École polytechnique fédérale de Lausanne

CHEMINA
Laboratory of Chemical Nanotechnology

Solid-Solid Interfaces
Lesson 5

MSE 304

Nako Nakatsuka

Nako.Nakatsuka@epfl.ch

October 10th 2025

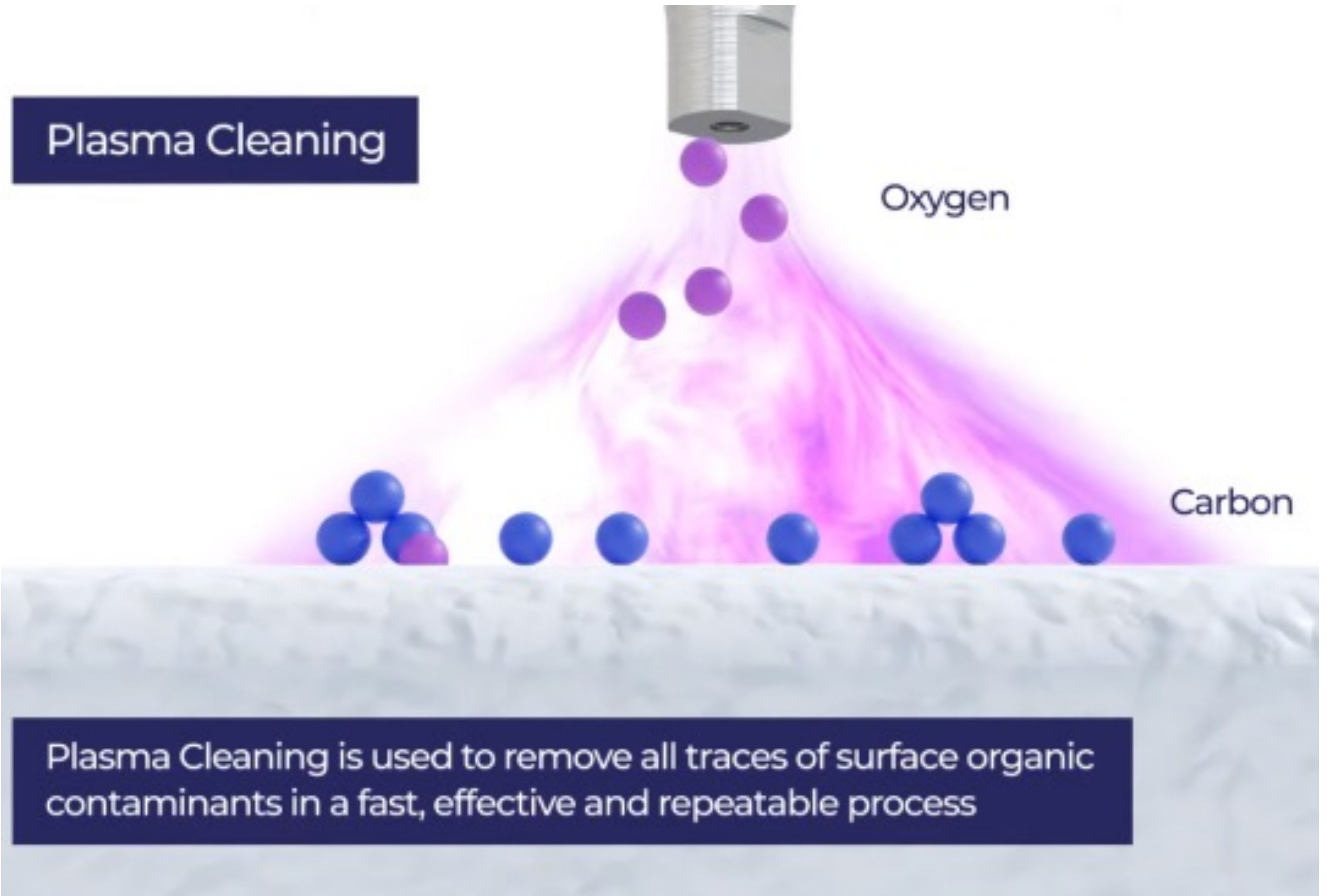
Indicative Feedback – Open Until Sunday 12 October

Single question: *“the running of the course enables my learning and an appropriate class climate”*

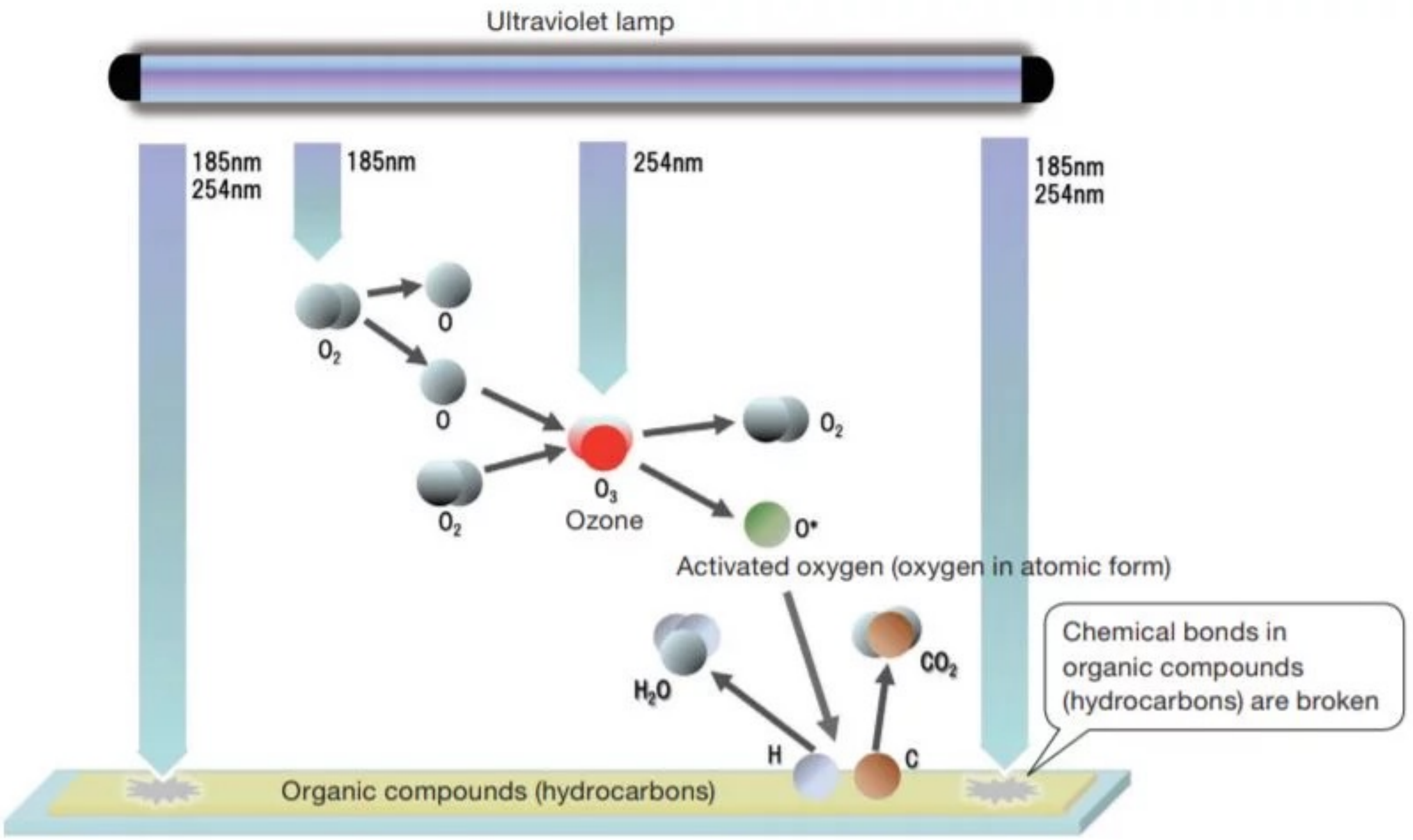
BUT there is a comments section where you can consider:

- How is the pace of the course?
- Do you find the amount of material covered each week manageable?
- Do you understand the key concepts so far?
- How are you finding the exercise session with the TAs?
- Are you comfortable engaging in class and in the exercise session?

Recap on Questions During Exercise Session : Plasma/UV Ozone

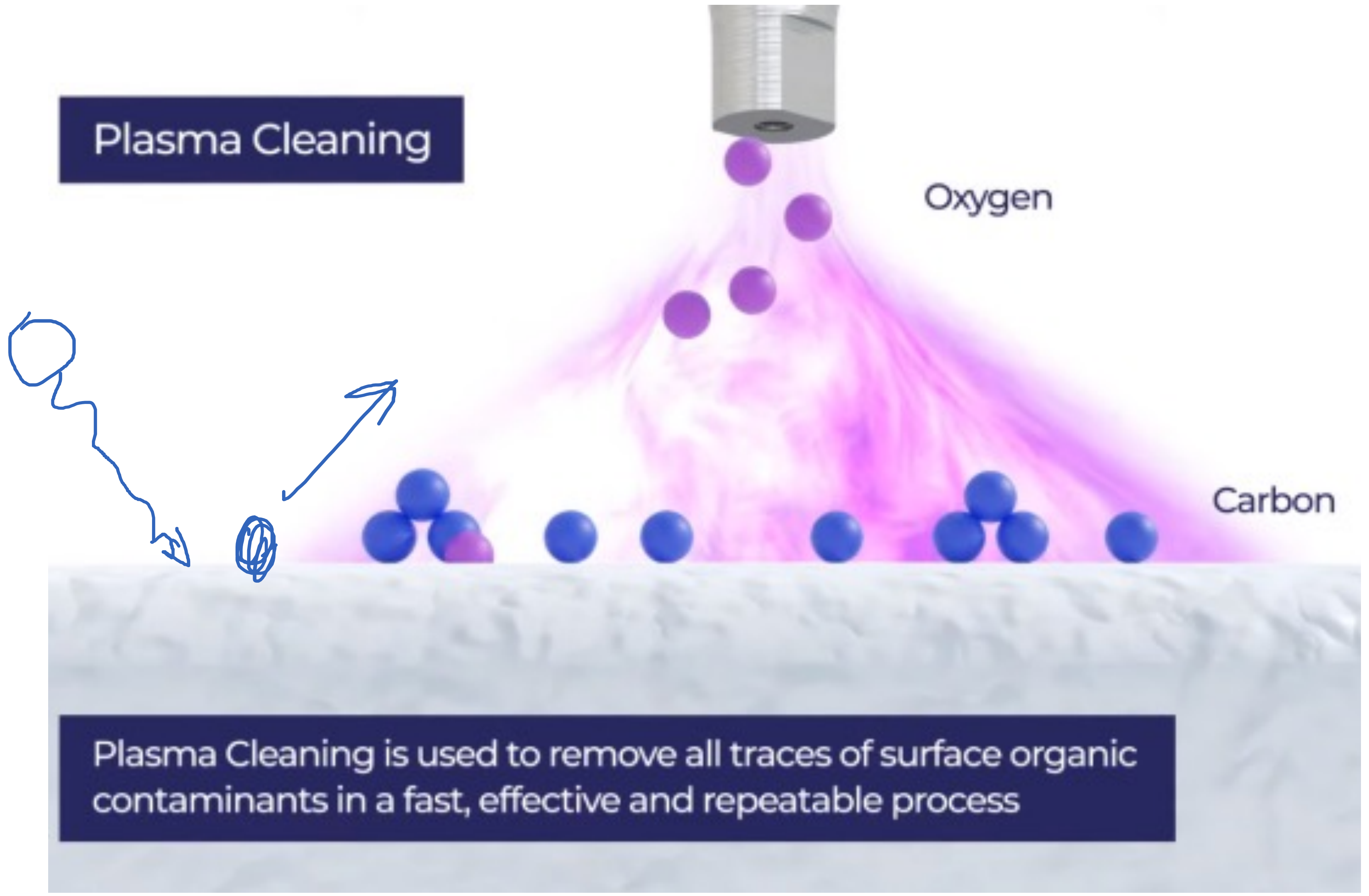


Plasma Cleaning is used to remove all traces of surface organic contaminants in a fast, effective and repeatable process



Energy source	Electrical discharge	UV light (185, 254 nm)
Speed	Fast (seconds – minutes)	Slow (minutes – hours)
Aggressiveness	More aggressive, can etch surface	Gentler treatment, mainly oxidizes

Recap on Questions During Exercise Session : Plasma/UV Ozone



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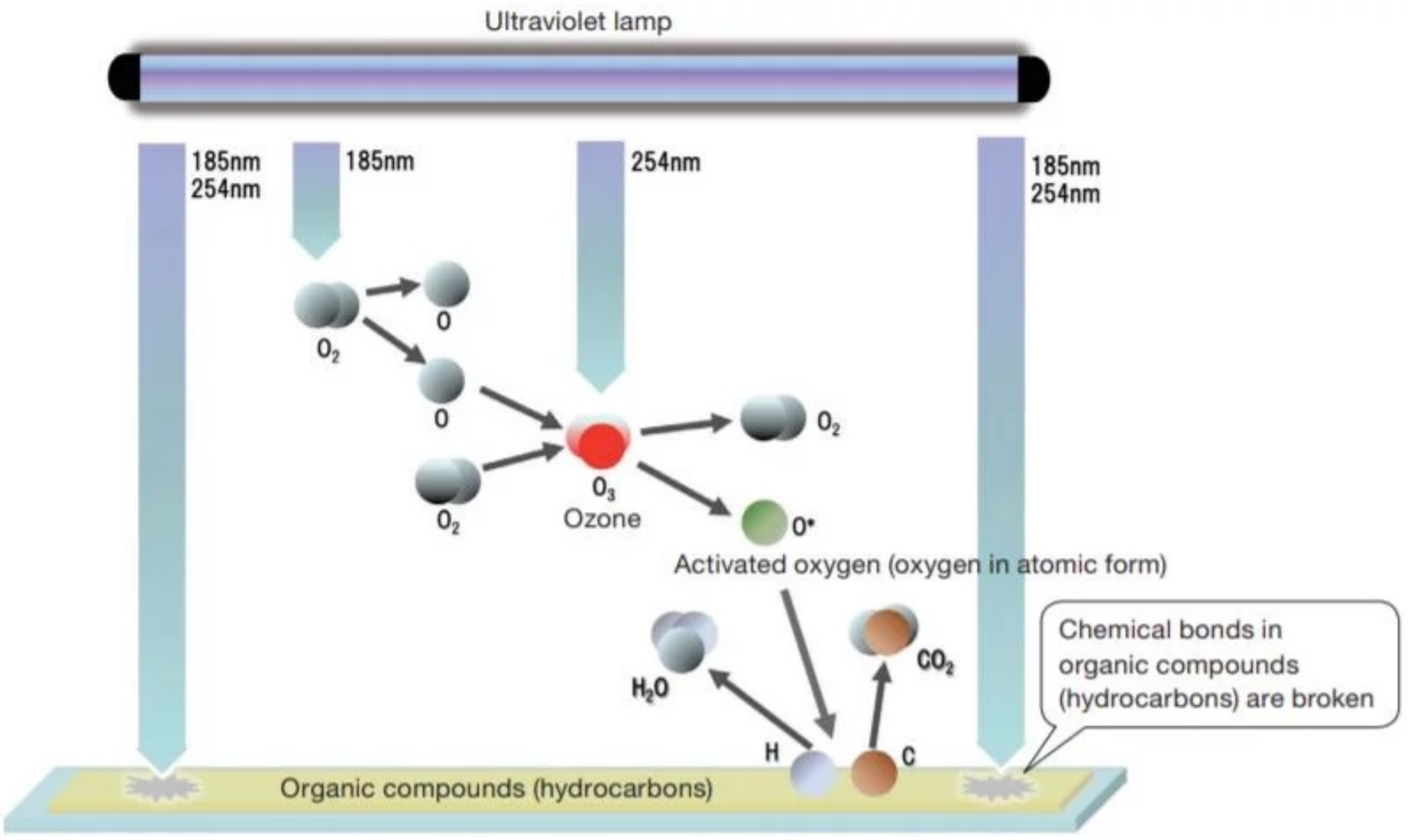


Main reactive species	O radicals (O·), O^+ ions, electrons, excited O_2*	Atomic oxygen (O·) and ozone (O_3)
Cleaning mechanism	Physical sputtering and chemical oxidation — radicals and ions remove contaminants	Oxidize organic contaminants. The UV also helps decompose organics directly via photolysis.

C–H

Various Species Get Generated in Plasma

Plasma is an ionized gas – state of matter where neutral molecules, ions, electrons, and excited species coexist and constantly interact (network of reactions)

Species	Charge	Lifetime	Main role	Acts by
O· (atomic oxygen radicals)	Neutral	microseconds–milliseconds	Chemical oxidation of organic contaminants	Reacts chemically to form CO_2, H_2O
O^+ (positive oxygen ions)	Positive	nanoseconds	Physical sputtering, activation	Bombards surface, transfers momentum, creates dangling bonds
e^- (electrons)	Negative	very short	Ionization, excitation	Keeps plasma sustained, can break bonds or excite O_2
O_2* (excited oxygen)	Neutral (excited state)	microseconds	Energy transfer, mild oxidation	Can emit UV photons or react to form radicals

High E

$e^- + O_2 \rightarrow 2O^{\cdot} + e^-$

$e^- + O_2 \rightarrow O_2^+ + 2e^-$

$\hookrightarrow O_2^+ + O_2 \rightarrow O^+ + O_2 + O$

Low E $e^- + O_2 \rightarrow O_2^* + e^-$

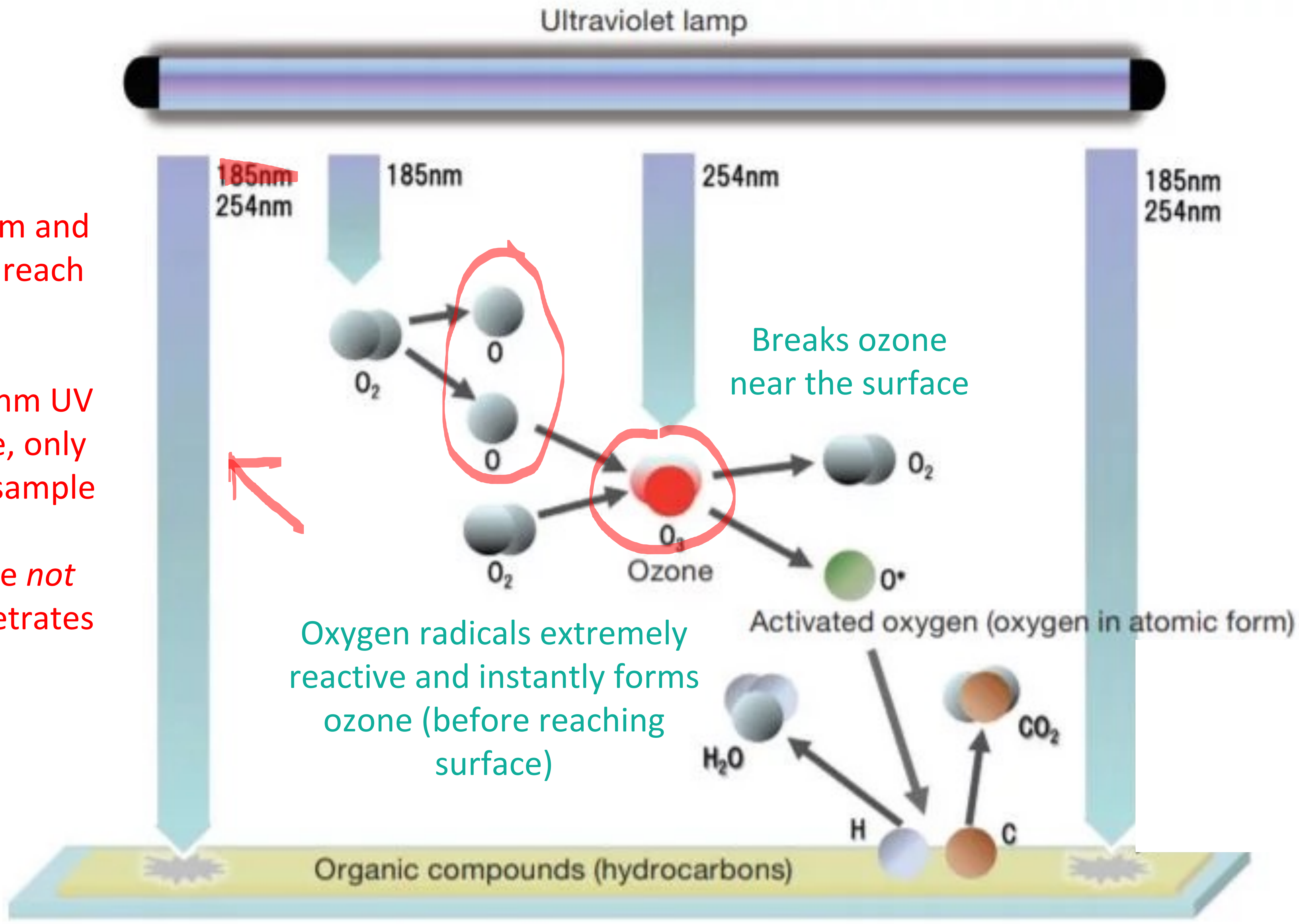
Roles of Different Wavelengths in UV Ozone Cleaning

Question: Why can't the oxygen radicals formed by the 185 nm UV directly clean surface?

Misleading – both 185 nm and 254 nm photons do not reach surface equally

Almost none of the 185 nm UV light reaches the surface, only acts in gas phase above sample

The 254 nm photons are *not* absorbed by O_2 and penetrates closer to surface



Breaks ozone near the surface

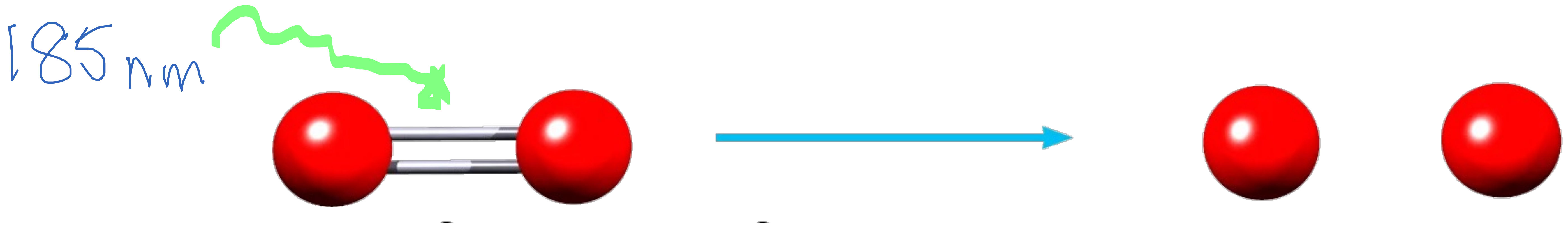
Oxygen radicals extremely reactive and instantly forms ozone (before reaching surface)

Upper gas layer

Near surface

Different Wavelengths Break Different Bonds

Calculate the energy of 185 nm vs. 254 nm UV light – which can break the double bond in O_2?



Bond dissociation energy (E required to break one mole of double bond) for O=O: **498 KJ/mol**

Energy of 185 nm photon:

$$E = \frac{hc}{\lambda} \qquad E = \frac{(6.63 \times 10^{-34}\ \text{J s}) \times (3.00 \times 10^{8}\ \text{m/s})}{1.85 \times 10^{-7}\ \text{m}} = 1.08 \times 10^{-18}\ \text{J (per photon)}$$

$$1.08 \times 10^{-18}\ \text{J} \times 6.022 \times 10^{23} = 6.51 \times 10^{5}\ \text{J/mol} = \boxed{\textbf{651 kJ/mol}}$$

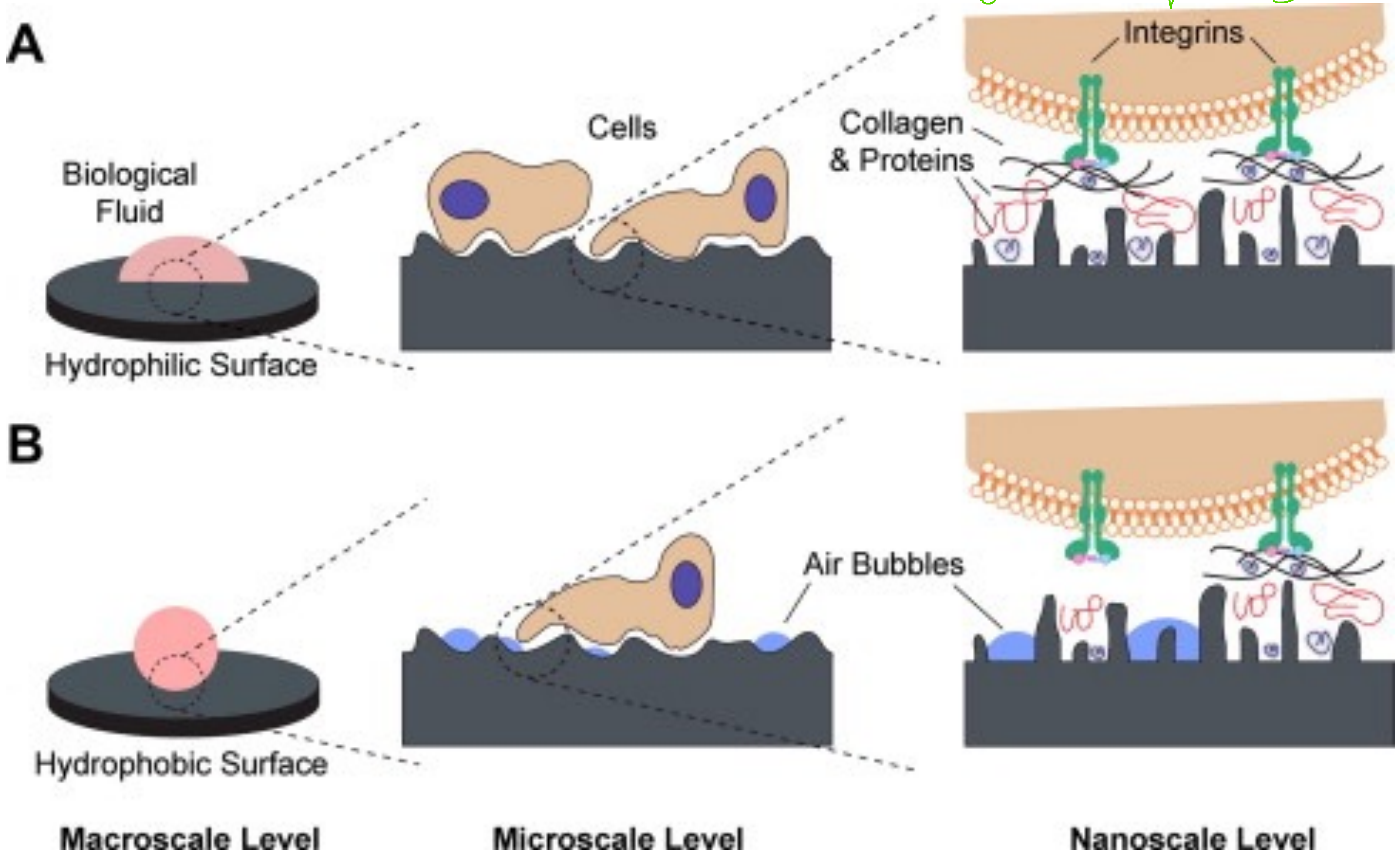
✓

Energy of 254 nm photon: **472 kJ/mol** vs. 489

Real-life Applications For Hydrophobic/Hydrophilic Coatings

Question: Should medical implants be hydrophobic or hydrophilic?

biocompatible



Gittens *et al.* |Acta Biomaterialia| 2014

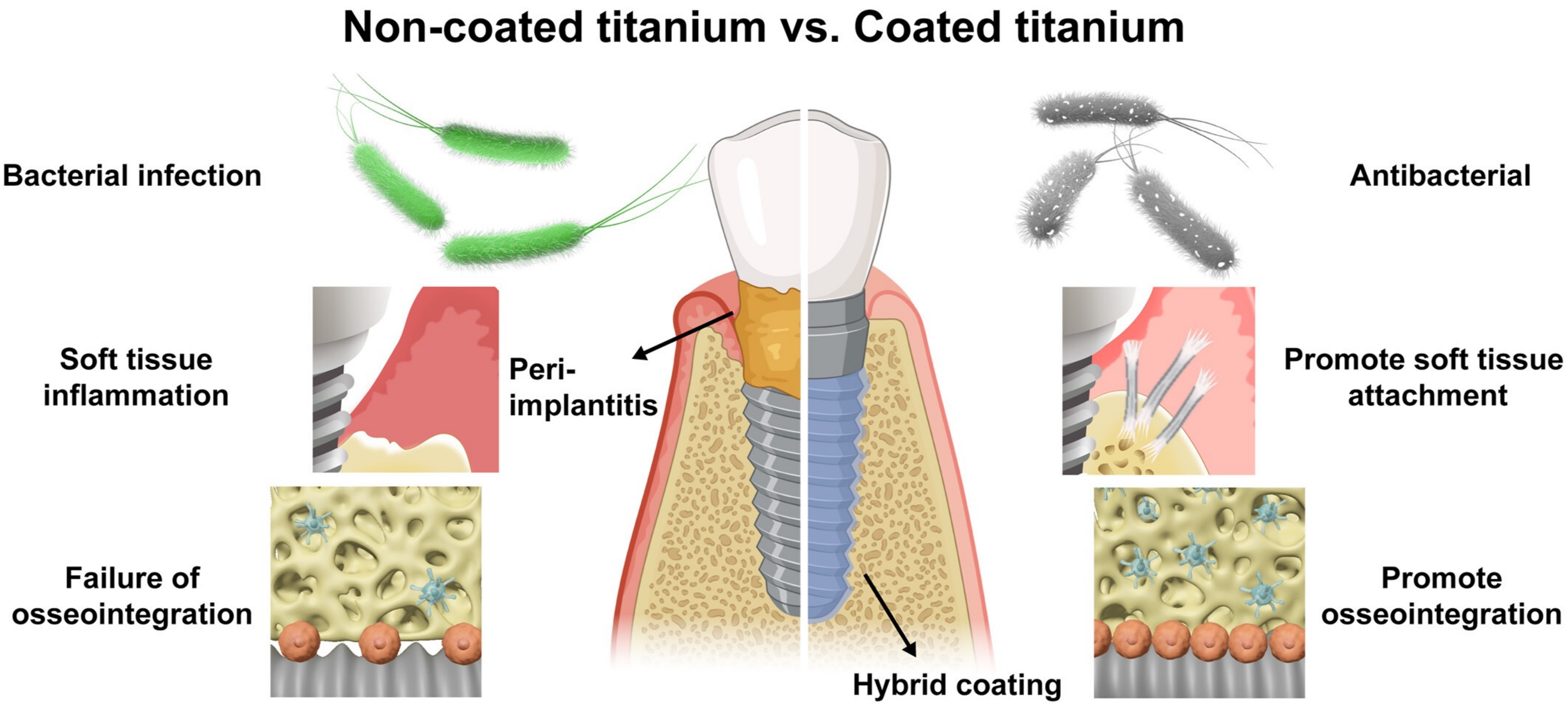
Nonspecific Bind

"Recent studies suggest a general stimulating effect of higher surface hydrophilicity on hard and soft tissue integration with the implant, yielding accelerated healing and early tissue integration.

The optimal degree of hydrophilicity for best biological and clinical outcomes remains unclear."

Real-life Applications For Hydrophobic/Hydrophilic Coatings

Hybrid coatings that integrate hydrophilic and hydrophobic components



Tang *et al.* |BME Mat | 2024

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: Solid-Solid Interfaces

6: Recap?

7: Characterization of Real Surfaces

8: Solid-Liquid Interfaces

9: Surface Chemistry

10: Biological Processes at Surfaces

11: Electronic Properties of Surfaces

12: Thin Film Technologies

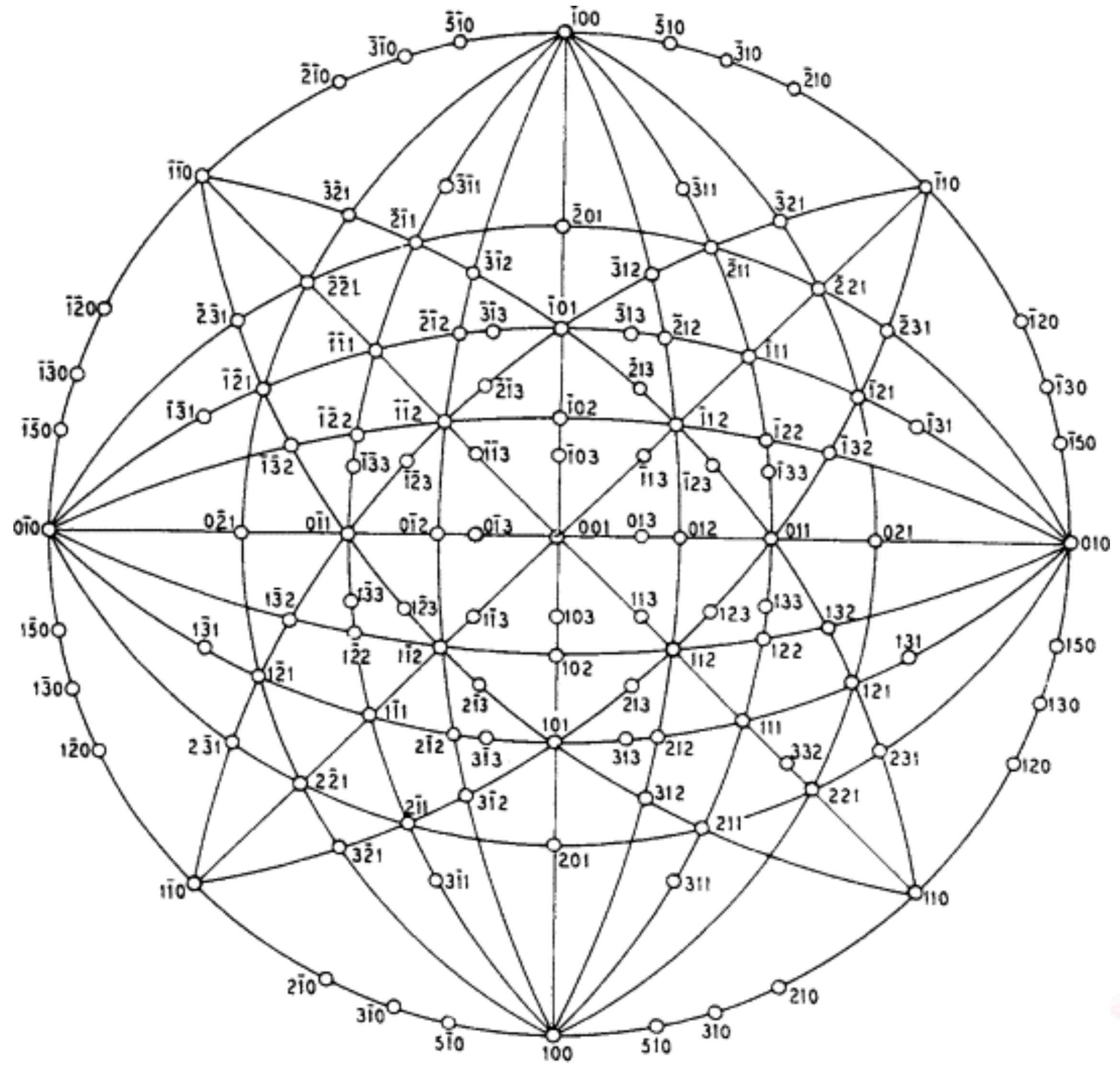
13: Biosensor Fundamentals

14: Biosensing applications

Would you like a recap session next week?

Recap from Lesson 4

- Crystals are never perfect
- Crystal structures driven by planes of surfaces having different surface energies
- Wulff construction shows equilibrium crystal shape
- Surfaces cost energy because bonds are broken
- Controlling surface energy, we can control material morphology

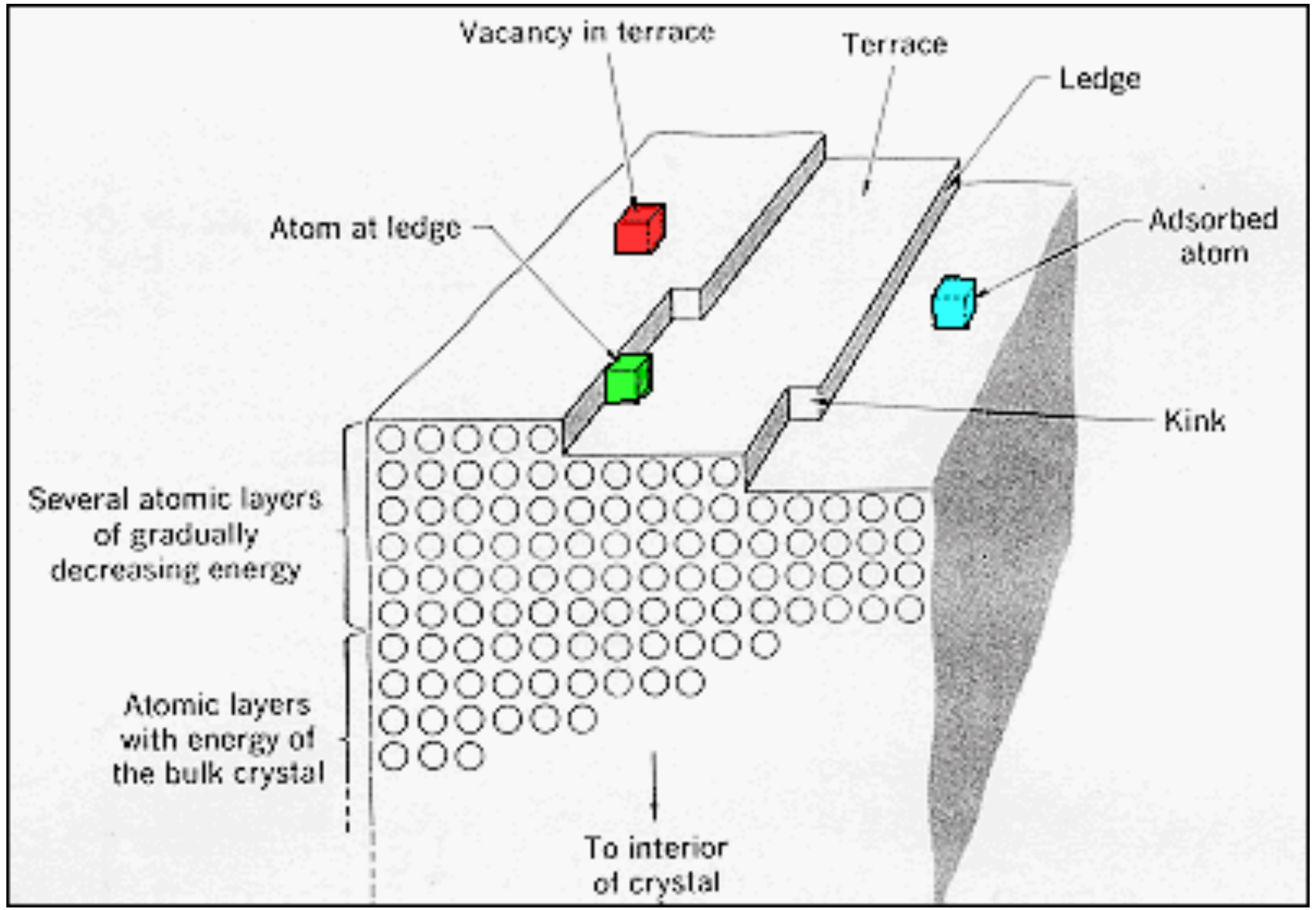


Recap from Lesson 4 – From 0-D to 3-D Defects

- Surface defects are based on energy minimization
- Defects are inevitable – even in perfect equilibrium defects exist
- Challenges and opportunities of defects

- ➢ **Point Defects** - vacancies, interstitials, adatoms 0D
- ➢ **Line Defects** – dislocations, terraces, ledges, kinks
- ➢ **Surface reconstructions**
- ➢ **Bulk (volume) Defects** – voids, inclusions, pores

3D



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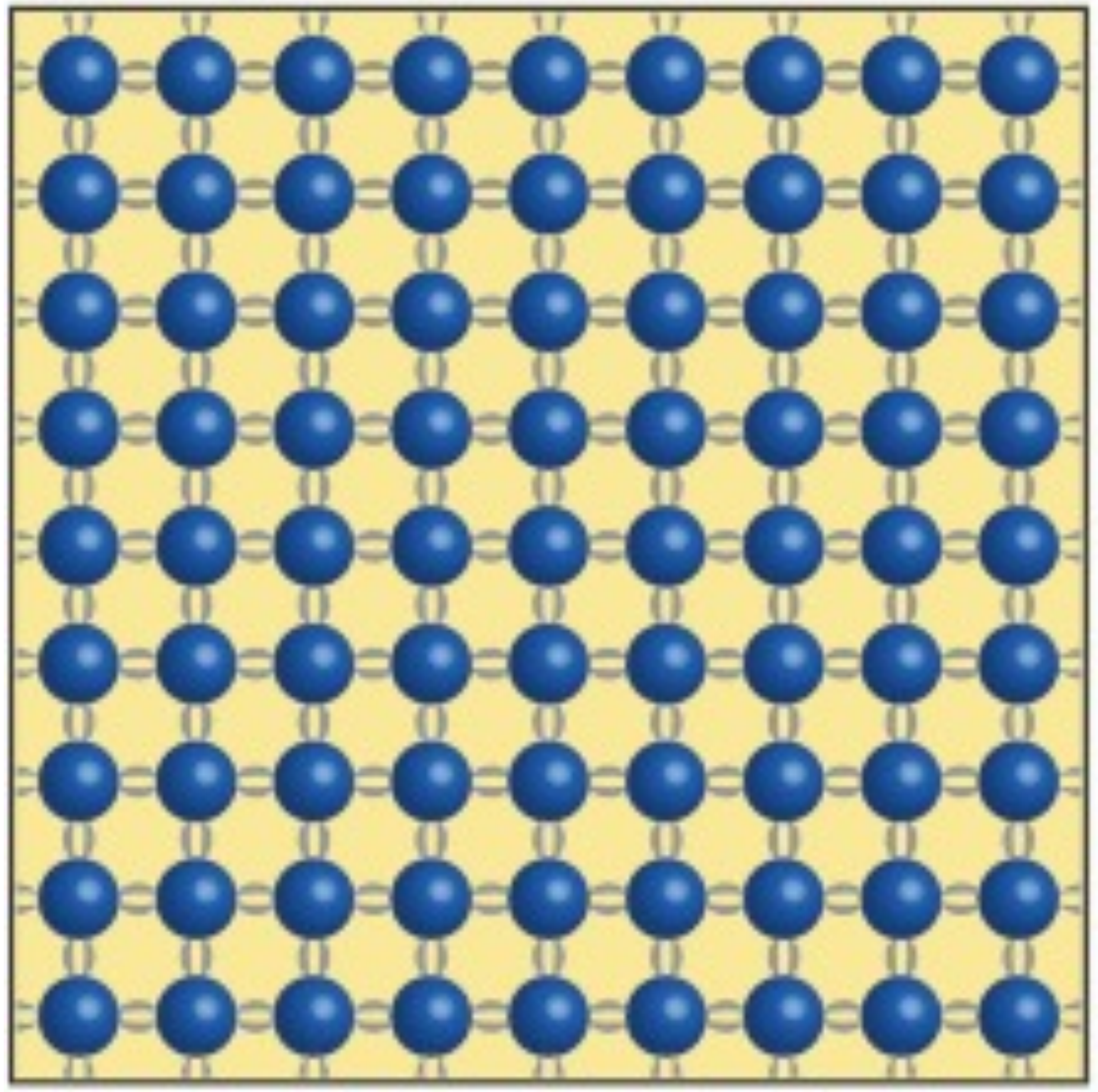
Outline of Lesson 5

- Homophase/heterophase solid-solid interfaces
- Introduction to grain boundaries (2-D defects)
- Energetics of grain boundaries
- Different types of grain boundaries
- How defects influence properties
- Electron microscopy techniques

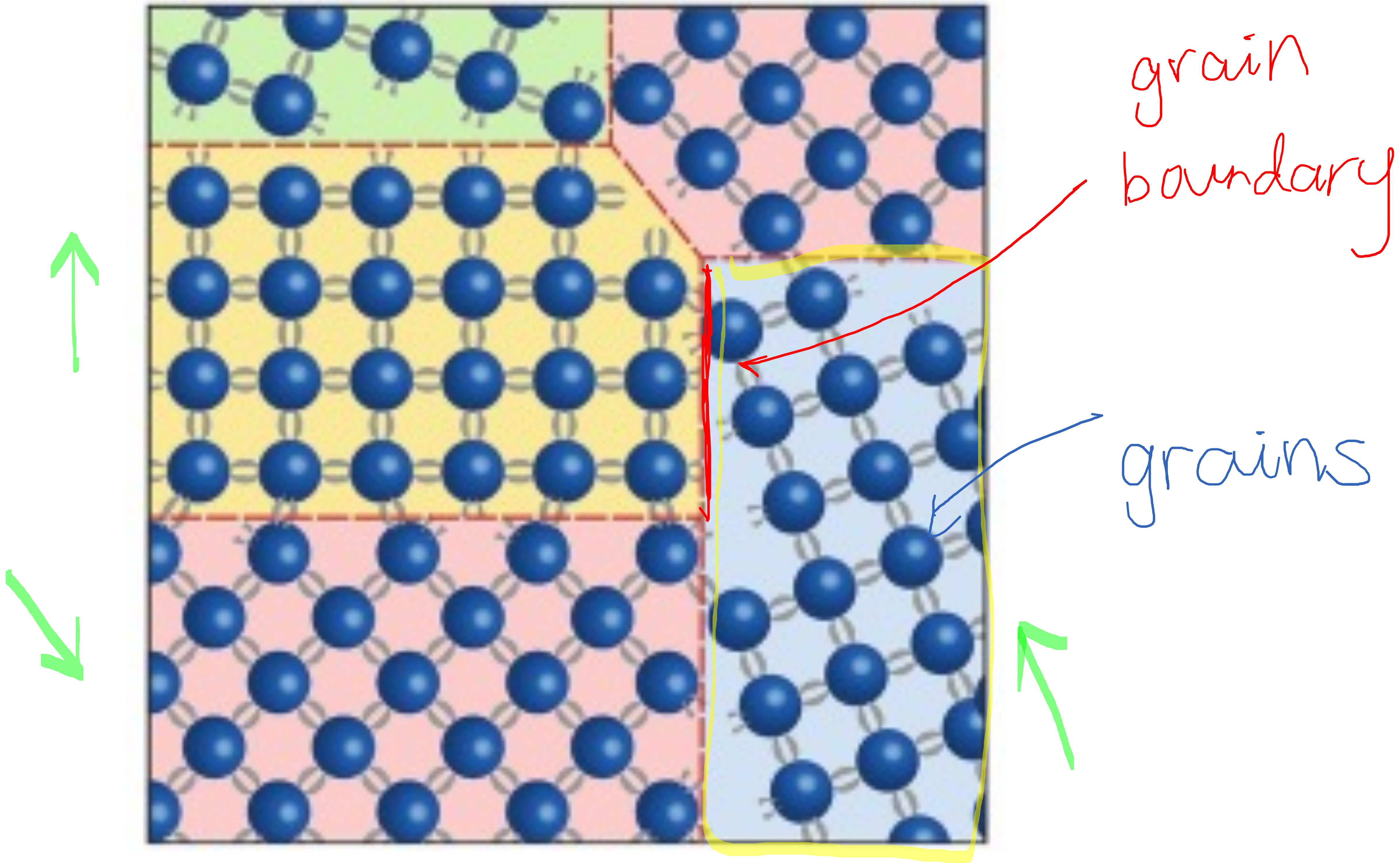
Real Materials Made of Many Small Crystals

Single crystals
(monocrystalline solids)



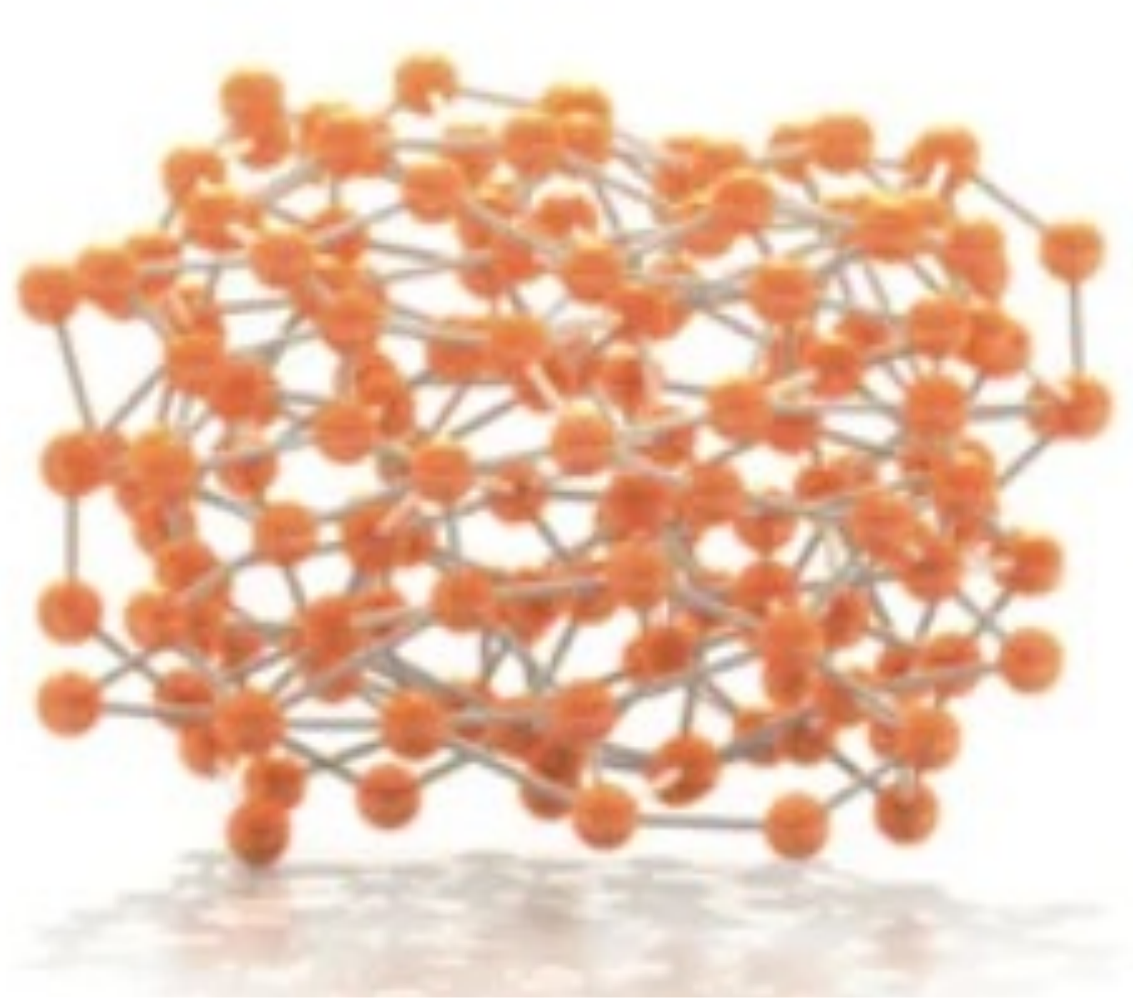
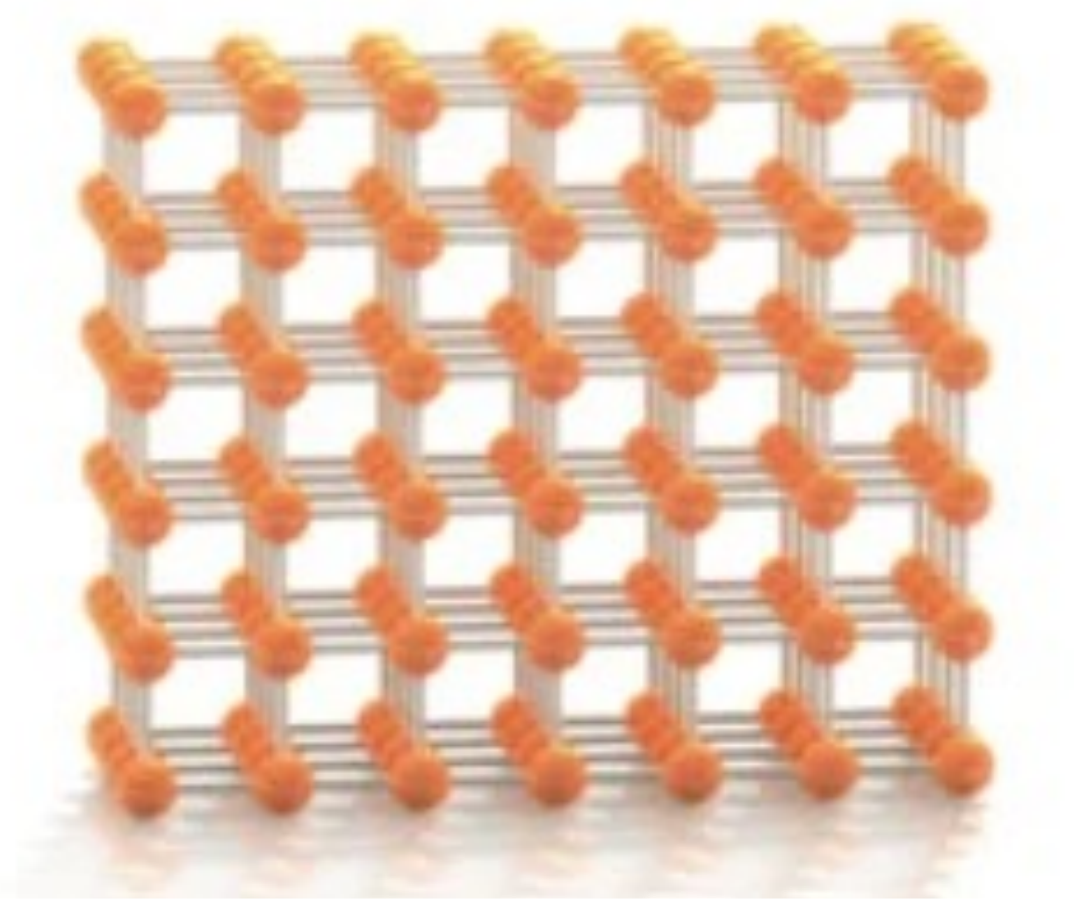
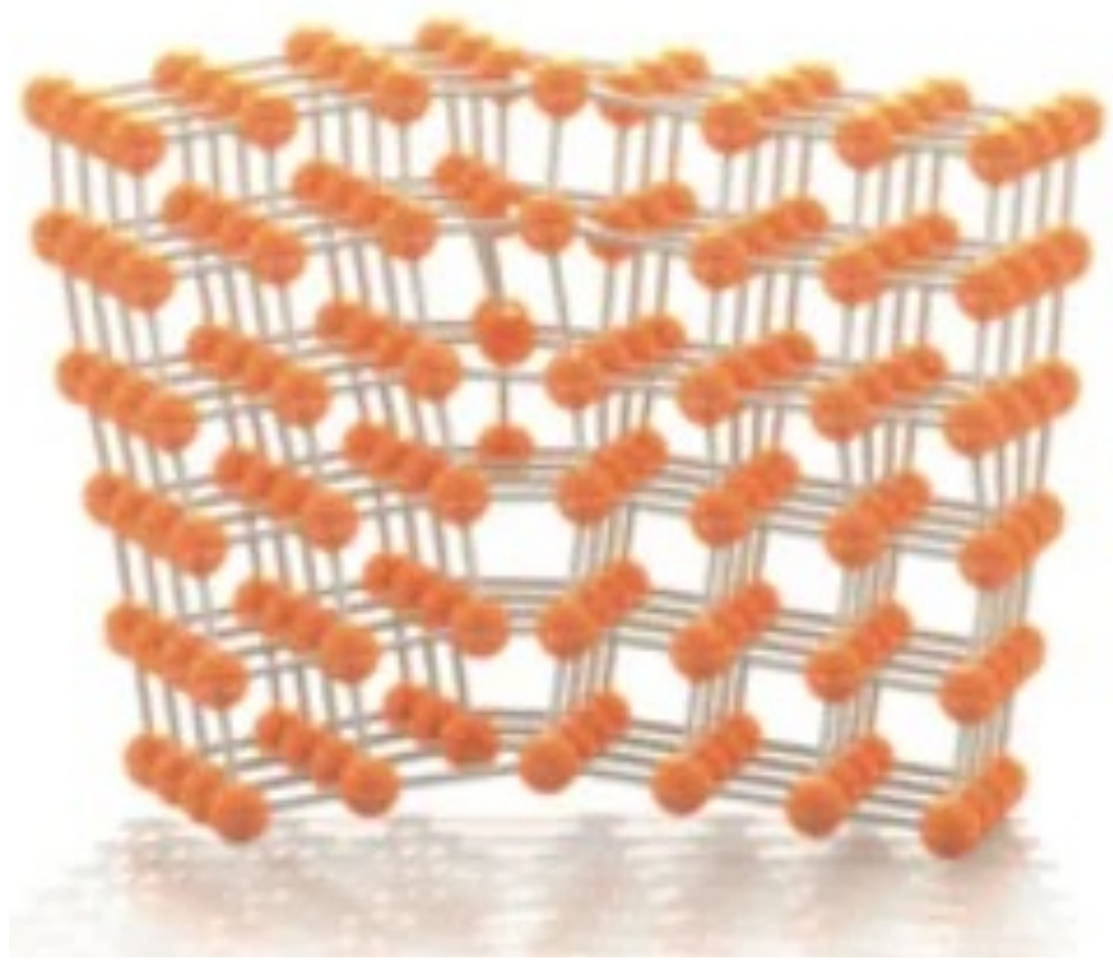
Relative spacing and orientation of neighboring atoms governed by chemical bonding

Patchwork of individual crystals (grains)
(Polycrystalline solids)

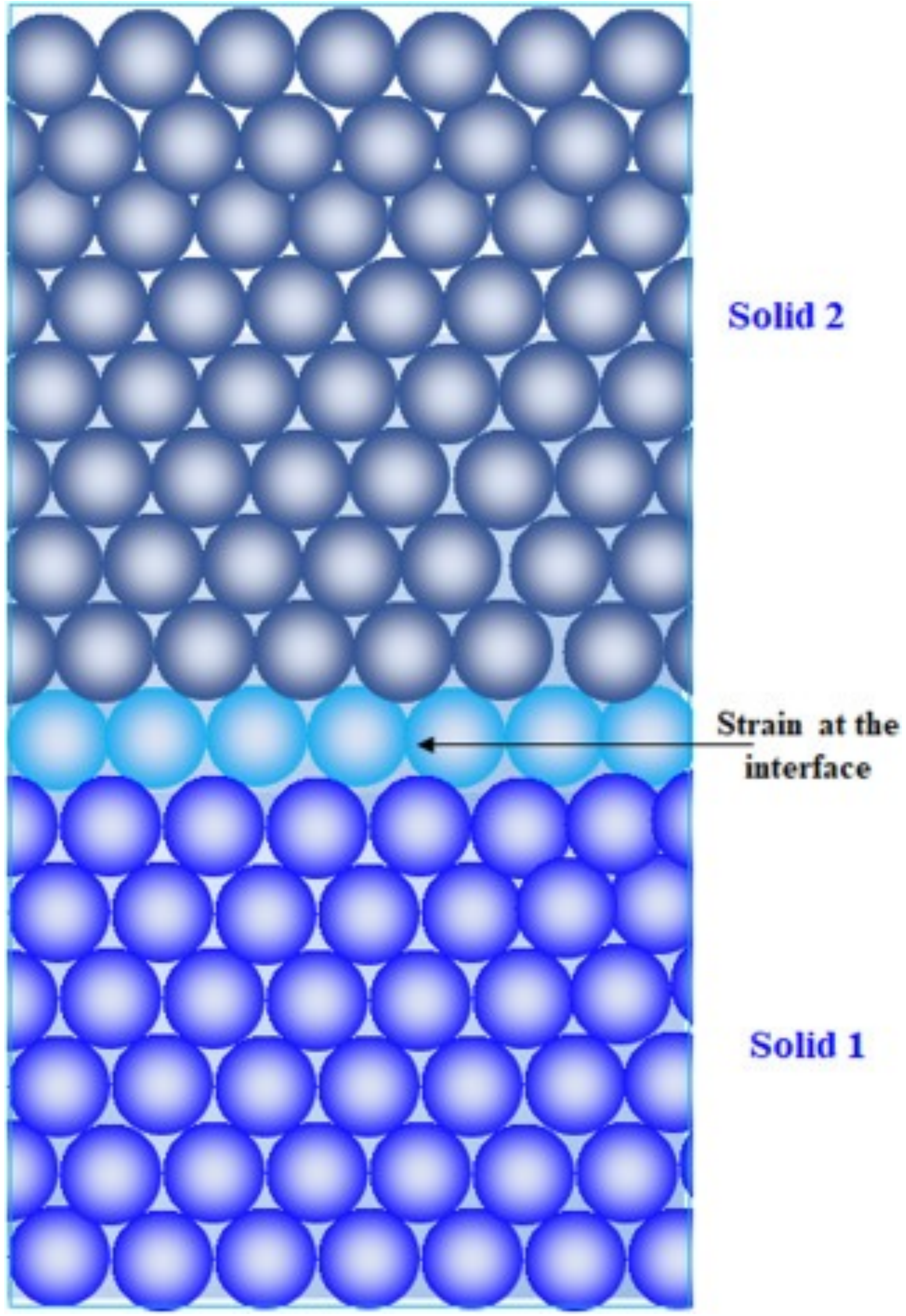


Individual grains differ in size and orientation and joined by planar interfaces called grain boundaries

Polycrystalline Solids in 3-D

Amorphous	Crystalline	Polycrystalline
		
Random arrangement	Regular repeating lattice	Grains with different orientations
No definite shape, moldable	Definite geometric shape	Separated by grain boundaries
Softens over temp. range	Sharp melting point	Grain boundaries control properties
Glass, plastic, gels	Salt, diamond, sugar	Most metals, ceramics

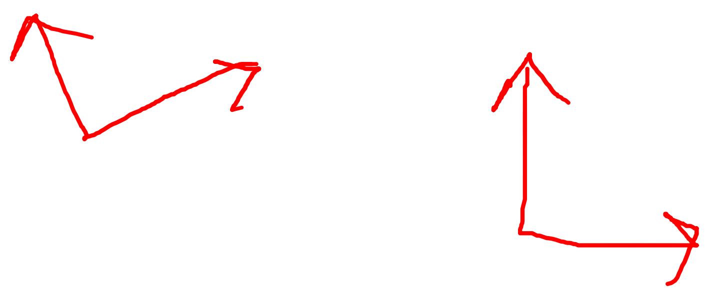
Solid-Solid Interfaces are Common in Nature



A B

α | β heterophase

α | α



α ➔ solid crystalline phase

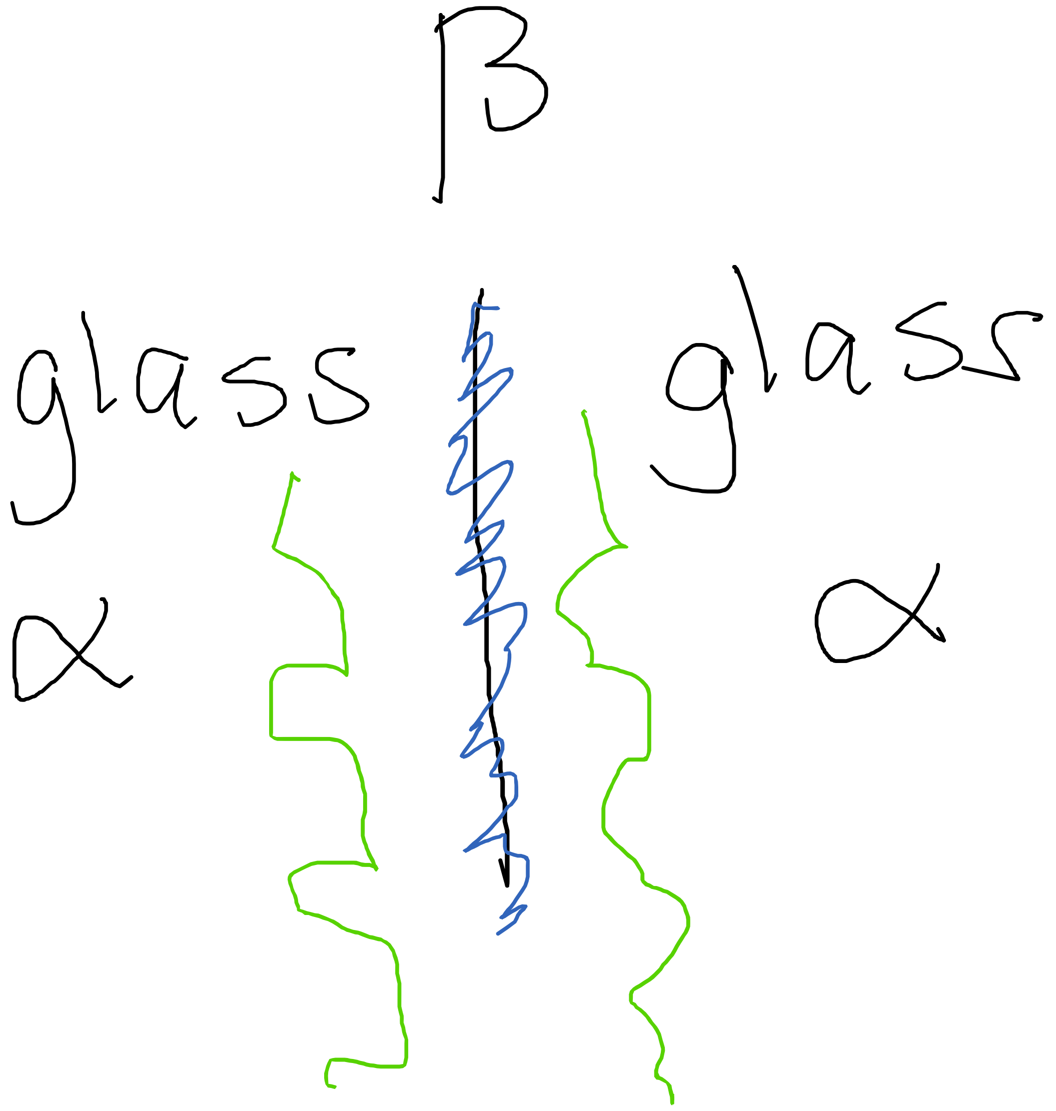
Any pure material that is in a single phase but in a polycrystalline solid, will have plenty of α| α interfaces

Homophase and Heterophase Solid-Solid Interfaces

α | β

Crystalline or amorphous

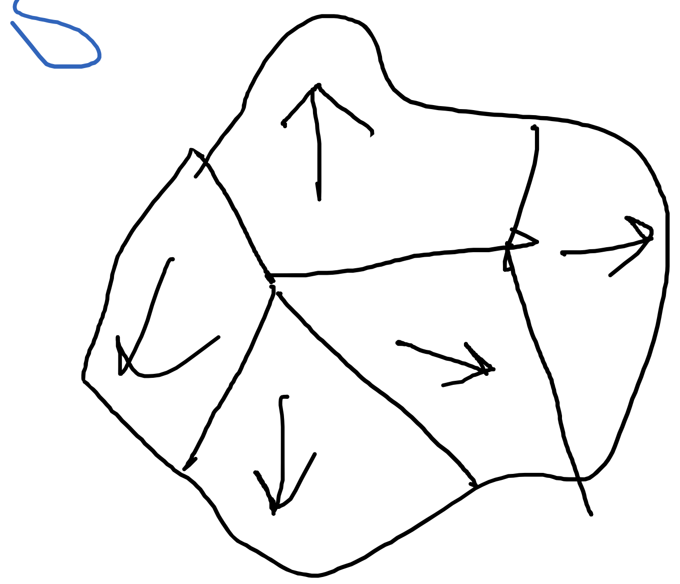
chemical structure of atoms are distinct



α | α

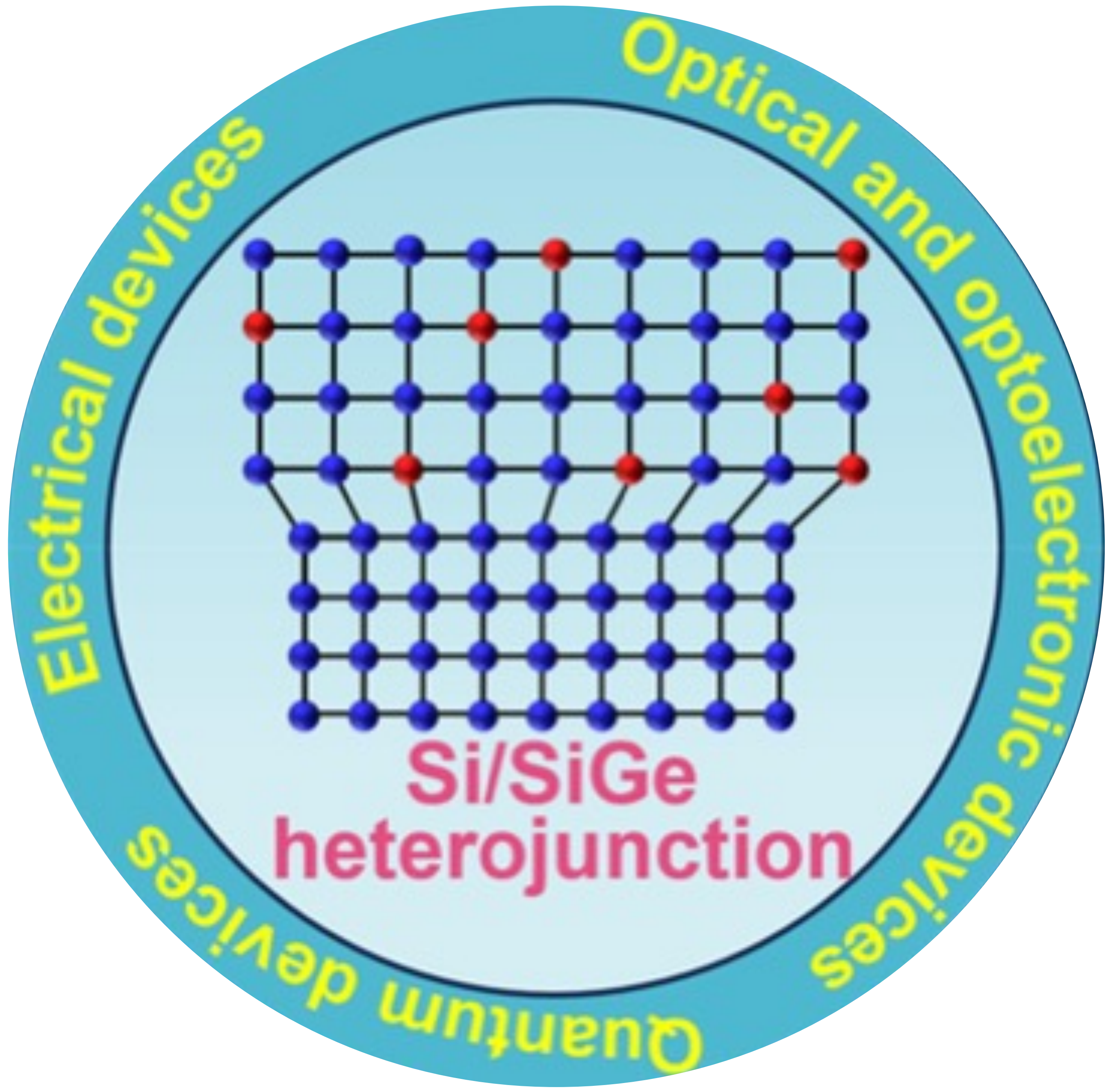
Crystalline material

determine orientation of grains



Types of Heterophase α | β Solid-Solid Interfaces

Crystalline | Crystalline

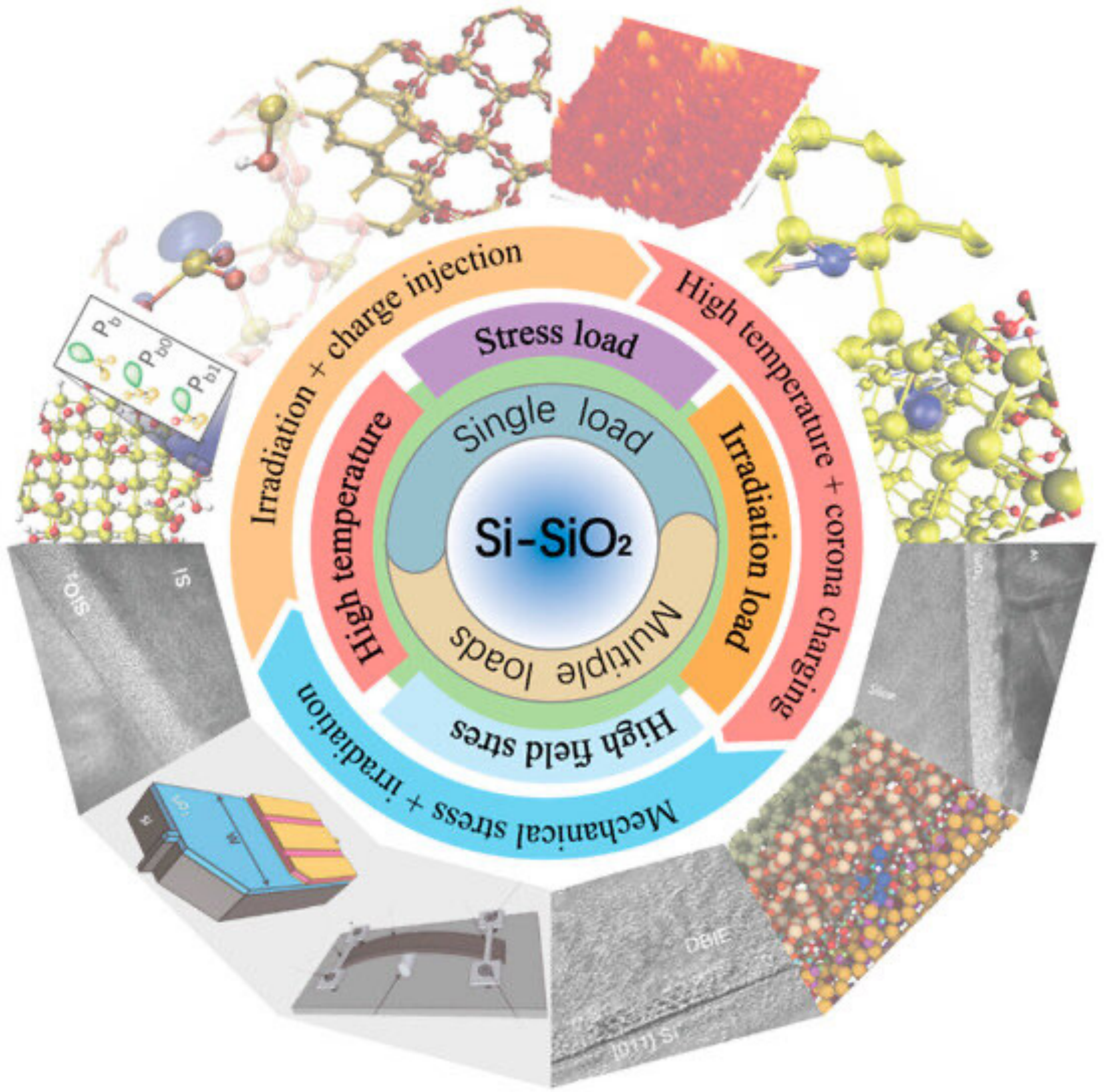


High atomic order

Li *et al.* | Electron | 2024

2 monocrystalline semiconductors

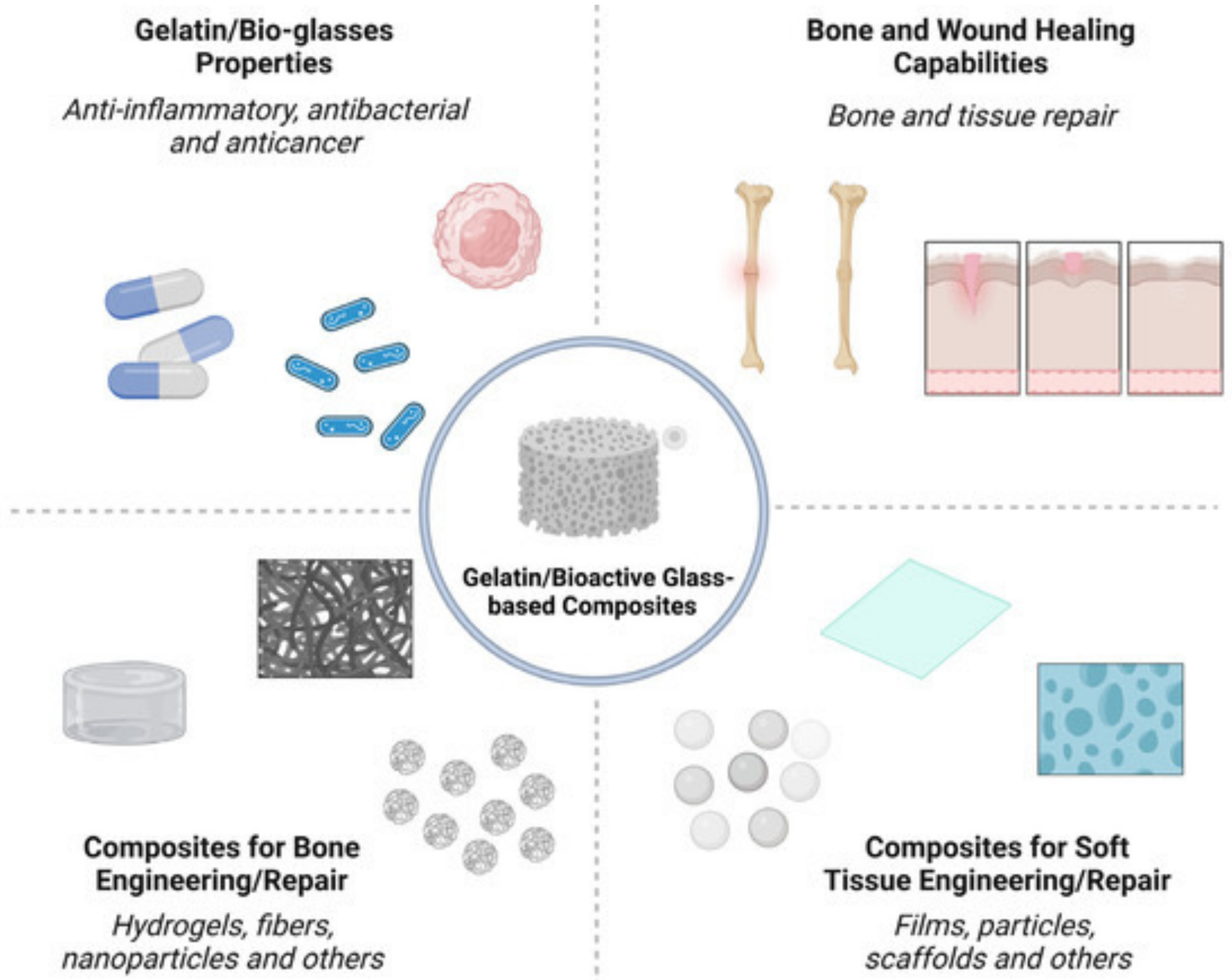
Crystalline | Amorphous



Disordered at boundary

Zhang *et al.* | Symmetry | 2025

Amorphous | Amorphous



Random atomic arrangement

Barreto *et al.* | J. Funct. Biomater. | 2023

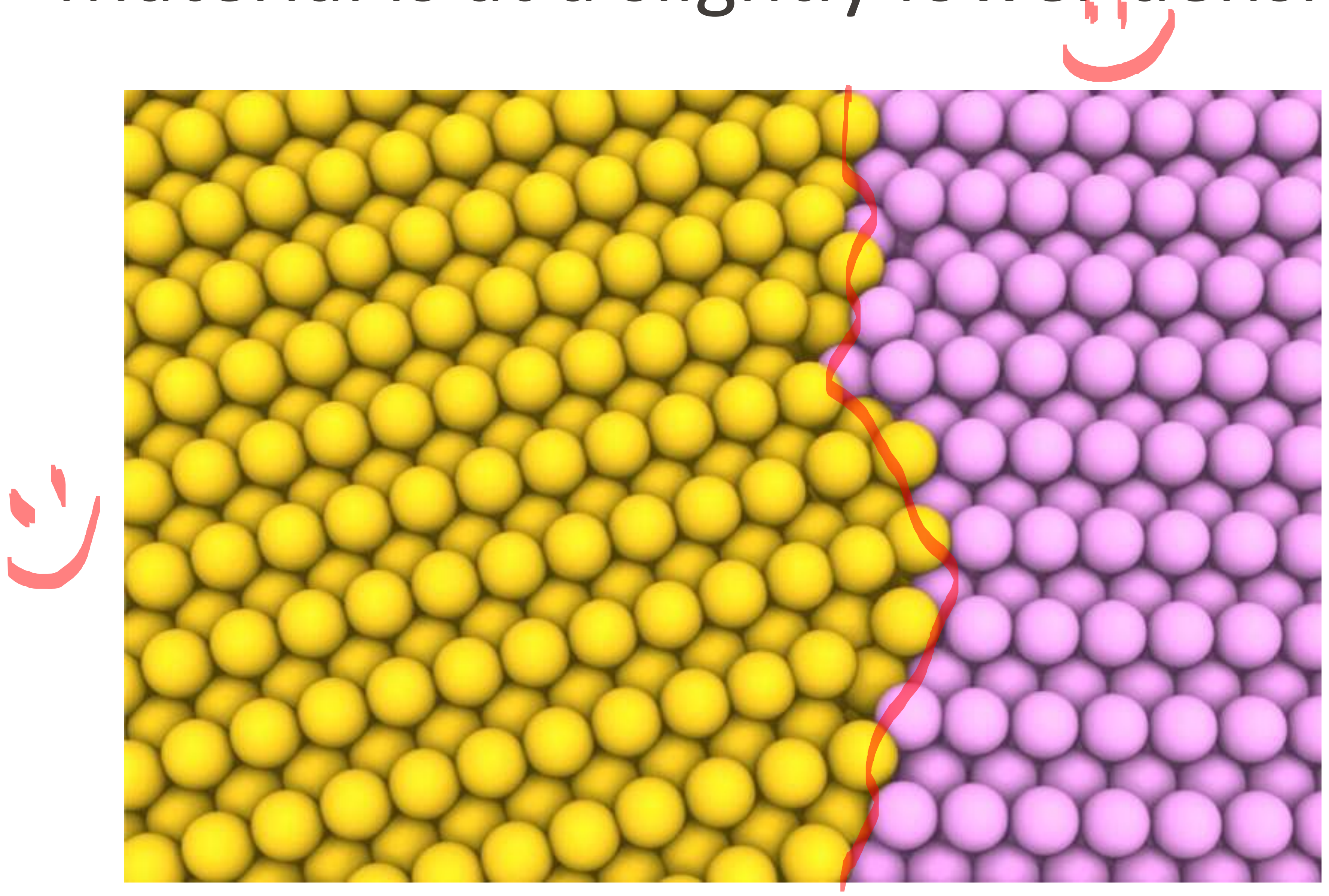
Grain Boundaries Are 2-D Defects

Grain boundaries cause a disruption in periodicity (atoms are in the wrong positions):

Higher energy

Broken distorted bonds

Material is at a slightly lower density



Atoms at a grain boundary **lower the energy** by arranging themselves so their rows line up better and match the atomic pattern on the other side

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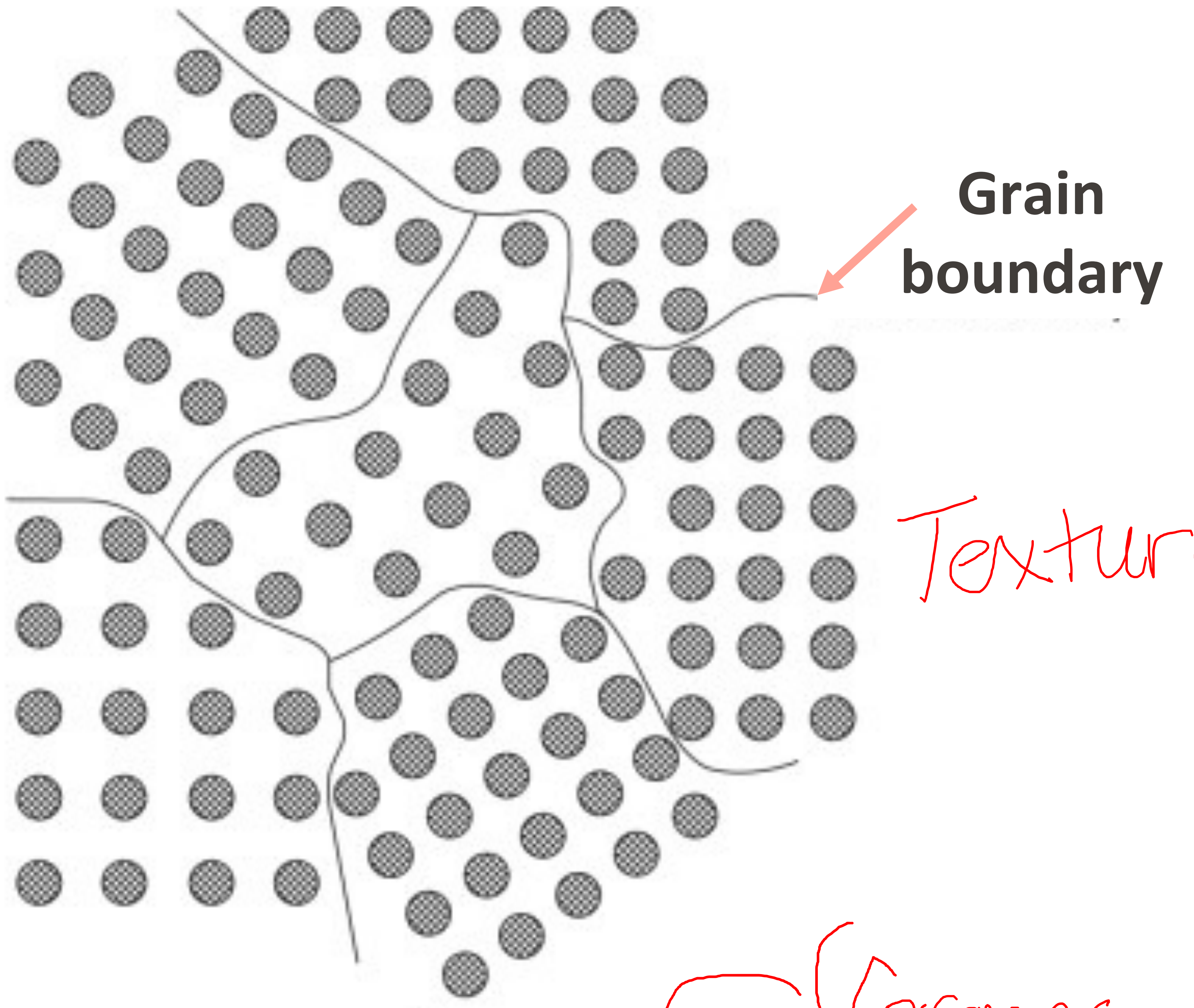
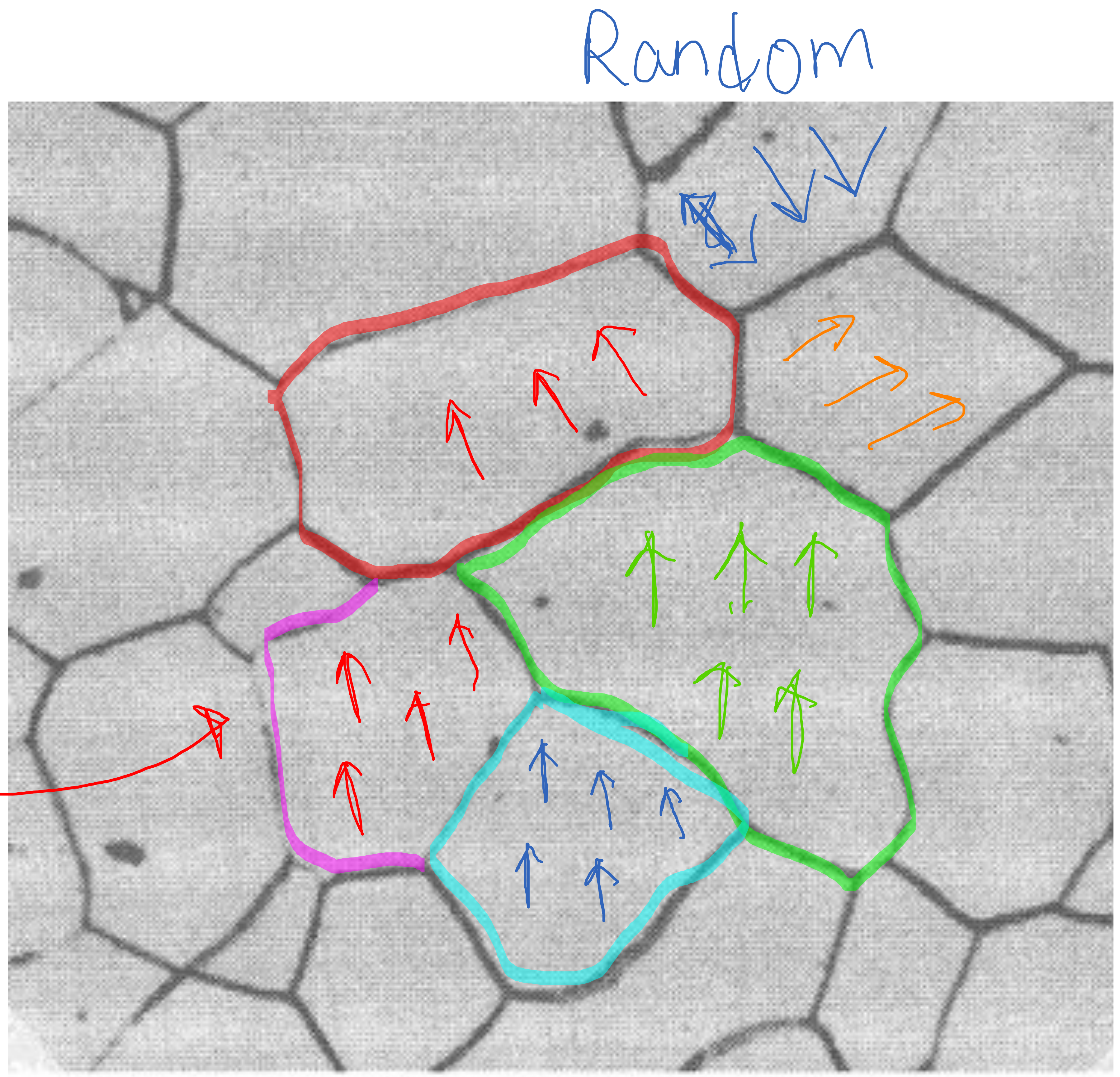
Grain Boundaries Form Microstructure

Grain boundaries are planar defects across which the crystal orientation changes





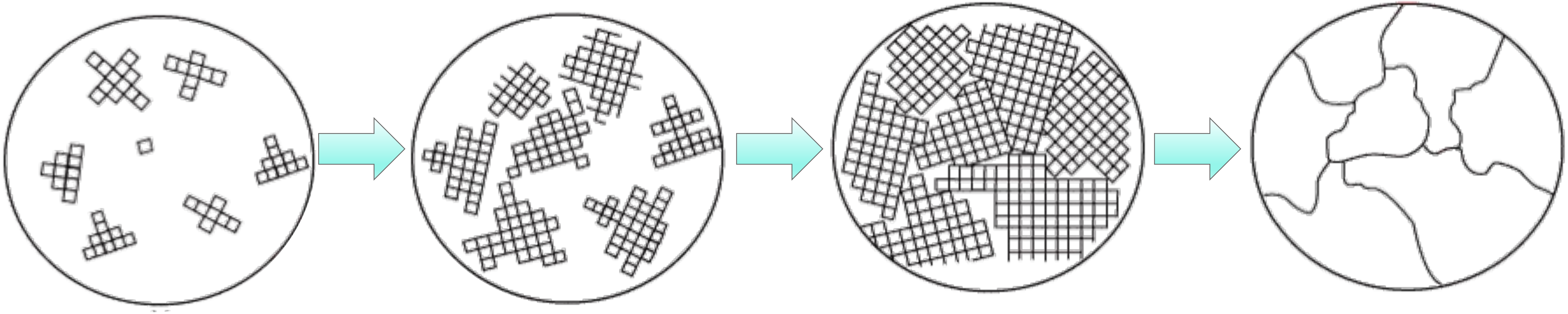
Texture

← (Grains + Boundary + Tex + Dist)

Microstructure influences properties: strength, toughness, corrosion, resistance, electrical

Why do Grain Boundaries Form?

In engineering materials, a crystal is usually referred to as a “grain”



Nucleation of crystals

Crystal growth

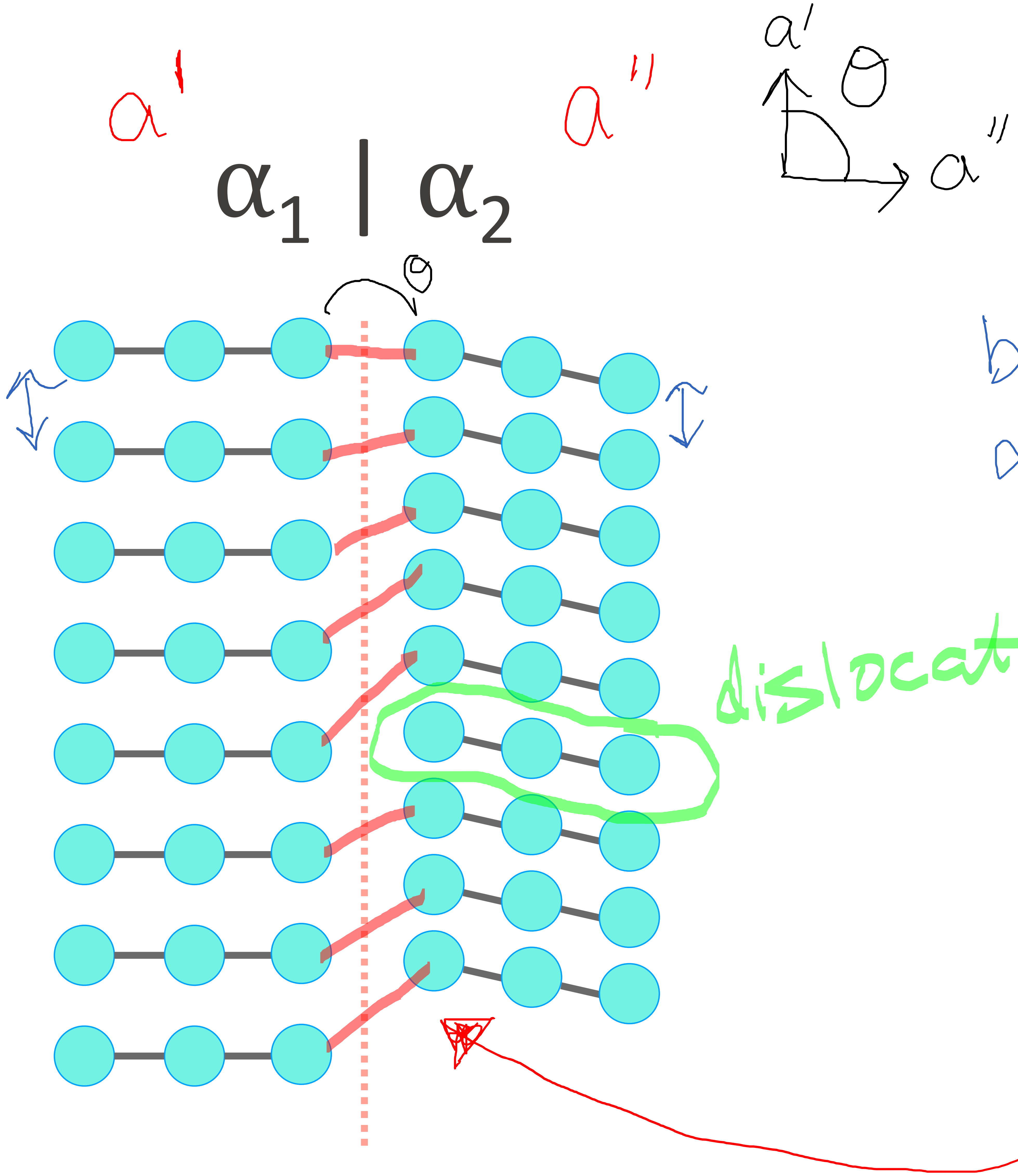
Irregular grains form as crystals grow together

Grain boundaries form

Rapid cooling ➔ more nucleation points and smaller grains, stronger material

Slow cooling ➔ larger grains with lower strength, hardness, and ductility

Thermodynamics of Homophase Solid-Solid Interfaces

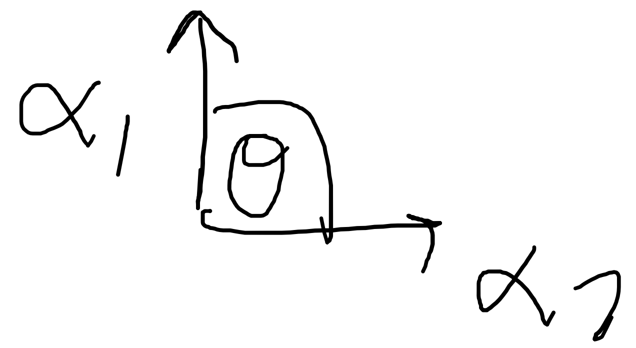


$$\overset{\text{between } \alpha_1 \ \& \ \alpha_2}{\boxed{\gamma_{\alpha_1\alpha_2}}} = \overset{\text{break}}{\gamma_{\alpha_1}} + \overset{\text{break}}{\gamma_{\alpha_2}} - \underset{\text{reform}}{\overset{\text{work of adhesion}}{W_{\alpha_1\alpha_2}}}$$

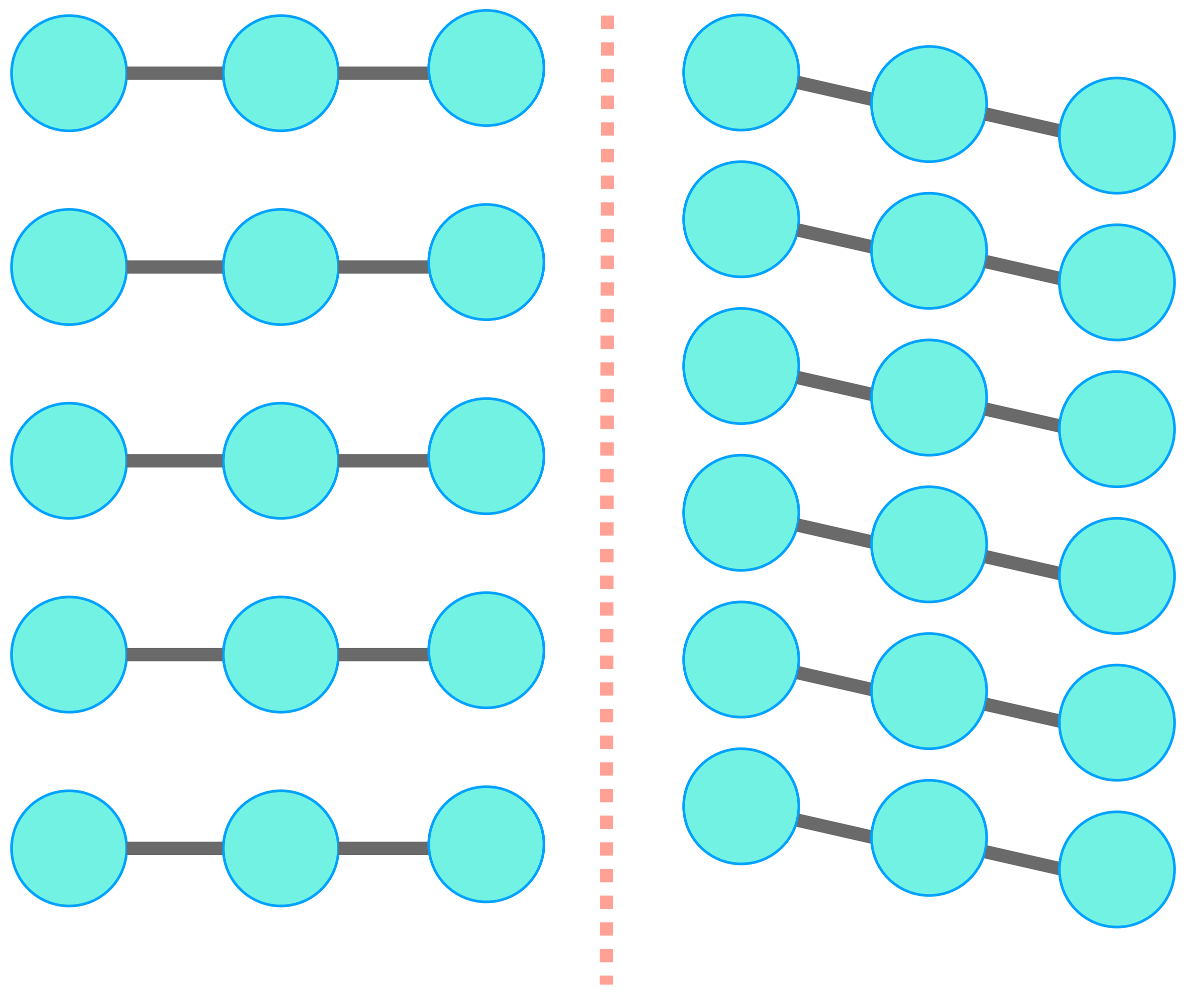
energy of a single bond broken + elastic energy to stretch all the red reformed bonds past equilibrium lengths.

Thermodynamics of Homophase Solid-Solid Interfaces

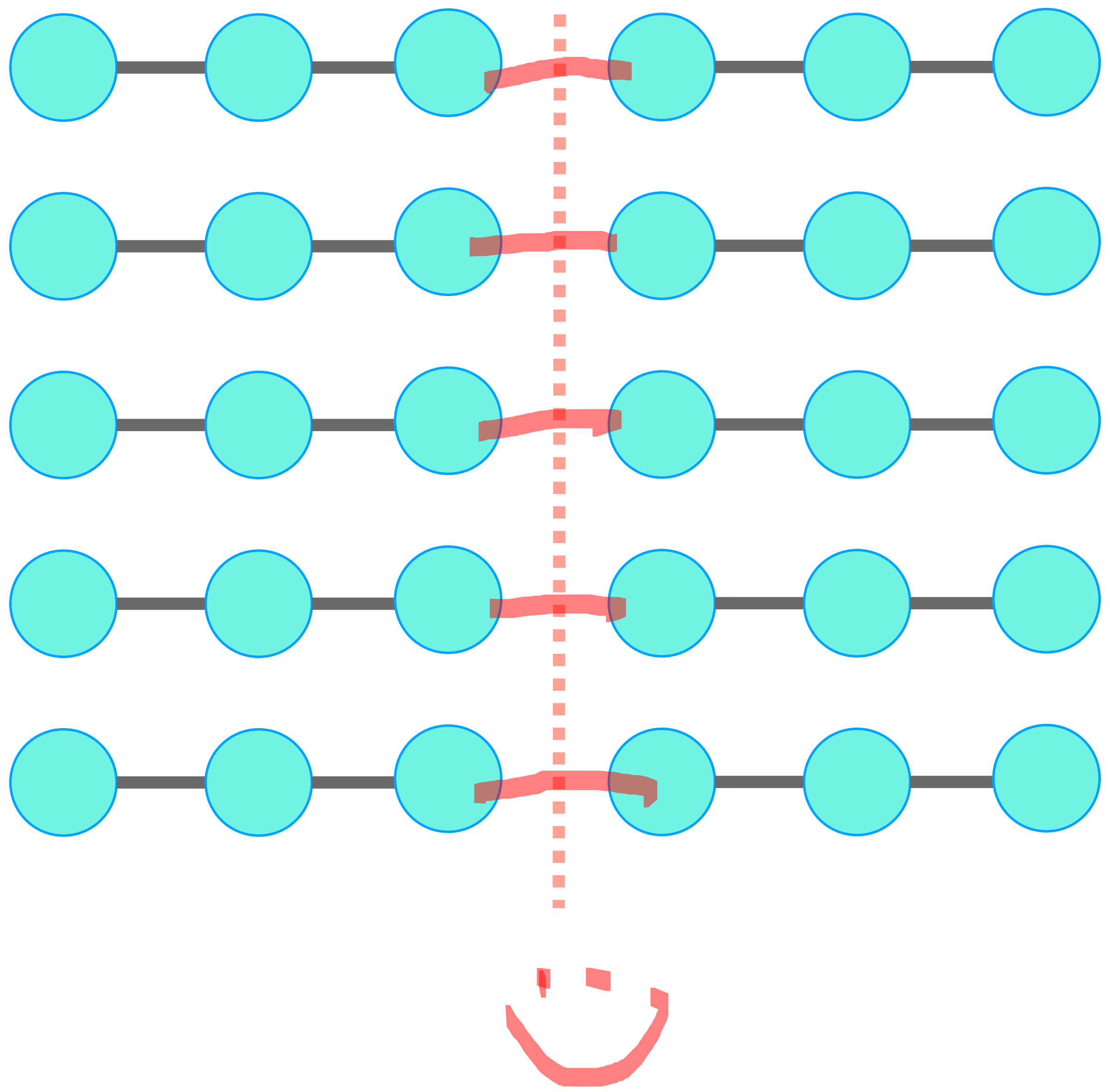
$$\lim_{\theta\to 0} \gamma_{\alpha_1\alpha_2} = \gamma_{\alpha_1} + \gamma_{\alpha_1} - W_{\alpha_1\alpha_1} = 0$$



$\alpha_1 \mid \alpha_2$



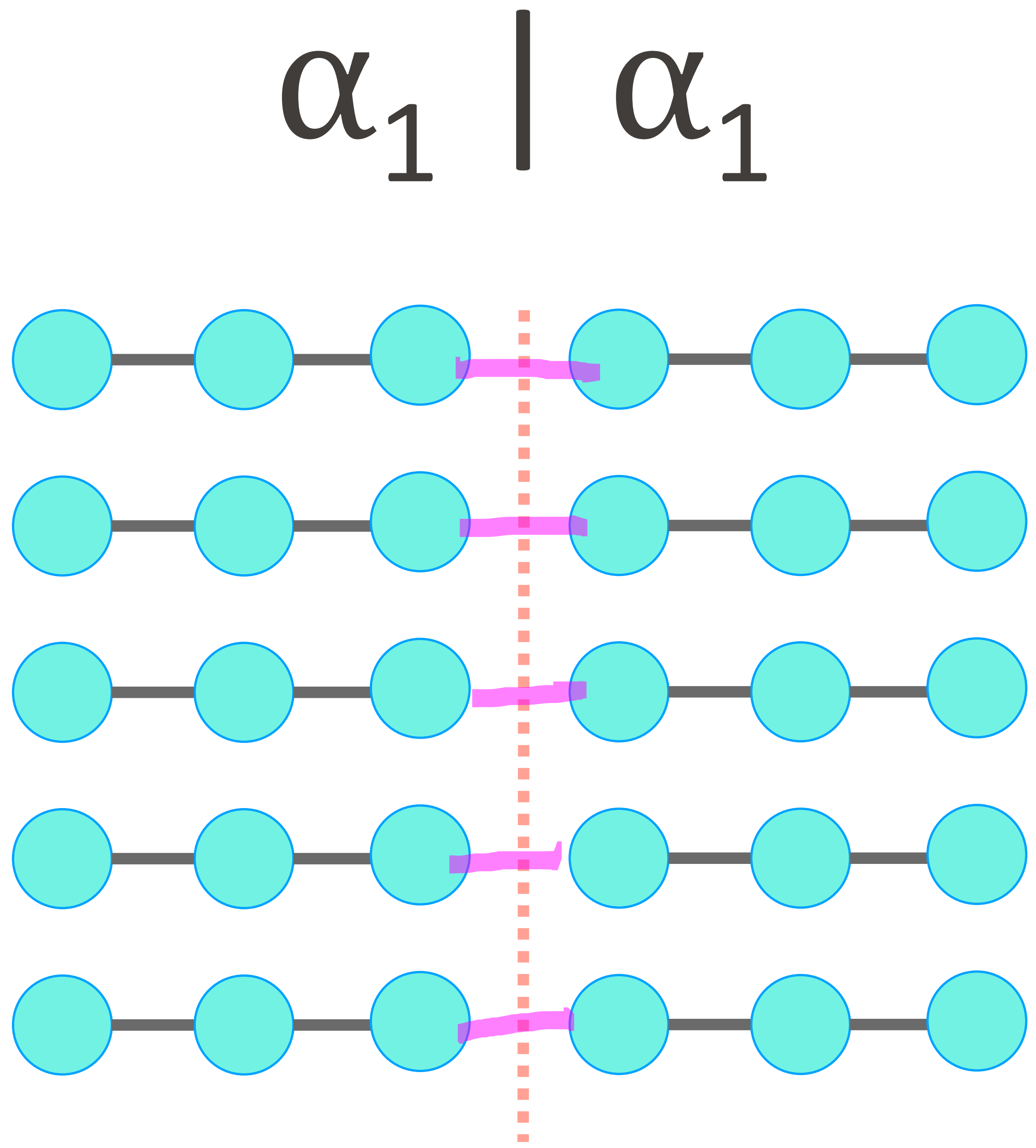
$\alpha_1 \mid \alpha_1$



$$\lim_{\theta\to 0} W_{\alpha_1\alpha_1} = 2\gamma_{\alpha_1}$$

homophase
solid
surfaces

Thermodynamics of Homophase Solid-Solid Interfaces

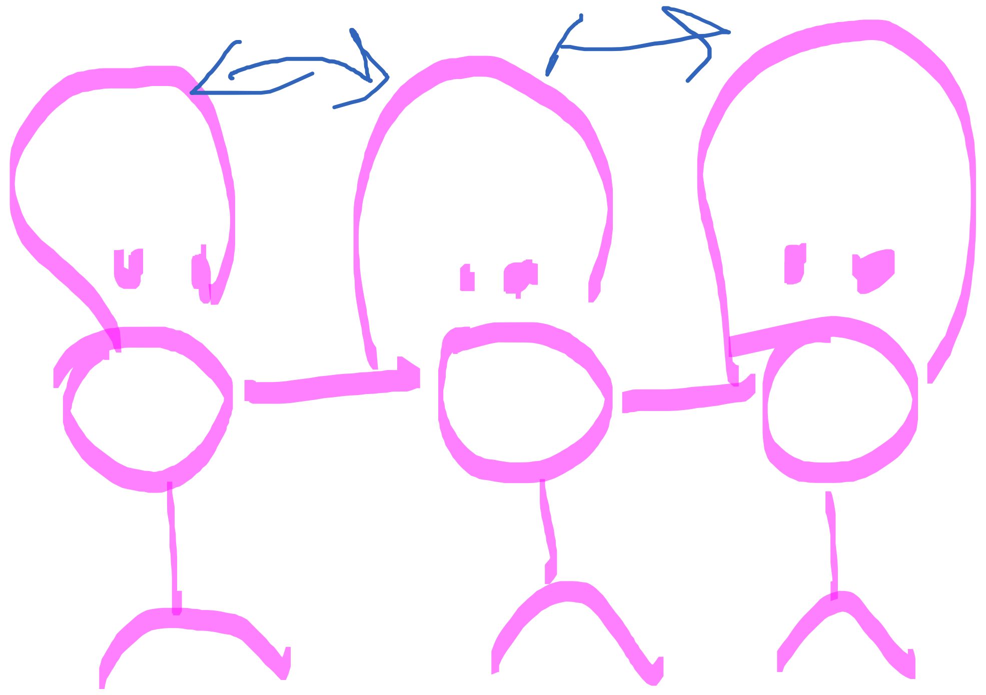


Homophase solid surfaces

$$W_{\propto_1\propto_1} \cong \gamma_{\propto_1} + \gamma_{\propto_2}$$

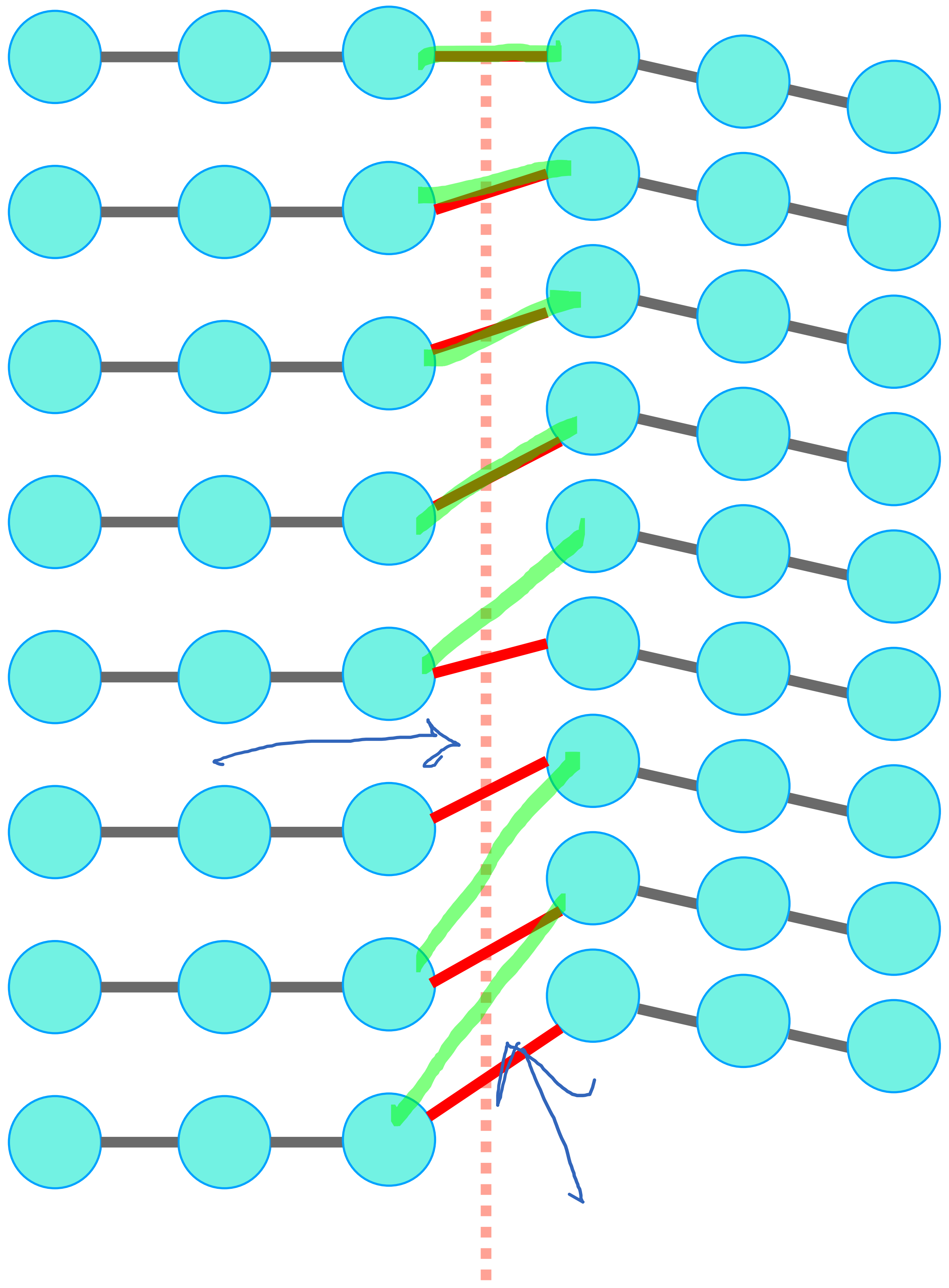
A few dangling bonds
+ elastic energy

defects
strain
misalignment



Thermodynamics of Homophase Solid-Solid Interfaces

$\alpha_1 \mid \alpha_2$



Dislocation!

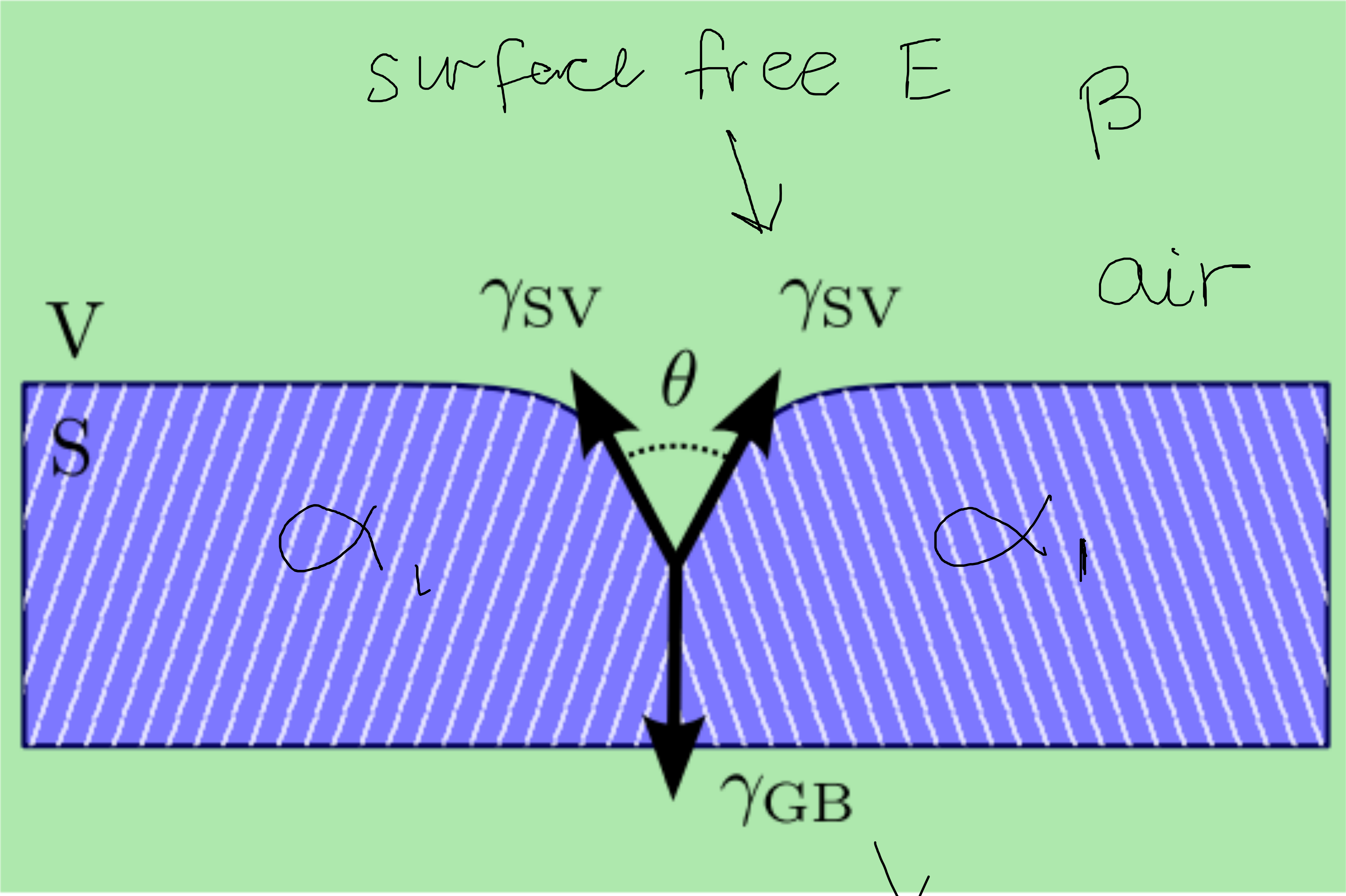
Homophase solid surfaces

$$W_{\propto_1 \propto_1} \cong \gamma_{\propto_1} + \gamma_{\propto_2}$$

A few dangling bonds
+ elastic energy

Measuring the Grain Boundary Energy

We can associate a surface free energy term γ_{GB} to the presence of grain boundaries



grain boundary

At equilibrium:

$$\boxed{\gamma_{GB} = 2\gamma_{SV}\cos\frac{\theta}{2}}$$

When two grains meet at a surface, their boundary has an energy (γ_{GB})

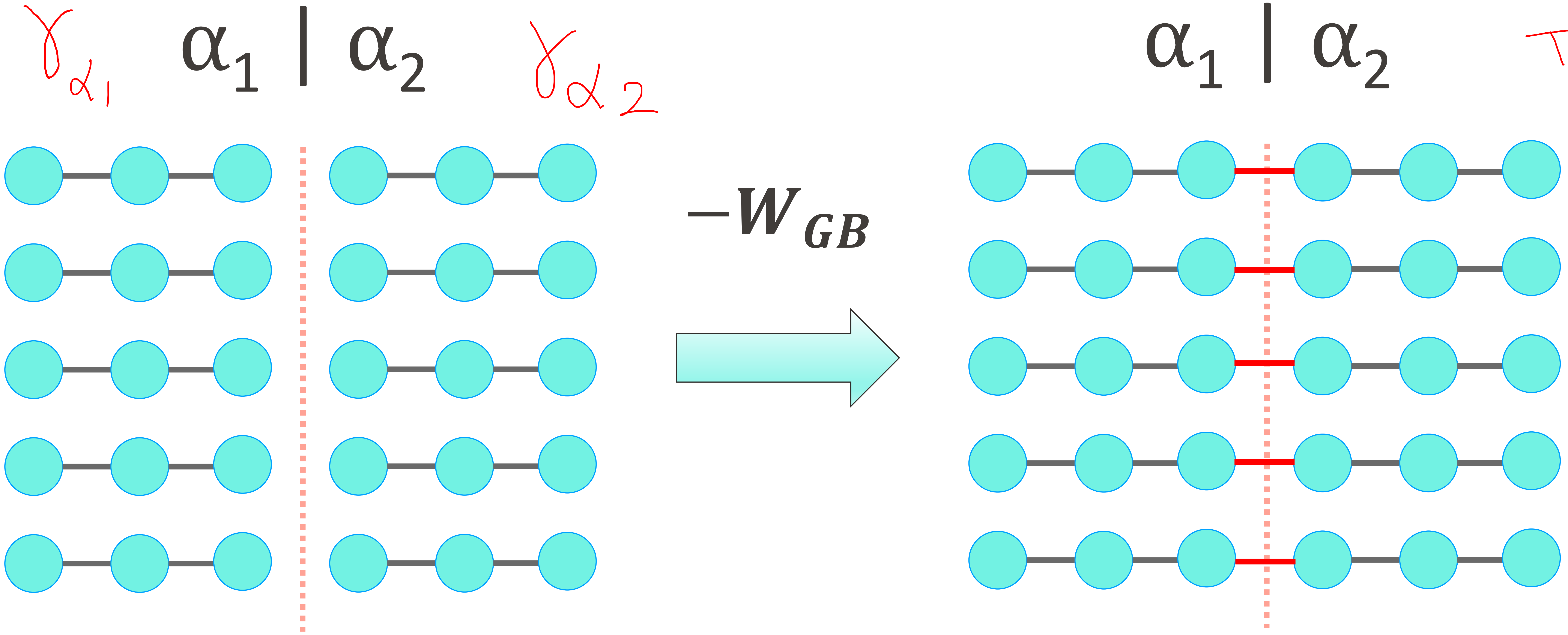
Atoms at intersection rearrange to minimize total energy, creating a small groove

Measuring groove angle θ, we can estimate grain boundary energy

Measuring the Grain Boundary Energy

$$\gamma_{GB} = \boxed{2\gamma_{SV}} - W_{GB}$$

Bonding Lowers Total E of System



Two separate crystal surfaces have total energy = $\underline{2\gamma_{SV}}$

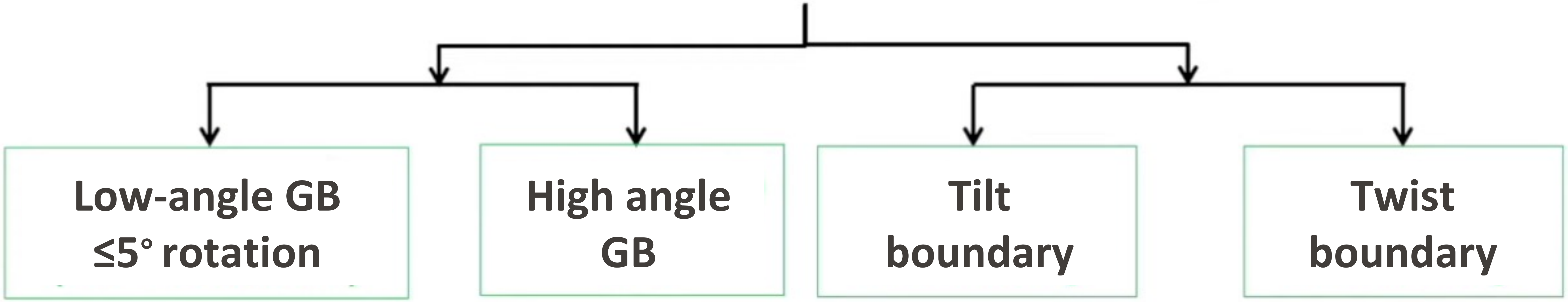
New interface (grain boundary) with its own energy per unit area

$\boxed{\text{The } \gamma_{GB}\ \alpha \text{ \# of dislocations}}$

Key Takeaways

- Real materials are polycrystalline consisting of small grains with different orientations separated by grain boundaries
- Grain boundaries are planar 2-D defects
- Interfaces can be homophase or heterophase
- Grain boundaries cost energy but can lower total system energy overall
- Groove angle at the surface gives a measure of the interfacial energy – linking thermodynamics to microstructure

Different Types of Grain Boundaries



Different types of grain boundaries (GB)

Low-angle GB ≤5° rotation

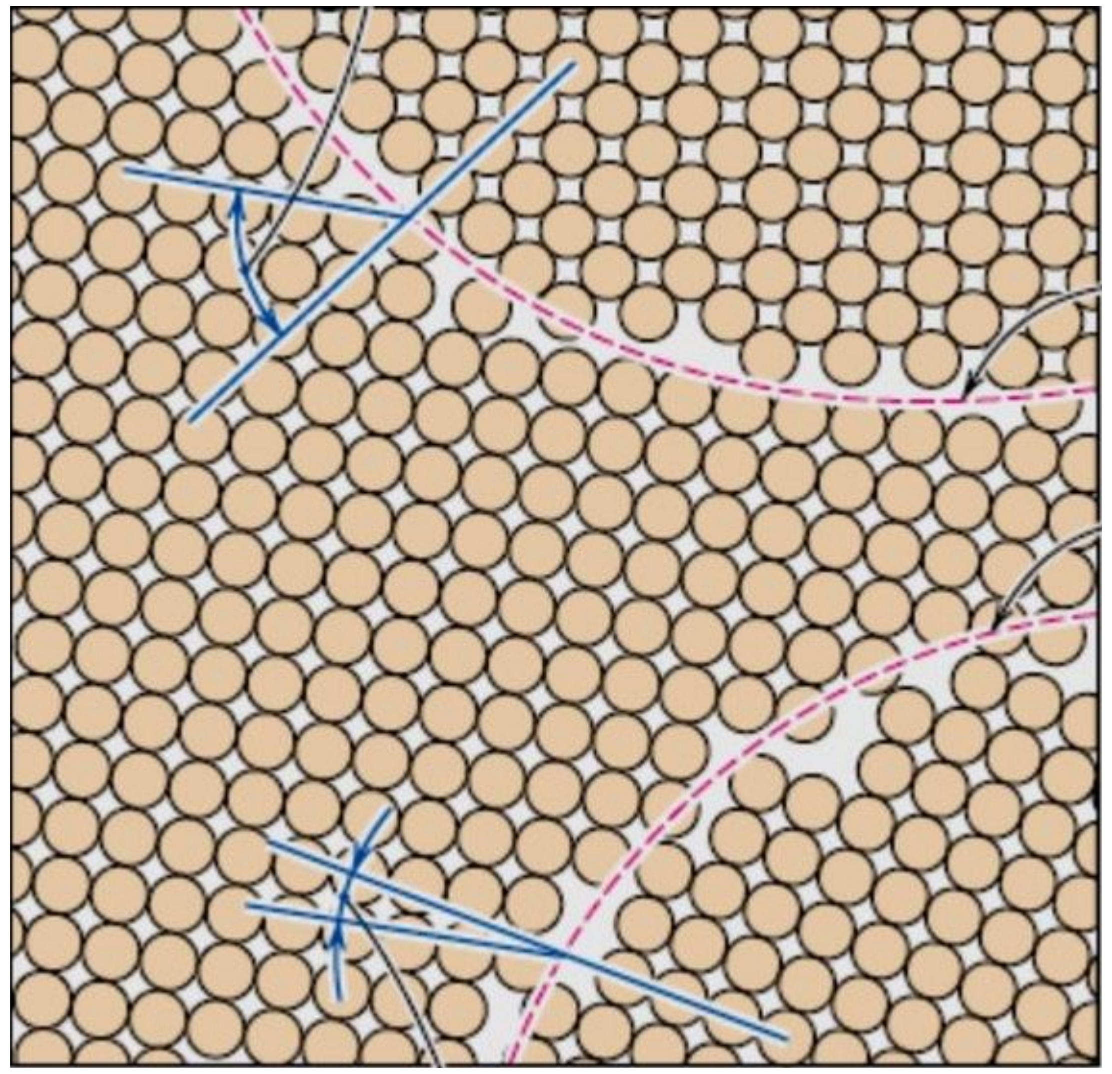
High angle GB

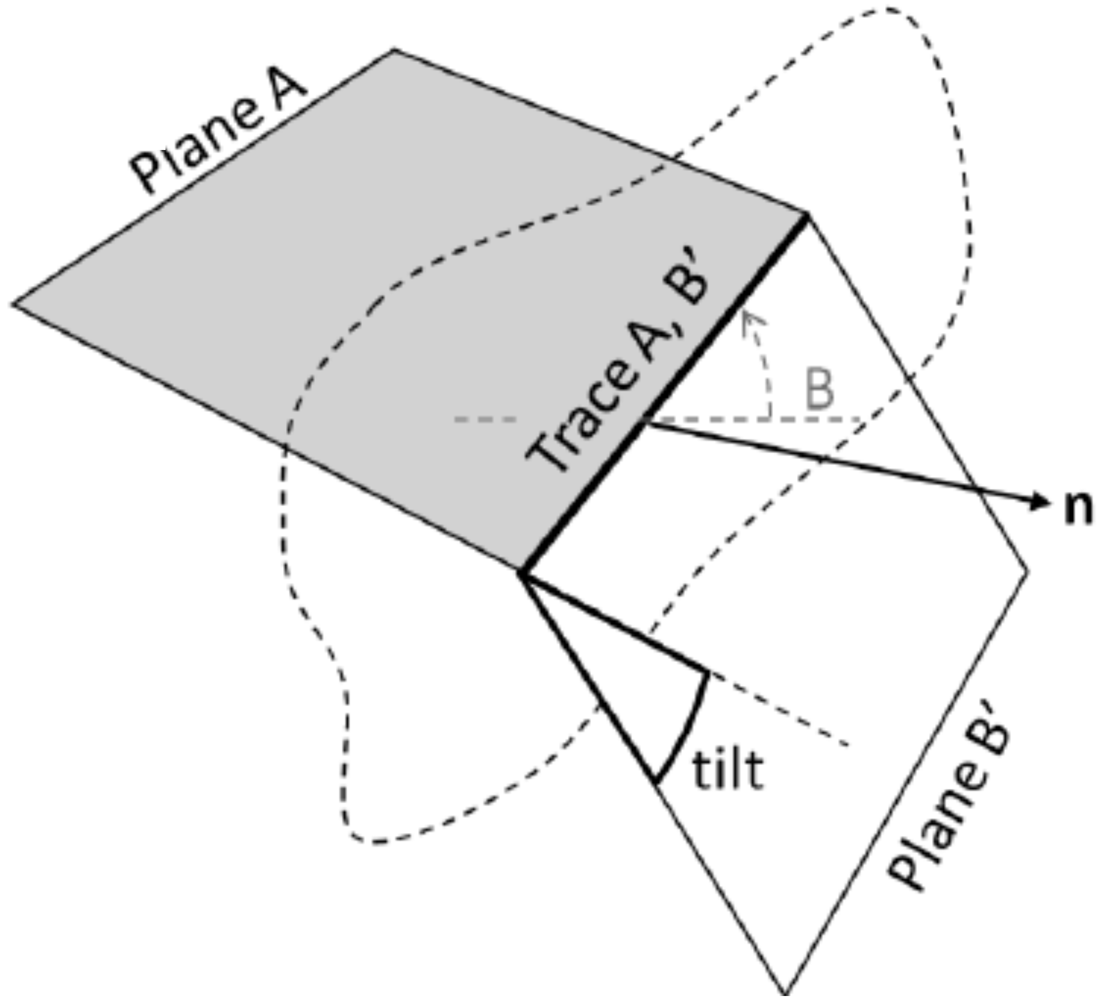
Tilt boundary

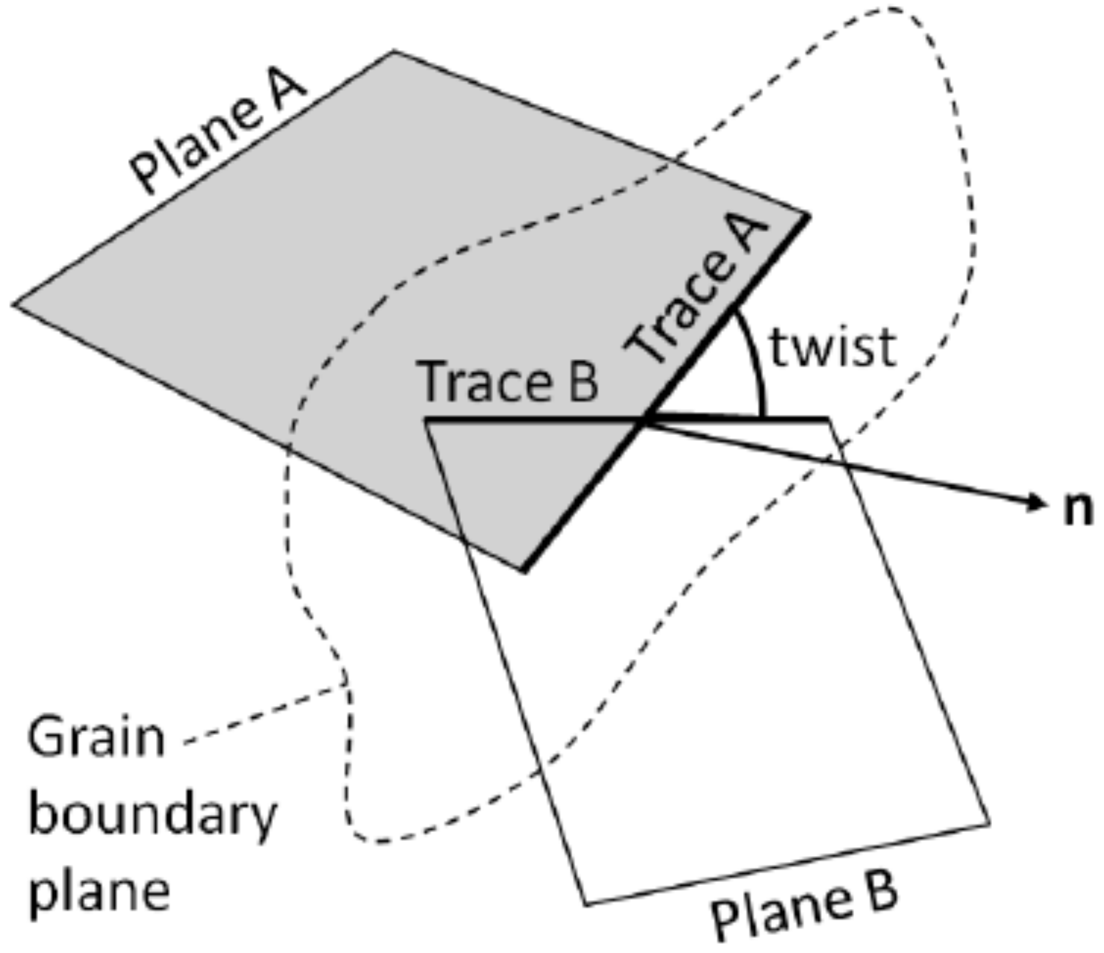
Twist boundary

High angle GB

Low angle GB





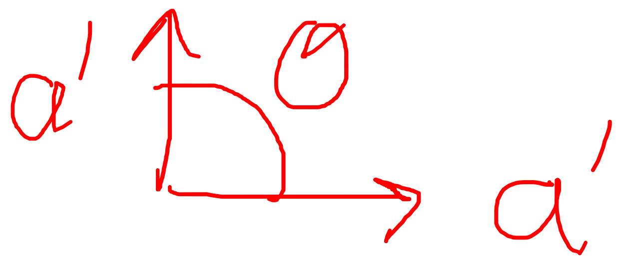


King *et al.* | Acta Materialia| 2011

Low Angle Symmetric Tilt Grain Boundaries

Low angle grain boundaries can be described as an array of edge dislocations

Crystal/grain misorientation related to dislocation spacing

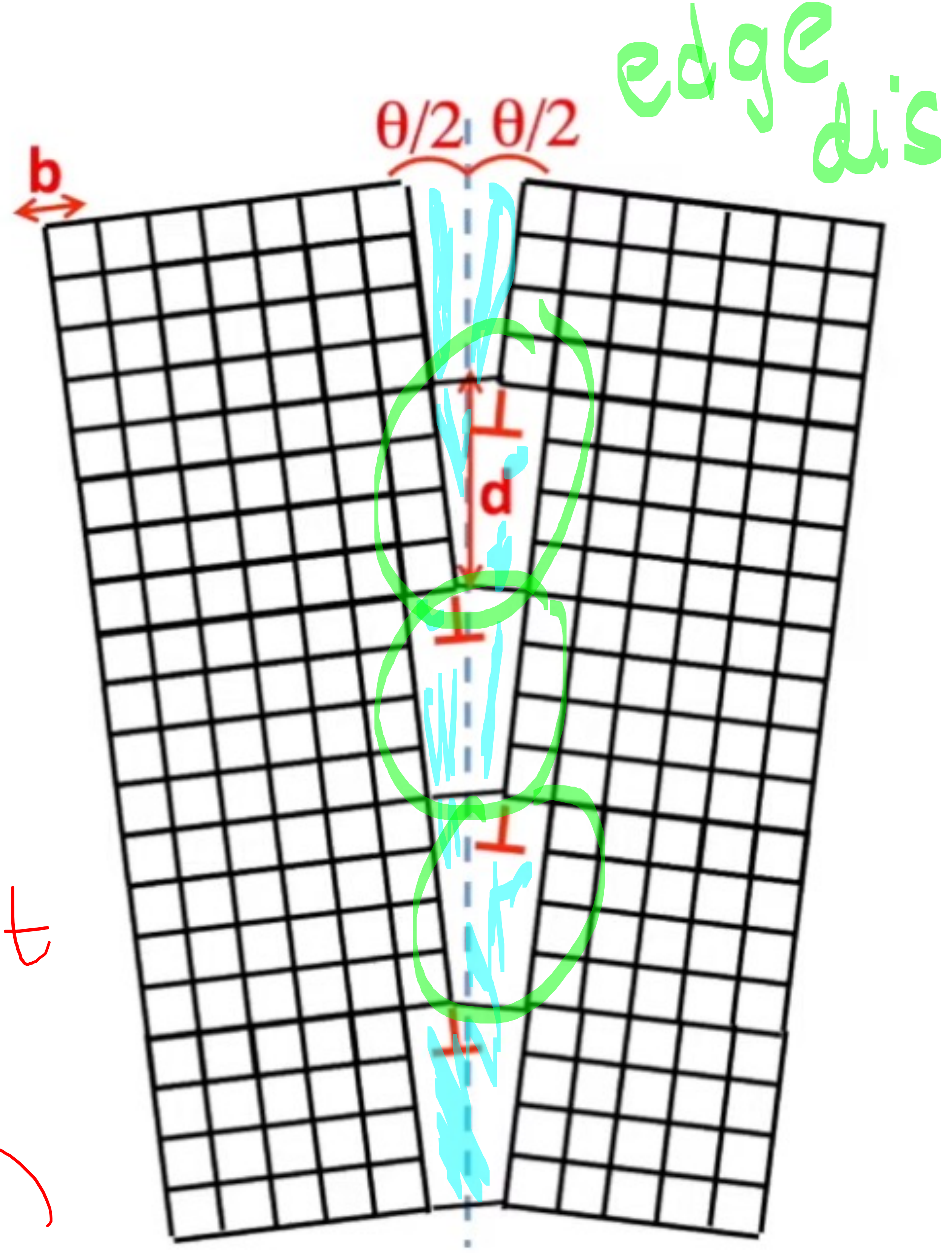


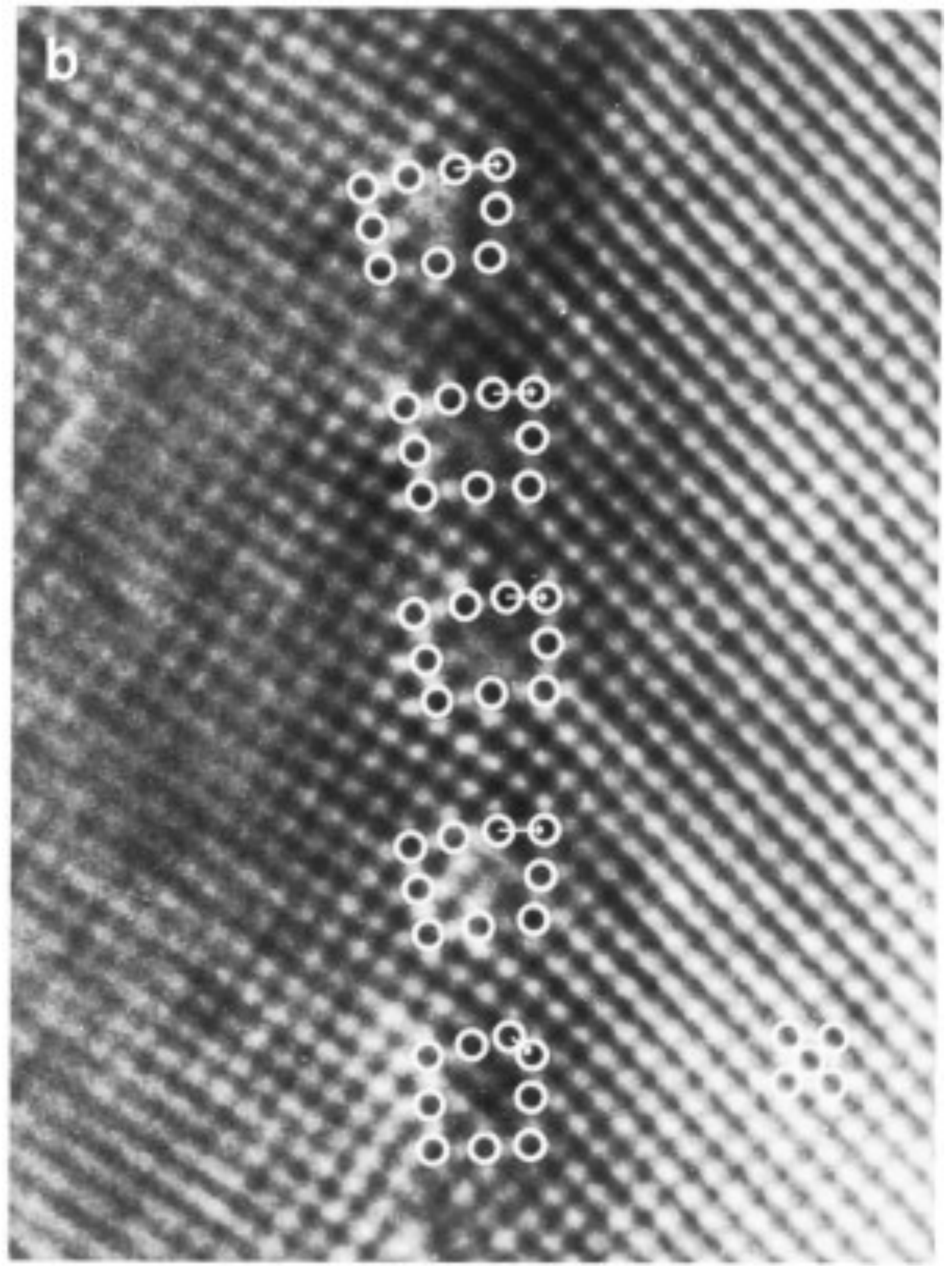
θ : tilt angle

d : dislocation separation

b : Burger's vector

↳ lattice shift caused by dislocation





Atomic resolution image of low-angle boundary in Mo

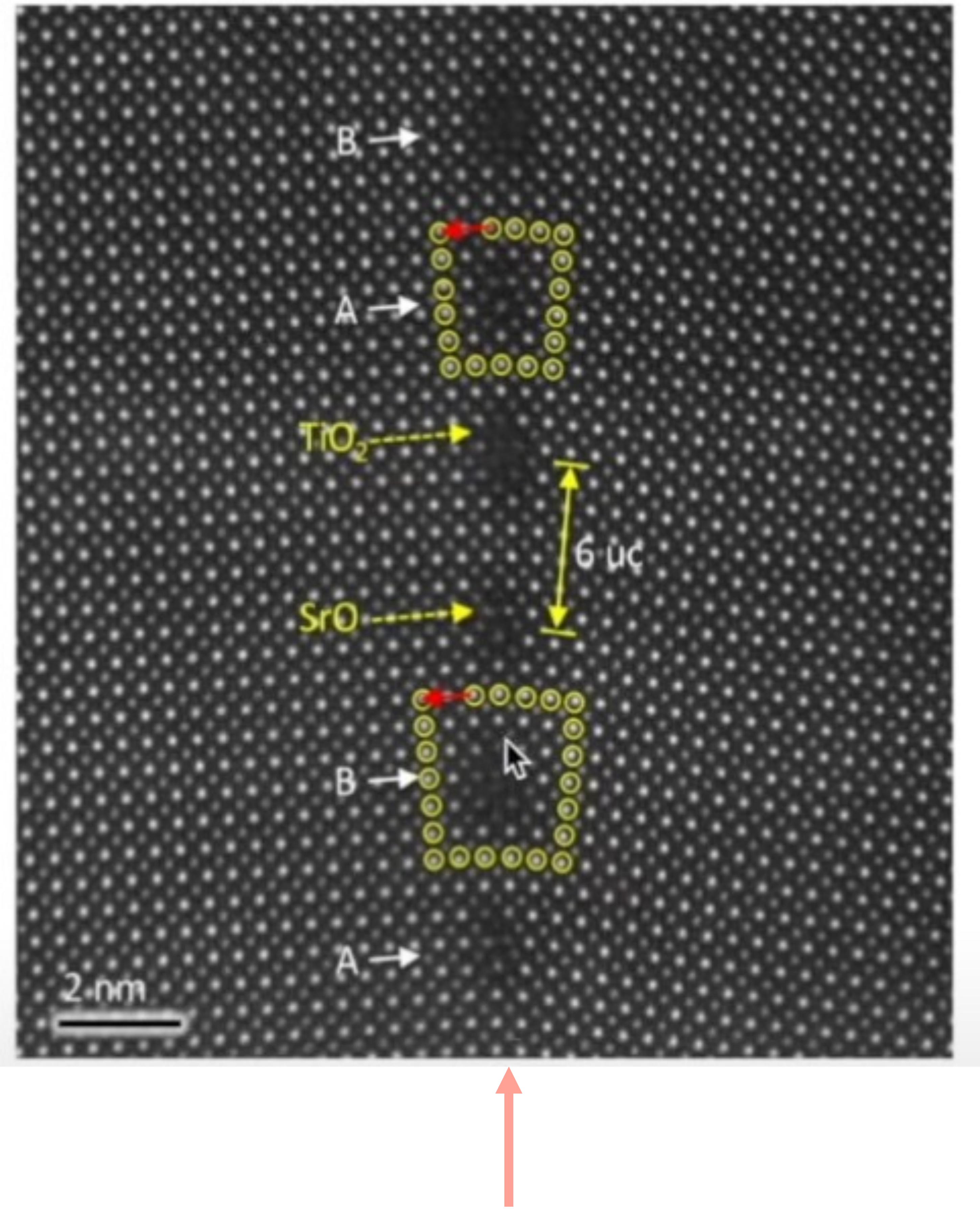
$$\theta \approx \frac{b}{d}$$

Dahmen | Phase Transformations, Crystallographic Aspects | 2003

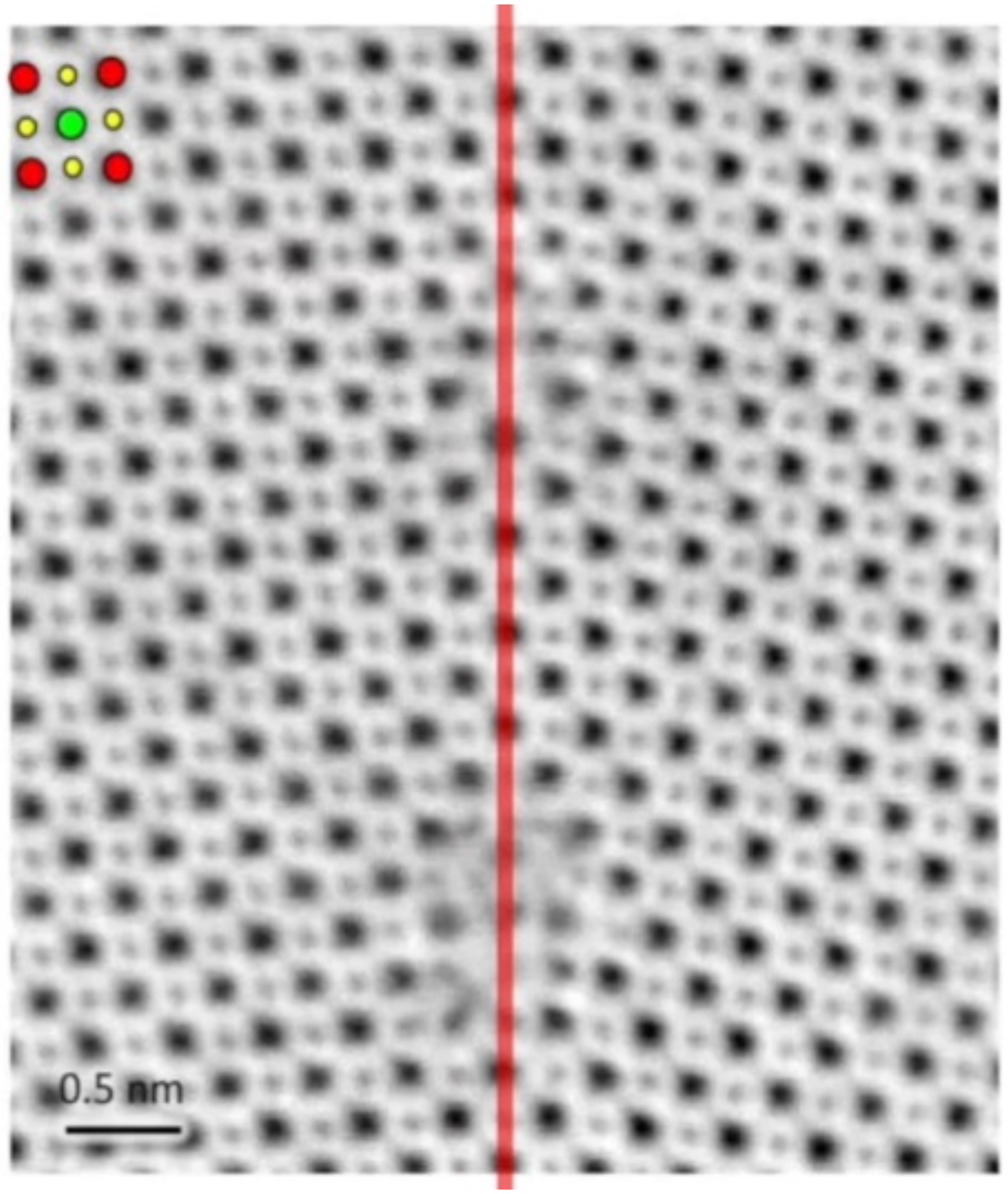
Low Angle Symmetric Tilt Grain Boundaries

Boundary energy clearly higher than bulk crystal

BUT disruption minimized by forming ordered arrays or dislocations



Grain boundary



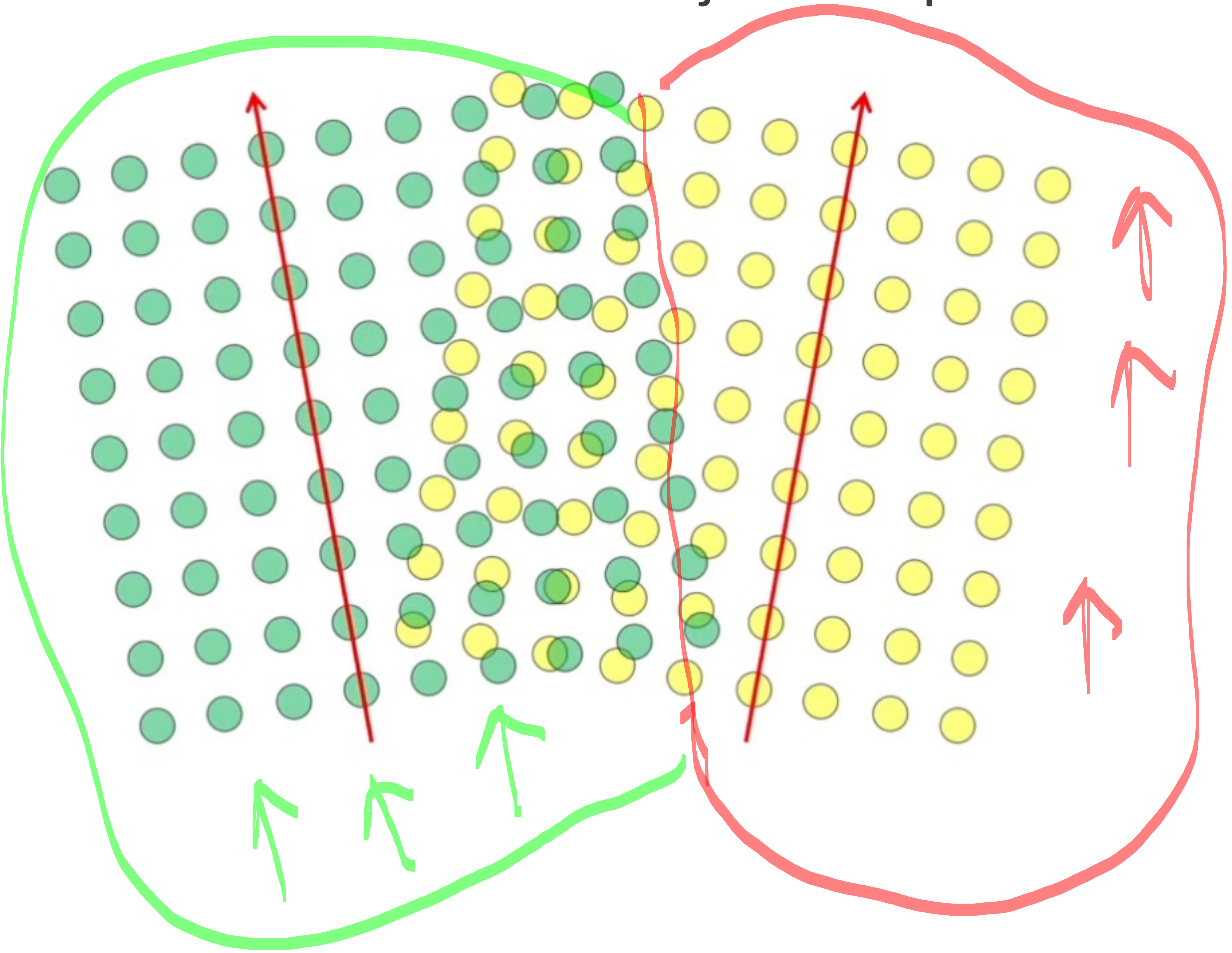
10° grain boundary in $SrTiO_3$ crystal

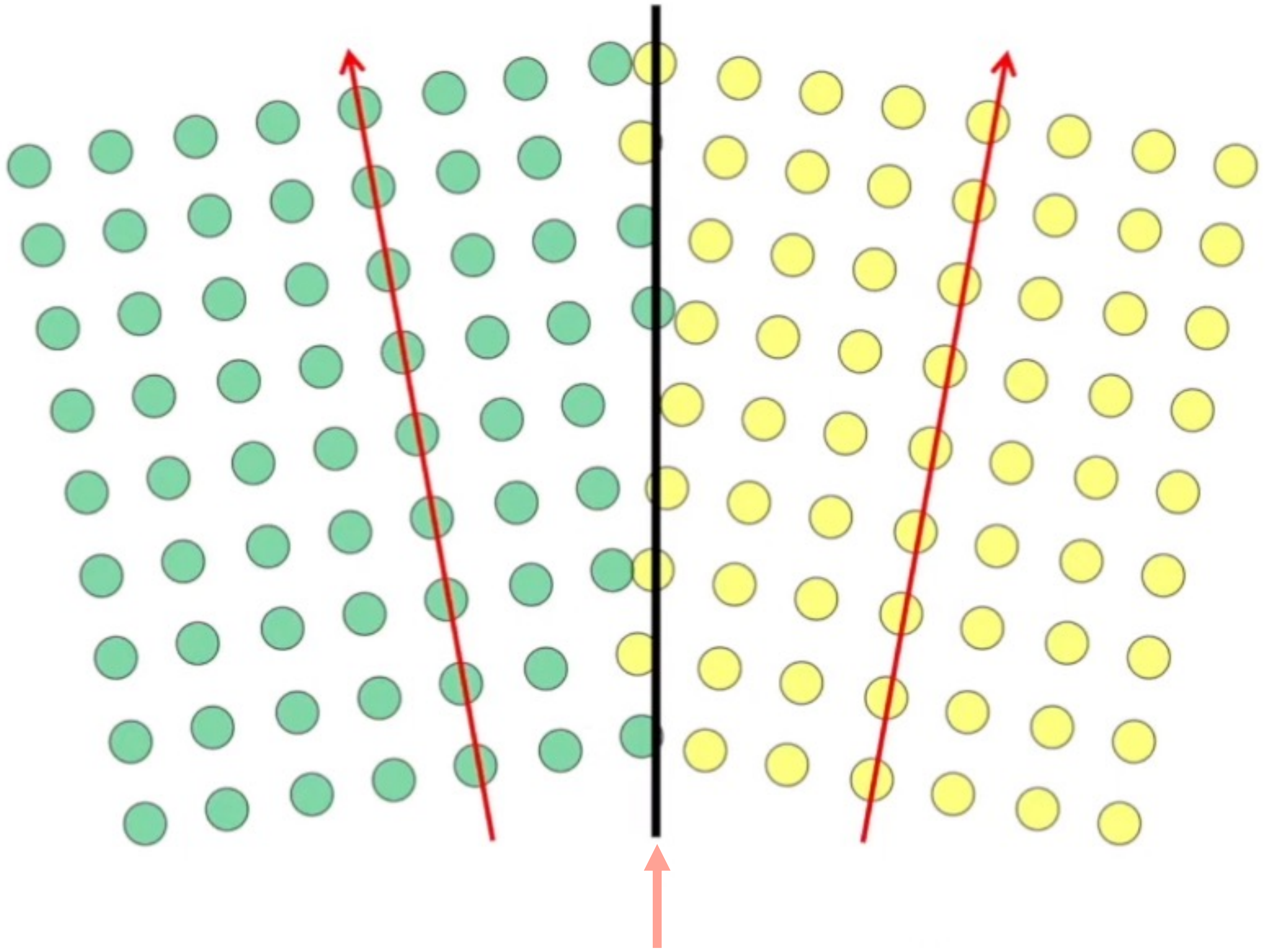
Sternlicht *et al.* | Ceramics | 2018

High Angle Tilt Grain Boundaries

Adjacent grain rotated with respect to each other

Can cause major disruptions in both lattices at the grain boundary





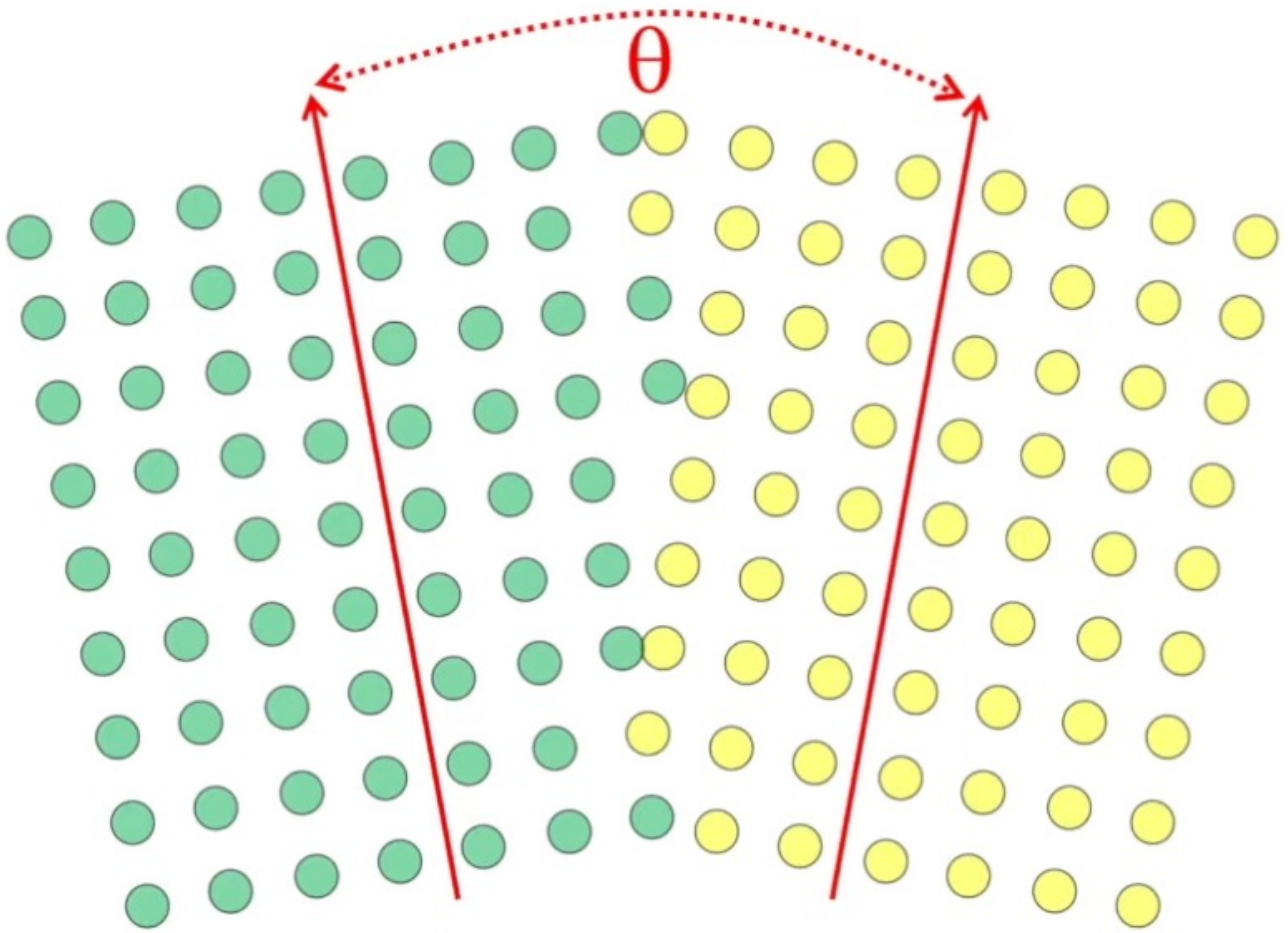
Disruption – high energy

Greater disruption ➔ Higher grain boundary energy

Grain Boundary Energy

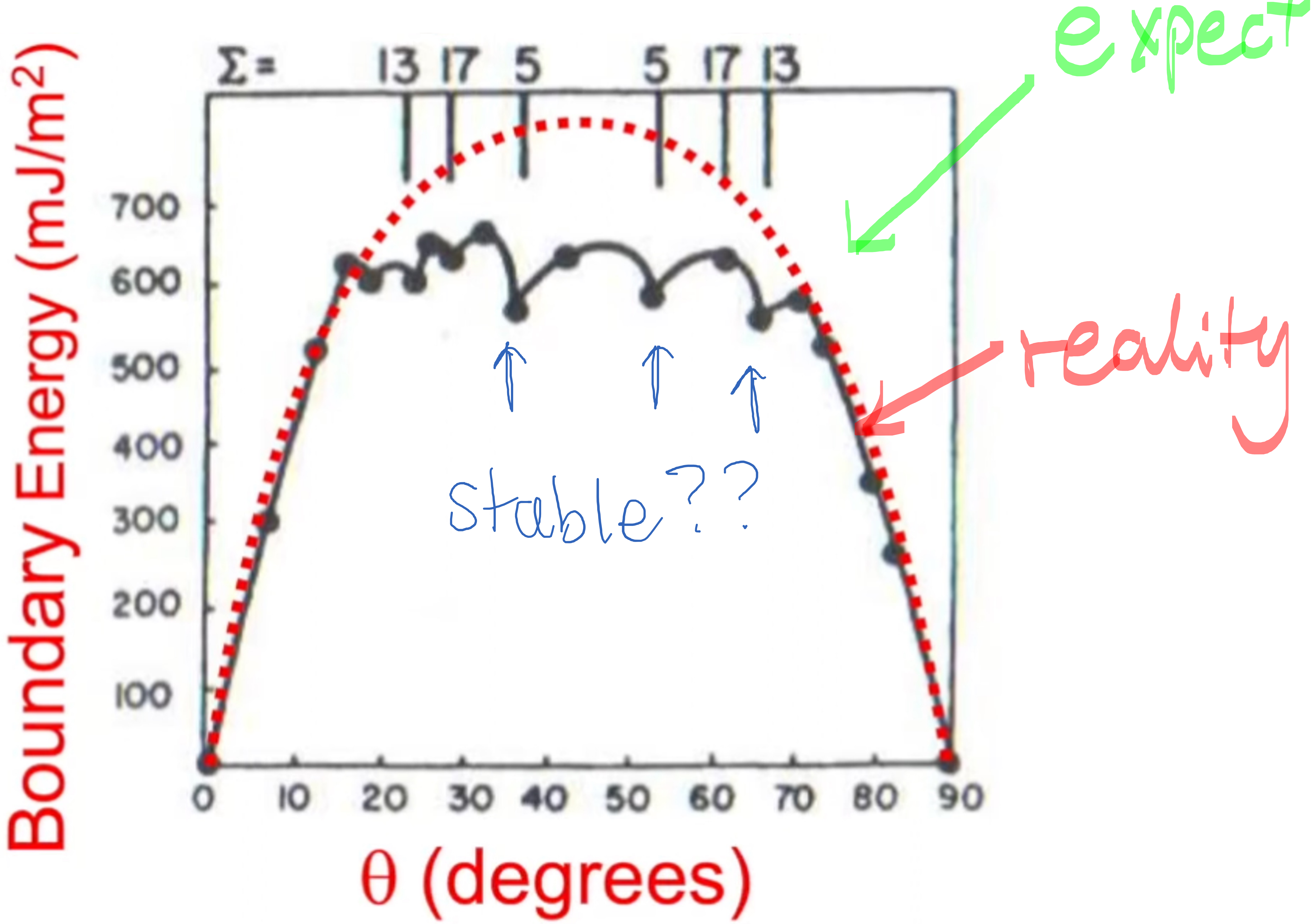
Greater misorientation – energy of boundary systematically increases

square or
simple cubic



Square lattice or simple cubic lattice

Maximum misorientation at 45° - highest energy?

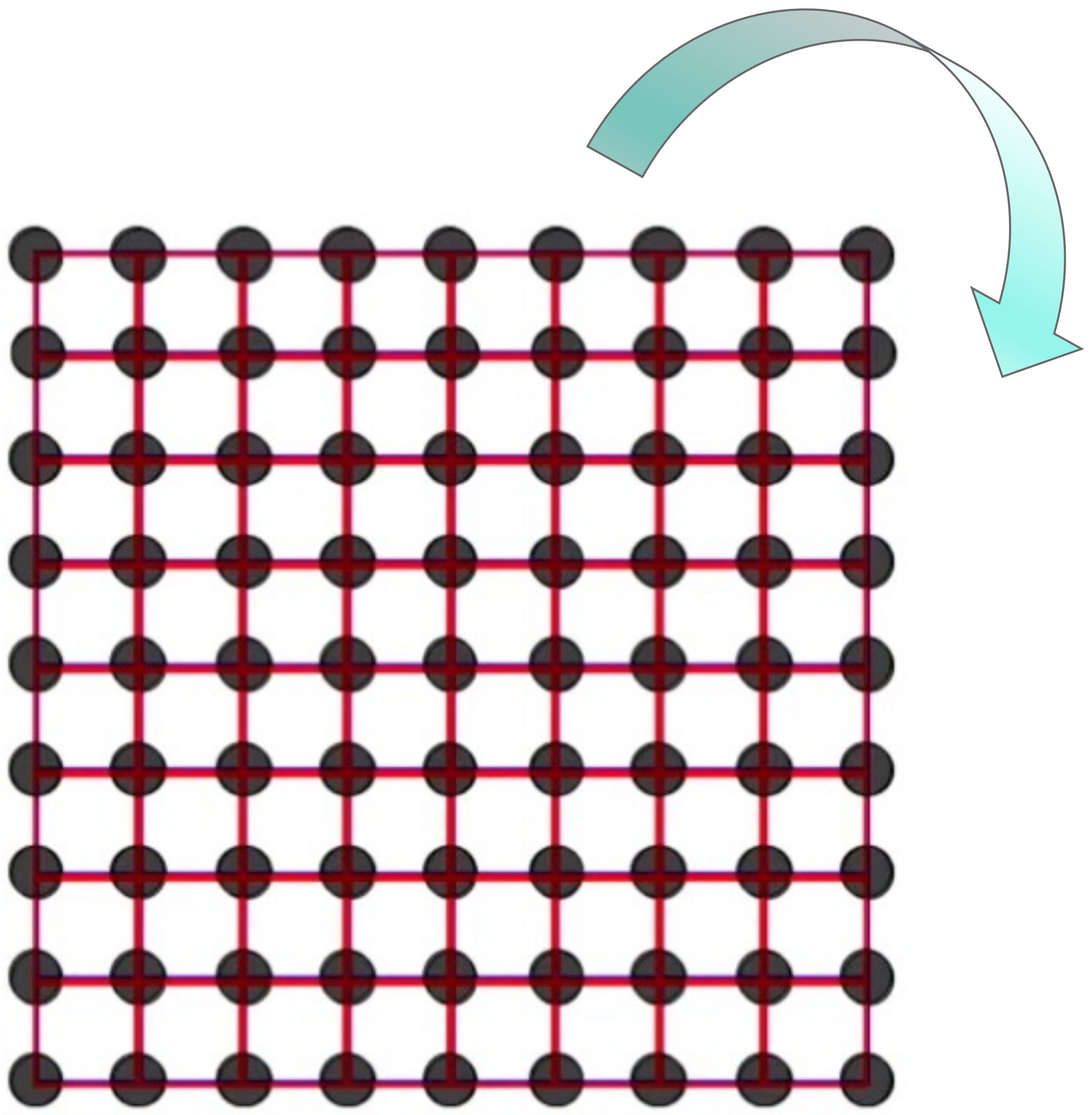


Lower energies at certain rotation angles

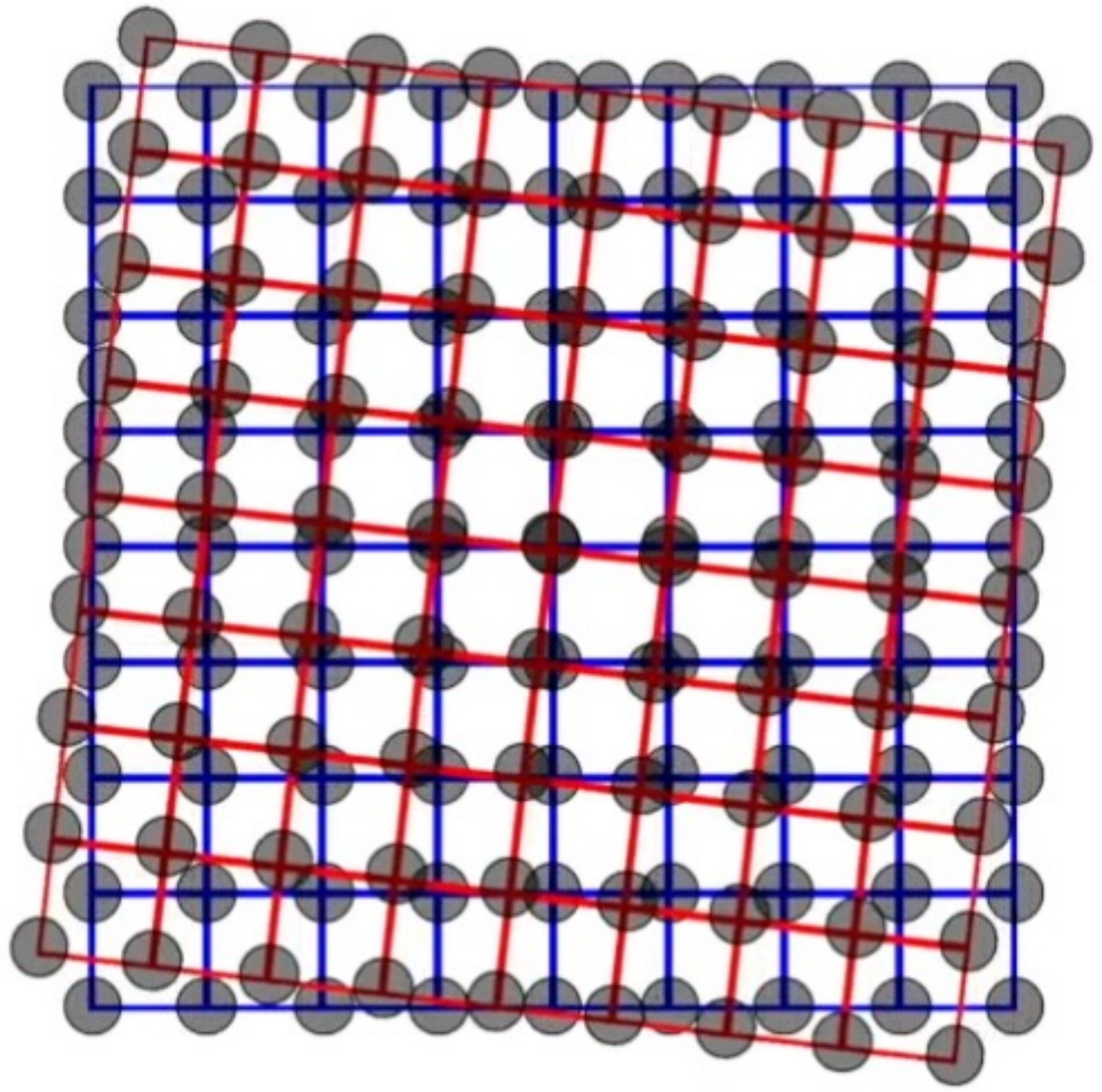
Grain Boundaries: Coincidence Site Lattice

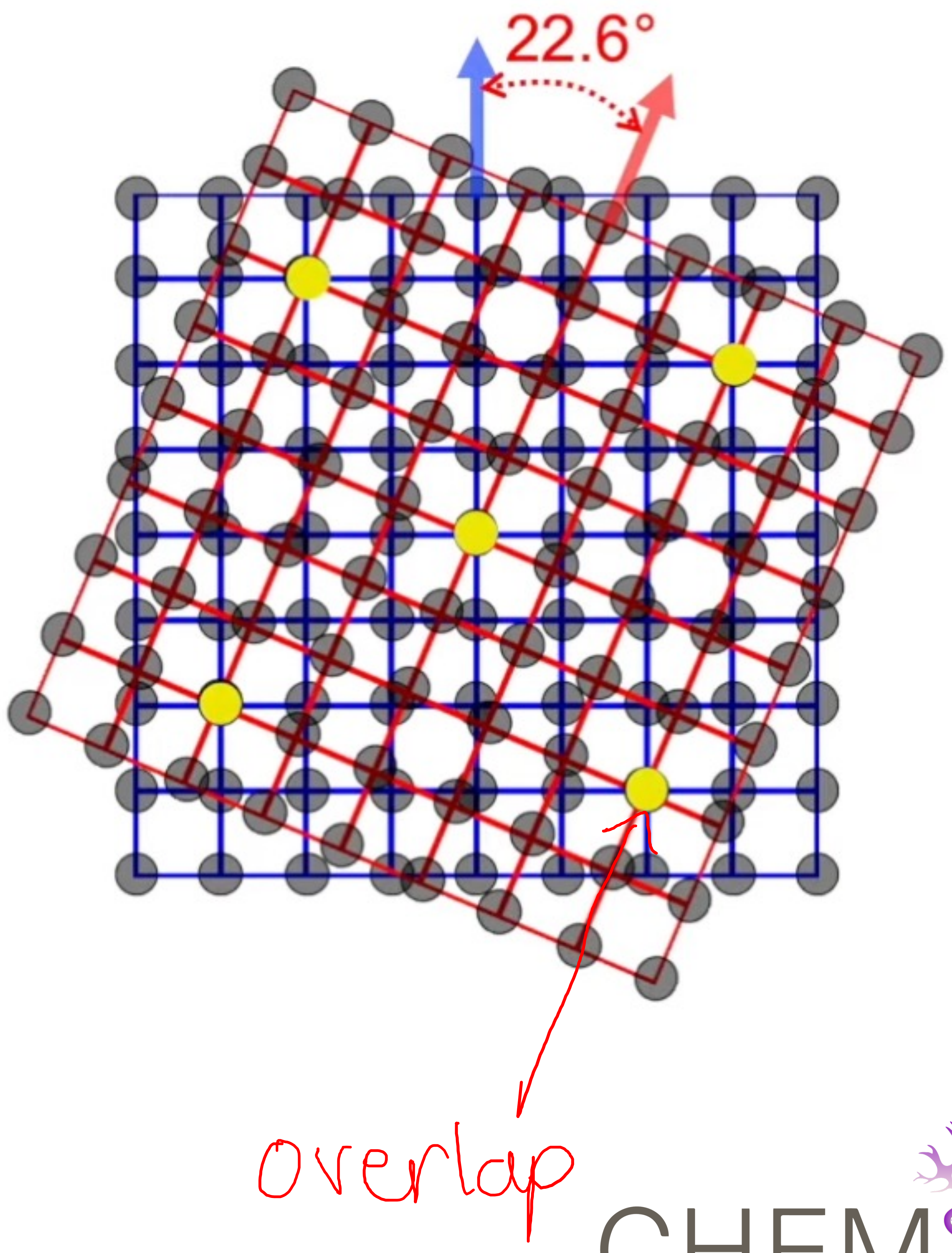
At certain angles, some lattice sites in rotated grains coincide at the boundary

Coincidence site lattice: at certain angles sites in both grains coincide ➔ more stable boundary



Superimposed grains





Grain Boundaries: Coincidence Site Lattice

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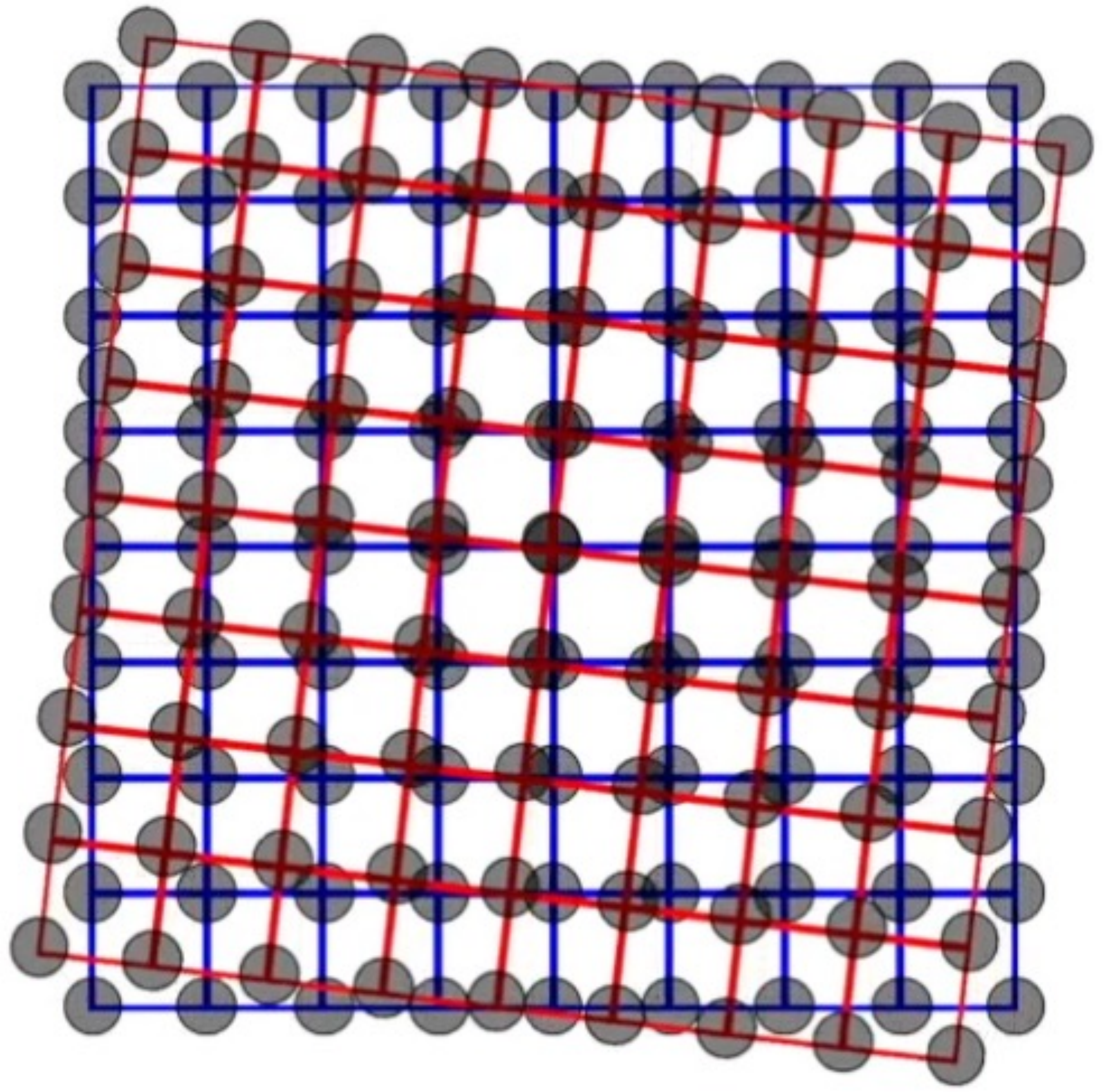
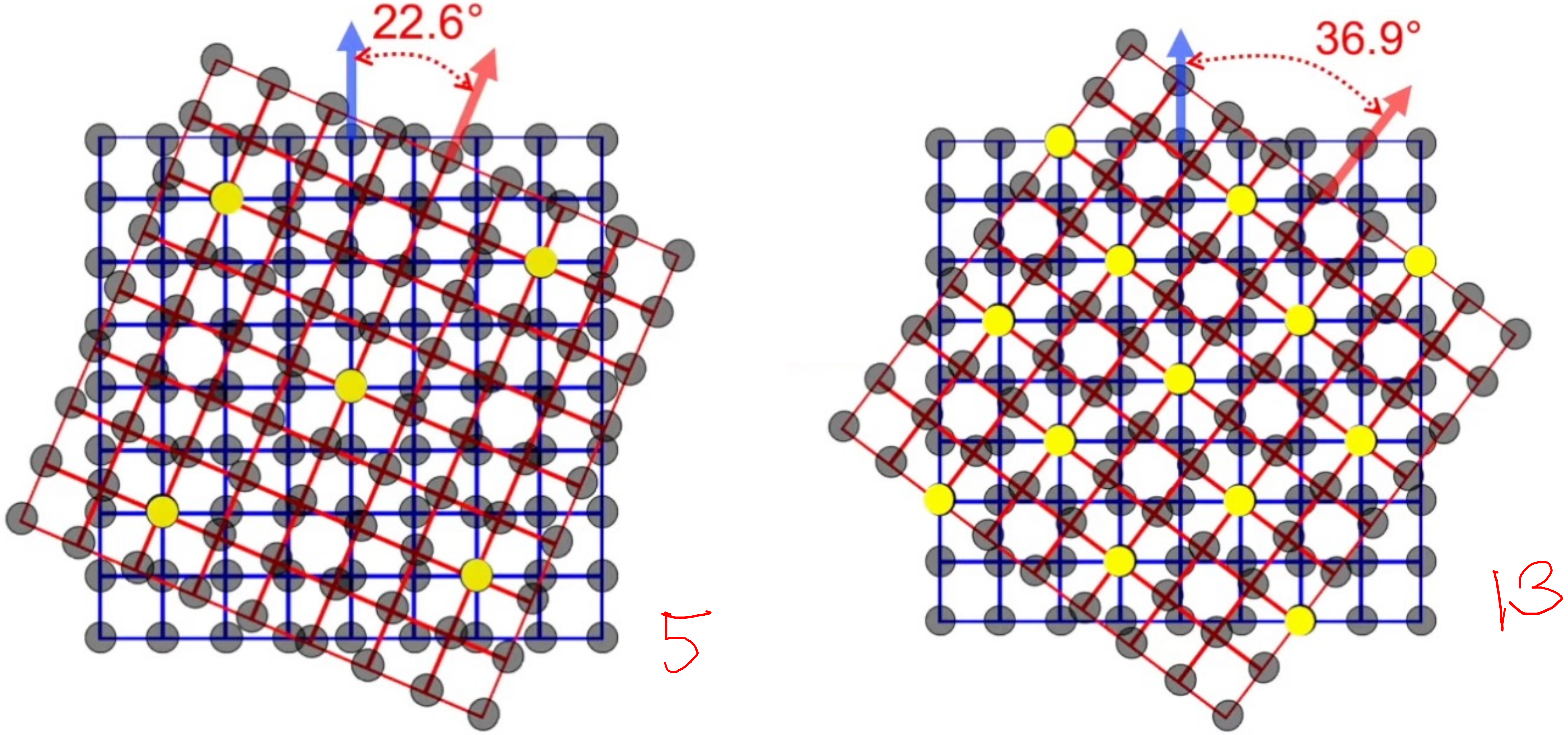


Superimposed grains



5

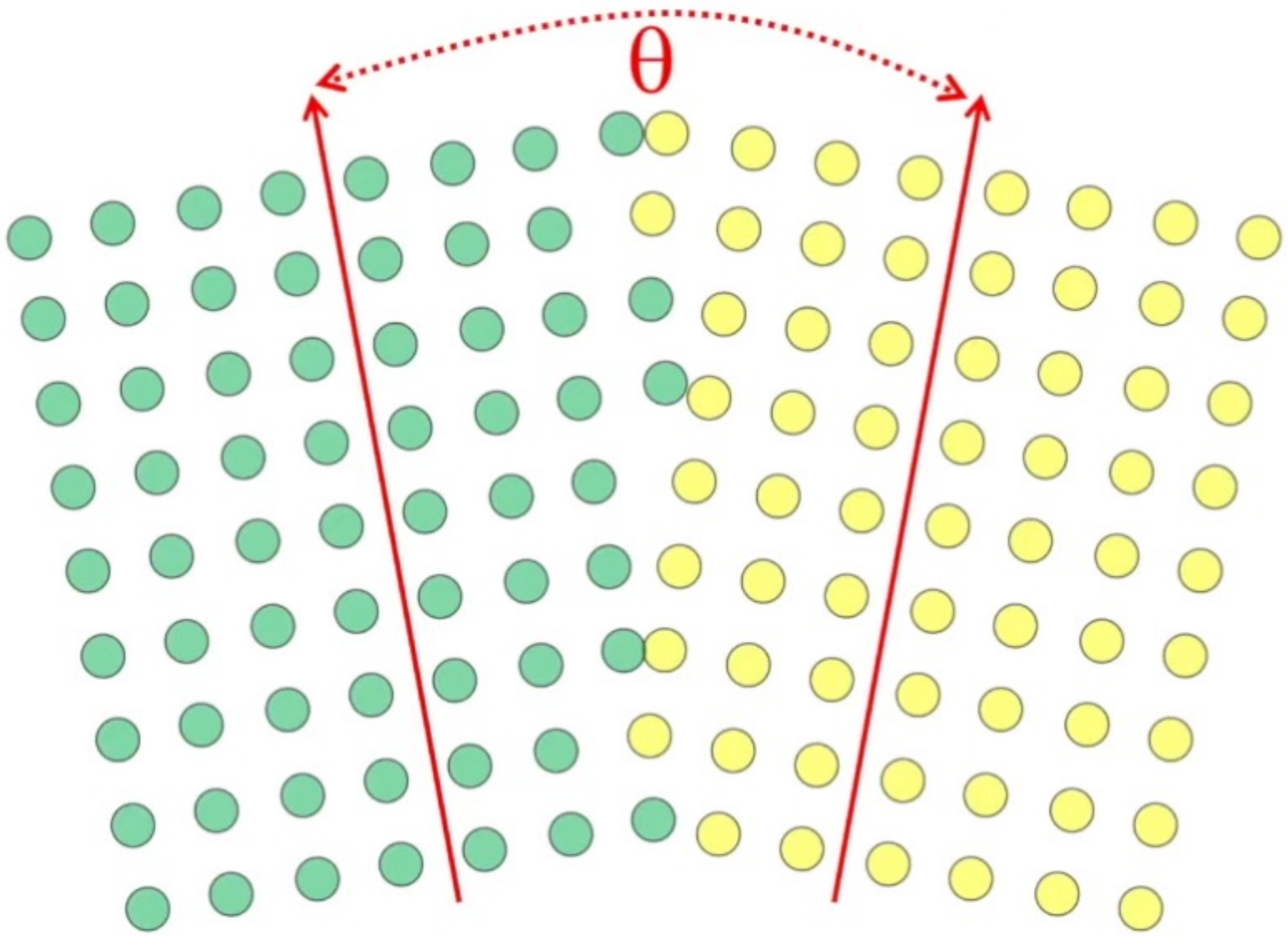
13

Some atoms in red and blue grains superimpose (yellow points)

Coincident site (super) lattice

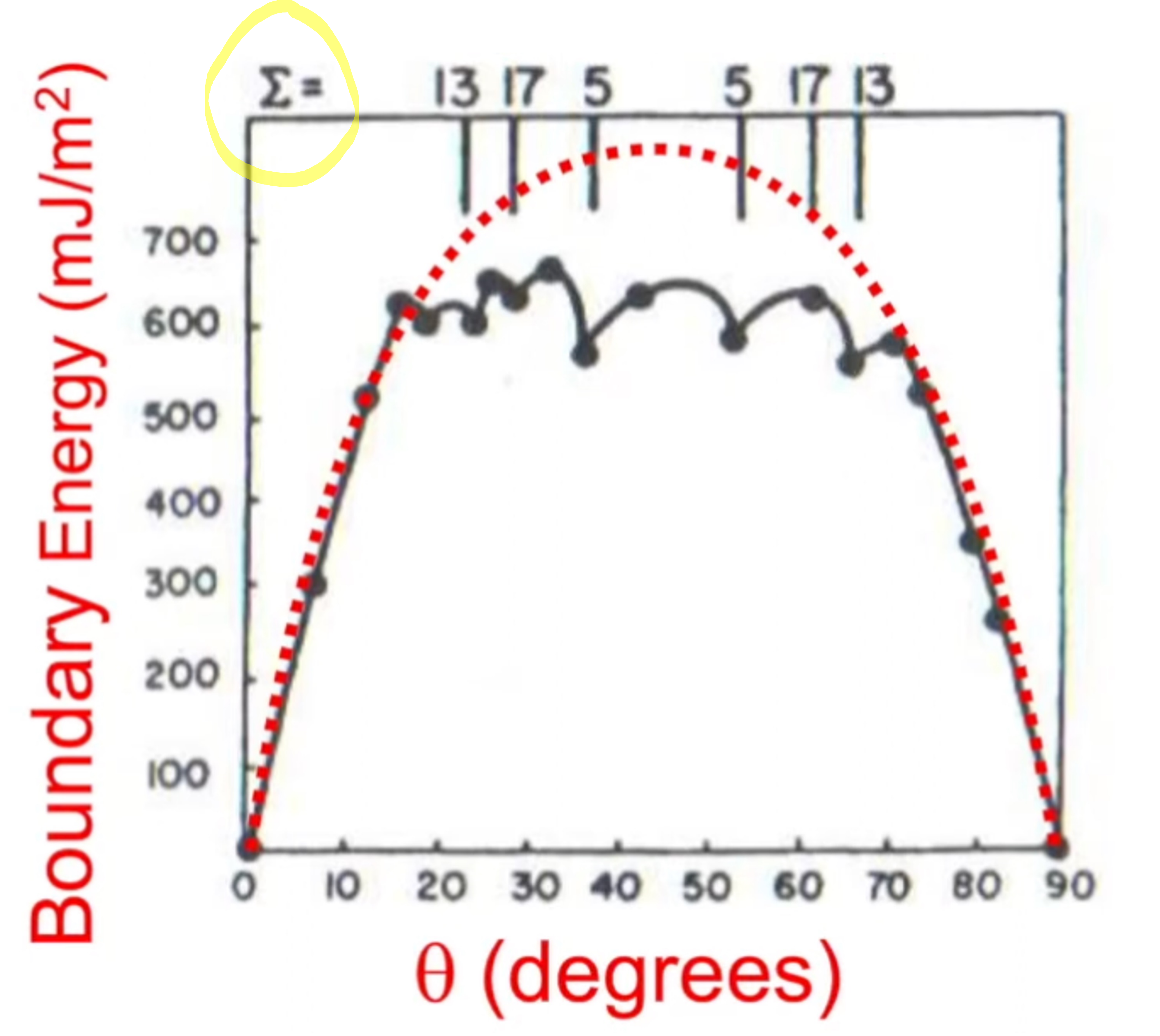
Grain Boundary Energy

Greater misorientation – energy of boundary systematically increases



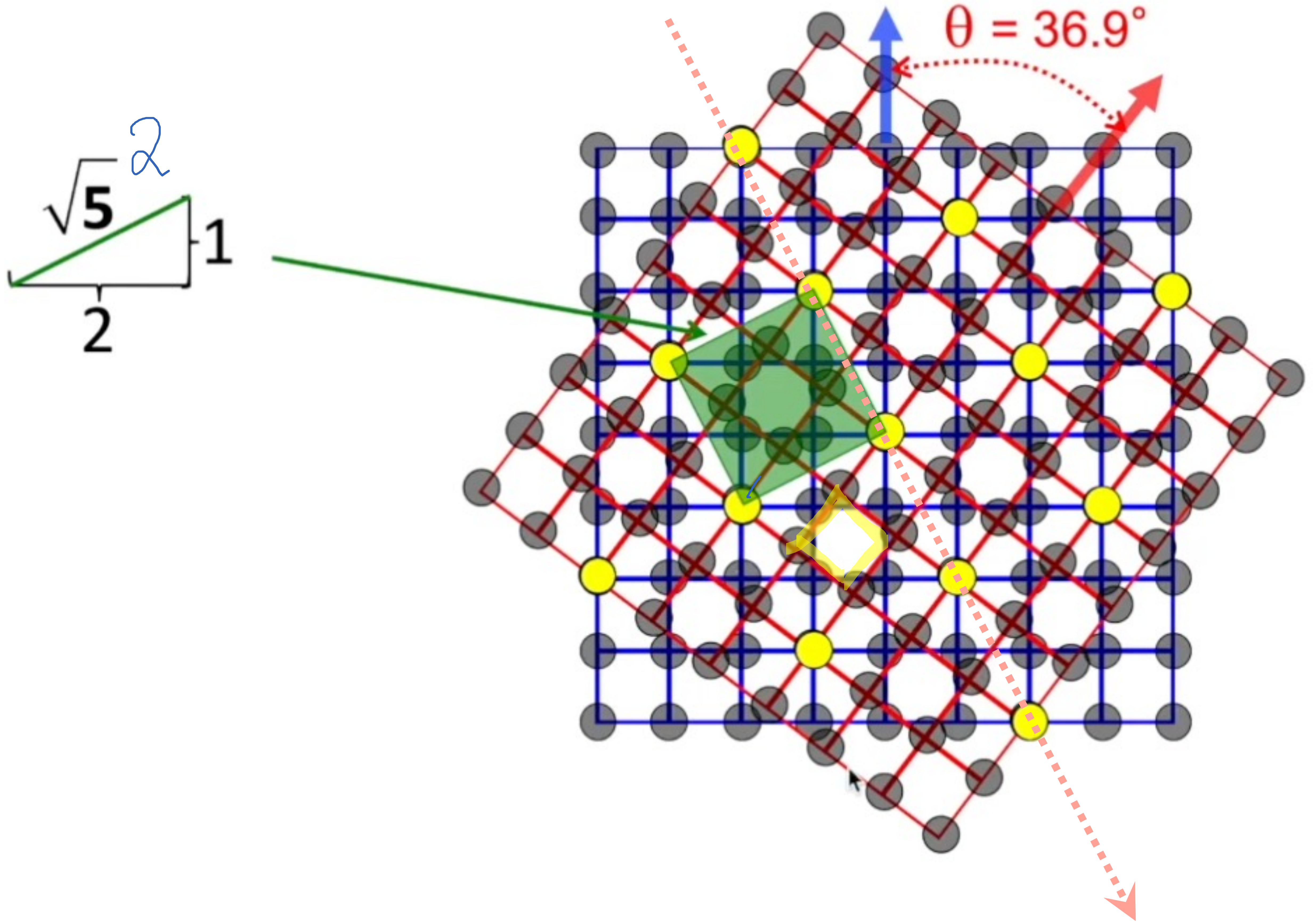
Square lattice or simple cubic lattice

Maximum misorientation at 45° - highest energy?



Lower energies at certain rotation angles

Coincidence Site Lattice Quantification



Quantify the coincidence site lattice using:

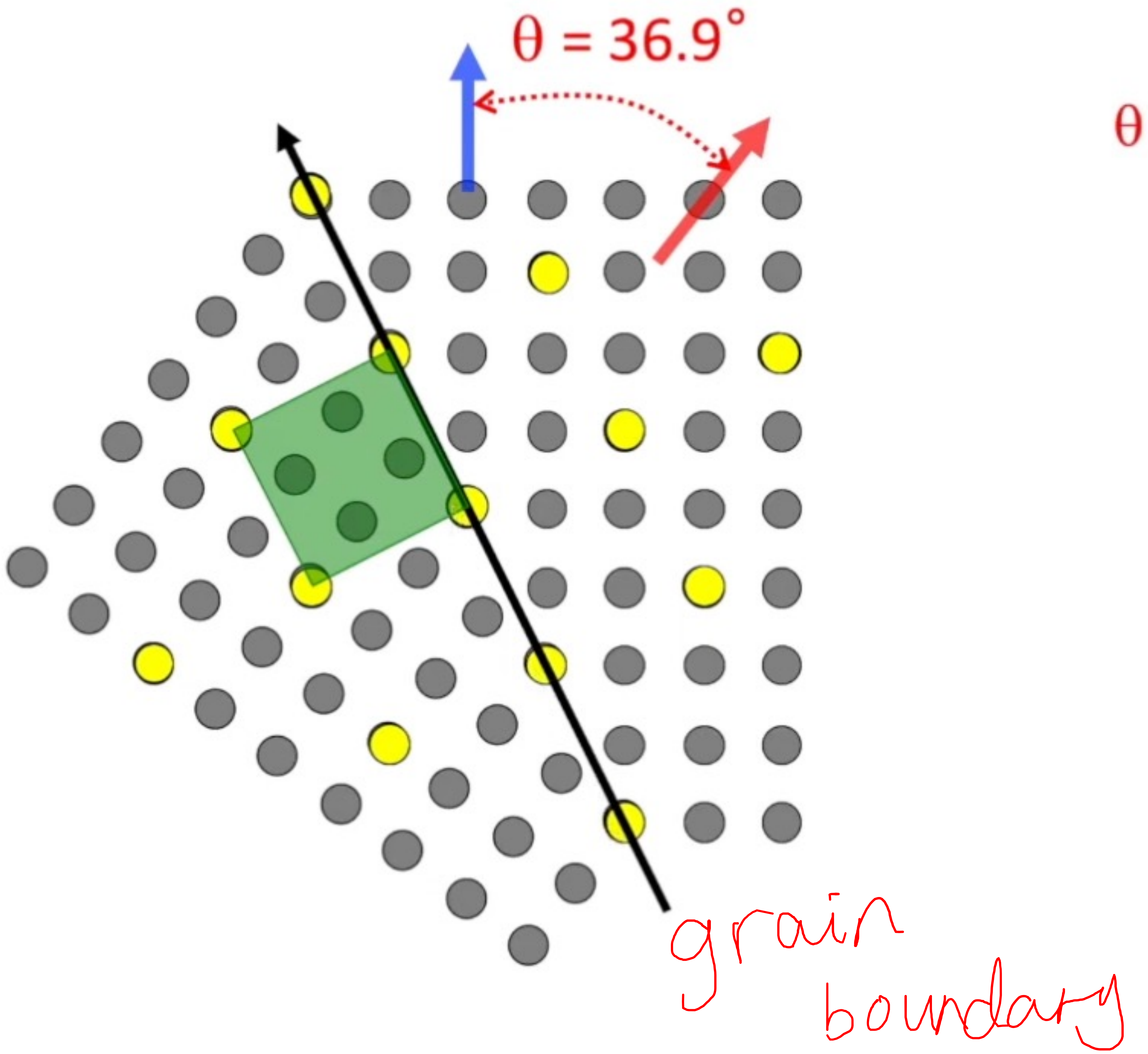
$$\Sigma = \frac{Area\ Coincidence\ Site\ Lattice}{Area\ Fundamental\ Lattice}$$

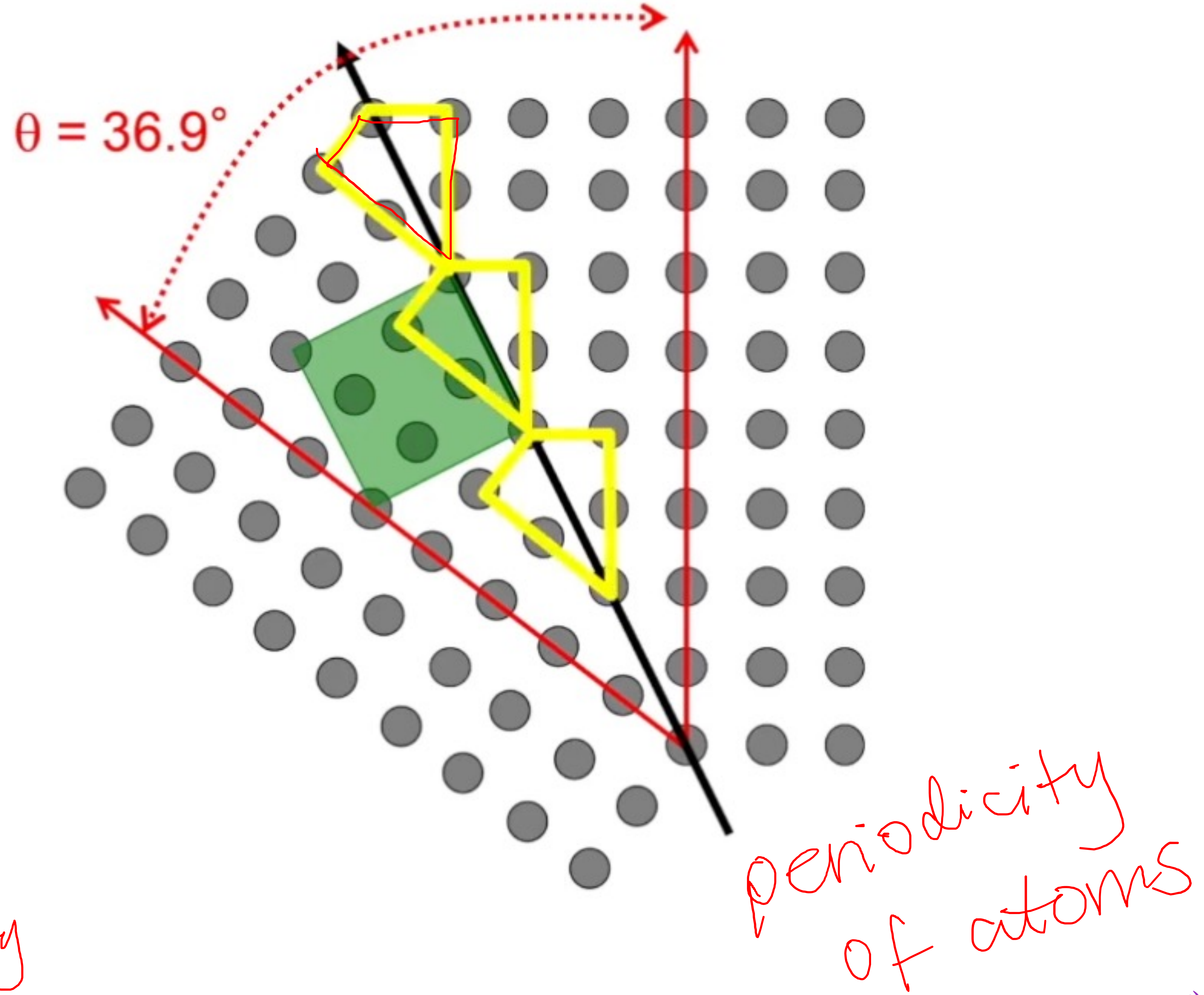
$$\Sigma = \frac{\sqrt{5}\ \text{x}\ \sqrt{5}}{1\text{x}1} = 5$$

Most stable grain boundary lies along the direction with the **highest density of coincident sites**

Coincidence Site Lattice Quantification

Σ = 5 grain boundary structure





Ordered repeat of atoms at grain boundary

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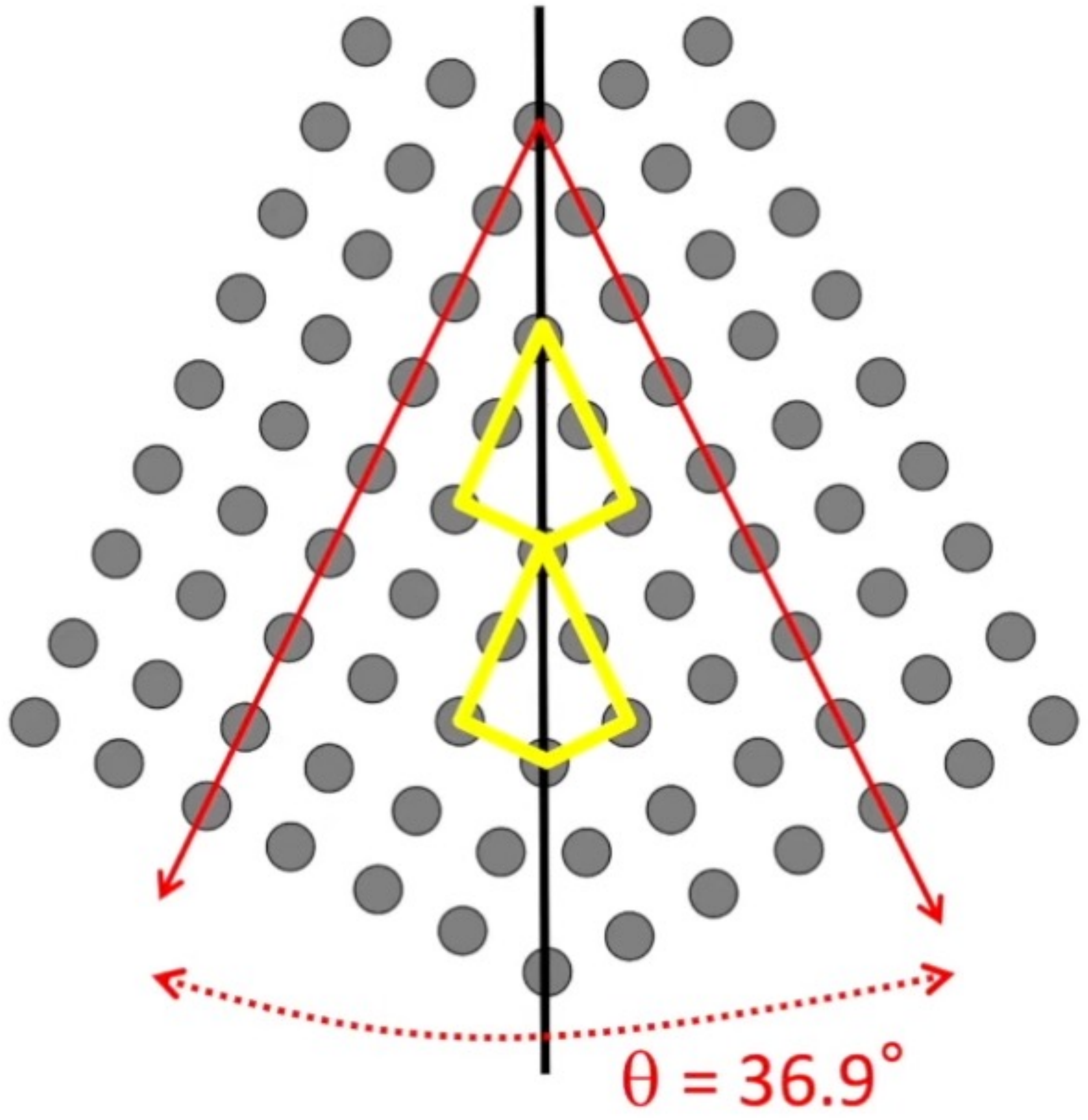
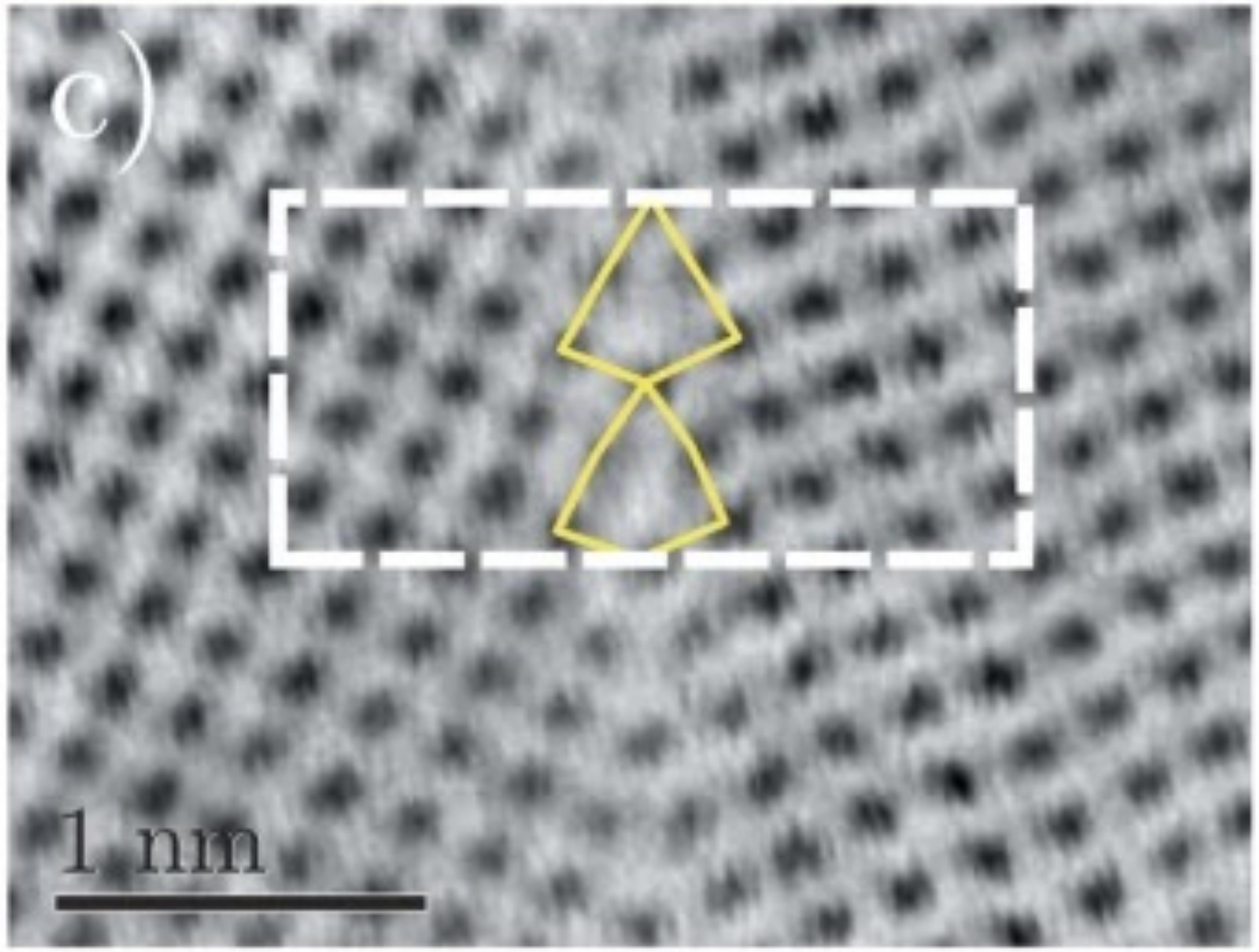
Do Such Lattices Exist In Reality?

Σ = 5 grain boundary structure



Atomic-scale imaging of MgO films



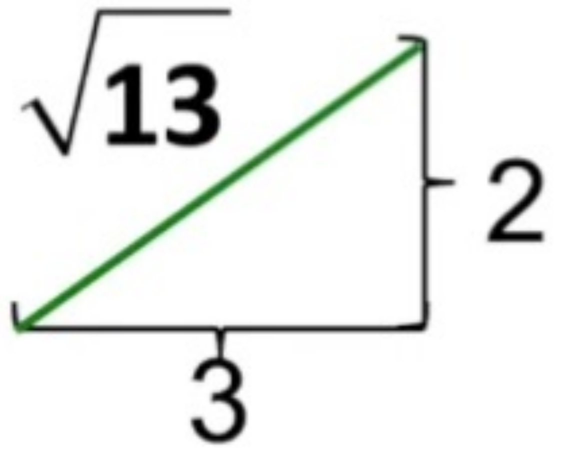
Polycrystalline metal oxides have diverse applications in nanoelectronics

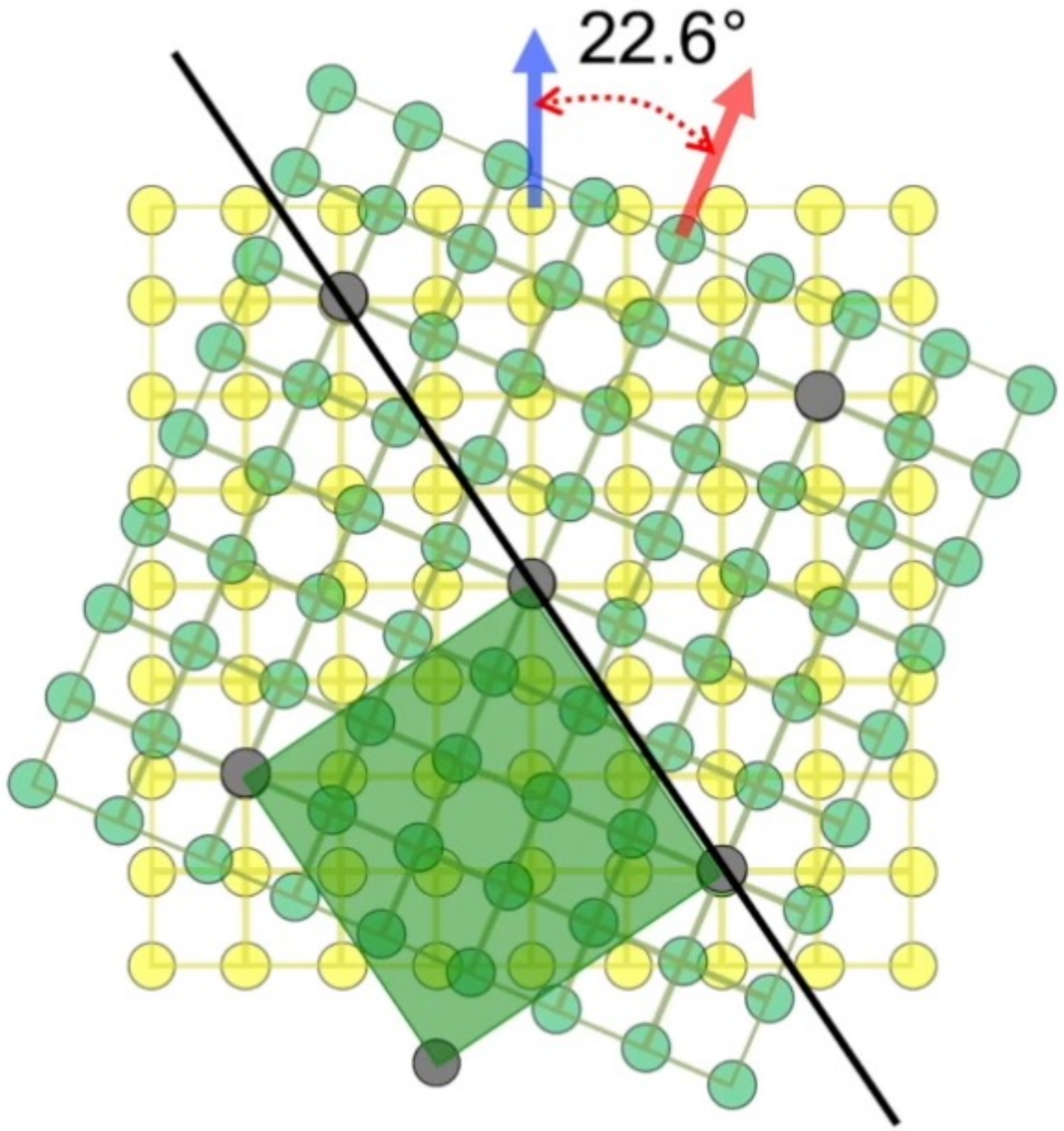
While grain boundary defects are ubiquitous, their structure and electronic properties are poorly understood

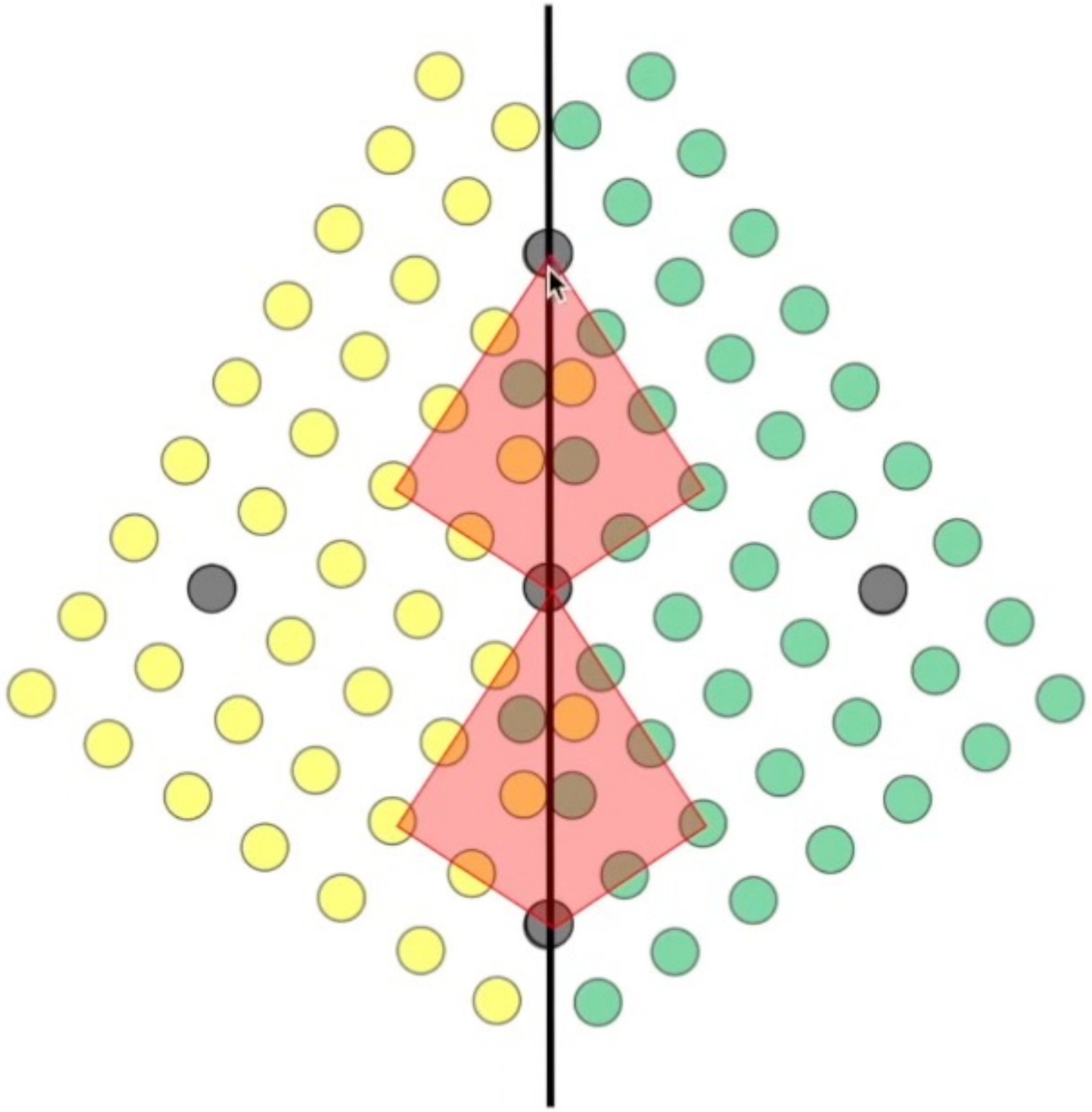
Bean *et al.* | Scientific Reports | 2017

Other Coincidence Site Lattices

Σ = 13 grain boundary structure

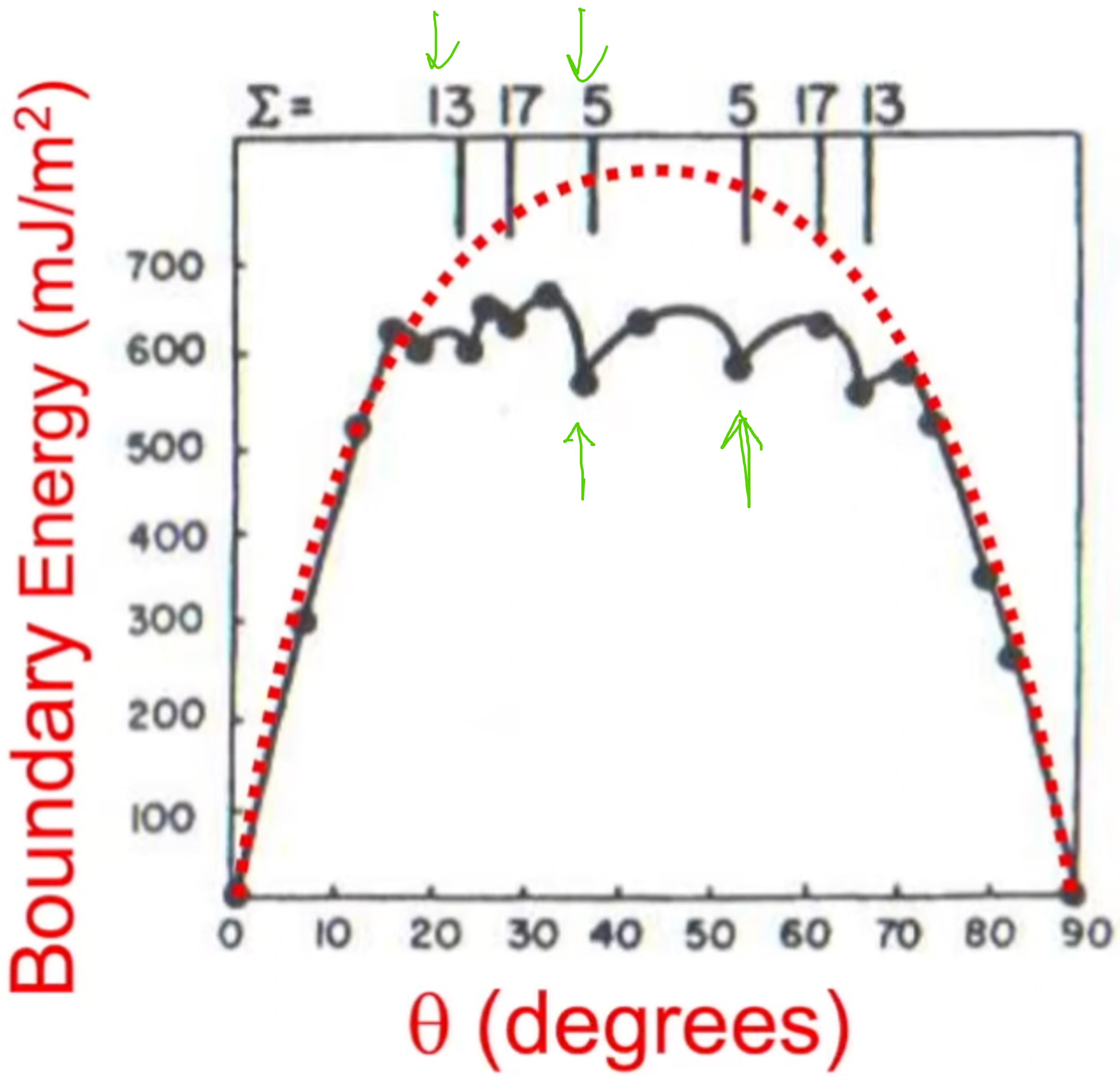






Periodic repeat of atoms at grain boundary

Grain Boundaries are Essentially Organized Defects



Lower energies correspond to angles for forming coincidence site lattices

As Σ increases ➔ less sites overlap ➔ less stabilization

Σ=1 ➔ perfect fit of all sites (no rotation)

Nature prefers order even when the structure is imperfect

The **coincidence site lattice** is a way the crystal partially restores order at an interface

Key Takeaways

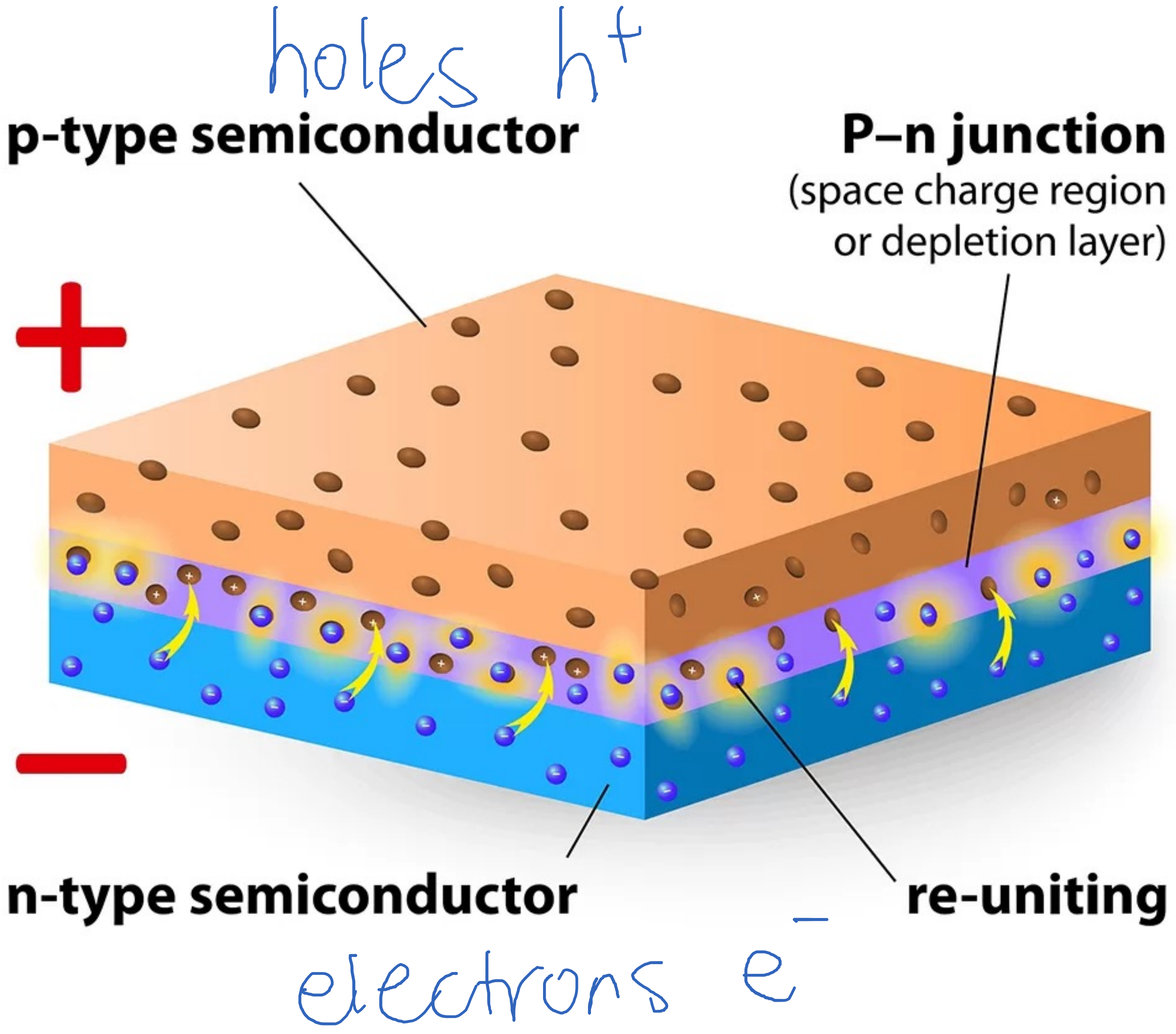
- Grain boundaries are 2-D defects between misoriented crystals
- As the angle of misorientation increases, crystal mismatch grows ➔ higher grain boundary energy
- Coincidence site lattice models determine low-energy orientations
- Such lattices exist in various polycrystalline materials

Why do we care about grain boundaries as defects?

Grain Boundaries Affect Electrical Properties

Polycrystalline materials are everywhere, and their grain boundaries strongly affect electronic properties (e.g. efficiency in solar cells)

Polycrystalline silicon solar cell



Grain boundaries act as “roadblocks” to the movement of charge carriers (electrons and holes) and trap or scatter these charges

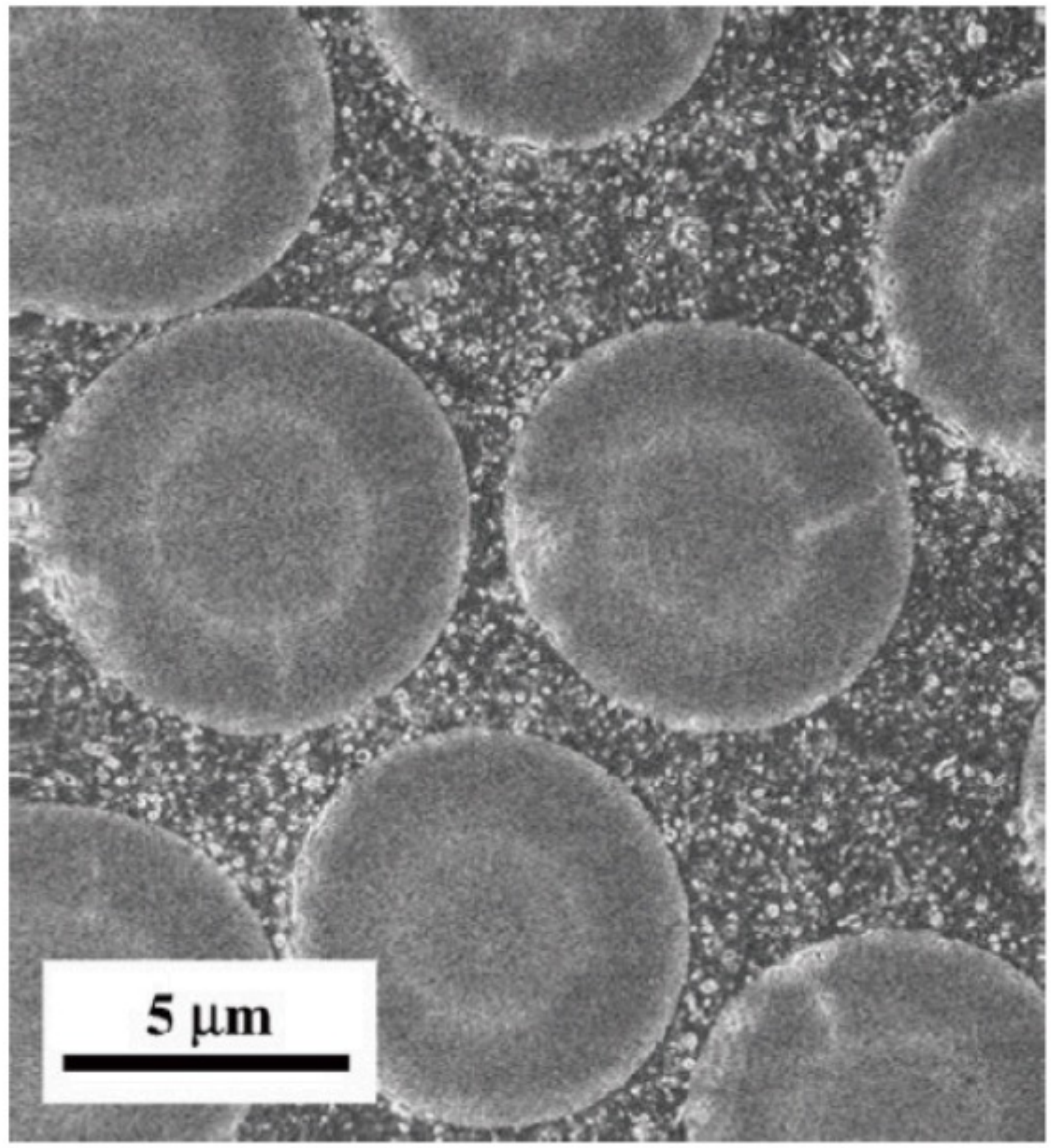
Polycrystalline silicon solar cells are cheaper to make but less efficient than single-crystal silicon

Grain Boundary Engineering: Tune Mechanical/Electrical Properties

Optical microscopy of metal alloy microstructure

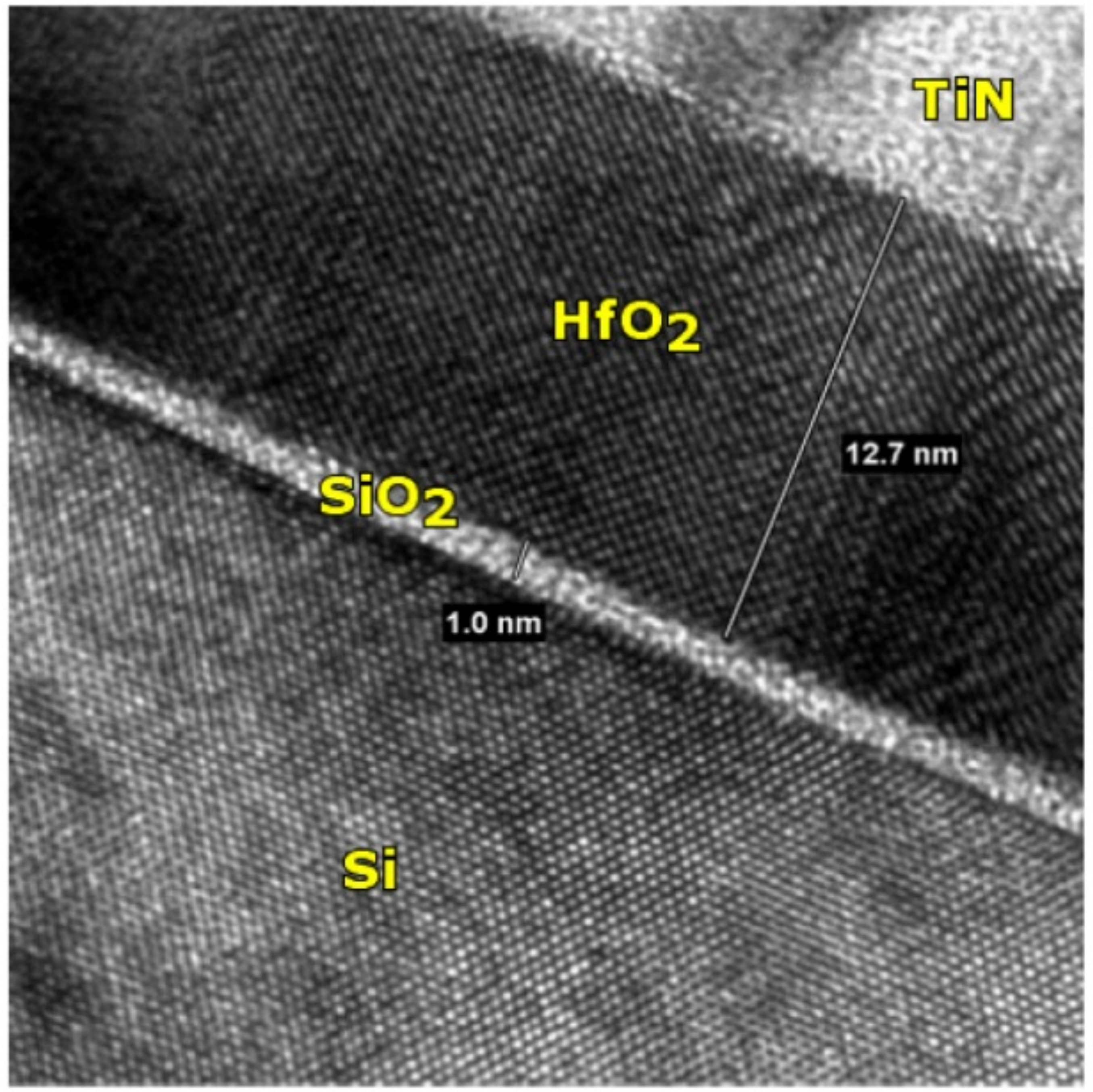
Grain size/shape influence ductility (mechanical)

Scanning electron microscopy inclusions in matrix



Inclusions block fractures/movement

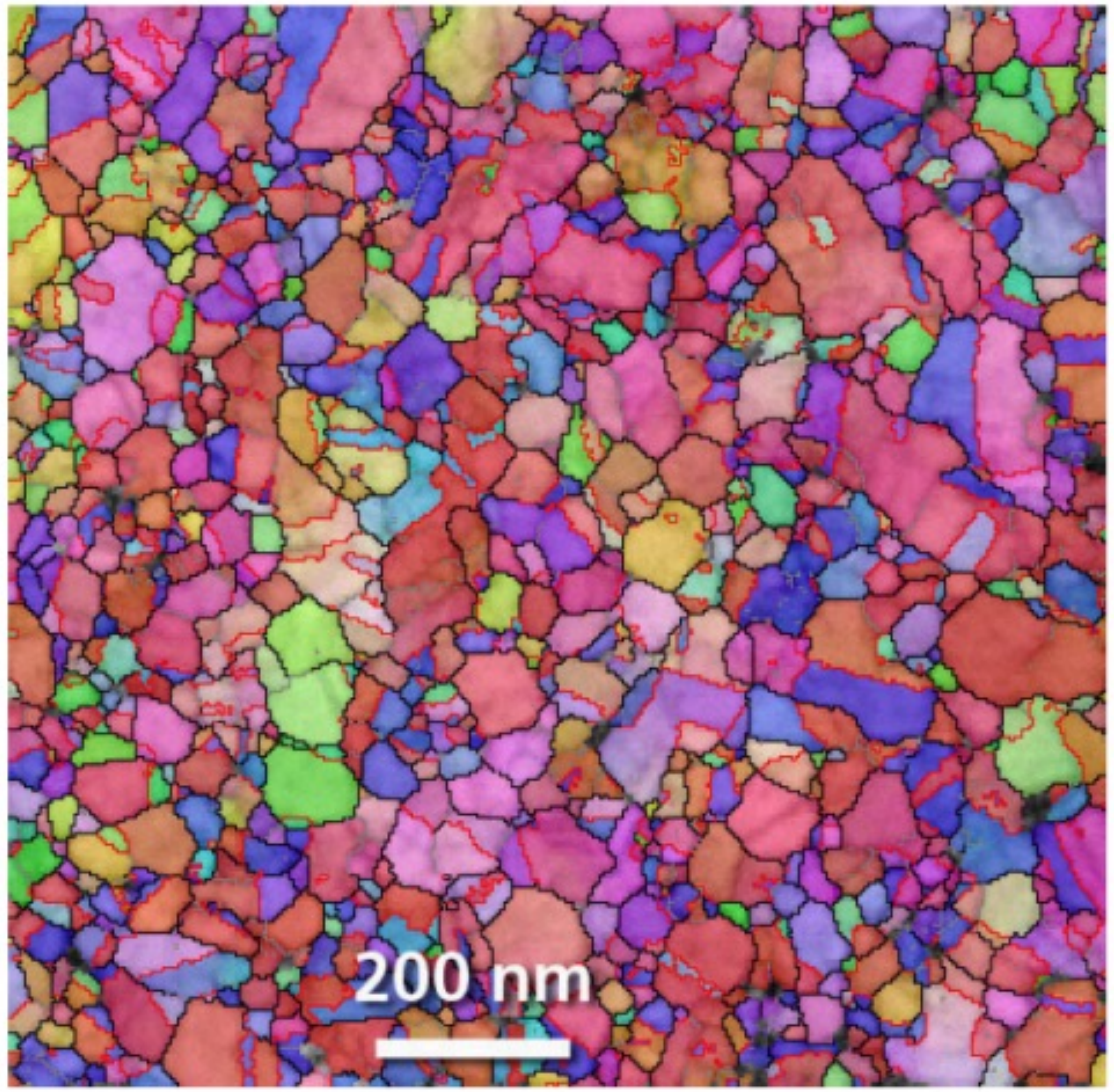
Transmission electron microscopy cross-section



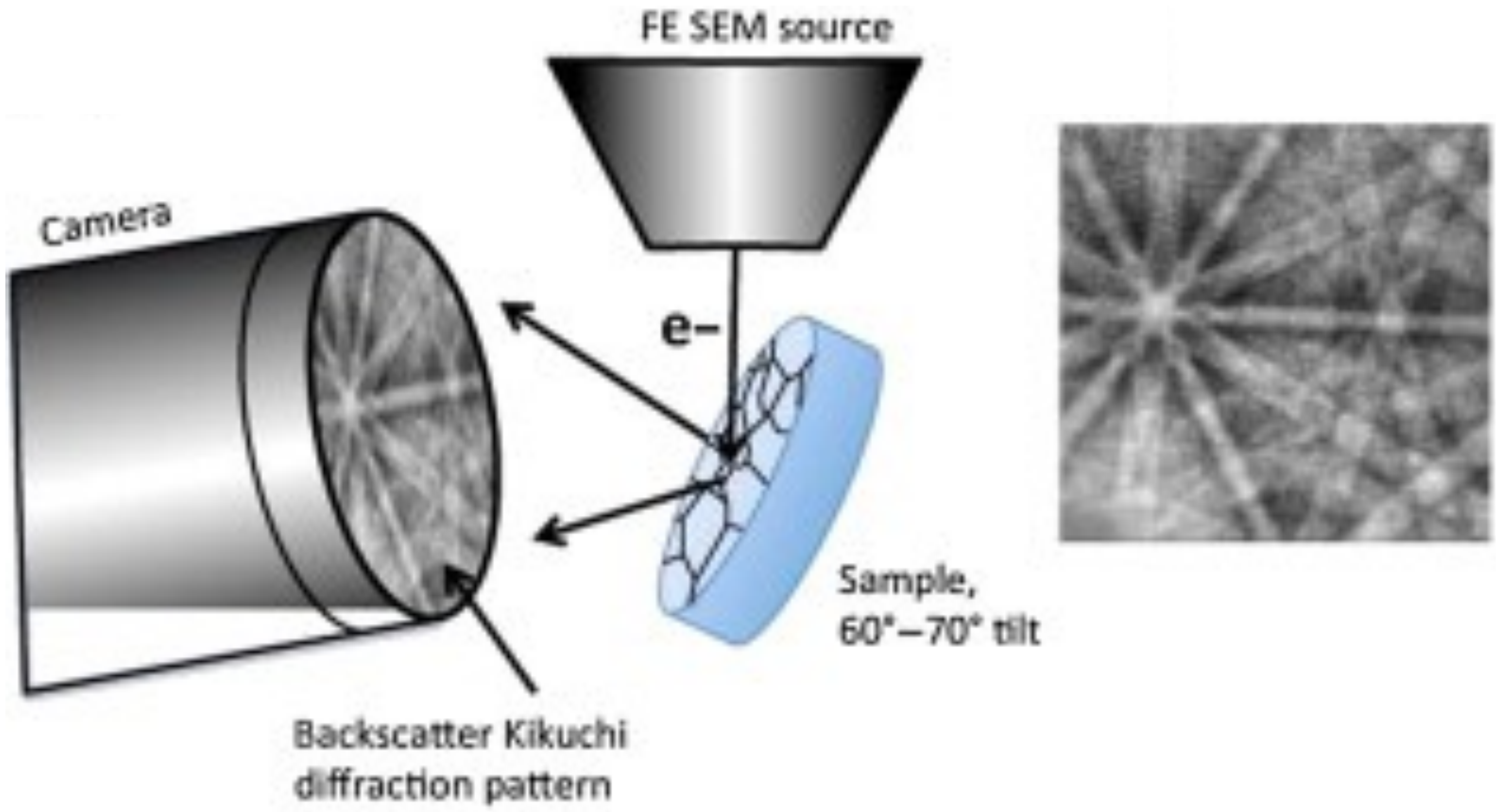
Sharpness of boundaries control electronic properties in semiconductors

electrical performance

Characterizing Polycrystalline Grain Boundaries



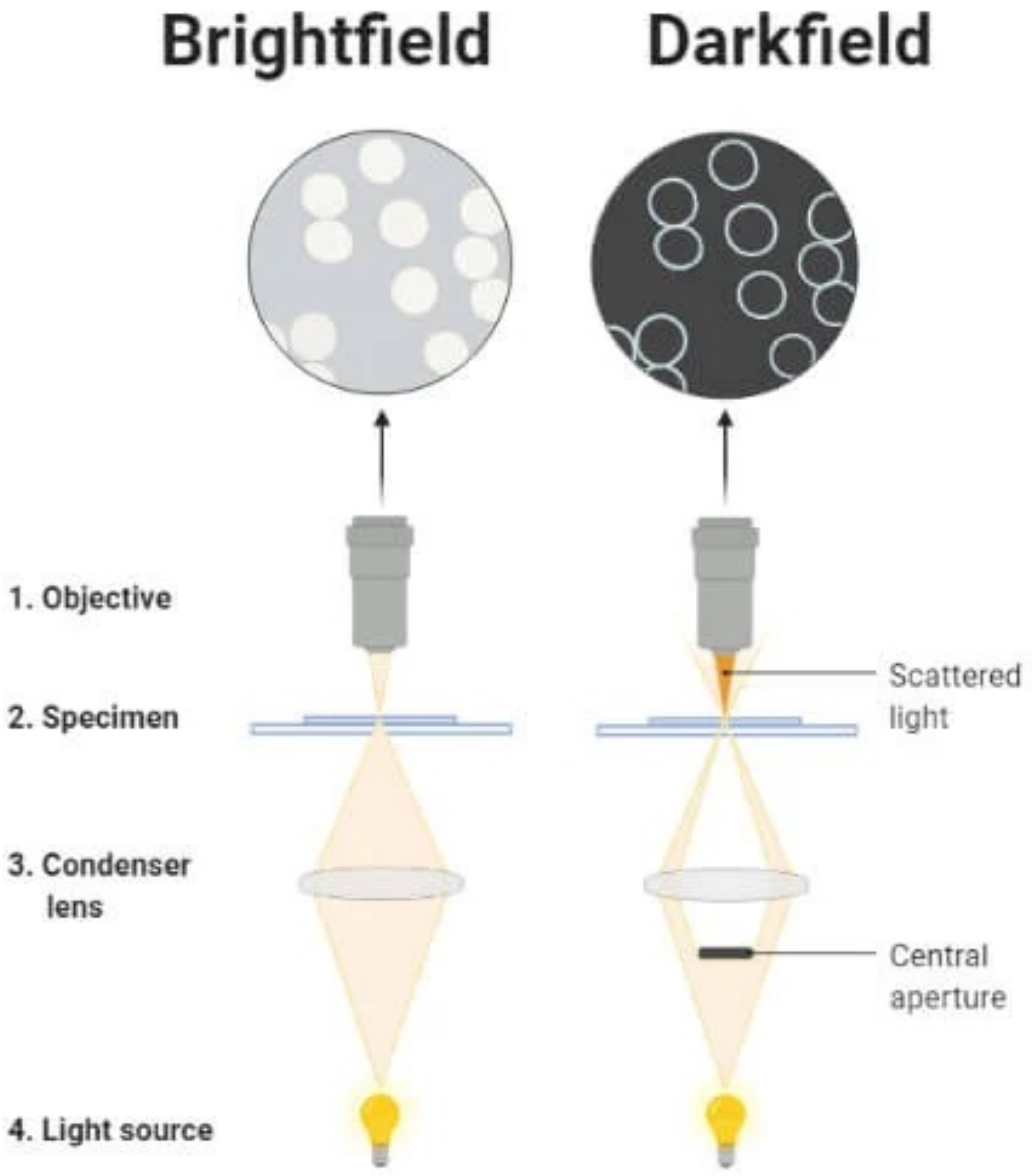
Electron Backscatter Diffraction (EBDS)



Inkson | Materials Characterization using NDE Methods | 2016

Electron Microscopy to Visualize Real Surfaces and Materials

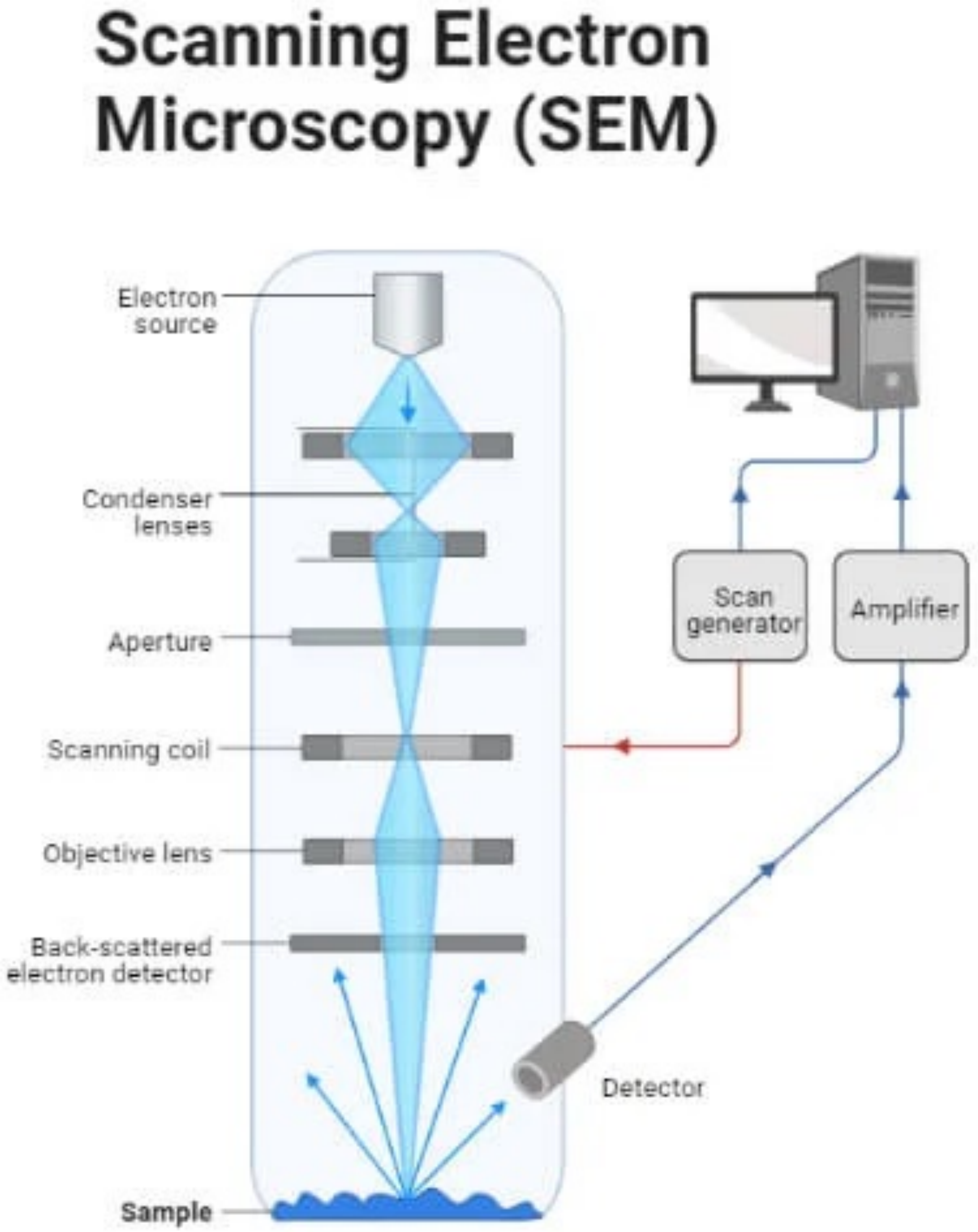
Light Microscopy



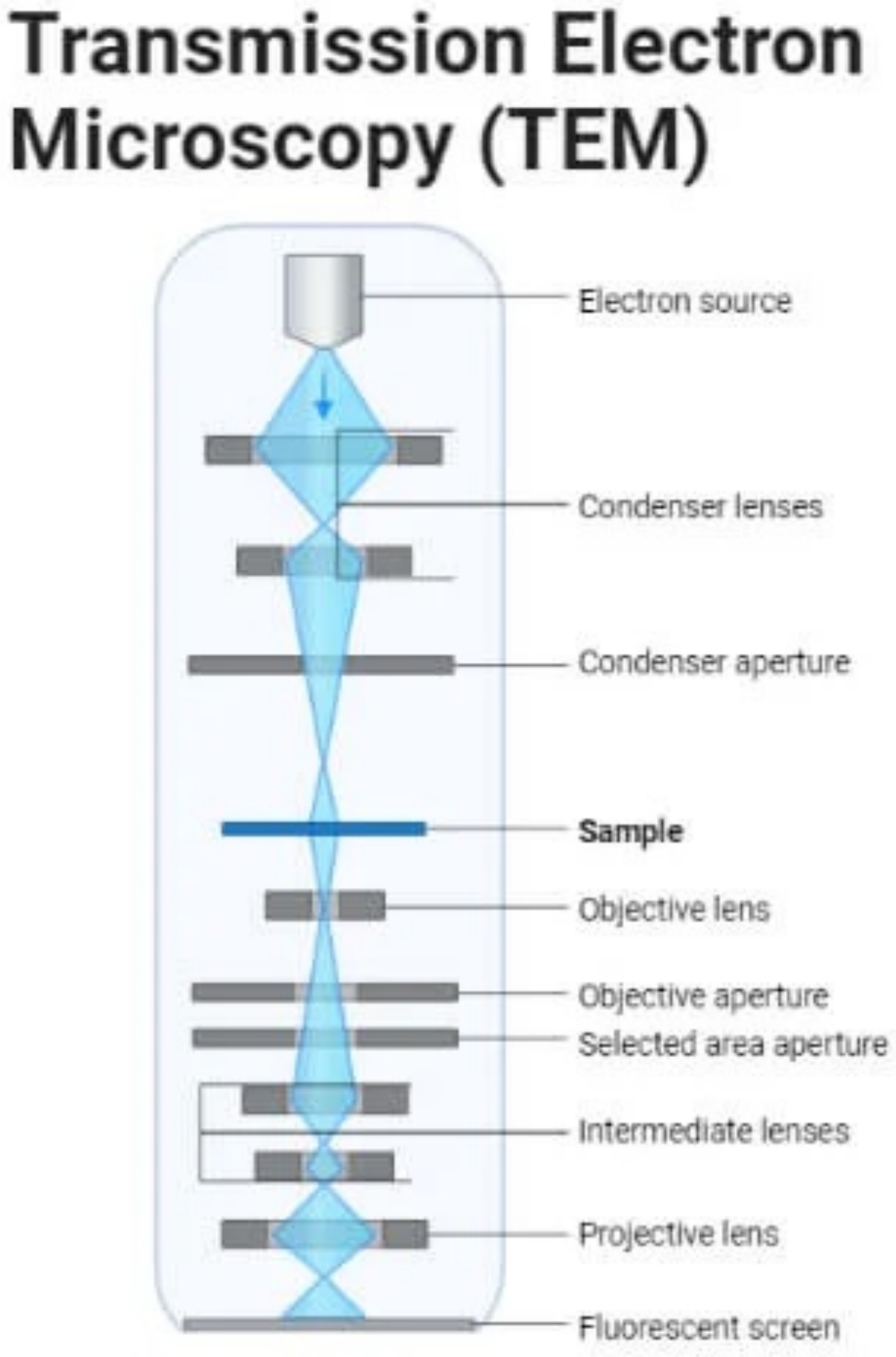
Brightfield

Darkfield

Electron Microscopy



Scanning Electron Microscopy (SEM)



Transmission Electron Microscopy (TEM)

Electron Microscopy to Visualize Real Surfaces and Materials

	Light Microscopy	Electron Microscopy
Illumination source	Light (400-700 nm)	Beam of electrons
Principle	Image formed by absorption of light waves	Image formed by scattering/transmission of electrons
Vacuum	Not used under vacuum	High vacuum
Thickness of specimen	5 µm or thicker	Ultra-thin, <0.1 µm
Magnification power	Low magnification (up to 1500x)	High magnification (up to 1,000,000x)
Complexity	Less complex	Complex

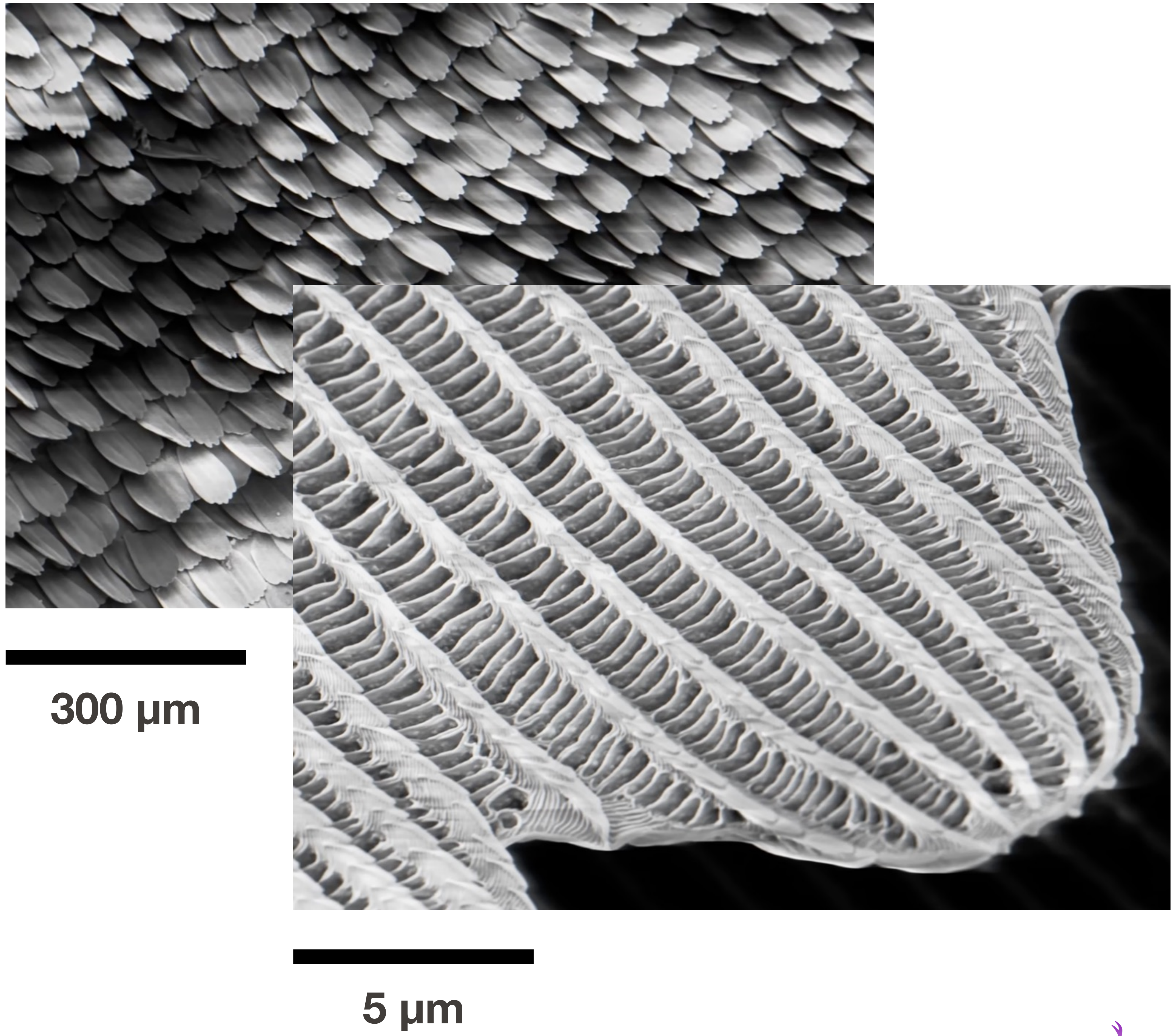
Microbe Notes CHEMINA

Electron Microscopy to Visualize Real Surfaces and Materials

Light Microscopy

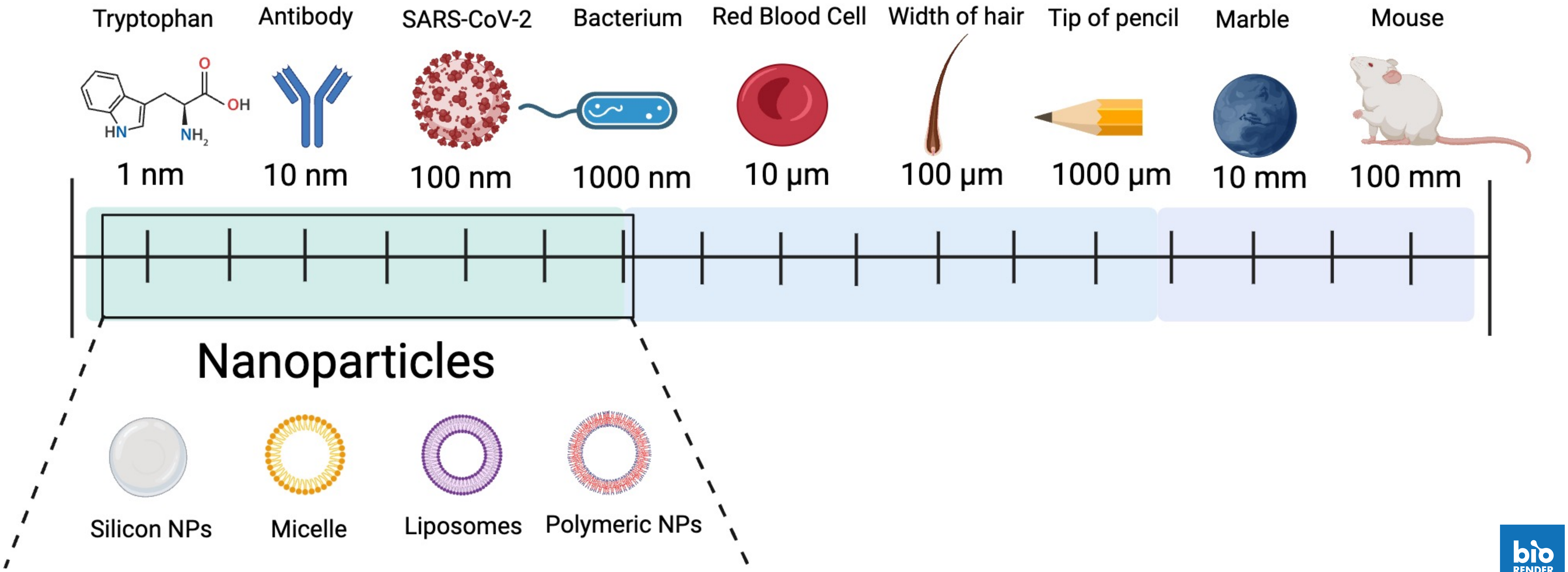
Peacock butterfly

Electron Microscopy

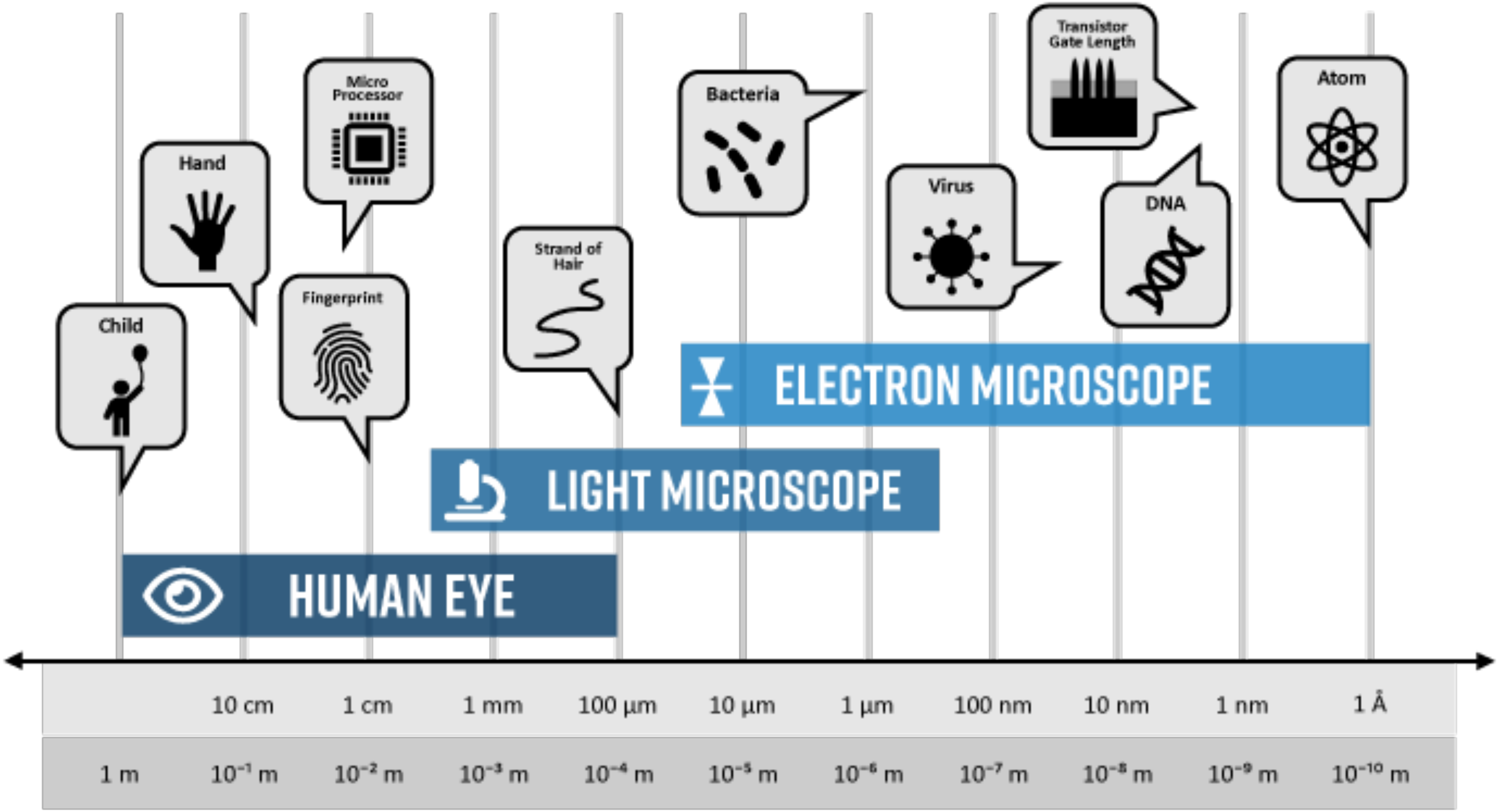


Visualizing at the Nanoscale

Nanoscience: Study of objects and systems in which at least one dimension is 1-100 nm



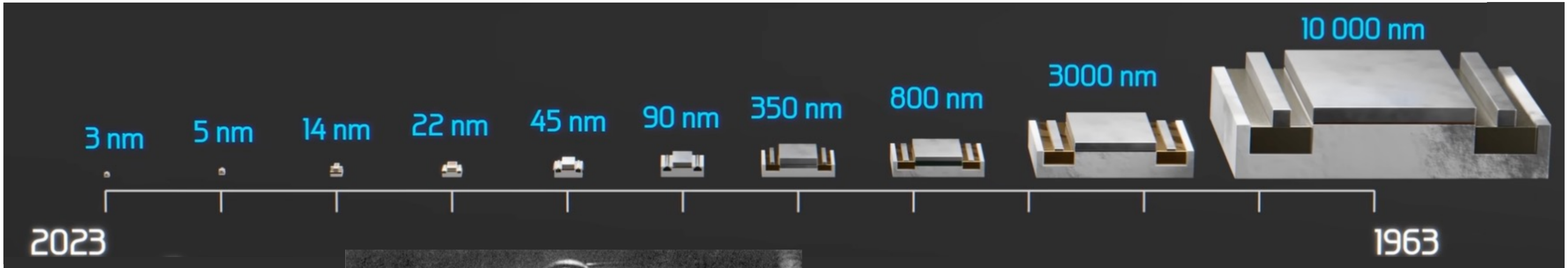
Length Scales Accessible with Different Microscopes

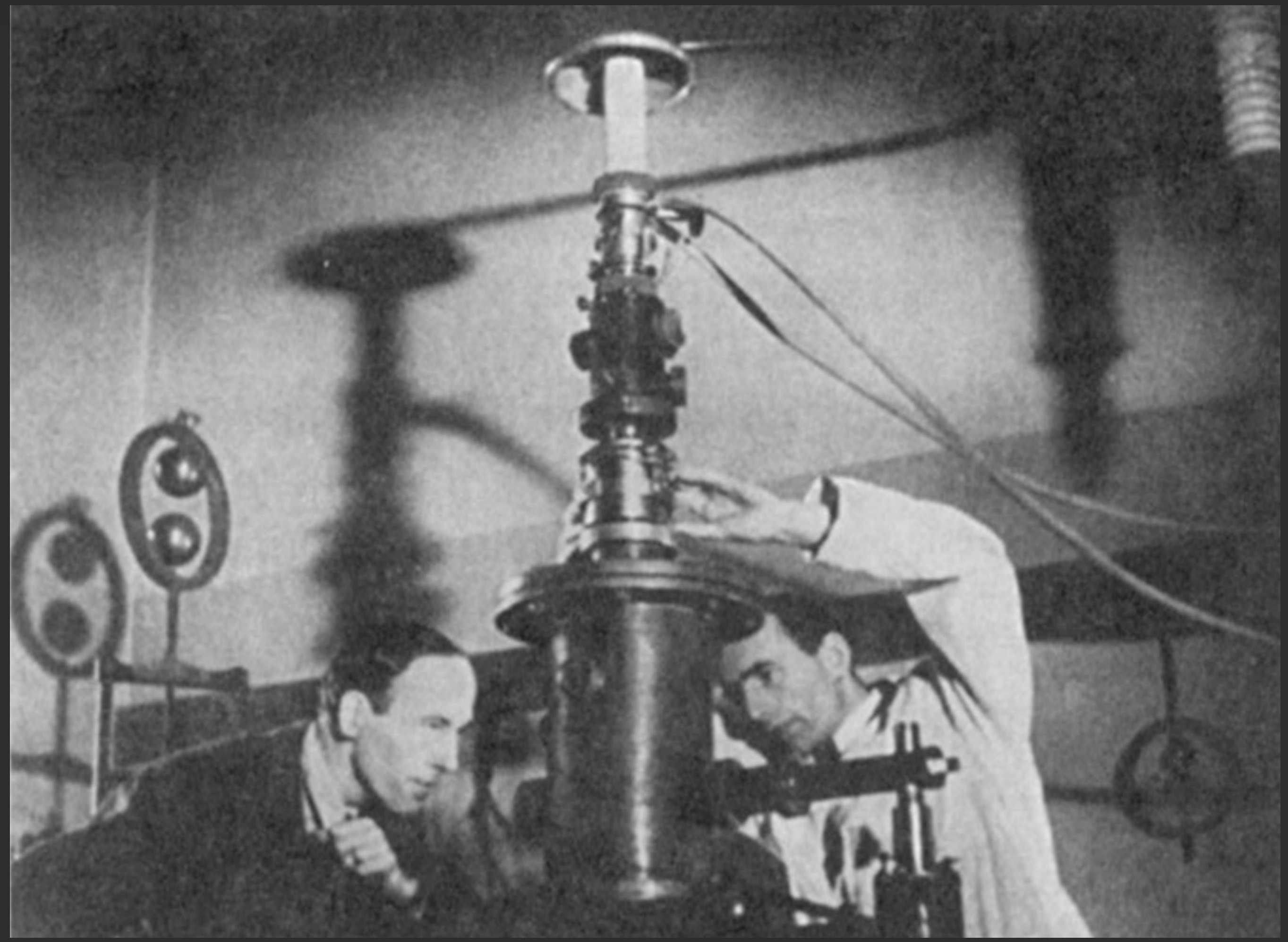


Electron Microscopy to Visualize Real Surfaces and Materials

Over six decades of development to the instruments we have today

Goal to develop smaller and smaller transistors – semiconductor devices that are the fundamental building blocks of modern electronics



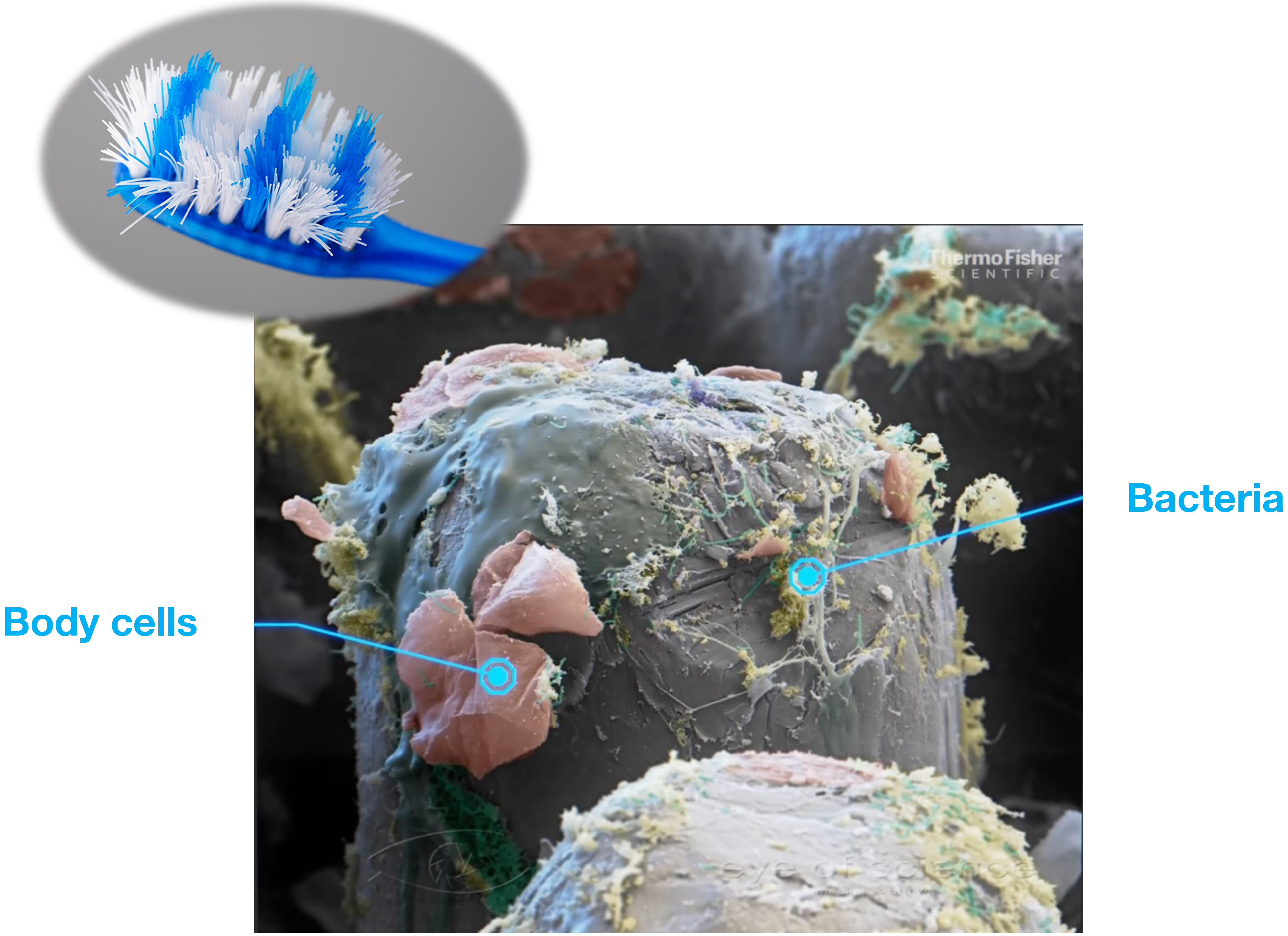


First electron microscope being checked by Ernst Ruska & Max Knoll in 1931

Branch Education

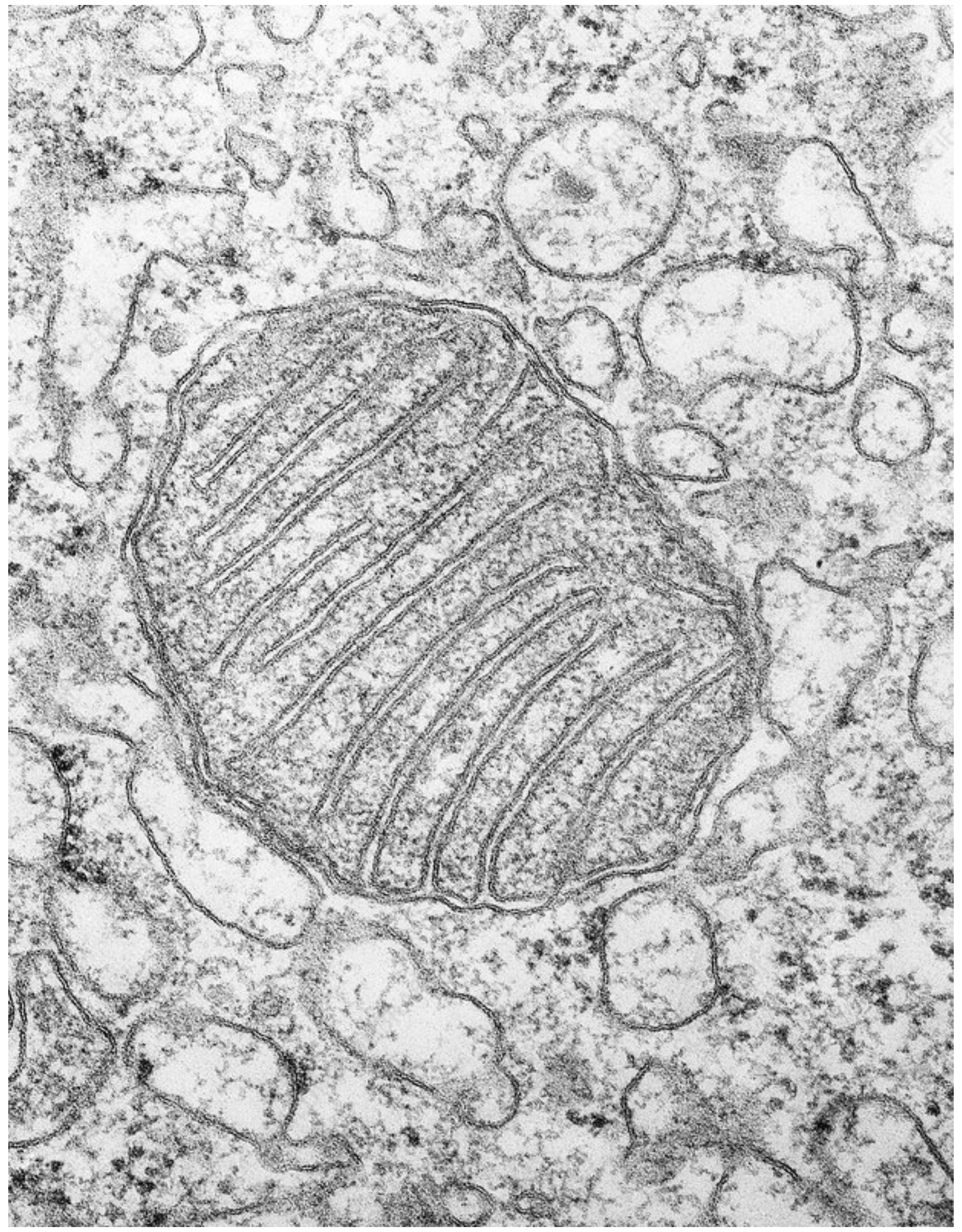
Electron Microscopy Techniques

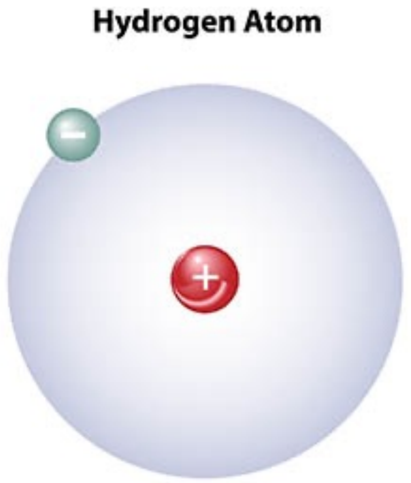
Scanning Electron Microscopy (SEM)



Max resolution: 1 nm

Transmission Electron Microscopy (TEM)





Max resolution: 50 pm

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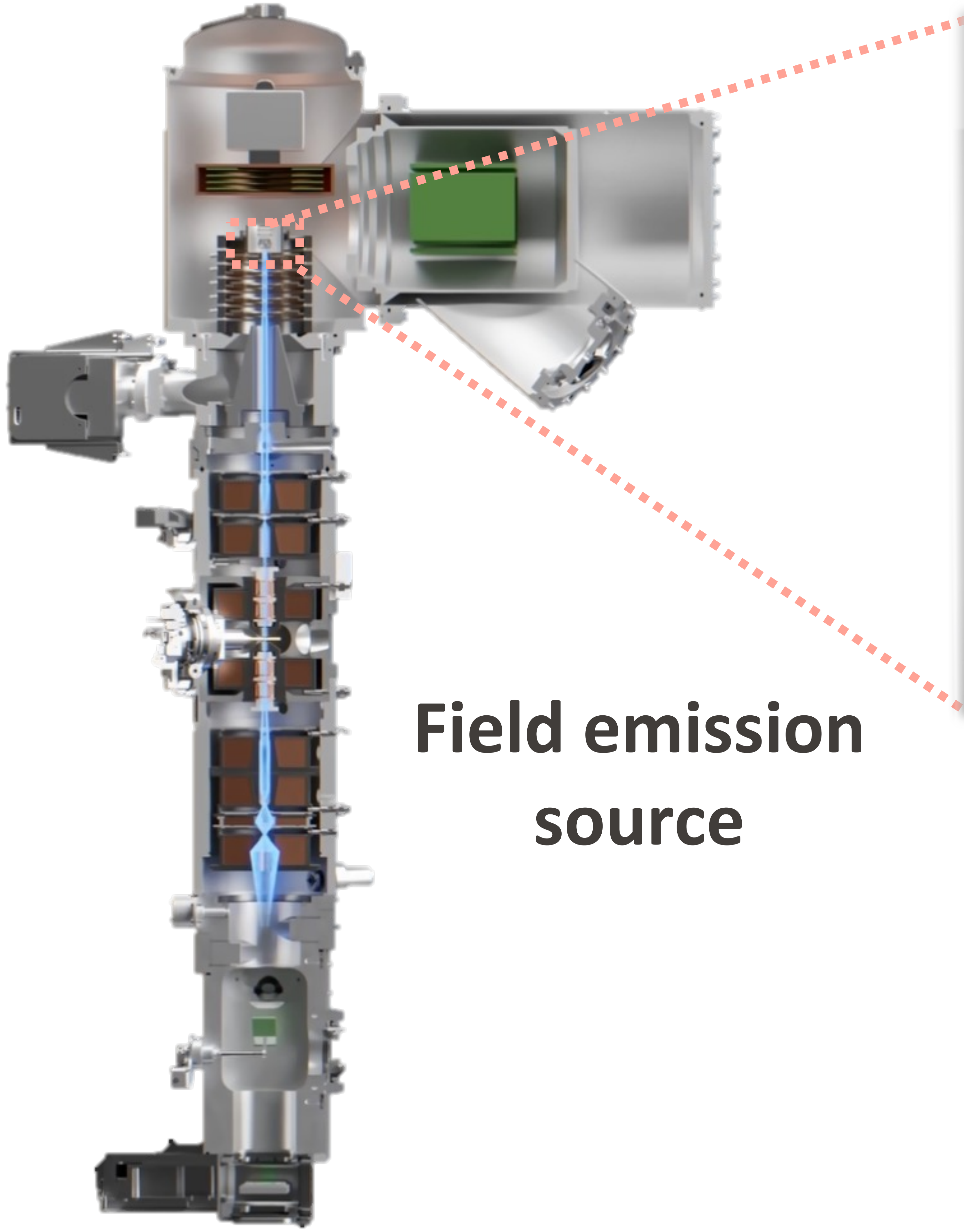
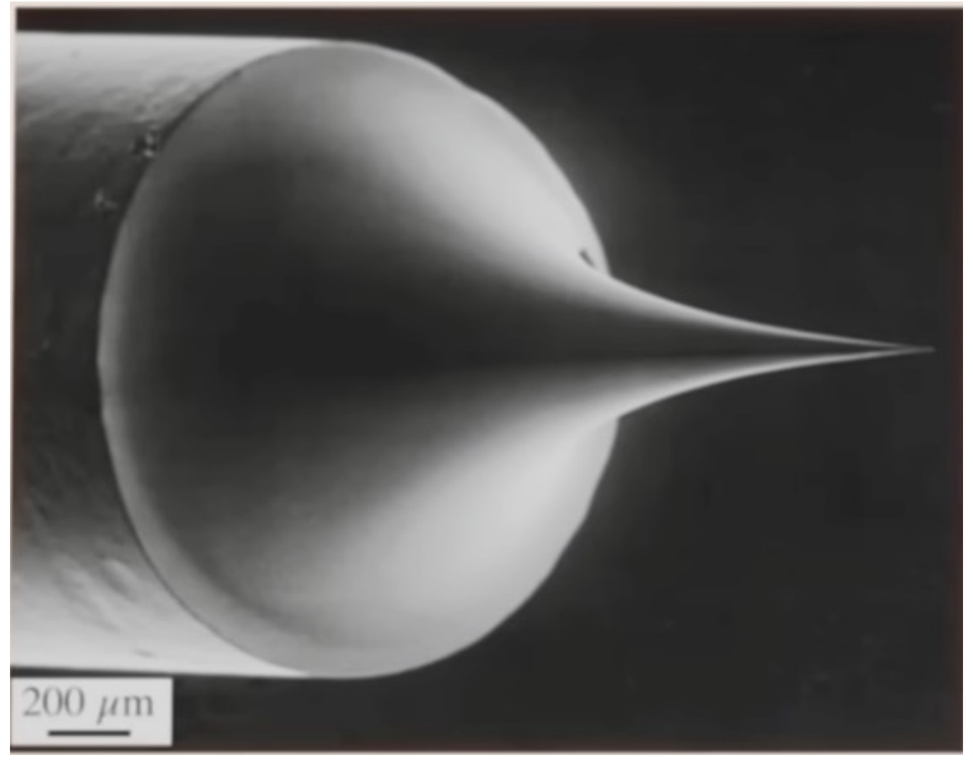
Transmission Electron Microscopy – Electron Generation

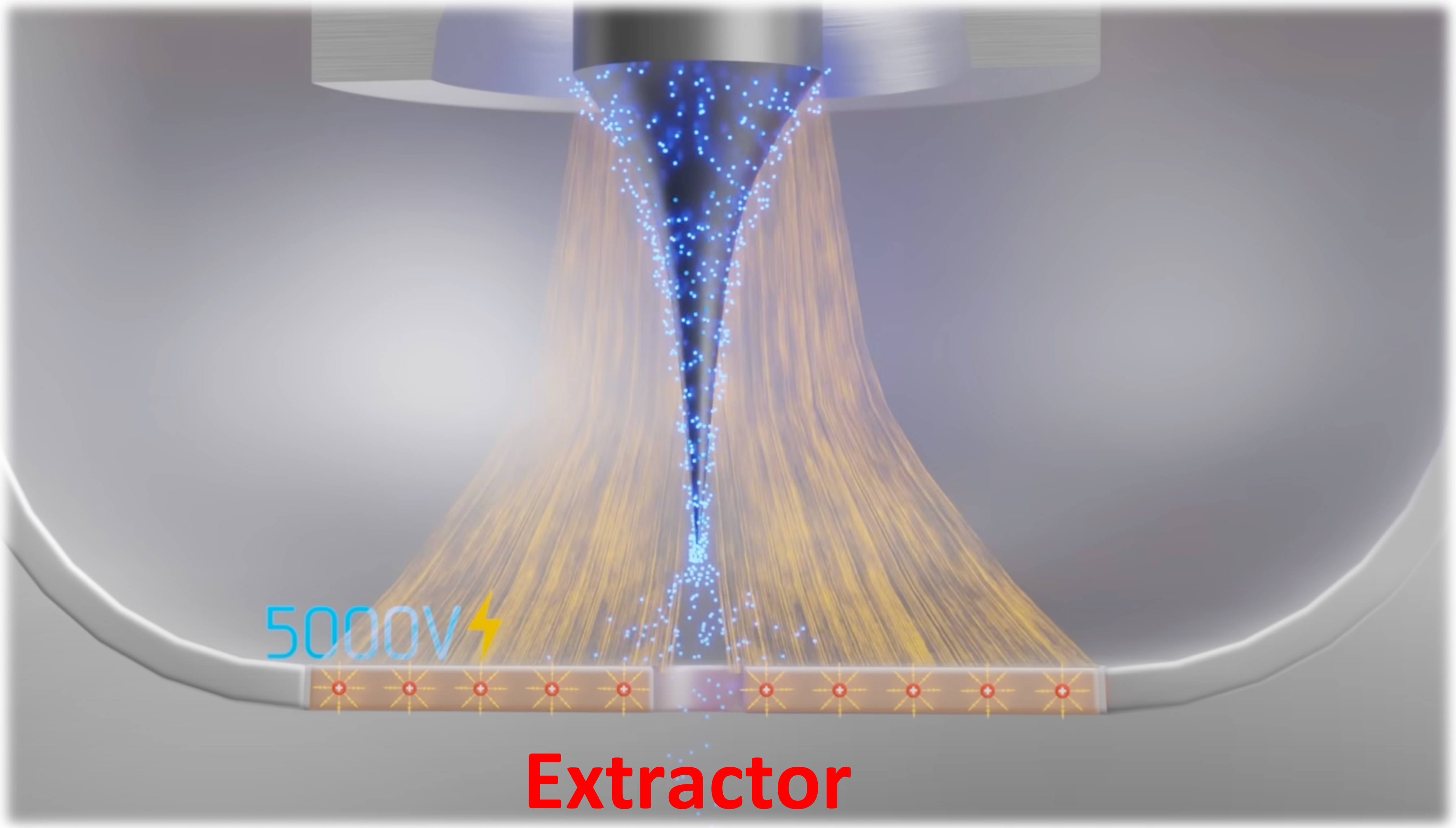


Field emission source



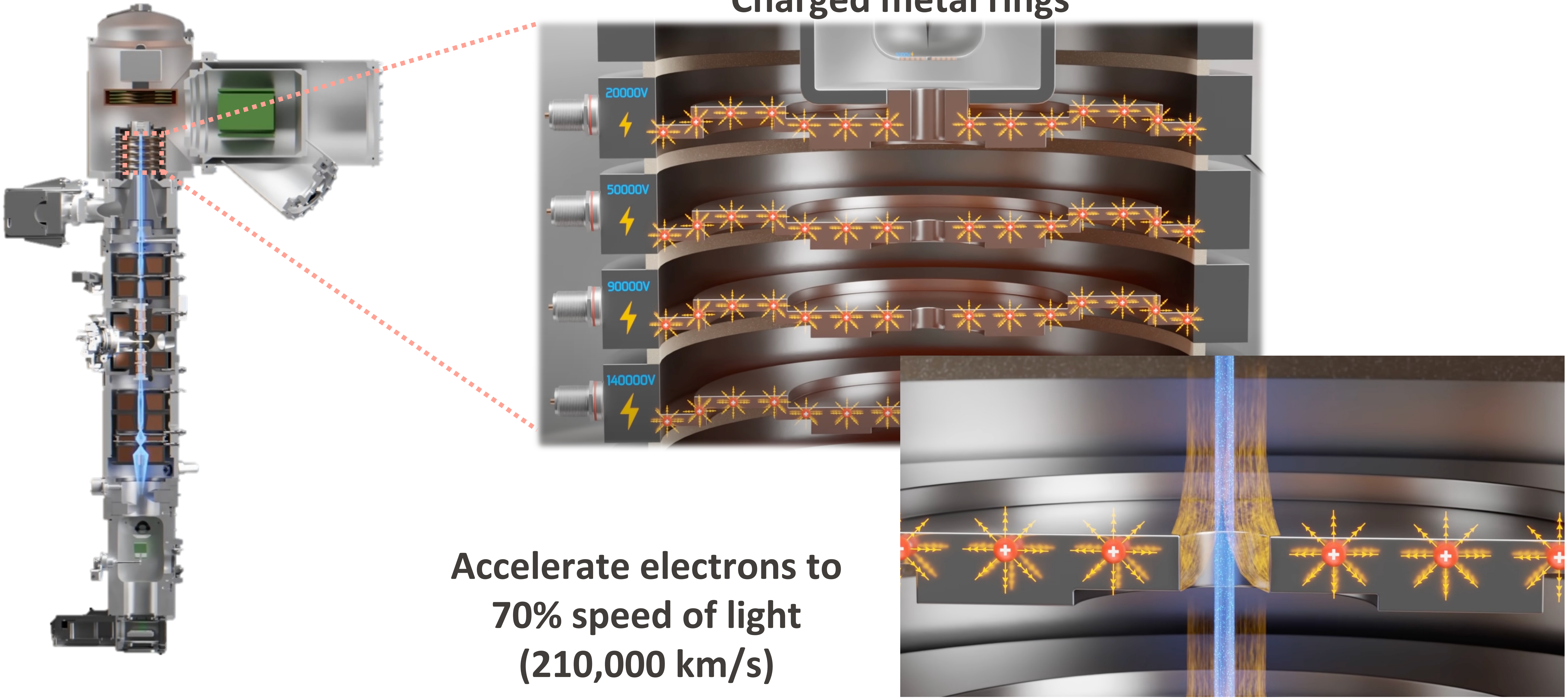
Few nanometers wide

Tungsten crystal needle



Generates free electrons

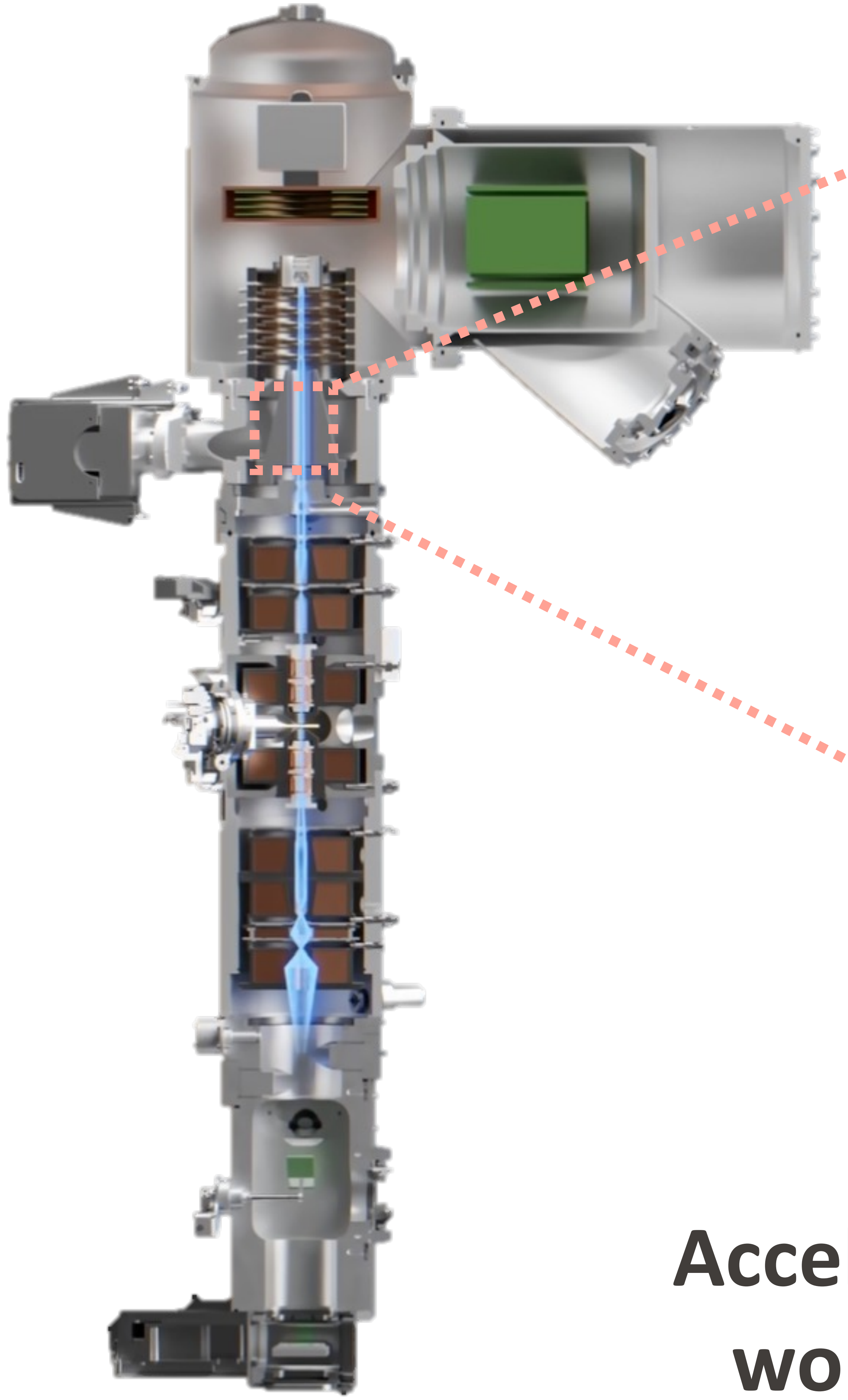
Transmission Electron Microscopy – Electron Acceleration



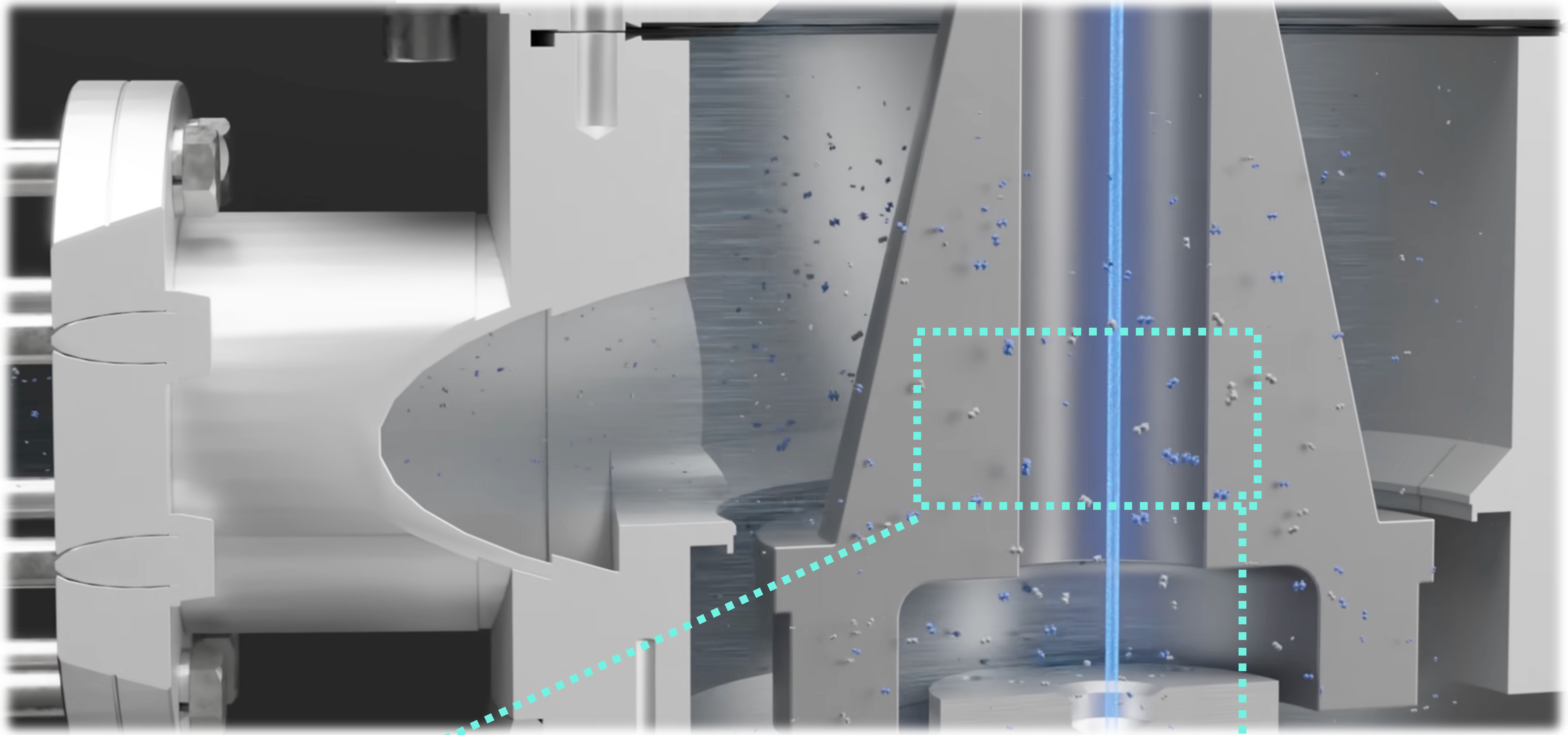
Charged metal rings

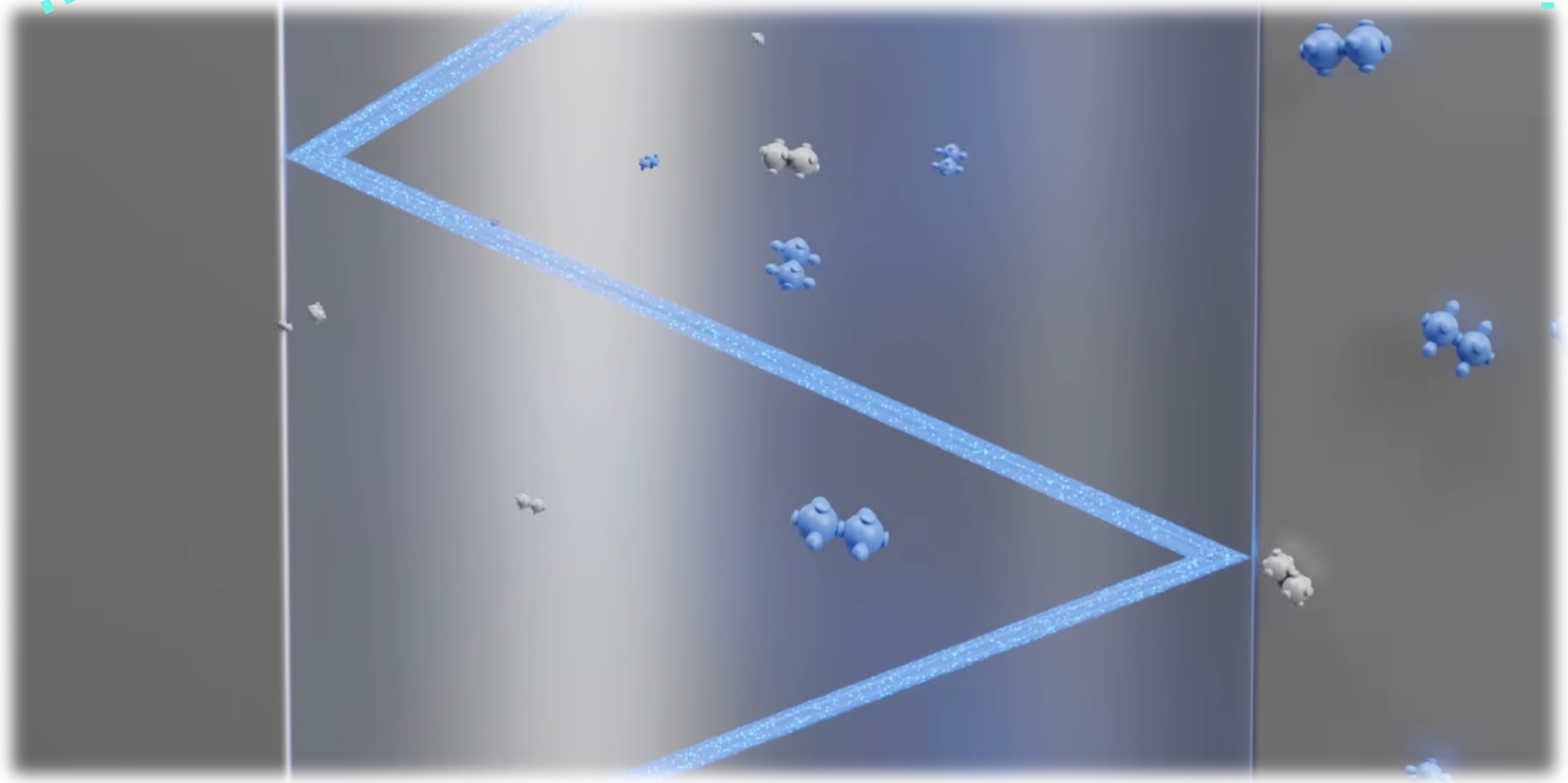
Accelerate electrons to 70% speed of light (210,000 km/s)

Transmission Electron Microscopy – Vacuum Pumps



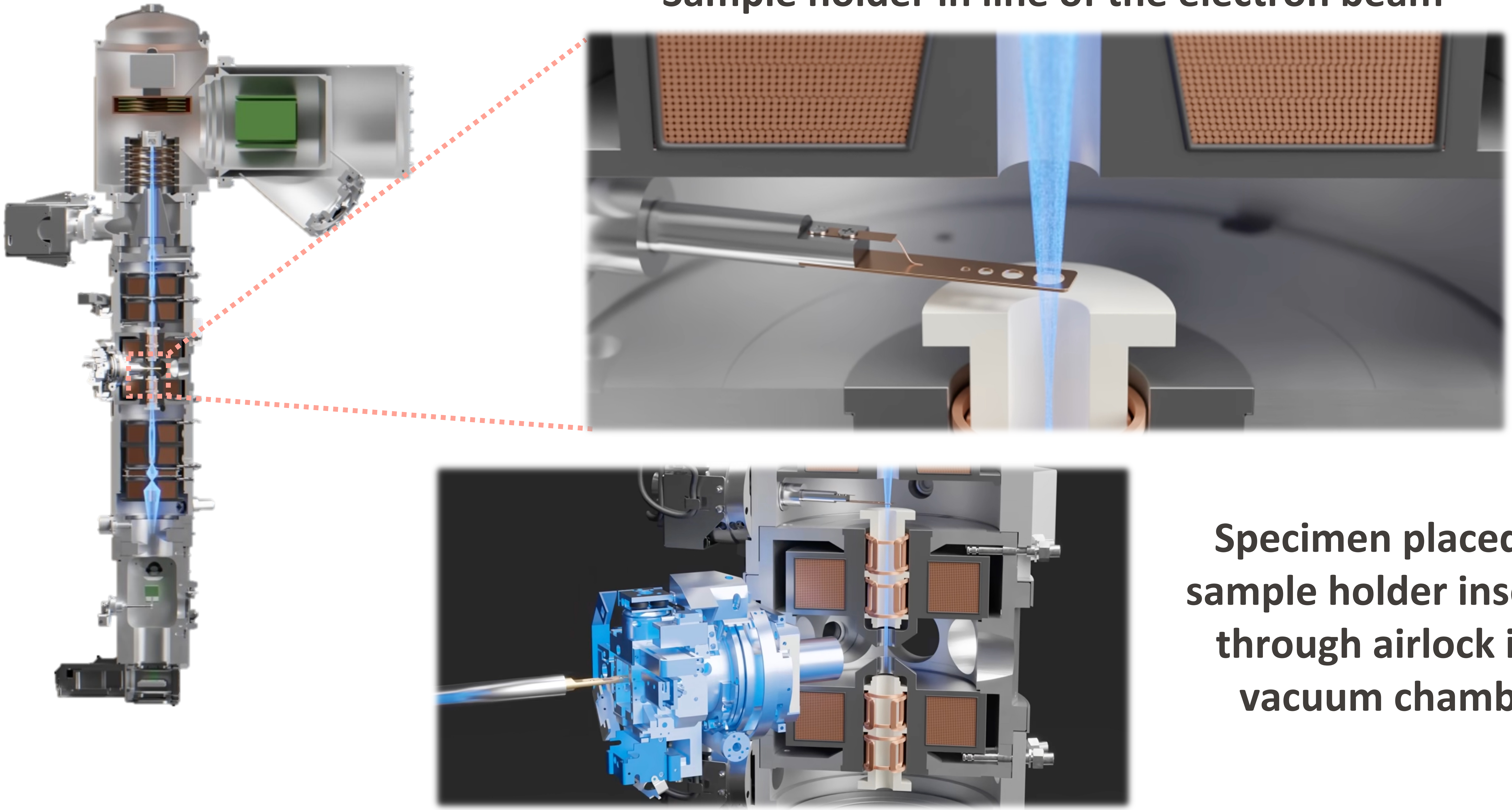
Vacuum pumps remove all atmospheric molecules





Accelerated electrons would collide with atmospheric molecules

Transmission Electron Microscopy – Specimen Handling

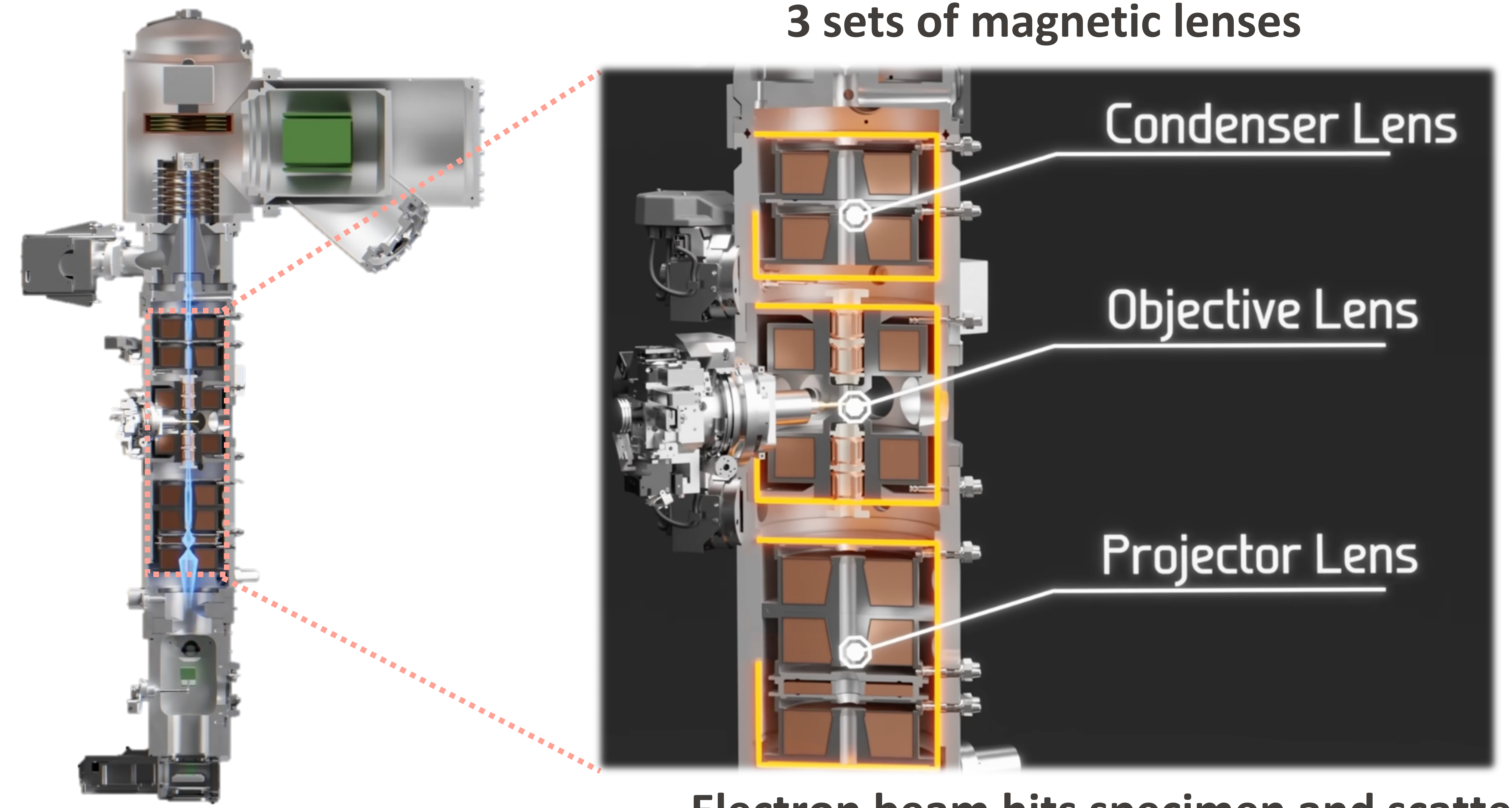


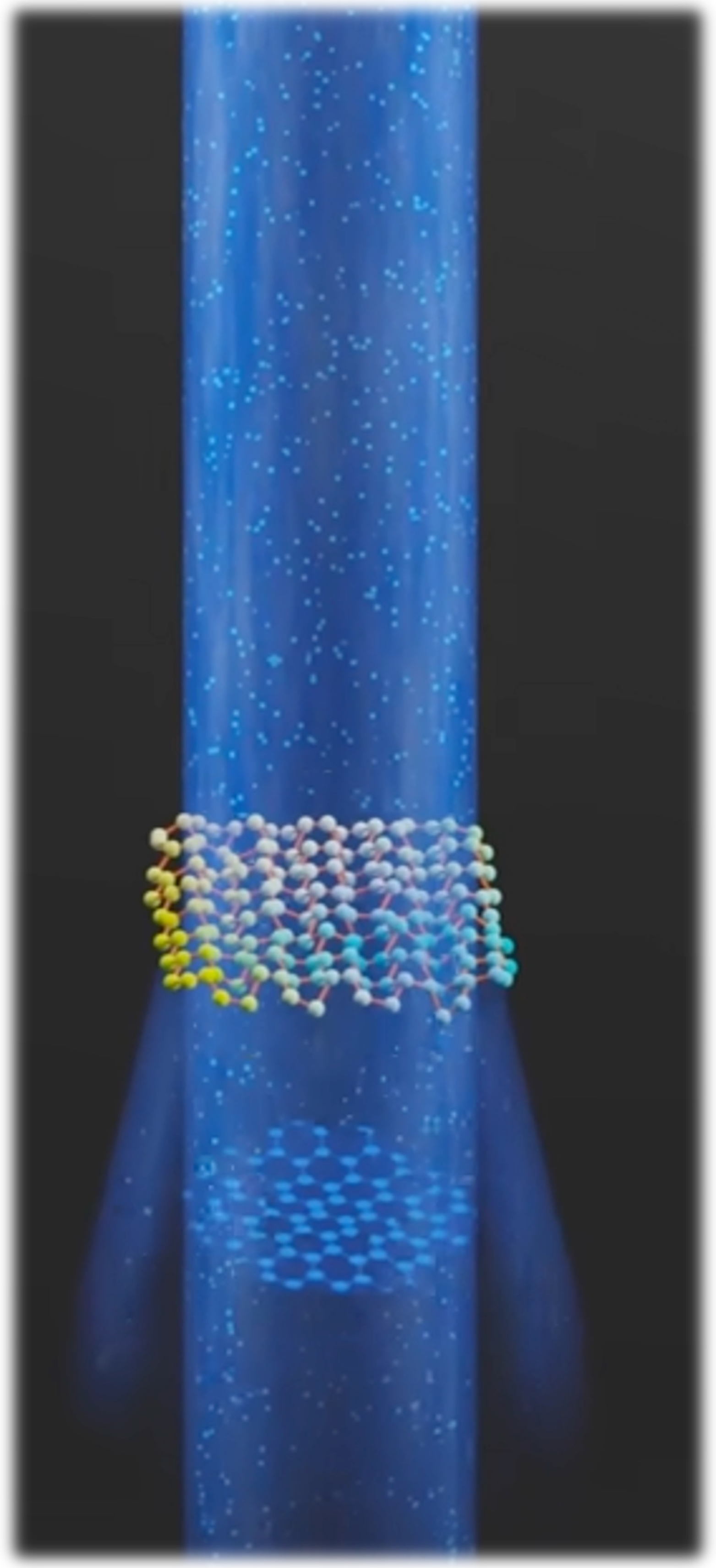
Sample holder in line of the electron beam

Specimen placed on sample holder inserted through airlock into vacuum chamber

Transmission Electron Microscopy – Magnetic Lens

3 sets of magnetic lenses

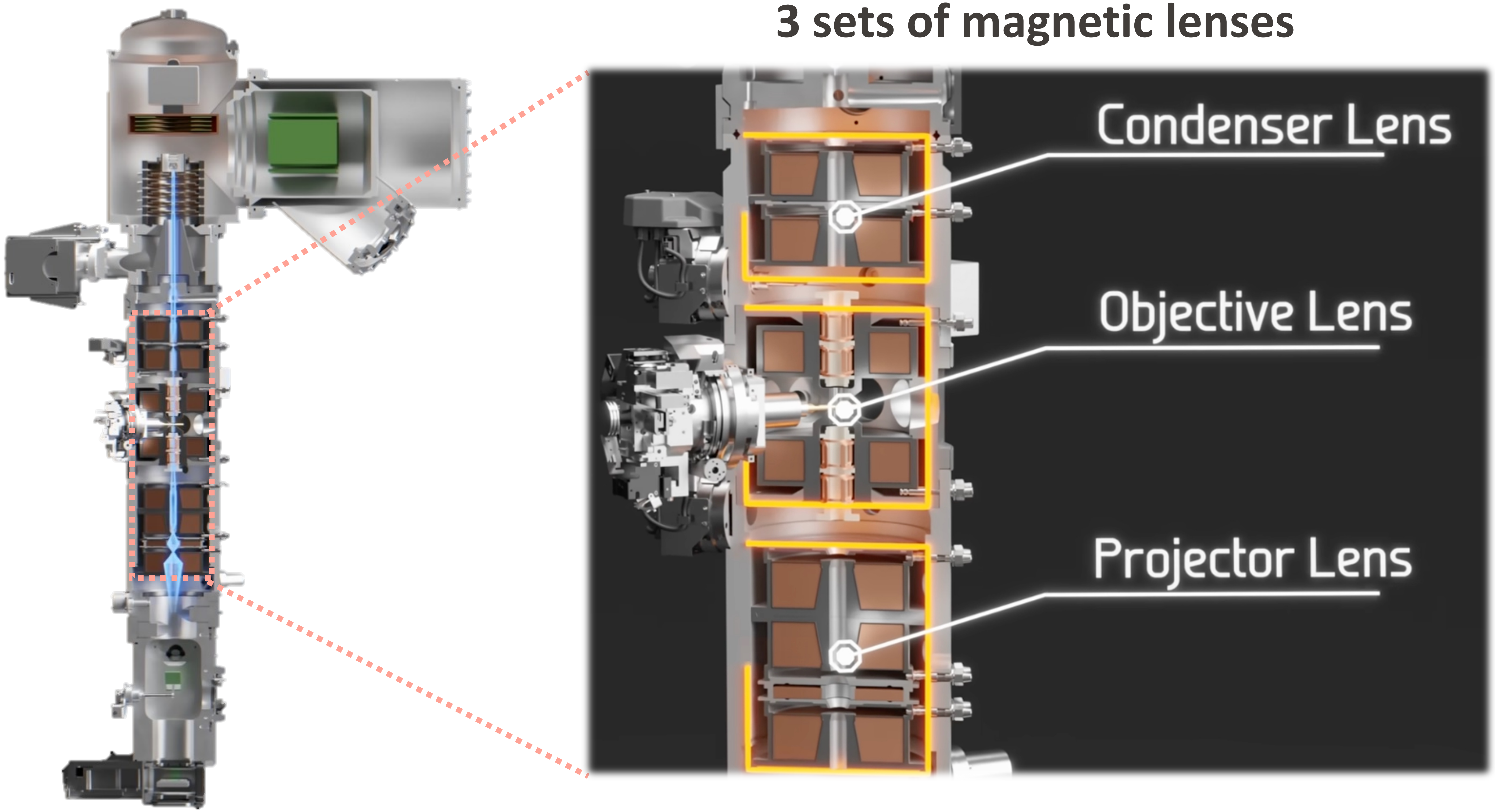


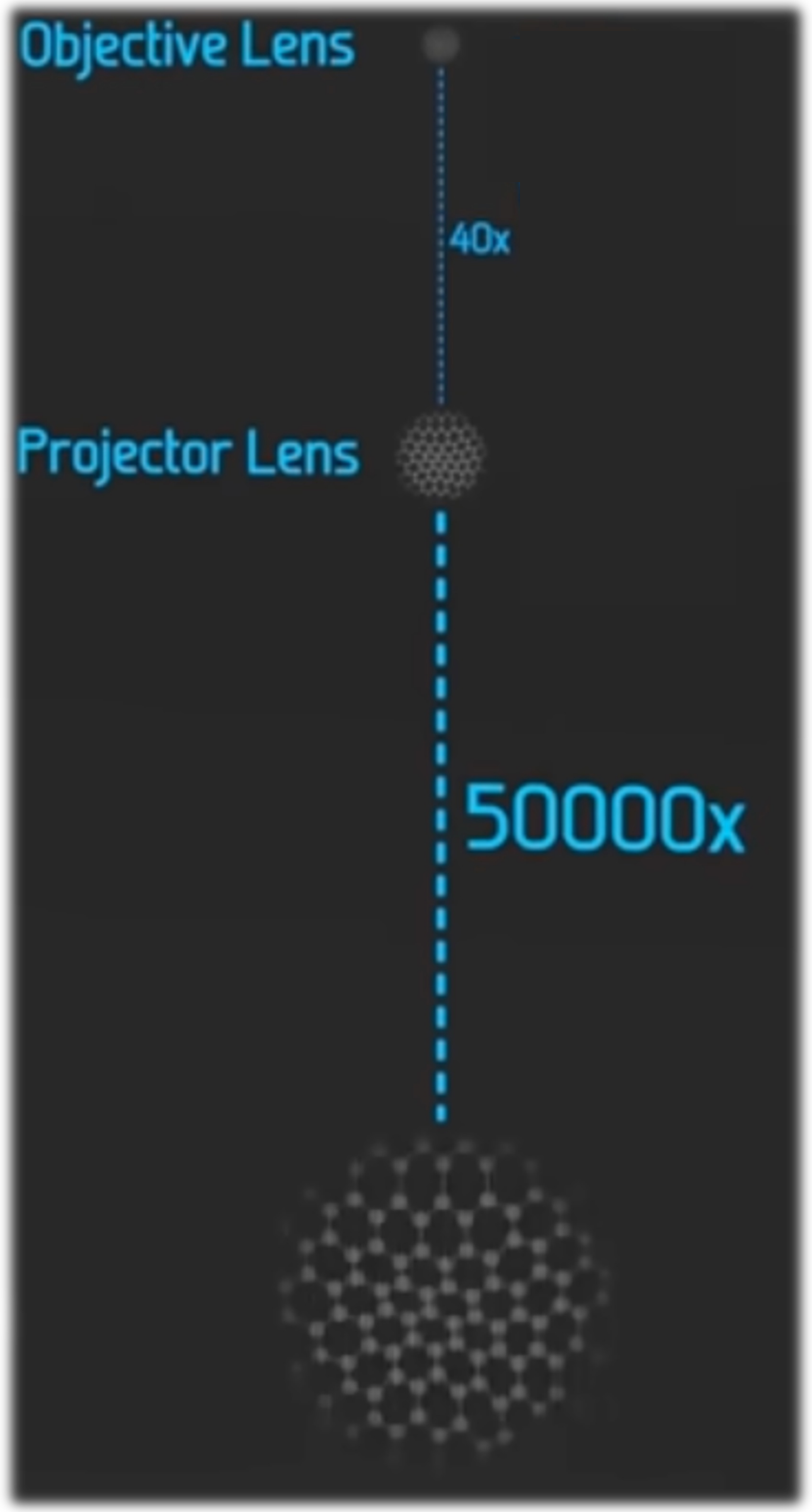


Electron beam hits specimen and scatters electrons, imprinting an image onto transmitted beam

Transmission Electron Microscopy – Magnetic Lens

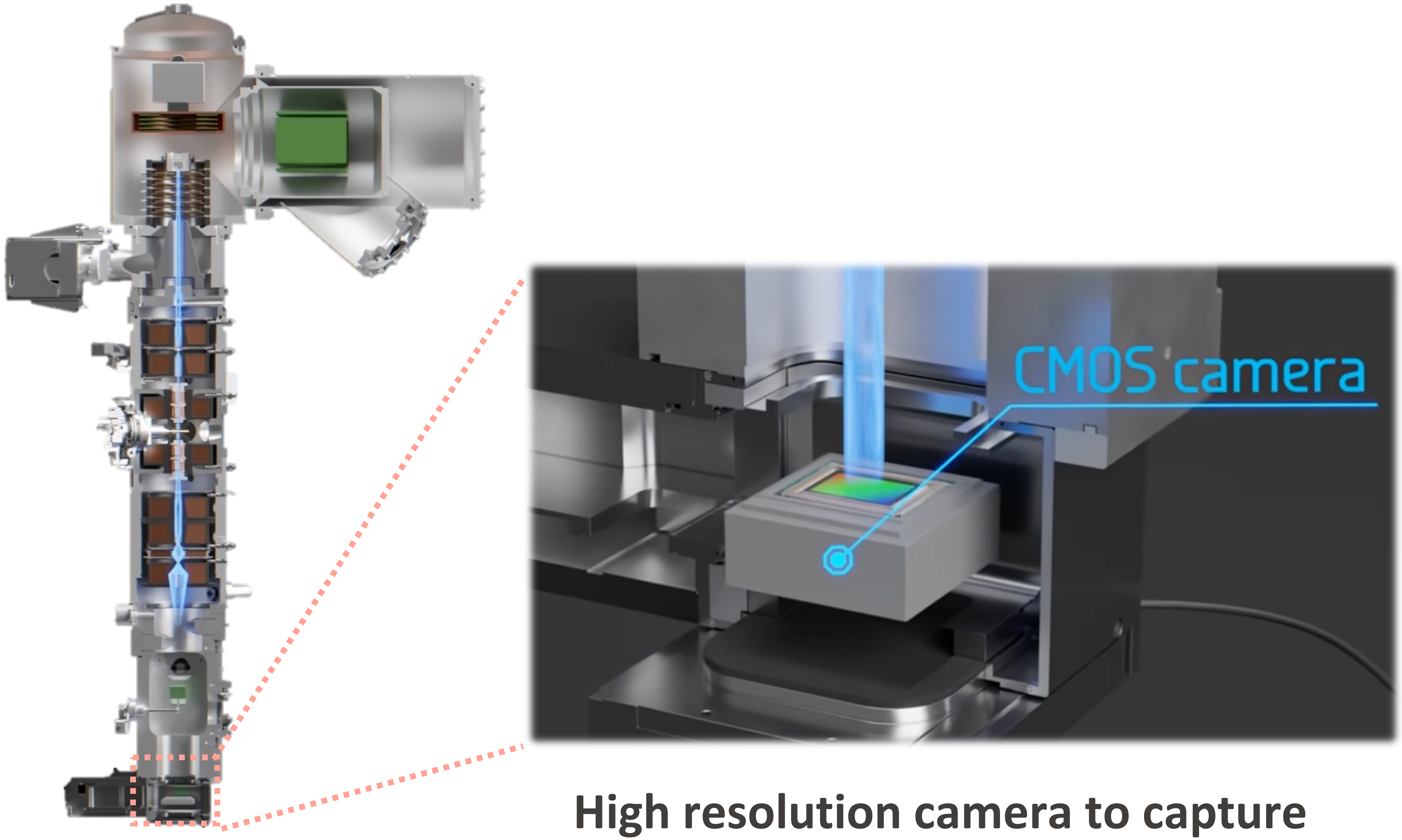
3 sets of magnetic lenses





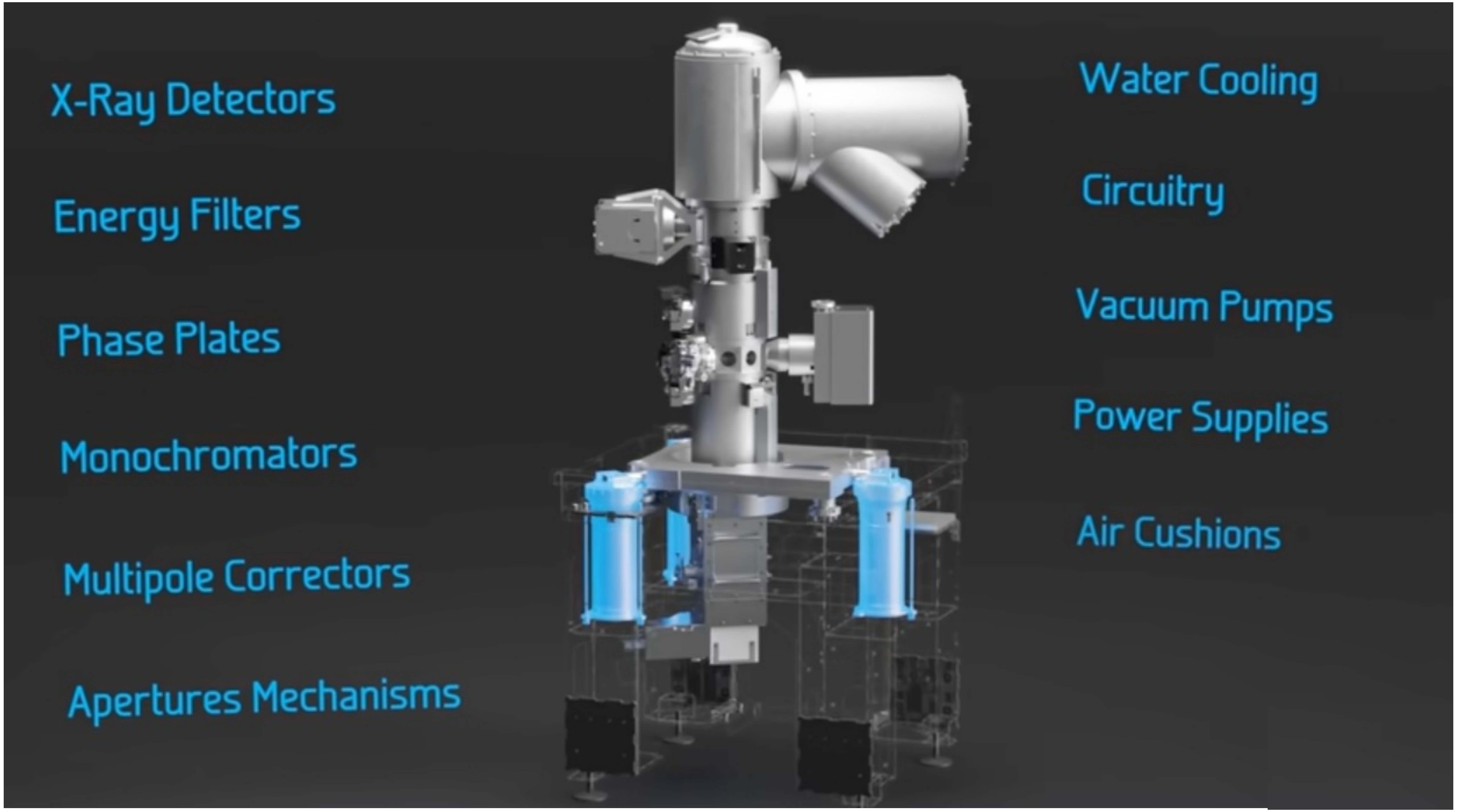
Magnify image imprinted by the electron beam

Transmission Electron Microscopy – Image Detection



High resolution camera to capture image

Simplified System – Complicated Details



X-Ray Detectors

Energy Filters

Phase Plates

Monochromators

Multipole Correctors

Apertures Mechanisms

Water Cooling

Circuitry

Vacuum Pumps

Power Supplies

Air Cushions

Branch Education CHEMINA

Key Takeaways

- Grain boundaries are important to characterize as they affect mechanical and electrical properties
- We can visualize polycrystalline grain boundaries using certain techniques
- Introduction to electron microscopy to visualize real surfaces
- You can access the nanoscale using a beam of electrons

Summary of Today's Class

- Solid-solid interfaces can be homophase or heterophase
- Grain boundaries are 2-D defects that form microstructures
- Grain boundaries cost energy but can lower total system energy overall
- Different types of grain boundaries at surfaces
- Electron microscopy techniques (TEM) to visualize the nanoscale

EPFL
École polytechnique fédérale de Lausanne

CHEMINA
Laboratory of Chemical Nanotechnology

Prof. Nako Nakatsuka
nako.nakatsuka@epfl.ch

EPFL
Laboratory of Chemical Nanotechnology
Campus Biotech
Chemin des Mines 9
1202, Geneva

https://www.epfl.ch/labs/chemina/