École polytechnique fédérale de Lausanne

Laboratory of Chemical Nanotechnology

Atomic Structure of Real Surfaces
Lesson 4

MSE 304

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Plan of the Course: Fundamentals, Characterization, and Applications

1: Intro to Surfaces & Interfaces

2: Surfaces in the Real World - Adsorption

3: Surface Energetics & Interfacial Phenomena

4: Atomic Structure of Real Surfaces

5: Characterization of Real Surfaces

6: Solid-Liquid Interfaces + Techniques

7: Solid-Solid Interfaces

8: Charged Solid-Liquid Interfaces

9: Surface Chemistry

10: Biological Processes at Surfaces

11: Electronic Properties of Surfaces

12: Thin Film Technologies

13: Biosensor Fundamentals

14: Biosensing applications

Things may be adapted in real time – thank you for your patience!
Midterm feedback (Week 5) – Recap session Week 7?

Recap from Lesson 3 – Thermodynamic Lingo of Surface Energy

Surface Energy (ɣ)

Work to create a surface of unit area at constant temperature and pressure, while keeping all the atomic positions fixed to their bulk position – mechanical definition.

Surface stress (f) – solids only

Mechanical stress when the surface is strained

In solids: $\gamma \neq f$

Surface Tension (σ) – liquids only

Work to extend the surface of a liquid of a unit area

In liquids: $\gamma = \sigma$

Surface free energy ($\tilde{\gamma}$)

Excess Gibbs free energy per unit surface area relative to the bulk.

Combination of cutting bonds and stretching bonds – thermodynamic definition

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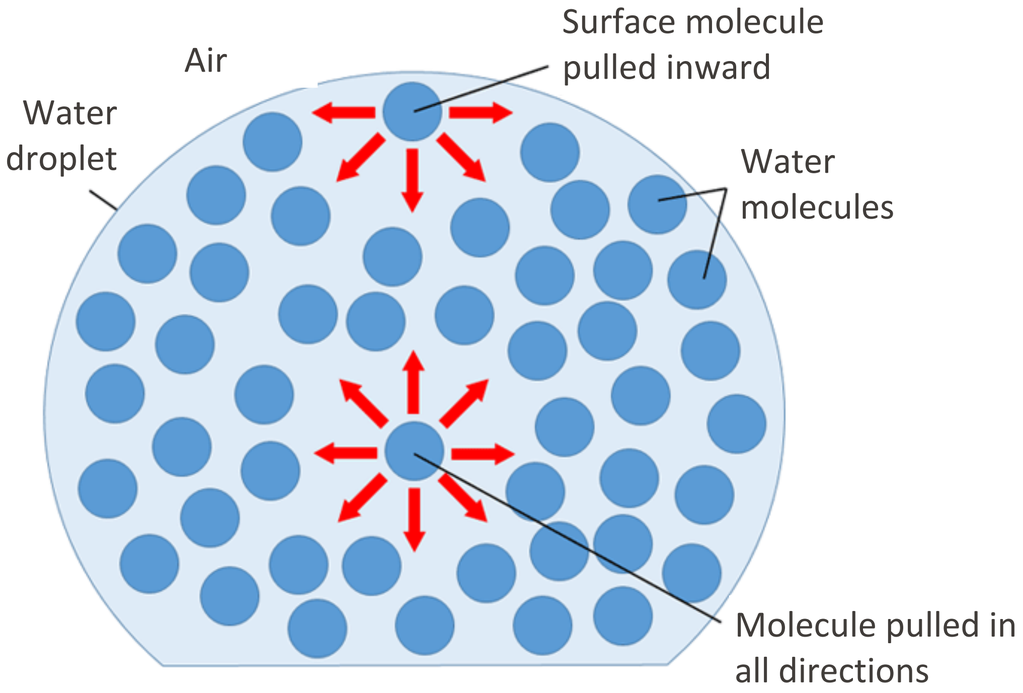
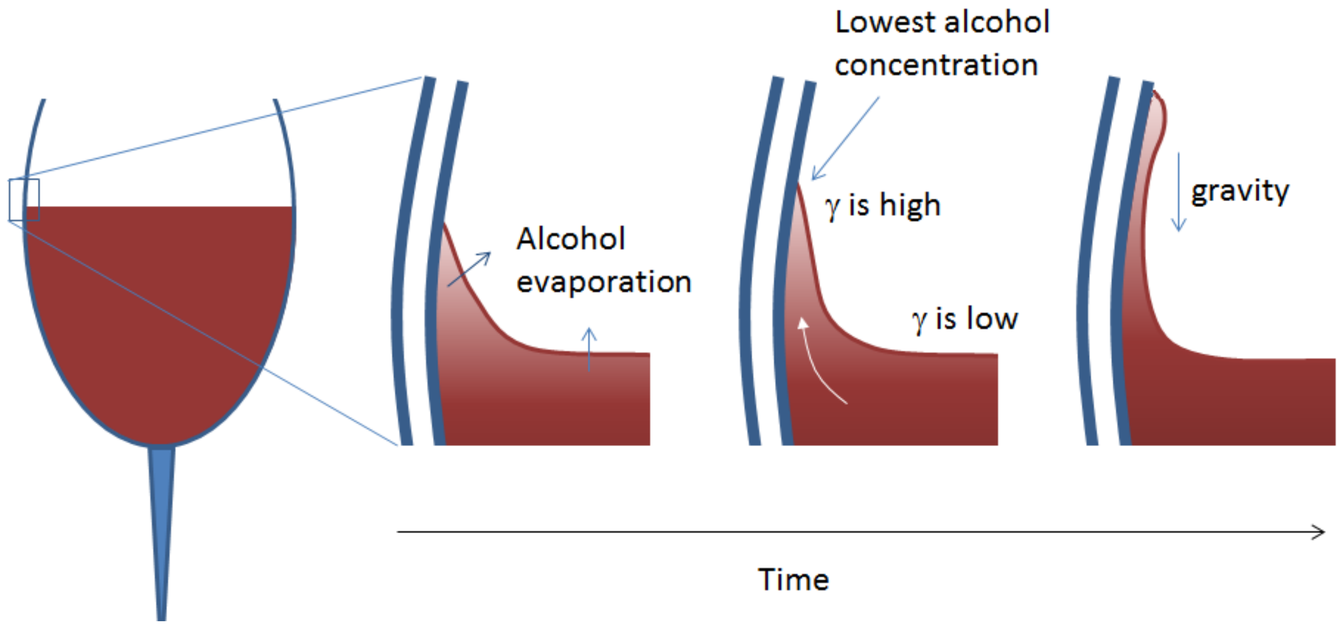
Recap from Lesson 3

- Young's equation bridges interfacial energies to something we can measure
- Methods to measure contact angle (sessile drop most common)
- Real surfaces lead to pinning, contact angle hysteresis
- Roughness amplifies wetting behavior – Wenzel and Cassie-Baxter models
- Nature shows examples of these effects that inspire research

Surface Energy Determines Shapes of Liquids





But what about solids? **Surfaces and energetics also determine how crystals look and behave**

Outline of Lesson 4

- Surface energetics and crystal morphology
- Wulff plot basics
- Why real crystals are never perfect
- Defects in real crystals across scales (1-D, 2-D, and 3-D)
- How defects influence properties

What Causes Crystals to Grow into Specific Shapes

Internal atomic structure

Lattice arrangement: Atoms arranged into repeating 3-D patterns

Symmetry: defines possible crystal face orientations

External factors

Growth conditions: temperature, pressure, impurities

Crystal chemistry and bonding: influence facets and shapes

Energy minimization

Crystals adopt shapes that minimize surface energy, making some configurations more stable than others

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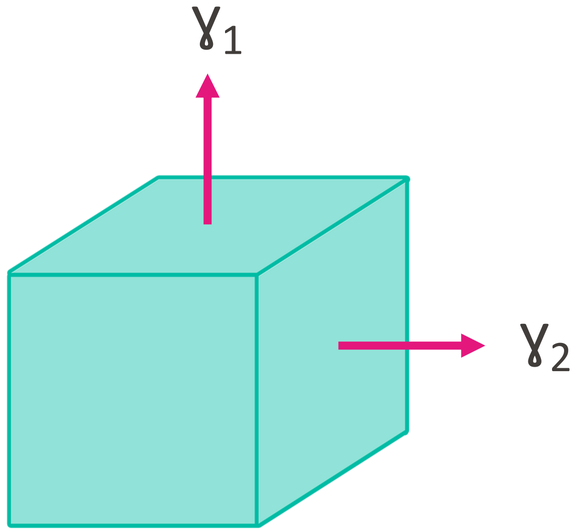
Equilibrium Shape of a Material of Finite Dimensions

In a liquid, γ is constant, so the system just wants to minimize area at fixed volume ➔ spherical droplets

In a solid, the surface energy γ is orientation-dependent.

Minimize total surface energy at constant volume



Different crystal faces don't have the same surface free energy γ (thermodynamic work required to create surface per unit area) – accounting for broken bonds and interactions with neighbors

Stereographic projection can show how surface energy depends on orientation

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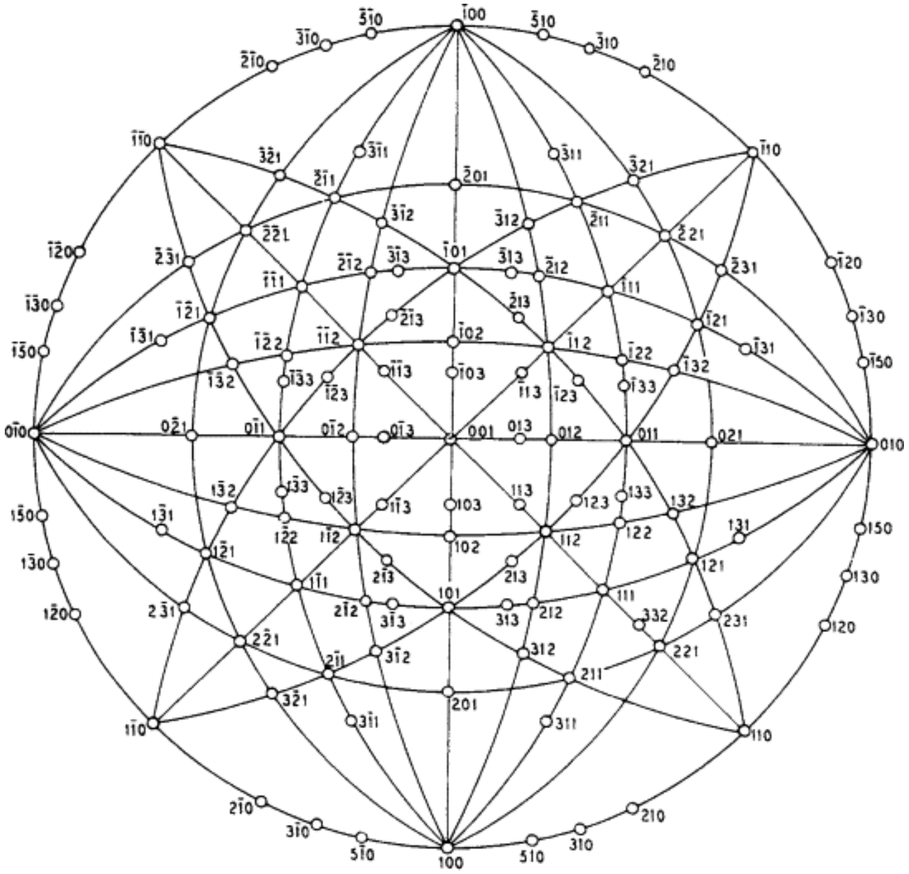
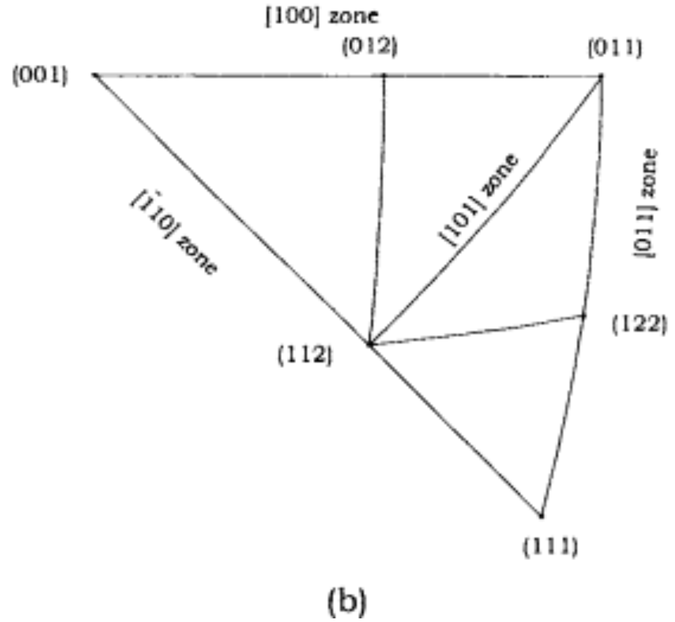
Equilibrium Shape of a Material of Finite Dimensions

Crystals are 3-D objects but to study orientation and symmetry, we can flatten them to 2-D
Stereographic projection: circular 2-D diagram that shows the arrangement of directions in space



The stereographic projection for a face-centered-cubic lattice with the [001] direction as the center,

The stereographic triangle for shown projection



Unertl | Handbook Surface Science | 1996

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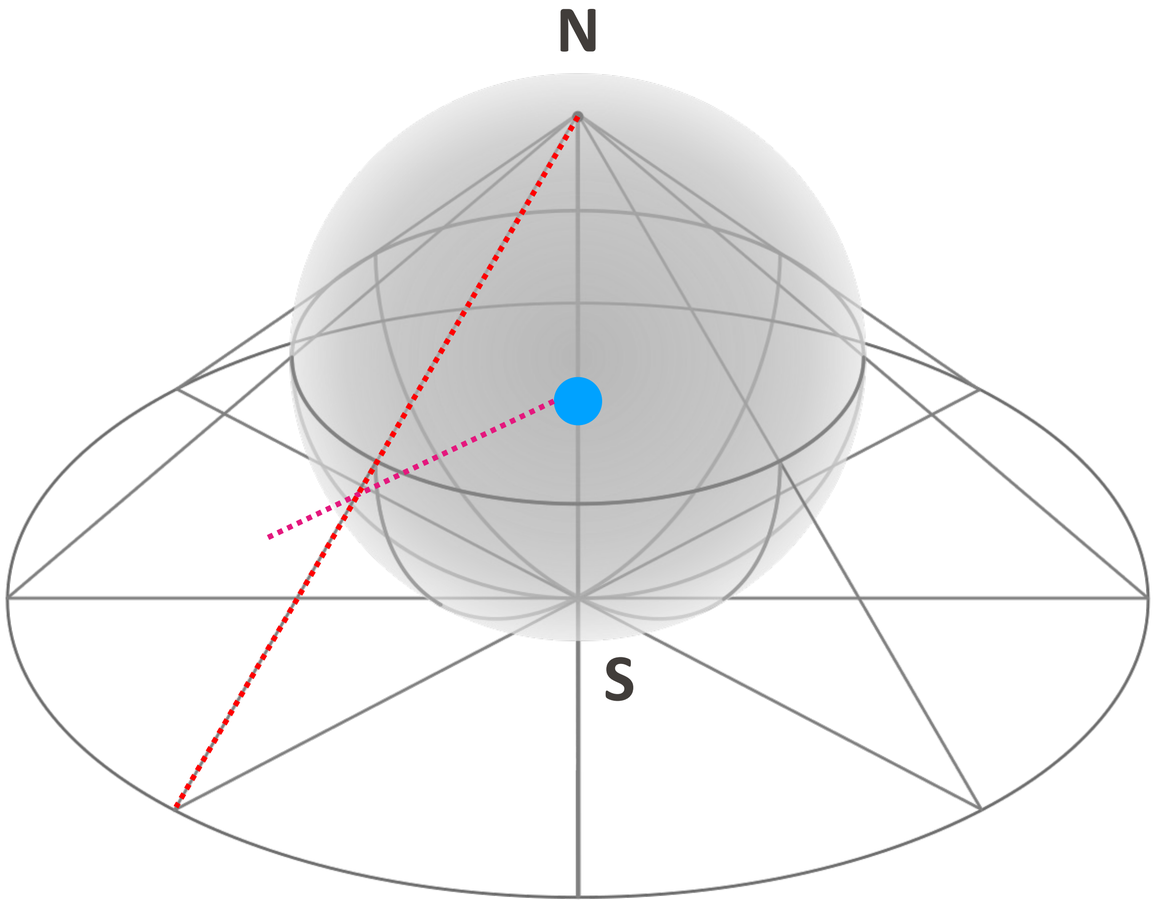
Stereographic Projections – Reduce 3-D to 2-D

Stereographic projection: circular 2-D diagram that shows the arrangement of directions in space



Stereographic projection

Source: Wikipedia

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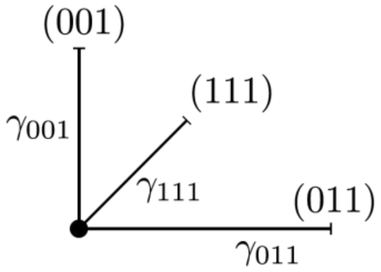
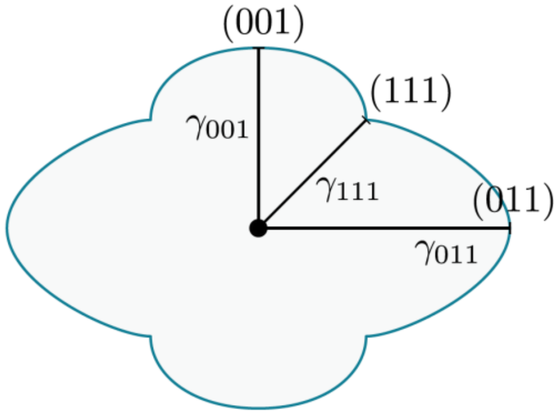
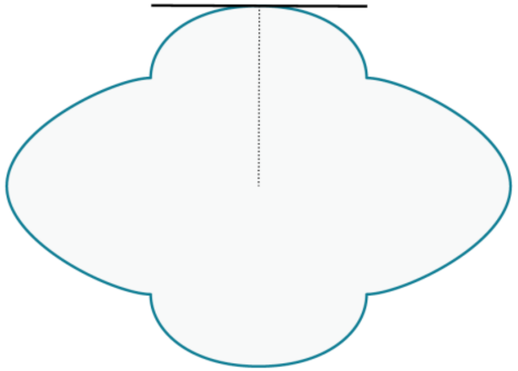
Wulff Construction

Stereographic projection: circular 2-D diagram that shows the arrangement of directions in space







Source: Francesco Stellacci

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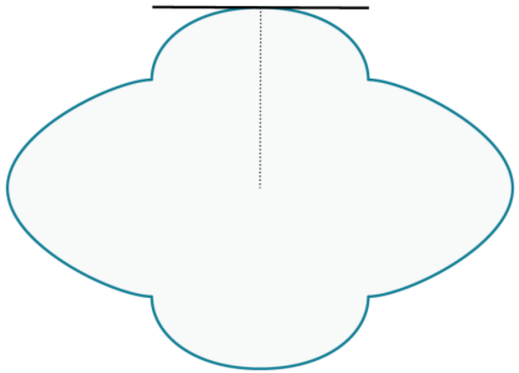
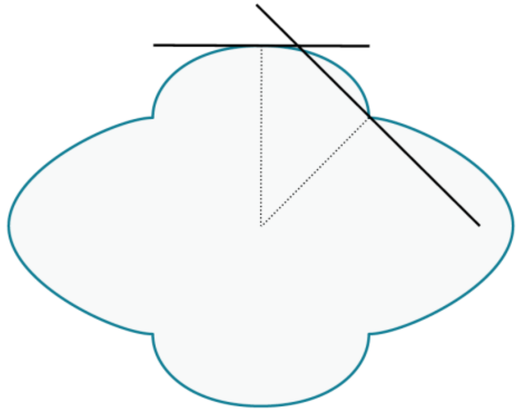
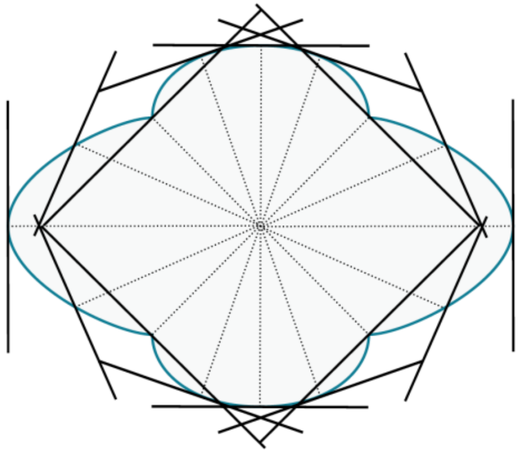
Wulff Construction – Draw Tangents

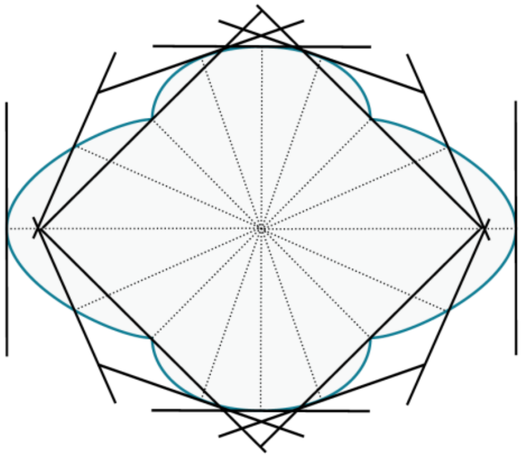




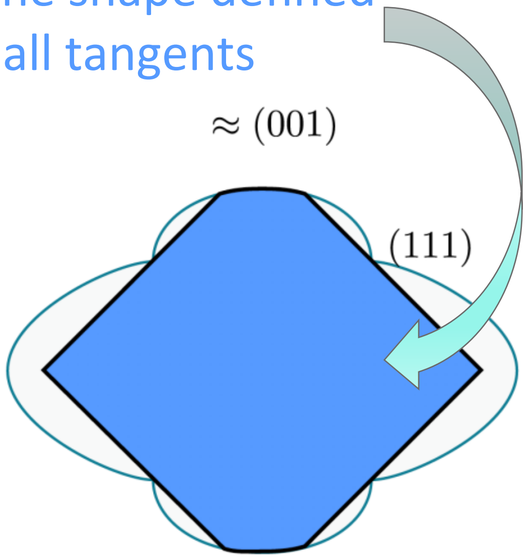


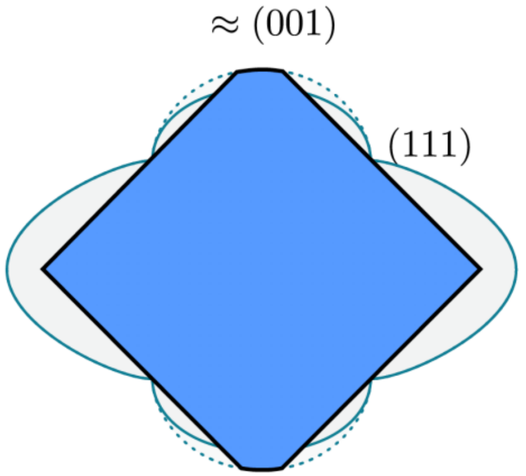
Source: Francesco Stellacci

Wulff Construction – Draw Internal Minimum Area



Internal minimum closed area of the shape defined by all tangents





Do this in all planes to construct 3-D shape

Source: Francesco Stellacci

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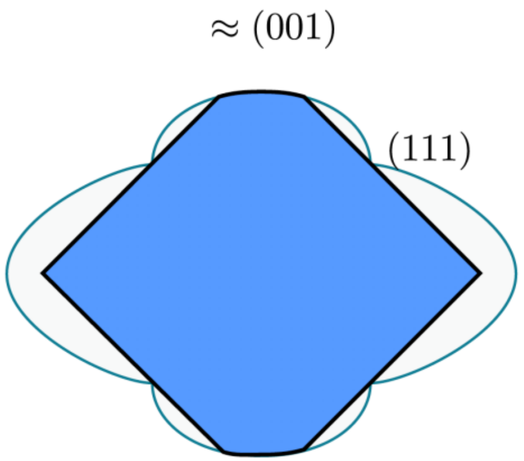
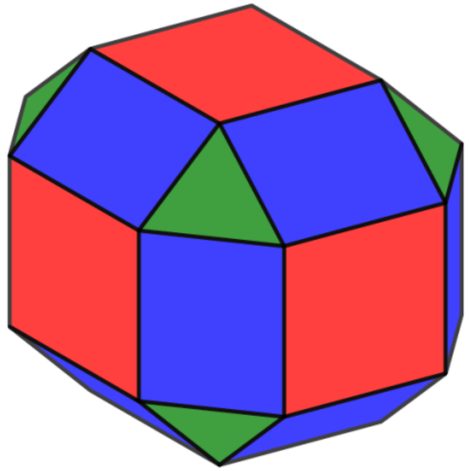
Wulff Construction – Equilibrium Shape



Equilibrium shape for material in a single plane

Do this process for all planes



Equilibrium crystal shape in 3-D

Experimentally proven

Source: Francesco Stellacci

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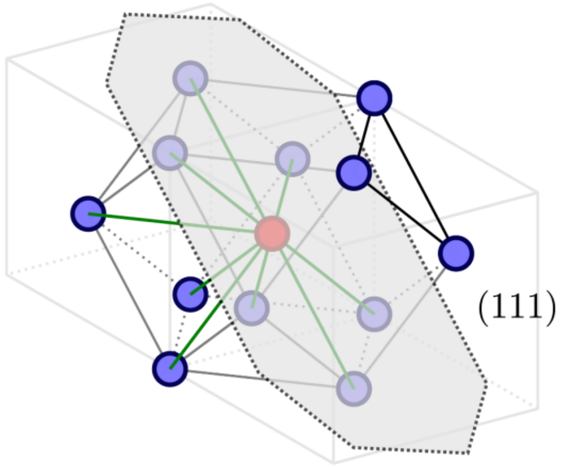
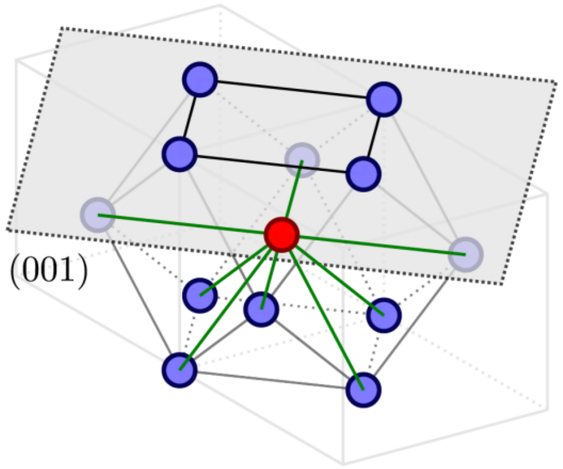
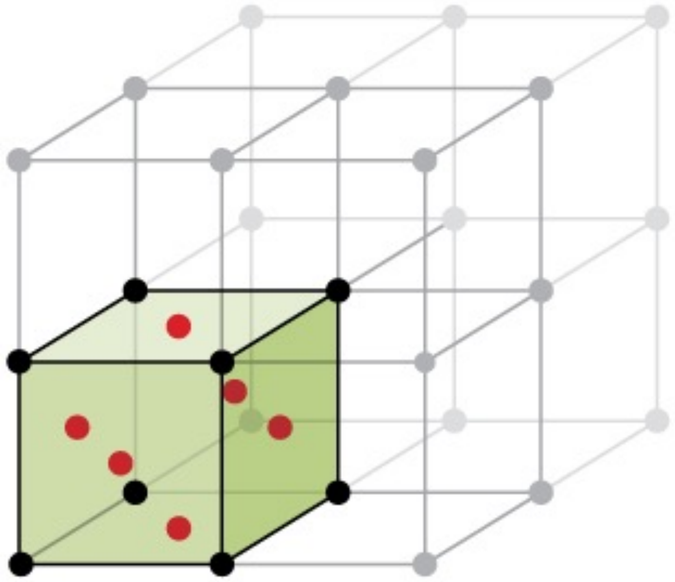
Why Crystallographic Planes Have Different Surface Energies







Surface energy basically proportional to the **number of broken bonds per surface atom** when you cut the crystal

Source: Wikipedia

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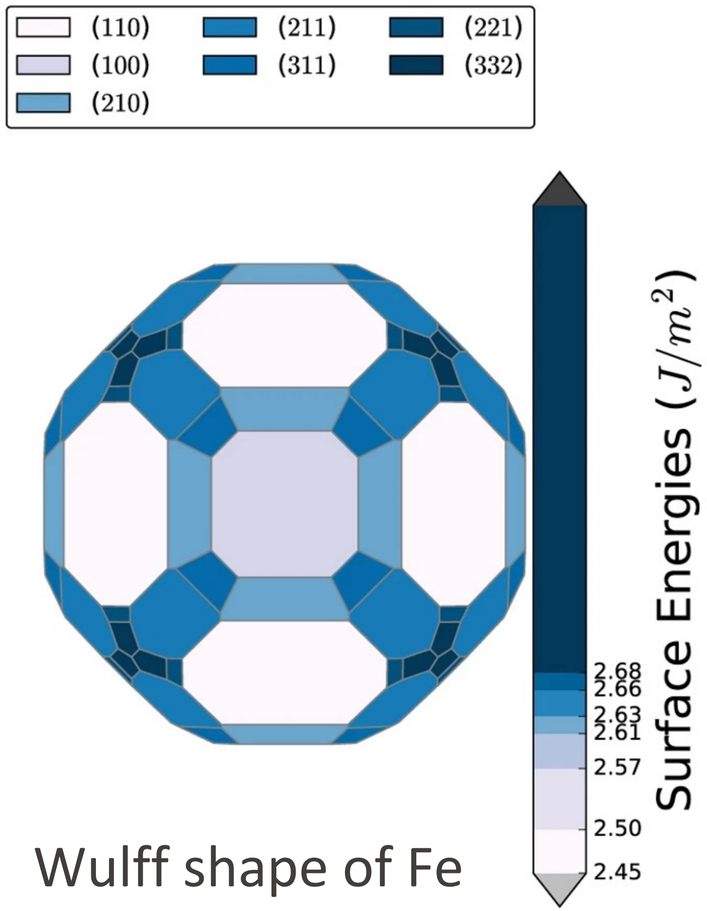
Crystals have Planes with Various Surface Energies

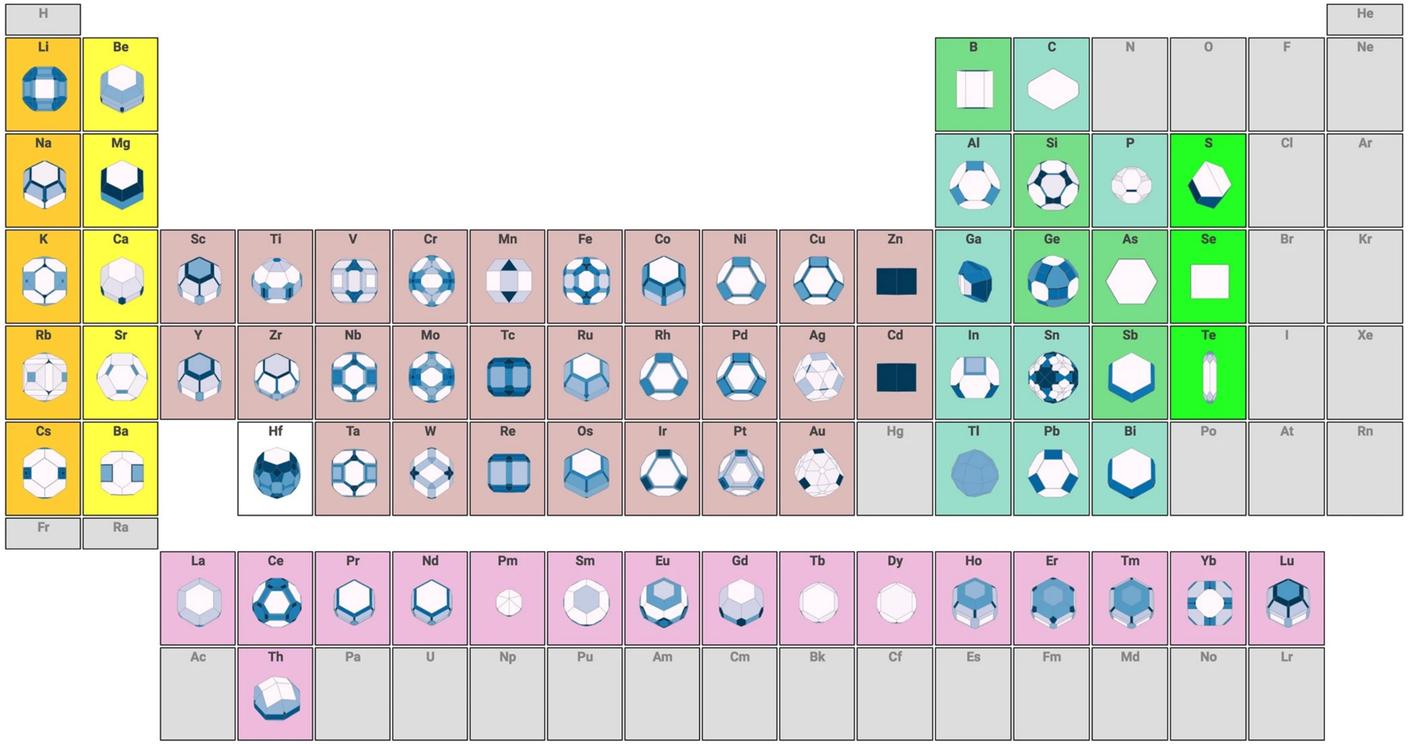


Wulff shape of Fe

Lower energy planes occupy larger areas of shape

Crystalium web application

An exploration of Surfaces and Wulff Shapes of Elements



Tran *et al.* | Scientific Data | 2016

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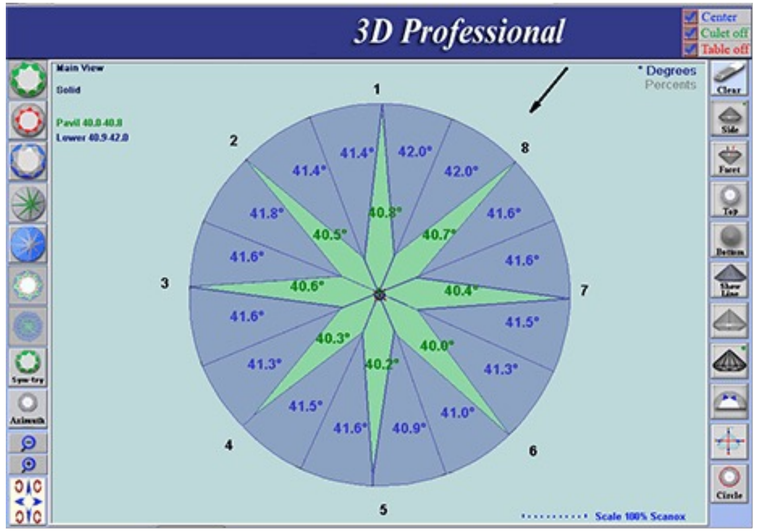
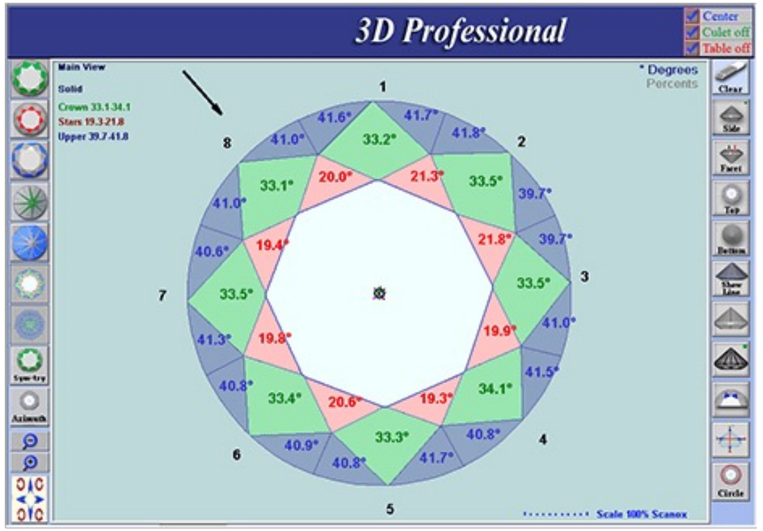
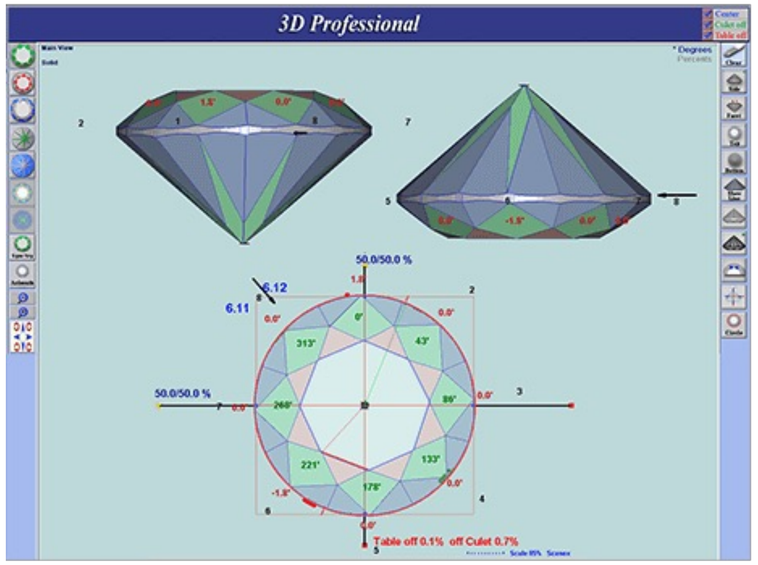
Art of Making Jewelery – Cutting Crystals Through Planes







OGI SYSTEMS
Inventions & Performances

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Key Takeaways

- Wulff construction shows equilibrium crystal shape
- Surfaces cost energy because bonds are broken
- Different planes = different surface energies

- By controlling surface energy, we can control the morphology of materials.
- Understanding planes in crystals has applications for gemstones

Not all crystals are “perfect” – there are many defects

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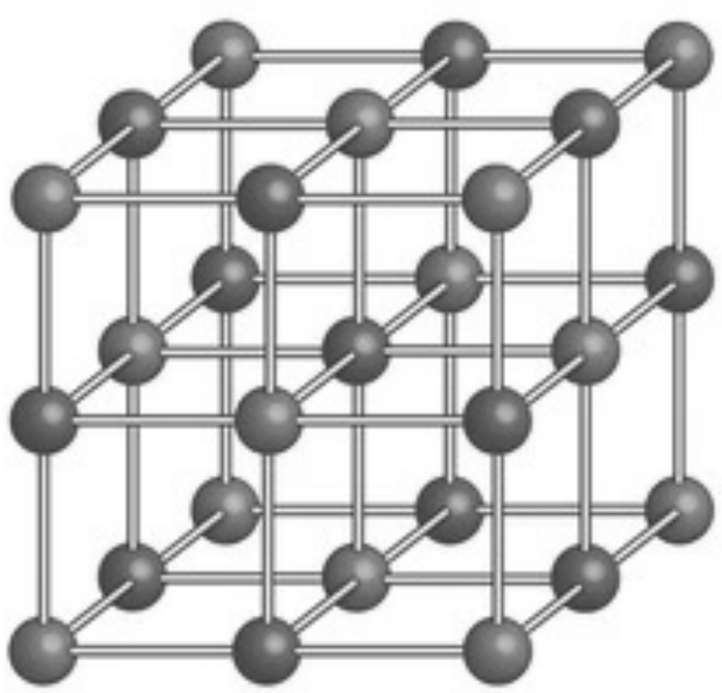
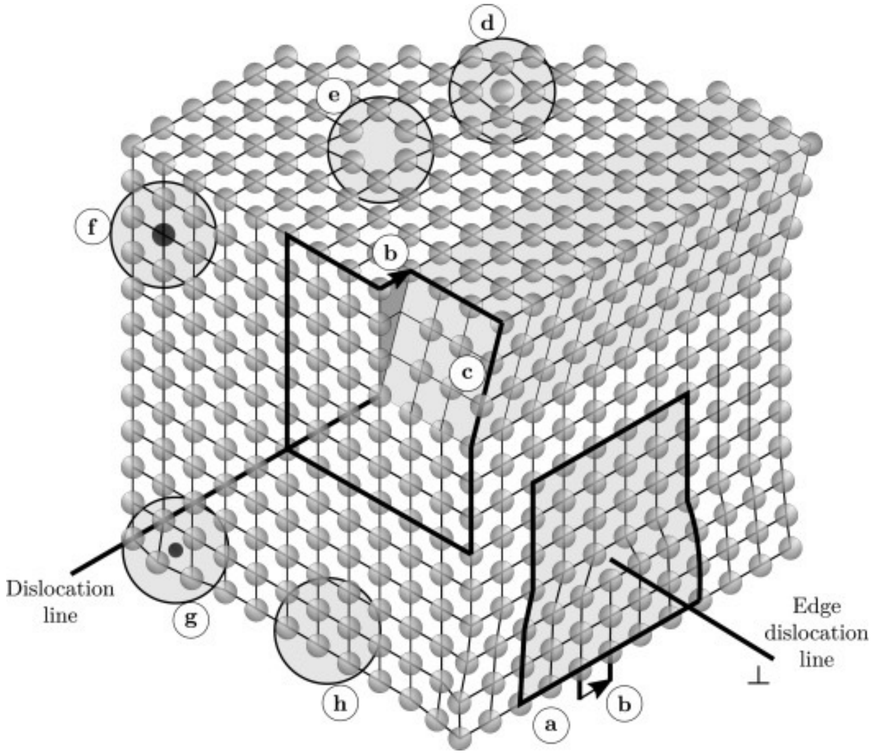
Crystals: Ideal *vs.* Real

Crystal lattices represent an idealized system - important principles for the behavior of solids

Real crystals contain large numbers of defects (>10^4 per milligram)





Source: Handbook of Surface Science, 1996

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Origins of Defects – Why Imperfections Exist

1. **Impurities are unavoidable**

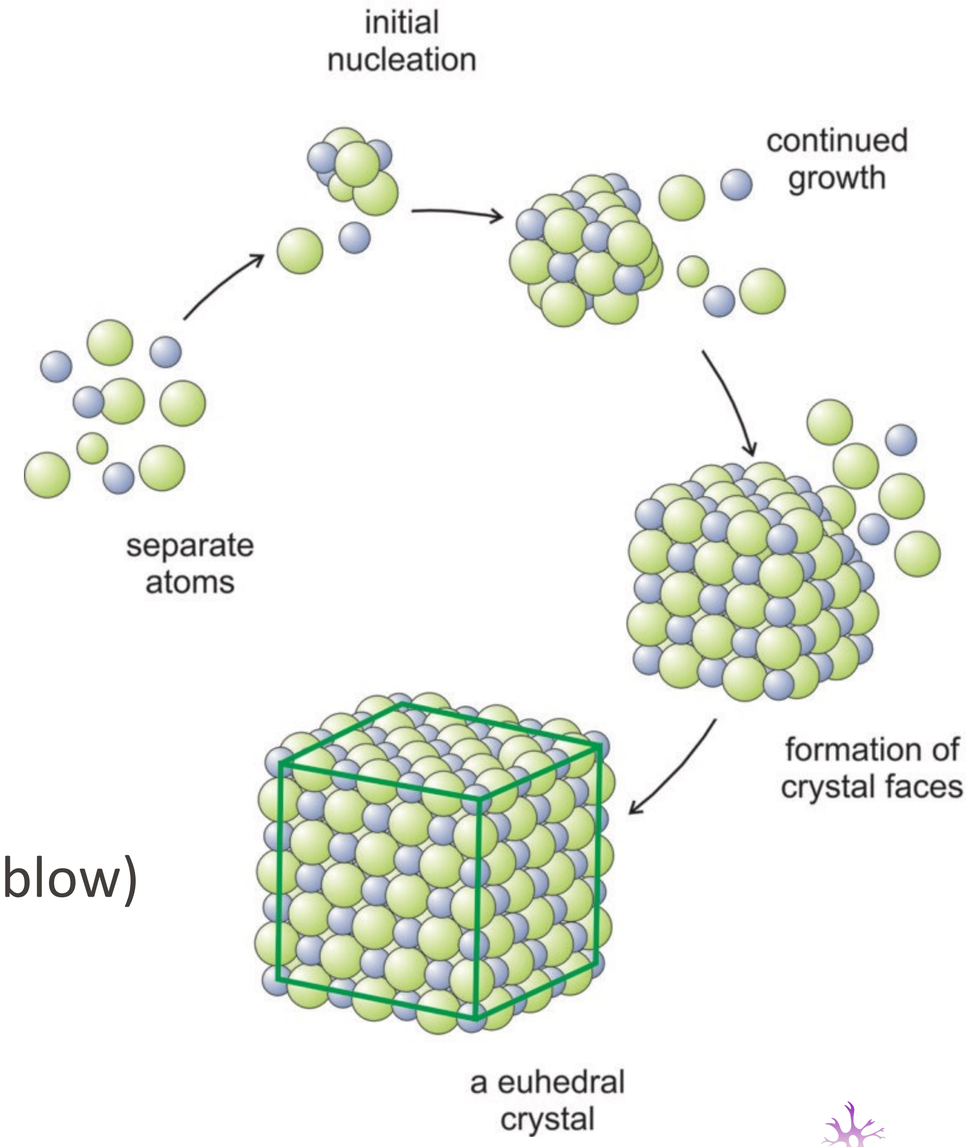
   No material is ever 100% pure

2. **Crystal growth is imperfect**

   Atoms get trapped in the wrong positions

3. **Stress creates defects**

   External forces misalign regions of lattice (e.g. hammer blow)



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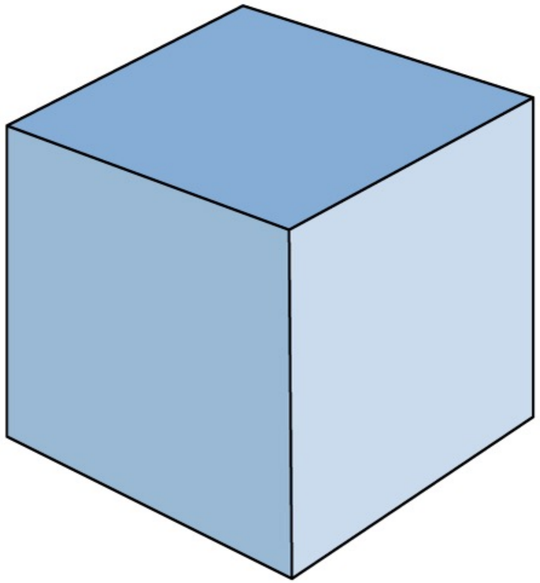
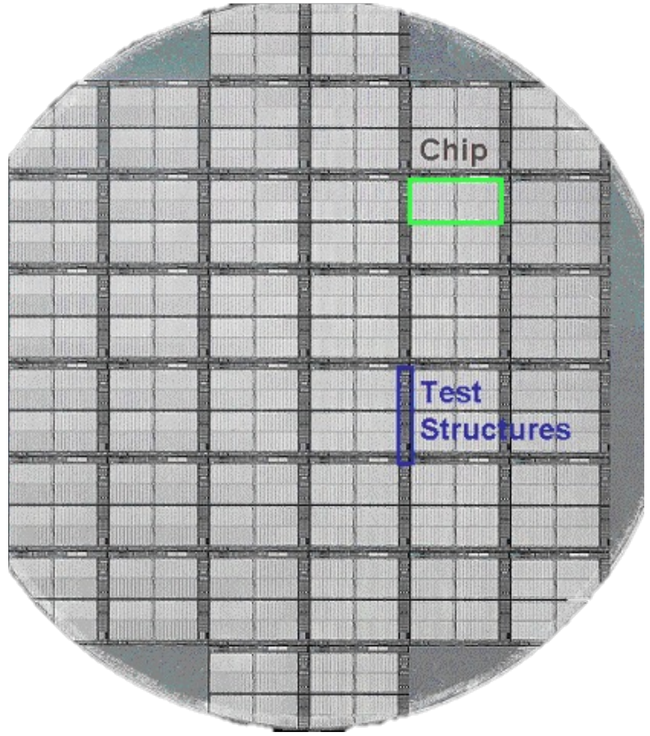
How Perfect Can We Get?



Si cube = 1 cm^3

How many defects in this volume?

Single crystal silicon
Biggest and most perfect crystsal



Processed silicon wafer
(memory chips)

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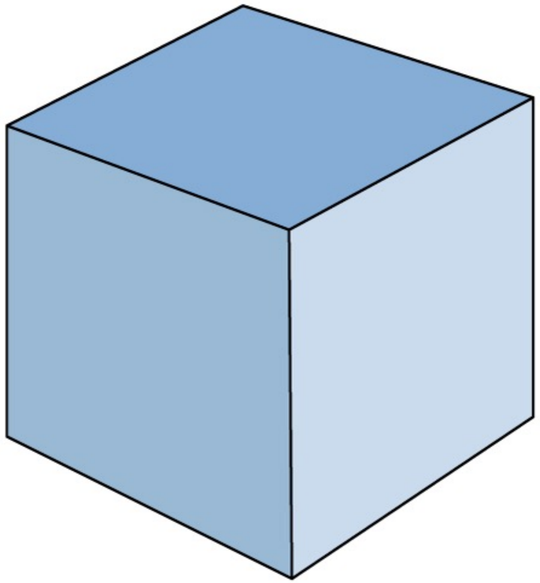
How Perfect Can We Get?



Si cube = 1 cm^3

How many defects in this volume?

Atomic density of silicon: 5 x 10^{22} atoms/cm^3

Chemically pure silicon: 99.99% silicon
0.01% impurities (100 ppm)
5 x 10^{18} atoms/cm^3 (impurities)

Electronic grade silicon: 99.9999999% silicon
1 ppm impurities
5 x 10^{13} atoms/cm^3 (impurities)

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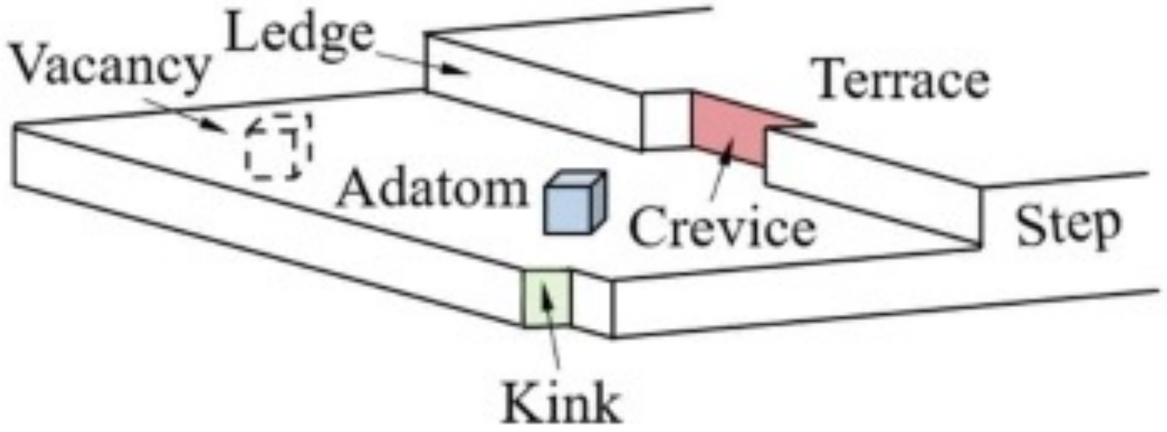
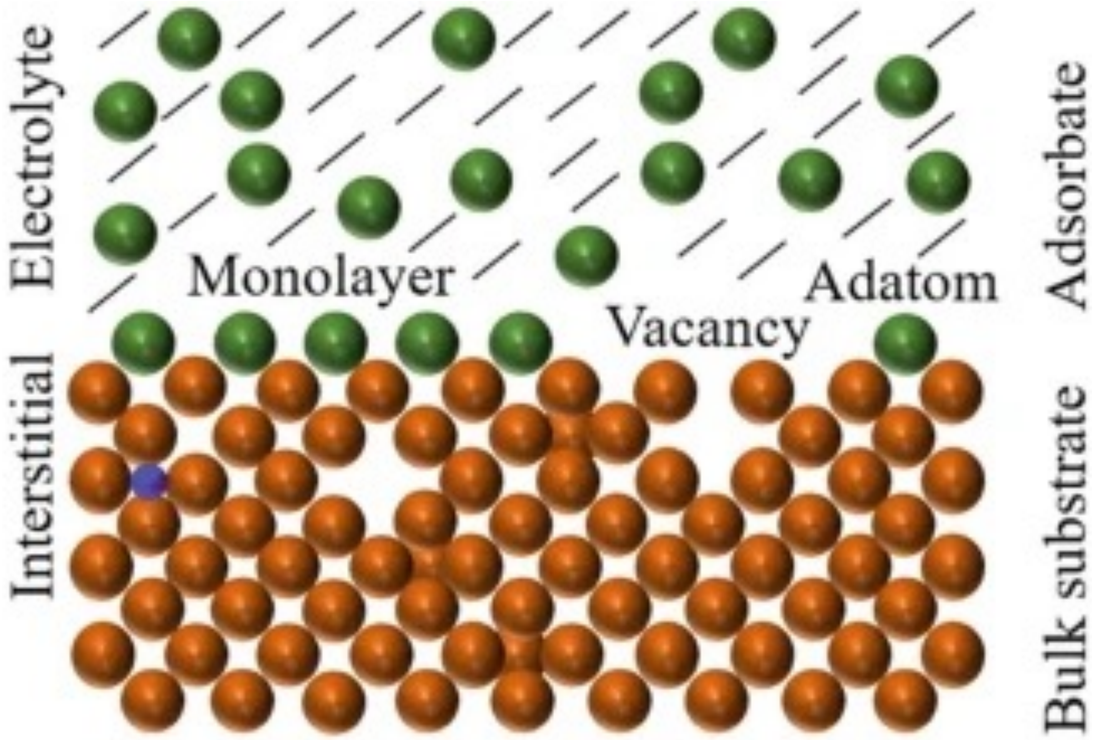
Various Defects In Chemically Perfect Crystals

Common surface defects



Defects and a partial monolayer on substrate in electrolyte



Perez |Materials Science: Theory and Engineering. Springer | 2024

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Surface Defects by Dimensionality (0-D to 3-D)

- **Point Defects** - vacancies, interstitials, adatoms
- **Line Defects** – dislocations leading to terrace, ledges, kinks
- **Surface reconstructions**
- **Bulk (volume) Defects** – voids, inclusions, pores

These are **Intrinsic Defects** that are native to the crystal structure
(even if formed during growth or annealing)

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Surface Defects Through Addition to Perfect Crystal

These are **Extrinsic Defects**
(foreign influences or environmental consequences)

- Residual Stress – lattice distortions
- Impurities – external atoms entering the crystal

Real-world perspective

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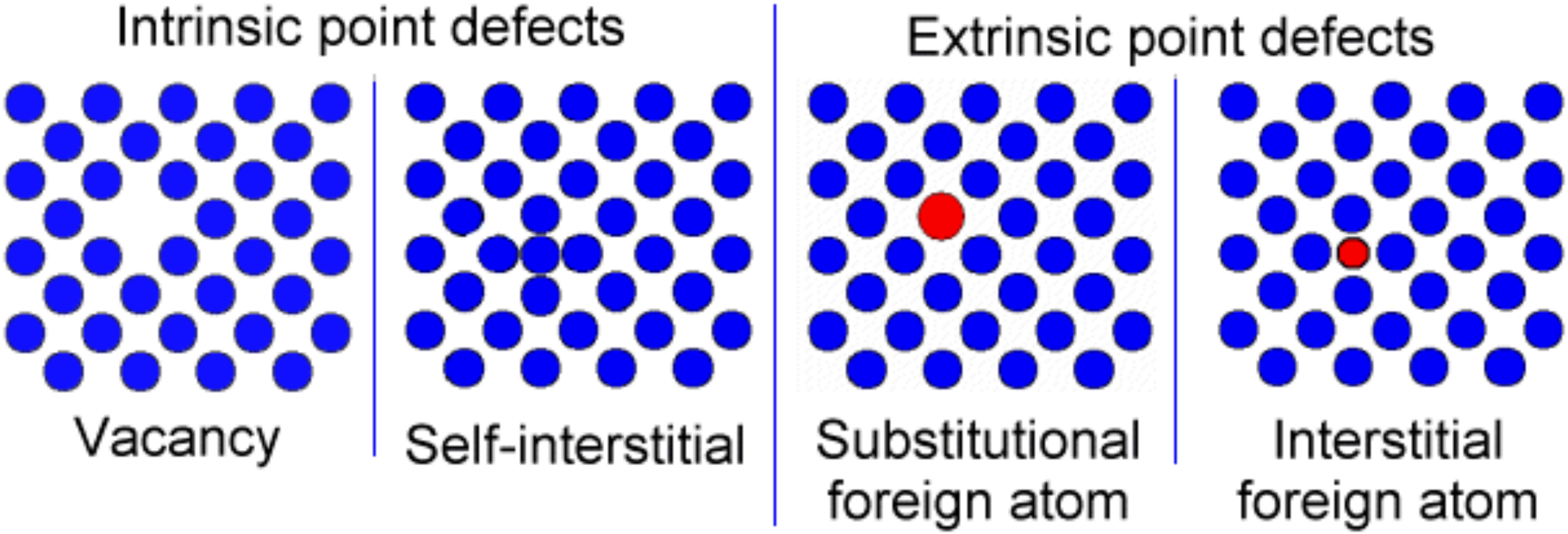
Classification of 0-D Defects



STUDYTRONICS

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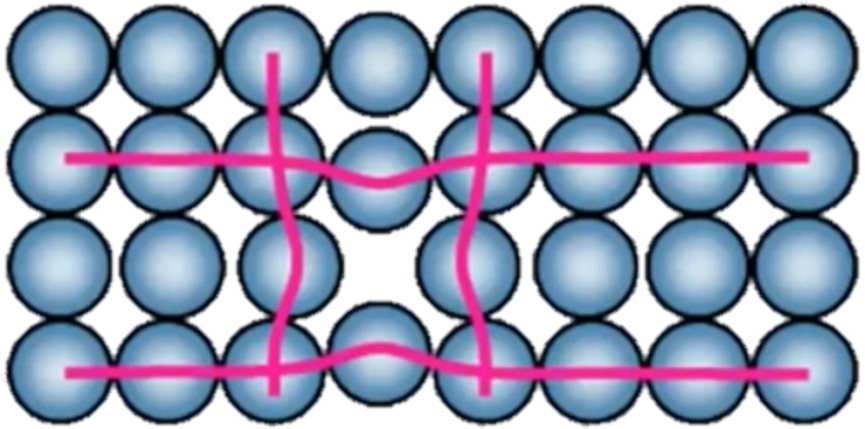
Basic Point Defects 1: Intrinsic Defects

Vacancies



Missing atom on lattice

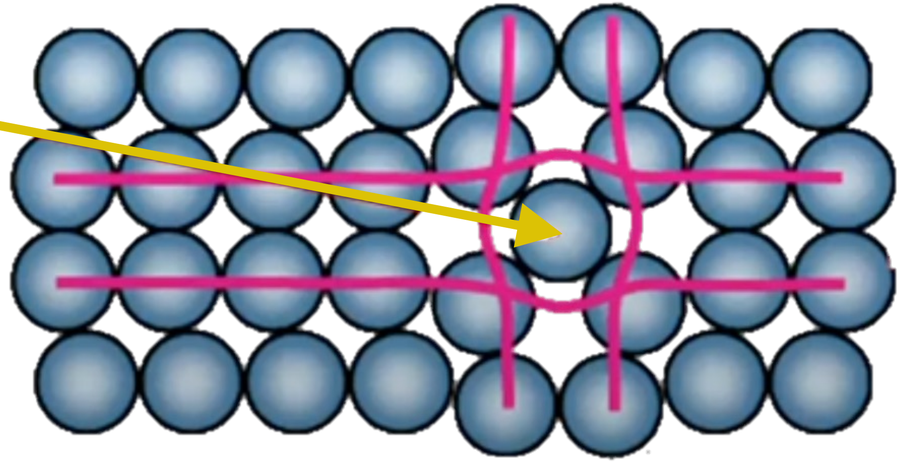
Surrounding vacancy, lattice is in:

- Tension (bond stretching)
- Compression

Self-interstitial

Distortion of planes

Interstitials



Additional atom in lattice

Surrounding interstitials, lattice is in:

- Compression

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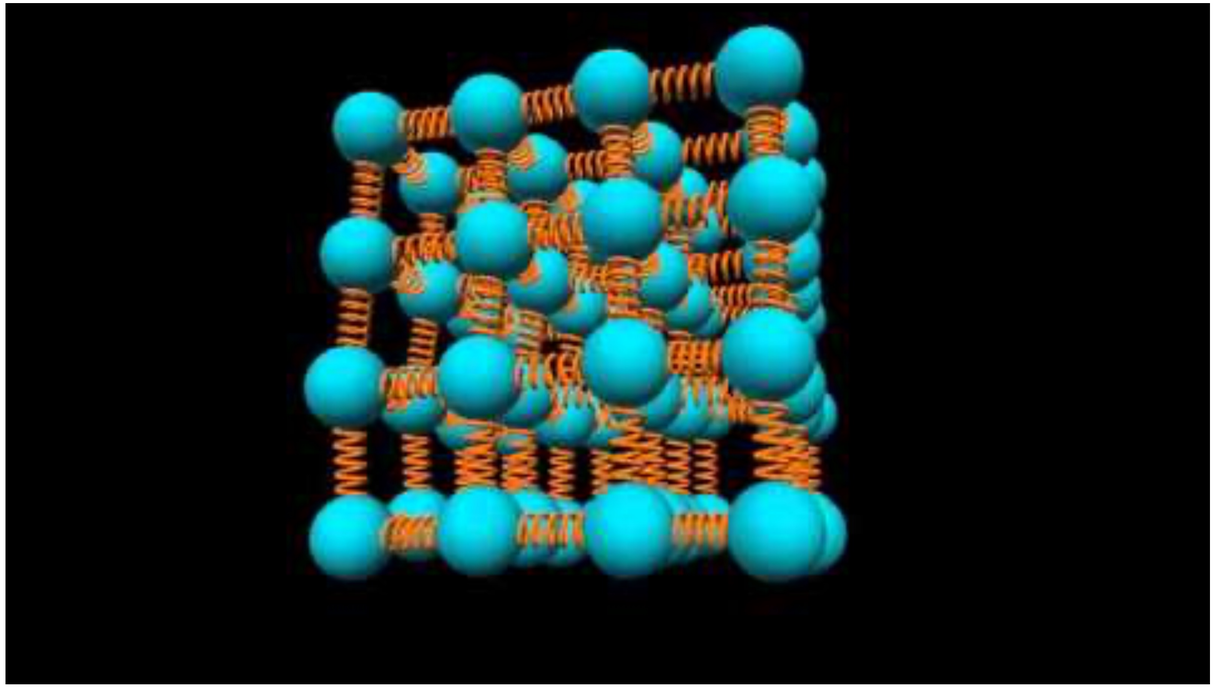
Where Do Intrinsic Defects Come From?

1. Thermal vibrations: at high temperatures, atoms vibrate with significant energy leading to creation of vacancies or shifting into interstitial positions



Simulation of a simple cubic lattice oscillating in response to thermal energy

Displacement in harmonic bond

$$\sqrt{\langle u^2 \rangle} \approx \sqrt{\frac{k_B T}{k_{\text{eff}}}}$$

Using a typical interatomic stiffness (k_{eff} = 100 N/m):

300 K: ~ 0.06 Å
2000 K: ~ 0.17 Å

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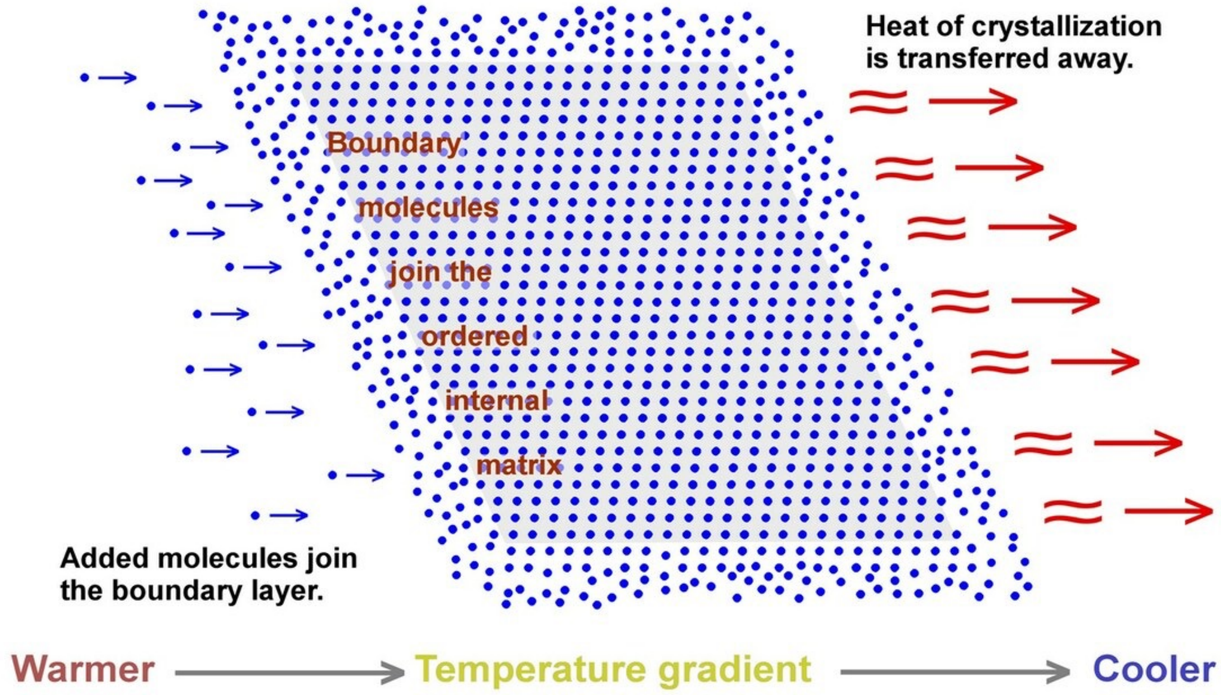
Where Do Intrinsic Defects Come From?

2. Crystal growth conditions: the rate at which the crystal grows and the temperature gradient at the melt-solid interface is critical. Atoms can shift or move from ideal lattice positions during crystal building process leading to structural imperfections preserved as crystal cools

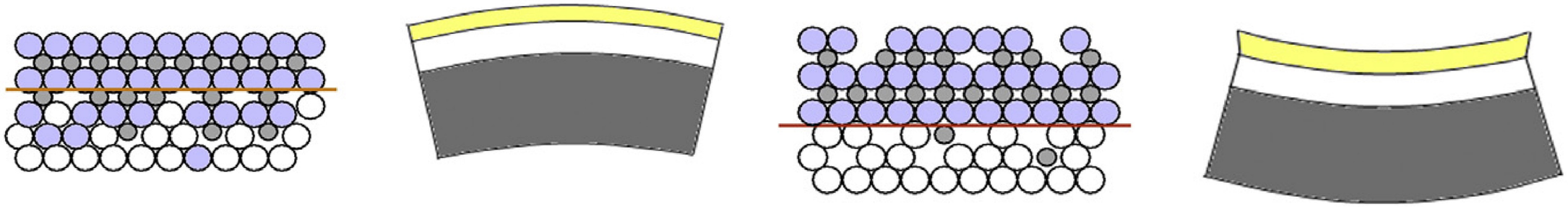


heartofavalonia.org CHEMINA

Where Do Intrinsic Defects Come From?

3. Ionizing radiation: High energy particles can knock atoms out of their positions

4. Mechanical stress and impact: physical forces can displace atoms from ideal lattice positions



Proost *et al.* | Encyclopedia of Interfacial Chemistry : Surface Science and Electrochemistry | 2017

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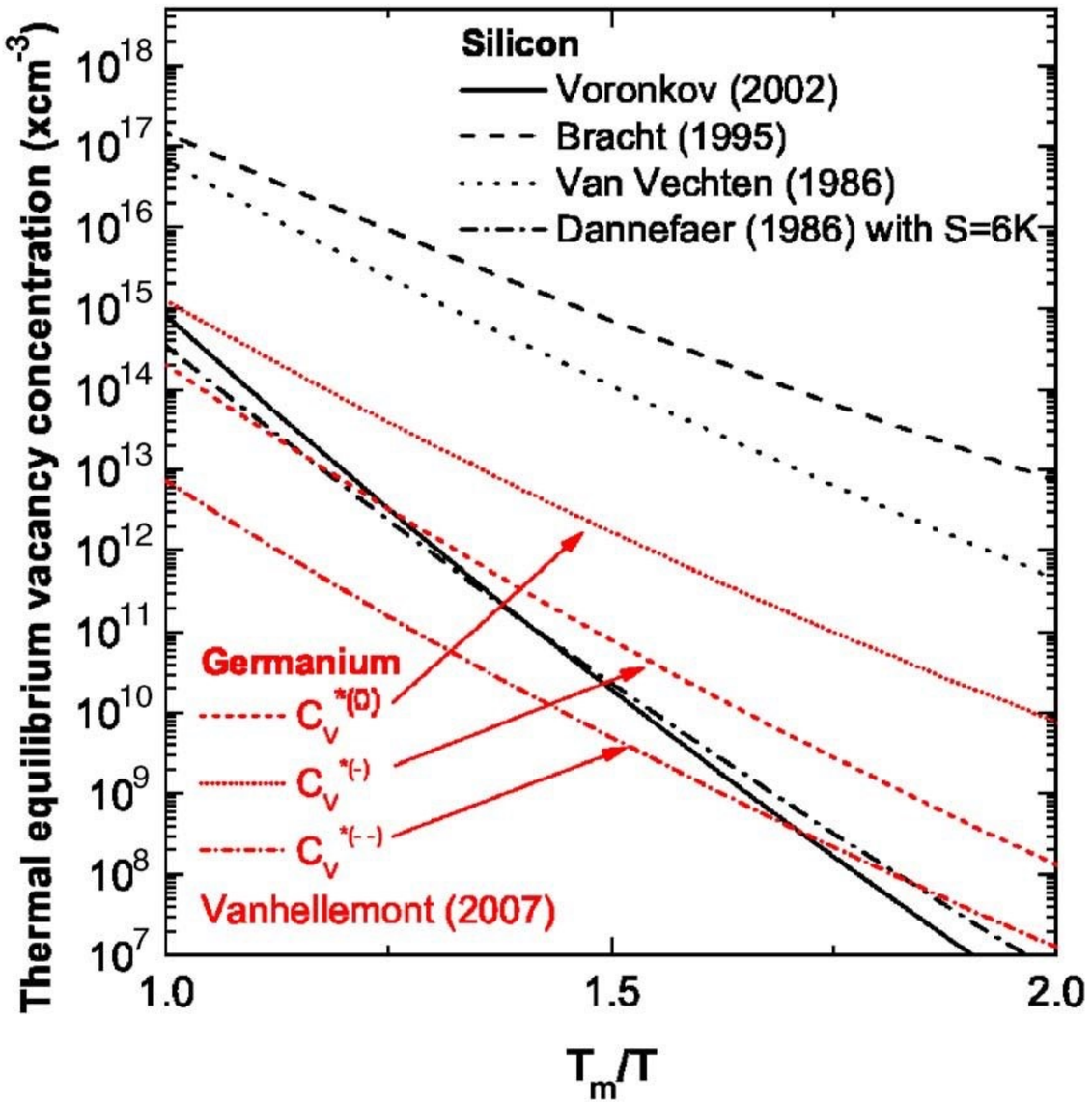
Vacancies Increases as Temperature Approaches Melting Point



Different theoretical and experimental models for vacancy concentrations in silicon and germanium

"Due to its high intrinsic carrier mobility, there is a renewed interest to use germanium as an active semiconductor in advanced nanoelectronic devices."

T_m: melting temperature
T: actual temperature

$T_m/T = 1$ – crystal at its melting point

Vanhellemont & Simoen | J. Electrochem. Soc. | 2007

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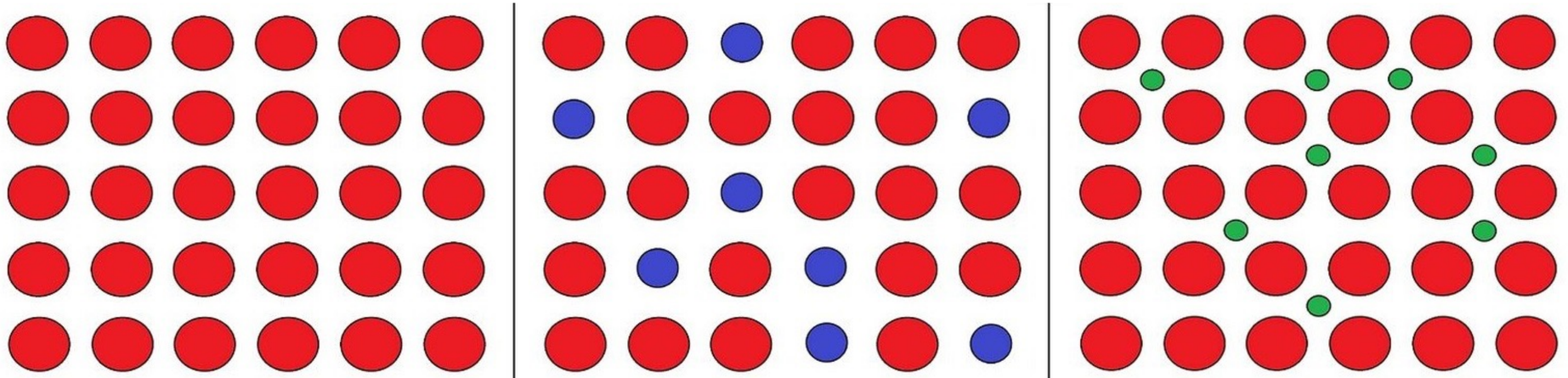
Basic Point Defects 2: Extrinsic Defects



Extrinsic atoms sitting on the lattice site, lattice conserved

Small atoms can occupy interstitial sites

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Where Do Extrinsic Point Defects Come From?

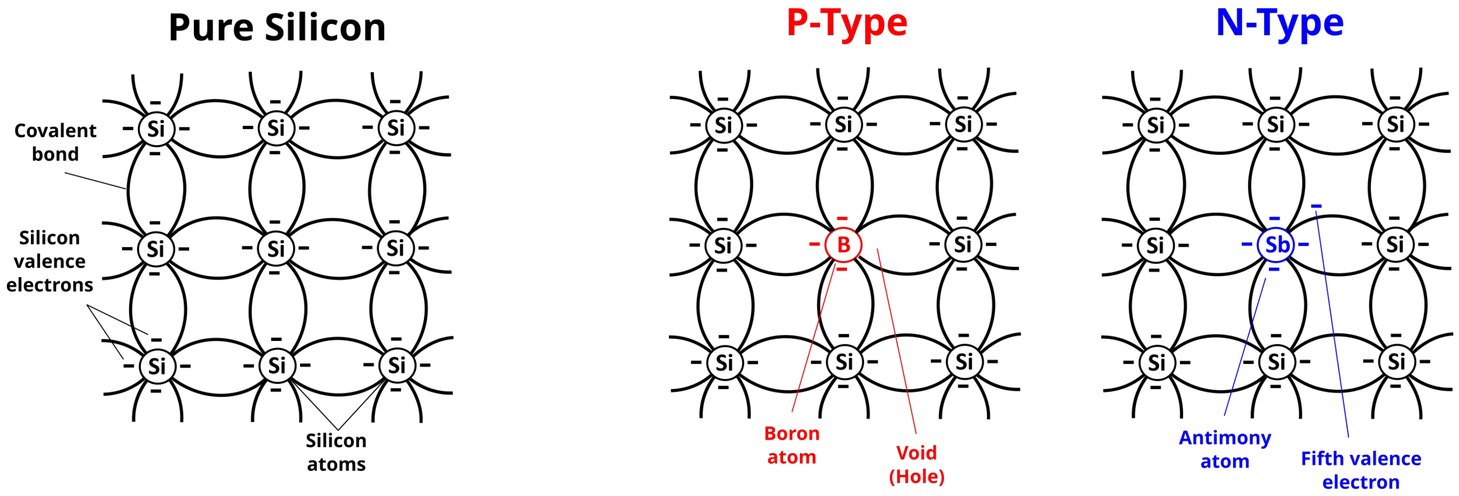
Foreign atoms within a material's crystal structure – can be intentional or unintentional

Intentional: Doping

Deliberate introduction of impurity atoms into a crystal lattice to modify properties. Small amounts of dopants in semiconductors can significantly change their electrical behavior.

Intrinsic (Undoped)

Extrinsic (Doped)



Modulate the electrical, optical and structural properties of semiconductors

Source: Wikipedia

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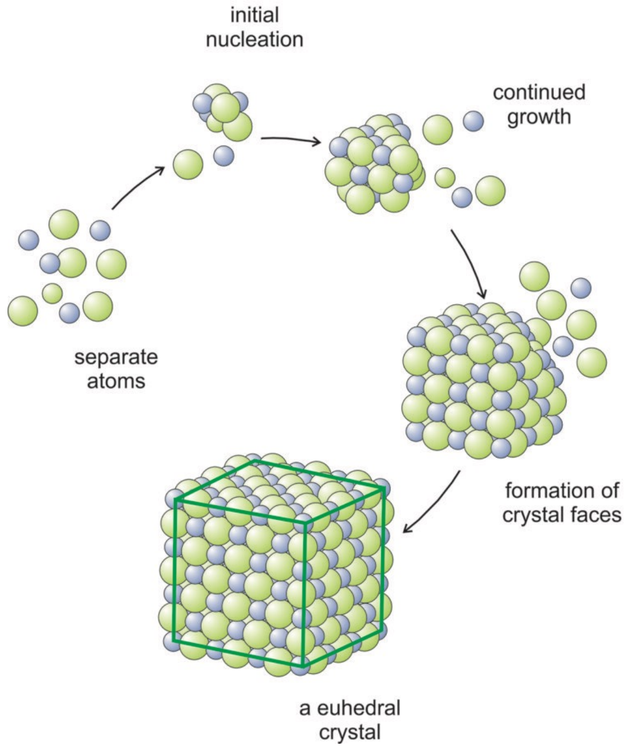
Where Do Extrinsic Point Defects Come From?

Foreign atoms within a material's crystal structure – can be intentional or unintentional

Unintentional: Impurities

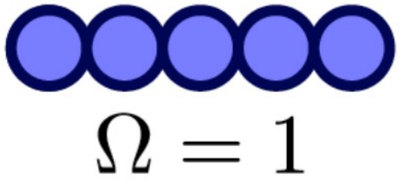
Unwanted foreign atoms incorporated into the material during its formation or processing.

- Impurities can be present in the original raw materials or introduced during extraction
- Manufacturing steps like welding can also introduce defects and impurities



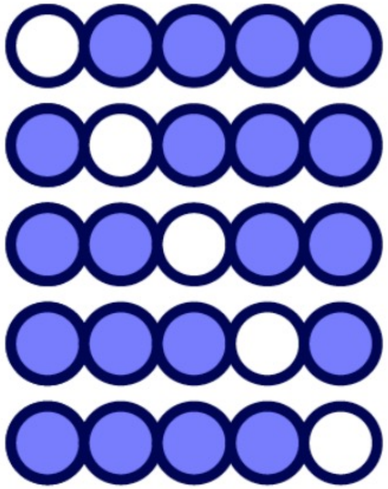
Point Defects Always Exist in Real Surfaces (Thermodynamics)

Point defects are unique – they are "**thermodynamic defects**", even in a perfect crystal grown under equilibrium conditions, they will exist

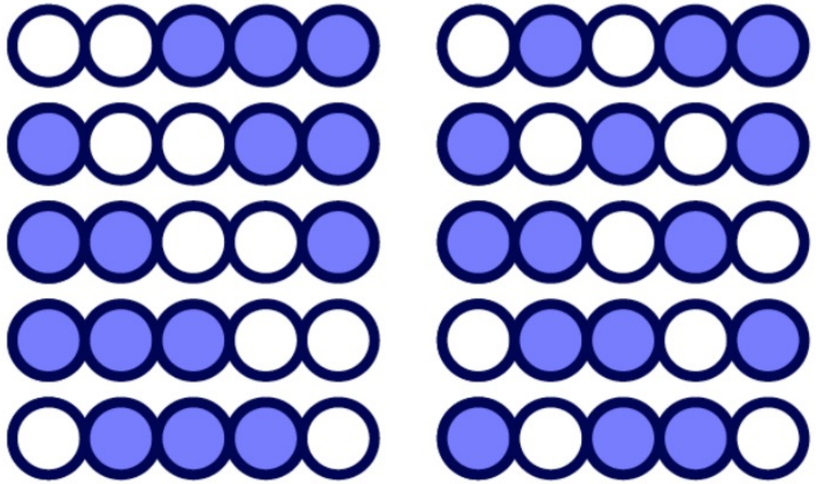


$\Omega = 1$

microstate



$\Omega = 5$



$\Omega = 5 \cdot 4/2 = 10$

Boltzmann entropy equation

$$S = k\, ln(\Omega)$$

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Energy-Entropy Balance for Vacancy Formation

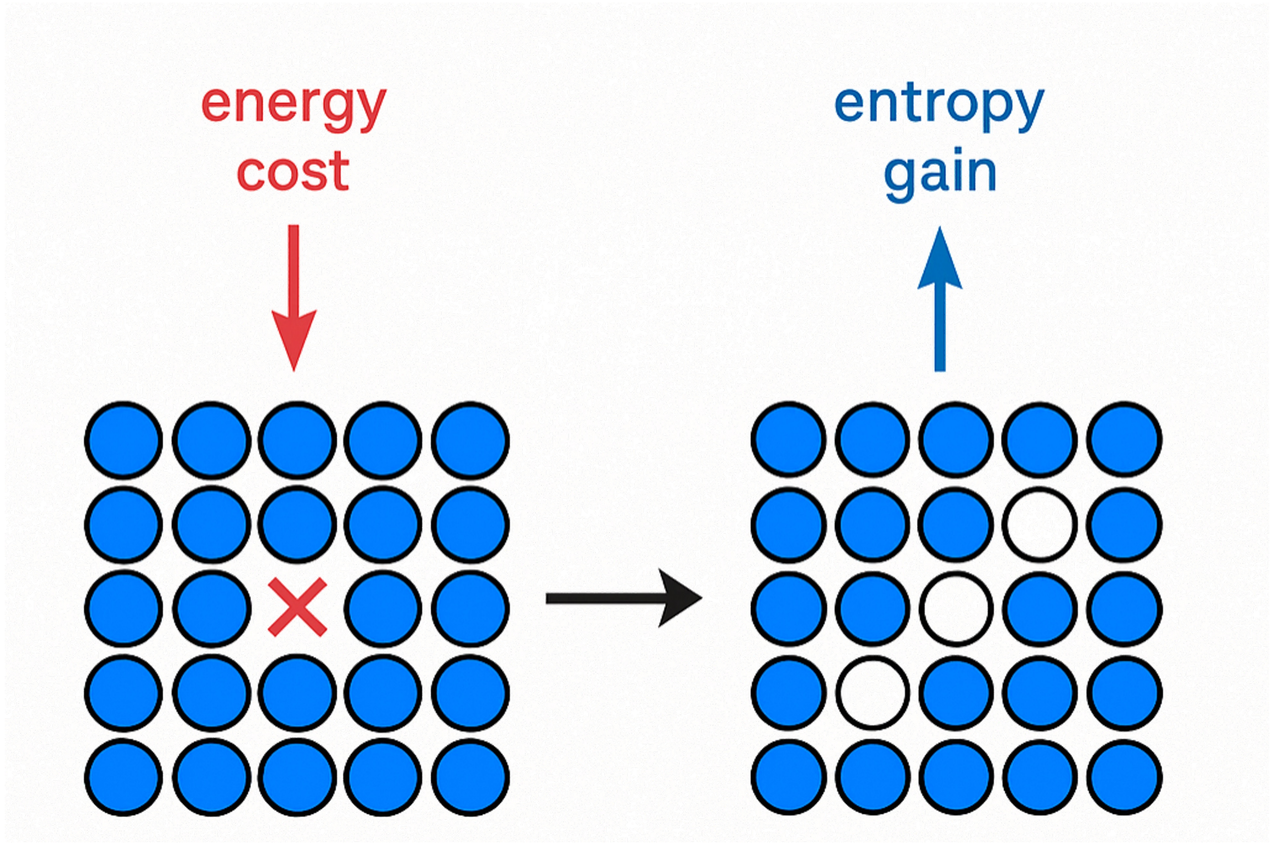
Creating a vacancy costs energy (breaking bonds) but system also gains entropy.

At equilibrium, the crystal balances these two effects.

Vacancy formation

Bonds broken

Energy penalty



More possible microstates (Ω)

Entropy gain

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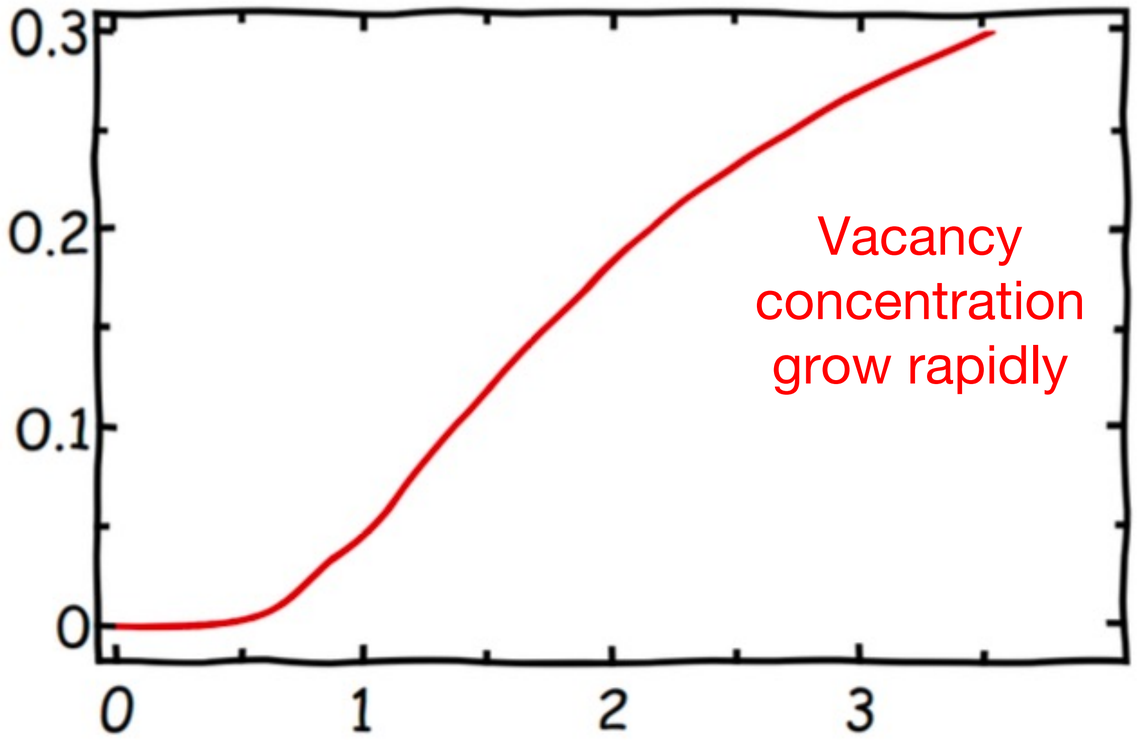
Effect of Temperature on Vacancy Formation

Vacancies cost energy ➔ increase entropy

Making a vacancy, costs an energy penalty (ϵ_v)



Fraction of lattice sites with vacancy X_V

$k_BT/(\epsilon_v)$ **Normalized temperature**

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Even at Lower Temperatures, Some Defects Exist

Intrinsic: ~10^8 vacancies/cm^3

~10^8 interstitials/cm^3

Extrinsic: ~10^{13} impurities/cm^3

Think about it as a statistical system

- Each defect has some formation energy (probability of occurring)
- Each defect has some potential impact on the system
- Goal is to understand which defects dominate and how they impact properties

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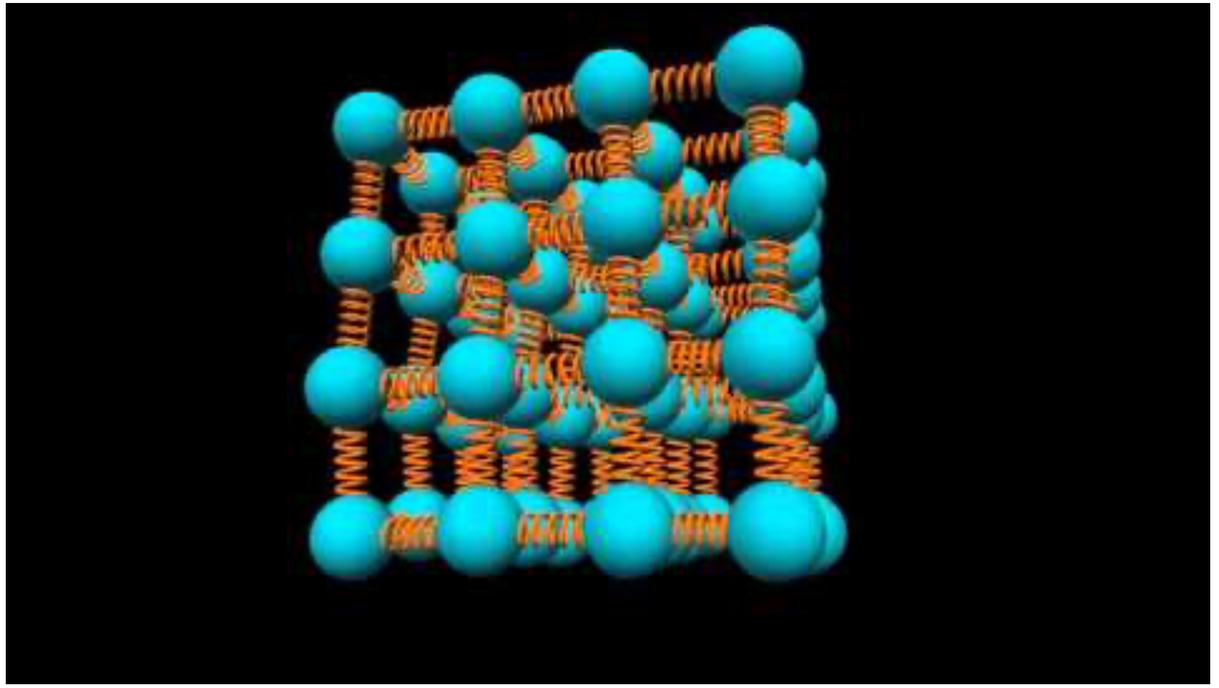
Point Defects are Not Static

Even if we could describe a location of a point defect, this can move

“Intrinsic defects” appear and disappear



Therefore, we describe **defect statistics** in the system, probability to occur, mobility (how easy it is for them to move)

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Point Defects in Real Surfaces – Vacancies & Adatoms

Point defects in 3-D

Point defects in 2-D

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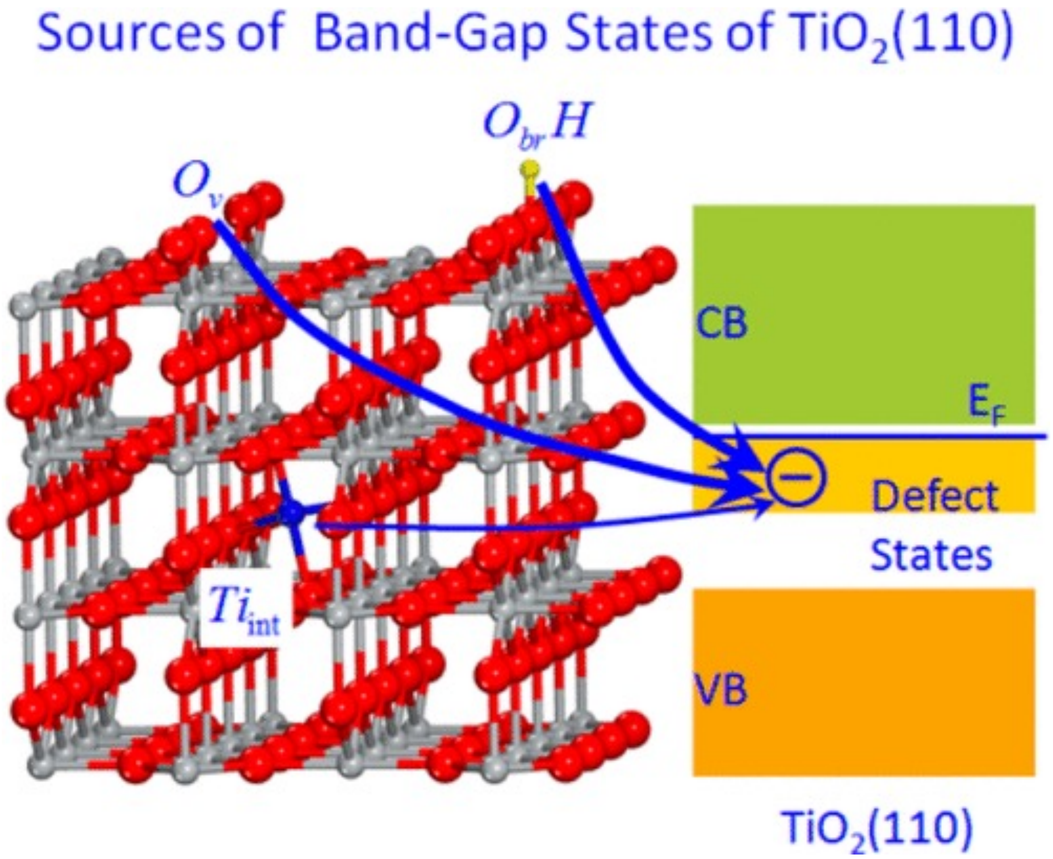
Point Defects – Why Do We Care?

Example 1: Electronic Materials – point defects can control electronic structure

Upon charged particle bombardment and UHV annealing, two kinds of major point defects arise in TiO_2: surface **O_{br} vacancies** and subsurface **Ti interstitials** (Ti_{int})



The Fermi level (E_F) is pinned to the bottom of conduction band (CB), and defect states appear at about 0.8 eV below the E_F.

Excess electrons originating from defect states affect the surface chemistry on TiO_2.

Mao *et al.* | J. Phys. Chem. Lett.| 2013

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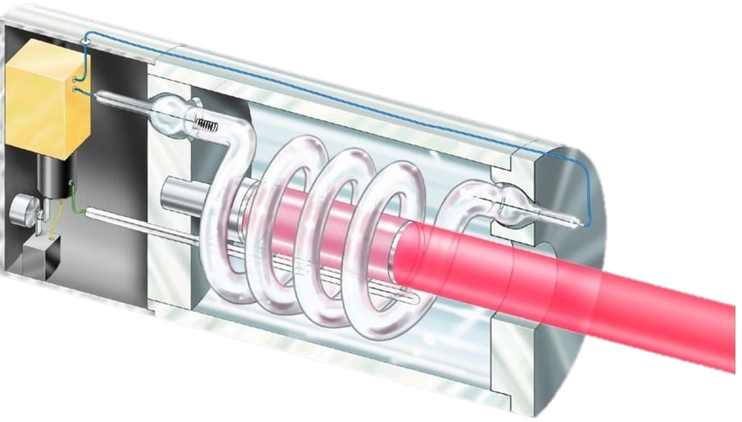
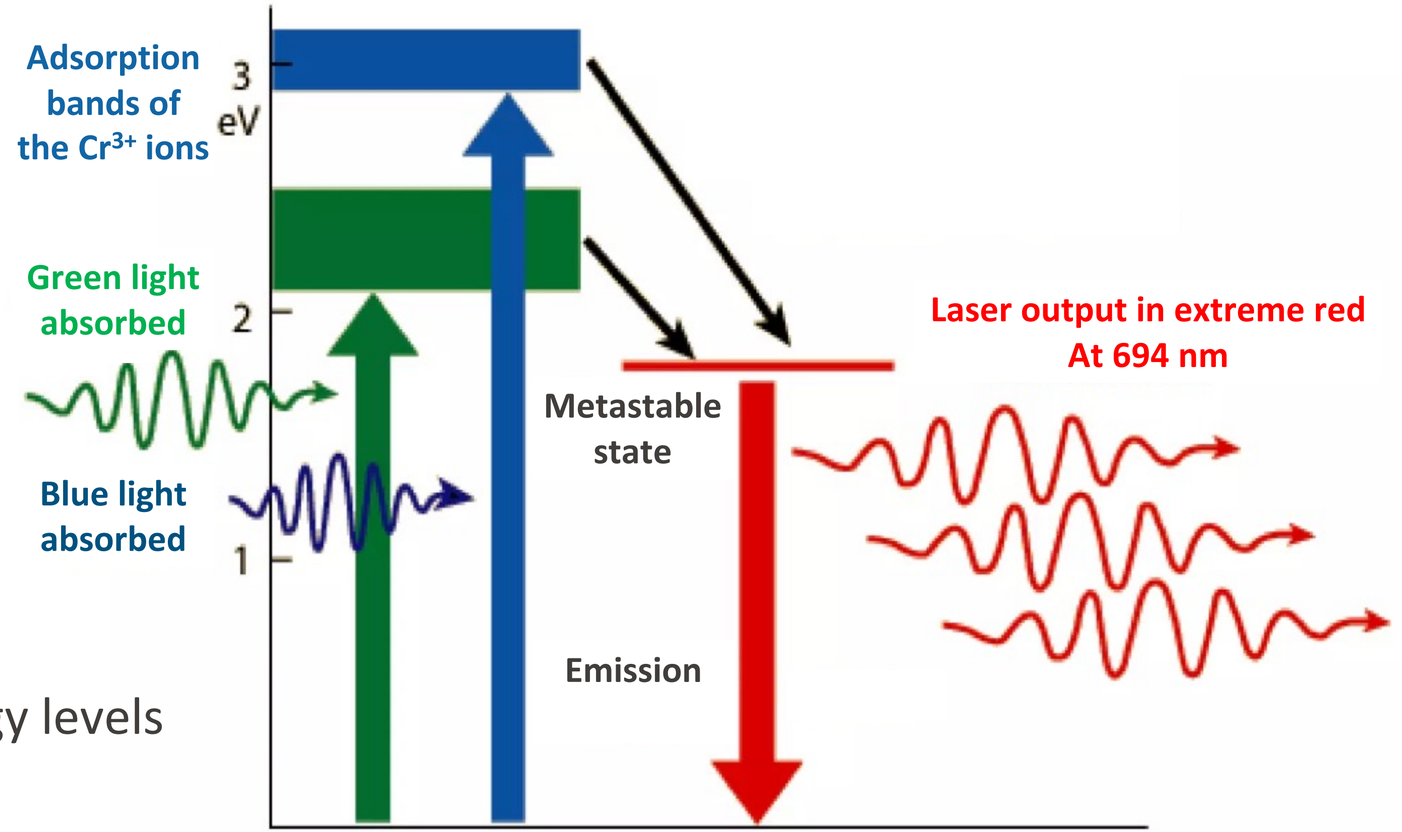
Point Defects – Why Do We Care?

Example 2: Optical transitions in the ruby laser (dermatology, tattoo removal)

Active laser medium is made of synthetic ruby, an aluminum oxide crystal where some aluminum atoms have been replaced with chromium atoms (extrinsic defect, 0.05% by weight)





Dopants absorb at specific energy levels

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Key Takeaways

- There are intrinsic and extrinsic point defects
- Defects are inevitable – even in perfect equilibrium, defects exist
- Point defects cost energy to form but increase entropy
- Point defects are not static but mobile
- Point defects influence the properties of materials for applications

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Surface Defects by Dimensionality (0-D to 3-D)

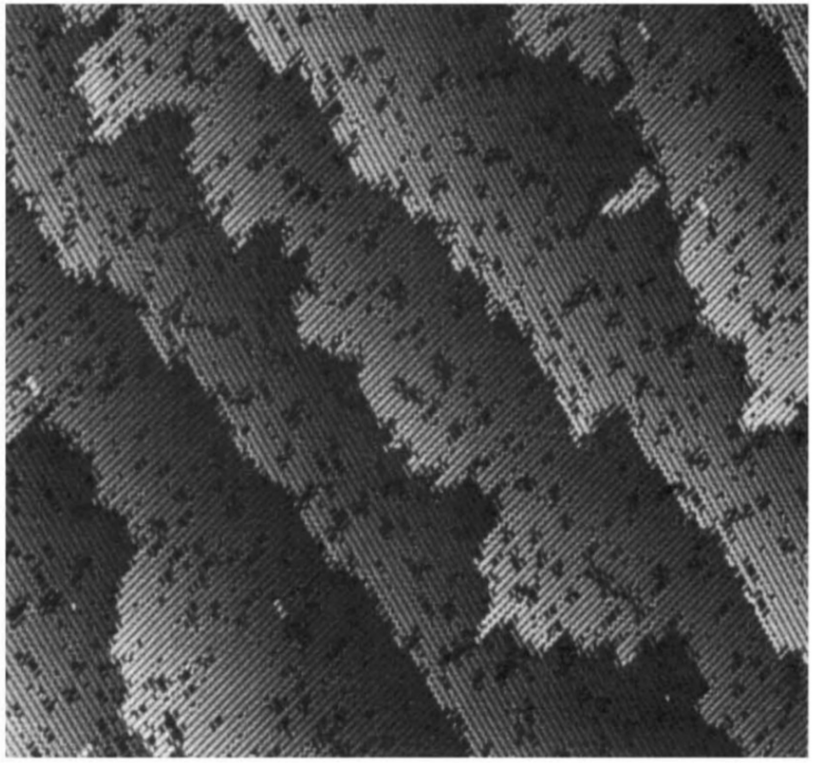
- **Point Defects** - vacancies, interstitials, adatoms
- **Line Defects** – dislocations leading to terrace, ledges, kinks
- **Surface reconstructions**
- **Bulk (volume) Defects** – voids, inclusions, pores

Line Defects (Dislocations) Arise in High Energy Planes

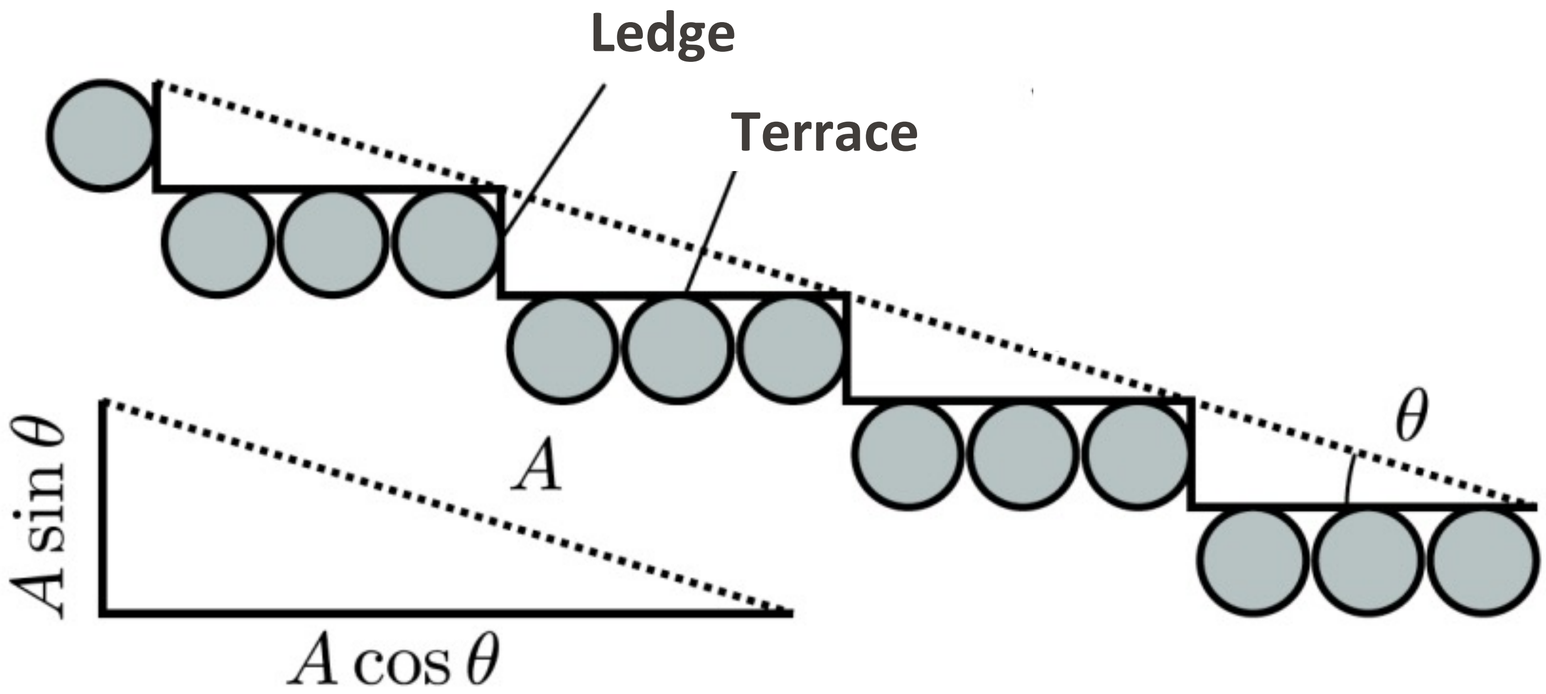
Not all surfaces of a crystal are perfectly flat

Singular surfaces ➔ atomically flat, very stable (lowest-energy crystal face)

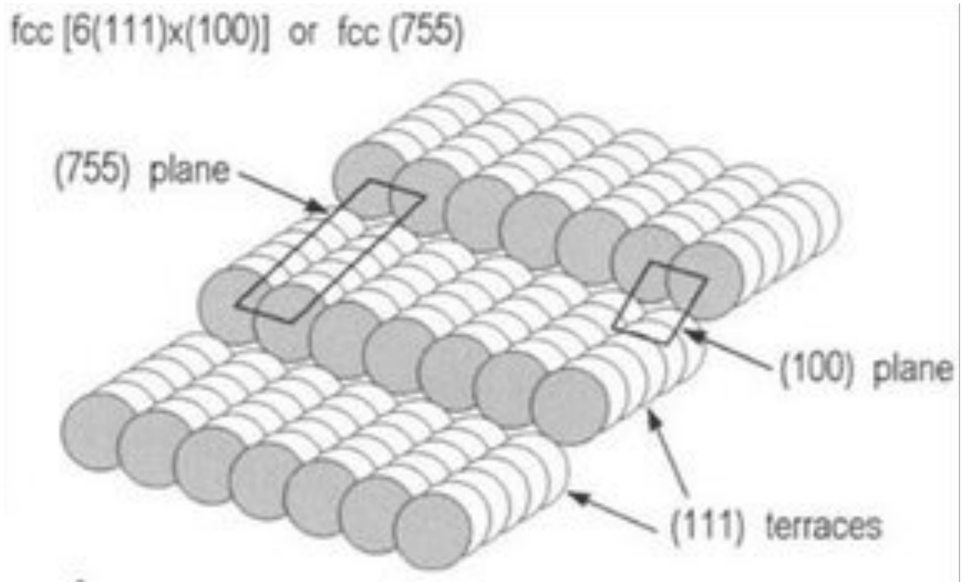
Vicinal surfaces ➔ slightly tilted surfaces exhibit faceting: flat, terraces separated by ledges



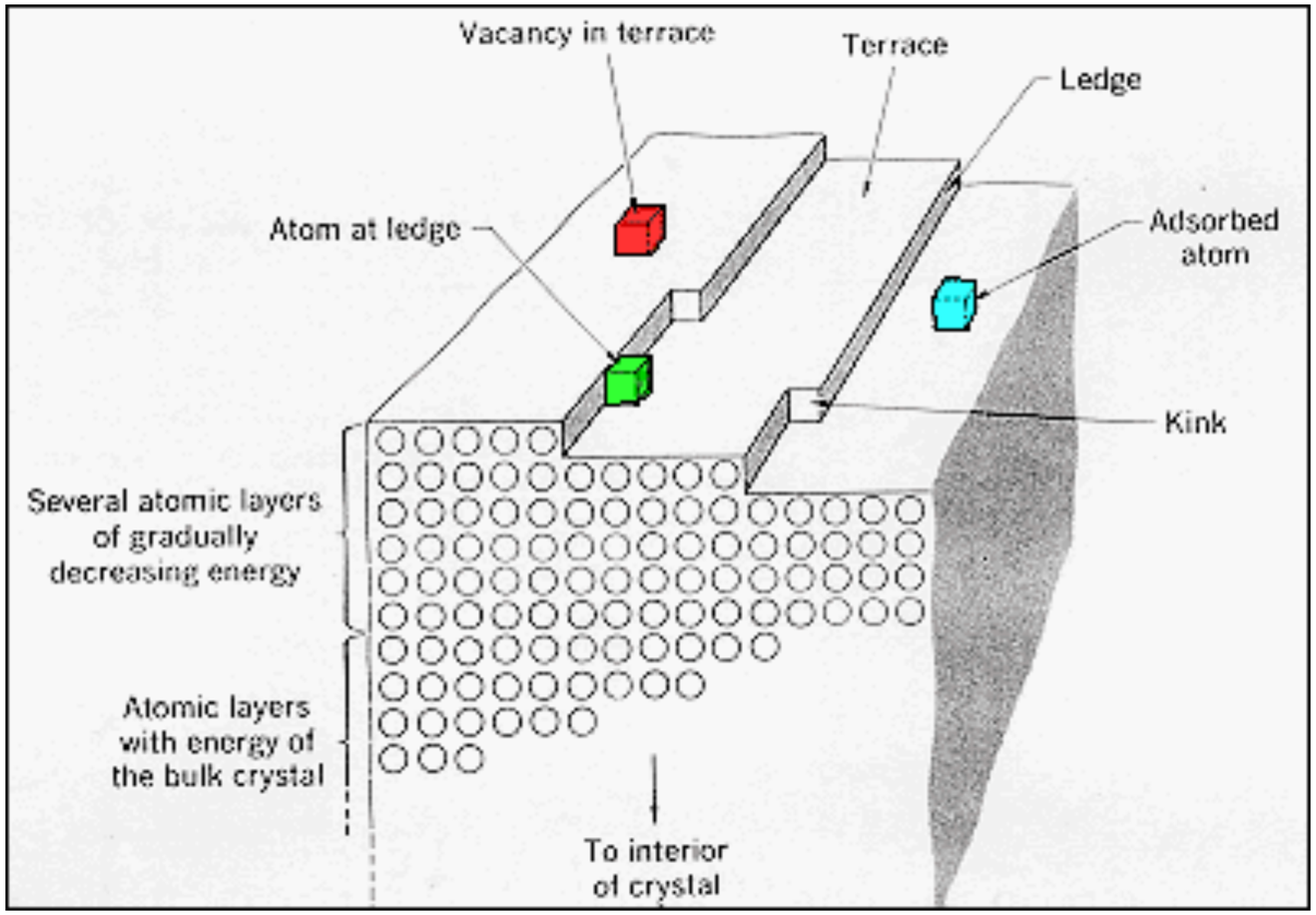
High Energy Planes Separate into Terraces and Ledges



Atomic View of Terraces and Ledges

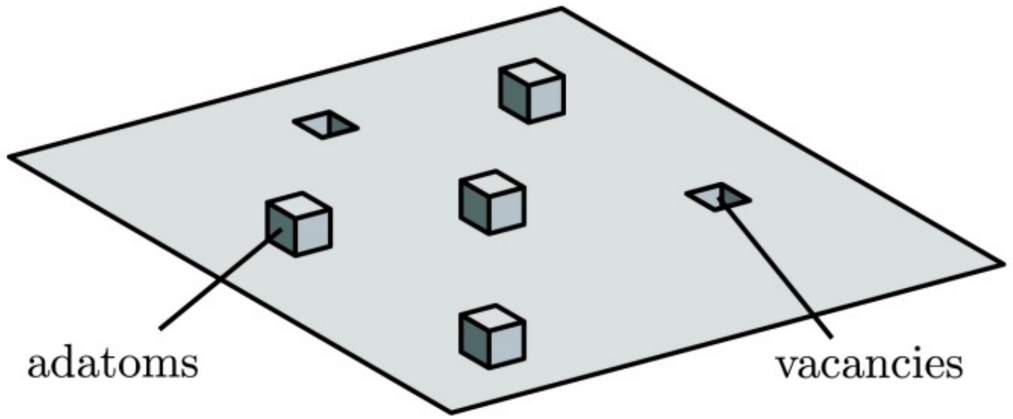


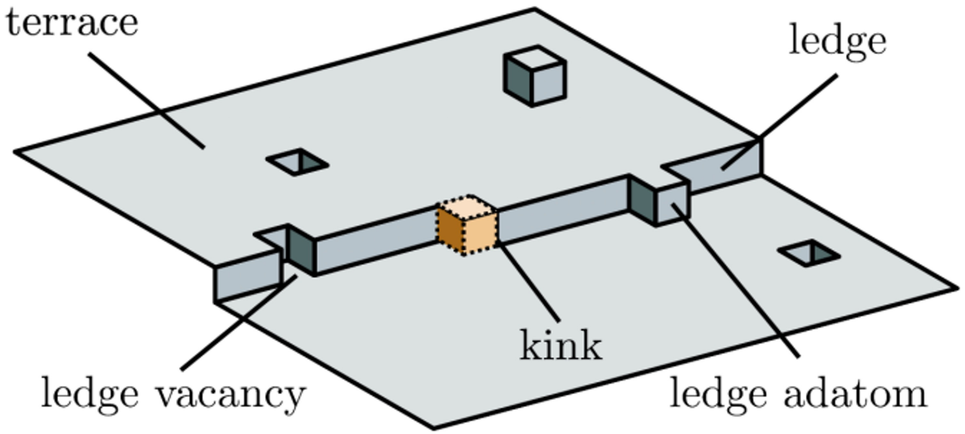
Nowicki & Wandelt | Surface and Interface Science | 2020



Complexity of Line Defects in Real Surfaces (TLK Model)

In a real surfaces with ledges and kinks in addition to vacancies and adatoms…the story is complex





Terraces ➔ atoms fully coordinated ➔ low reactivity

Ledges ➔ atoms at a step edge have fewer neighbors than terraces ➔ moderate reactivity

Kinks ➔ atoms at a kink are the least coordinated ➔ highest reactivity

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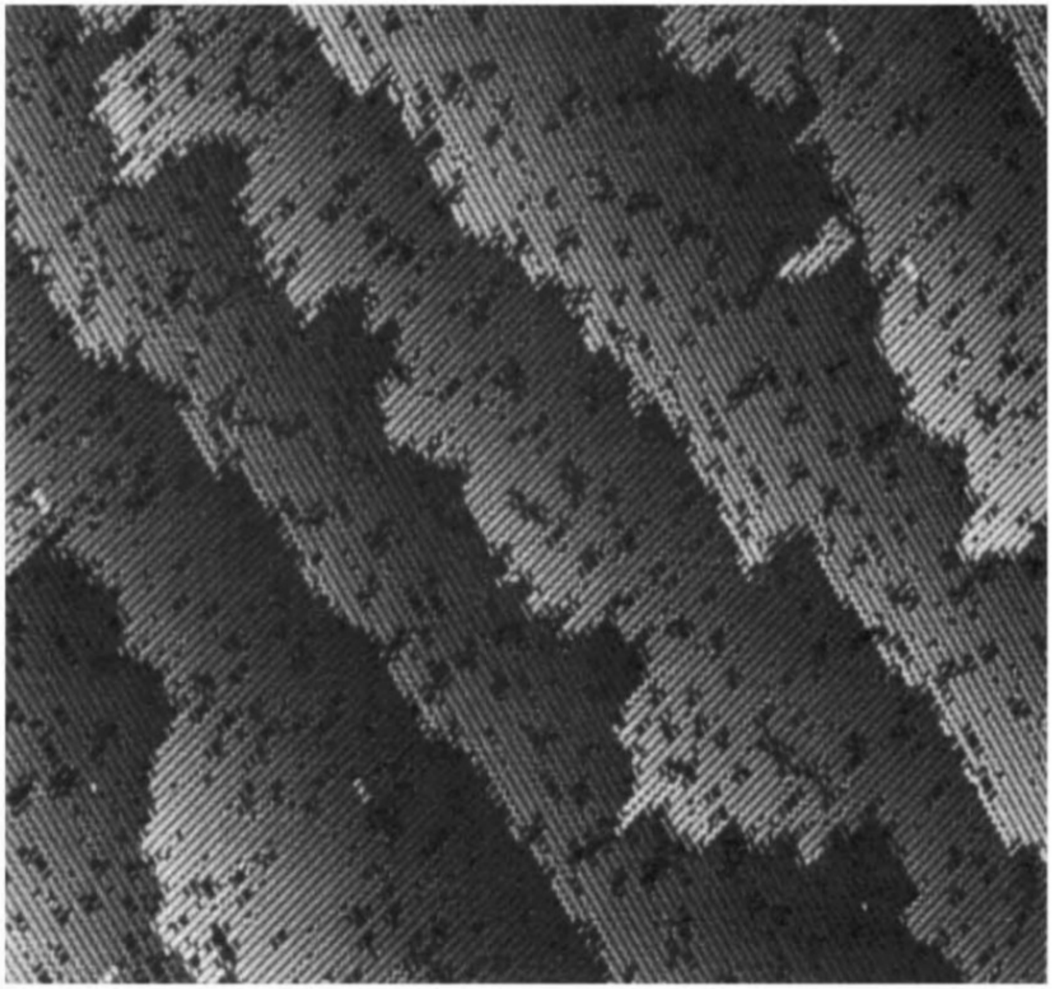
Why Line Defects (Dislocations) Matter



1. **Mechanical properties**

   Dislocations allow metals to deform

2. **Electronic properties**

   Dislocations can trap or scatter electrons (semiconductors and devices)

3. **Chemical reactivity**

   Kinks are often reactive sites for adsorption and hot spots for catalysis

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Surface Defects by Dimensionality (0-D to 3-D)

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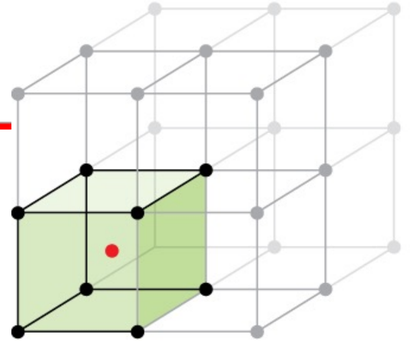
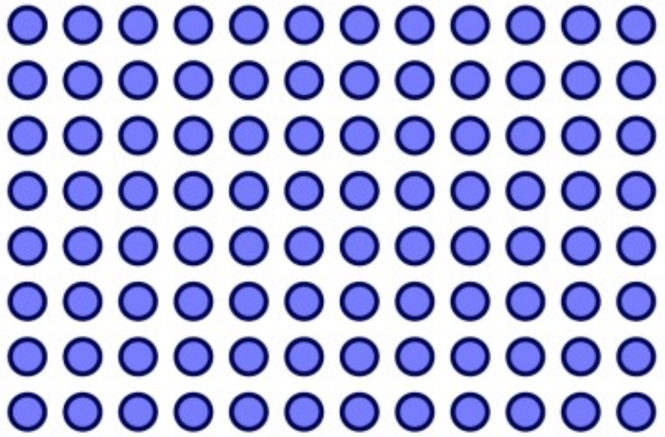
- **Line Defects** – dislocations leading to terrace, ledges, kinks
- **Surface reconstructions**
- **Bulk (volume) Defects** – voids, inclusions, pores

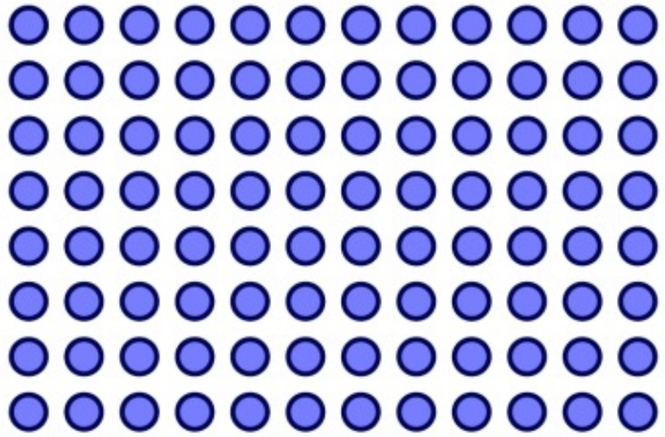
Reconstructions in Real Surfaces – Cubic Crystal



Side view



Top view



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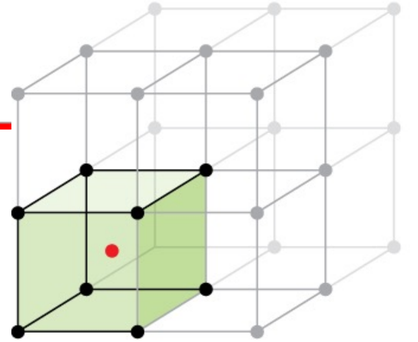
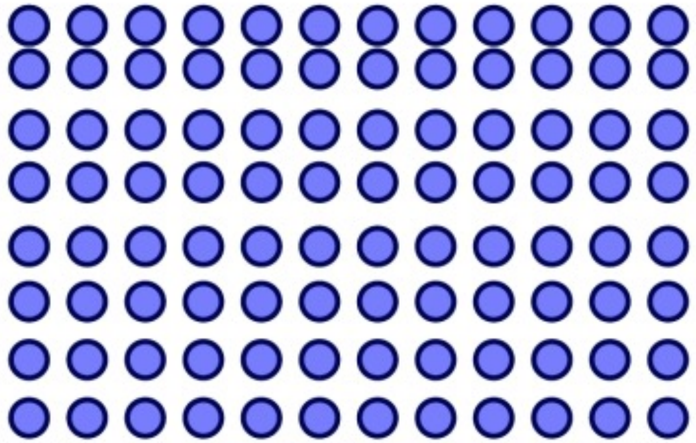
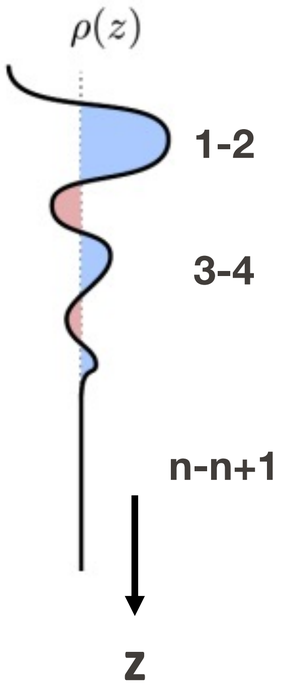
Reconstructions in Real Surfaces – Cubic Crystal



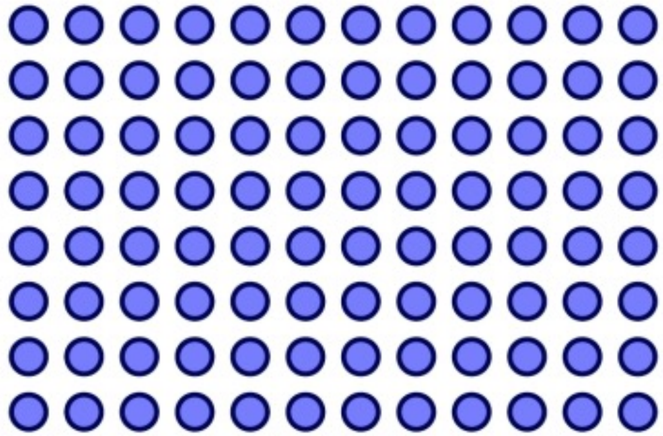
Side view



Density as function of position



Top view



Symmetry

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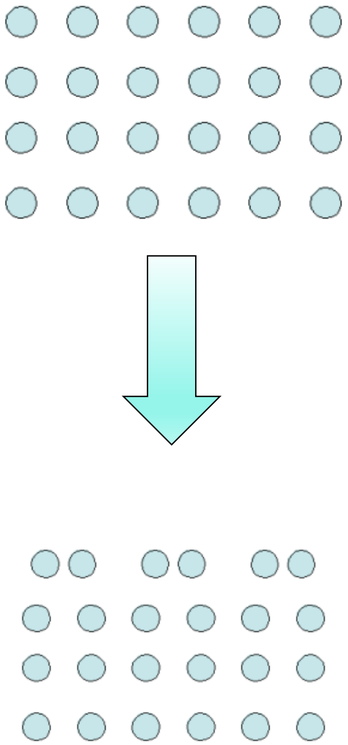
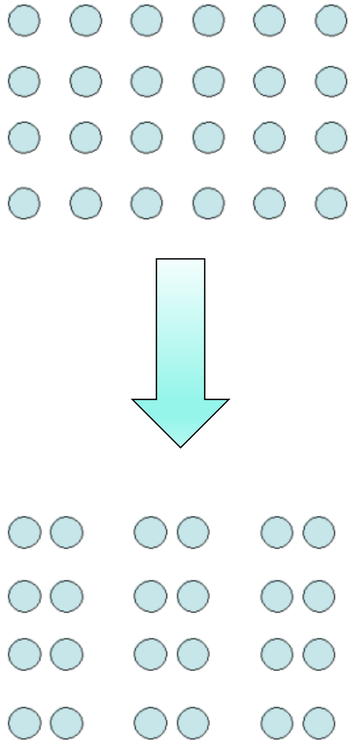
Reconstructions in Real Surfaces – Dangling Bonds

Side view



Top view



Problem: Now we broke symmetry at the surface

Surface Reconstruction: Energy penalty from unsymmetric pulling of surface bonds compensated by gain of forming bonds with two dangling orbitals

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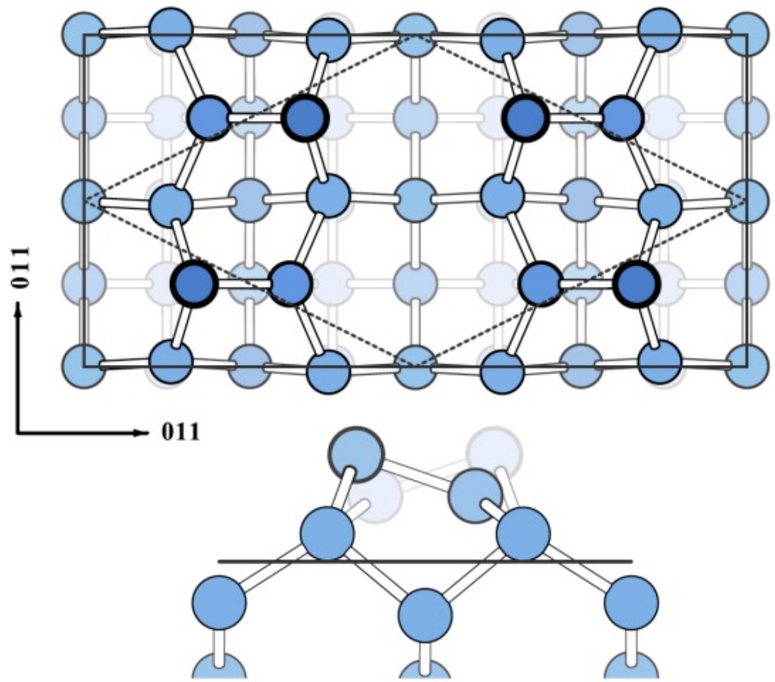
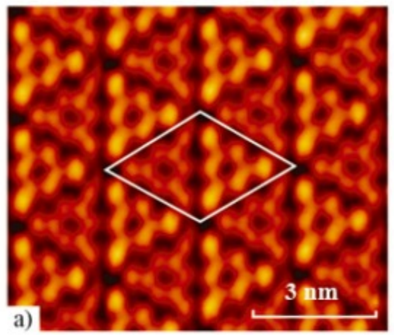
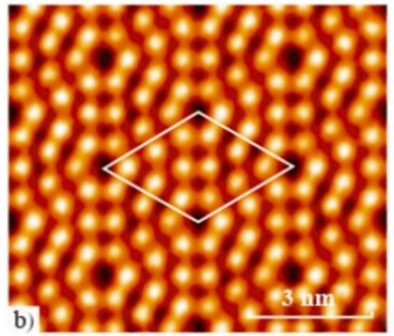
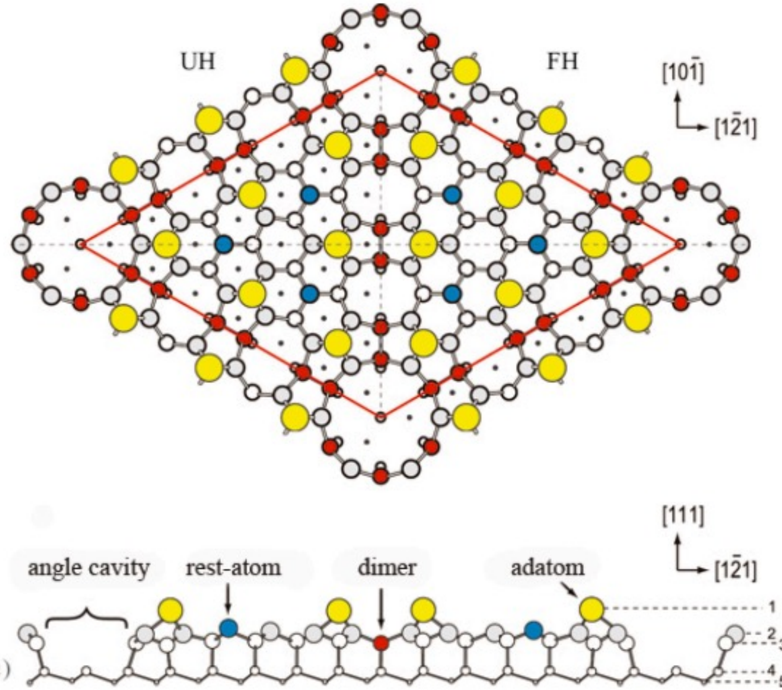
Reconstructions in Real Surfaces – Reality is Complex









Si (111) – one of the most technologically most important surfaces

Surface reconstructions determines electrical properties of semiconductors

Influence adsorption and device performance

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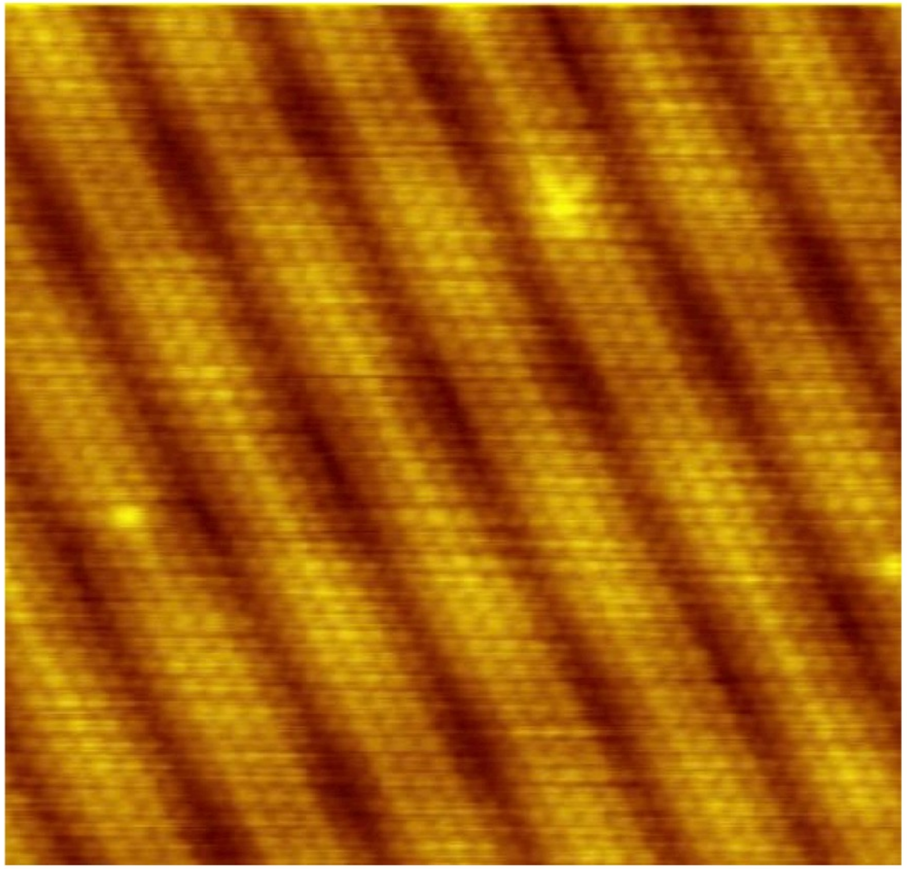
Reconstructions in Real Surfaces – Why They Matter



Au (100) – simpler reconstructions

Flat, stable surfaces for experiments

Silicon	**Gold**
Covalent bonds	Metallic bonds
Dangling bonds at the surface high in energy	Delocalized electrons screen dangling bonds
Complex reconstruction to minimize surface energy	Small relatively uniform rearrangement

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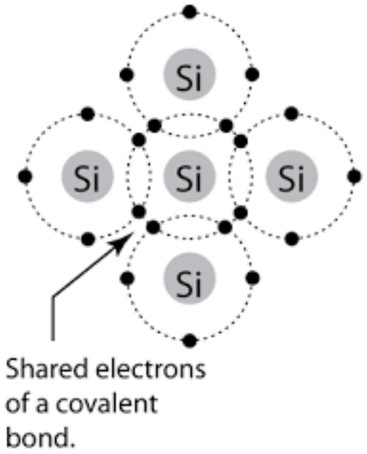
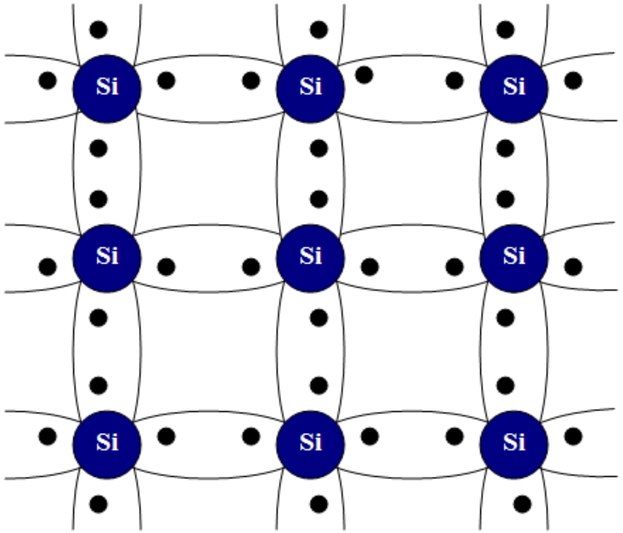
Dangling Bonds – Metals *vs.* Semiconductors

Silicon

Covalent bonds

Dangling bonds at the surface high in energy

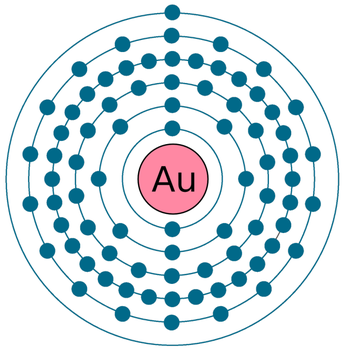


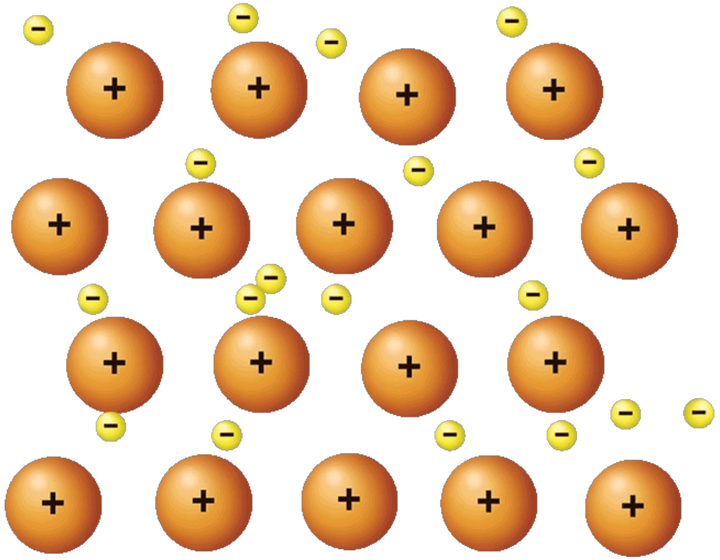


Gold

Metallic bonds

Delocalized electrons screen dangling bonds





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Key Takeaways

- Not all surfaces of crystals are flat ➔ high energy planes become TLK
- Reactivity depends on coordination of atoms T < L < K
- Line defects influence mechanical, electronic, and chemical properties
- Dangling orbitals forming dangling bonds lead to surface reconstructions
- Surface reconstructions differ between silicon and metal surfaces

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Surface Defects by Dimensionality (0-D to 3-D)

- **Point Defects** - vacancies, interstitials, adatoms
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- **Bulk (volume) Defects** – voids, inclusions, pores

Bulk (Volume) Defects in Crystals

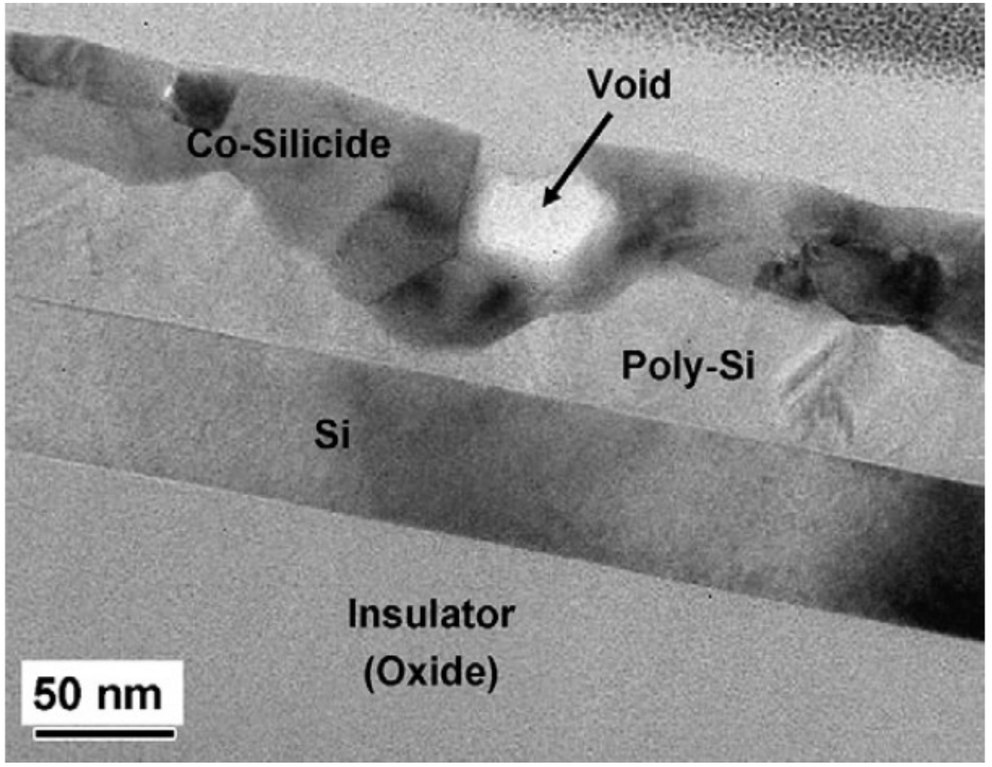
Extend over large regions of a crystal (not just a few atoms)

Caused by processing, impurities, or stresses

Types of bulk defects:

- **Voids**: empty regions
- **Inclusions**: foreign particles or phases inside
- **Cracks**: micro- or macroscale
- **Porosity**: many small voids

Voids in silicon



Raghaw & Swaminathan | Progress in Crystal Growth and Characterization of Materials | 2009

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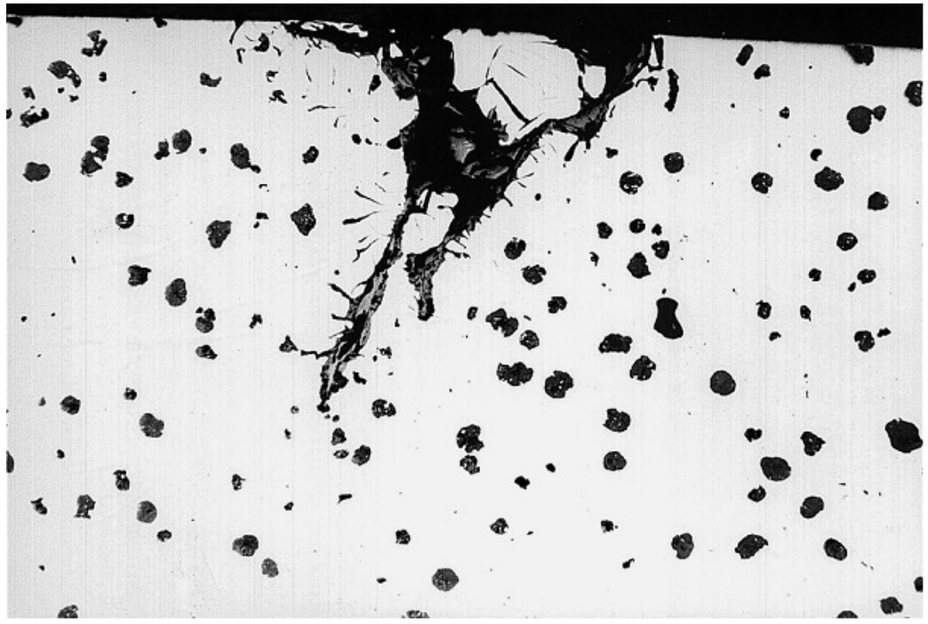
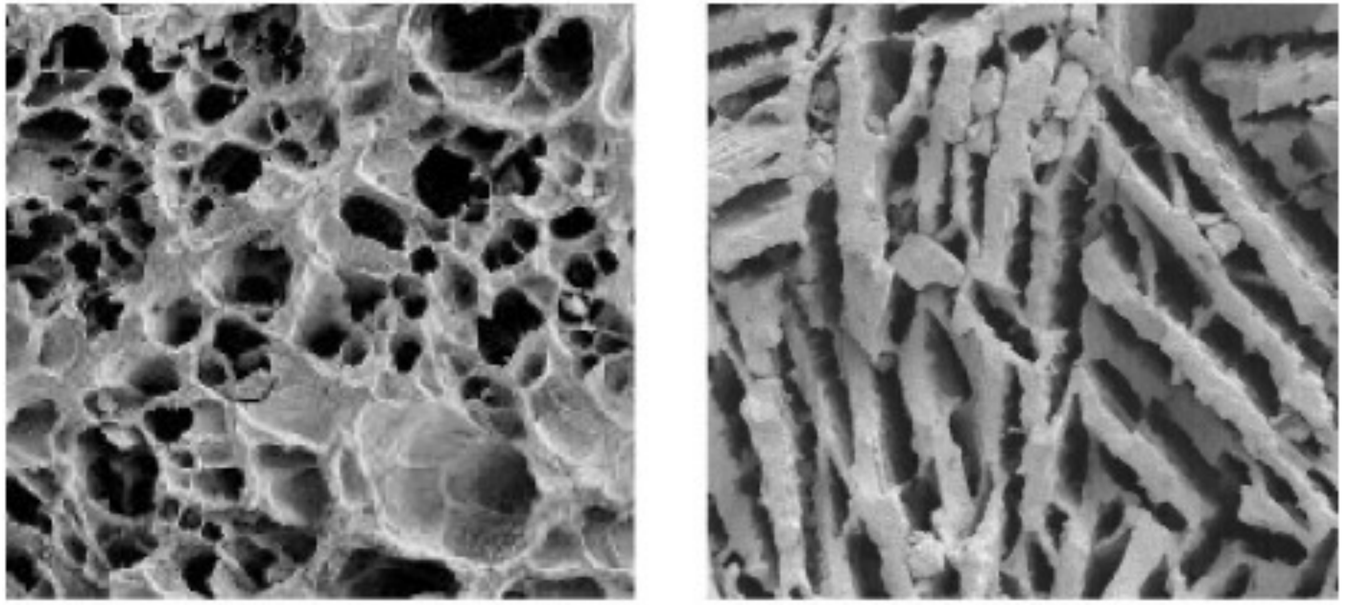
Examples of Bulk (Volume) Defects in Crystals

Oxide inclusions in iron



FOUNDRY

Porous ceramics



Orbray

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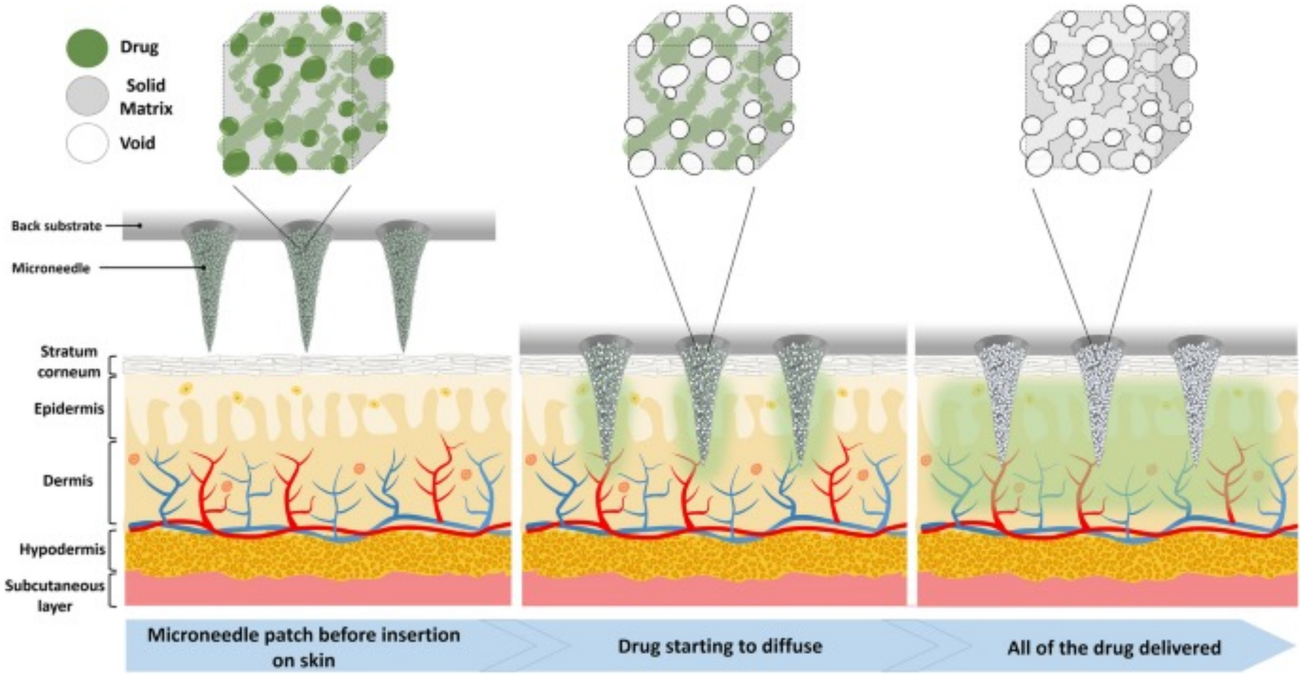
Why Bulk (Volume) Defects Matter

Destructive

PHYS.ORG

Constructive



Sadeqi| Scientific Reports | 2022

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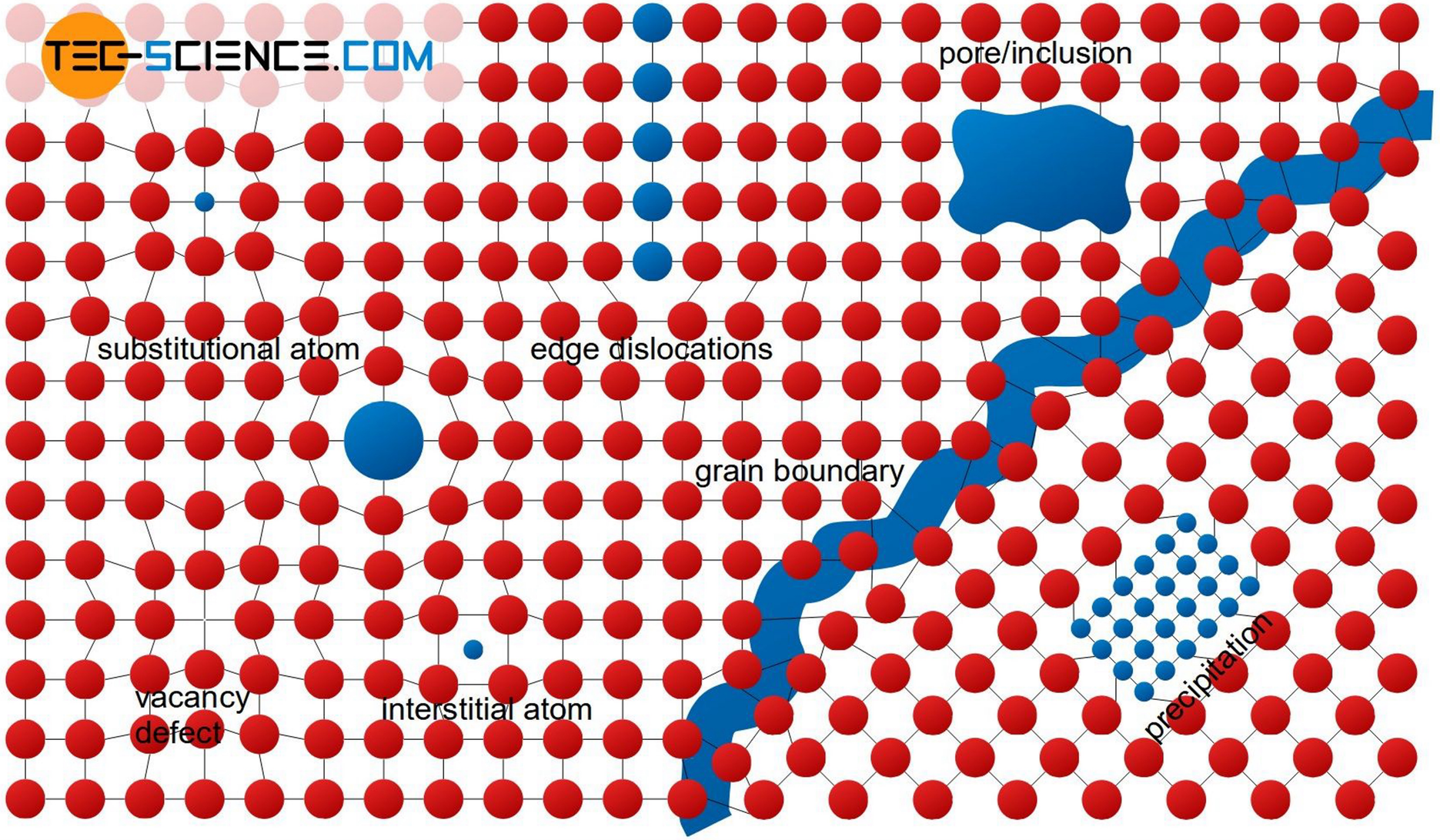
Summary of Various Crystal Defects



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Summary of Today's Class

- Different planes of surfaces have different surface energies ➔ Crystal shape
- By controlling surface energy, control morphology of materials
- Perfect crystals do not exist
- Surface defects from 0-D to 3-D exist - all about energy minimization
- Defects can be harnessed or cause problems in various applications

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