained when each atom in the irradiated volume has been displaced once in average, i.e. the FP concentration becomes equal to the atomic density of the irradiated material

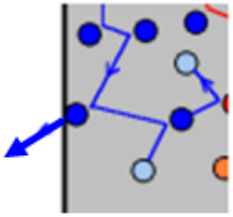
$$\Phi_{am} = \frac{2nR_p(E_0)}{N_F^{eff}(E_0)}$$

n atomic density

Correspondingly, in radiation damage studies the fluence is often given in units of dpa = displacements per atom

$$\frac{\Phi_{dpa}}{dpa} = \frac{c_F}{n} = \frac{N_F^{eff}(E_0)}{2nR_p(E_0)}\Phi$$

Collisional sputtering



Cascade atom overcomes surface binding energy

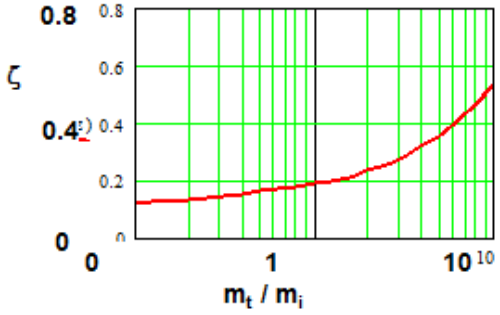
$$Y_s = \frac{nr.\ of\ \ sputtered\ \ atoms}{nr.\ of\ \ incident\ \ ions}$$

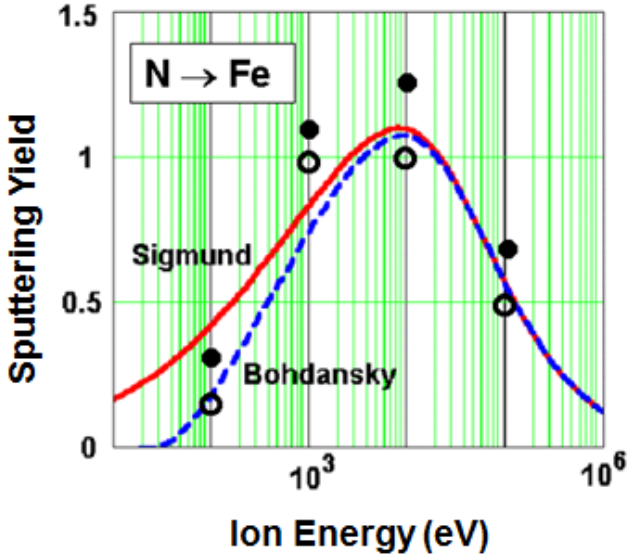
Sputtering yield

Analytical transport theory by Sigmund

$$Y_s(E_i) = \frac{4.2 \cdot 10^{14}\ cm^2}{U_s} \cdot \zeta\left(\frac{m_t}{m_i}\right) \cdot S_n(E_i)$$

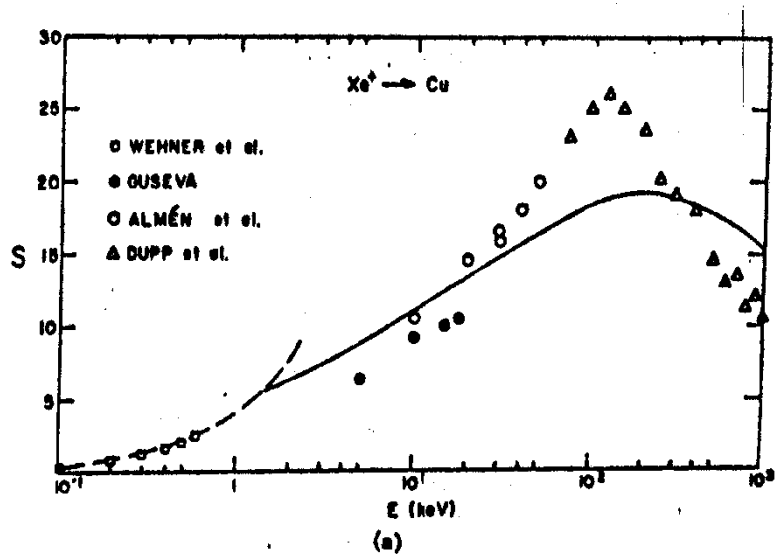
U_s surface binding energy (enthalpy of sublimation: 3 ... 8 eV depending on material)
S_n nuclear stopping power
ζ momentum reversal factor
m_t target atomic mass

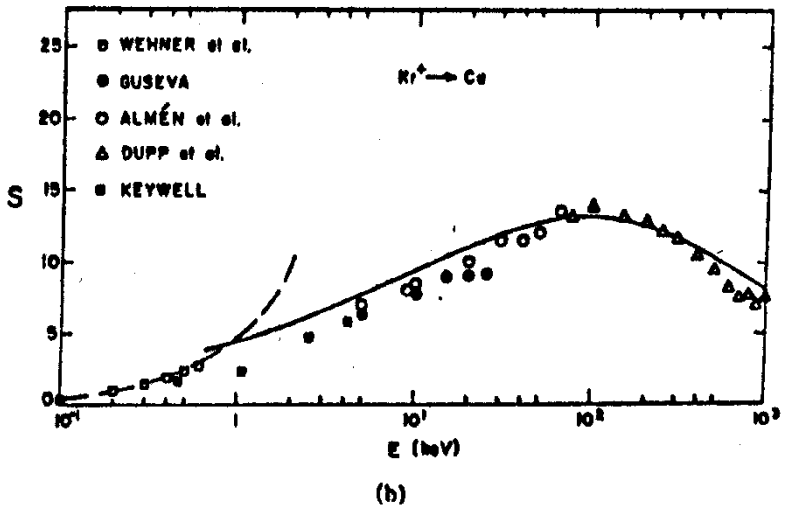


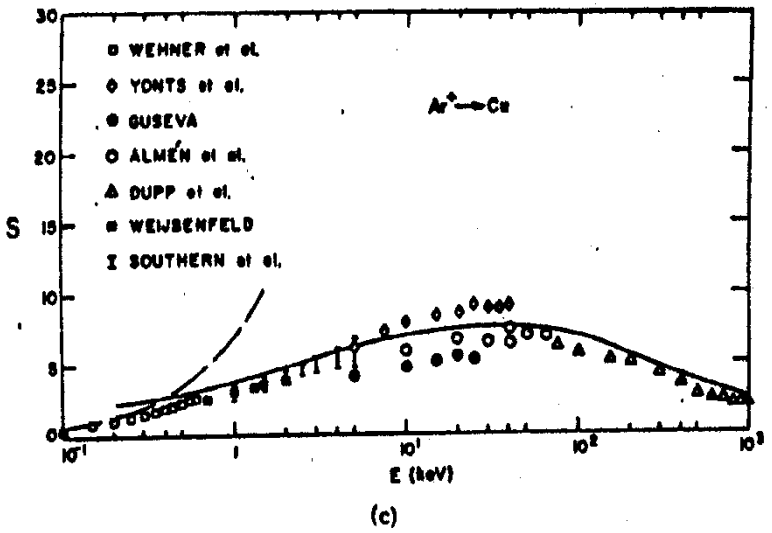


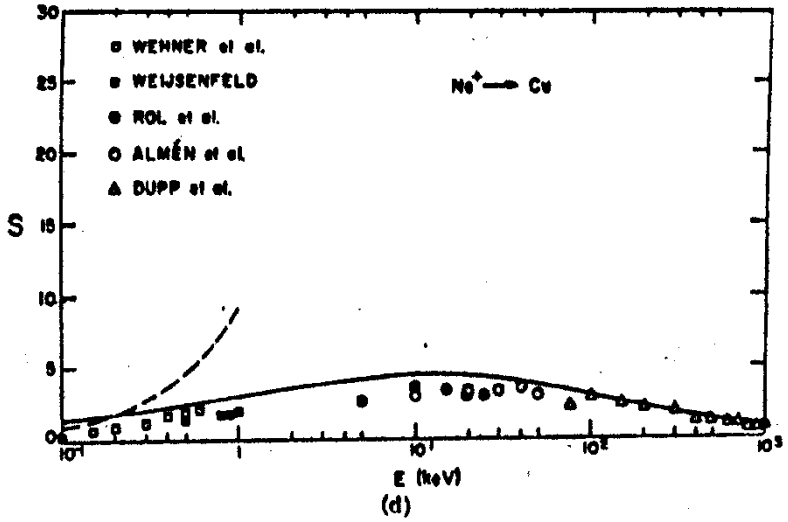
Read line: Sigmund formula
Blue line: Corrected for threshold effects
Dots: From computer simulation (TRIM, TRIDYN)

Collisional sputtering









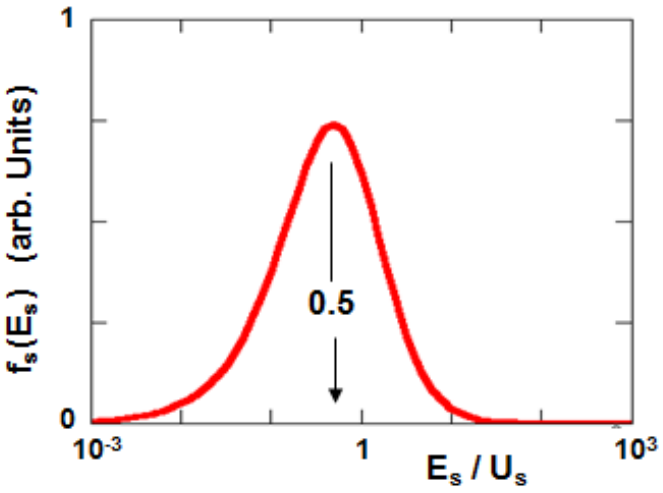
Sputtered atom angle and energy distributions

Thompson energy distribution of sputtered atoms

$$f_s(E_s) \sim \frac{E_s}{(E_s + U_s)^3}$$

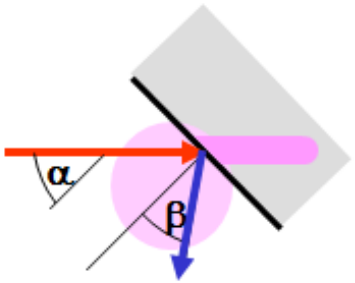
Mean energy of sputtered atoms

$$\overline{E} \approx 2 \ln \frac{E_0}{U_s} - 3$$



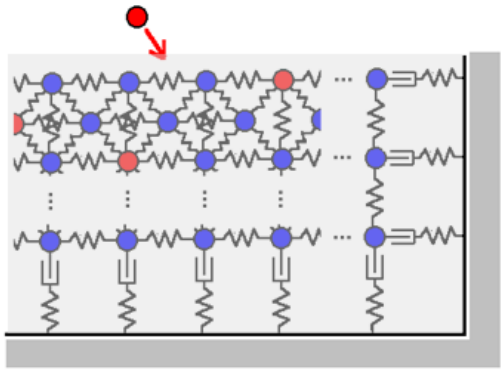
Dependence on angles of incidence and emission (amorphous substance)

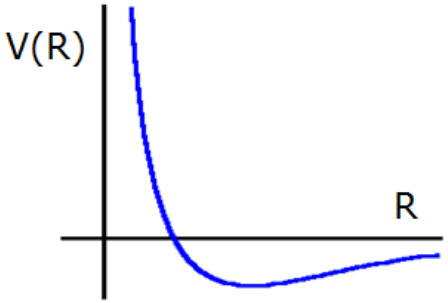
$$f_\Omega(\alpha,\beta) \sim \frac{\cos\beta}{\cos\alpha}$$



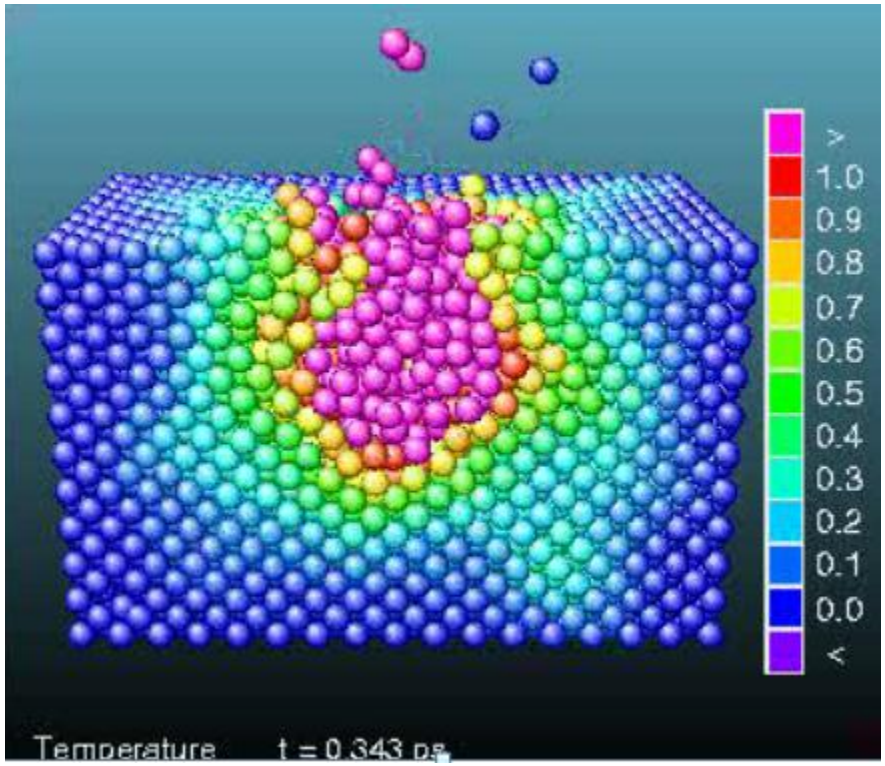
Thermal spike: molecular dynamics computer simulation

Classical Molecular Dynamics (MD)

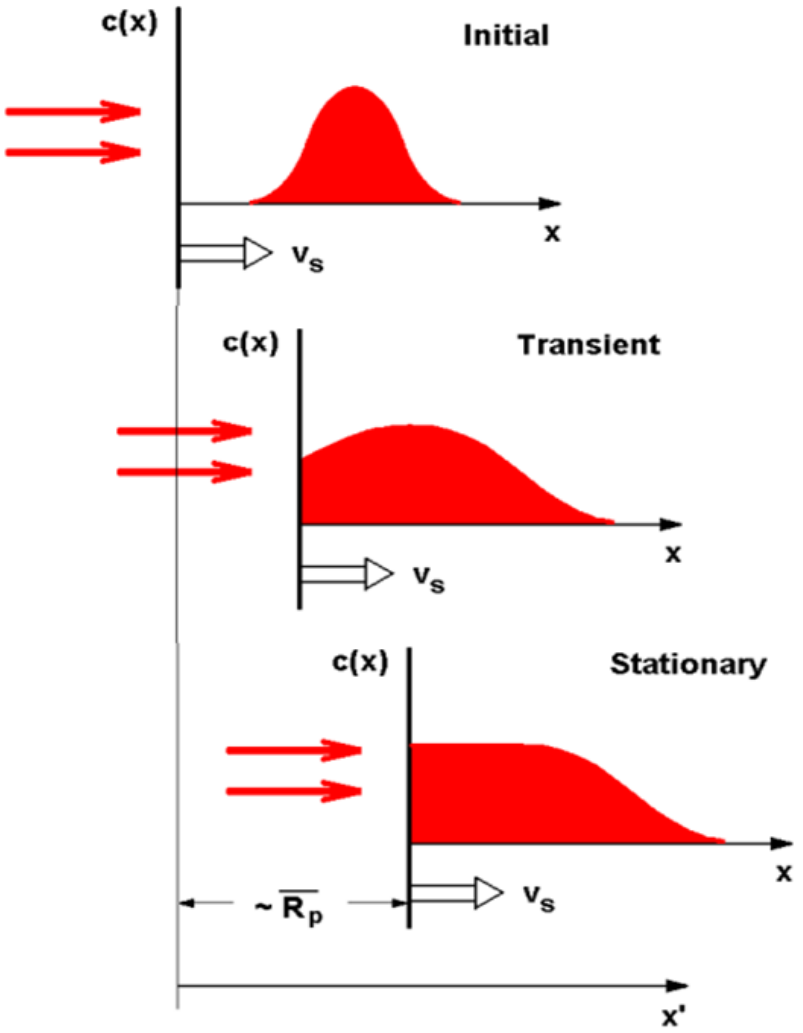




1 keV $Ar^+ \rightarrow Cu$



Sputter-controlled implantation profile

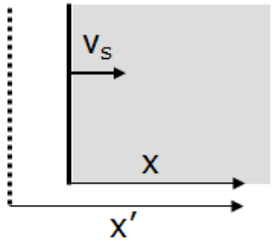


Deposition Profile $Q(x) = j_0 f_R(x)$

j_0 Ion Flux
f_R Range Distribution

Sputtered Flux $j_s = Y_s j_0 = n \upsilon_s$

Surface Recession $x' = x + \upsilon_s t$



Concentration at Time t $c(x',t) = \int_0^t Q(x' - \upsilon_s t')dt'$

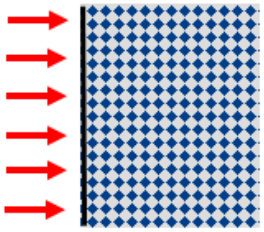
Gaussian range distribution

$$c(x,t) = \frac{n}{Y_s}\left[erf\left(\frac{x + \upsilon_s t - \overline{R}_p}{\sigma}\right) - erf\left(\frac{x - \overline{R}_p}{\sigma}\right)\right]$$

$$\xrightarrow{t\to\infty} \frac{n}{Y_s}\left[\frac{1}{2} - erf\left(\frac{x - \overline{R}_p}{\sigma}\right)\right]$$

Surface Concentration $\frac{c(x=0, t\to\infty)}{n} = \frac{1}{Y_s}$ $(\sigma << \overline{R}_p)$

Preferential sputtering of compounds



Irradiation of two-component substance A_nB_m

Example: B is preferentially sputtered

Partial sputtering yields

$$Y_k^p = c_k^s Y_k^c$$

k = A,B
Y_k^c "component" sputter yields
c_k^s surface atomic fractions

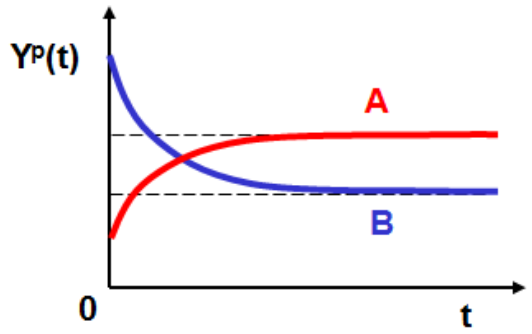
are generally different

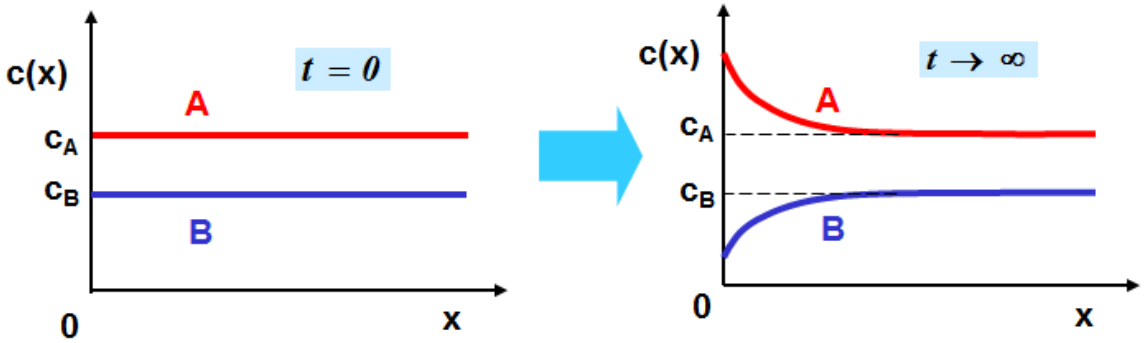
Preferential sputtering if

$$\frac{Y_A^p}{Y_B^p} \neq \frac{c_A^s}{c_B^s}$$

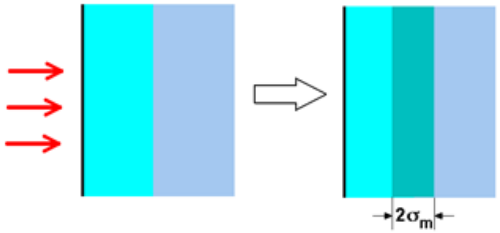
Mass conservation requires

$$\frac{Y_A^p(t \to \infty)}{Y_B^p(t \to \infty)} = \frac{c_A}{c_B}$$

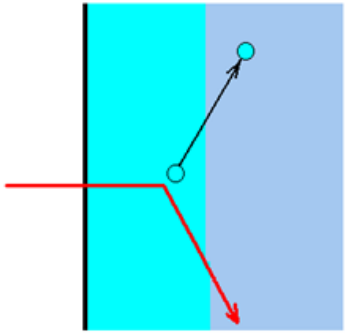




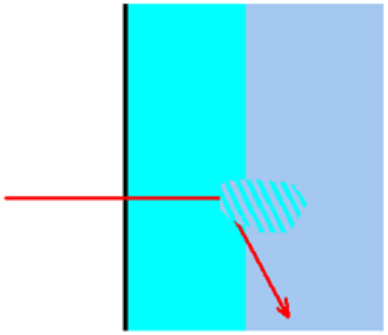
Ion mixing in multilayer stacks



Intermixing of layered materials by ion-induced atomic relocation



Recoil Mixing



Cascade Mixing

Analytical transport theory only for cascade mixing (Sigmund and Gras-Marti)

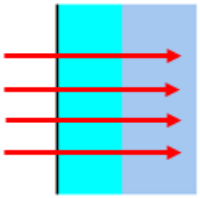
$$\sigma_m^2 = \frac{2\gamma}{\pi^2} S_n(\overline{E}) \frac{(R(E_c))^2}{E_c} \Phi$$

$$\gamma = \frac{4 m_1 m_2}{(m_1 + m_2)^2}$$

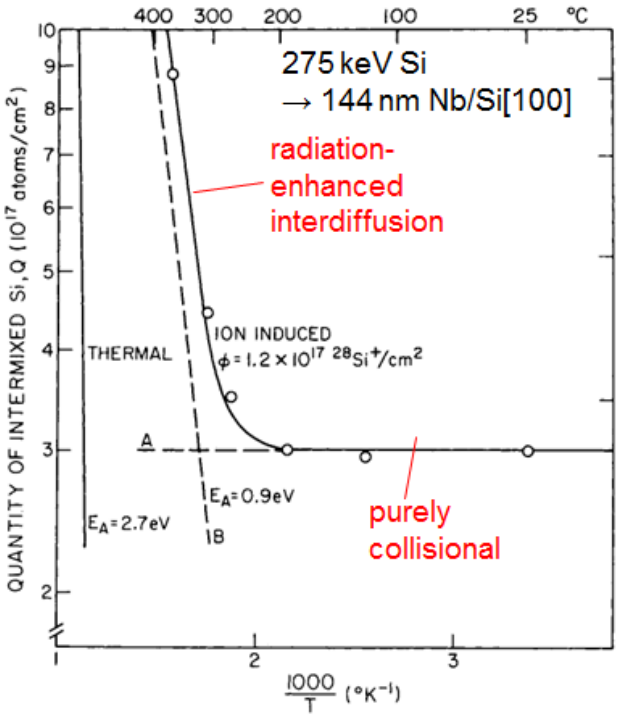
E_c min. recoil energy for relocation
$R(E_c)$ Recoil range at E_c
Φ Ion fluence

Fluence dependence of recoil implantation and mixing difficult to describe analytically

Ion mixing: thermal and chemical effects



Radiation-enhanced interdiffusion

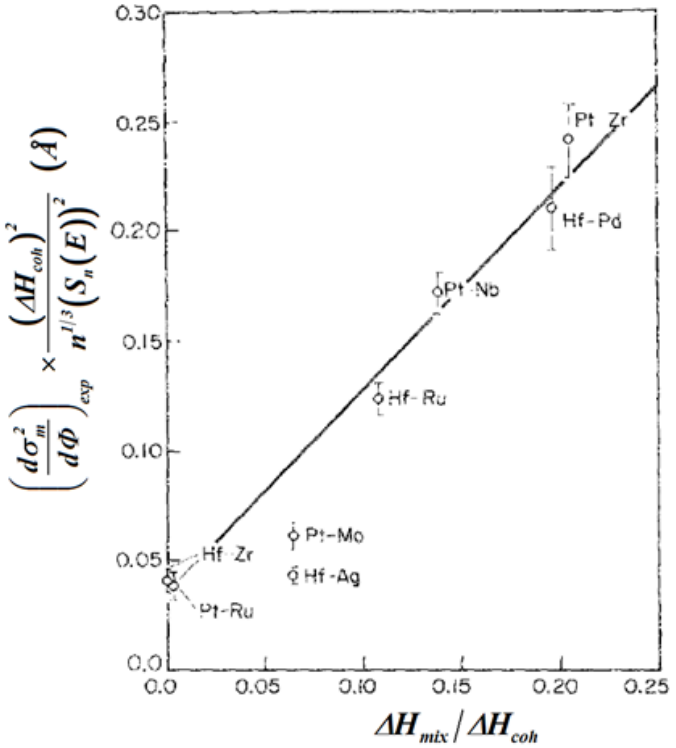


S. Matteson et al., Rad. Eff. 42(1979)217

Chemical driving forces: Enthalpy of mixing and cohesive energy

$$\frac{d\sigma_m^2}{d\Phi} = K_1 \frac{n^{1/3}(S_n(E))^2}{(\Delta H_{coh})^2}\left(1 + K_2 \frac{\Delta H_{mix}}{\Delta H_{coh}}\right)$$

K_1, K_2 Constants



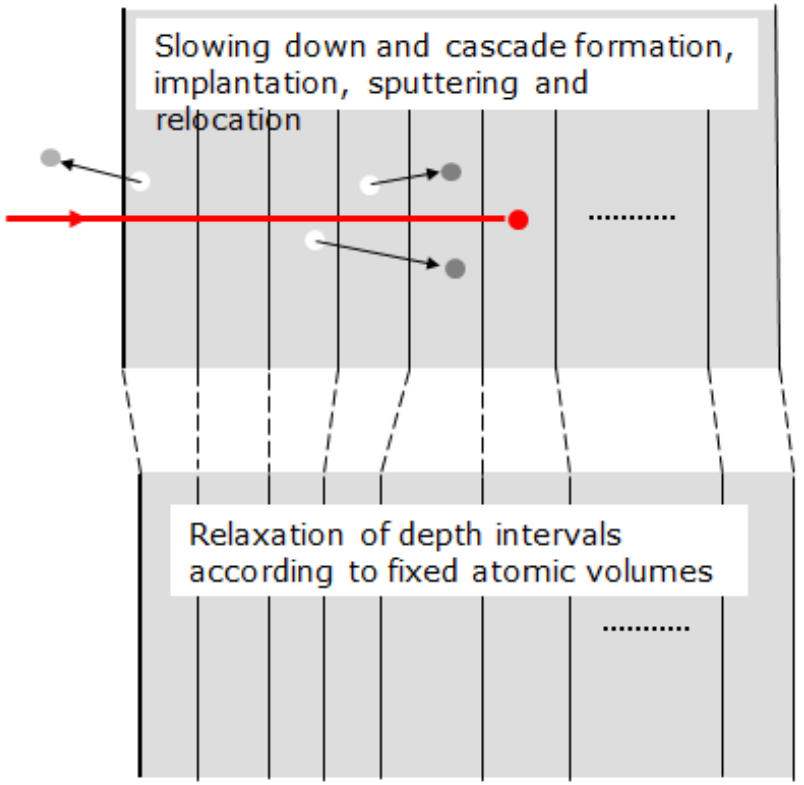
T.W. Workman et al., Appl. Phys. Lett. 50(1987)1485

TRIDYN: BCA simulation of compositional modification

- Collision cascade simulation as in TRIM
- Initially equidistant depth slabs (i=1,...,N) with thickness Δx_0 and fractional compositions c_{ik} (k=1,...,M) for M different elements (including projectile)
- Each pseudoparticle (deposited, relocated or sputtered atom) in the computer simulation corresponds to an increment in areal density
- $$\Delta\nu = \frac{\Phi_{tot}}{N_{pp}}$$

  Φ_{tot} Total Ion Fluence
  N_{pp} Total Number of Pseudoprojectiles
- Only compositional information is provided. BCA is unable to treat sructure or morphology.

- For each incident pseudoprojectile, simulation in two steps:



Möller, Eckstein and Biersack 1984

TRIDYN: BCA simulation of compositional modification

- After termination of pseudoprojectile and recoil histories, new areal densities ν_{ik} are calculated all components and depth intervals. From these

- Fractional Compositions

$$c_{ik} = \frac{\nu_{ik}}{\sum_j \nu_{ij}}$$

- Total Atomic Densities

$$\frac{1}{n_i^{tot}} = \sum_j \frac{c_{ij}}{n_j^0}$$

n_j^0 Pure Element Atomic Densities

- Slab Thicknesses

$$\Delta x_i = \frac{1}{n_i^{tot}} \sum_j \nu_{ij}$$

- Limitation of Slab Thicknesses

$$0.5 < \frac{\Delta x_i}{\Delta x_0} = 1.5$$

Otherwise Splitting or Combination

- For reasonable statistics and precision, the relative change per slab has to be kept sufficiently small, by choosing Δv small enough. From experience,

$$max_i \left(\frac{\Delta \nu_i}{\nu_i} \right) < 0.05$$

per pseudoprojectile

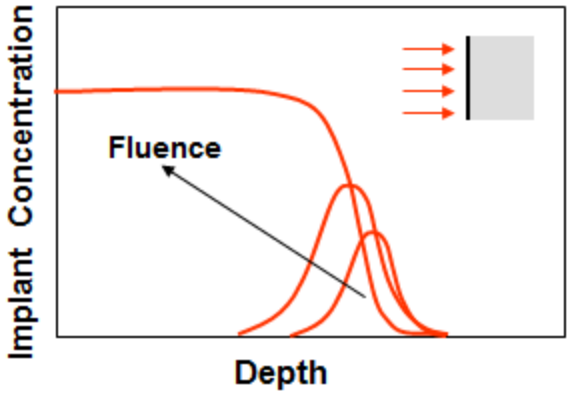
- Surface binding energies in componds variable with surface composition

$$U_{s,i} = \sum_j U_{ij} c_{s,j}$$

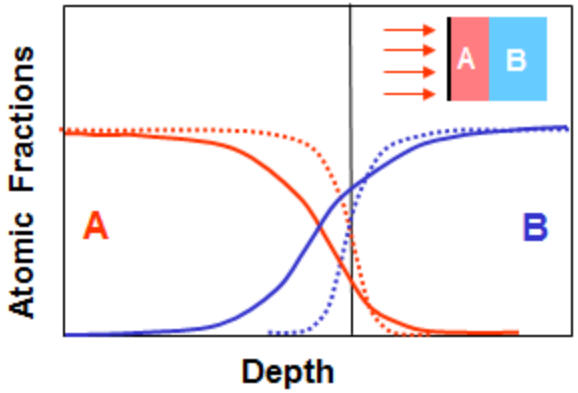
where U_{ij} are obtained from thermochemical data (heats of sublimation and compound formation)

TRIDYN applications

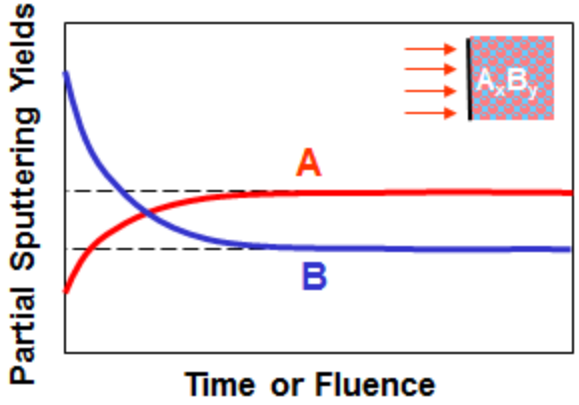
High-Fluence Implantation



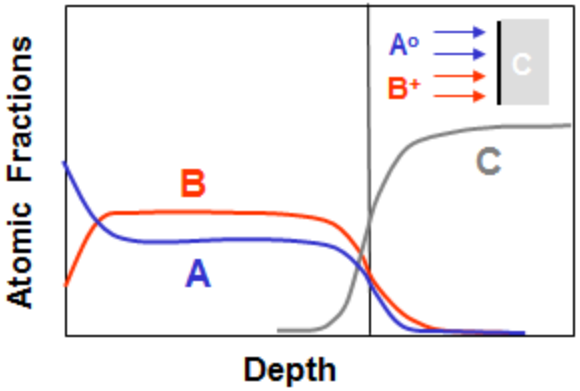
Ion Mixing



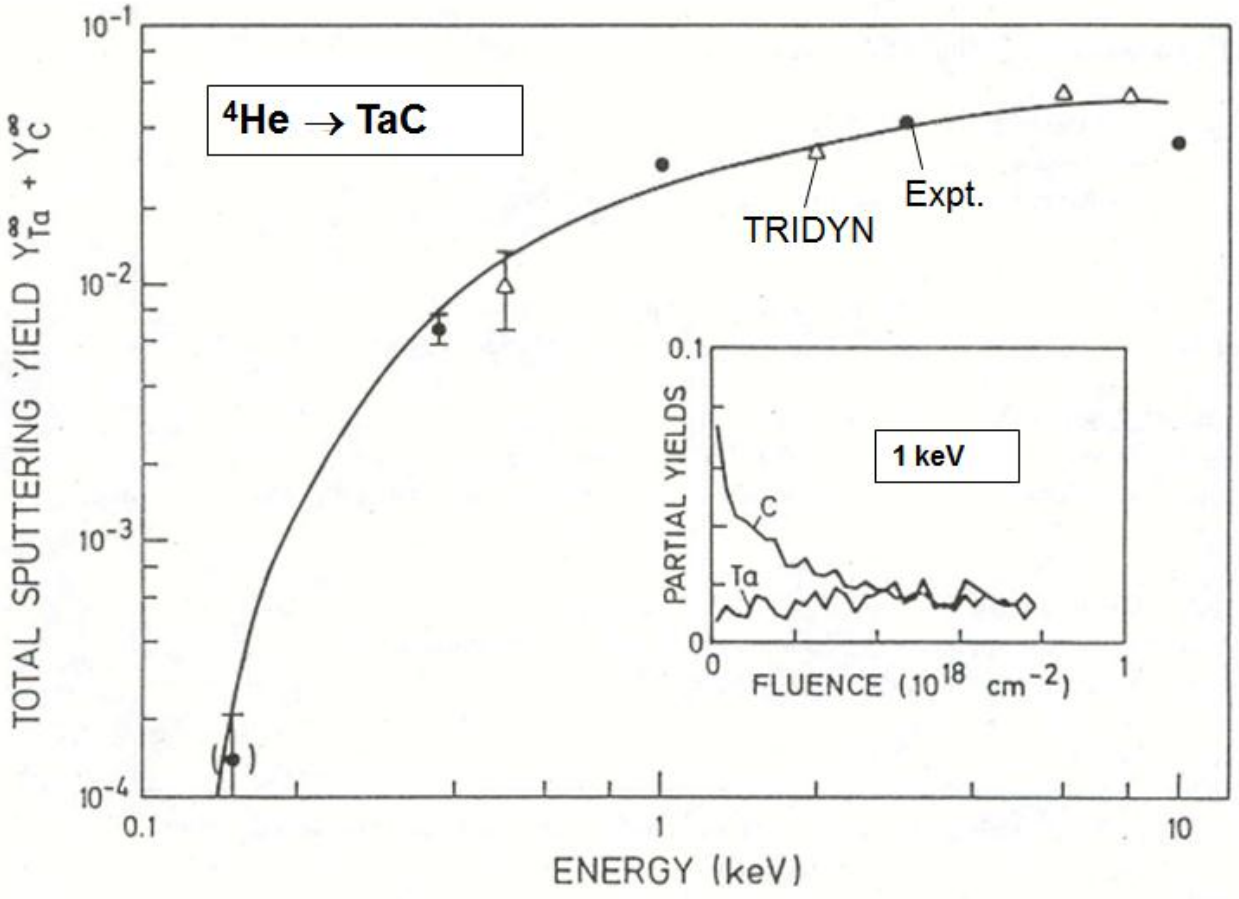
Preferential Sputtering



Ion-Assisted Deposition



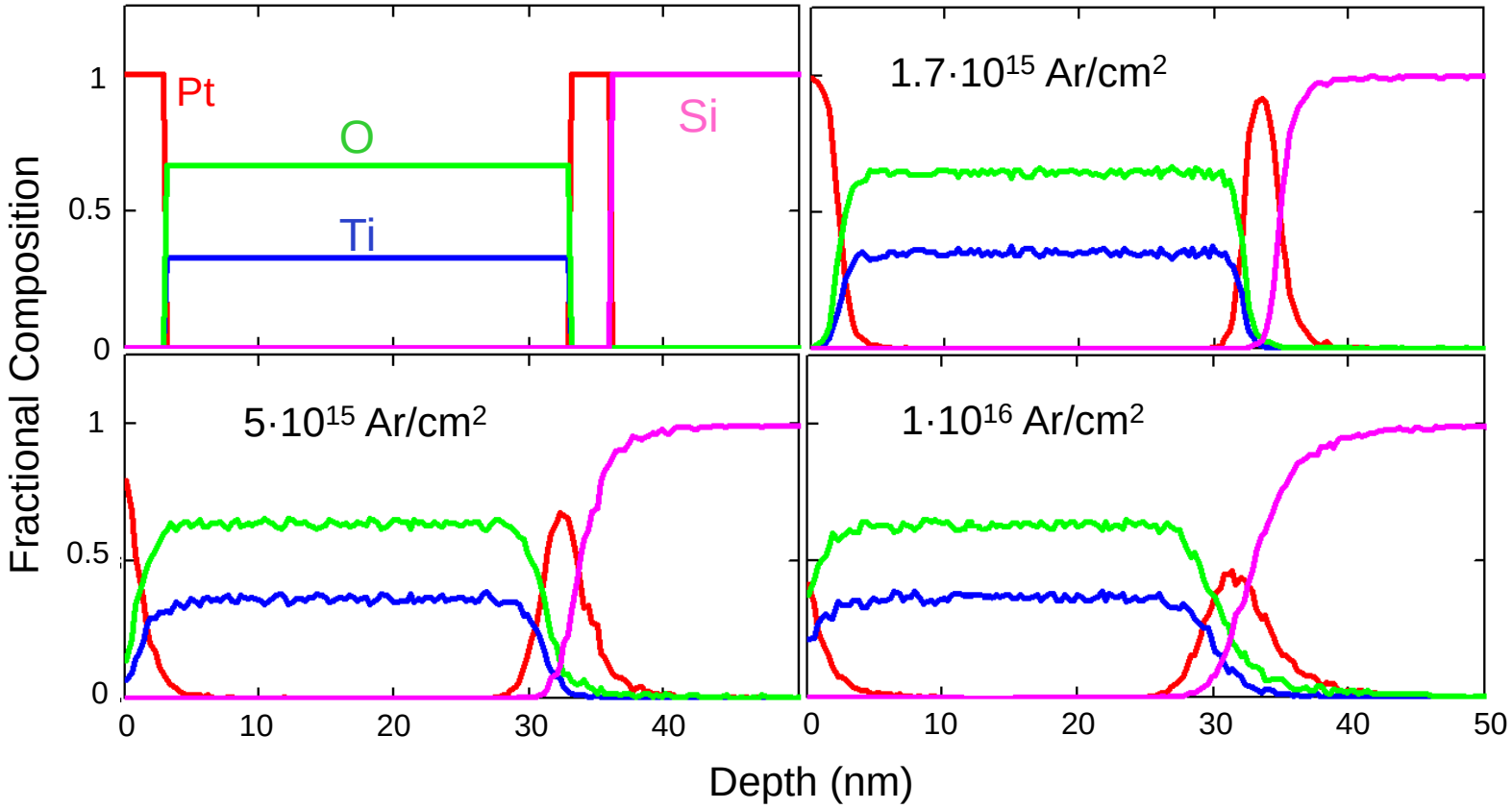
Preferential sputtering



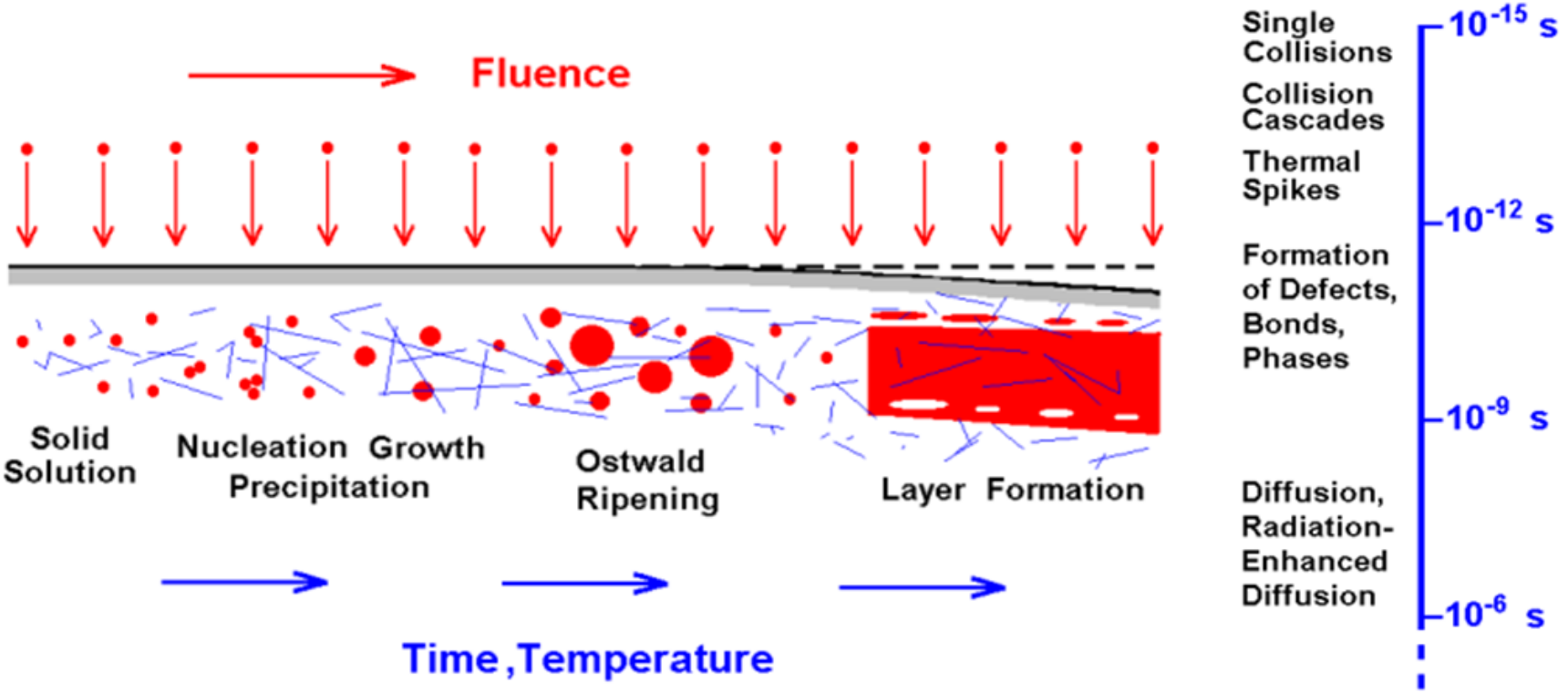
W. Eckstein and W. Möller, Nucl. Instr. Meth. B 7/8(1985)727

Multilayer sputtering and mixing

50 keV Ar^+ → 3 nm Pt / 30 nm TiO_2 / 3 nm Pt / Si

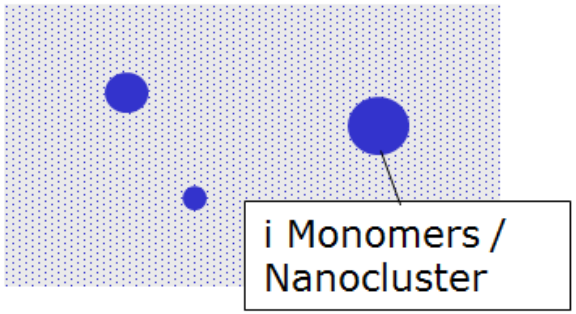


Ion implantation and ion beam synthesis



Nucleation of precipitates

Supersaturated Solution of Monomers



Change in Gibb's Free Energy

$$\Delta G(i) = -\delta\mu \cdot i + \gamma \cdot i^{2/3}$$

Volume Gain

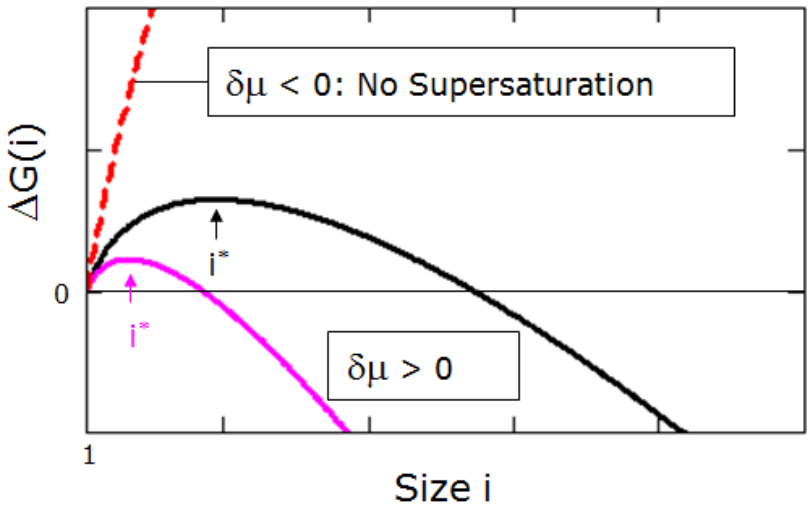
Creation of Interface

$$\gamma = \left(36\,\pi V_{at}^{2}\right)^{1/3}\sigma$$

V_{at} Atomic Volume
σ Surface Tension

Nucleation Threshold $i^* = \left(\frac{2\gamma}{3\,\delta\mu}\right)^3$

$$\Delta G(i^*) = \frac{4\gamma^3}{27\,(\delta\mu)^2}$$



Nucleation by Fluctuations!

Ostwald ripening

Monomer Concentration
around Precipitate
(Gibbs-Thomson Equation)

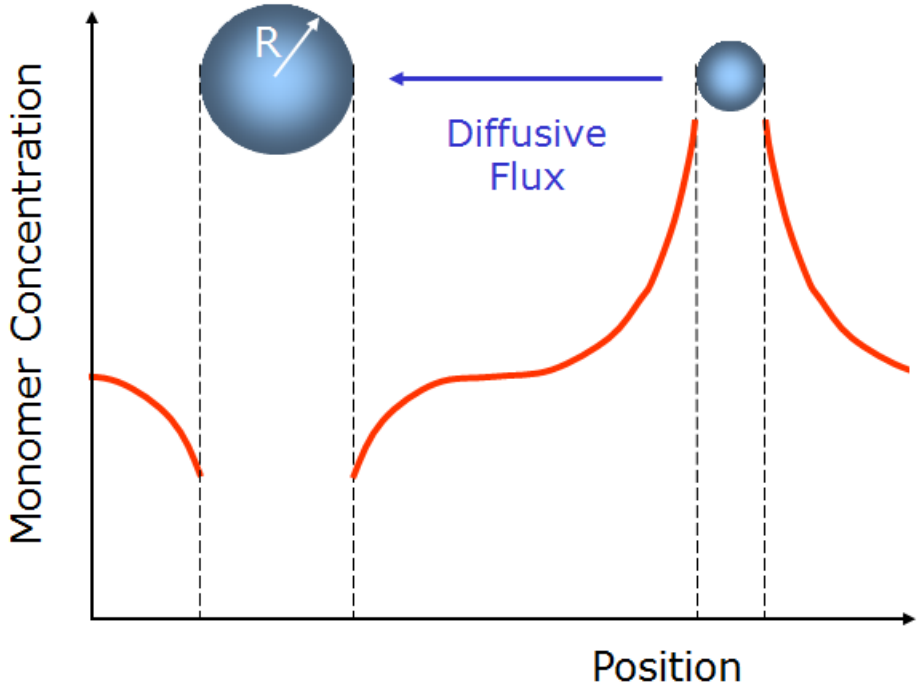
$$c(R) = c_\infty \, exp\left(\frac{R_c}{R}\right) \approx c_\infty\left(1 + \frac{R_c}{R}\right)$$

c_∞ Solubility

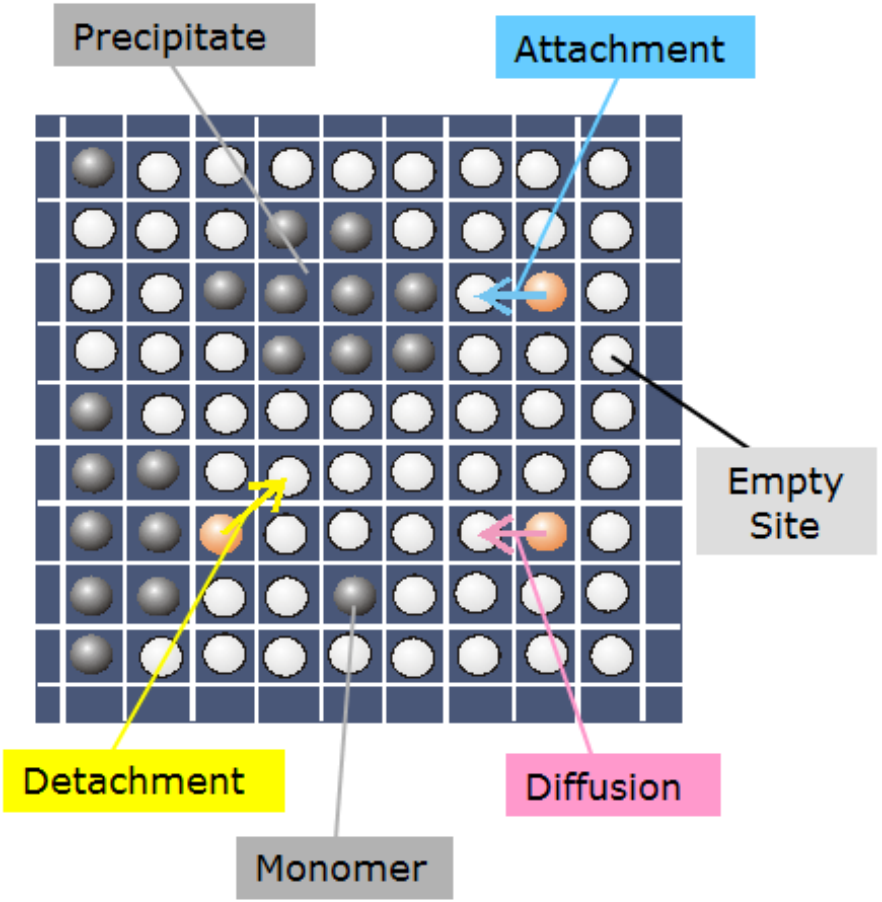
"Capillary" Length

$$R_c = \frac{2\sigma V_{at}}{kT}$$

σ Surface Tension
V_{at} Atomic Volume



Kinetic Monte Carlo simulation



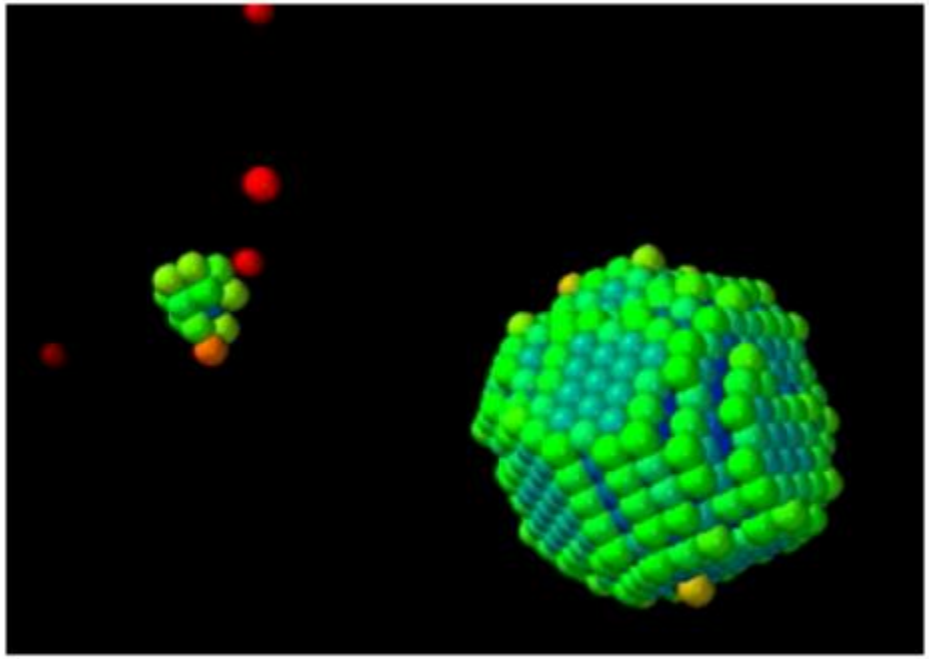
"Ising" Model: Configurational energy of each atom depends only on number of nearest neighbours

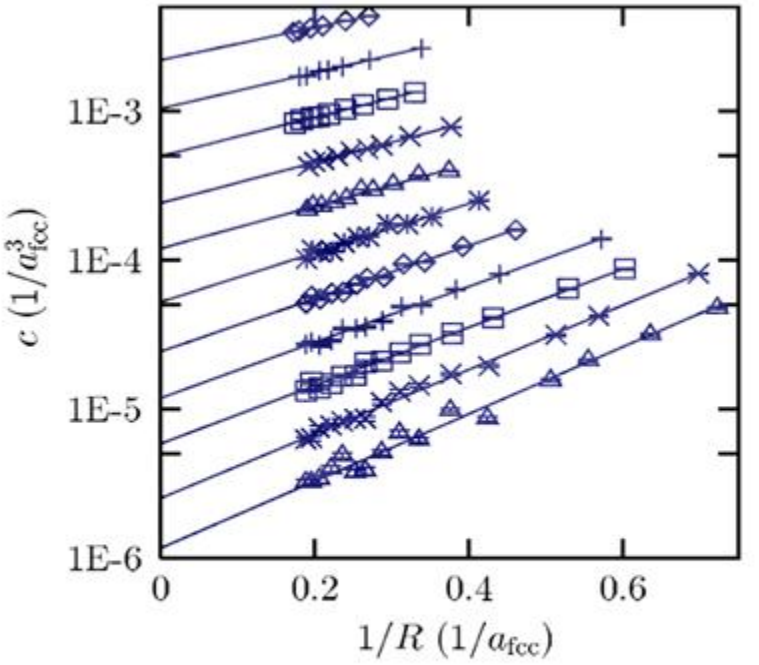
Probability of jump from initial site i to final site f

$$w_{if} = \nu_0 e^{-\frac{E_d}{kT}} \cdot \begin{cases} 1 & if \quad N_i < N_f \\ e^{-\frac{E_p}{kT}(N_i - N_f)} & else \end{cases}$$

ν_0	Attempt frequency
E_d	Activation energy of diffusion
E_p	Energy gain per nearest neighbour
$N_{i,f}$	Initial and final number of nearest neighbours

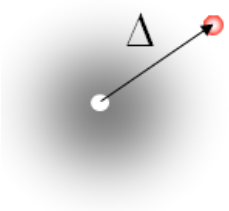
Ostwald ripening by 3D lattice Monte Carlo simulation





GT Equation Reproduced

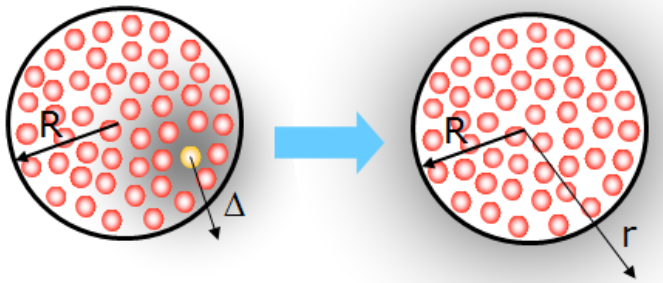
Ion mixing at precipitates



Atomic relocation probability per incident ion (Assumed to be isotropic)

$$w_r(\Delta) \propto exp\left(-\frac{\Delta}{\lambda}\right)$$

$\lambda = \lambda(E_{ion}, m_{ion}, m_{target})$
Characteristic Relocation Length



Angular and spatial integration yields radial relocation field $W_r(r)$

Atomic relocation is counteracted by diffusion.
In local equilibrium

$$-\frac{D}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial c(r)}{\partial r}\right) = j\,W_r(r)$$

D Diffusion Coefficient
j Ion Flux

After minor approximations (e.g., r-R > λ)

$$c(R) = \tilde{c}_\infty\left(1+\frac{\tilde{R}_c}{R}\right)$$

(Linearized) Gibbs-Thomson equation holds for ion mixing !

with

$$\tilde{c}_\infty = c_\infty(1+\delta)$$

$$\tilde{R}_c = \frac{R_c - 5\lambda\delta/4}{1+\delta}$$

$$\delta = \frac{q\lambda^2}{Dc_\infty}$$

q Nr. of displacements per Atom and Unit of Time

K.-H. Heinig et al., Mat.Res.Soc.Proc. vol. 650 (2001)

Inverse Ostwald ripening

Conventional Ostwald ripening

$$c_s = c(R) = c_\infty \left(1 + \frac{R_c}{R}\right) \qquad R_c \propto \frac{1}{kT}$$

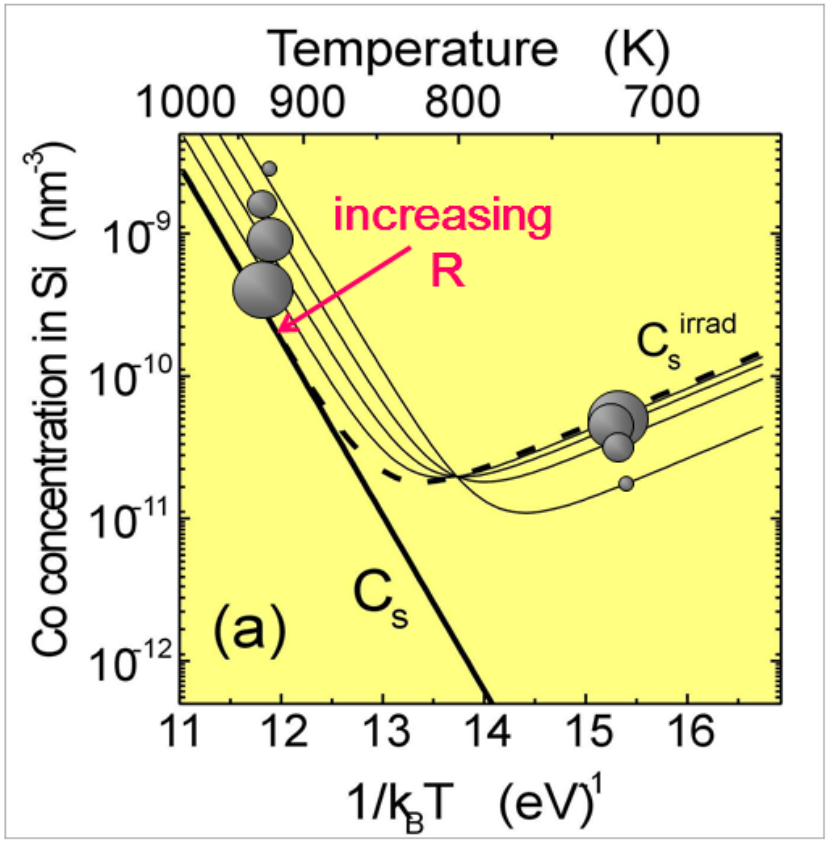
Under irradiation

$$c_s^{irr} = c^{irr}(R) = \tilde{c}_\infty \left(1 + \frac{\tilde{R}_c}{R}\right)$$

$$\tilde{R}_c = \frac{R_c - 5\lambda\delta / 4}{1 + \delta}$$

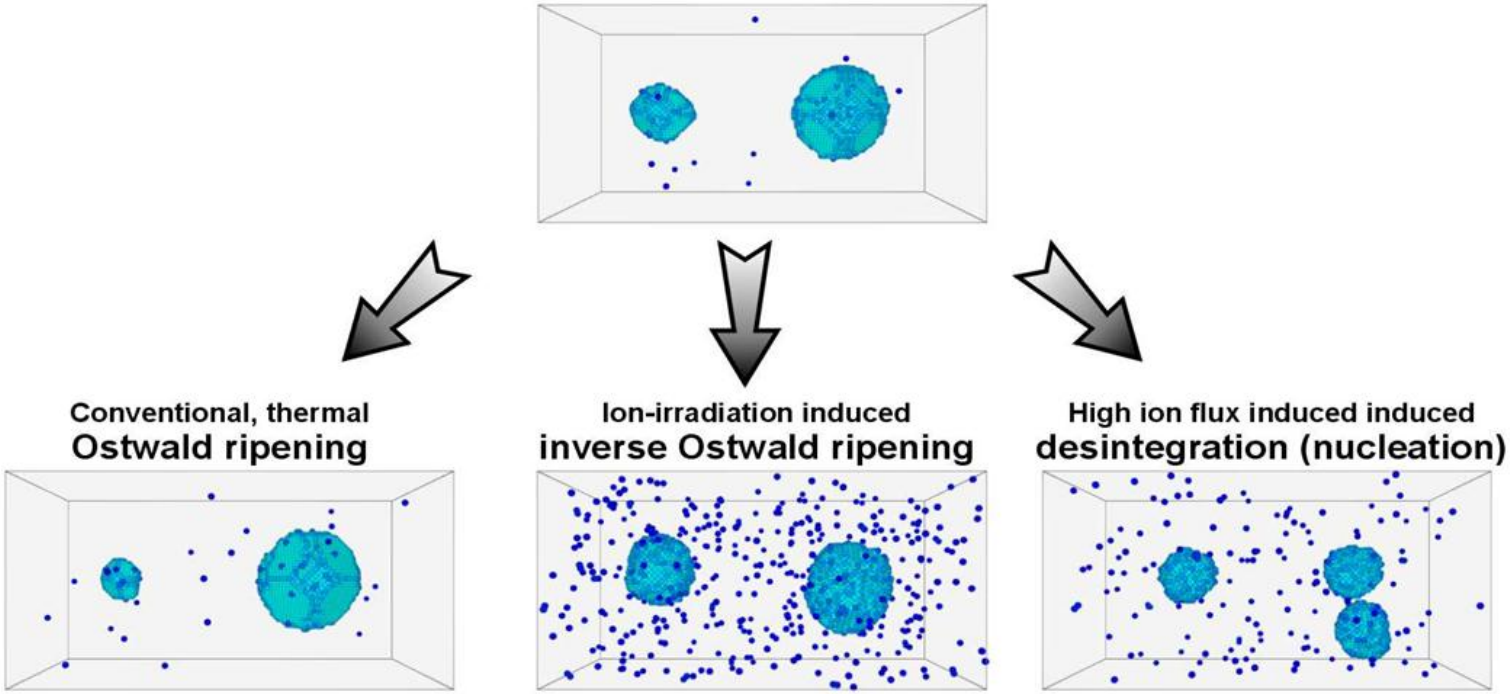
Capillary length may become negative !

- Growth of smaller precipitates
- Towards homogeneous size distribution



K.-H. Heinig et al., Mat.Res.Soc.Proc. vol. 650 (2001)

Nanocluster evolution under ion irradiation



(Kinetic Monte Carlo simulation)