Ion-Solid Interactions and Defect Formation

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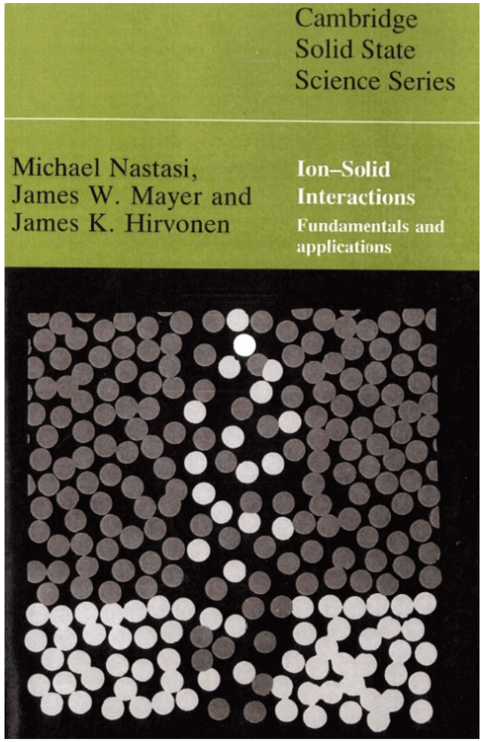
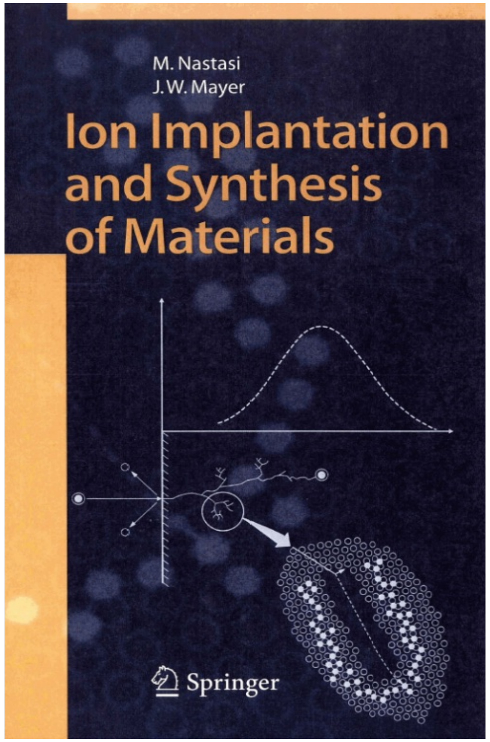
This tutorial will be primarily derived from information contained in the following books



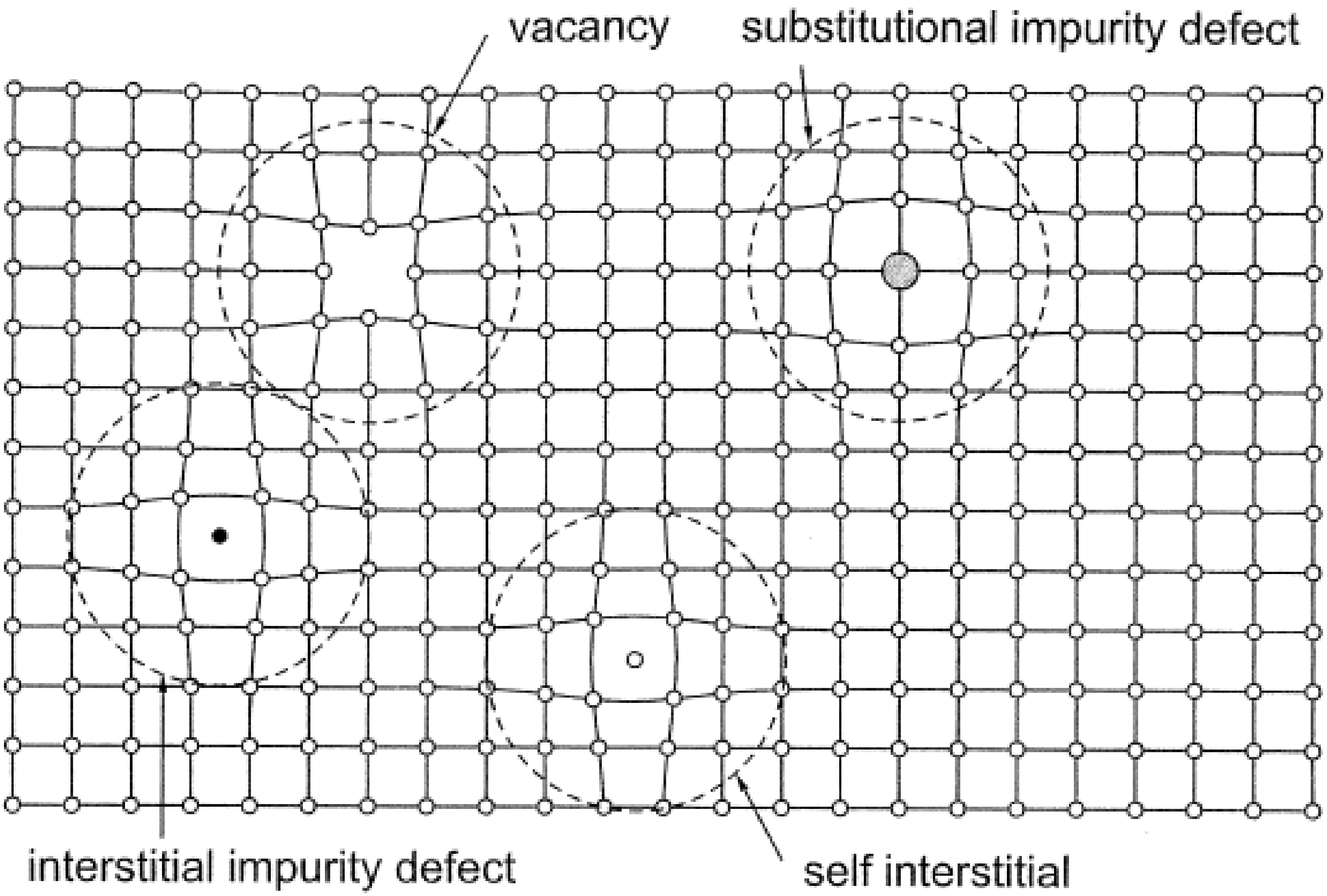


Why Do We Care About Defects in Solids?

Defects Affect Many Properties of Materials

- **Electrical – transport, bandgap engineering, etc.**
  - **all defects, especially point defects and anti-sight defects**
- **Optical – color centers, opacity, etc.**
  - **all defects, especially point defects**
- **Mechanical – strength, toughness, hardness, etc.**
  - **all defects, especially dislocations**
- **Magnetic – magnetism, magnetic order, etc.**
  - **all defects**
- **Kinetics – diffusion, phase transformations**
  - **all defects, especially point defects**

Some Examples of Point Defects



(Imperfections in Crystalline Solids, Cai and Nix, Cambridge/MRS, 2016)

Outline: Ion-Irradiation-Induced Defects in Solids

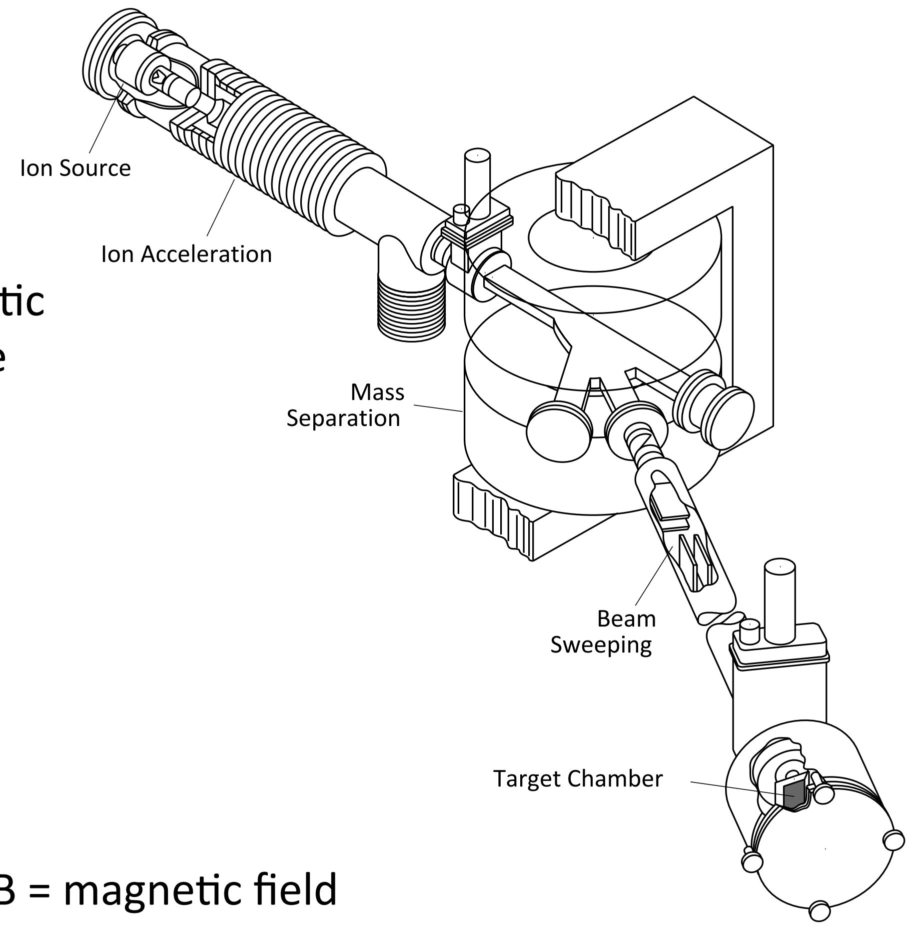
- Sources of ion irradiation
- Ion implantation as a model system for ion-solid interactions
- Ion stopping
- Nuclear stopping, displacements and defect formation

Sources of Ion Irradiation

- Accelerator based Ion Implantation Systems
- Nuclear Environments (fusion, fission)

Ion Implantation System with Mass Separation

Schematic drawing of an ion implantation system. A mass-separating magnet is used to select the ion species (elements and isotopes) of interest. Beam-sweeping facilities are required for large-area uniform implantations



Magnetostatic field can not change the kinetic energy (K.E.) of the particle, only change the direction of its velocity.

$$K.E. = 0.5\ mv^2 = eV$$

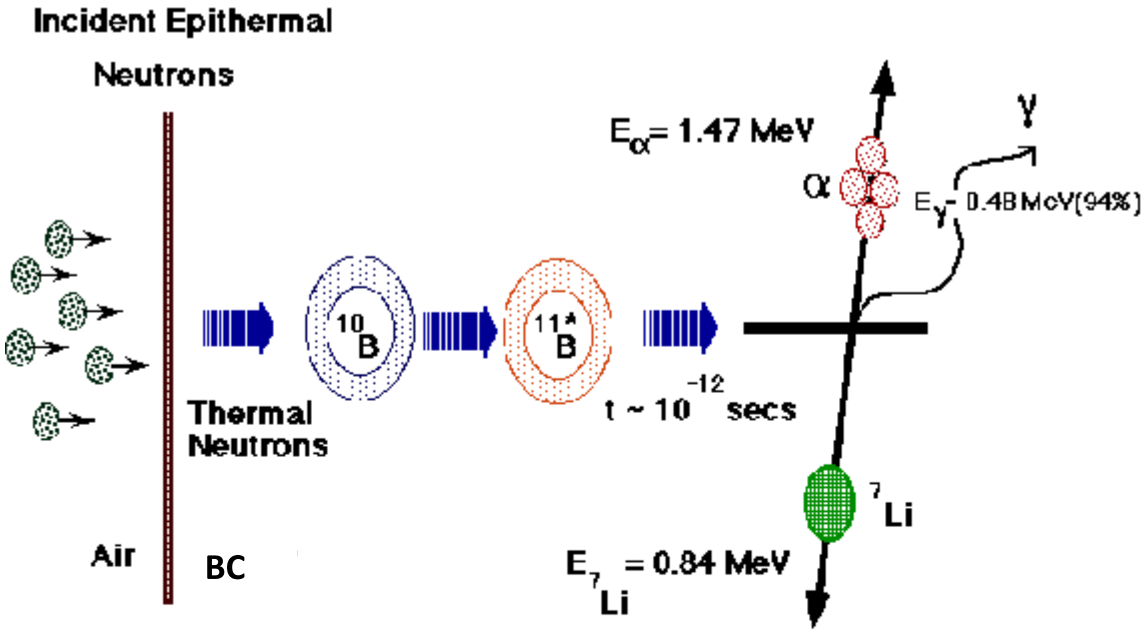
The radius (R) of the circular path is proportional to the velocity of the particle.

$$\mathbf{R = m\ v\ /\ q\ B}$$

m = ion mass, v = ion's velocity, q = charge, B = magnetic field

Neutron Sources of Ion Irradiation

^{10}B neutron capture and boron disintegration



$^{10}B + n \rightarrow {}^{7}Li$ (0.84 MeV) + ^{4}He (1.47 MeV) + γ (0.48 MeV) (94%)
$^{10}B + n \rightarrow {}^{7}Li$ (0.84 MeV) + ^{4}He (1.78 MeV) (6%)

The energetic He and Li ions give rise to radiation damage

This damage process can be simulated with energetic ions produced by an ion accelerator

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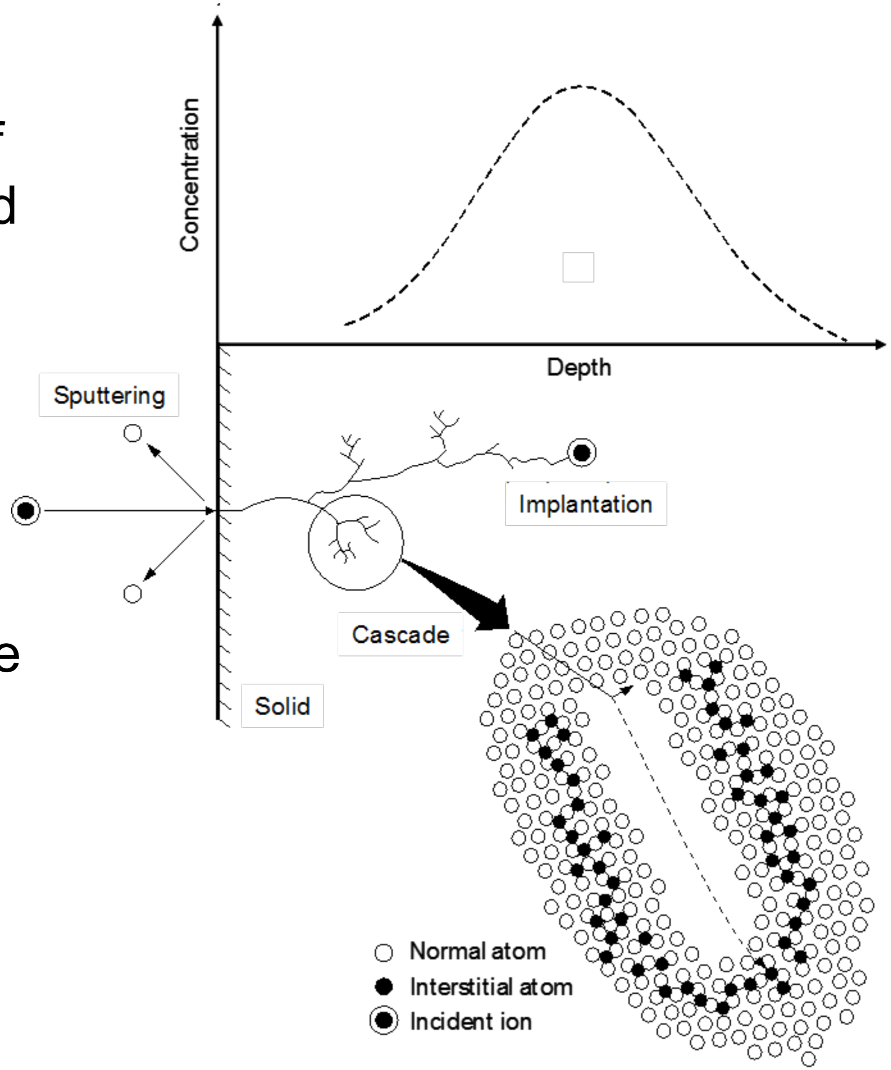
What is Ion Implantation?

Ion implantation is the introduction of atoms into the surface layer of a solid substrate by bombardment of the solid with ions in the electron-volt to mega-electron-volt energy range.



The use of energetic ions affords the possibility of introducing a wide range of atomic species, independent of thermodynamic factors, thus making it possible to obtain impurity concentrations and distributions of particular interest; in many cases, these distributions would not otherwise be attainable.

Why Do We Care About Ion Implantation

- Ion implantation is one of the key processing steps in silicon-integrated circuit technology
- Some integrated circuits require up to 35 implantation steps, and circuits are seldom processed with fewer than 10 implantation steps
- Controlled doping at controlled depths is an essential feature of implantation
- Ion beams are a favored method to achieve controlled modification of surfaces and near-surface regions
- Ion implantation provides an alternative and non-equilibrium method of introducing dopant/alloying atoms into the lattice.
- In addition to integrated circuit technology, ion beams are used to modify the mechanical, tribological, and chemical properties of metals, intermetallics, and ceramics without altering their bulk properties.
- Can be used to simulate nuclear environment based radiation damage

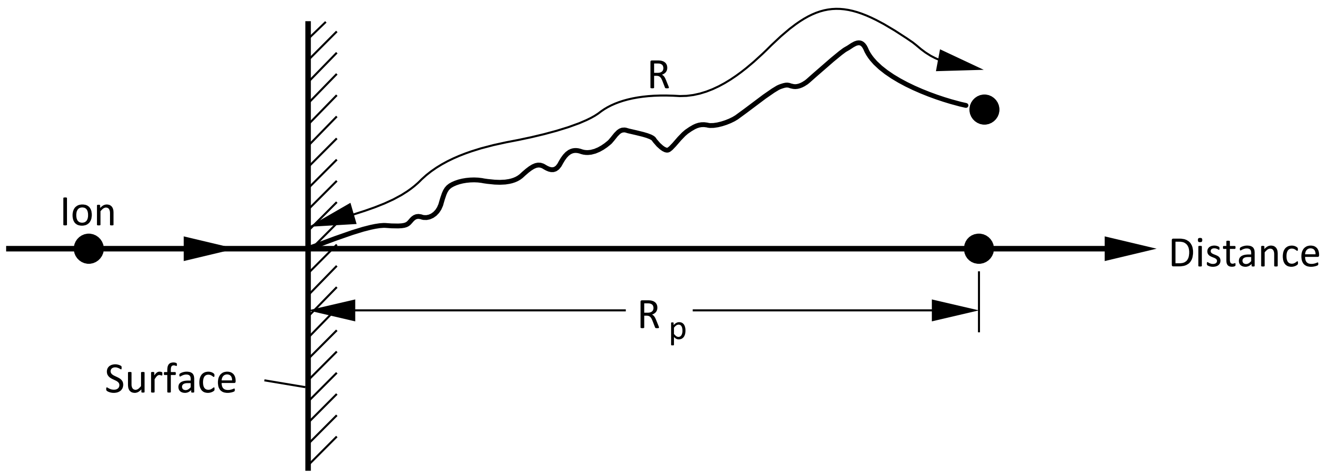
Ion-Solid Interactions

Ion-solid interactions are the foundation that underlies the broad application of ion implantation to the irradiation and modification of materials.

The physics of ion-solid interactions controls:

- The location of the energetic ions in the crystal lattice (the range distribution of the energetic ions)
- The amount and nature of the lattice disorder that is created
- Sputtering
- Ion-mixing
- Ion-induced defect formation, phase formation and the transformation of one phase to another (i.e., the transformation of a crystalline material into an amorphous material).
- Defect Engineering

Ion Range



As an implanted penetrates the solid it slows down and ultimately comes to rest.

R = total path length

R_p = projected range, along the direction parallel to that of the incident ion

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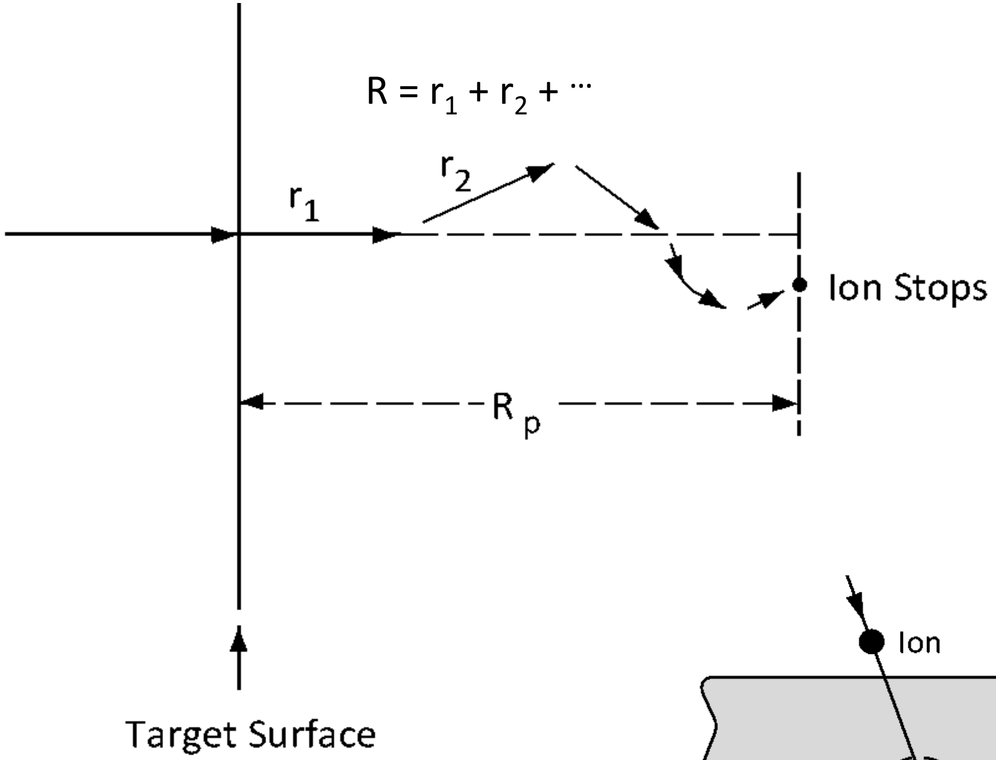
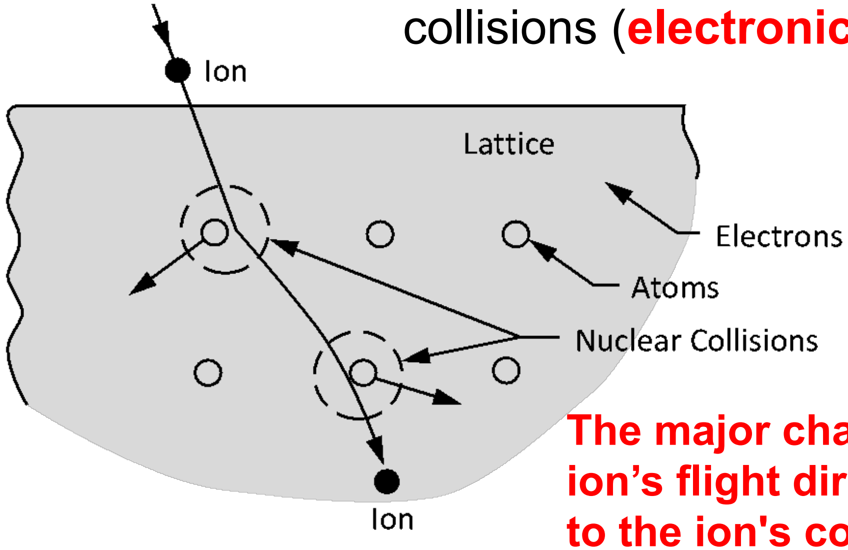
Ion Stopping: The Process of Slowing Down the Ion



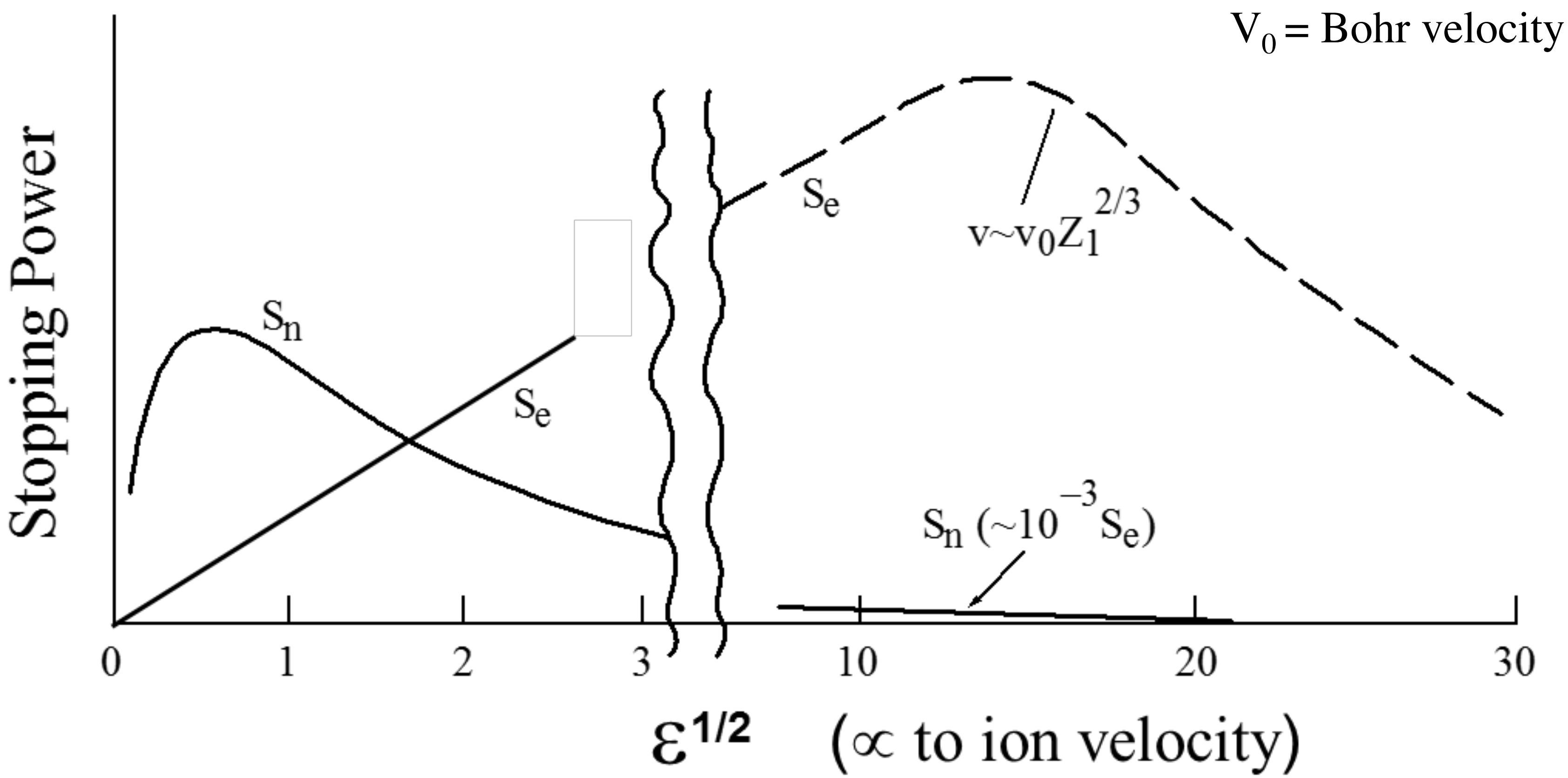
The passage of an energetic ion in a solid during an ion implantation. As the ion travels across the solid, it undergoes collisions with stationary target atoms, which deflect the ion from its initial direction (**nuclear stopping**).

The ion also collides with electrons in the solid and loses energy in these collisions (**electronic stopping**).



The major changes in the ion’s flight direction are due to the ion's collision with individual lattice atoms (nuclear collisions).

Energy loss: Ion Stopping



Nuclear stopping dominates as the ion slows down

$Z_1^{2/3}$

Electronic Stopping

at low ion velocities stopping is proportional to ion velocity

$$S_e(E) = 3.83 \frac{Z_1^{7/6} Z_2}{\left(Z_1^{2/3} + Z_2^{2/3}\right)^{3/2}} \left(\frac{E}{M_1}\right)^{1/2} = K_L E^{1/2}$$

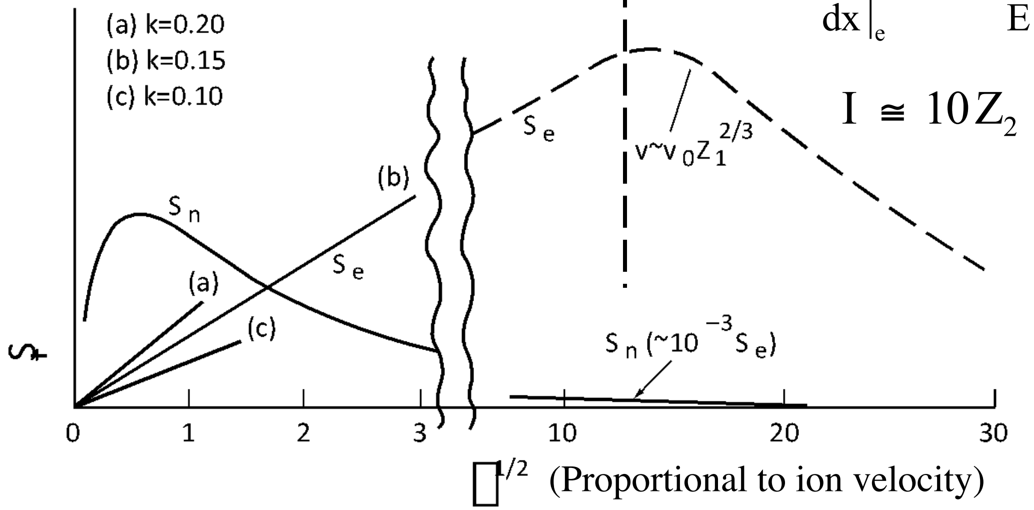
$$K_L = 3.83 \frac{Z_1^{7/6} Z_2}{M_1^{1/2}\left(Z_1^{2/3} + Z_2^{2/3}\right)^{3/2}}$$

At higher velocities, the charge state of the ion increases and ultimately becomes fully stripped of all its electrons at $v \geq v_0 Z_1^{2/3}$

$V_0 =$ Bohr velocity

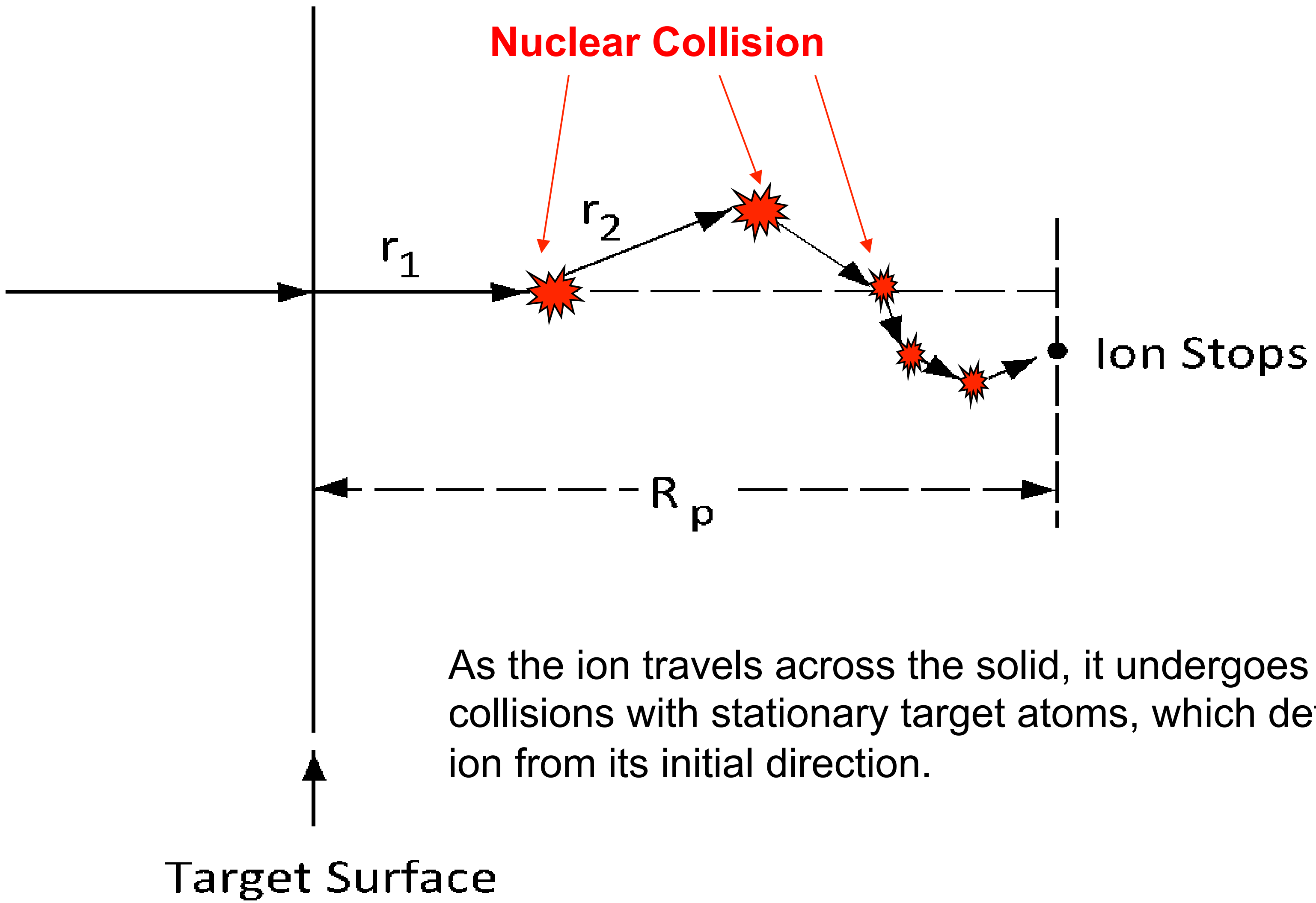
$$-\left.\frac{dE}{dx}\right|_e = \frac{2\pi Z_1^2 e^4}{E} N Z_2 \left(\frac{M_1}{m_e}\right) \ln \frac{2 m_e v^2}{I}$$

$I \cong 10 Z_2$ average excitation energy of an electron



Nuclear energy deposition dominates as the ion slows down, which leads to defect production and damage of the local atomic structure

Dynamics of Binary Elastic Collisions

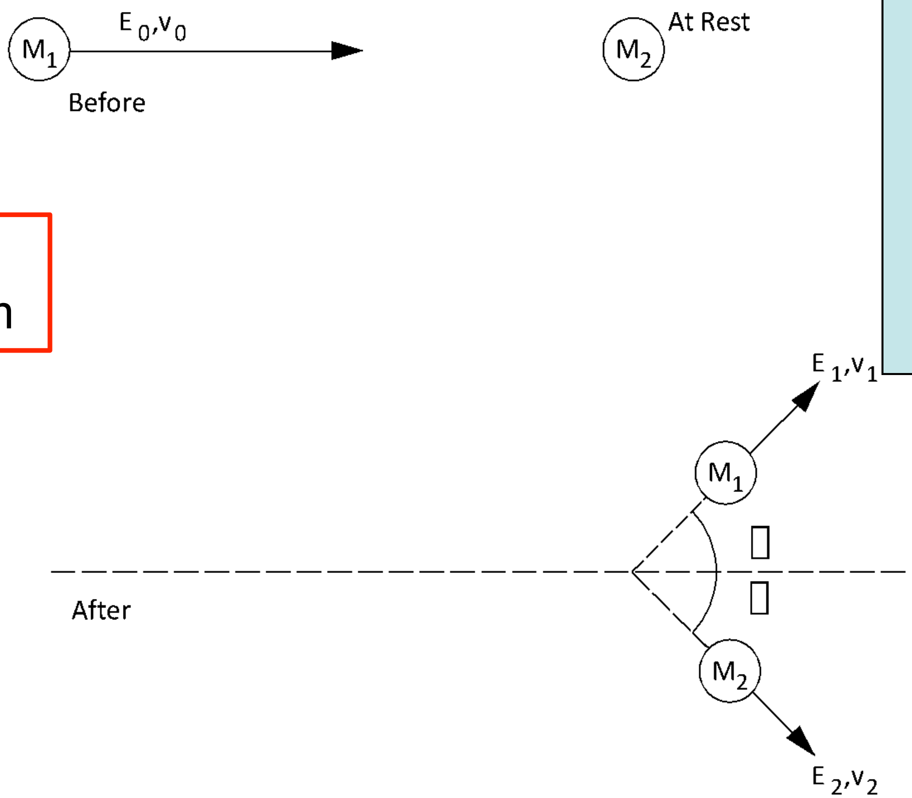


As the ion travels across the solid, it undergoes collisions with stationary target atoms, which deflect the ion from its initial direction.

Kinematics of Elastic Collisions

The energy transfers and kinematics in elastic collisions between two isolated particles can be solved fully by applying the principles of *conservation of energy and momentum*.

Conservation of energy and conservation of momentum parallel and perpendicular to the direction of incidence are expressed by the equations:



= ion
= target atom

$$E_0 = \frac{1}{2} M_1 v_0^2 = \frac{1}{2} M_1 v_1^2 + \frac{1}{2} M_2 v_2^2 \qquad (1)$$

$$M_1 v_0 = M_1 v_1 \cos\theta + M_2 v_2 \cos\phi \qquad (2)$$

$$0 = M_1 v_1 \sin\theta - M_2 v_2 \sin\phi \qquad (3)$$

These three equations can be solved in various forms to give relationships between energy and scattering angle for both laboratory and center of mass coordinates

Nuclear Stopping

Energy Transferred to Target Atom by an Energetic Ion in an Elastic Collision

$$T = E_2 = E_0 \frac{4M_1 M_2}{(M_1 + M_2)^2} \cos^2\phi$$

(ϕ = scattering angle of the target atom)

The maximum energy transferred is for a head-on collision ($\phi = 0$)

$$T_M = \frac{4M_1 M_2}{(M_1 + M_2)^2} E_0 = \gamma E_0 \qquad \gamma = 4M_1 M_2 / (M_1 + M_2)^2$$

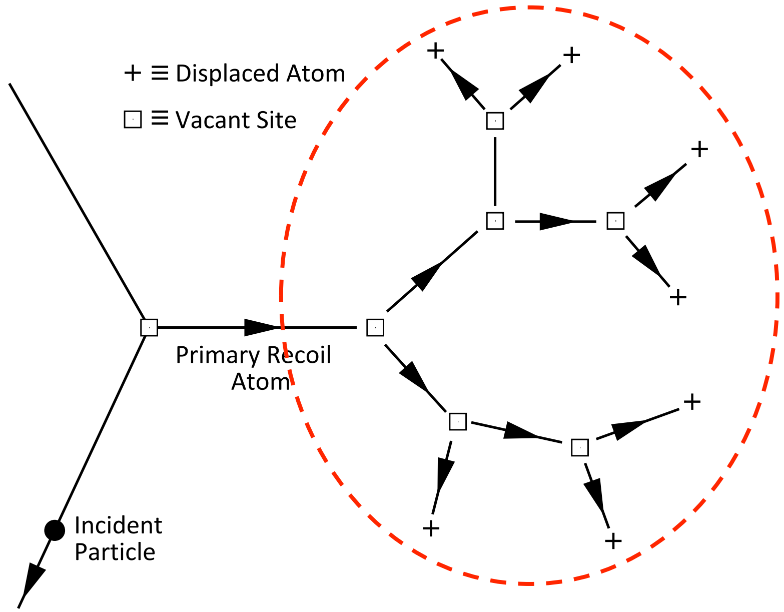
For the equal mass case, all the energy may be transferred,

For a larger mismatch in particle masses, only a fraction of the energy may be transferred.

For $M_1 << M_2$ $\quad T = E_0 \frac{4M_1}{M_2} \cos^2\phi$

For $M_1 >> M_2$ $\quad T = E_0 \frac{4M_2}{M_1} \cos^2\phi$

Nuclear Stopping, Displacements and Defect Formation



Collisions between ions and target atoms result in the slowing down of the ion. In these collisions, sufficient energy may be transferred from the ion to displace an atom from its original site

Atoms that are displaced by incident ions are called *primary knock-on atoms* or PKAs.

The PKAs can in turn displace other atoms, i.e., secondary knock-on atoms, tertiary knock-ons, etc., thus creating a *cascade of atomic collisions*.

This leads to a distribution of vacancies, interstitial atoms and other types of lattice disorder in the region around the ion track.

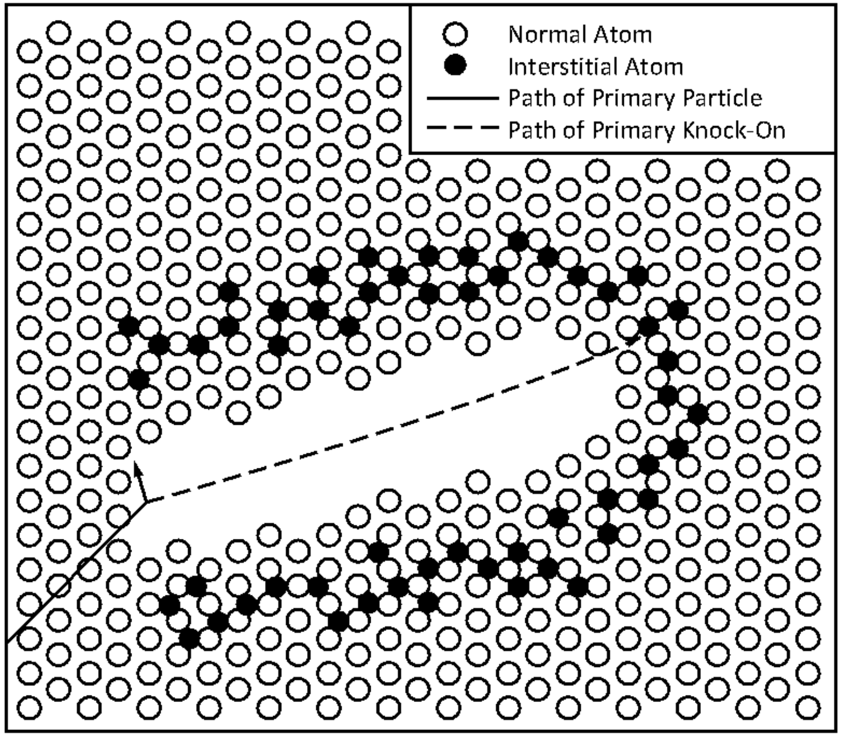
In semiconductors these defects are charged and therefore add electronic states in the band gap and serve as scattering centers to charge carriers thereby **reducing the carrier mobility**

This process is also responsible for:

- Sputtering
- Ion-mixing
- Ion-induced phase formation and the transformation of one phase to another (i.e., the transformation of a crystalline material into an amorphous material).
- Defect clustering and material embrittlement

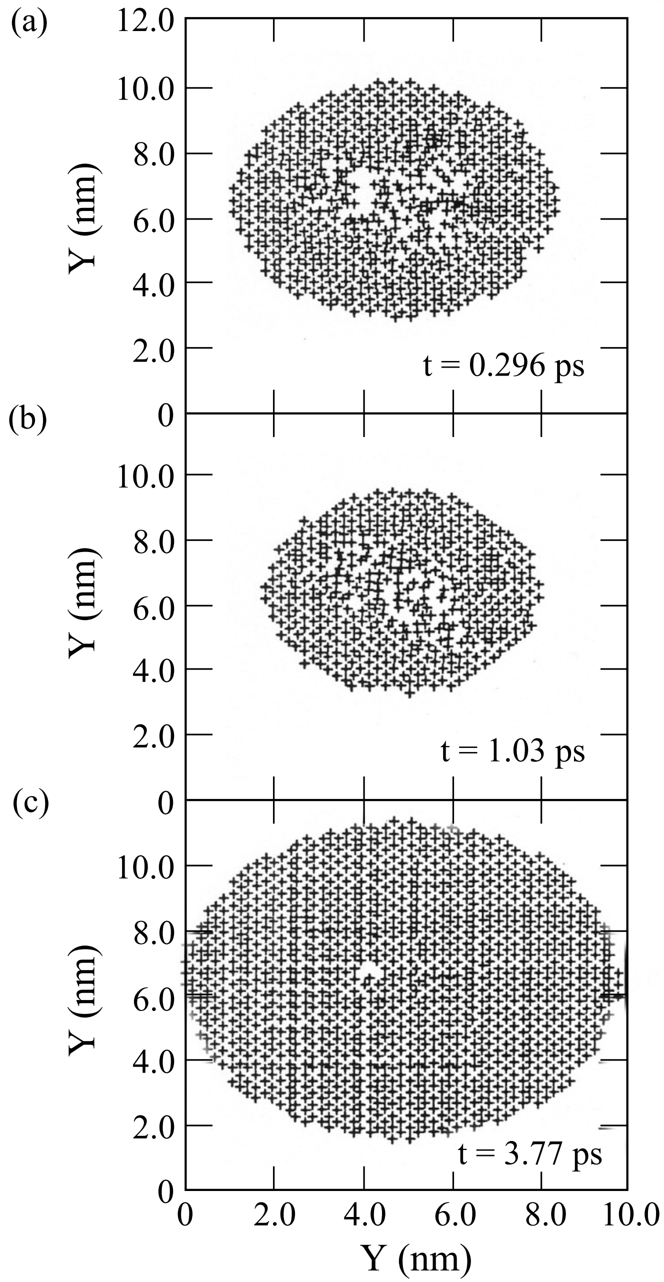
Displacement (Thermal)Spike

We will define a **spike** as a *high density cascade that possesses a limited volume in which the majority of atoms are temporarily in motio*n (implies lattice heating/melting)



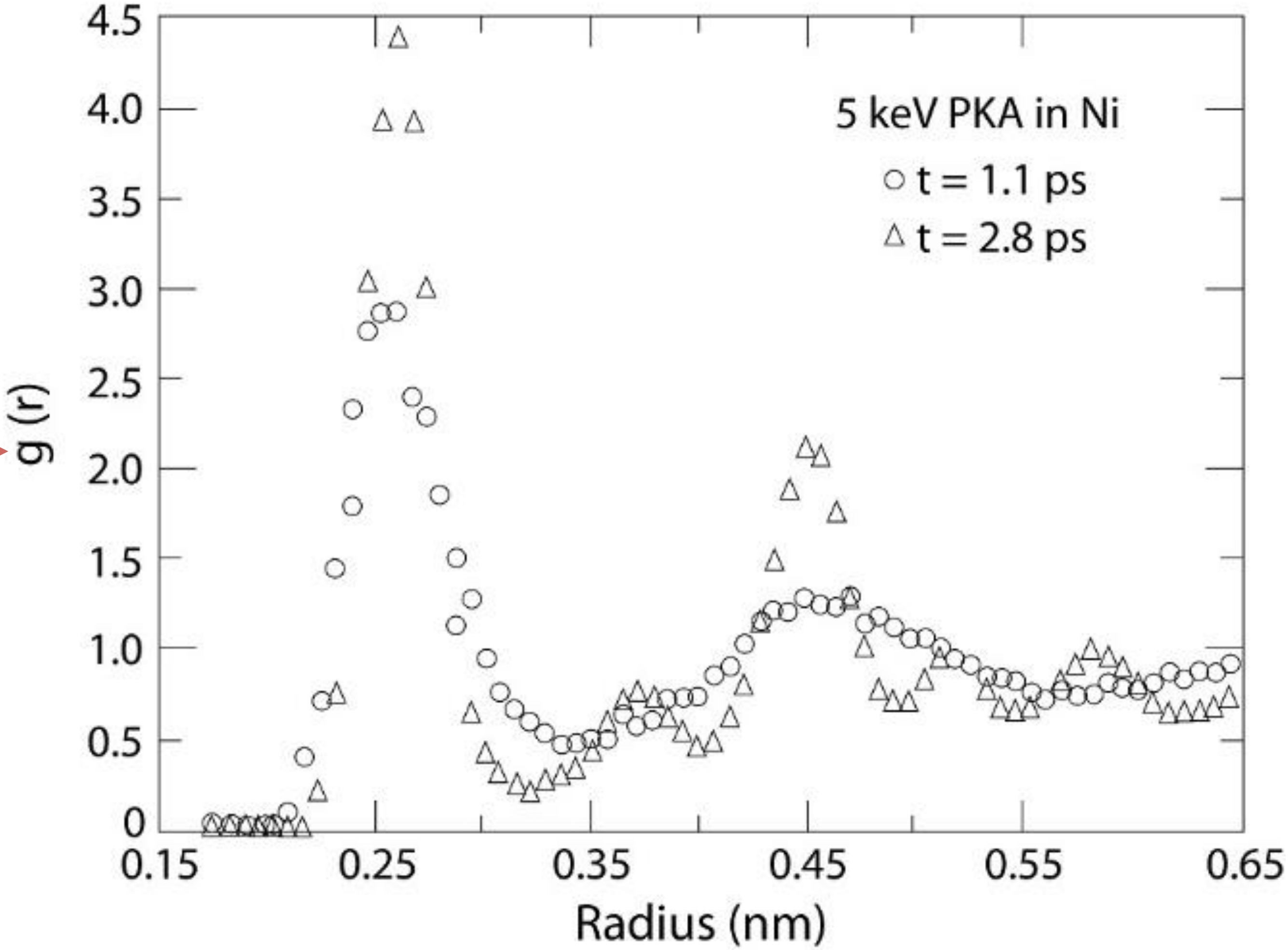
Displacement Spike: A core of vacancies surrounded by a cloud on interstitials

5 keV Cascade in Ni: MD (100) Projection

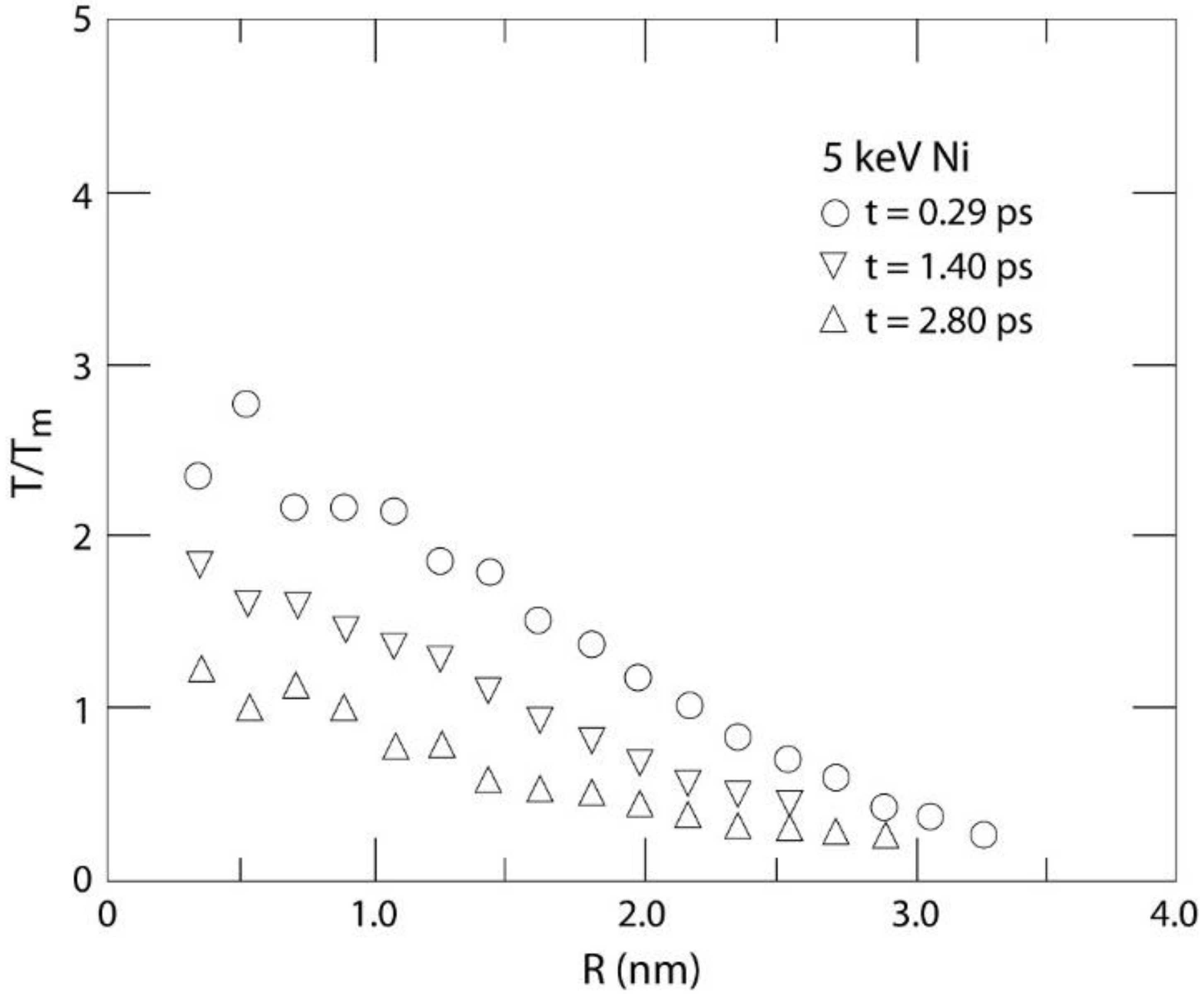


Structural Evolution of a Displacement Spike by MD

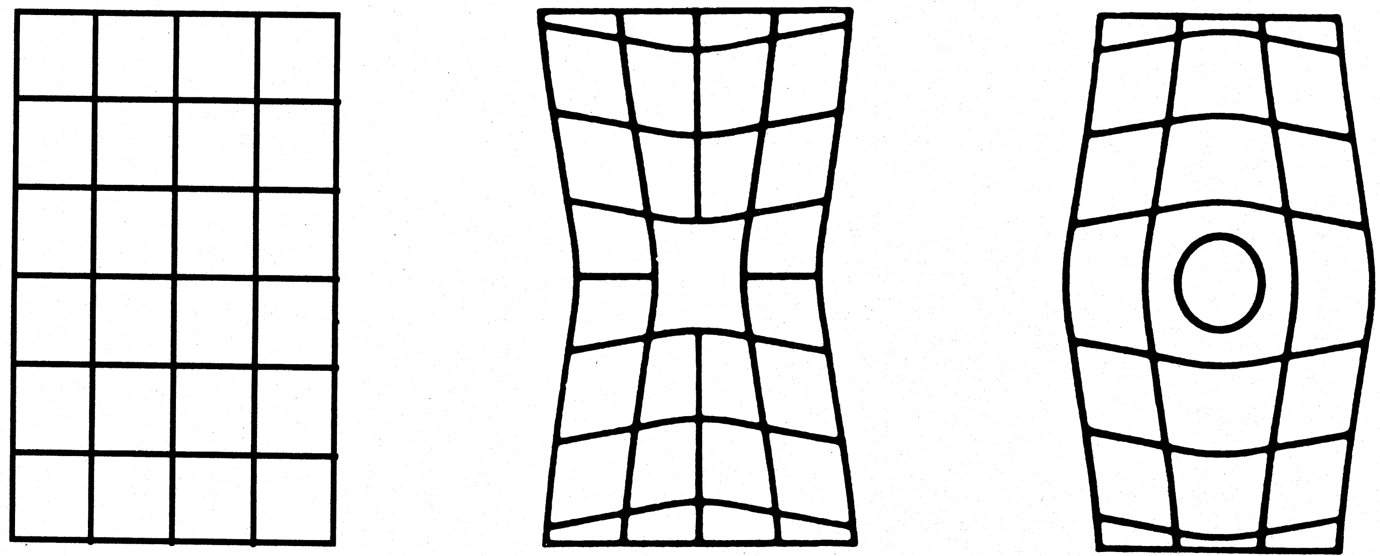
Radial Pair Distribution function



Thermal Evolution of a Displacement Spike by MD

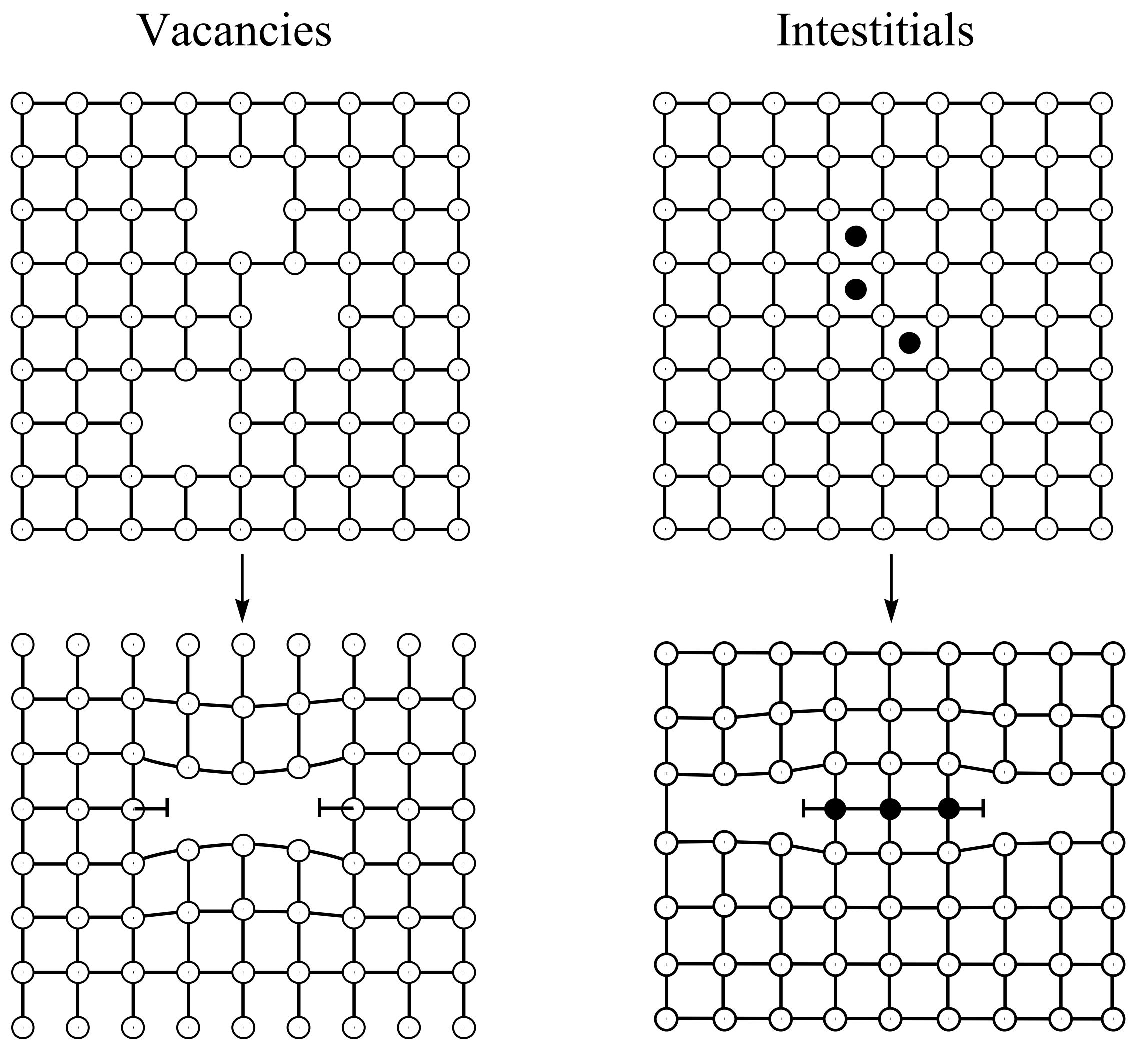


Radiation Damage and Point Defect Production



Perfect Lattice   Vacancy   Interstitial

Collapse of Point Defects in to Dislocations

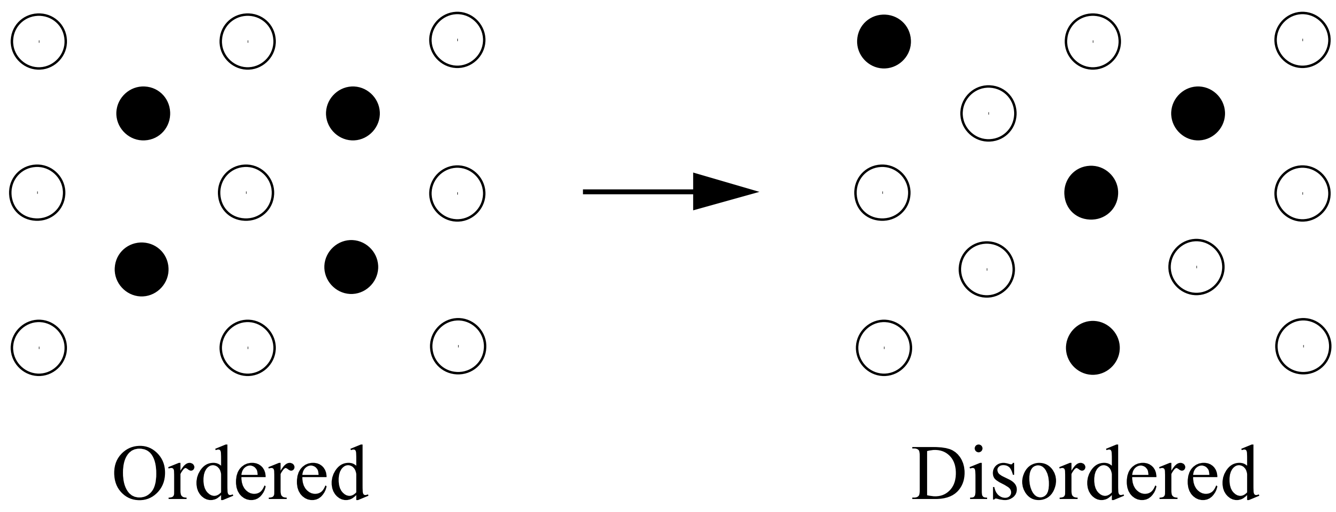


Collapse of Point Defects in to Dislocations

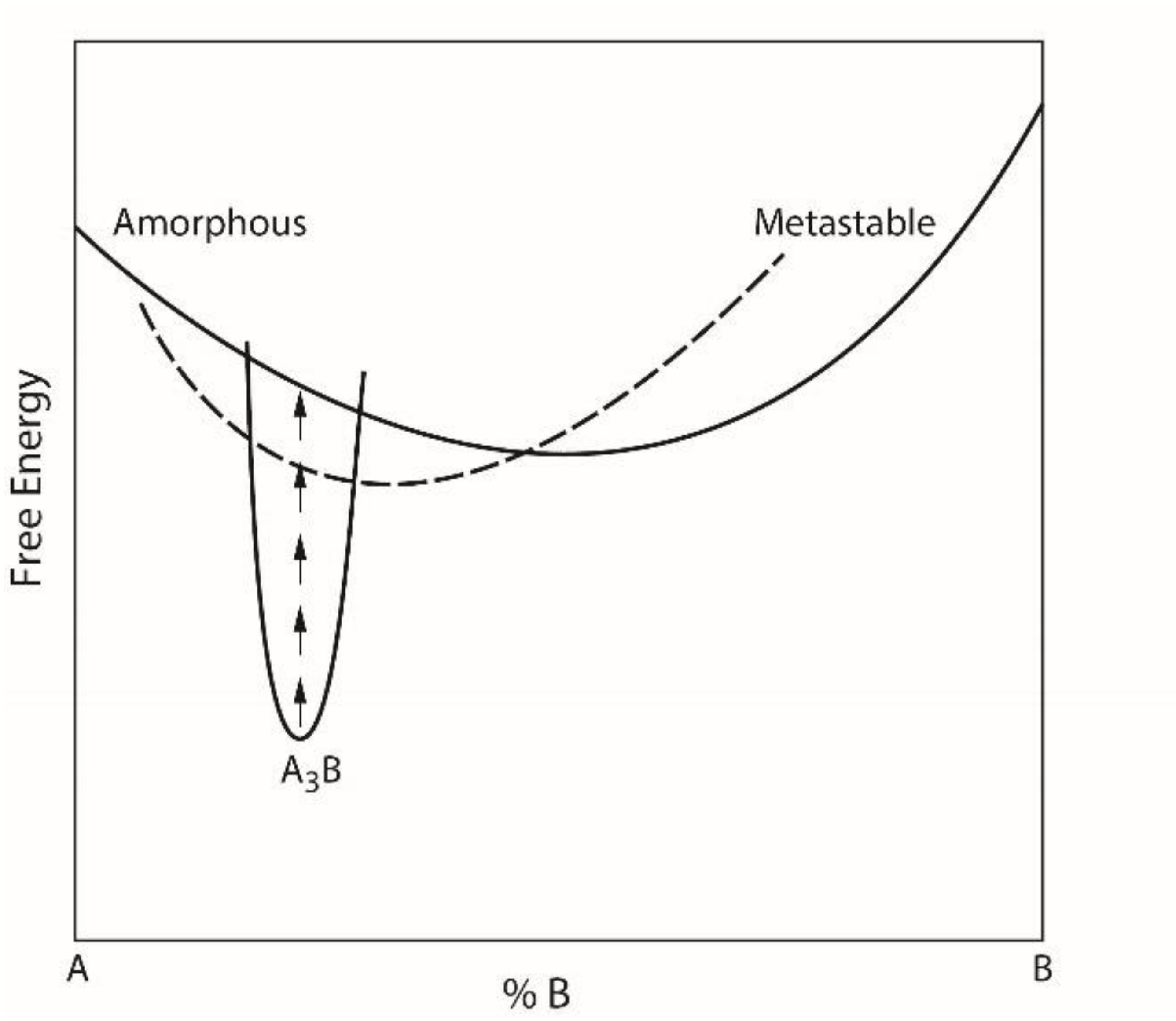
Quenched Al: Hexagonal loops with enclosed stacking fault

Anti-Site Defects: Chemical Disorder

(Important in compounds and alloys, e.g. GaAs, Ni_3Al, etc.)



Defect Accumulation Can Lead to Transformations to Metastable Phases



Radiation Damage: Amorphization

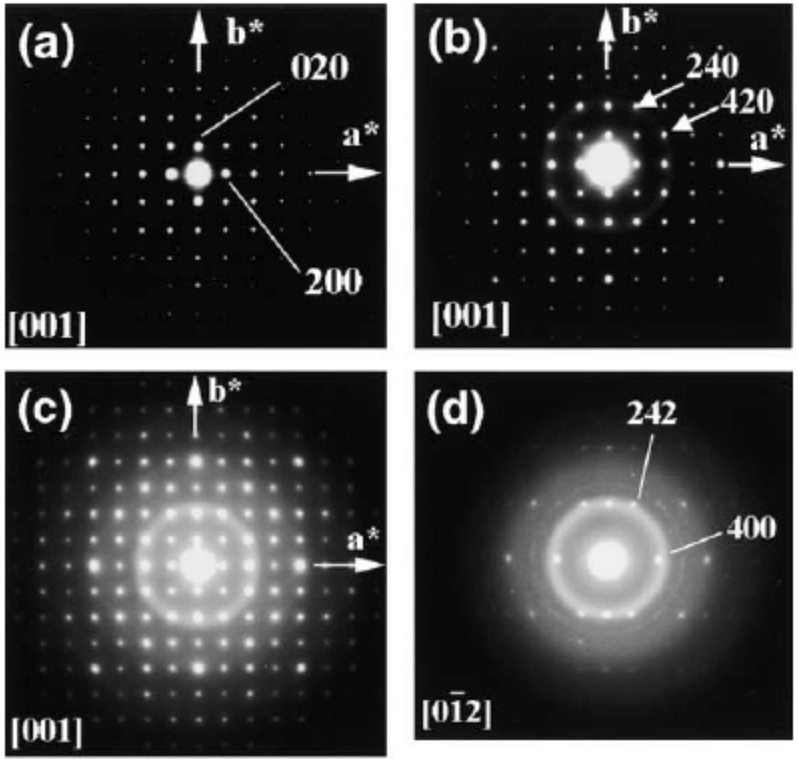
1.00 MeV Kr irradiation of Garnet

0 dpa

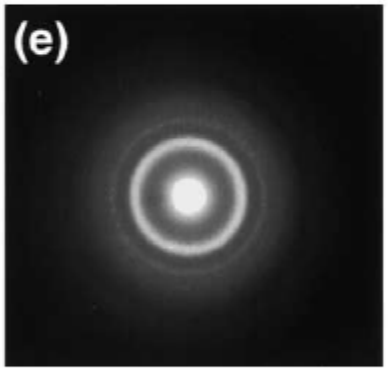
0.091 dpa

0.14 dpa

0.18 dpa



0.22 dpa



dpa = Number of displacemen
per unit volume/atomic densit

A unit of 1 dpa means that, on average, every atom in the irradiated volume has been displaced from its equilibrium lattice site one time.

This is a typical result for semiconductor, ceramic and intermetallic materials

Fig. 4. SAED patterns of G3 garnet irradiated by 1.0 MeV Kr^{2+} at 25 °C: (a) 0 dpa, (b) 0.091 dpa, (c) 0.14 dpa, (d) 0.18 dpa and (e) 0.22 dpa.

S. Utsunomiya et al. / Journal of Nuclear Materials 303 (2002) 177–187

SUMMARY/CONCLUSIONS

- **Sources of ion irradiation: ion accelerators & neutron irradiation (e.g. (n, α) reactions)**
- **Ion accelerators can be used simulate nuclear energy environments**
- **For typical ion implanter energies, nuclear stopping dominates atomic displacements and defect formation**

Ion-Solid Interaction: Where to Find Recent Progress

Conferences:

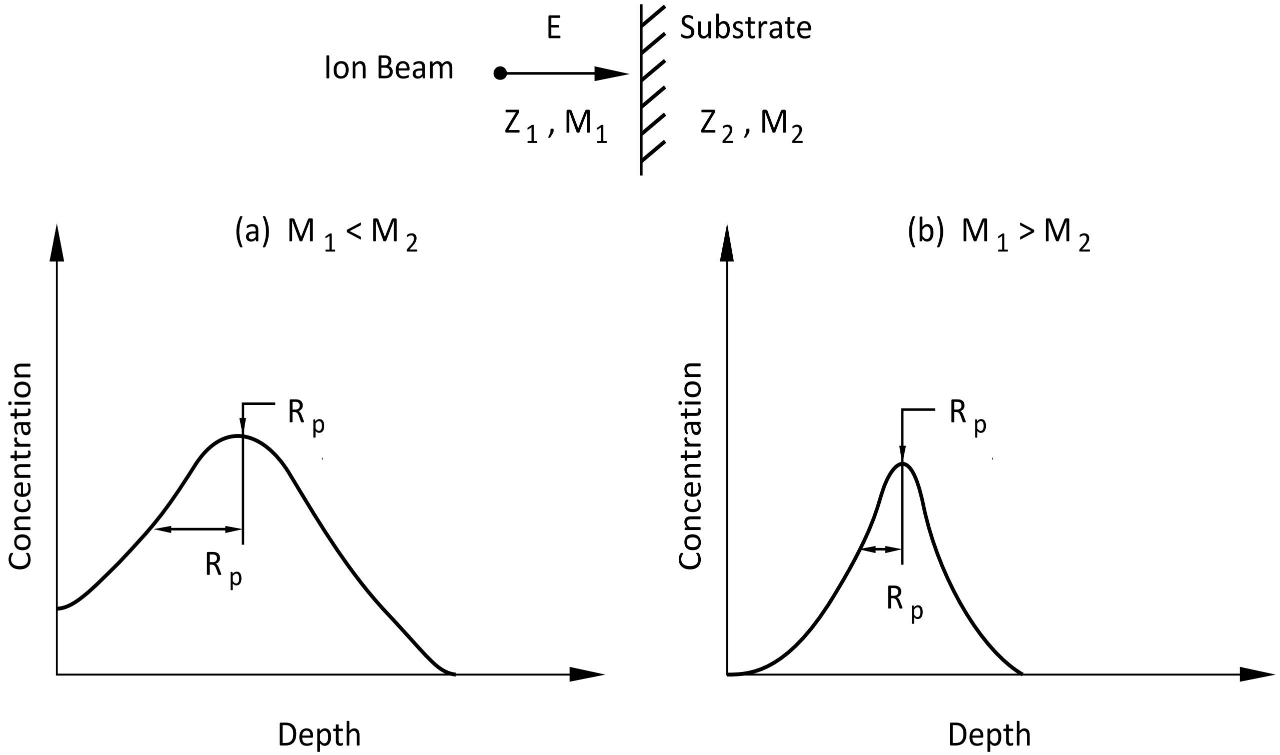
IBMM *International Conference on Ion Beam Modification of Materials*
IBA *International Conference on Ion Beam Analysis*
REM *International Meeting on Recent Developments in the Study of Radiation Effects in Ma*tter
SMMIB *International Conference on Surface Modification of Materials by Ion Beams*
CAARI *Conference of Application of Accelerators in Research and Industry*
IIT *International Conference on Ion Implantation Technology*
ECAART *European Conference on Accelerators in Applied Research and Technology*
ICACS *International Conference on Atomic Collisions in Solids*
SHIM *International Symposium on Swift Heavy Ions in Matter*
REI *International Conference on Radiation Effects in Insulators*
HEFIB *International HeFIB Conference*

Application areas:

Nanomaterials Synthesis
Semiconductor Fabrication
Simulate Nuclear Energy (Fission, Fusion) Environments
Ion Beam Analysis
Tribology
Corrosion

EXTRA SLIDES

Range Distribution



Z = atomic number
M = atomic mass,

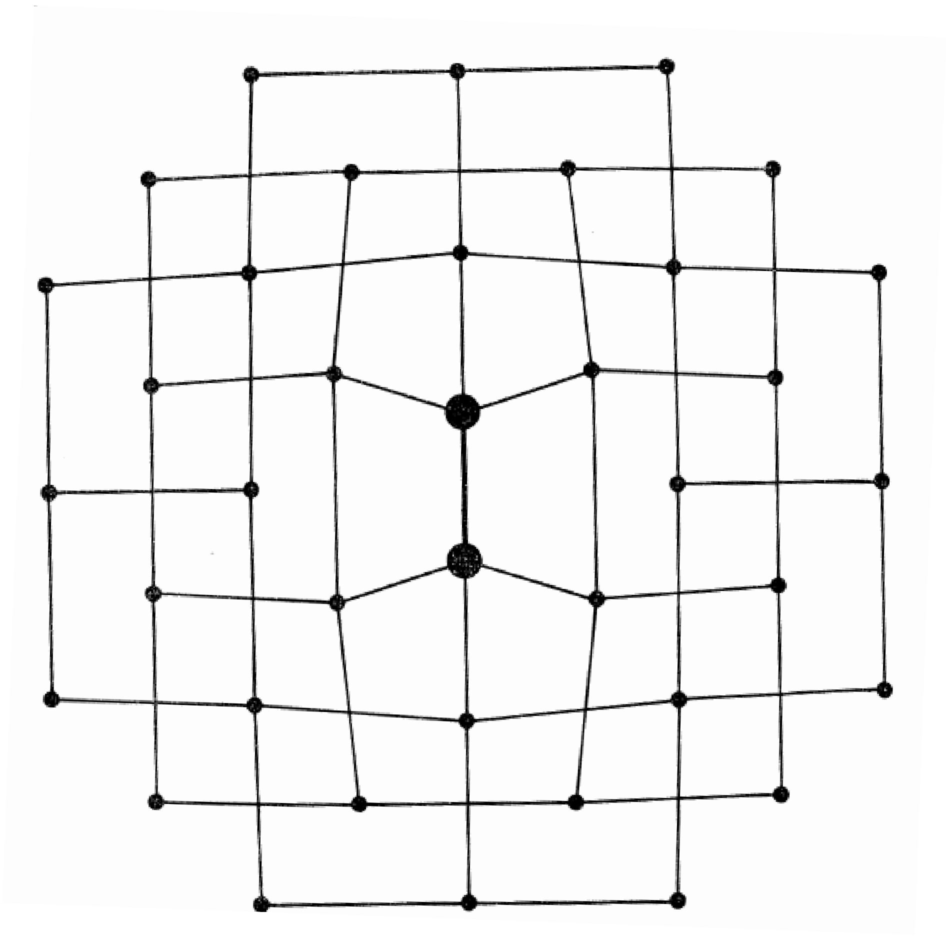
subscript 1 -> incident ions

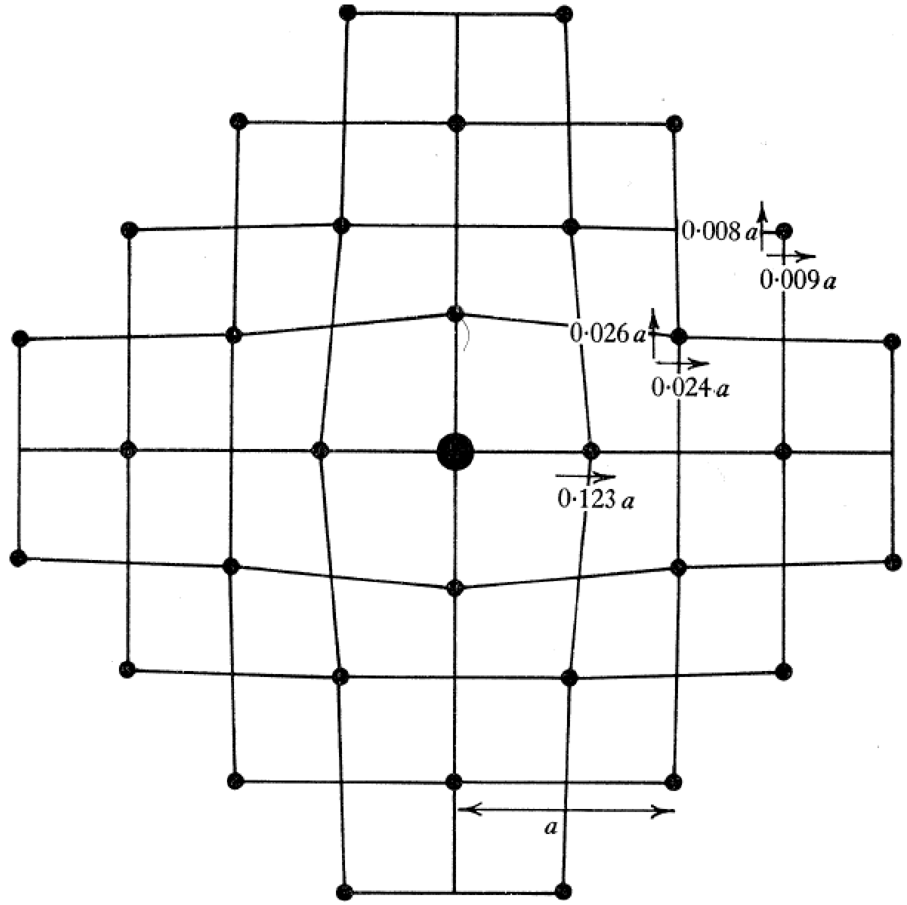
subscript 2 -> ion bombard
sample or target

ΔR_p= straggling (variance)

To a first approximation, the mean depth, R_p, depends on ion mass, M_1, and incident energy, E, whereas the relative width, $\Delta R_p/R_p$, of the distribution depends primarily on the ratio between ion mass and the mass of the substrate atom, M_2.

Radiation Damage and Point Defect Production

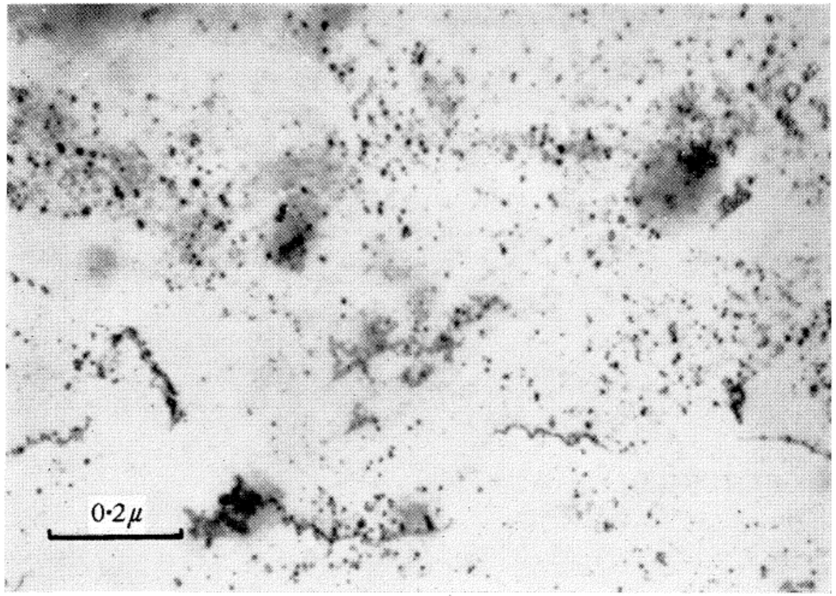


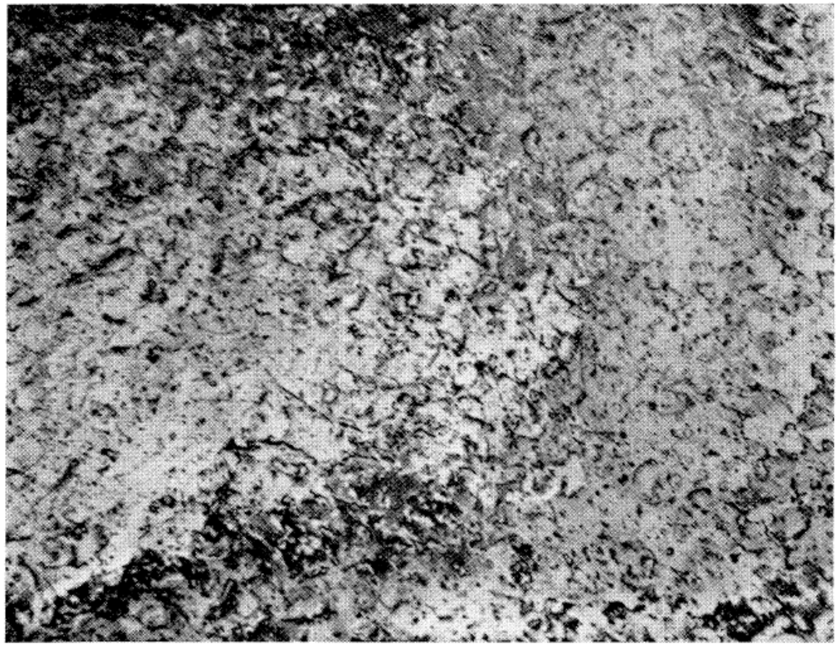


Dumb-bell interstitial

Body-centered interstitial

Dislocation Networks formed by Ion Irradiation



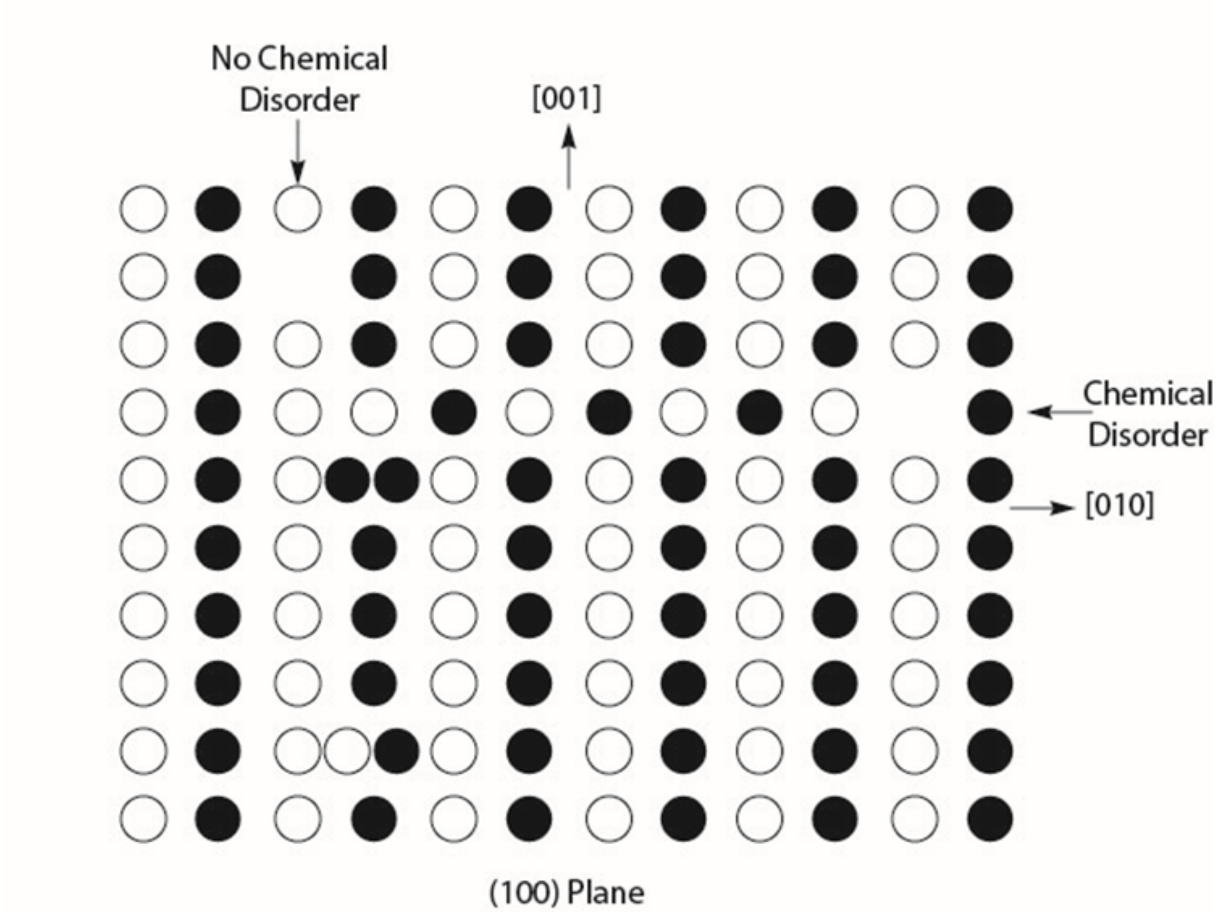


High energy He irradiate Mo. Dislocation loops and point defect clusters

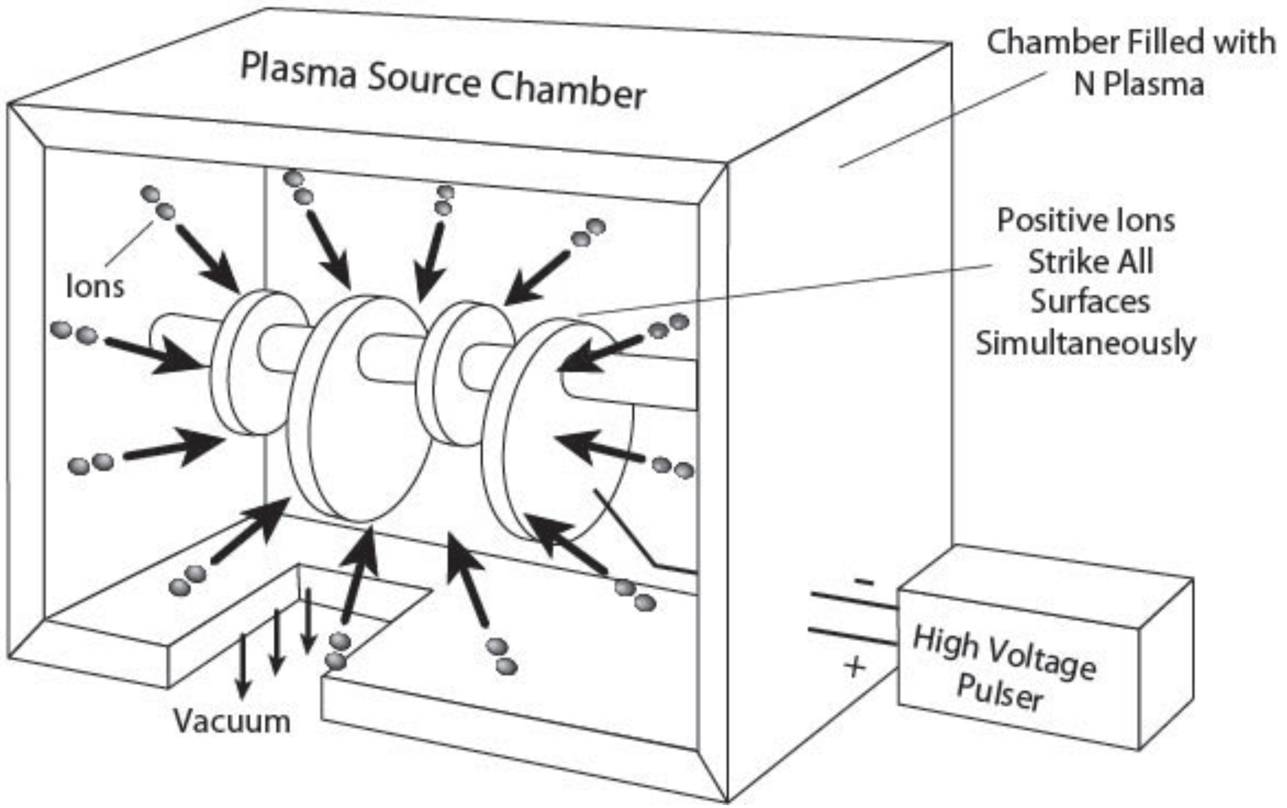
Xe irradiated Al showing dislocation networks

Anti-Site Defects: Chemical Disorder

Effect of Collison Direction



Simplest form of ion implantation: Plasma Source Ion Implantation



Issues:

1) **All ions in gas are implanted (impurities, etc…)**
2) **Energy varies due to different charge states, charge transfer collisions, molecular ions… Results in different implantation depths**