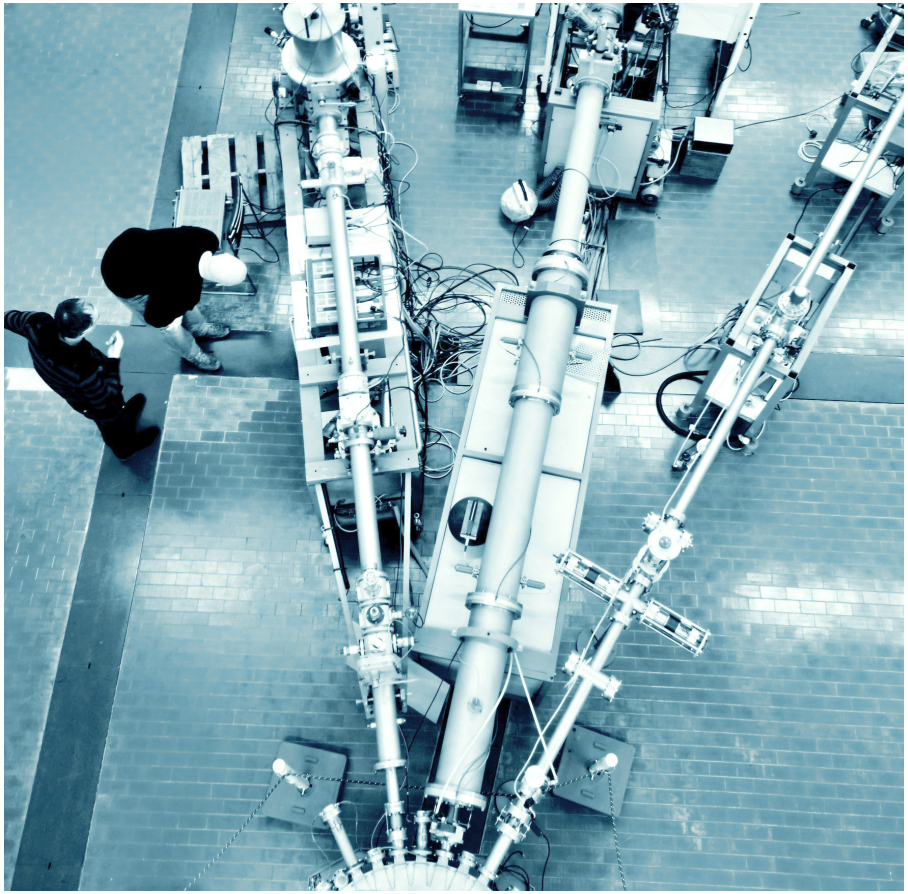

tandem accelerator lab. at CNR-IMM Bologna

INTRODUCTION TO ION IMPLANTATION

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G. Lulli - Scientific background

- Optics of charged particles (electrons, ions)
- Electron irradiation of solids
- Ion implantation of crystalline semiconductors (Si, SiC)
- Ion-Beam Analysis for structural characterization of ion-induced damage in semiconductors
- Developement of models and computer codes for the simulation of ion-matter interactions (ion implantation, ion beam analysis)

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web (to see online and download this presentation and other):

http://webarch.bo.imm.cnr.it/lulli/didattica/index.html

Premise

Although ion implantation (**II**) is a *processing technique* widely used in both research labs and industries, the underlying physics is quite complicated. The fundamentals of this physics are in the ***theory of atomic collisions,*** first developed by the great phisicist and Nobel laureate **Niels Bohr** about one century ago.

The purpose of this lesson is to give a brief, and unavoidably incomplete, overview of ion implantation, both from fundamental and practical points of view.

The level is intermediate, with little mathematics. Those who want to go deeper into the matter, especially in the fundamental part, may refer to the textbooks listed in the bibliography or download the additional material in the web page: http://webarch.bo.imm.cnr.it/lulli/didattica/download.html

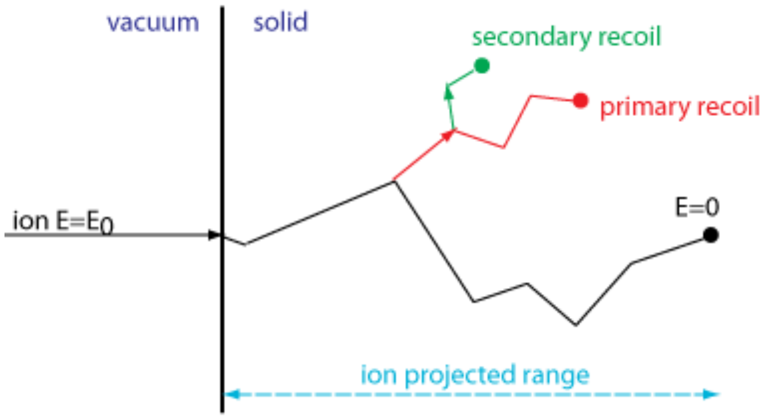
Lesson overview

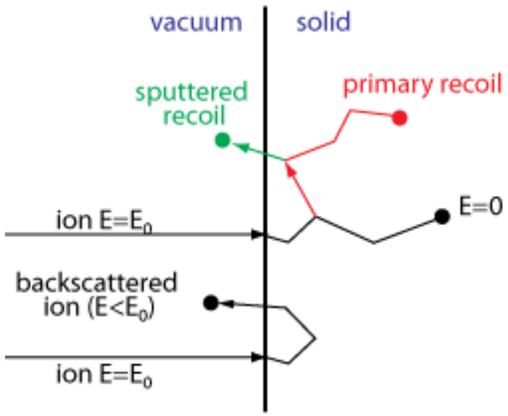
- Intro to ion implantation
    - what is ion implantation?
    - main features of ion implantation equipment
    - applications in microelectronics: electrical doping of semiconductors
- The physics of ion implantation: elements of ion-matter interactions, with examples from atomistic computer simulation[1]
- Brief survey of ion-beam processing techniques and their applications
- Example of application at the CNR-IMM Institute
- Bibliography (textbooks and recent articles), links and contacts

[1] All simulation results reported in the following have been performed using computer codes originally developed by myself and E. Albertazzi at CNR-IMM in Bologna.

What is ion implantation, in short ?

- bombardment of a solid target with an energetic ***ion beam*** (tipically **1keV - 1MeV**) ⇒ ions penetrate through the material, slow down by transferring their energy to the target atoms/electrons and eventually stop at a certain depth (**~0-1μm**) below the surface





- It is basically a **surface** or **near-surface** processing technique. Due to their stronger interactions with target atoms, ions penetrate much less in matter than electrons, for the same energy.

Projected ranges of charged particles - electrons, protons, alpha particles, heavy ions - in **Silicon**

particles		*energy (MeV)*	*range (μm)*
electrons (e^-)	(1)	2	~ 0.5 cm
protons (H^+)	(1)	2	~ 50 μm
alpha (He^{++})	(1)	2	~ 7 μm
B ions	(2)	2	~ 3 μm
P ions	(2)	2	~ 2 μm
As ions	(2)	2	~ 1.3 μm

EM radiation (**X**- or **ϒ -Rays**) and neutral particles (**neutrons**) interact much less with target atoms and have much longer (> cm) penetration ranges → *bulk* process.

Sources:

(1) http://www.nist.gov/pml/data/star/ (NIST Stopping Power and Range Tables)

(2) http://www.cleanroom.byu.edu/rangestraggle.phtml (BYU - Brigham University)

Why ion implantation ?

- To modify/improve properties (physical, chemical) of materials in a thin (**50nm-1µm**) surface layer
- Changes occur because (main reasons):

1) we implant chemical species different from the target, which, although in a small total amount, may still reach high relative concentrations on a microscopic scale (***chemical modification***)

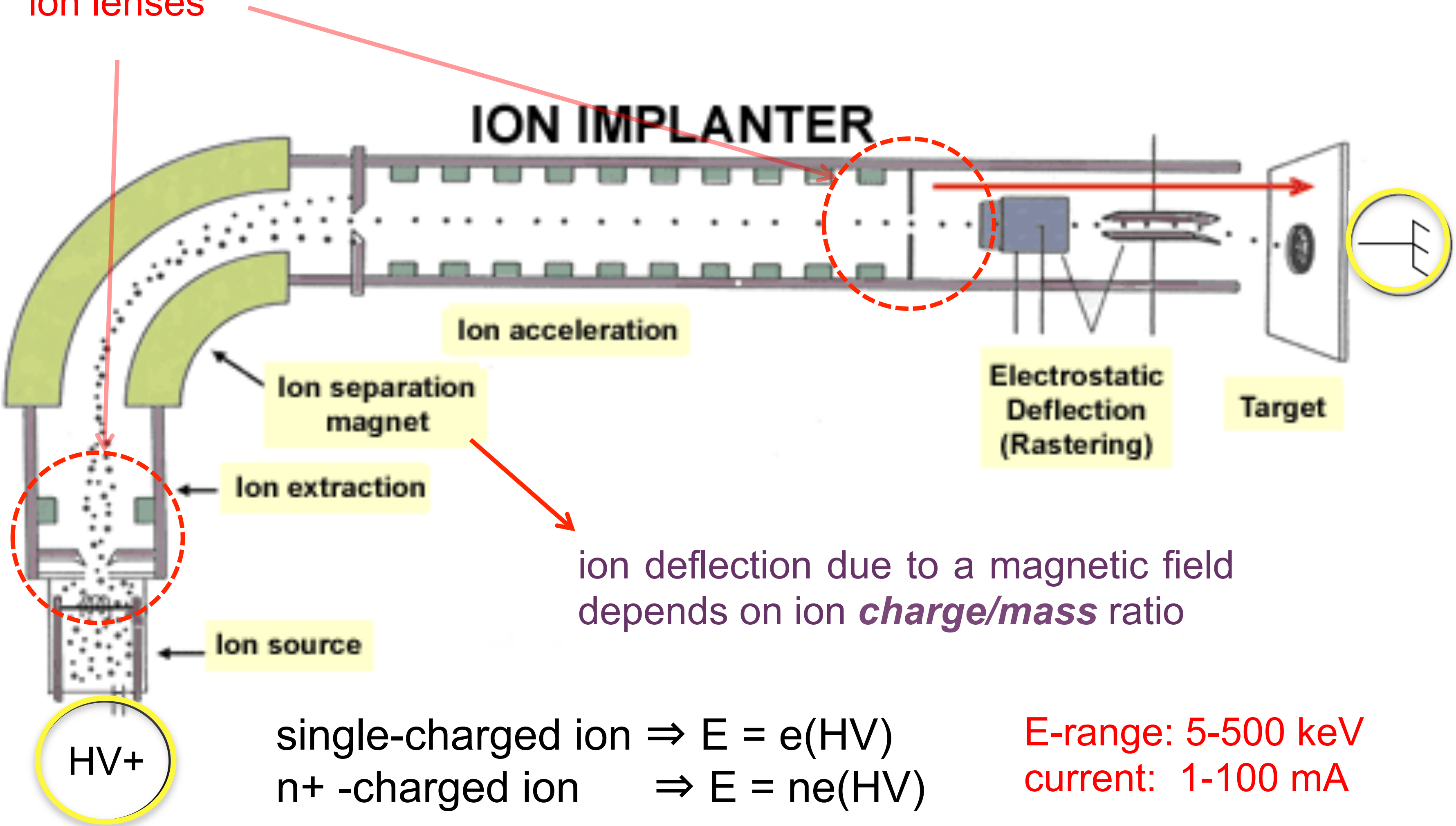
2) ion irradiation damages the structure of the target, generating radiation defects, changes of phase, atom removal, etc. (***structural modification***)

What do we need to perform ion implantation ?

- Produce a beam of ions (***ion source***)
- Select among beam atoms just the chemical species we want to implant (***magnetic mass filter***)
- Accelerating ions at the desired energy (***acceleration column***)
- Bring the ion beam to hit the surface of the target material (***beamline: ion lenses, beam scanner, neutral trap,...***)

Schematics of a *single-ended* ion implanter

ion lenses



ion deflection due to a magnetic field depends on ion ***charge/mass*** ratio

single-charged ion ⇒ $E = e(HV)$
n+ -charged ion ⇒ $E = ne(HV)$

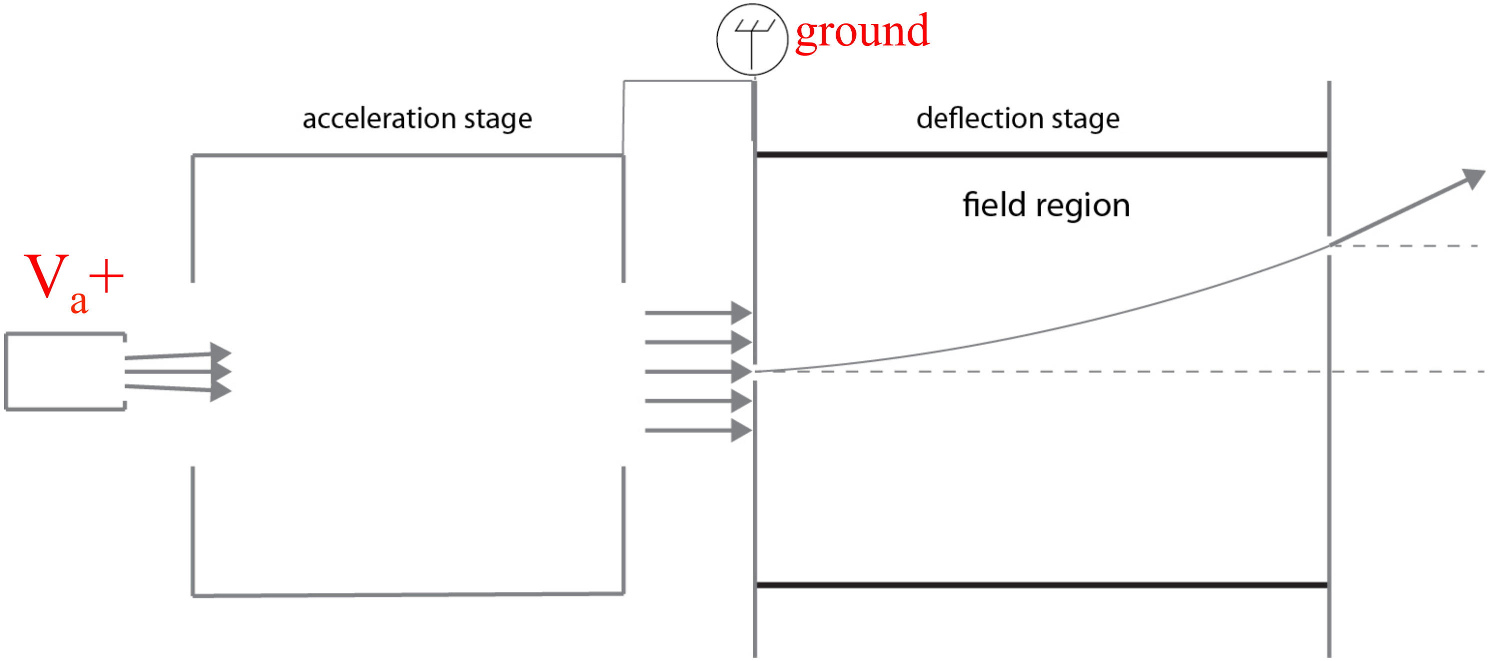
E-range: 5-500 keV
current: 1-100 mA

Ion beam manipulation by electromagnetic fields

- force acting on an ion of positive charge *q* and velocity *v* in an electromagnetic field:

$$\vec{F} = q\vec{E} \quad + \quad q\vec{v}\times\vec{B}$$

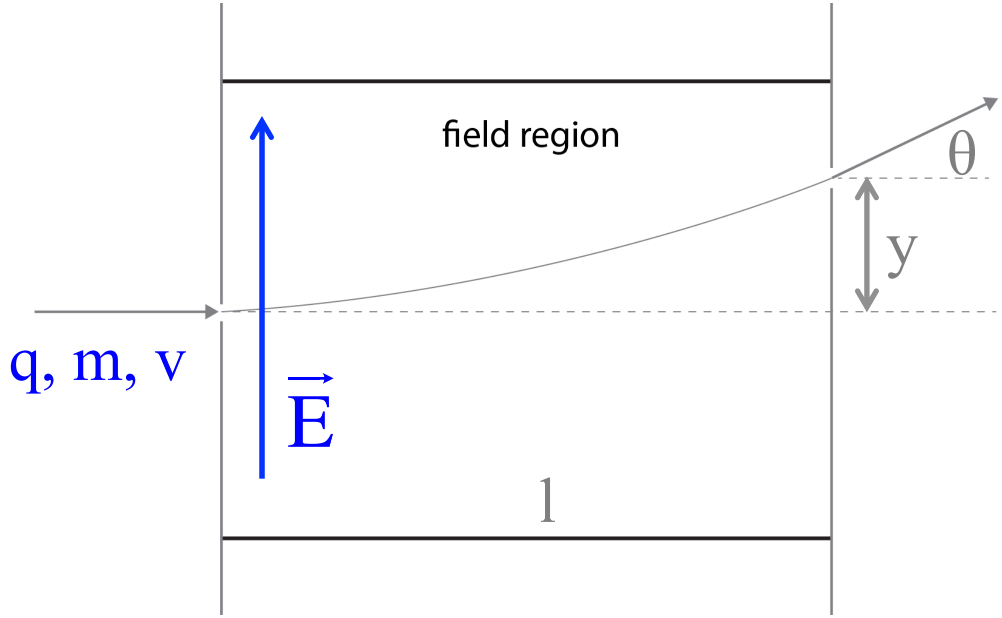
(electrostatic + Lorentz force)



Ion beam manipulation by electromagnetic fields

- Pure electrostatic

$$\vec{F} = q\vec{E}$$



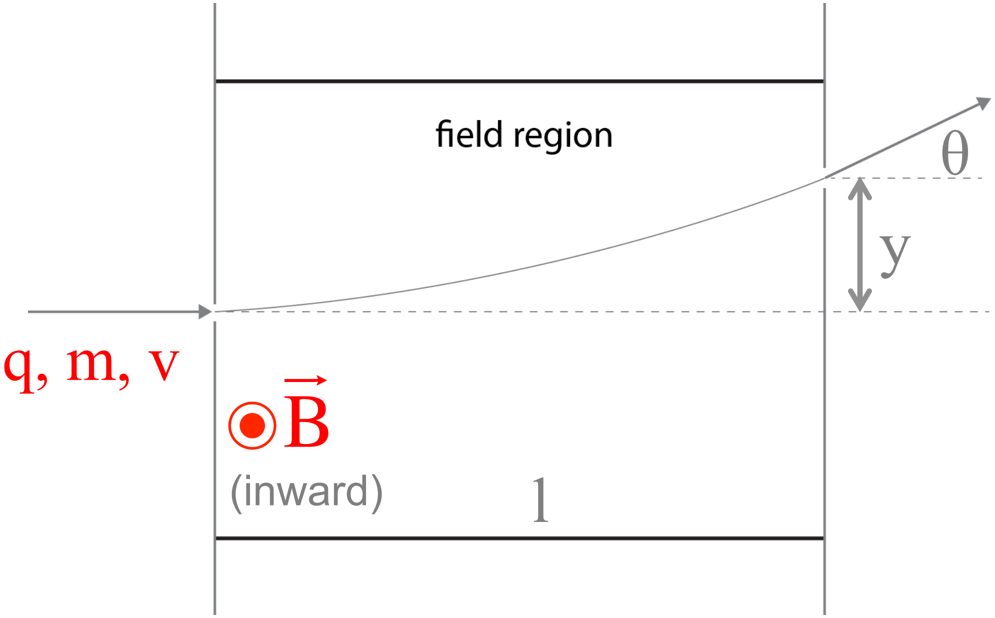
$$\boxed{\vartheta \simeq \frac{E}{2V_a} l}$$

ion deflection independent of ion mass or ion charge

Ion beam manipulation by electromagnetic fields

- Pure magnetic

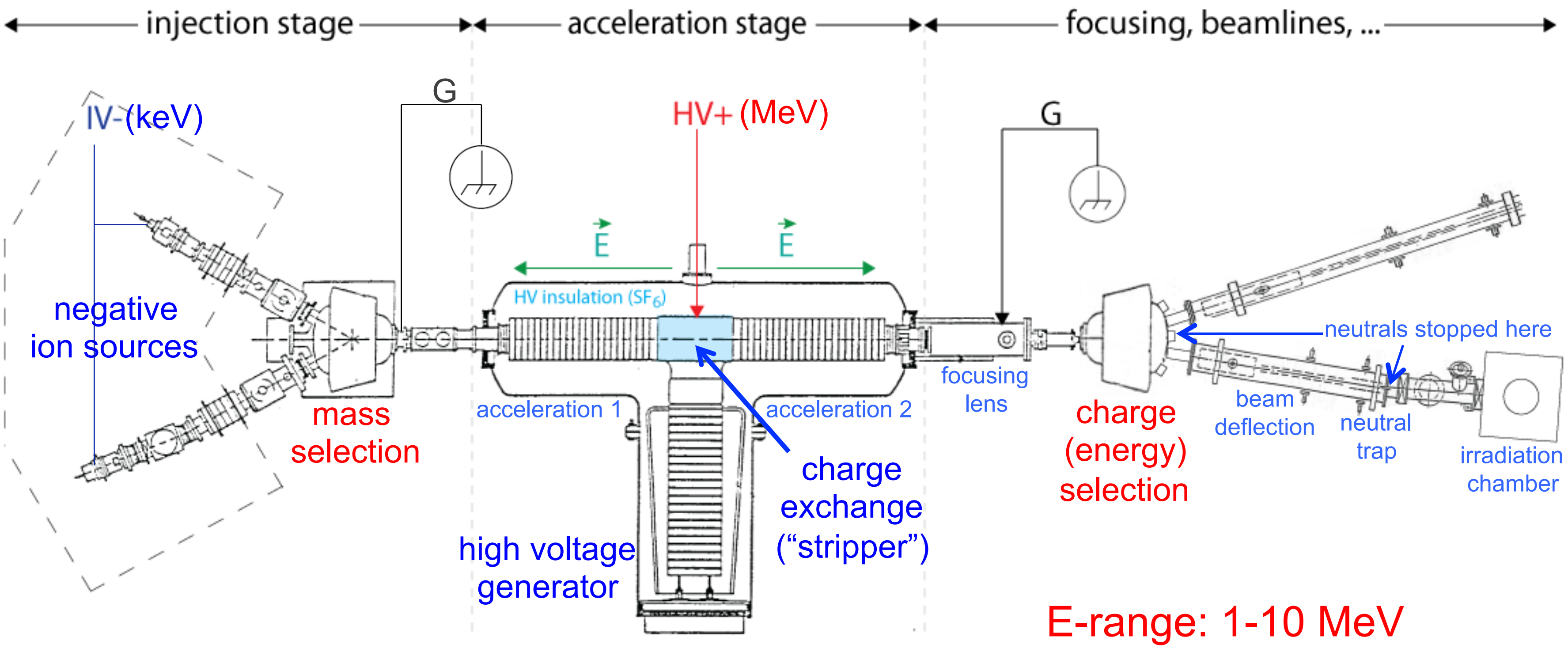
$$\vec{F} = q\vec{v} \times \vec{B}$$



$$\boxed{\vartheta \simeq \left(\frac{q}{m}\right)\frac{B}{v}l}$$

for the same velocity/energy (not changed by the magnetic field) deflection depends on charge to mass ratio

Schematics of a tandem (*double-ended*) ion implanter



E-range: 1-10 MeV
current: 1-100 µA

single-charged ion ⇒ $E = (IV) + e(HV) + e(HV) = IV + 2e(HV)$

n - stripped ion ⇒ $E = (IV) + e(HV) + ne(HV) = IV + (n+1)\,e(HV)$

Negative ion sources used in tandem accelerators

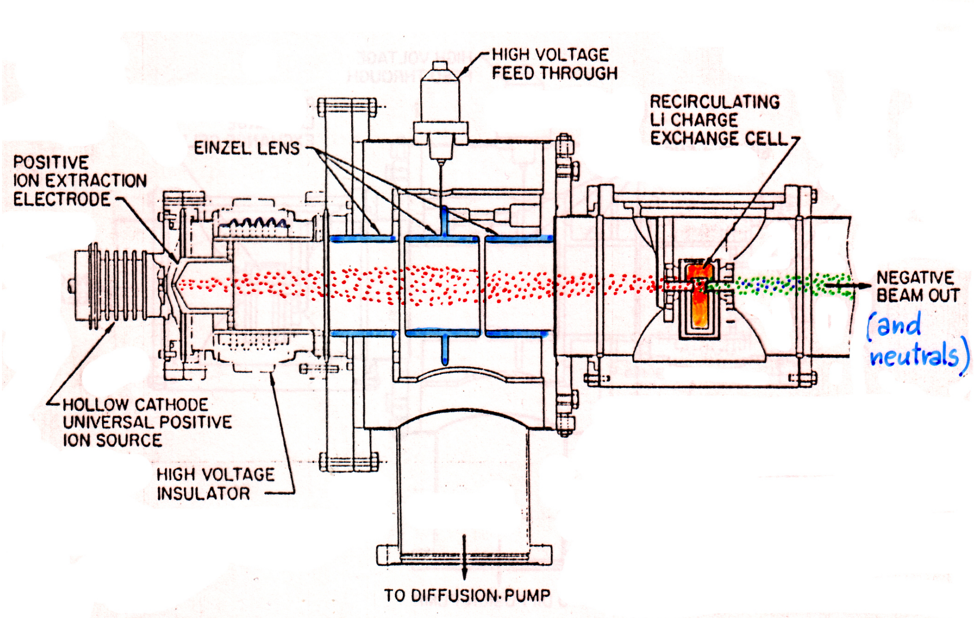
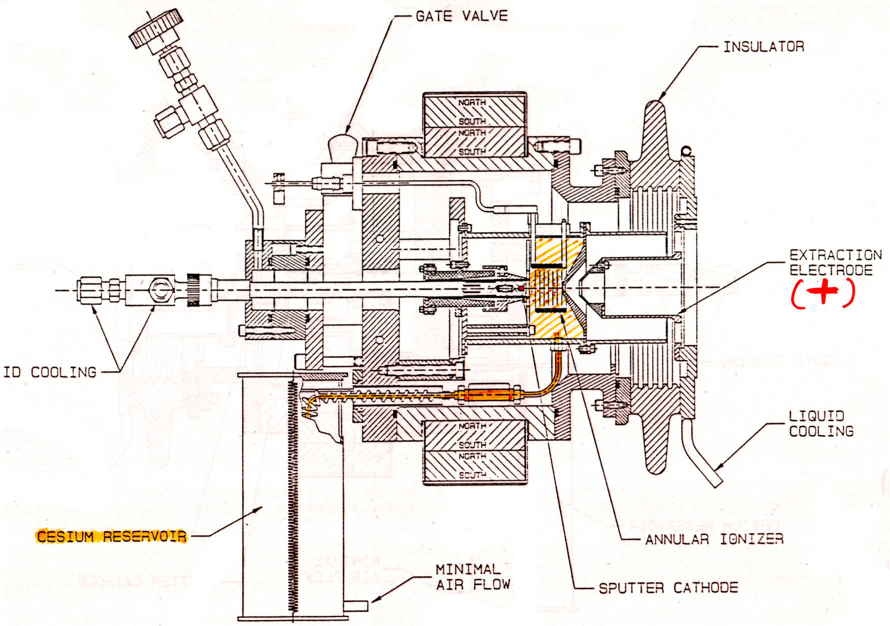


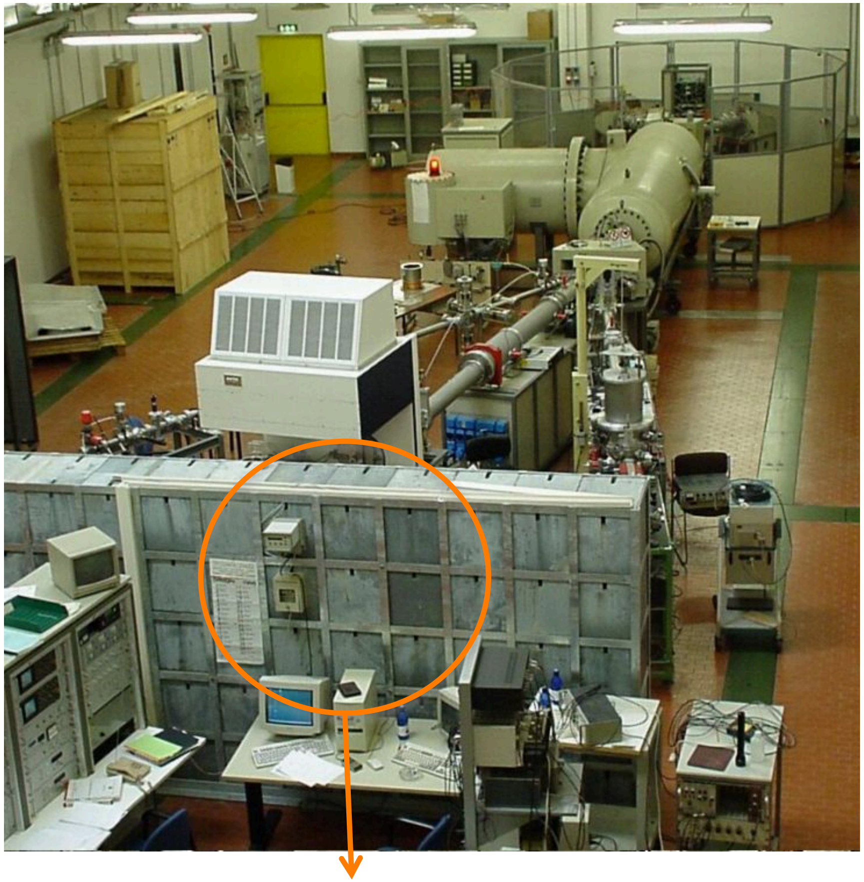
Fig. 57. Schematic drawing of a universal charge-exchange source [231].



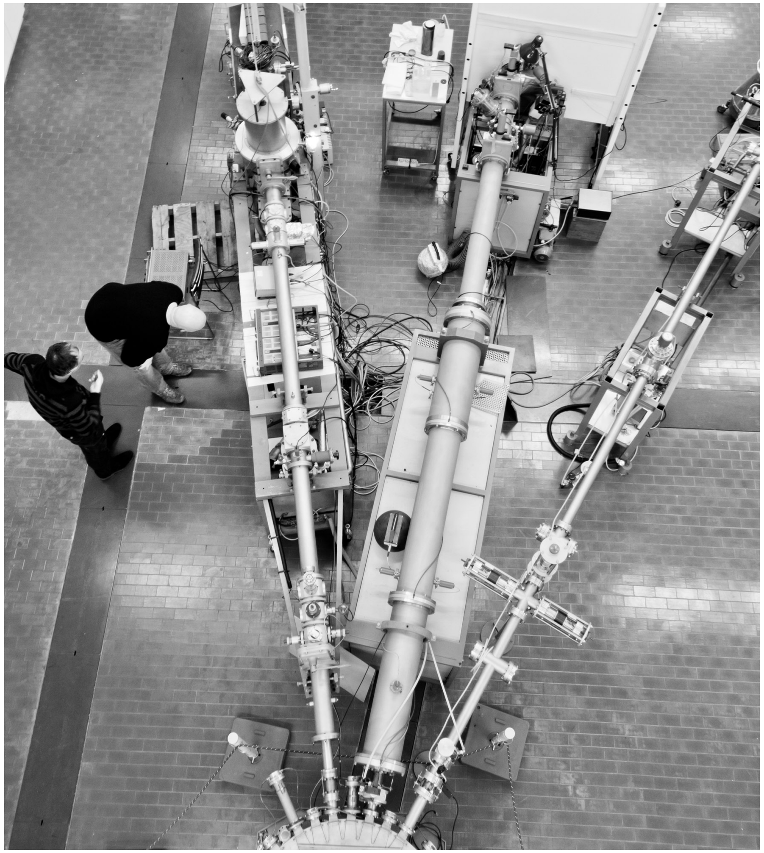
Duoplasmatron: for gases, produces positive light ions (H^+, He^+) turned negative by interaction with a low-pressure lithium gas

Sputtering: for solid targets, produces directly negative heavy ions, obtained by cesium ion bombardment of target surface

Tandem accelerator lab. at CNR-IMM



barite concrete wall and neutron detector with alarm – all prescribed by the radiation safety protocol.

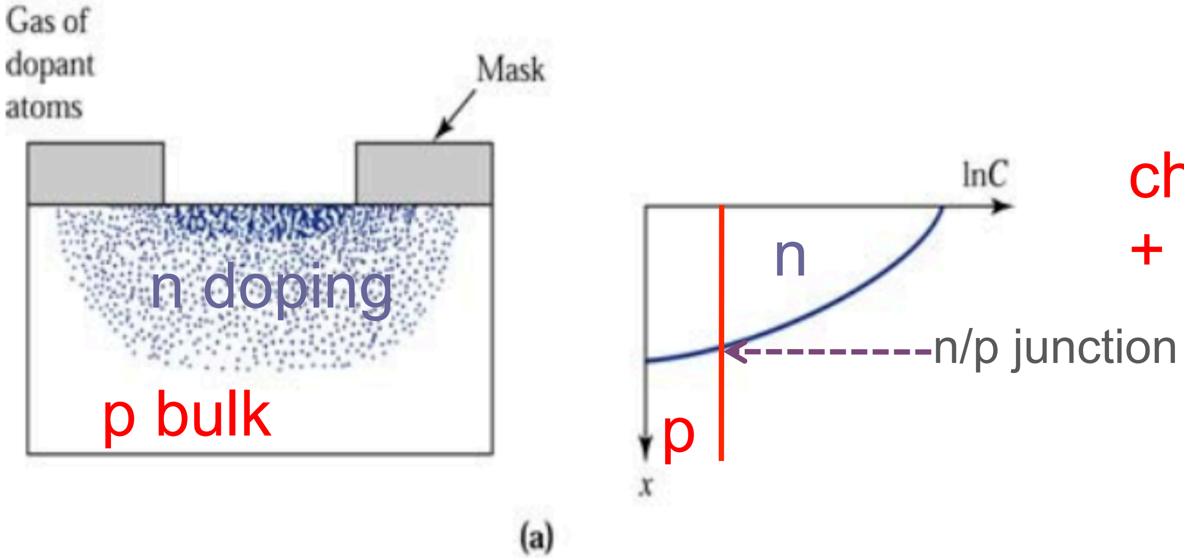


beamlines after the charge-selection magnet

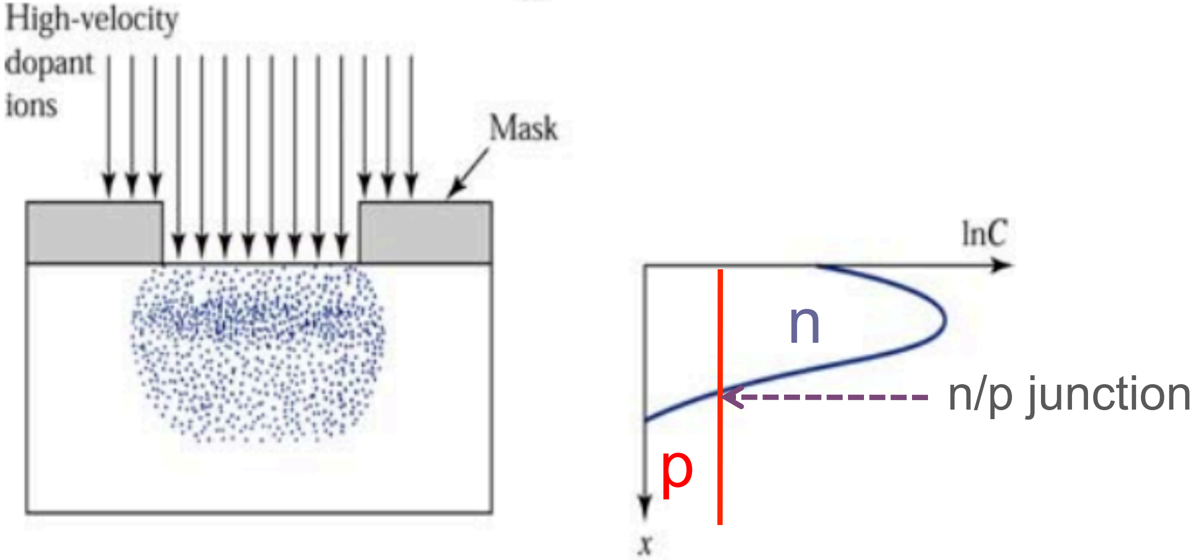
Summary of electric and magnetic fields for ion beam manipulation

electric field *(deflection independent on mass and charge)*	**magnetic field** *(deflection dependent on the charge/ mass ratio)*
accelerate ions to reach desired beam energy	***mass filter***: select ion mass (for ions of the same charge)
optics: focus ion beams across the implanter column to optimize beam transmission	***energy filter***: select ion charge (for ions of the same mass)
scan a small beam to cover a large irradiation area	
deflect the beam to separate charged from neutral particles (*neutral trap*)	

Different techniques for *electrical doping* of semiconductors

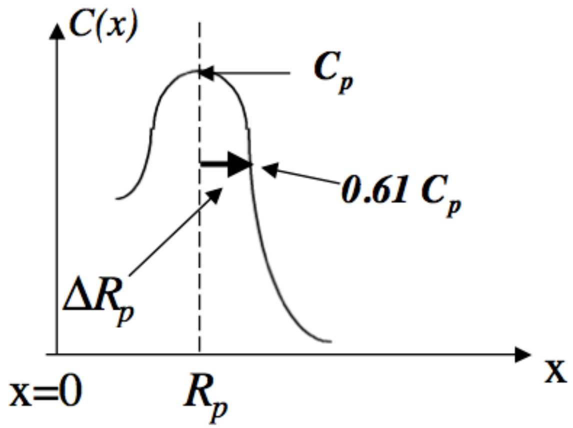


chemical deposition
+ thermal “drive-in”



ion implantation

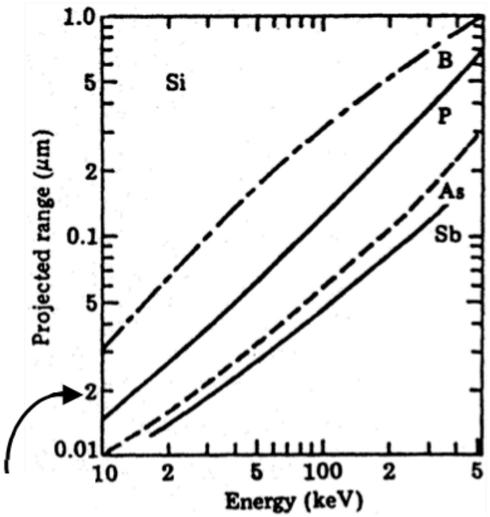
First approximation to implantation profile: the *gaussian*

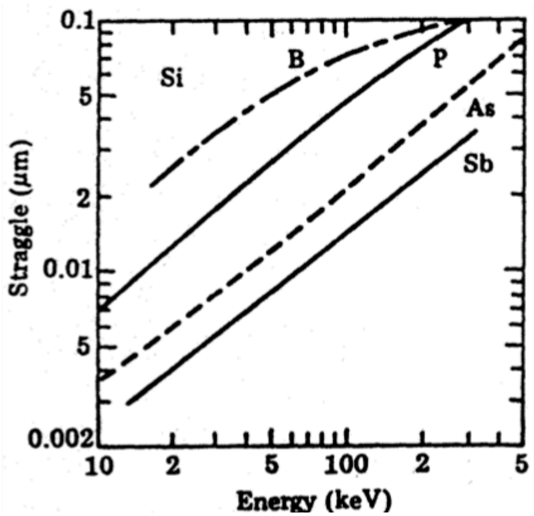


$$C(x)=Cp\cdot e^{\frac{-(x-R_p)^2}{2(\Delta R_p)^2}}$$

R_p = *projected range*

ΔR_p = *longitudinal straggle*





Tables of R_p and ΔR_p allow a first approximate evaluation of ion profiles and of maximum concentration:

$C_p \sim 0.4\phi/2\Delta R_p$

ϕ = **fluence** (*ions cm*$^{-2}$)

Typical range of ϕ in a standard implantation equipment ≈ **10^{12} - 10^{16} ions cm^{-2}**

Numerical example

P ion, **100 keV**, **$\phi = 10^{15}$ ions cm^{-2}**

From the graphs in previous slide:

$\Delta R_p \simeq$ **0.05×10^{-4} cm** ($R_p \simeq$ **0.15×10^{-4} cm**)

$C_p \simeq 0.4\phi/2\Delta R_p =$ **4×10^{19} cm^{-3}**

For a Si target (5×10^{22} atoms cm^{-3}) the maximum relative P concentration at the peak of the distribution will be $4 \times 10^{19} / 5 \times 10^{22}$ = **0.08%**

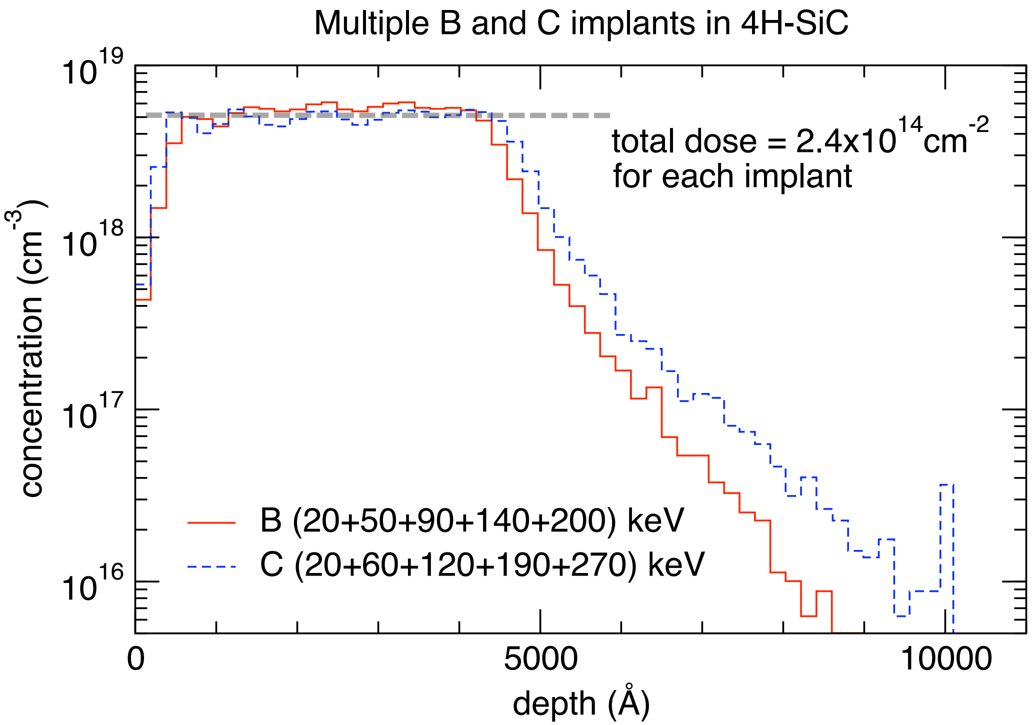
For the same energy and fluence the result for **As** would be **0.2%**

Ion implantation: **PROS**

- Good control (≤ 10%) of the ***fluence*** (ions cm^{-2}), or total amount of implanted atoms

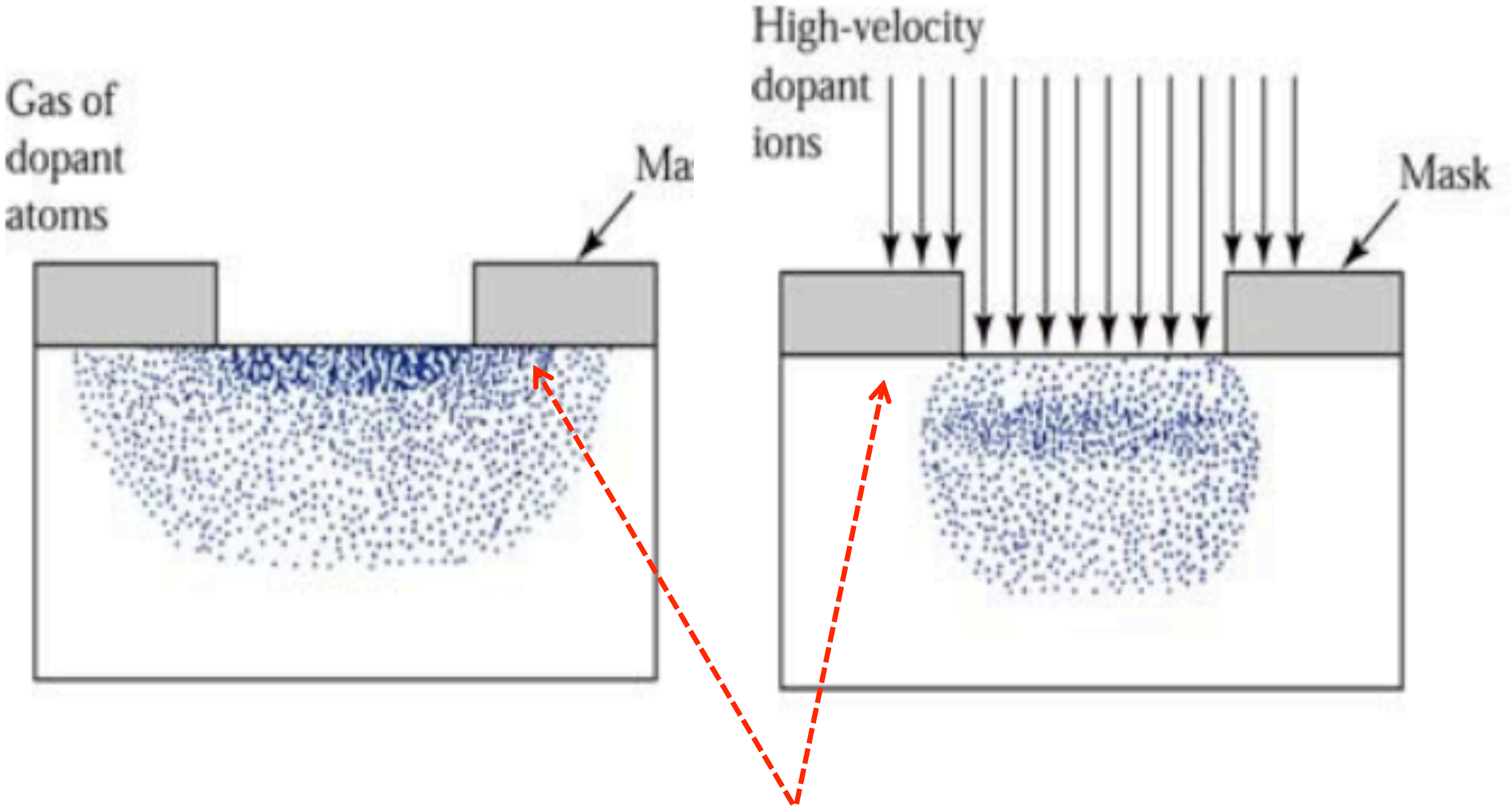
- It's a *cold* process: very limited amount of thermal ***diffusion*** during implantation ⇒ accurate control of depth distribution of ions.

- using ***multiple implants*** at different fluences, one has large degrees of freedom in designing ion distribution profiles that would be impossible by chemical deposition + drive in (*example on the left: multiple implantation in 4H-SiC – BCA simulation*)



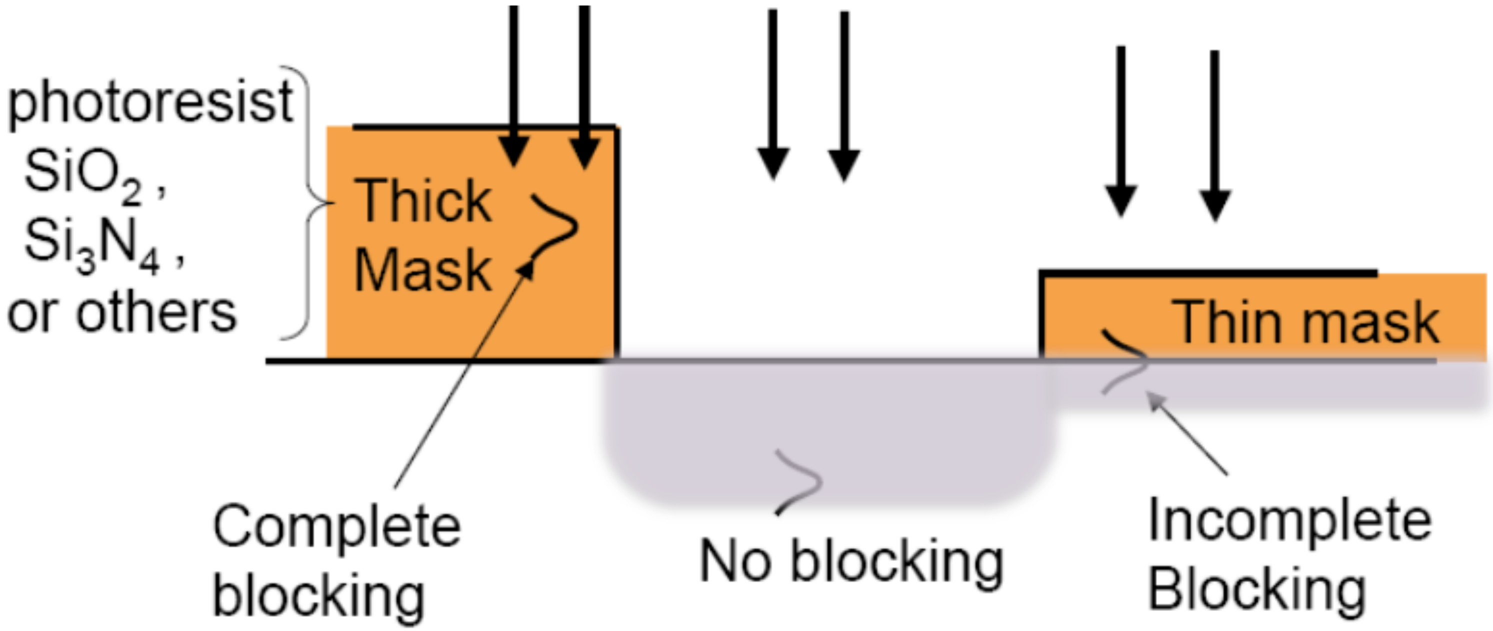
Ion implantation: **PROS**

- Reduced *lateral* (under-mask) penetration of dopant

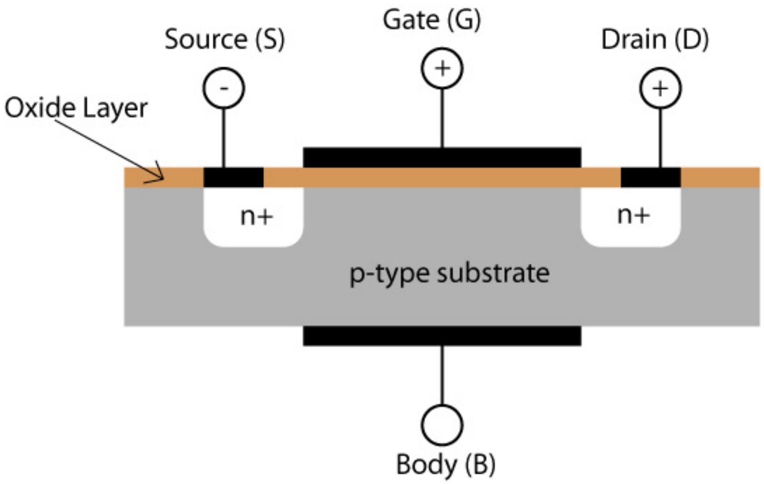


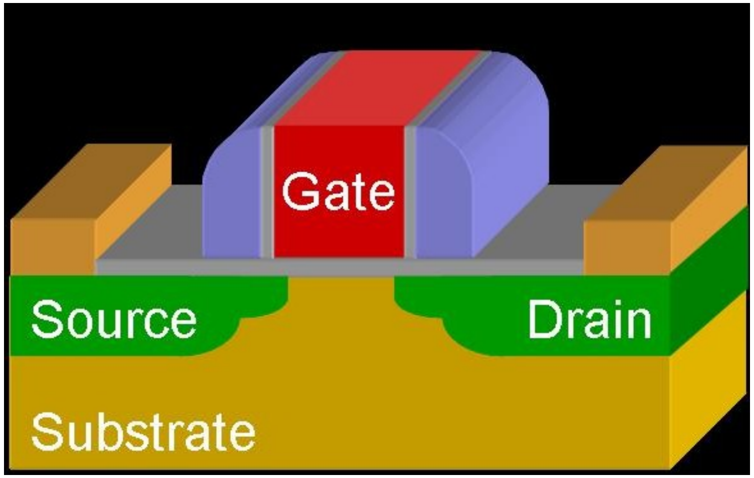
Ion implantation: **PROS**

- ***ion masking*** allows ***lateral selectivity*** and ***in-depth modulation*** of ion distribution in a single implant step



A simple microelectronic device: the **MOSFET**



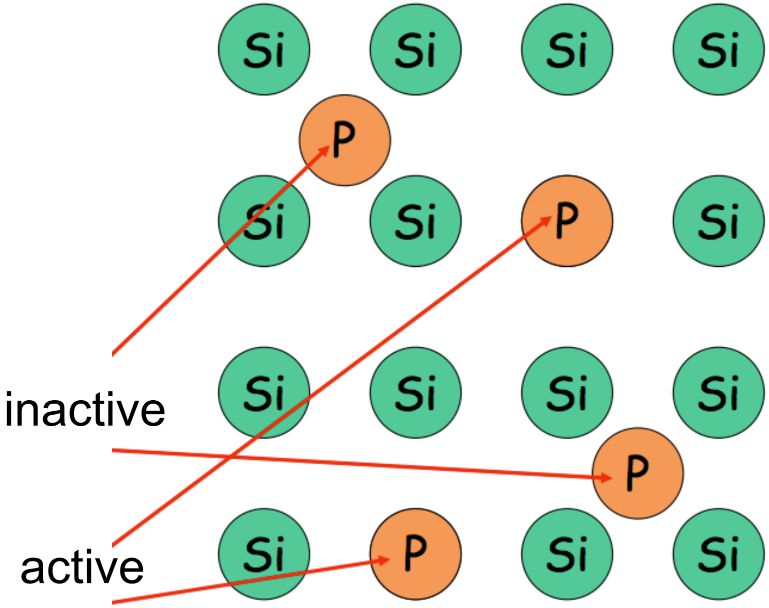


The sequence of many processes like: *epitaxial growth*, *film deposition*, *masking*, *selective etching*, *ion implantation*, *oxidation*, *thermal tratment* ... allows the design and fabrication of complex microelectronic devices in Silicon and other semiconductor materials. For its characteristics, ion implantation is particolarly suitable to be integrated in such a complex process flow.

Figures on the left show the schematics of a Metal-Oxide-Semiconductor Field- Effect Transistor (MOSFET), the relatively simple device most widely used in modern digital microcircuits.

Ion implantation: **CONS**

- ***Radiation damage***: for many applications such as electrical doping of semiconductors, damage must be recovered by subsequent thermal processing (typically in the range 500-900 C for 5’ – 60’)

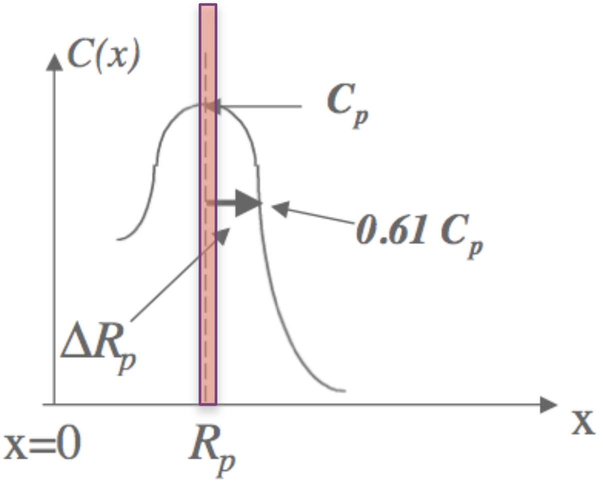


A n-type dopant atom in Silicon (P in this case) to be electrically active (i.e. to supply one electron for electrical conduction) must occupy a ***substitutional site*** in the perfect Si lattice. Soon after ion implantation most of P atoms are in ***interstitial*** positions, while the Si lattice may be heavily damaged (which leads to carrier trapping, etc.)

It is during subsequent high temperature ***annealing*** that the Si lattice recovers its crystallinity and that P atoms can rearrange to substitutional sites, thus becoming electrically active as *donors*.

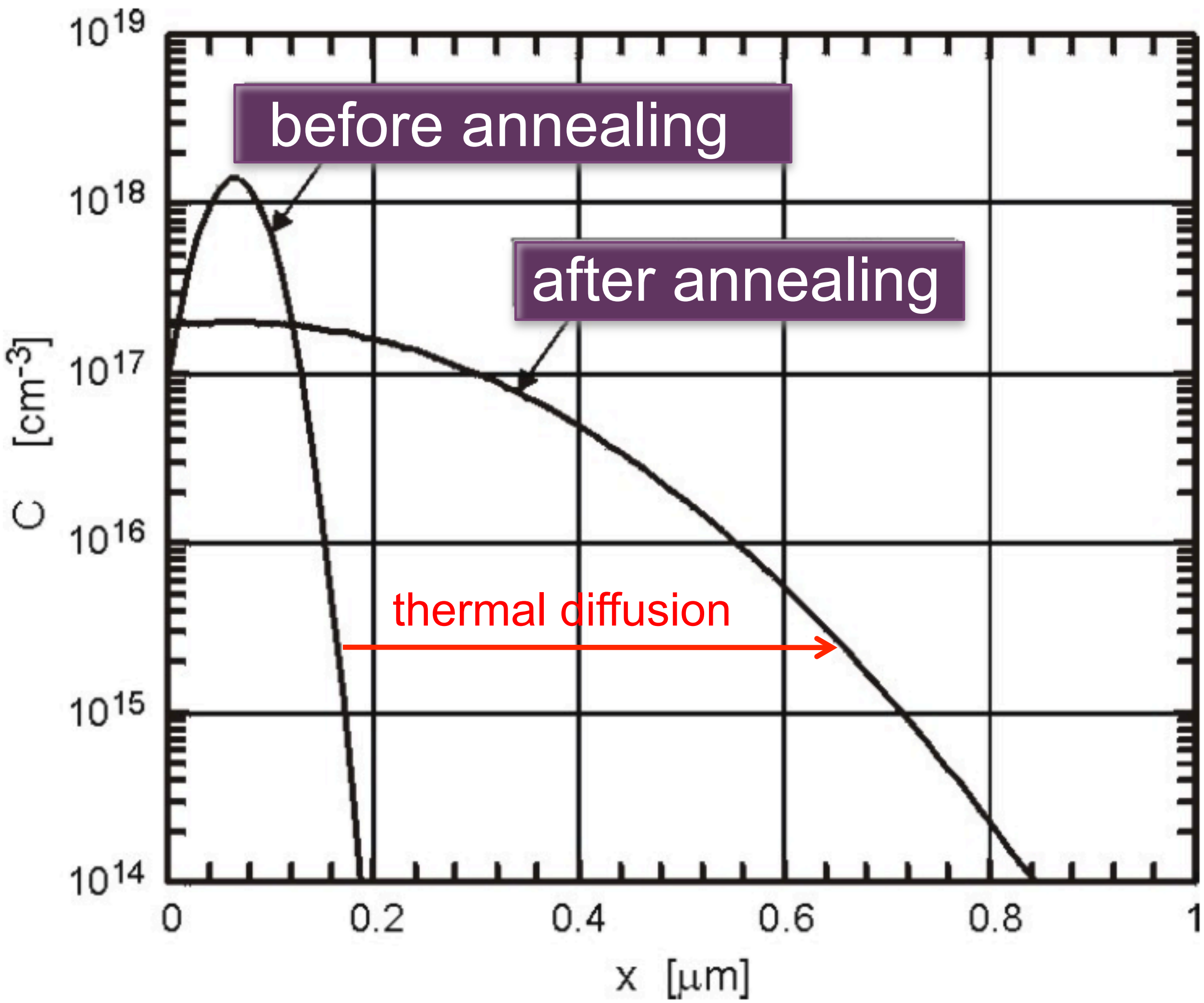
Ion implantation: **CONS**

- ***Straggling****:* ion-target scattering at the atomic level is a *stochastic process* ⇒ ions with same macroscopic parameters (ion species, energy, angle of incidence) penetrating a solid do not stop at the same depth, but generate a *distribution*, with a certain *spread* (the ΔR_p introduced before). This can be a limitation for those applications where an accuracy in the position of the implanted atoms smaller than the ion straggling is needed. A similar situation occurs more often today, due to the ever decreasing size of electronic devices or nanostructures.



With ion implantation it is not possible to have a thin, sharp, box-shaped distribution of dopants, like the one depicted in the example on the left. To get such a profile different techniques must be used, such as ***Molecular Beam Epitaxy*** (MBE).

Conventional post-implantation thermal processing of silicon wafers at the clean room facility of CNR-IMM in Bologna. This process, necessary to remove ion-implantation damage, also induces thermal ***diffusion*** of dopants ....



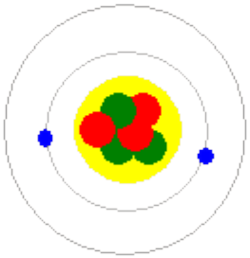
... which causes further penetration and widening of the profile.
This means that most advantages of ion implantation can be lost ! To reach the best compromise, the process (implantation + damage annealing) must be carefully optimized.

Ion implantation is the technique used for most standard semiconductor doping processes in the microelectronics industry.

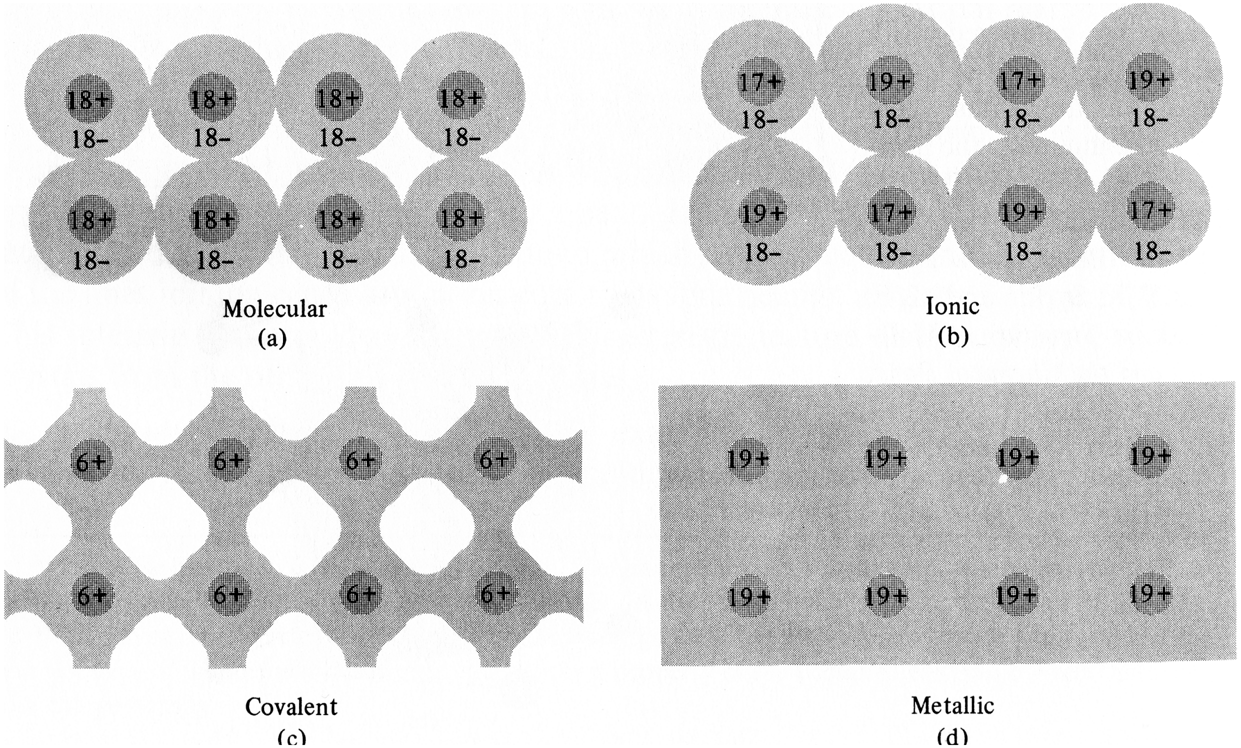
A major part of the research in this field has been on reducing implantation damage, thus maximizing the electrical activity of dopants, while minimizing diffusion, and consequent in-depth and lateral shift of electrical junctions.

This task has become more and more difficult with shrinking the size of electronic devices, today of the order of a few tens of nm.

Elements of ion-solid interaction



Li^+



Molecular
(a)

Ionic
(b)

Covalent
(c)

Metallic
(d)

ion → solid

(i.e. an atom which has lost or gained some electrons)

(i.e. not just an ensemble of isolated atoms)

The *atomistic* view

- We will look at the problem from the ***atomistic*** point of view, as opposed to the one based on ***transport*** theory
- Under this approach, ion collisions and trajectories are considered in detail, while the cumulative effects of the process are deduced from the statistical analysis of a large number of individual events
- This is the approach typically used in ***computer simulation*** of ion-matter interactions and processes

The physics of ion-solid interaction is a very complex, ***many-body*** problem

ion $M_1,\ Z_1,\ \mathbf{R}_1,\ \mathbf{r}_{1,i}\ \ (i=1,n_1\ n_1\neq Z_1)$

target $M_2,\ Z_2,\ \mathbf{R}_{2,k},\ \mathbf{r}_{2,k,j}\ \ (j=1,Z_2\ \ k=1,N)$

M: masses, Z: atomic numbers, R: nuclei coordinates, r: electron coordinates, N: number of target atoms

$n_1 \neq Z_1$ means that the ion may have been "stripped" of part of its electrons when moving through the solid

Time dependent Schrödinger equation of the system

$$H\Psi(\mathbf{R}_1,\mathbf{R}_{2,k},\mathbf{r}_{1,i},\mathbf{r}_{2,k,j},t)=i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{R}_1,\mathbf{R}_{2,k},\mathbf{r}_{1,i},\mathbf{r}_{2,k,j},t)$$

where

$H = (T + V)$ Hamiltonian (kinetic + potential) energy of the system

$\Psi(\mathbf{R}_1,\mathbf{R}_{2,k},\mathbf{r}_{1,i},\mathbf{r}_{2,k,j},t)$ Wave function of the system (ion+target atoms)

Actually, , to calculate ion trajectories and defects generated by displacement and relocation of target atoms, we are interested in the *motion of nuclei* only ...
.. but nuclei and electrons interact, their coordinates are not independent, so, in principle, the problem cannot be separated into a nuclear and an electronic one

... ***however***

reasonable *approximations* are possible, which allow us to simplify the problem, still having a satisfactory and predictive physical description of the phenomenon.

The approximations that are applied under most circumstances are:

1) adiabiatic (*quasi-elastic*) approximation, to treat nuclear and electronic subsystems separately

2) classical mechanics to treat the motion of ion nuclei

3) Binary Collision Approximation (**BCA**) to calculate ion trajectories in matter

Adiabatic (quasi-elastic) approximation

It can be demonstrated that if ions/atoms velocities are much lower that velocities of target electrons (which is fullfilled in most ion implantation conditions), *the electronic and nuclear sub-systems can be treated separately*.

It is as if nuclei move in an *effective average electronic potential*, which at each time does not depend on the detailed positions of electrons, but *only on the coordinates of the nuclei*.

Approximations: classical mechanics

Once the potential, and therefore forces, acting on nuclei, are determined, ion trajectories can be calculated using *classical mechanics*, since the De Broglie wavelenght associated with the ion:

$$\lambda_{ion}[nm] = \frac{h}{M_1 v} = \frac{2.87 \times 10^{-2}}{\sqrt{M[amu]E[eV]}}$$

(Example: B ion, $E = 1\text{keV} \Rightarrow \lambda \cong 3\times10^{-4}$ nm)

is much smaller than the typical interatomic distance in a solid (~0.13 nm in Si). Ions then move as **classical particles**: quantum effects (wave-like, such as diffraction, interference ..) are negligible under usual circumstances.

Much complication has gone, however the problem is still a *many-body* one.

Binary Collision Approximation (BCA)

When the ion energy is much larger than the binding energy between atoms in the solid (~ a few tens of eV) its movement can be treated as a series of successive two-body interactions (***binary collisions***).

The binary collision between an ion and a target nucleus is described with a ***screened, two-body Coulomb potential***, derived from the *Thomas-Fermi* atomic model:

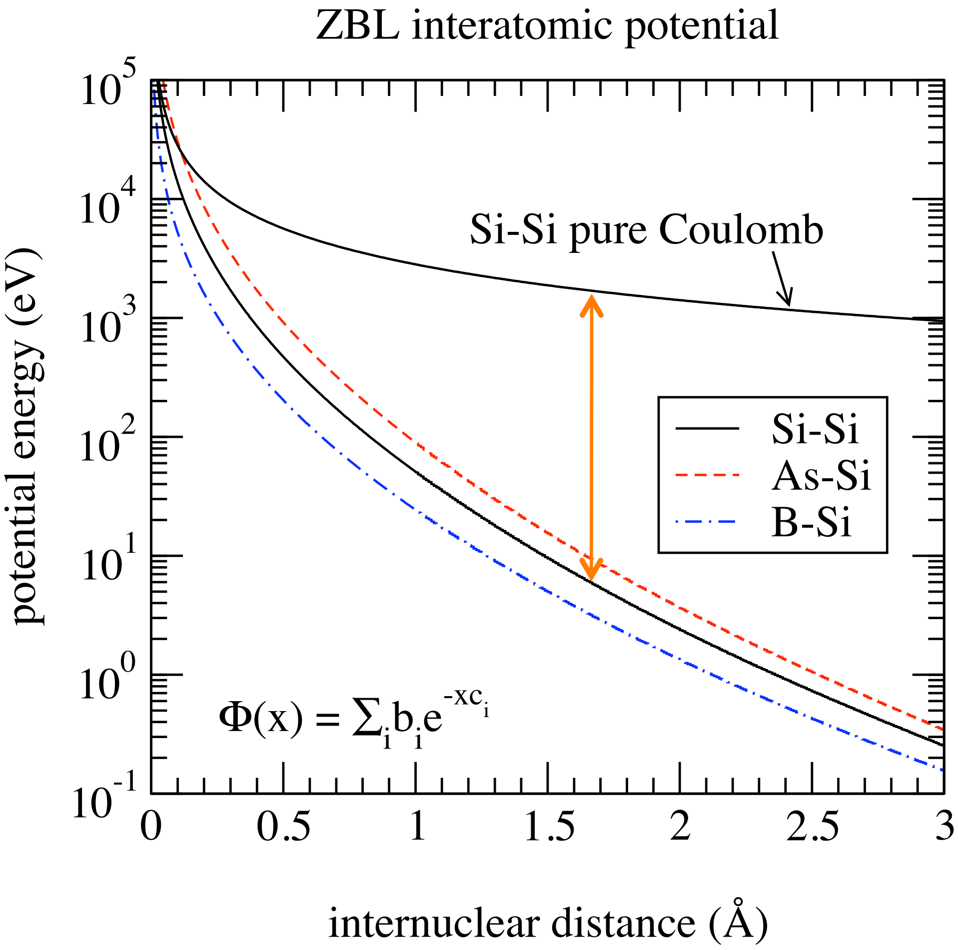
$$V(r) = \frac{Z_1 Z_2 e^2}{r} \Phi(r, Z_1, Z_2)$$

$\Phi(r, Z_1, Z_2) = \Phi(r/a) \leq 1$ screening function

$a = a(Z_1, Z_2)$ screening radius

Why screened? Because the negative charge of both target and ion electrons reduces the strength of the pure Coulomb repulsion between positive nuclei.

Example: the ZBL[1] universal interatomic potential for Si target



Electrons located around both ion and target nuclei *screen* the positive charges and strongly reduce the pure Coulomb force between them.

Here we deal only with collisions for which the ion energy is not large enough to penetrate the *coulomb barrier* of the target nuclei. This condition, usually fullfilled in ion implantation, excludes the occurrence of ***nuclear reactions.***

[1] Ziegler, Biersack and Littmark

Schematic of the binary collision between ion and target

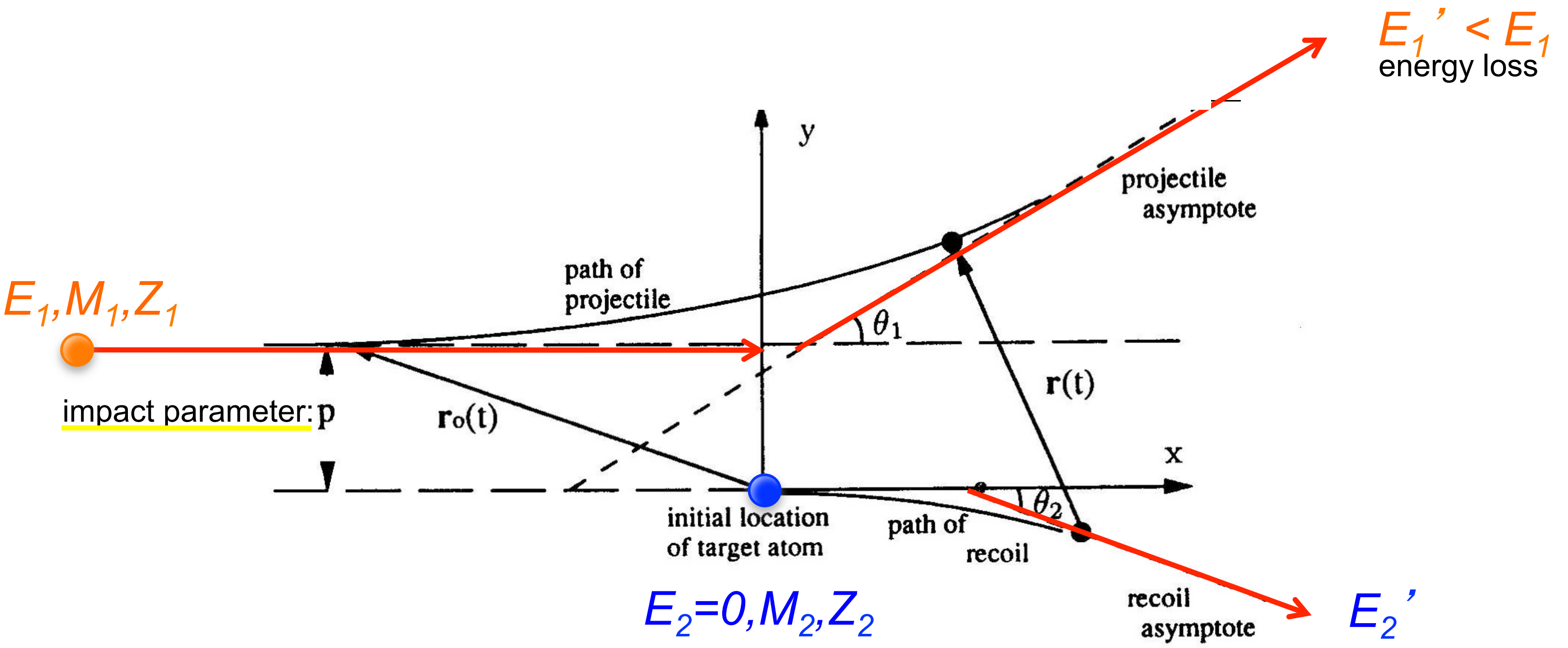


Fig. 2.3 The trajectories of the projectile (incoming particle) and the recoil

The binary collision between nuclei is treated as ***elastic***, i.e. obeying both *energy* and *momentum conservation.* Solving this classical scattering problem (if you like, you can find more mathematics in the supplementary material on the web site), we can determine the paths of ion and recoil, and the energy which is transferred from the ion to the target recoil. But the ion loses energy also by interactions with target electrons...

Stopping power: nuclear and electronic contributions

Another feasible approximation under typical ion-implantation conditions, is to treat separately the ion energy loss due to the interaction with target nuclei and the energy loss due to the interaction with electrons. Total ***stopping*** $\boldsymbol{S}$ (energy loss/unit path length) can thus be written as:

$$S = \left(-\frac{dE}{dx}\right)_{nuclear} + \left(-\frac{dE}{dx}\right)_{electronic} = S_n + S_e$$

- S_n can be obtained by the solution of the classical two-body scattering problem seen before;
- S_e is due to the interactions (ion nucleus)-(target electrons) - dominant at high ion velocities, and (ion electrons)-(target electrons) - dominant at low ion velocities. These interactions originate complex phenomena (**excitation** and **ionization** of target atoms, **capture** and **loss** of electrons by the moving ion) which need *quantum mechanics* to be properly treated. Due to the complexity of these phenomena, for practical purposes (simulation) electronic stopping is usually treated with semi-empirical models.

Main qualitative features of electronic stopping:

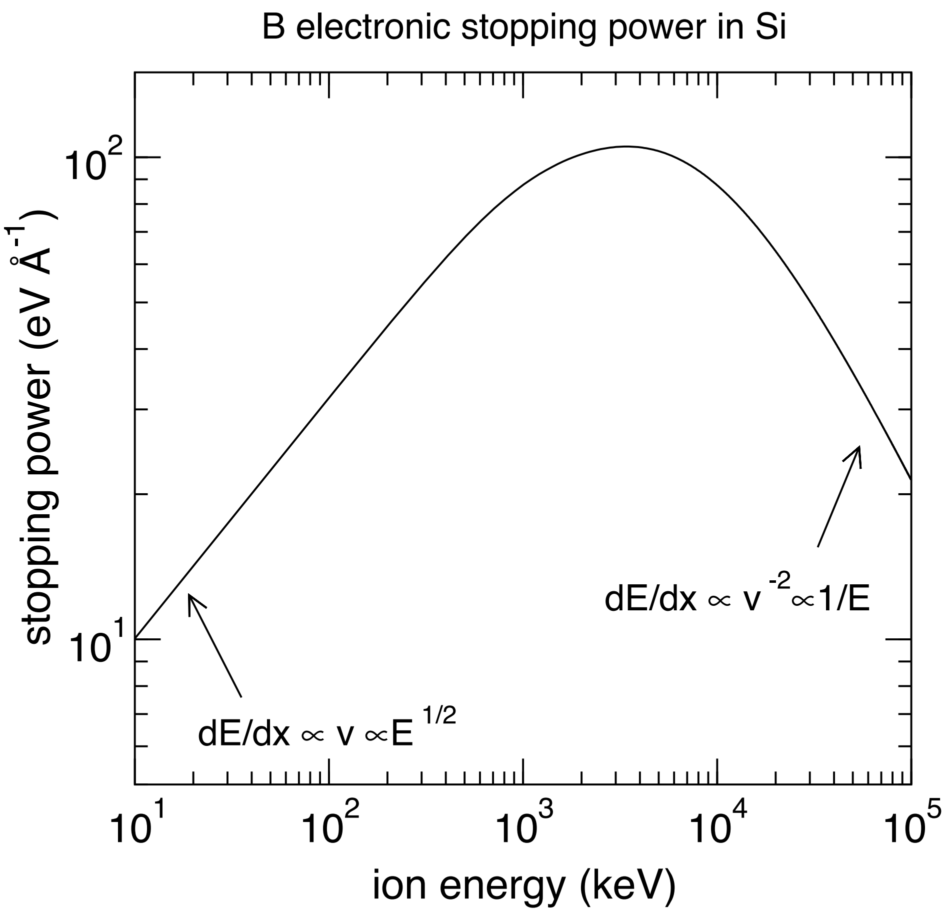
- $S_e = f(v_1)$ i.e. electronic stopping is basically a function of the ion ***velocity***

- the ***charge*** of the ion moving through the target may change by electron capture and loss

- the momentum transferred from electrons to ion nucleus is small, and it does not cause relevant deviation of the ion path

- the interaction depends on the electron density seen from the ion while moving through the material, which is *not uniform*, so the energy loss may depend on the detailed ion path through the material (see the case of ***ion channeling*** reported in the following) . Usually the term “electronic stopping” is meant to indicate the value averaged over all possible paths in the material.

Low- and high-velocity regimes of electronic stopping



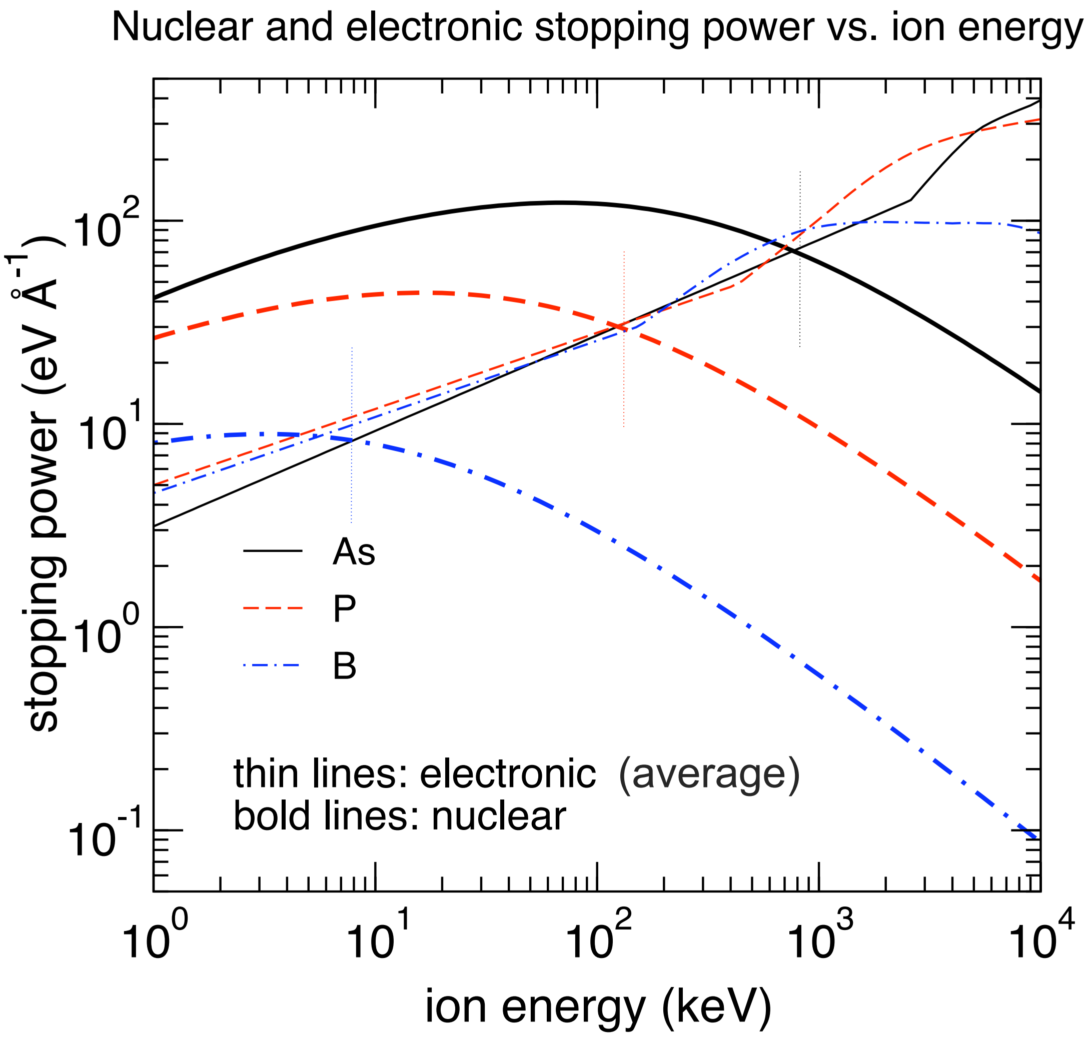
In the limits of low- and high-ion velocity[1], the problem can be simplified. It is possible to demonstrate that:

$S_e \propto v$ (for low v)
$S_e \propto 1/v^2$ (for high v)

S_e must therefore have a ***maximum***. This maximum shifts to higher energies with increasing ion mass

[1] Low or high is intended in comparison with the *Fermi velocity* of electrons in the target medium

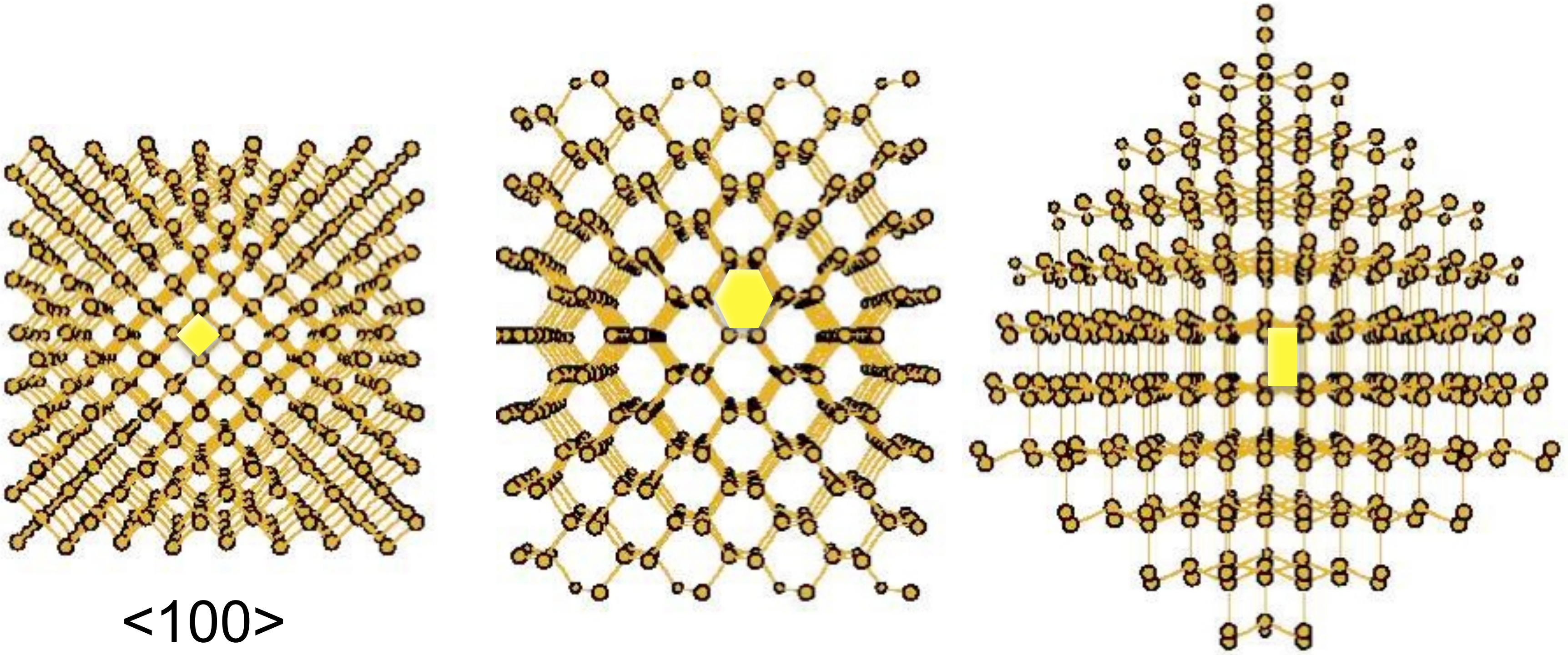
Comparison of nuclear and electronic stopping power



The example refers to common dopant species in Silicon.

At the energies typical of ion implantation, differences in S_e between different ion species are smaller than differences in S_n . The latter dominates the stopping at low energy, whereas electronic stopping is more effective at high energy. The crossing between the regimes of dominant S_n and S_e shifts to higher energy with increasing the ion mass.

Ion channeling in crystalline materials

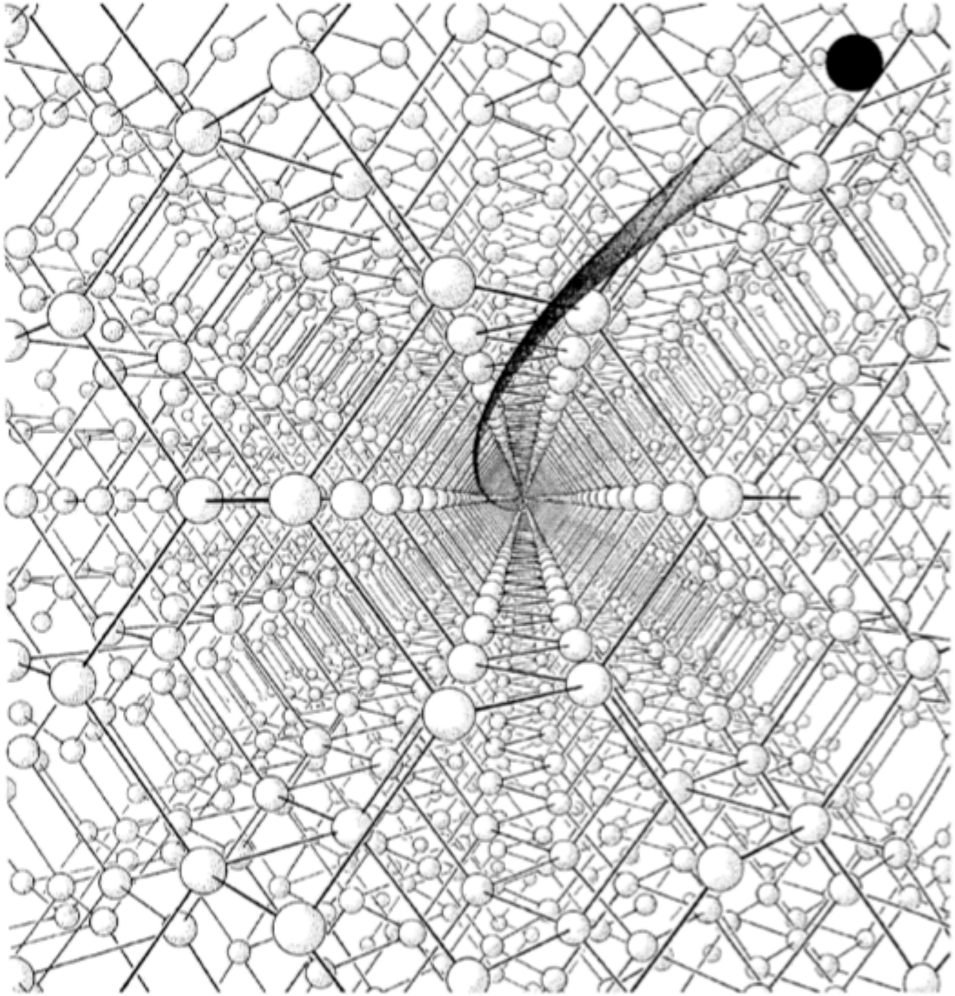


<100>

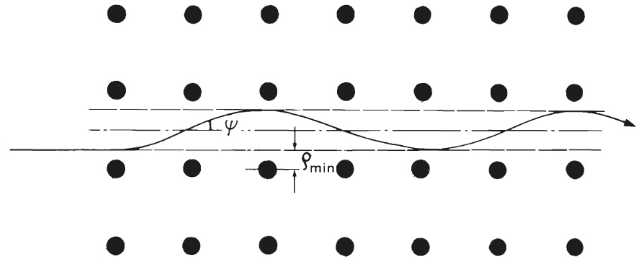
<110>

<112>

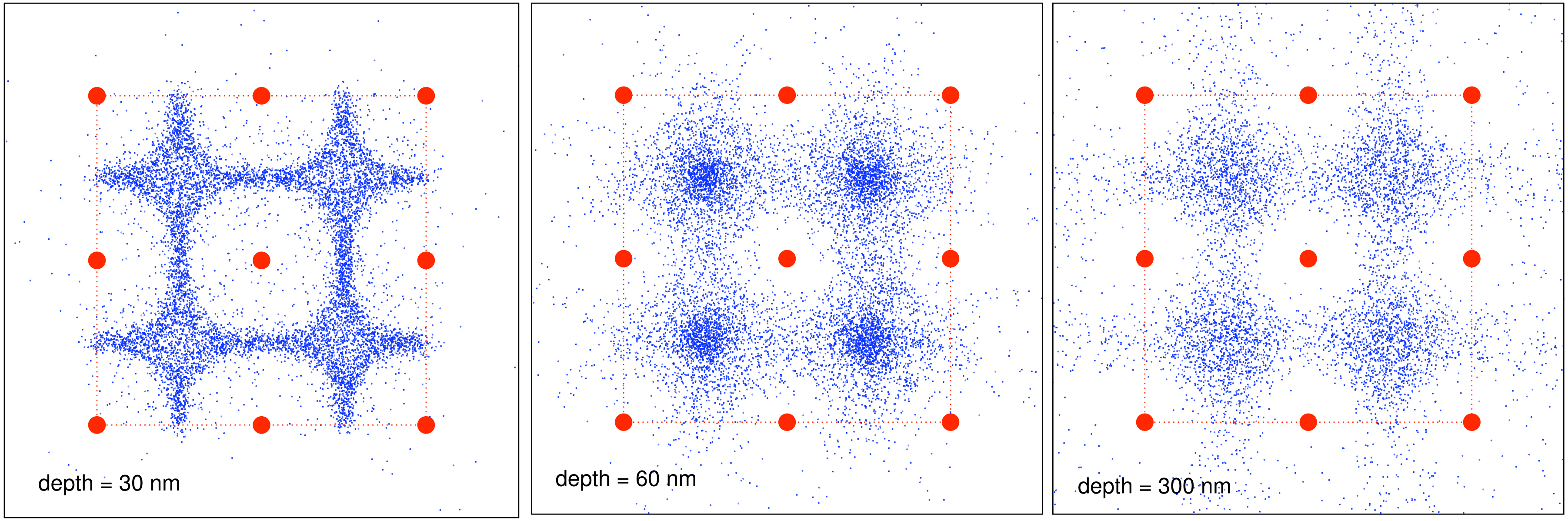
The Si lattice, as seen from three different low-index crystallographic orientations: the yellow regions bounded by atomic rows aligned with the view direction, indicate axial *channels.*



Axial ion channeling in <110> Si



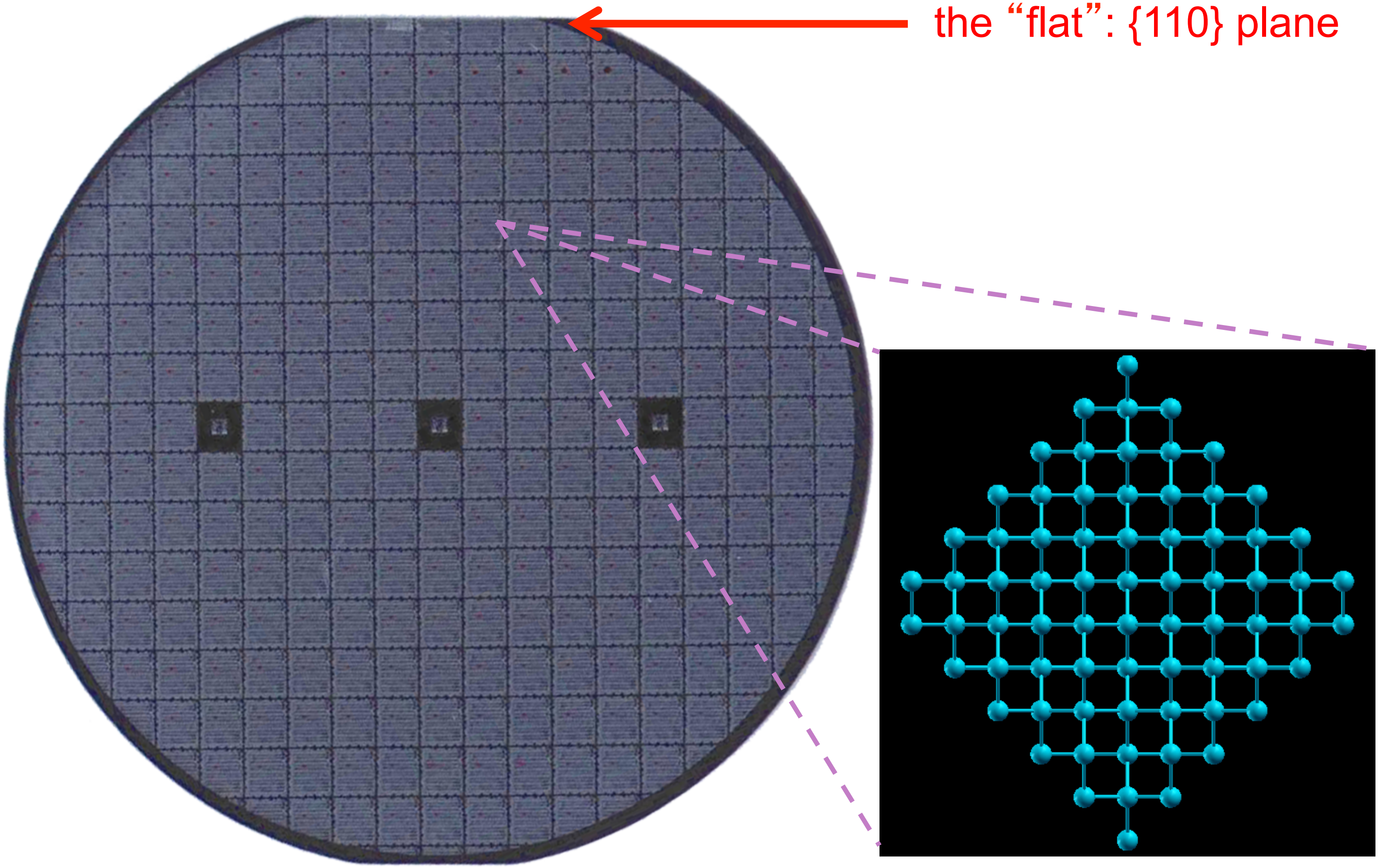
Nuclear scattering in a periodic structure, may “confine” ion trajectories into regions (***channels***) bounded by atomic rows (***axial*** channeling) or planes (***planar*** channeling). Interactions of ***channeled ions*** with target nuclei and electrons are weaker in comparison to those of ions following “random” trajectories or penetrating a disordered material. Their average stopping (both S_n and S_e) is *lower*, and their penetration depth *larger*.



Example of ion confinement in Si lattice channels (from BCA simulation).

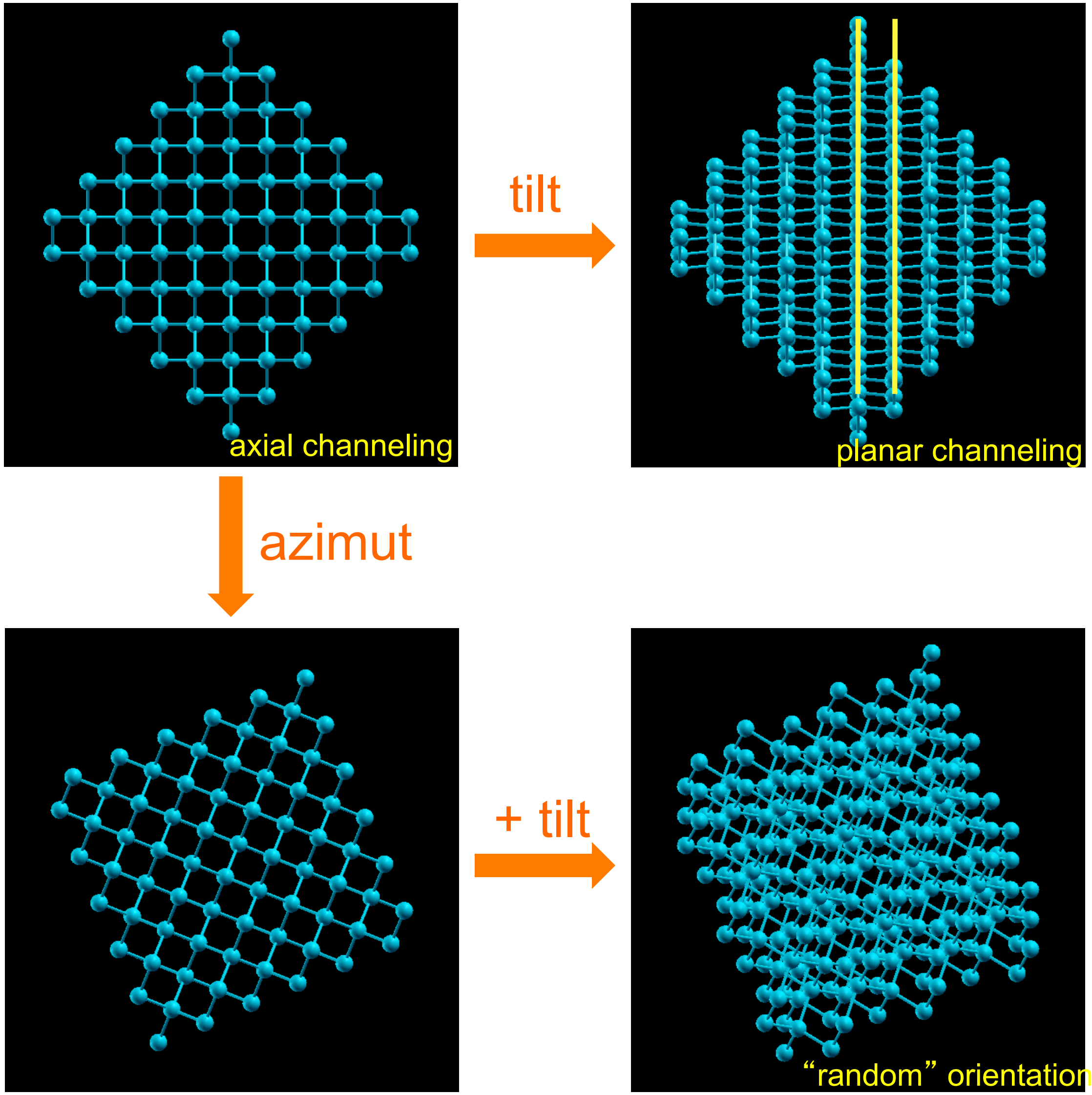
Snaphots of the flux of 2MeV He ions incident perpendicular to the (100) surface of Silicon at different depths below the surface.

Lattice orientation of a Si(100) wafer



the “flat”: {110} plane

Minimizing channeling in Si(100) ion implantation



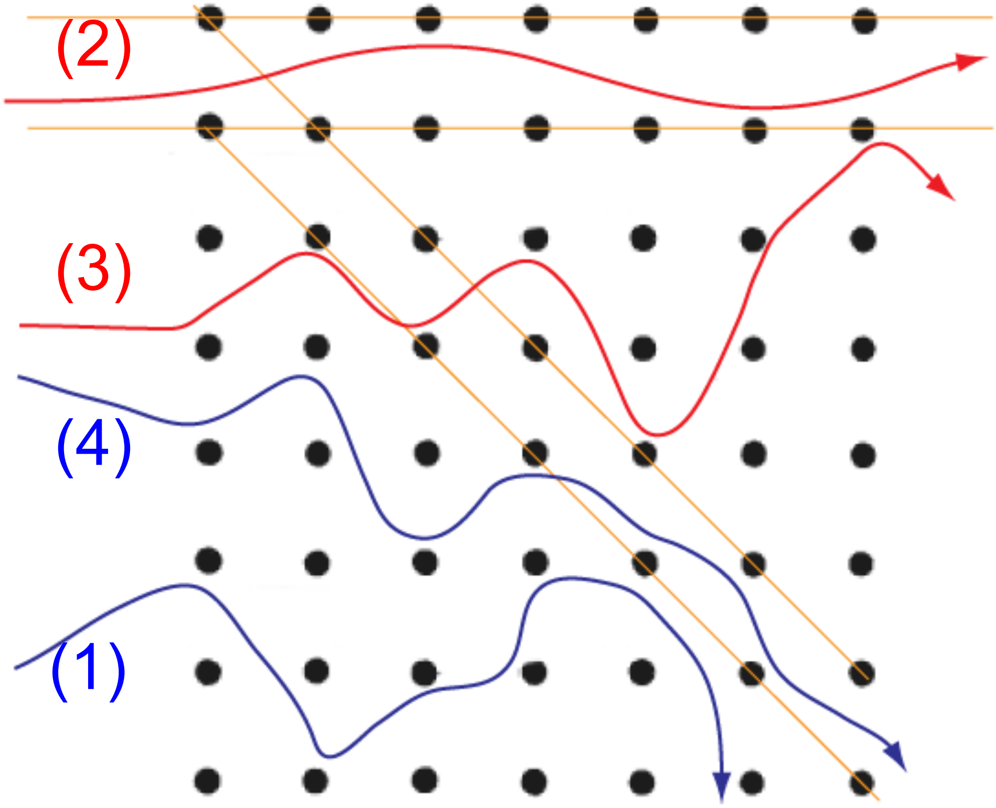
Channeling gives origin to an often unwanted increase of ion penetration. How getting rid of it ?

If the wafer is tilted around one <100> axis only, *axia*l channeling disappears, but *planar* channeling still occurs.

The procedure to get a so-called “***random***” orientation is first to rotate azimutally of an angle ϕ,

then tilting of an angle θ the Si wafer. In Si(100) typical values for “random” implantation (which minimize, but do not eliminate !) channeling are **θ ≈ 7-8°** and **ϕ ≈ 19-22°**

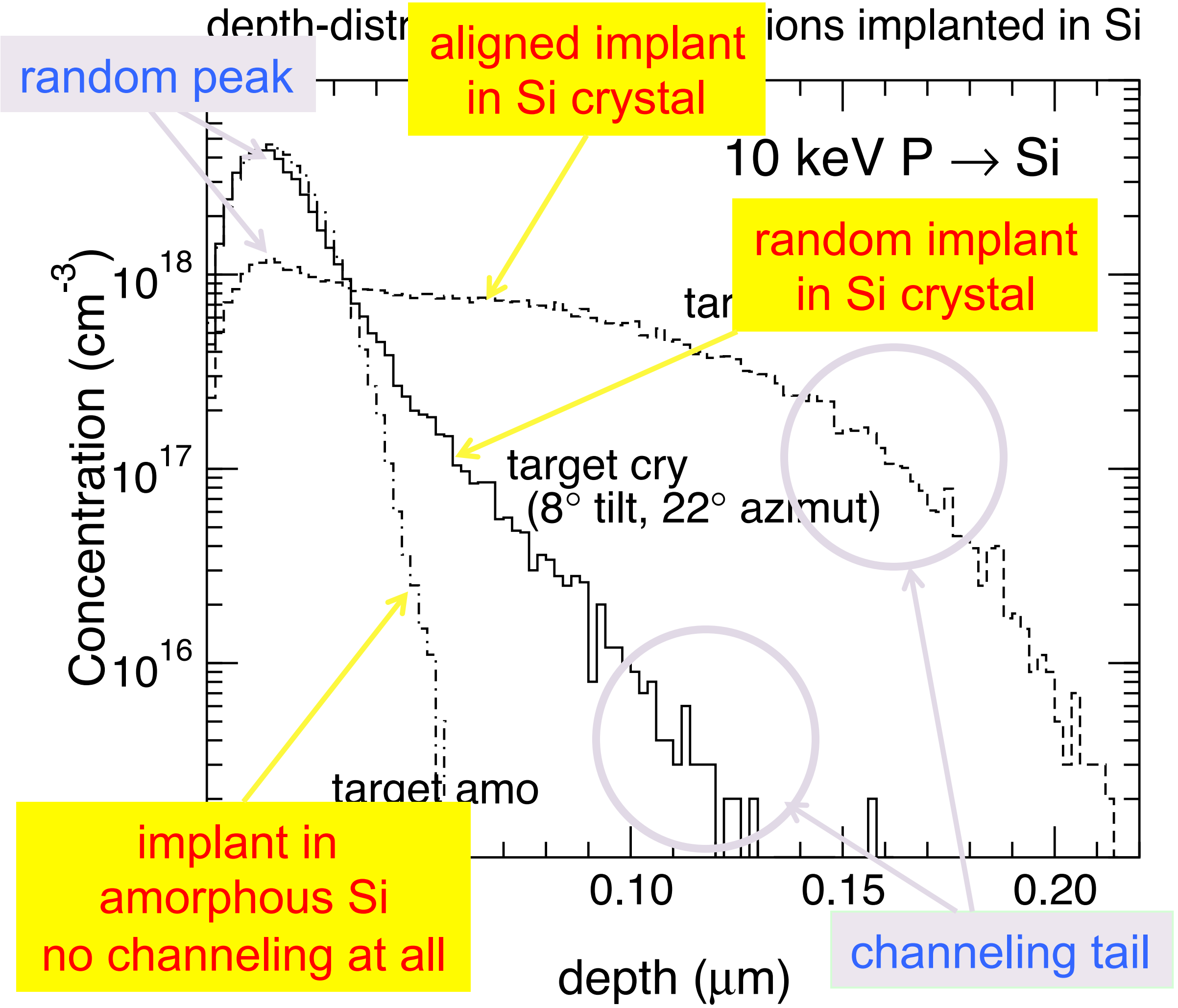
The interplay of channeling and *dechanneling*



Trajectories of ions moving through a crystal maybe random (1), channeled (2), or they maybe channeled at the beginning, then are ***dechanneled*** and become random (3), or, just the opposite way, i.e. they start as random and then may become channeled afterwards (4), even along a direction not perpendicular to the surface. The occurrence and relative abundance of (1)-(4) events changes with changing the beam-lattice orientation. Looking at the depth distribution profile of ions we can observe the contributions of all these different paths.

,

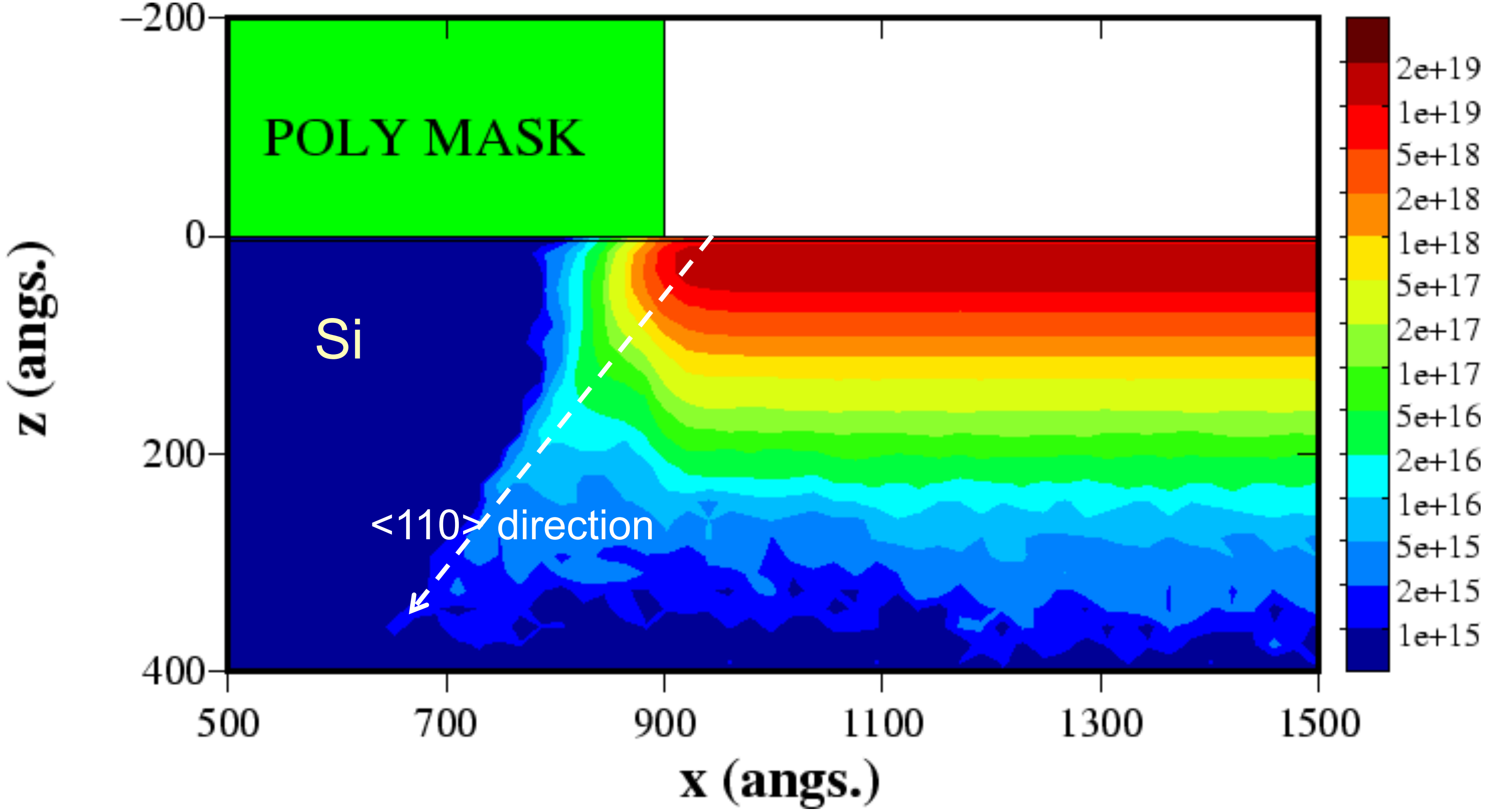
Channeling effects studied by Monte-Carlo BCA simulation



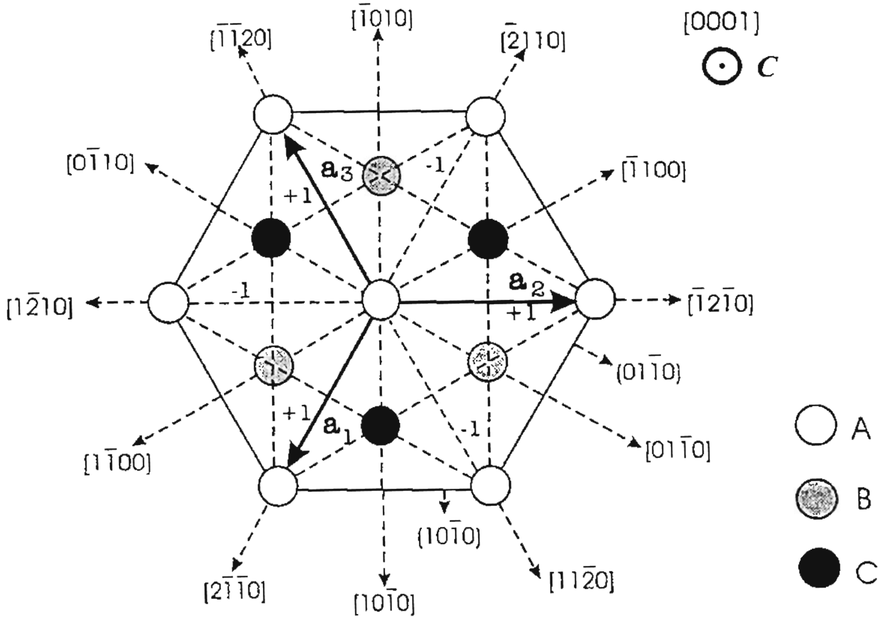
Channeling effects cannot be completely eliminated in a crystal, even if implantation is performed under so-called "random" conditions.

A certain fraction of ions, deflected by nuclear collisions, may become aligned with major axes or planes, being "trapped" in axial or planar channels and giving origin to the so called "***channeling tails***".

Channeling effects in 2D distribution of implanted ions



Channeling effects in crystalline SiC



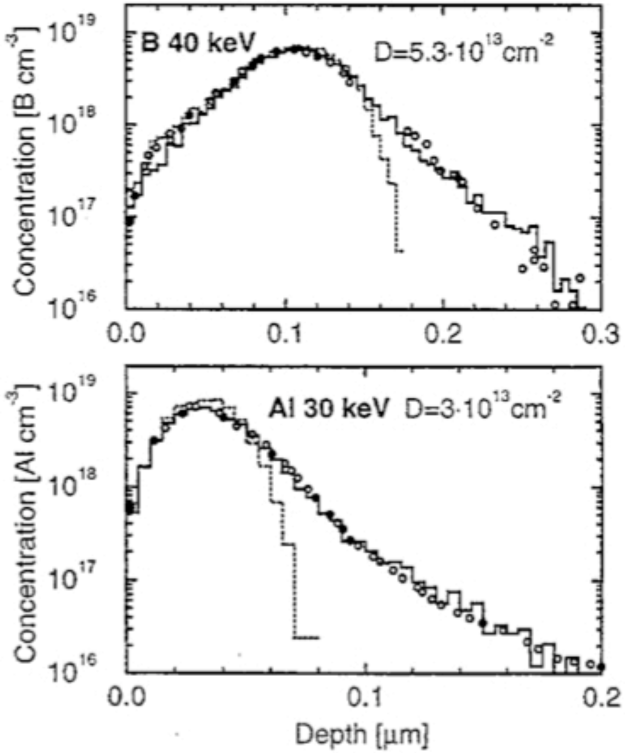
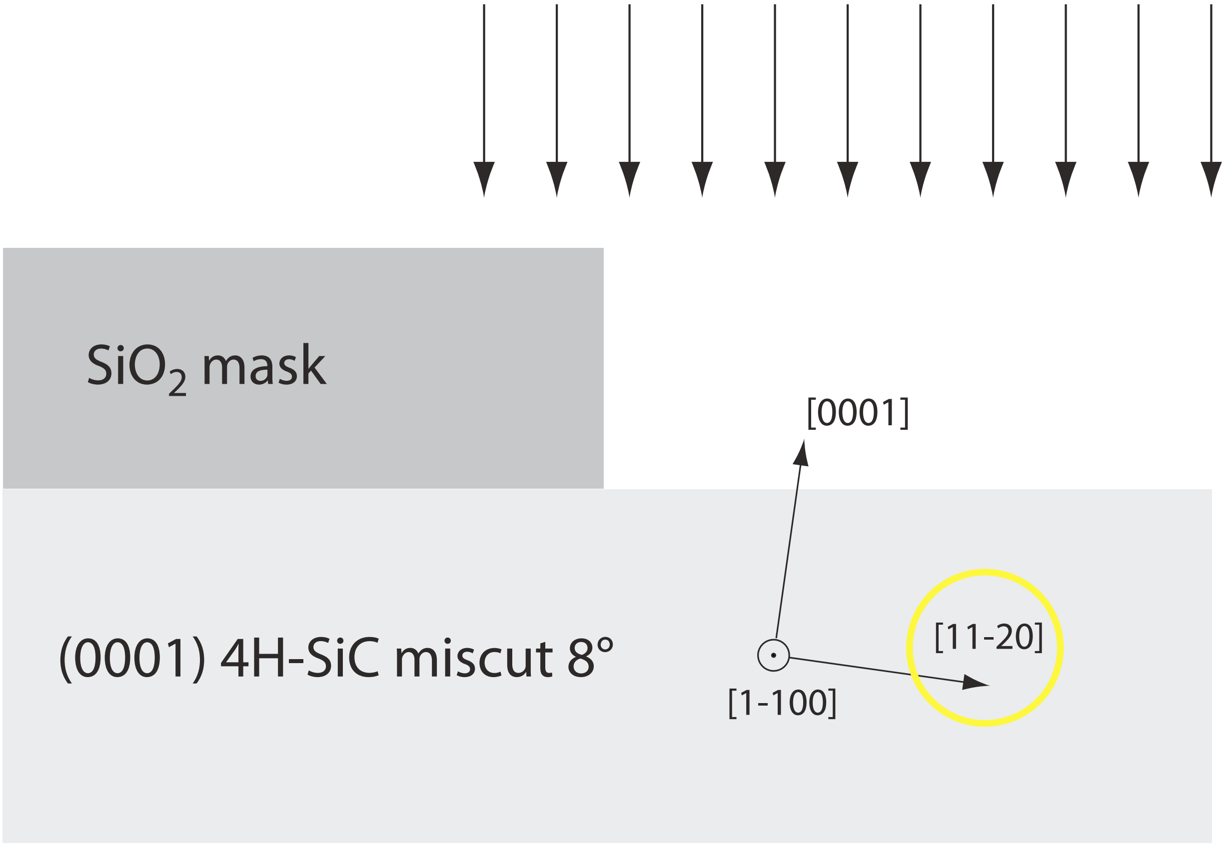
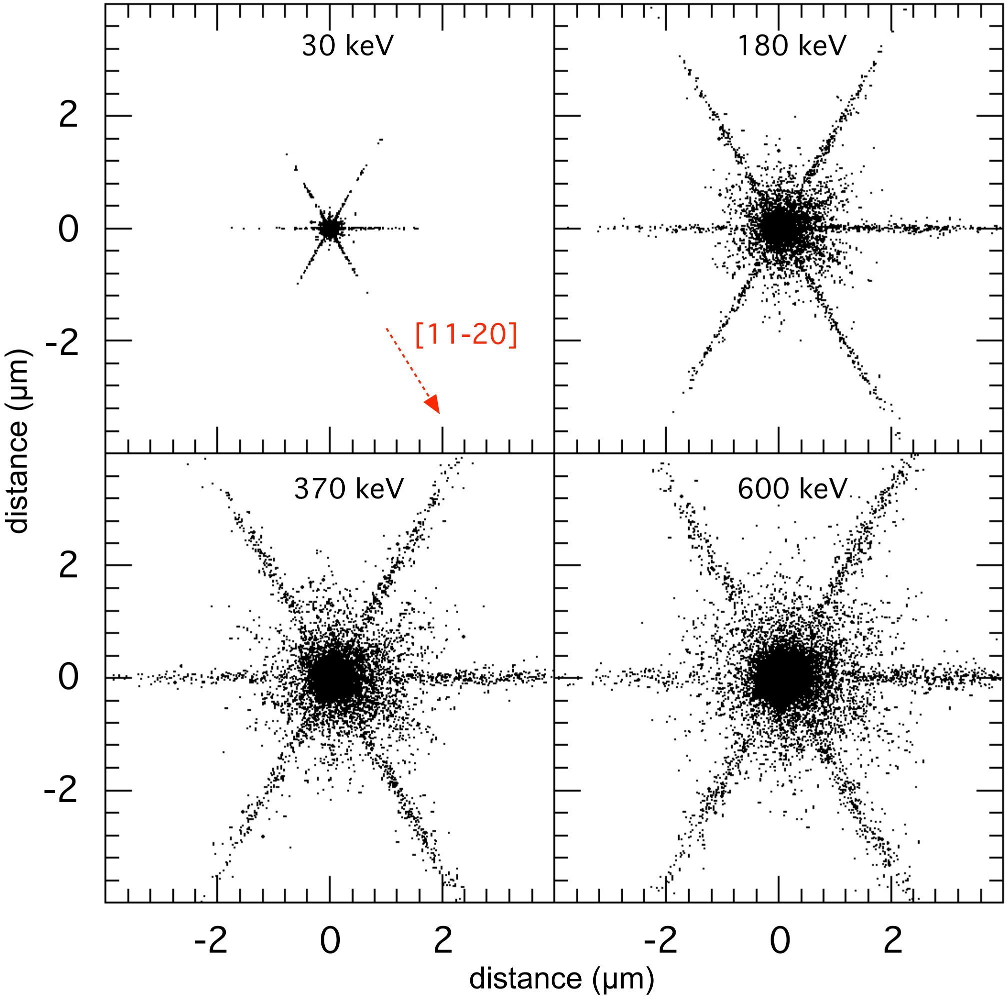


Fig. 1. Examples of the comparison of MC simulations (histograms) of ion-implantation into 6H-SiC with experimental SIMS profiles (symbols) reported in Ref. [11]. Dotted histograms are the results of TRIM-like simulations in the amorphous material, while continuous ones refer to the simulations in the crystal. Orientation conditions were ϕ (azimuth) = 30° measured from the (11$\bar{2}$0) plane and θ (tilt) = 12.5° performed towards the (11$\bar{2}$0) plane from the (0001) surface normal. Parameters of electronic energy loss model (see text) were $f = 0.42$, $s = 0.55$ for Al, $f = 0.16$, $s = 0.35$ for B.

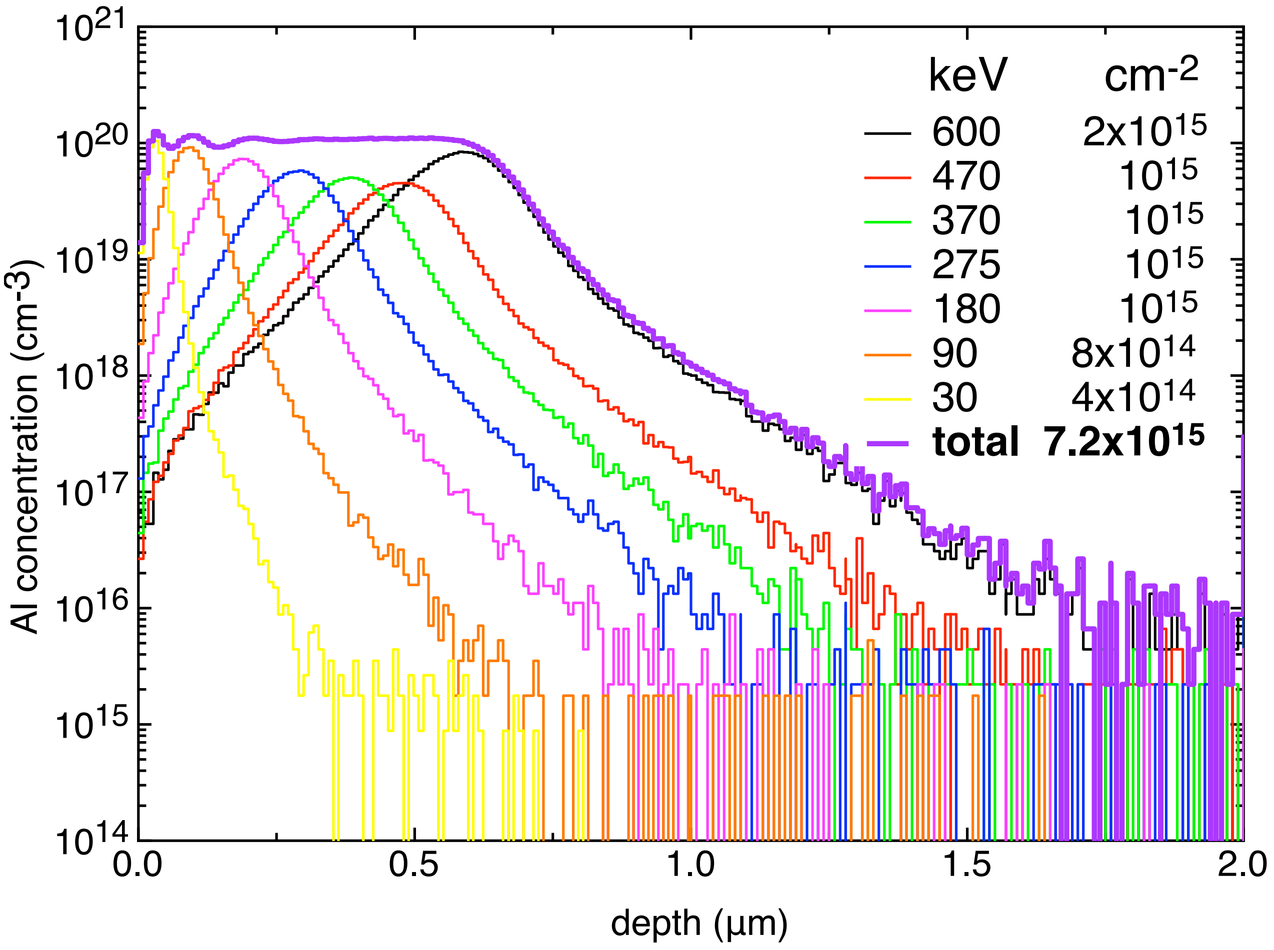
E. Albertazzi, G. Lulli / Nucl. Instr. and Meth. in Phys. Res. B 120 (1996) 147–150



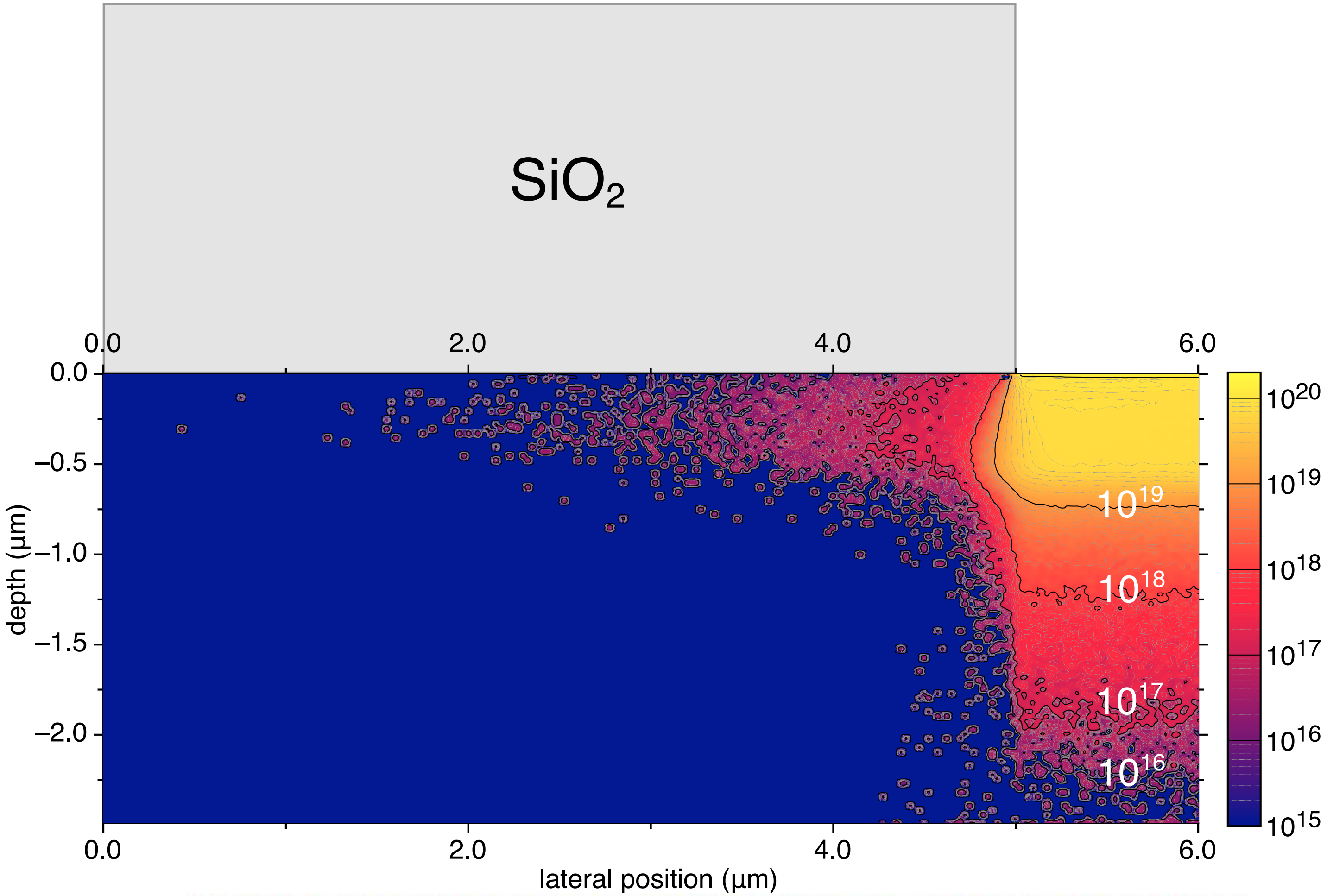
[11-20] orientation is perpendicular to a rather “open” channel in SiC: the question of practical interest is: how much the implanted dopant distribution will extend laterally in the under-mask region, due to channeling?



Surface projection of the distribution of ions implanted in 4H-SiC perpendicularly to the surface and impinging all in the same point (0,0)



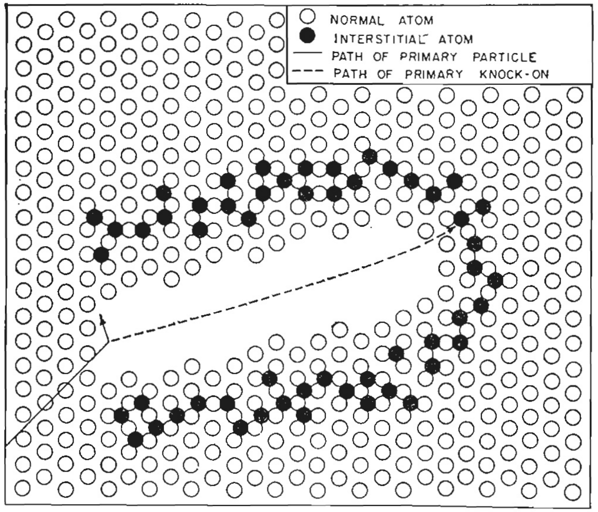
1D simulation of implantation conditions designed to have a nearly constant dopant concentration of 10^{20} atoms cm^{-3} in a 0.5 µm surface layer



G. Lulli IEEE TRANSACTIONS ON ELECTRON DEVICES, VOL. 58, NO. 1, JANUARY 2011

2D simulation allows to evaluate the phenomenon of lateral under-mask penetration, which in this case is rather pronounced and may have consequences on the electrical behavior of the final device.

Radiation damage induced by ion implantation



Displacement cascade induced by a primary recoil in an ordered material: black dots: ***interstitial*** *atoms.*

Radiation damage in a crystalline target consists of atoms which are permanently displaced from their regular lattice sites as a result of irradiation.

The elementary radiation defect consists of the displaced atom (***interstitial)*** plus the related ***vacancy*** (the site left empty by the interstitial). More complex defects form as a result of accumulation and clustering of interstitials and vacancies.

Effects of ion-implantation damage:

- *change of physical and chemical properties* of the target, such as electrical, optical, mechanical ...
- *loss of long-range structural order*, leading eventually to the transition to a fully disordered phase (crystal ⇒ ***amorphous***).

Radiation damage induced by ion implantation

Main mechanisms of ion-induced damage:

An elementary defect (interstitial + related vacancy) is formed if one nucleus of the target receives enough energy to be pushed out of its regular lattice site. This may occur as a result of:

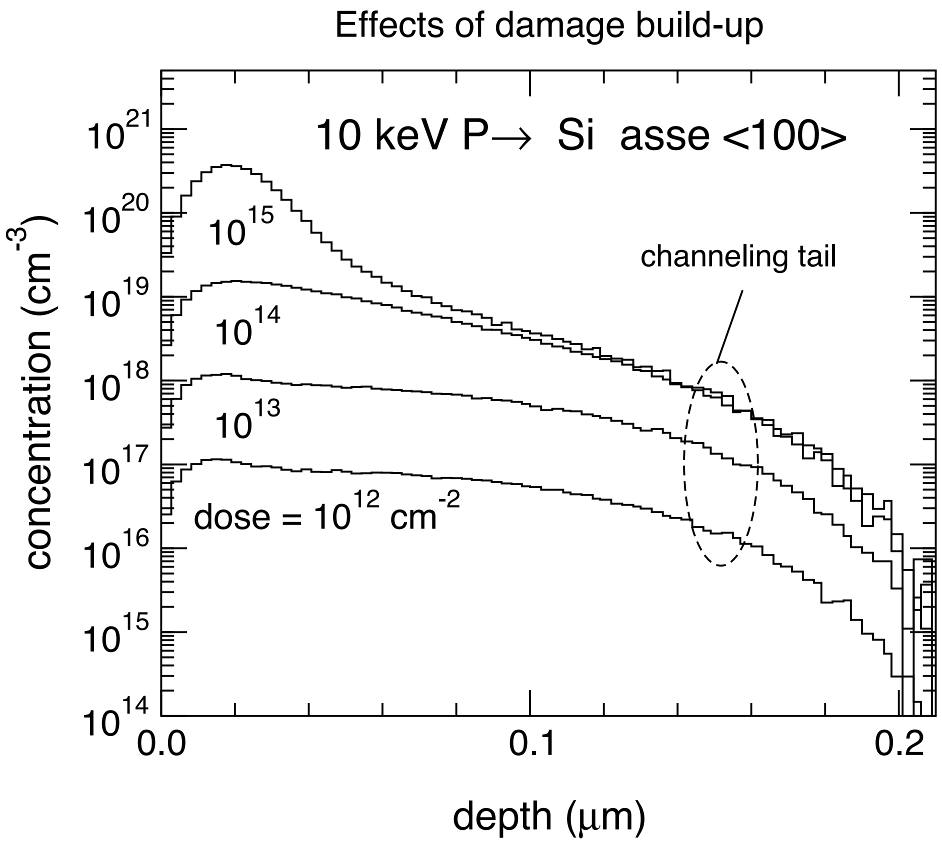
1. direct transfer of momentum in the elastic collision between ion-target and target-target nuclei (***nuclear damage***)

2. energy transferred to target electrons, subsequently transferred to target nuclei by *electron-phonon coupling* effects (***electronic damage***)

While nuclear damage is effective in almost any material, electronic damage may not work in materials (as ***metals*** and ***semiconductors***) in which electron-phonon coupling is weak. Typical materials which are instead sensitive to electronic damage are ***insulators*** and ***organic materials*****.**

Effects of damage accumulation in channeling implantation

One consequence of damage accumulation during ion implantatation is the *reduction of channeling effects with increasing fluence*, as a consequence of the progressive loss of structural order.



The simulation takes into account the dynamic modification of crystal structure with increasing ion fluence.

Ion damage progressively destroys the crystal order, until channeling is no more possible.

Channeling tail increases at low fluence but **saturates** at high fluence.

BCA modelling of of damage formation during ion-implantation: the Kinchin-Pease (KP) approximation

Simple considerations lead to write the approximate number of ***atomic displacements*** (or *Frenkel pairs*) $N_d(T)$ originated by a ***primary recoil*** of the target which has received an energy T in a nuclear collision with the primary ion:

$$N_d(T) = \begin{cases} 0 & T \leq E_d \\ 1 & E_d < T < 2E_d \\ \frac{T}{2E_d} & 2E_d < T \end{cases}$$

where E_d is the ***threshold energy for atomic displacement***

Under the KP approximation, ion damage is estimated without calculating the detailed trajectories of primary, secondary, and nth order Si recoils, therefore the simulation is rather fast.

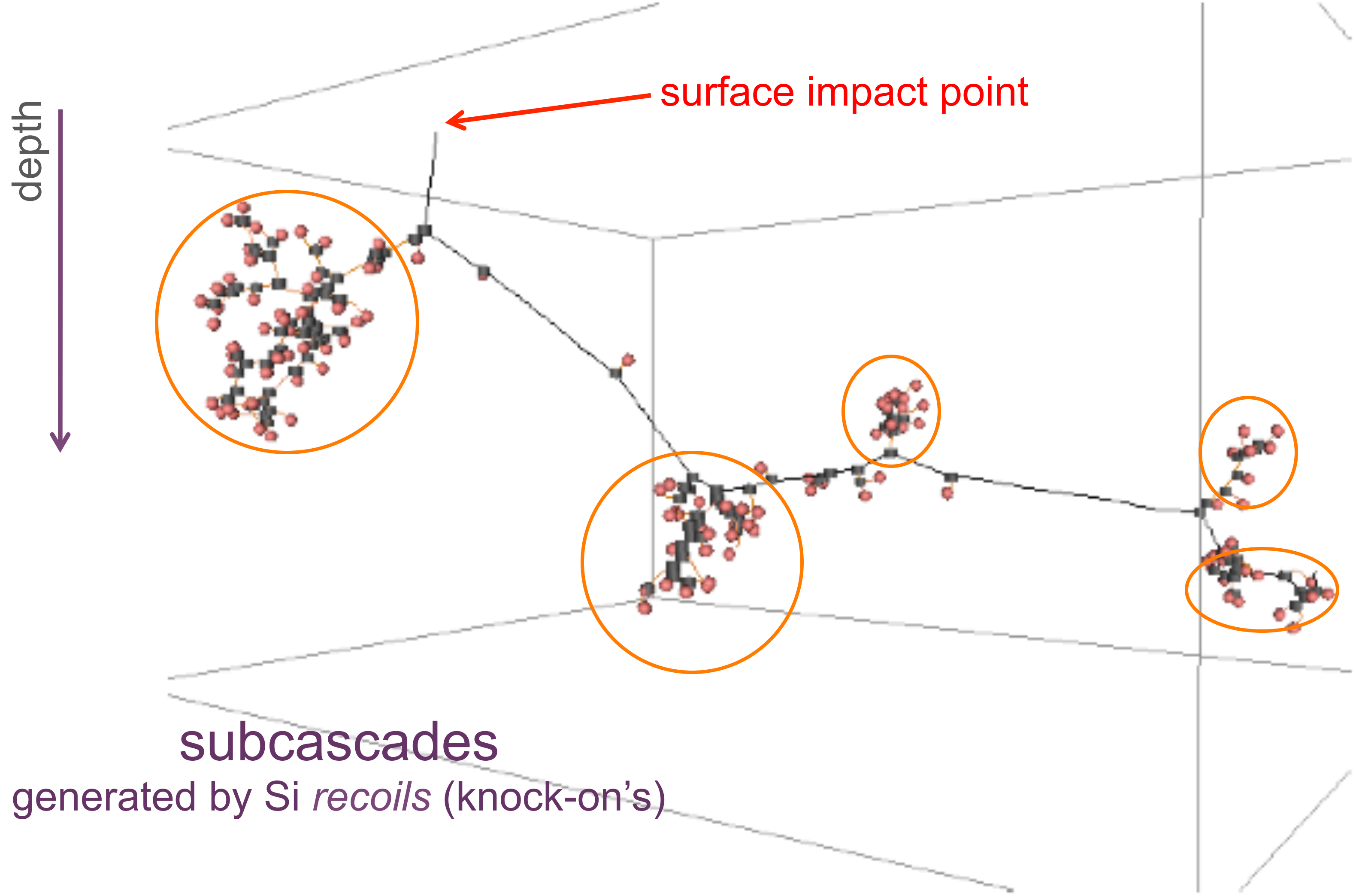
BCA modeling of of damage formation during ion-implantation: full recoil calculation

Target recoils which receive energy $T > E_d$ are *displaced* and their trajectories followed in details until their kinetic energy is fully dissipated. The same is done for secondary (i.e. recoils displaced by primary recoils) and nth order recoils ...

This simulation method is more computer intensive, but allows a much better insight into the structure of ion-induced damage.

In the following a few examples are presented, which show qualitatively how the shape of the ***displacement cascade*** varies with varying ion mass and orientation, keeping the ion energy fixed at 10 keV. Grey cubes represent lattice Si vacancies (V) whereas red spheres represent interstitial Si atoms (I). Obviously, for mass conservation, the total number of Si interstitials must equal the number of total Si vacancies.

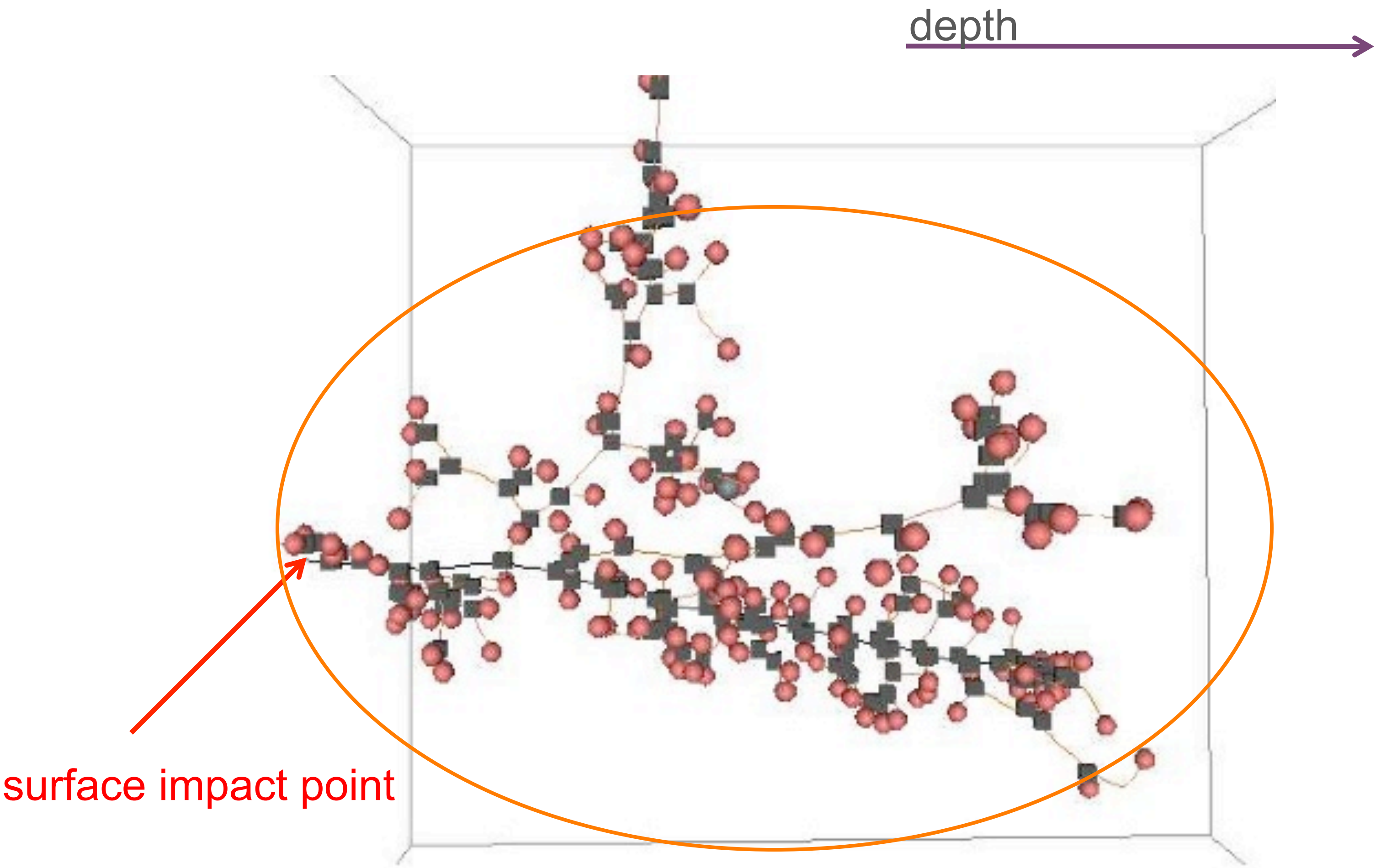
B 10 keV – random impact



subcascades

generated by Si *recoils* (knock-on's)

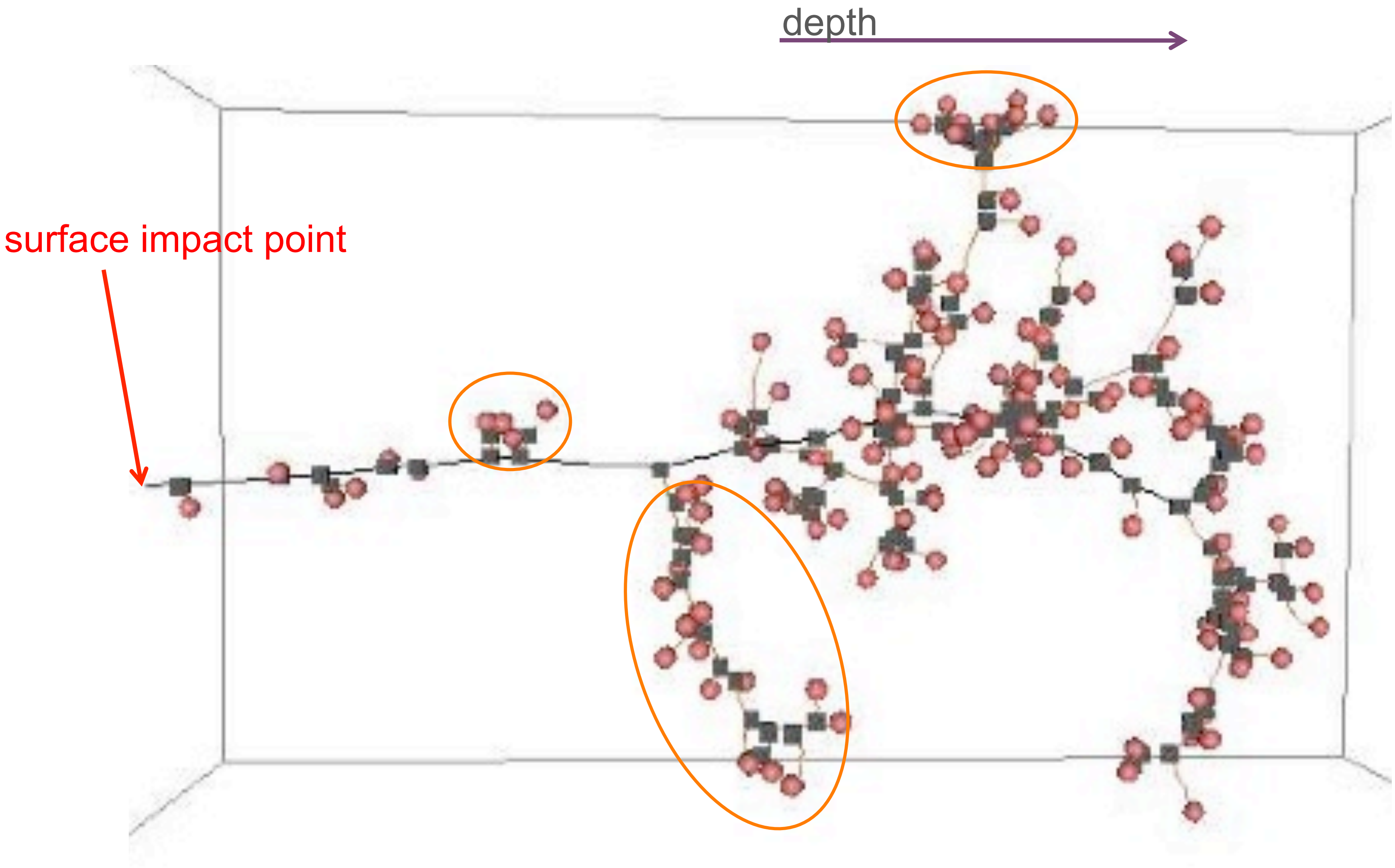
As 10 keV – random impact



depth

surface impact point

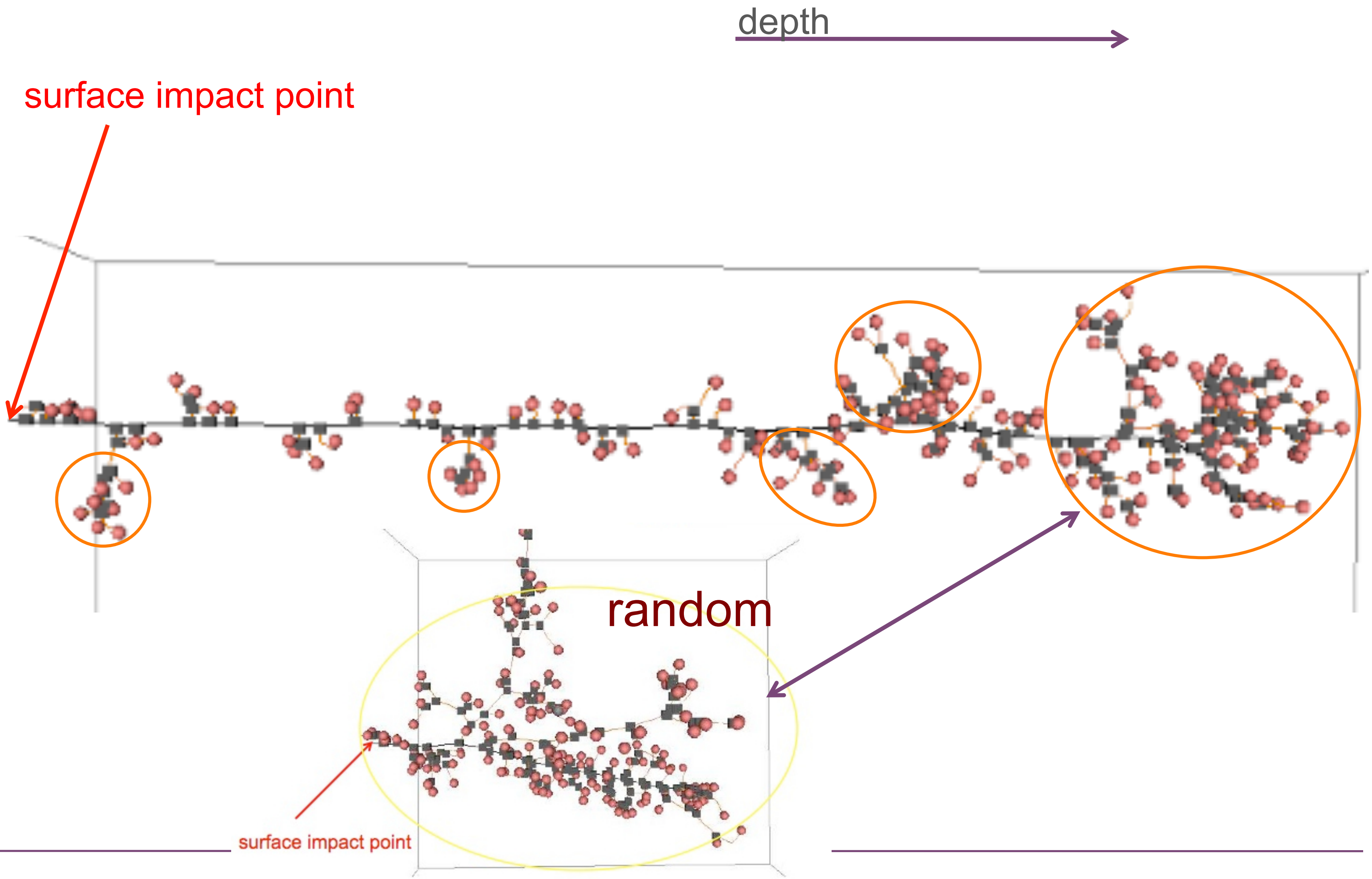
Si 10 keV – random impact



depth

surface impact point

As 10 keV – aligned <100> impact



depth

surface impact point

random

Other damage-related phenomena: sputtering

Surface atoms are more easily displaced than bulk atoms (E_d surface < E_d bulk). As a consequence of ion bombardment, they can be ejected from the surface to the surrounding vacuum. If the number of atoms ejected from the target overcomes the number of implanted atoms, the net effect is a loss of matter through ***surface sputtering***. The occurrence of surface sputtering and its amount depends on ion-irradiation parameters. The sputtering effect requires high fluences (**>> 10^{16}** ions cm^{-2}) to be observed, and usually is negligible in conventional ion implantation doping applications. The effect increases with :

- increasing ion mass
- decreasing ion energy
- increasing ion-surface incidence angle

There are specific ion beam-based techniques (for example Secondary Ion Mass Spectroscopy – **SIMS** - or Focused Ion Beam – **FIB** – nanofabrication) which take advantage of the sputtering effect of an intense, highly focused ion beam.

Limitations of BCA in the simulation of ion implantation damage

- While most part of the trajectory of an implanted ion is described quite accurately by the BCA, the low-energy (E≤100 eV) events occurring in the final part of ion and recoil paths (where most of the energy elastically transferred to the lattice is dissipated) are not.

- Here the binary approximation of atom-atom interaction breaks down, *multiple atomic interactions* and *collective effects* (such as ***melting*** and ***resolidification*** of microscopic regions of the material), which play an important role in the formation of damage, cannot be neglected.

- To overcome these limitations, *empirical corrections* can be used in BCA simulation of damage. However, multiple interactions, collective effects and their influence on defect formation can be properly treated only by ***molecular dynamics (MD)***

Classical Molecular Dynamics (MD)

It is a method widely used for the numerical simulation of *many-body* atomic and molecular processes.

The interactions between nuclei (ion-target and target-target) are described by an ***empirical many-body potential*** $V(R_{i,j})$.

One has to solve (numerically) the newtonian equations of motion of N nuclei:

$$M_i \frac{d^2\mathbf{R}_i(t)}{dt^2} = \sum_{j=1}^{N} \mathbf{F}_{ij} = \mathbf{F}_i(\mathbf{R}_i(t))$$

where the forces **F** are calculated as the gradients of the empirical potential. Critical issues are: the choice or setup of a "good" empirical potential (there is almost a dedicated science to do so) and the large computational effort required if the number of interacting atoms is large. In ion implantation, the penetration of a single ion of energy in the 1-100keV range, usually involves interactions of 10^3-10^6 atoms, which could be prohibitive for practical purposes, unless one can rely on a large computational resource.

Damage cascades in metals and semiconductors by MD

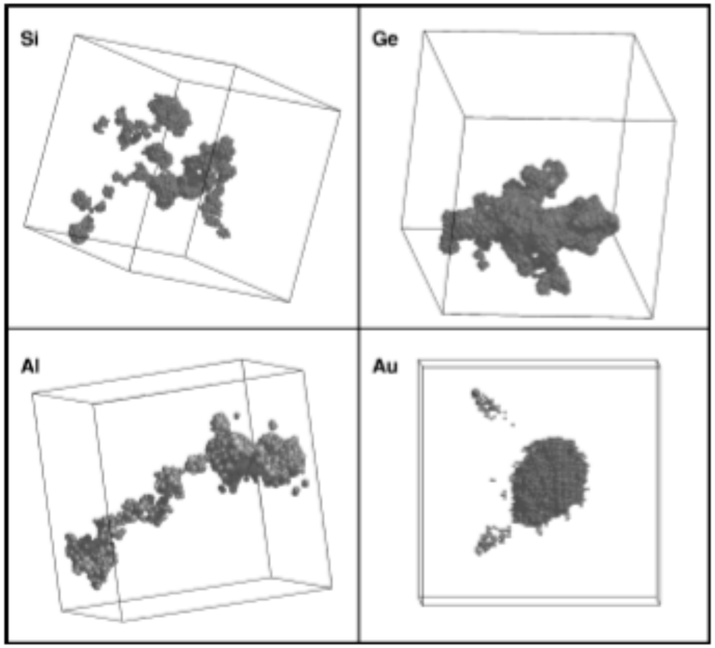


FIG. 2. Liquid atoms in 10 keV cascades in silicon (upper left), germanium (upper right), aluminum (lower left), and gold (lower right) (Ref. 61). The snapshots were chosen at times when the number of atoms in large continuous liquid regions was at a maximum. The atom size illustrates the kinetic energy of each atom, with the hottest atoms being larger. The bounding boxes show the total size of the simulation cells, which have been rotated to provide a clear view of the nature of the damage. In the gold cascade shown here, two replacement collision sequences emanate out from the center of the cascade, producing a trail of hot atoms in their wake.

K. Nordlund *et al.* Phys. Rev. B 57 (1998) 7556

⇒

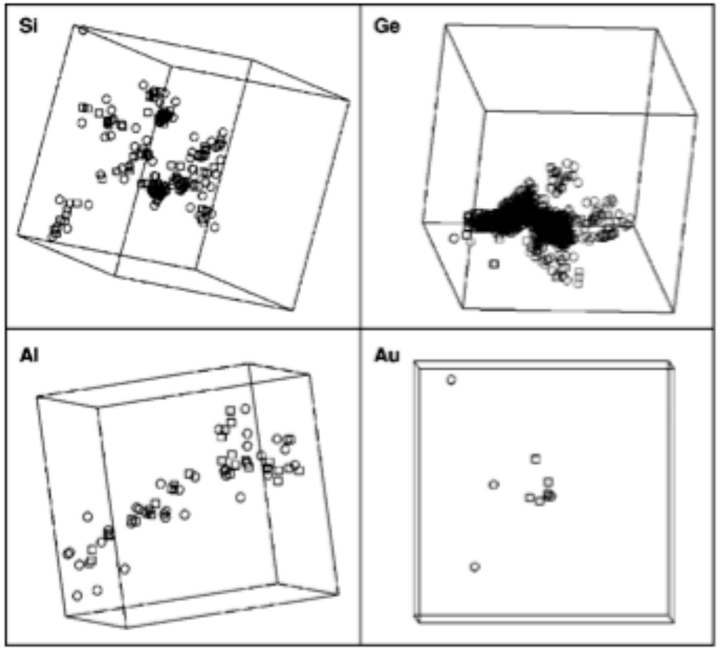


FIG. 3. Final defects created in 10 keV cascades in Si, Ge, Al, and Au. The cascades shown and the rotation of the cells are the same as in Fig. 2. Squares show the locations of vacancies and circles interstitials. The amorphous zones in Si and Ge appear as agglomerations of vacancies and interstitial in the figures.

the evolution depends on many physical properties of the target (structural, thermal, bonding ...)

MD: the influence of the model potential

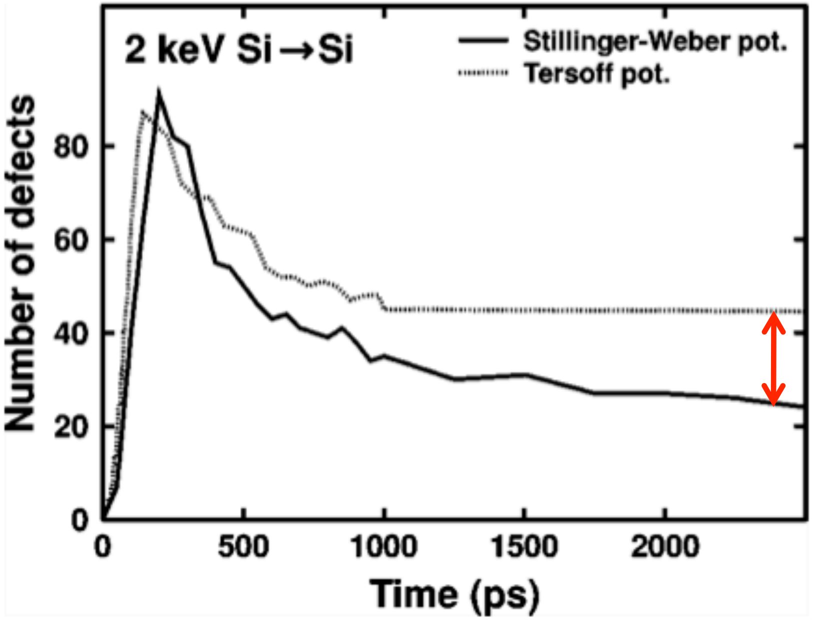
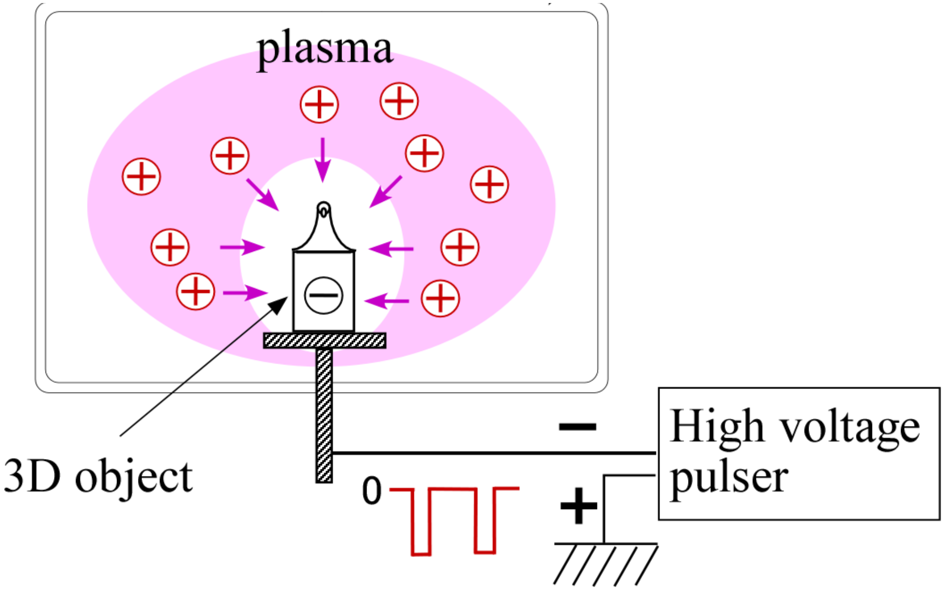


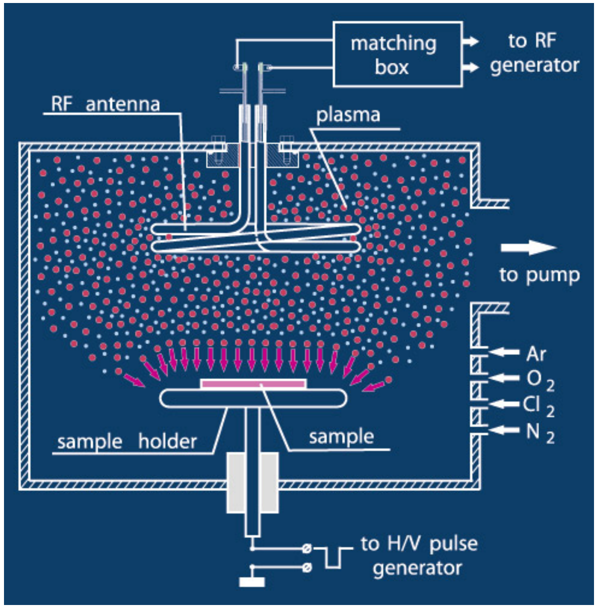
FIG. 1. Number of defects as a function of time in two representative 2 keV cascades simulated using the Tersoff and Stillinger-Weber interatomic potentials.

Quantitative results depend on the the empirical many-body potential used in MD. Its functional form and empirical parameters are chosen to fit some physical properties of the target material. Nevertheless, there is no empirical potential which can fit *every* property. So, there may be different possible choices, which lead, for instance, to different quantitative results in the calculation of radiation defects, as in the example shown on the left.

Brief survey of other ion-based processing techniques

Plasma Immersion Ion Implantation and Deposition (PIII&D)





Pros

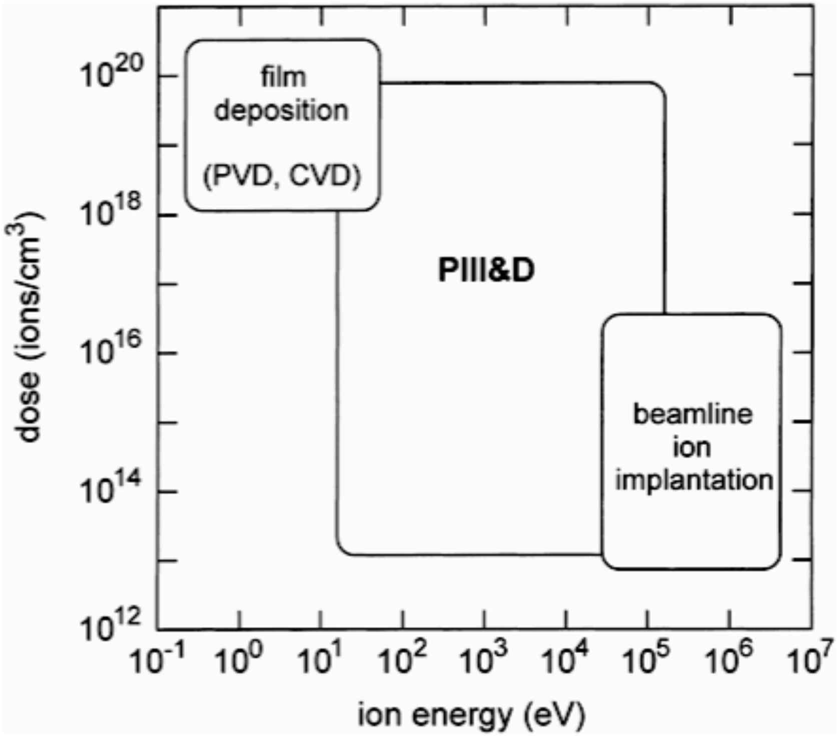
- conformal treatment of non-planar 3D surfaces
- very high fluence

Cons

- contamination
- poor process uniformity
- high ion energy spread

i.e. less process control

Plasma Immersion Ion Implantation and Deposition (PIII&D)

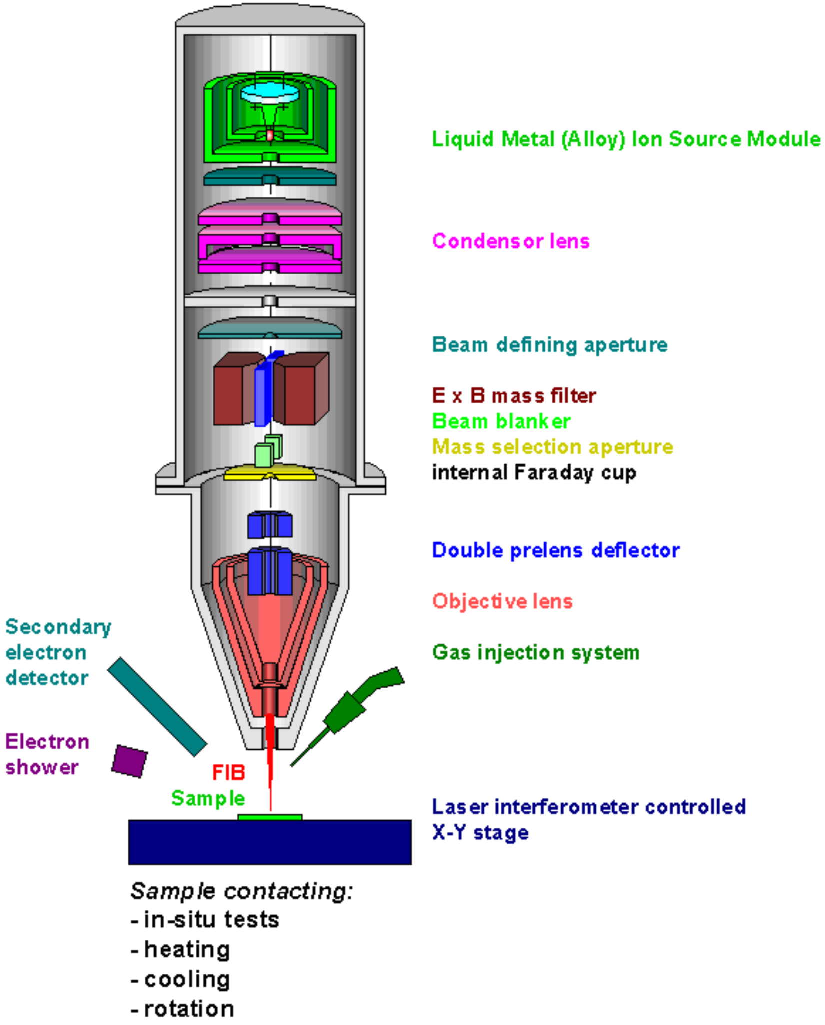


Relation of PIII&D to ion implantation and thin-film deposition.

Depending on experimental parameters (density of the plasma, substrate temperature, applied target-substrate voltage) the process may result in **ion implantation** or **film deposition**, just as in Plasma Enhanced Chemical Vapor Deposition (PECVD)

See for instance: Wolfhard Möller and Subroto Mukherjee *Plasma-based ion implantation* Current Science, Vol. 83, no. 3, 10 august 2002

Focused Ion Beam (FIB): a tool for fabrication, modification and analysis at the nano scale



Modes of FIB application

- milling (most used)
- induced chemical reaction: deposition & etch (by proper gas injection)
- implantation: damage or doping
- lithography: direct writing (resist exposure, as in high energy *proton beam writing*)
- high-resolution imaging (by secondary electrons or backscattered ions)

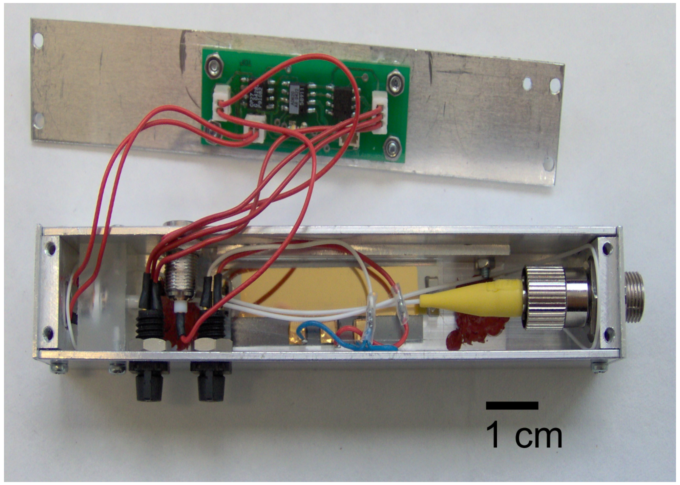
Applications of Ion-beam irradiation techniques in advanced research fields

nano	• doping and defect engineering of nanomaterials (graphene, nanowires ..) • single atom implantation (quantum devices) • fabrication of nanostructures/nanodevices	• low energy II • Focused Ion Beams
bio	• nanostructuring/funcionalizing surfaces of biomaterials for improving biocompatibility and creating new functionalities	• plasma II
photonics	• doping and defect engineering for tailoring optical properties and fabricating optoelectronic devices (waveguides, resonators,..)	• medium-high energy II
energy	• doping and defect engineering of photovoltaic devices • surface modification/nanostructuring of materials for energy storage (batteries, capacitors) and catalysis (TiO_2)	• low-medium energy II • plasma II

Example of application of ion implantation at CNR-IMM

Fabrication of Integrated optical devices in $LiNbO_3$

In this application the focus is on *radiation damage* induced by ion implantation. Damage changes the *refractive index* of an optical material such as $LiNbO_3$. By selectively damaging the $LiNbO_3$ crystal, both in depth (by varying *ion energy*) and laterally (by *ion masking*) one is able to spatially modulate the index of refraction. A region of high refractive index (damaged crystal) surrounded by a region of lower refractive index (good crystal) works as a ***waveguide*** for visible and infrared light.



Mach-Zender interferometer fabricated with $LiNbO_3$ processed by ion implantation.

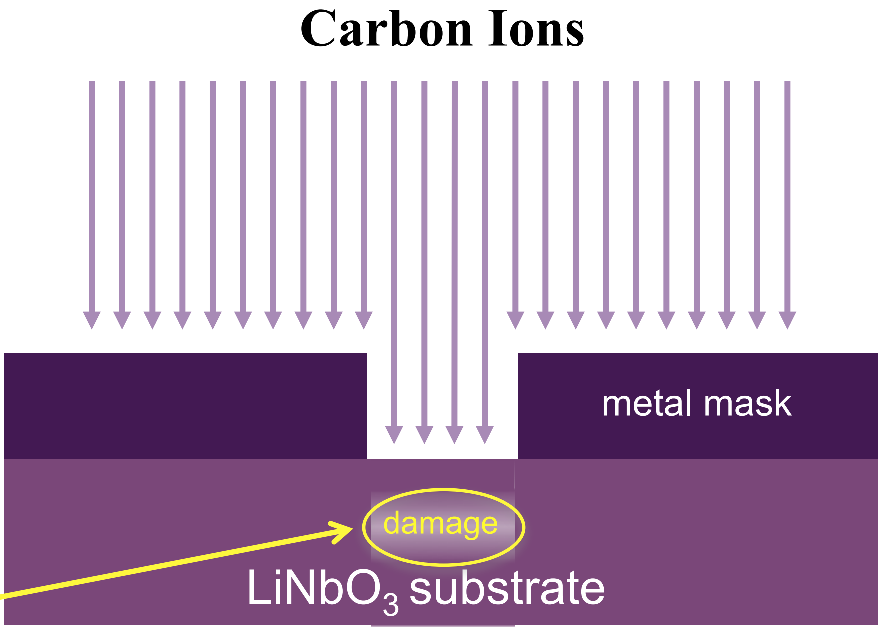
$LiNbO_3$ is an ***electro-optical*** material, whose index of refraction can be varied by the application of an electric field.

[1] Responsible of the research : Dr. **Marco Bianconi** (CNR-IMM and MIST-ER lab - bianconi@bo.imm.cnr.it)

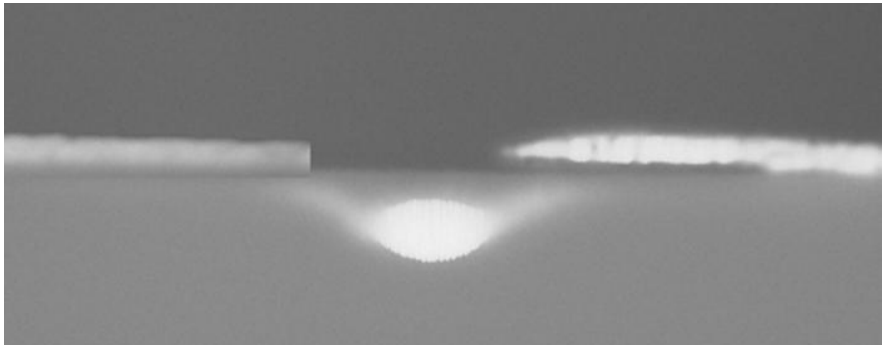
Fabrication of Integrated optical devices in $LiNbO_3$

Embedded Channel Waveguide (one-step process)

- Ion Implantation (MeV)
- Mask removal
- Result (Near Field)



embedded waveguide (damaged crystal)



The measured intrinsic optical loss is of the order of **0.3 dB/cm**.

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- J. F. Ziegler, J. P. Biersack, U. Littmark ***The Stopping and Range of Ions in Solids***, (Pergamon, New York, 1985).

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Bibliography: some recent papers to give the feeling of current trends in ion implantation (updated 2013)

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- C. Ronning , C. Borschel, S. Geburt, R. Niepelt ***Ion beam doping of semiconductor nanowires*** Materials Science and Engineering R 70 (2010) 30–43
- I.P. Jain , Garima Agarwal ***Ion beam induced surface and interface engineering*** Surface Science Reports 66 (2011) 77–172
- Tapash R. Rautray, R. Narayanan, Kyo-Han Kim ***Ion implantation of titanium based biomaterials*** Progress in Materials Science 56 (2011) 1137–1177
- Jeffrey C. McCallum et. al. ***Single-Ion Implantation for the Development of Si-Based MOSFET Devices with Quantum Functionalities*** Advances in Materials Science and Engineering Volume 2012, Article ID 272694
- N. G. Rudawski, B. L. Darby, B. R. Yates, K. S. Jones, R. G. Elliman et al. ***Nanostructured ion beam-modified Ge films for high capacity Li ion battery anodes*** Appl. Phys. Lett. 100, 083111 (2012)
- Feng Chen ***Micro- and submicrometric waveguiding structures in optical crystals produced by ion beams for photonic applications*** Laser Photonics Rev. 6, No. 5, 622–640 (2012)
- Chung-Soo Kima, Sung-Hoon Ahna,, Dong-Young Jang *Review:* ***Developments in micro/ nanoscale fabrication by focused ion beams*** Vacuum 86 (2012)
- Bill R. Appleton et al. ***Materials modifications using a multi-ion beam processing and lithography system*** Nuclear Instruments and Methods in Physics Research B 272 (2012) 153–157

Bibliography: some recent papers to give the feeling of current trends in ion implantation

- Wise, SG; Waterhouse, A; Kondyurin, A; Bilek, MM; Weiss, AS ***Plasma-based biofunctionalization of vascular implants*** Nanomedicine, 7, 1907 (2012).
- Hornberger, H; Virtanen, S; Boccaccini, AR ***Biomedical coatings on magnesium alloys - A review*** Acta Biomaterialia 8, 2442 (2012).
- Lu, T; Qiao, YQ; Liu, XY ***Surface modification of biomaterials using plasma immersion ion implantation and deposition*** Interface Focus 2, 325 (2012).
- Li, WQ; Xiao, XH; Stepanov, AL; Dai, ZG; Wu, W; Cai, GX; Ren, F; Jiang, CZ ***The ion implantation-induced properties of one-dimensional nanomaterials*** Nanoscale Res. Lett. 8, 175 (2013).
- Bangert, U.; Pierce, W.; Kepaptsoglou, D. M.; et al. ***Ion Implantation of Graphene-Toward IC Compatible Technologies*** Nano Letters 13, 4902 (2013).
- Chu, Paul K. ***Progress in direct-current plasma immersion ion implantation and recent applications of plasma immersion ion implantation and deposition*** Surf. Coat. Technol. 229, 2 (2013)

Underlined articles are available upon e-mail request to *lulli@bo.imm.cnr.it*

Links/contacts

- http://www.srim.org/ Here yu can freely download the **J. Ziegler**'s program **SRIM** for BCA simulation of ion implantation. The program runs on Windows. It is very useful both as an educational and as a research tool. The main limitation of this program is that it considers *amorphous* targets only. As a consequence, it is not possible to calculate channeling effects which occur when implantation is performed on a *crystalline* target.

- **KING** (by **G. Lulli** and **E. Albertazzi –** CNR-IMM Bologna) is a computer program for BCA simulation of ion implantation in crystalline Si. It is freely available (send me an e-mail if you are interested) and runs under Linux OS. It calculates advanced effects, including channeling and damage accumulation, but it can handle just Si and SiO_2 layers.

- http://webarch.bo.imm.cnr.it/lulli/didattica/index.html to see online/download updated versions of these slides, and find more links/material on the subject. Moreover, if you are interested in getting some of the articles (just articles, not textbooks) cited here, please contact me.

If you happen to be in Bologna and are interested in visiting us, contact me, and I'll be happy to welcome you in our acceleration lab.

thanks for your attention!