

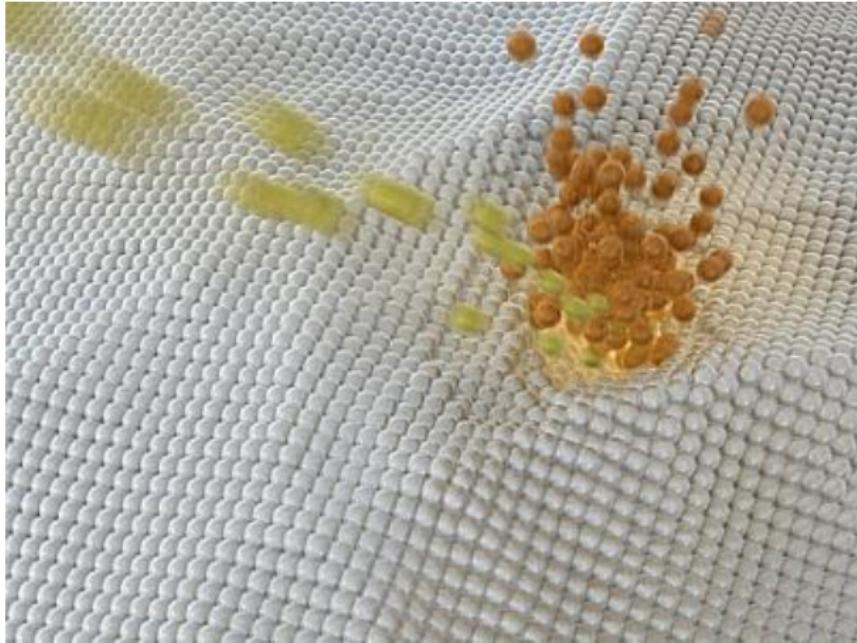


Physical techniques for nanofabrication

Ion implantation

Ion implantation

Atoms are introduced in the sub-surface zone of a solid substrate by accelerating ions with energy in the keV-MeV-GeV range.



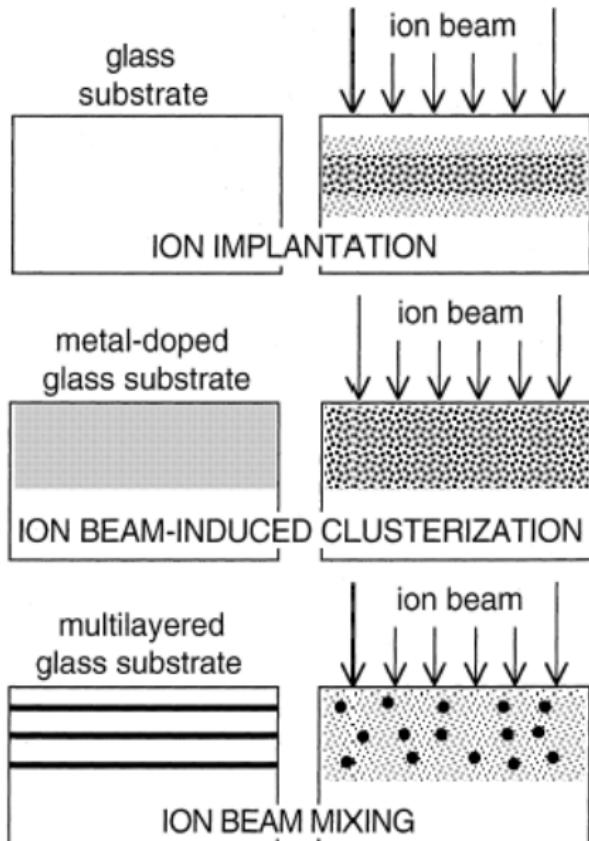
Ion implantation

- Possibility to introduce virtually **any element** into the matrix (out of thermodynamic equilibrium)
- **No solubility limit** (supersaturation)
- Depth **concentration profile** control
- **Patterning** on prescribed geometries
- **Compatibility** with micro-electronic processes (low temperature)
- **Multiple** ion implantation (alloys or compounds)
- **Ion-beam processing**

Ion implantation

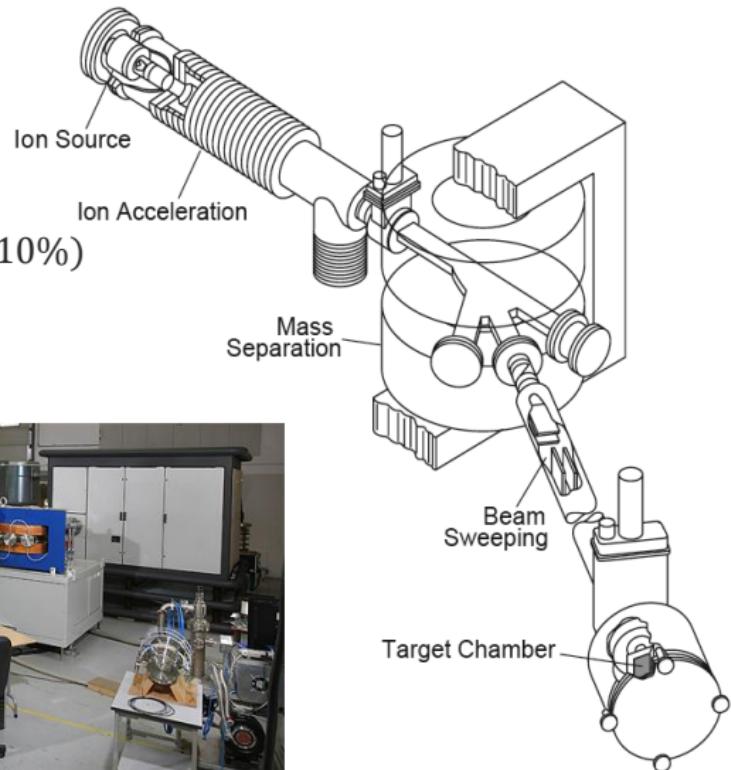
Ion-beam processing

1. **Implantation** to form clusters of the implanted species
2. **Light-ions irradiation** (He, Ne, ...) in glasses doped with the elements whose precipitation is to be promoted
3. **Heavy-ions irradiation** to induce mixing in multilayers



Ion implanter Danfysik 1090 (Legnaro, PD):

- $E_{ion} < 200 \text{ keV}$
- $J_{beam} < 2 \mu\text{A}/\text{cm}^2$
- $\text{Area}_{raster} < 20 \times 20 \text{ cm}^2$
- Fluence_{ion}: $10^{11} \div 10^{17} \text{ cm}^{-2} (\pm 10\%)$
- Double Faraday cage





Ion implanter Danfysik 1090 (Legnaro, PD)

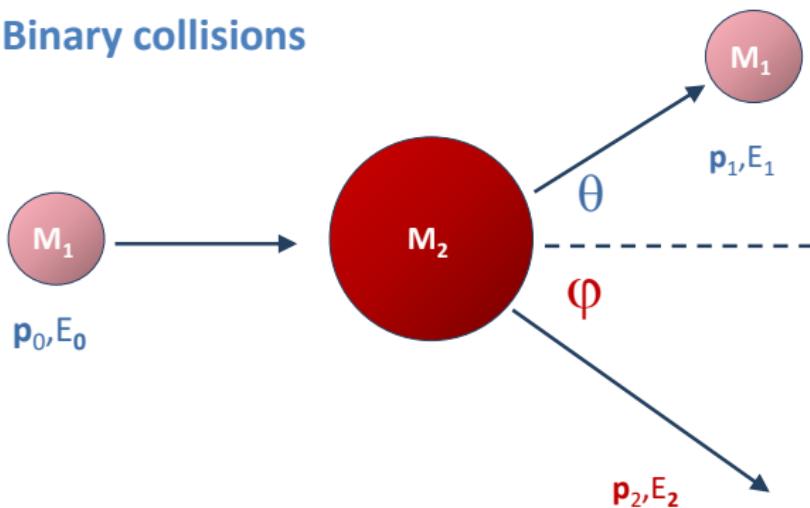
Implantable species

*Lanthanide Series

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

[†]Actinide Series

Binary collisions



$$V(r) = k \frac{Z_1 Z_2 e^2}{r} \chi(r)$$

Screening function

$$\chi(r) = \begin{cases} 0 & r \rightarrow \infty \\ 1 & r \rightarrow 0 \\ r & \end{cases}$$

$$\chi_{TF}(r) = 1 - \frac{r}{\sqrt{3 + r^2}}$$

$$T_E = 4 \frac{M_1 M_2}{(M_1 + M_2)^2} E_0 \sin^2 \frac{\theta_c}{2} = \gamma E_0 \sin^2 \frac{\theta_c}{2}$$

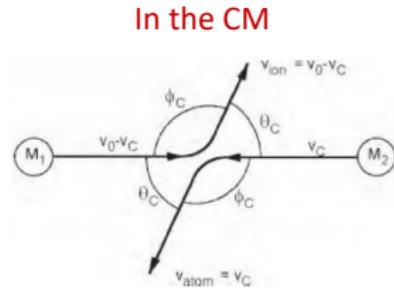
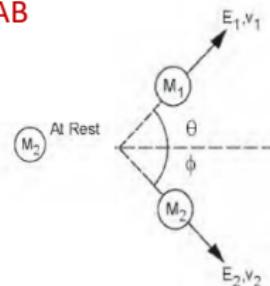
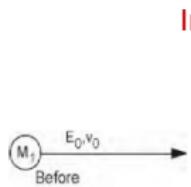
T_E transferred energy

$$\theta_c = \theta + \sin^{-1} \left(\frac{M_1}{M_2} \sin \theta \right) \quad \text{In the CM}$$

T_E is maximum when $M_1 = M_2$

When $T_E > E_B$ (binding energy, 3-10 eV): atoms are removed from the target

Ion implantation



Ex.: 100 keV B on Si at $\theta = 45^\circ$ (in the Lab)

$$\frac{M_1^B}{M_1^{Si}} = 10$$

$$\frac{M_1^{Si}}{M_1} = 28$$

$$\theta_c = \theta + \sin^{-1} \left(\frac{M_1}{M_2} \sin \theta \right) = 59.6^\circ \quad \text{CM}$$

$$T_E = 4 \frac{M_1 M_2}{(M_1 + M_2)^2} E_0 \sin^2 \frac{\theta_c}{2} = \gamma E_0 \sin^2 \frac{\theta_c}{2}$$

$$\gamma = 0.78$$

$$\sin^2 \frac{\theta_c}{2} = 0.247$$

$$\gamma \sin^2 \frac{\theta_c}{2} = 0.192$$

$$T_E = 19.2 \text{ keV}$$

Energy Loss

When an energetic ions enters a solid target it undergoes collisions loosing its initial energy at a typical rate of $dE/dx \sim 0.1\text{-}1 \text{ keV/nm}$

Energy Loss

Coulomb interaction with the screened nuclear charge
(elastic energy loss)

Stopping cross-section S

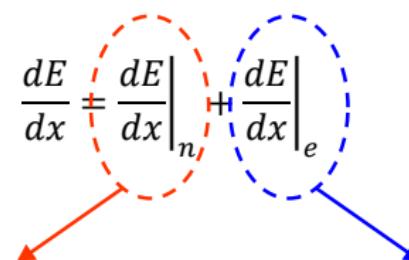
Stopping

$$\text{Energy loss per diffusion center } S \equiv \frac{1}{N} \frac{dE}{dx} = S_n + S_e$$

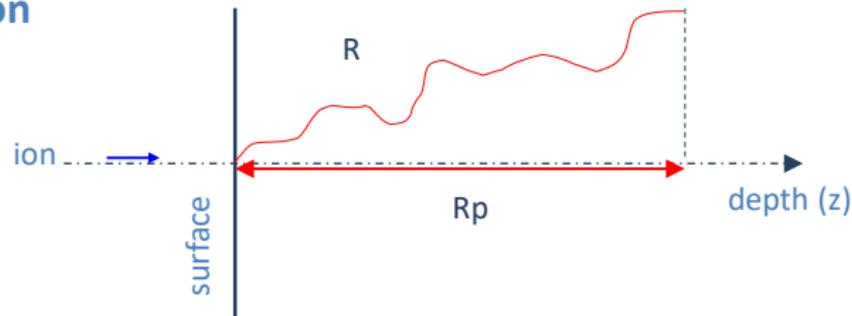
N: densità atomica target
(atomi/nm³)

S_n(E): stopping nucleare

S_e(E): stopping elettronico



Concentration



Ion Range

$$R \equiv \int_{E_0}^0 \left(\frac{dE}{dx} \right)^{-1} dE = \frac{1}{N} \int_{E_0}^0 \frac{dE}{S(E)}$$

Projected Range Rp:

$$R_P = \frac{1}{N_{ion}} \sum_j^{N_{ion}} z_j \cong \frac{R}{1 + \frac{M_2}{3M_1}}$$

}

Straggling ΔR_P : HWHM = semilarghezza picco di conc.

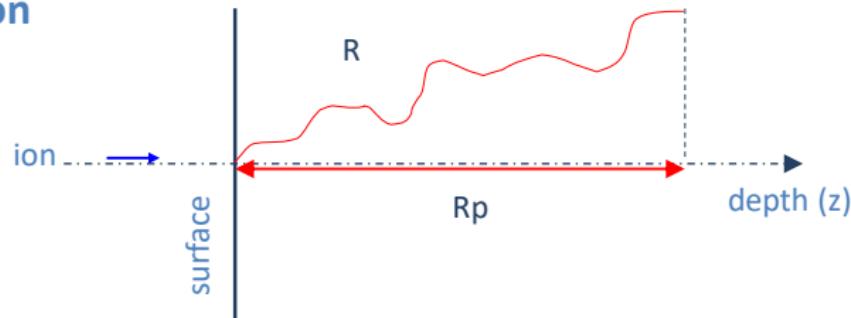
$$\Delta R_P = \sqrt{\frac{1}{N_{ion}} \sum_{j=1}^{N_{ion}} (z_j - R_P)^2}$$

}

(average over N_{ion} ions)

Ion implantation

Concentration

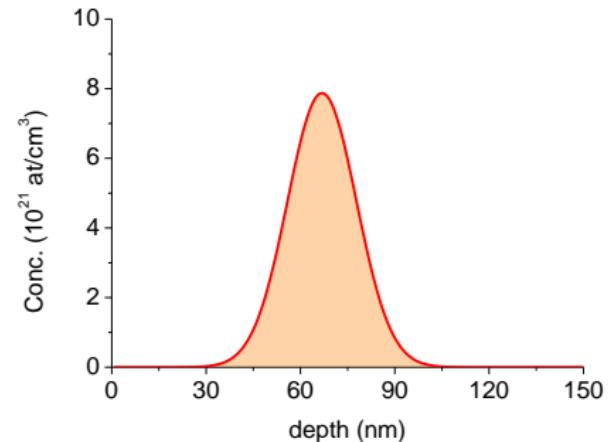


Concentration profile
(~ gaussian)

$$C(z) = A \exp \left[-\frac{1}{2} \left(\frac{z - R_p}{\Delta R_p} \right)^2 \right]$$

Dose or Fluence (atomi/cm²)

$$D = \int_0^{\infty} C(z) dz$$



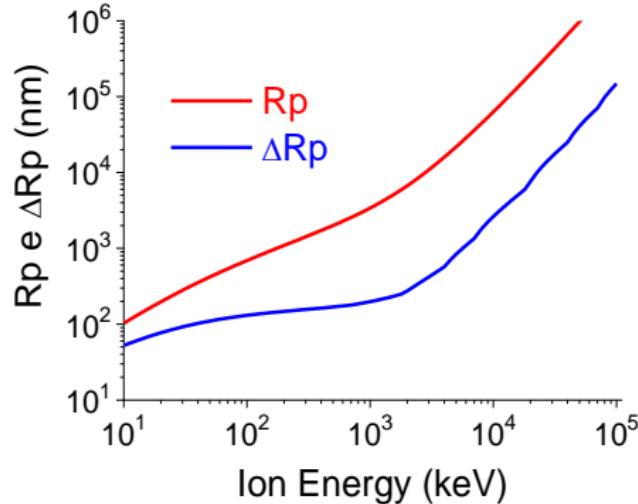
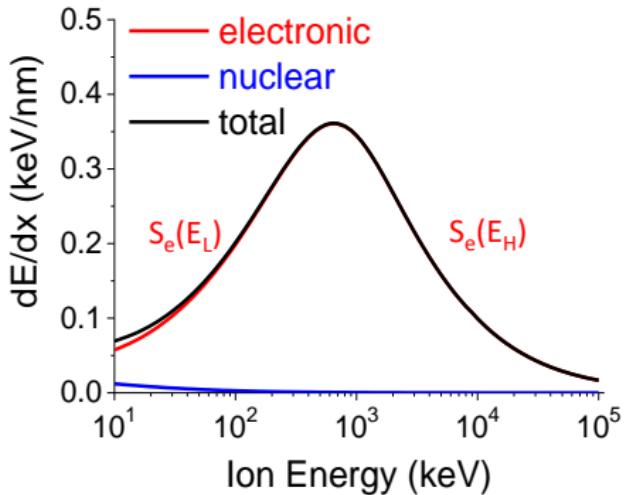
Example: He in SiO₂

Ion: He [2], Mass = 4.003 amu

Target: SiO₂

Target Density = 2.32 g/cm³ = 6.976 × 10²² atoms/cm³

Target Composition			
Atom Name	Atom Numb	Atomic Percent	Mass Percent
O	8	66.67	53.26
Si	14	33.33	46.74



Ion implantation

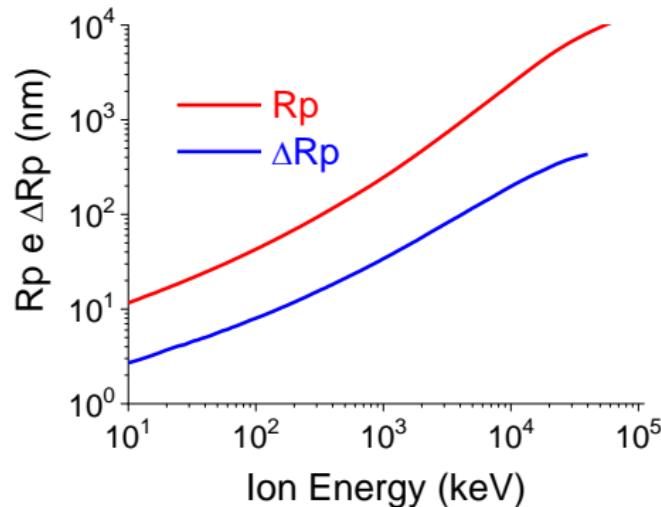
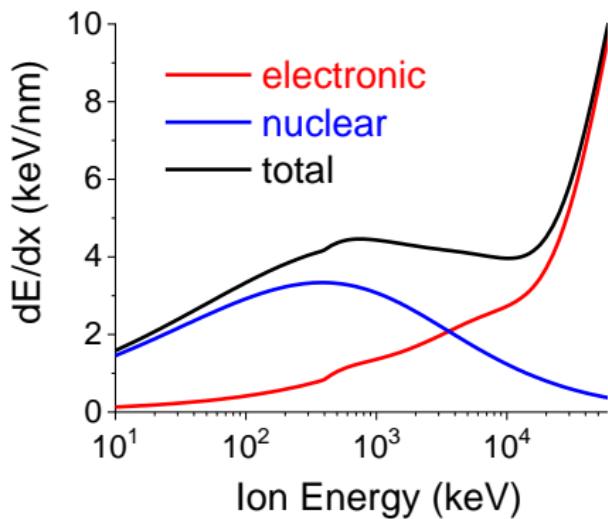
Example: Au in SiO₂

Ion: Au [79], Mass = 196.967 amu

Target: SiO₂

Target Density = 2.32 g/cm³ = 6.976 × 10²² atoms/cm³

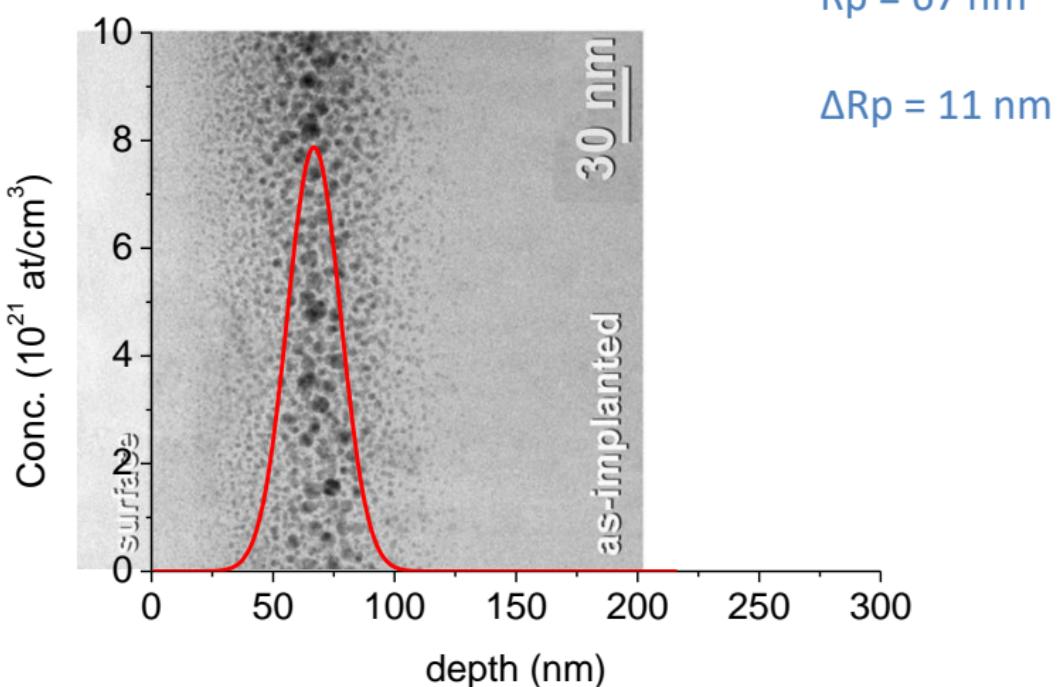
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J. P. Biersack and L. Hagmark, Nucl. Instr. and Meth., vol. 174, 257, 1980
SRIM code: <http://www.srim.org/>

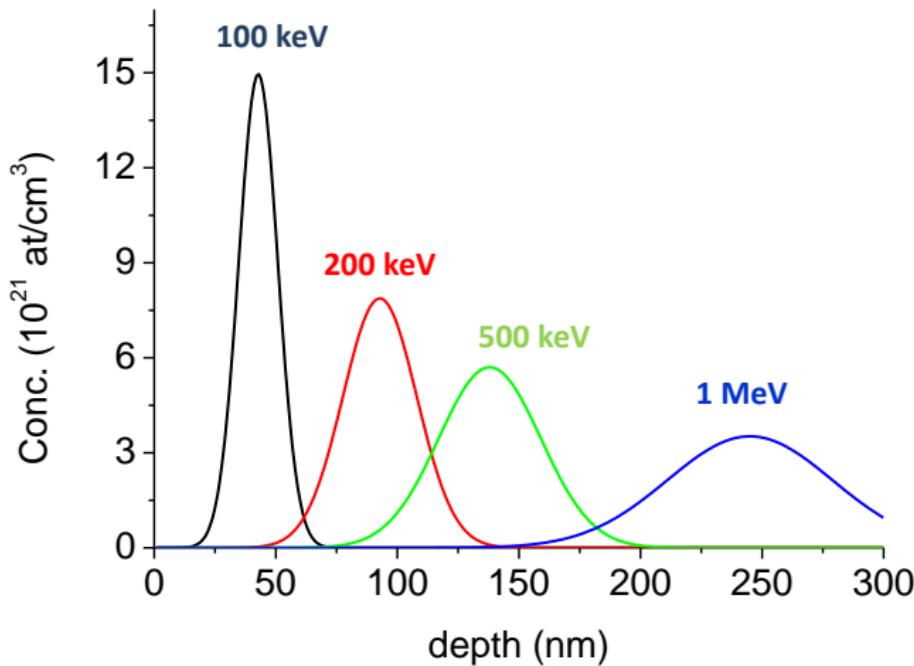
Ion implantation

Example: Au 190 keV, 3×10^{16} ion/cm² in SiO₂

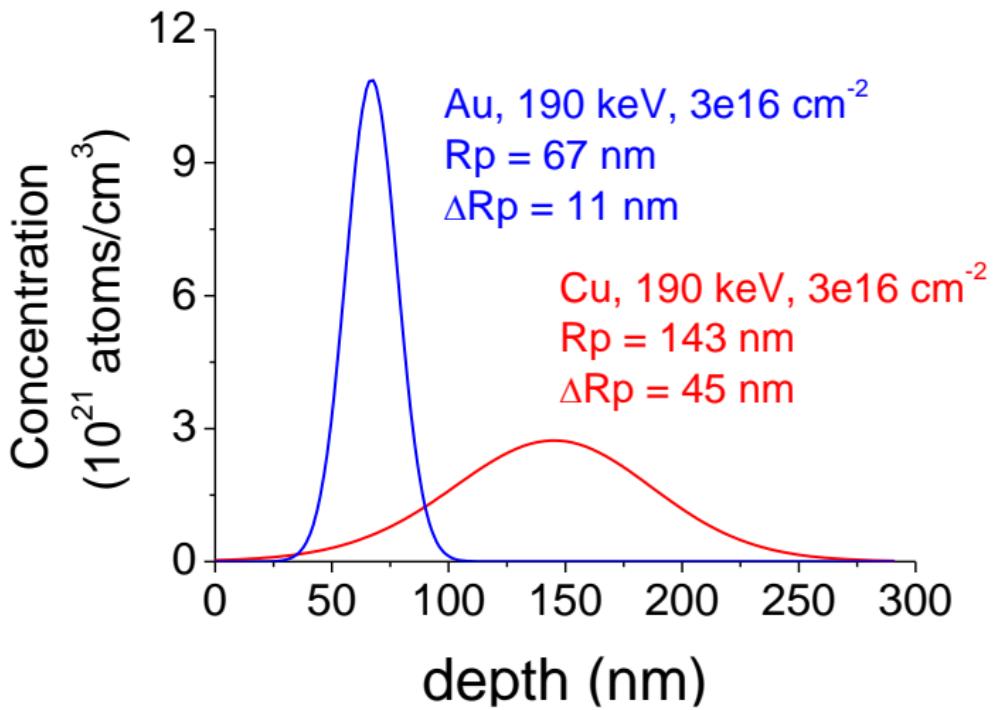


Ion implantation

Example: Au in SiO_2 – dose 3×10^{16} at/cm²

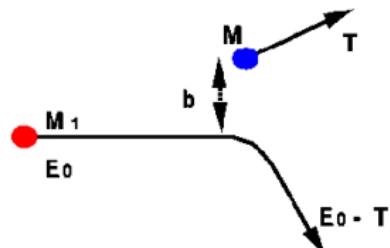


Example: Au o Cu in SiO_2



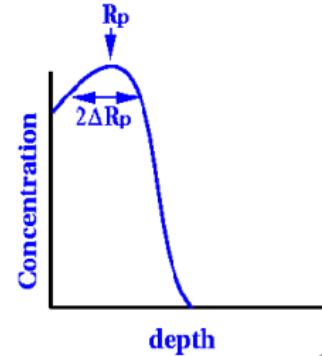
Some definitions for Defect Configurations

- **Displacement** = The process where an energetic incident atom knocks a lattice atom off its site.
- **Vacancy** = A lattice site without an atoms. Originally all lattice sites are occupied, and displacements cause vacancies.
- **Interstitial Atoms** = Atoms which were knocked out of their original site, and come to a stop in the solid. Also the incident ions, when they stop, are considered interstitial atoms.
- **Replacement Collisions** = Atom sites with new atoms, identical to their original atom. This is the only mechanism in which a vacancy may be re-occupied.



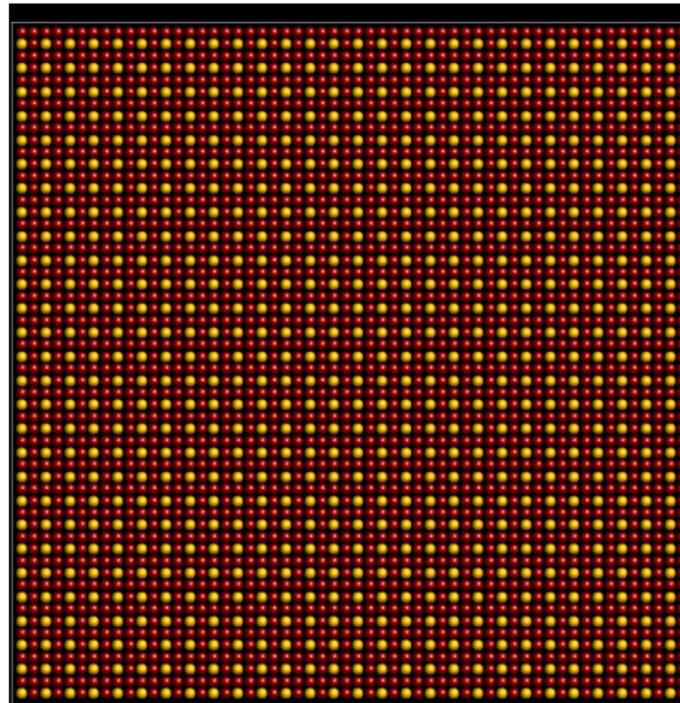
Some definitions for Energies

- E_d = **Displacement Energy**, the minimum energy required to knock a target atom far enough away from its lattice site so that it will not immediately return. This minimum energy produces a “**Frenkel Pair**” = a single vacancy and a nearby interstitial atom, which is the most fundamental type of damage caused by an ion. (~ **20-50 eV**)
- E_b = **Lattice Binding Energy**, the minimum energy needed to remove an atom from a lattice site (proportional to the sublimation enthalpy ΔH_s). It takes energy to break electronic bonds and displace an atom from a lattice site. The lattice binding energy must be smaller than the Displacement Energy ($E_b < E_d$) (**3-10 eV**)
- E_s = **Surface Binding Energy**. the energy required to remove a surface atom from its lattice site is less than if it was inside the solid and surrounded by other atoms. A surface atom has fewer electronic bonds which must be broken. Very important for sputtering (removal of surface atoms).

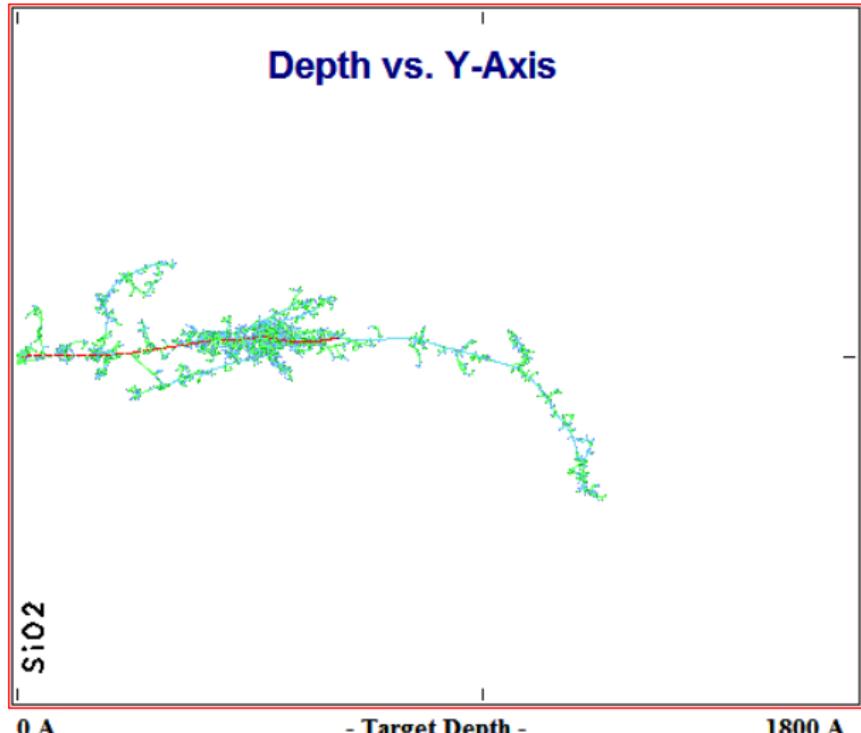


Ion implantation

Disordering by a 10 keV Au \rightarrow Cu₃Au cascade

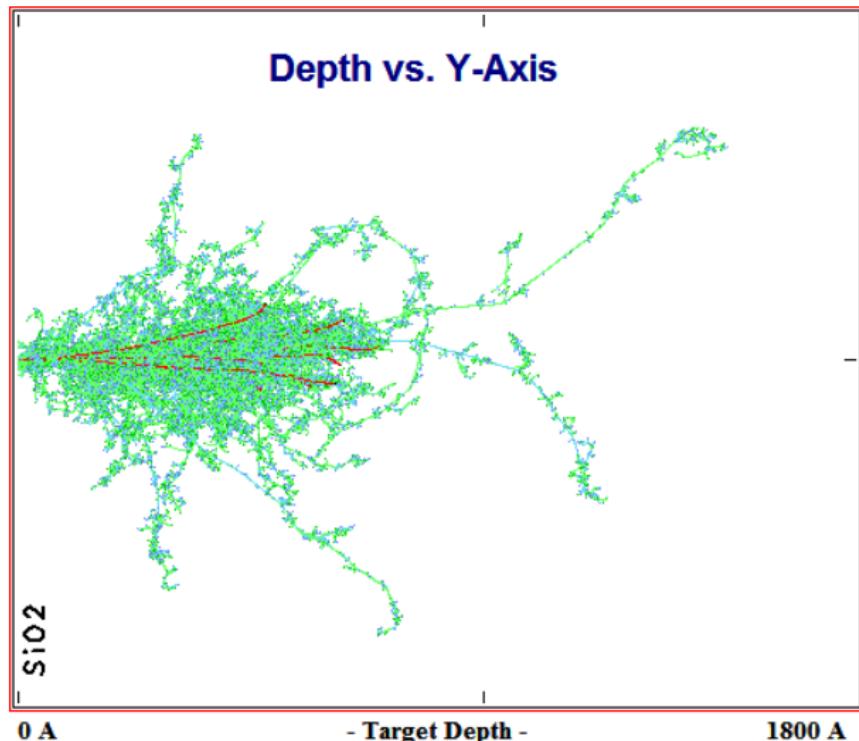


Collisional Cascade

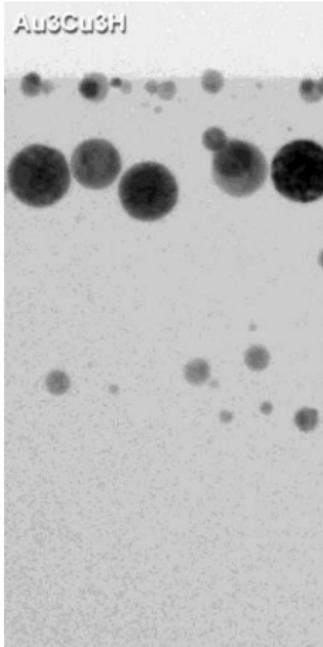
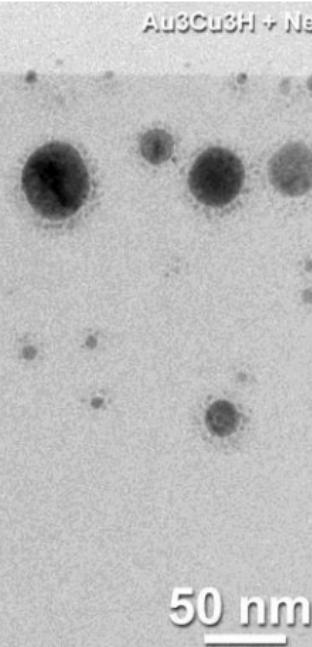
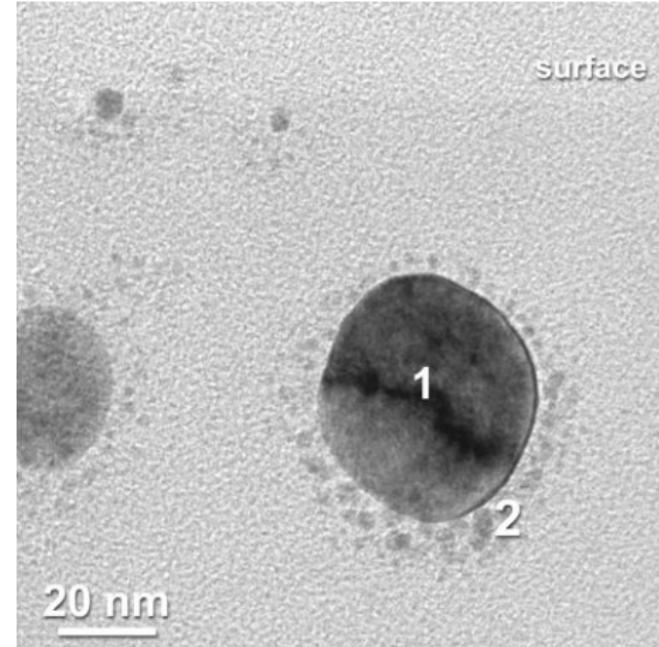
Au 190 keV in SiO_2

1 Au ion

Collisional Cascade

Au 190 keV in SiO_2

10 Au ions

Au_xCu_(1-x) alloy NCs in SiO₂Au₃Cu₃H + Ne**Ne⁺ irradiation**

1

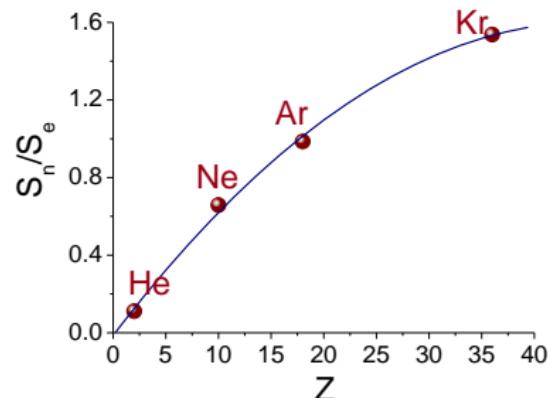
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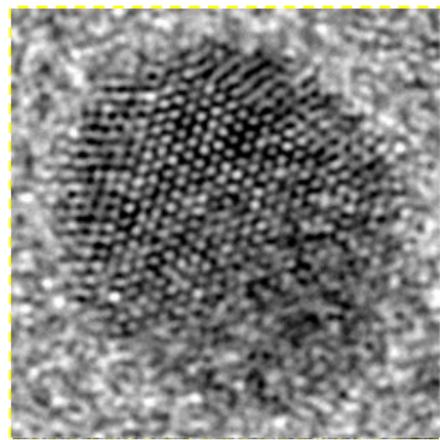
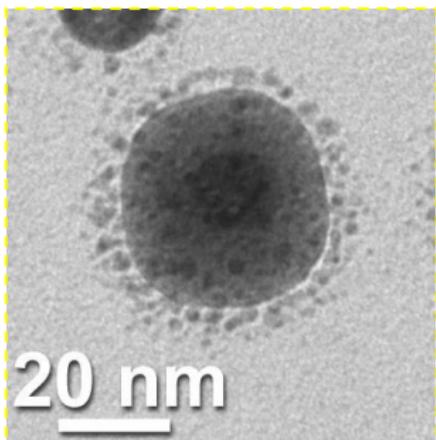
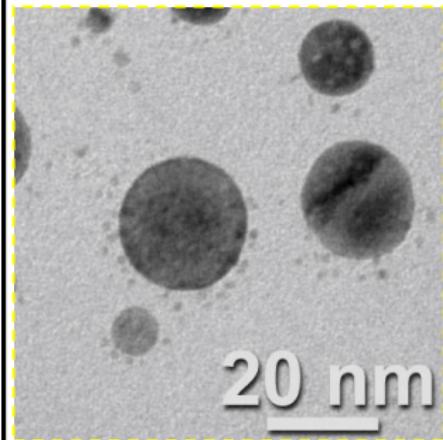
100 keV

 $5.2 \times 10^{16} \text{ Ne}^+/\text{cm}^2$

Ion	Energy (keV)	Fluence (ions/cm ²)	Current dens. (μA/cm ²)	$S_n = E_{nucl}/E_{tot}$ (%)	$S_e = E_{el}/E_{tot}$ (%)
He ⁺	25	$32 \cdot 10^{16}$	6.3	10	90
Ne ⁺	100	$5.2 \cdot 10^{16}$	1.6	43	57
Ar ⁺	190	$2.5 \cdot 10^{16}$	0.8	50	50
Kr ²⁺	380	$1.2 \cdot 10^{16}$	0.4	67	33

- Energy → Range $\sim 3 R_p^{(Au,Ag)}$
 $(\sim 210 \text{ nm})$
- Fluence → Constant energy density
 $(\sim 180 \text{ keV/nm}^3)$
- Current density → Constant power density
 $(\sim 2.5 \times 10^{-8} \text{ W/cm}^2)$



He^+ Ne^+ Kr^{++} 

25 keV

 $32 \times 10^{16} \text{ He}^+/\text{cm}^2$
 $J = 6.3 \mu\text{A}/\text{cm}^2$

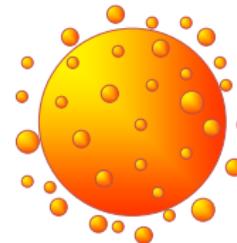
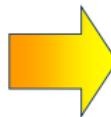
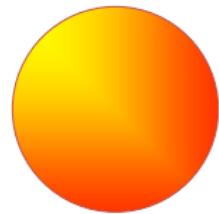
100 keV

 $5.2 \times 10^{16} \text{ Ne}^+/\text{cm}^2$
 $J = 1.6 \mu\text{A}/\text{cm}^2$

380 keV

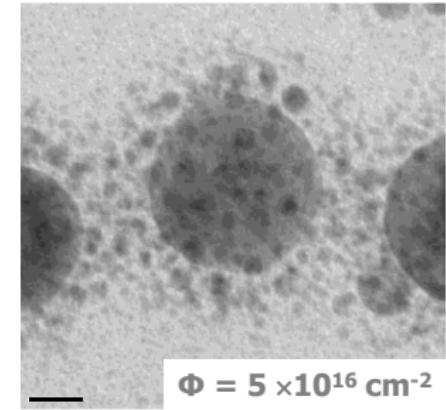
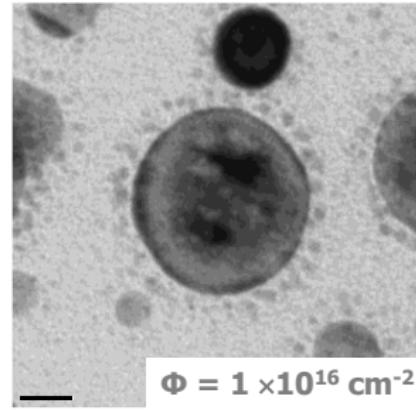
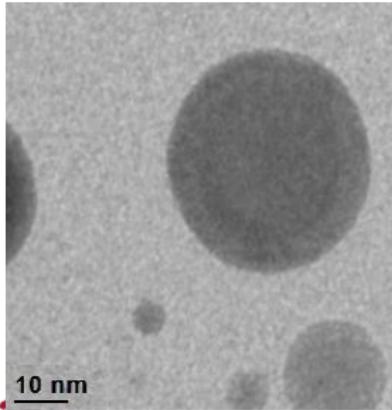
 $1.2 \times 10^{16} \text{ Kr}^{++}/\text{cm}^2$
 $J = 0.4 \mu\text{A}/\text{cm}^2$

Ion irradiation



Core + Satellites
=
NanoPlanets

$\text{Ar}^+ 190 \text{ keV}$

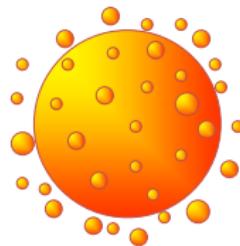
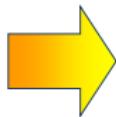
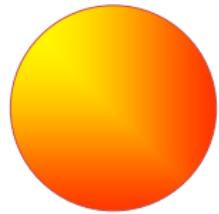


10 nm

$\Phi = 1 \times 10^{16} \text{ cm}^{-2}$

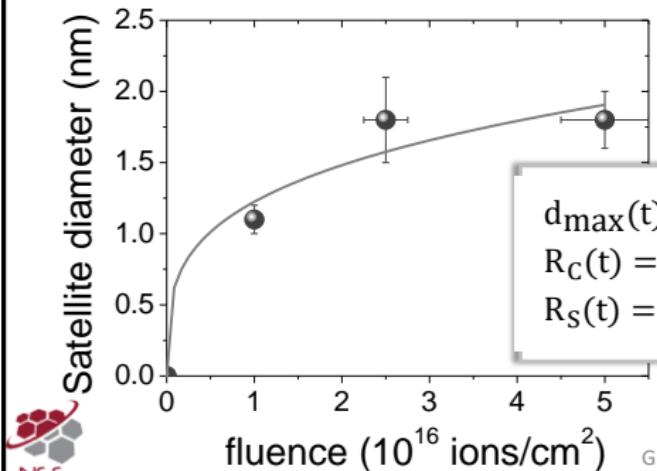
$\Phi = 5 \times 10^{16} \text{ cm}^{-2}$

Ion irradiation

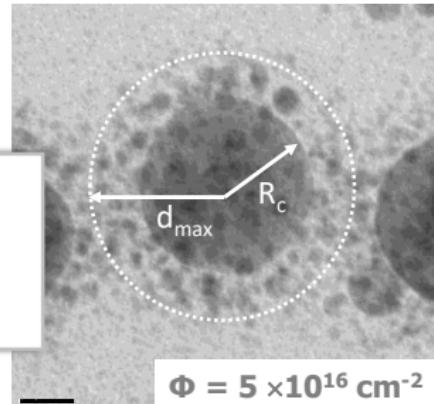


Core + Satellites
=
NanoPlanets

$\text{Ar}^+ 190 \text{ keV}$



$$\begin{aligned} d_{\max}(t) &= C_1 t^{1/2} \\ R_C(t) &= R_C(0) - C_2 t^{1/3} \\ R_S(t) &= C_3 t^{1/3} \end{aligned}$$



$\Phi = 5 \times 10^{16} \text{ cm}^{-2}$

Au NPs