MSE 160 – Semiconductor synthesis

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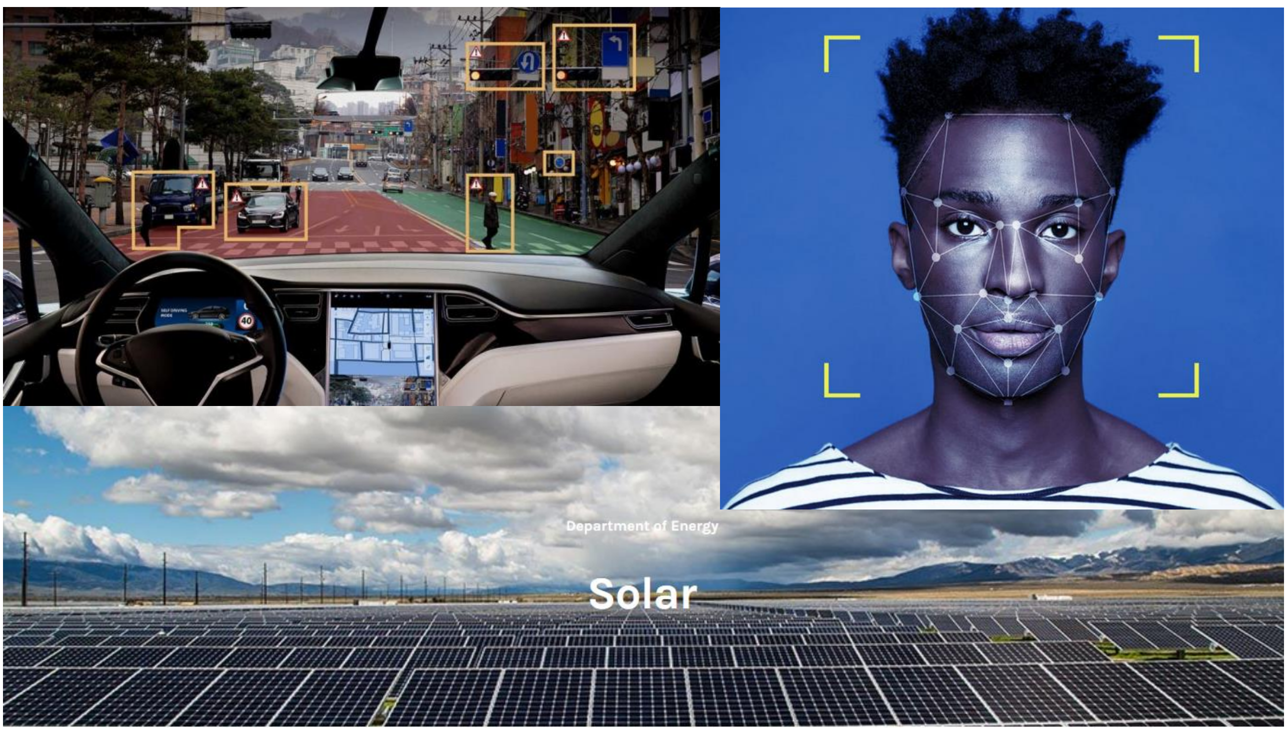

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What is a semiconductor?

Definition: a solid substance that has a conductivity between that of an insulator and that of most metals, either due to the addition of an impurity or because of temperature effects

Conductor

Insulator

Allows the flow of electricity

Metallic bonding => free electrons

Does not allow the flow of electricity

Covalent/ionic bonding => no free electrons

Semiconductors can do both!

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Outline

Semiconductor physics

Plasmonic nanocrystal synthesis

Silicon wafer synthesis

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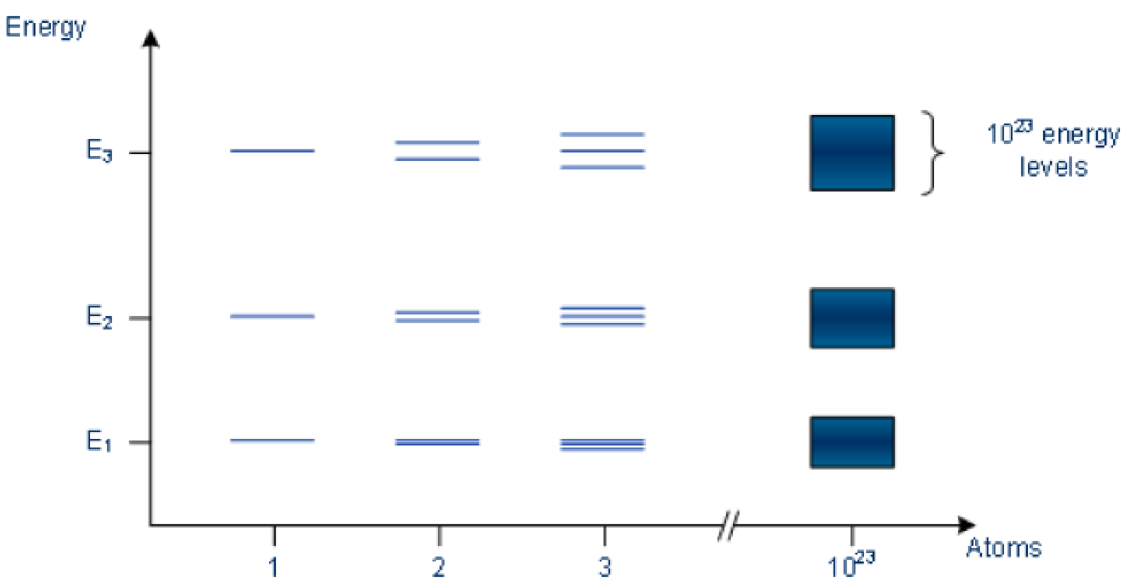

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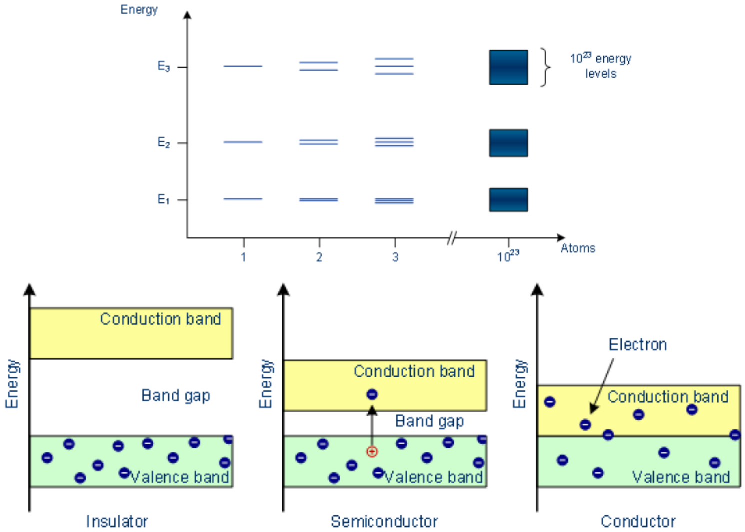
A semiconductor has a narrow bandgap



https://www.halbleiter.org/en/fundamentals/conductors-insulators-semiconductors/

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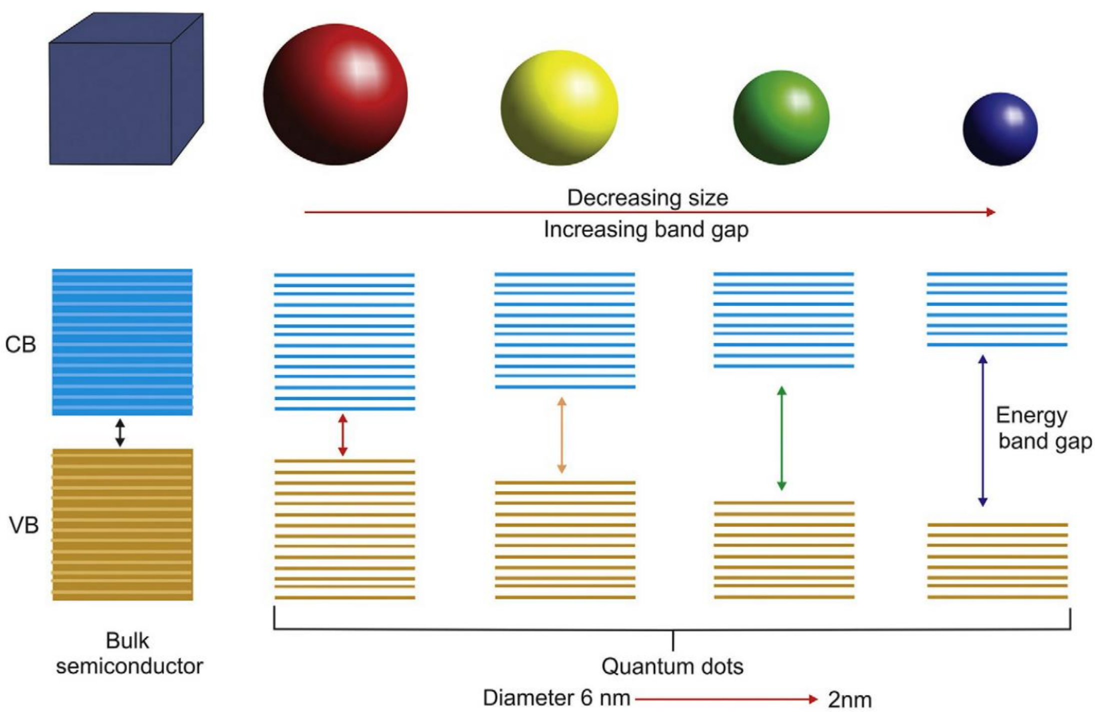

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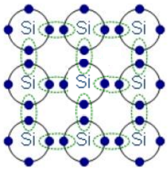
Intrinsic semiconductor is formed by pure covalent material

Intrinsic



https://www.halbleiter.org/en/fundamentals/doping/

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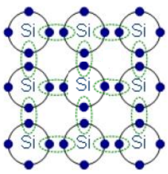
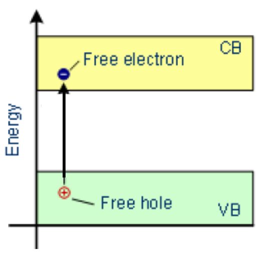
Intrinsic semiconductor has a relatively wide bandgap, E_g

Intrinsic





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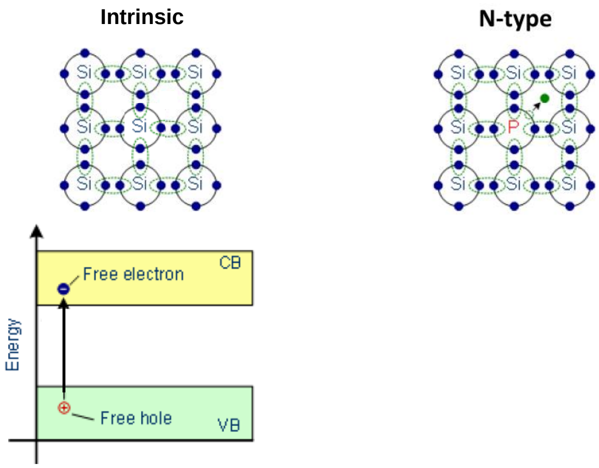
N-type dopants add (donate) electrons to the material



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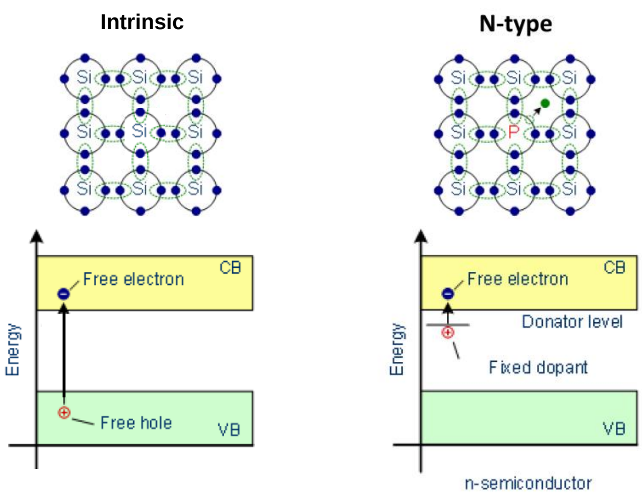

Dopant typically phosphorus or arsenic

https://www.halbleiter.org/en/fundamentals/doping/

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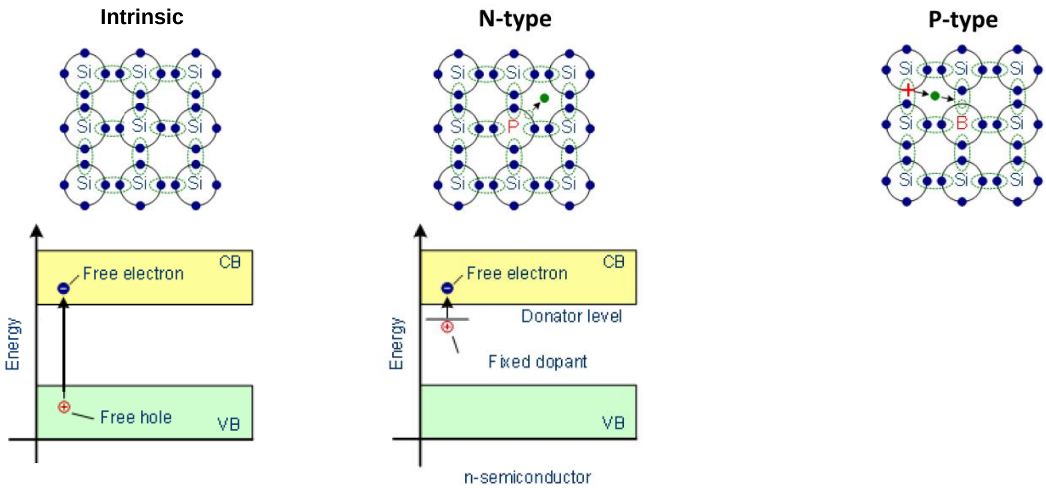
P-type dopants add holes (accept electrons) to the material



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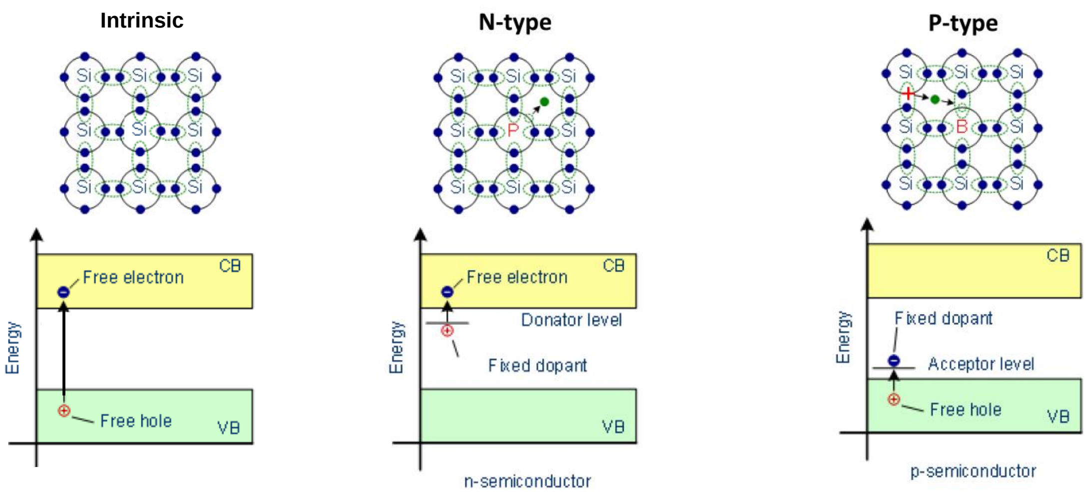

Dopant typically phosphorus or arsenic Dopant typically boron or gallium

https://www.halbleiter.org/en/fundamentals/doping/

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Question
Why is Bulk Silicon Black & Shiny?

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To Answer This:

- We need to know that the energy gap of Si is:

$$E_{gap} = 1.2eV$$

- We also need to know that, for visible light, the photon energy is in the range:

$$E_{vis} \sim 1.8 – 3.1eV$$

$$E_{vis} > E_{gap}$$

- So, all visible light will be absorbed & Silicon appears black

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Why is Si shiny?

- Photon absorption occurs in Si because there are many electrons in the conduction band. These electrons are delocalized *and they scatter photons*.

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Before we go on, let's consider why **bulk** (semi)conductors are shiny

Light is an electromagnetic wave

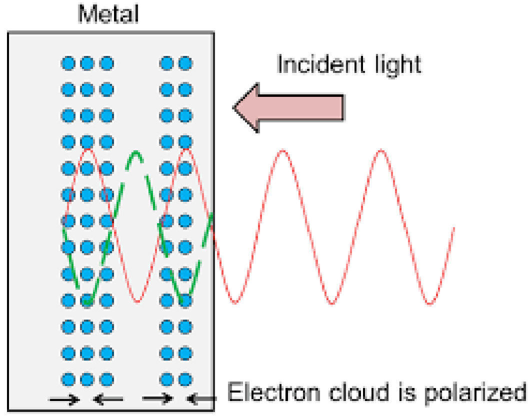
Light's electric field interacts with conduction electrons, causing them to oscillate

Creates a perturbation in the distribution of conduction electrons, "plasmon wave"

Light's energy is absorbed via plasmon standing wave in mostly bulk

Oscillating electron in plasmon re-emits the energy as photons, creating reflection

Composition of bulk material affects color (think Au, Ag)



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Why is GaP Yellow?

To Answer This:

- We need to know that the energy gap of GaP is:

$$E_{gap} = 2.26\text{ eV}$$

or ν= 549 nm.

- So photons with E = h ν > 2.26 eV (i.e. green, blue, violet) *are absorbed*.
- Also photons with E = h ν < 2.26eV (i.e. yellow, orange, red) *are transmitted*.
- Also, the sensitivity of the human eye is greater for yellow than for red, so

GaP Appears Yellow/Orange.

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Colors of Bulk Semiconductors

E_{vis}= 1.8eV → 3.1eV

I B G Y O R

If the Photon Energy is $E_{vis} > E_{gap}$

Photons will be absorbed

If the Photon Energy is $E_{vis} < E_{gap}$

Photons will transmitted

If the Photon Energy is in the range of E_{gap}

those with higher energy than E_{gap} *will be absorbed*.

We see the color of the light being transmitted.

If all colors are transmitted the light is ***White***

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What happens during the photon absorption process?

Photons interact with:

the lattice

defects

valence electrons

conduction electrons

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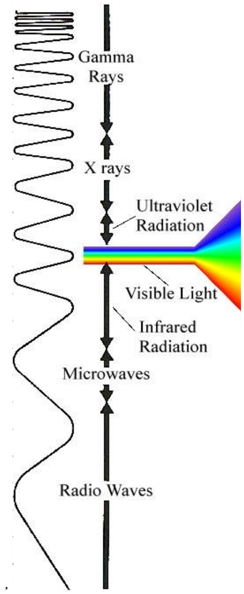
Semiconductors can have bandgap in the visible range



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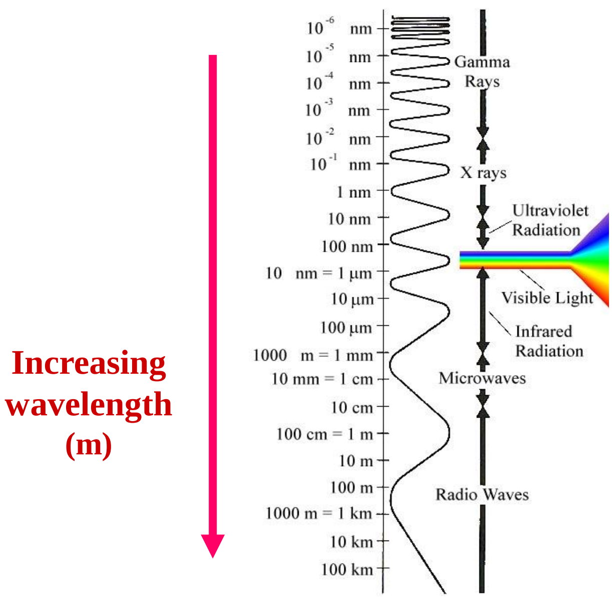
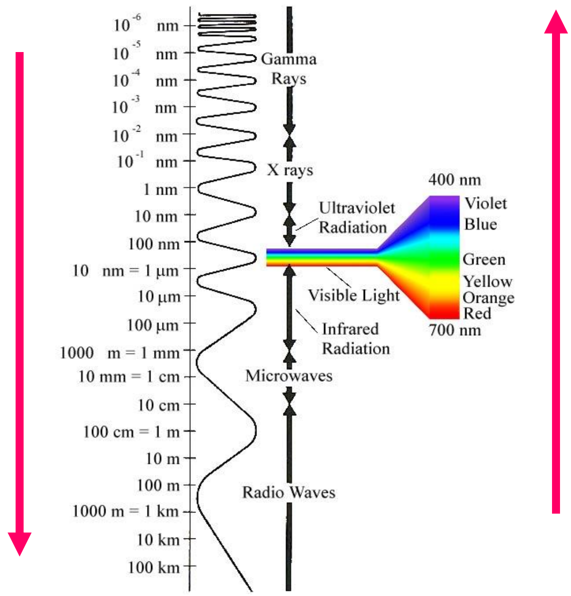


Semiconductors can have bandgap in the visible range

Increasing wavelength (m)



Increasing Photon Energy (eV)

Color & Energy
Violet ~ 3.17eV
Blue ~ 2.73eV
Green ~ 2.52eV
Yellow ~ 2.15eV
Orange ~ 2.08eV
Red ~ 1.62eV

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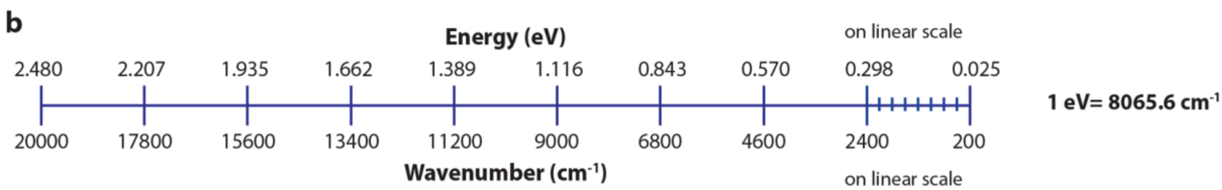

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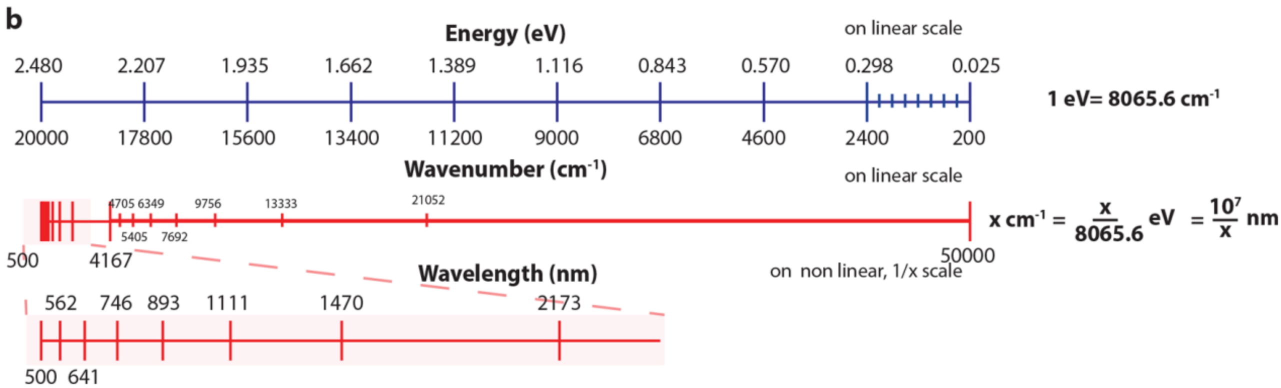

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Plasmonic nanoparticle synthesis

What is a plasmon? How it’s different than bulk semiconductor

Plasmonic nanoparticle synthesis

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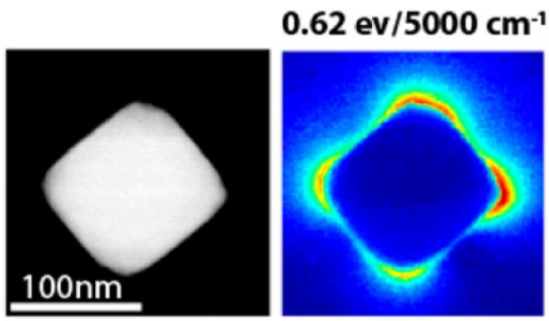
Plasmonic nanoparticle properties

Electromagnetic enhancement around the particles, which localize photon energy to specific locations on their surface

Absorption of light occurs at resonance frequencies; i.e. specific wavelengths of light excite plasmon waves, or “modes,” more strongly than others

Resonant frequency is tunable based on particle shape, size, composition, dielectric environment



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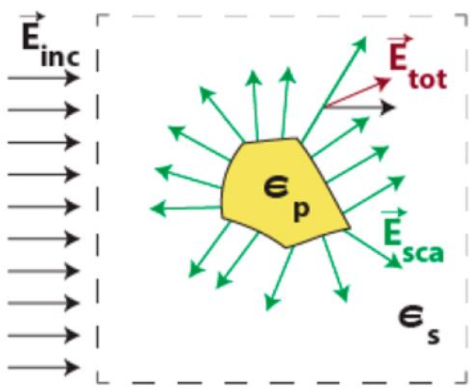
Light-matter interactions for plasmonic particles

Incoming oscillatory electromagnetic waves induce oscillatory charges set into motion inside a material.

Leads to:

Scattering = Reradiation of light by matter in all directions

Absorption = thermal losses associated with the interaction



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Plasmons are quasi particles

Quasi particles are described by a collection of interacting particles, in this case free electrons

Occur on the surface of a conductor nanoparticle, and are quantized (i.e. have discrete energy)

Consist of collective oscillations of the free electron gas

*Have different absorption and re-radiation property than bulk (semi)conductor due to small size

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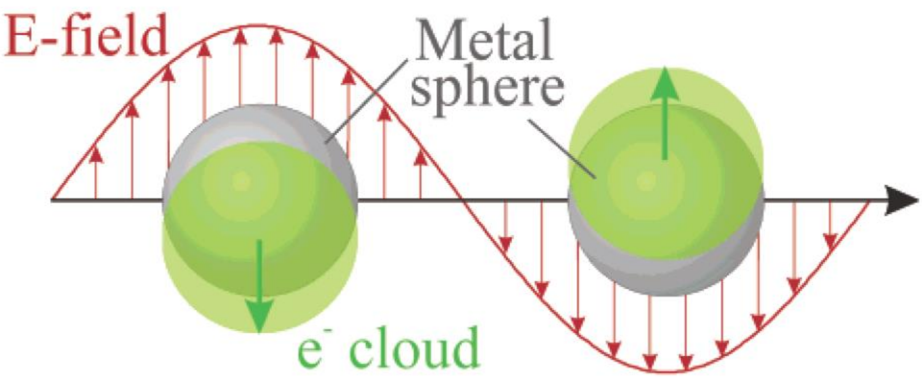
Plasmon: electric field of light displaces conduction electrons causing coherent oscillation



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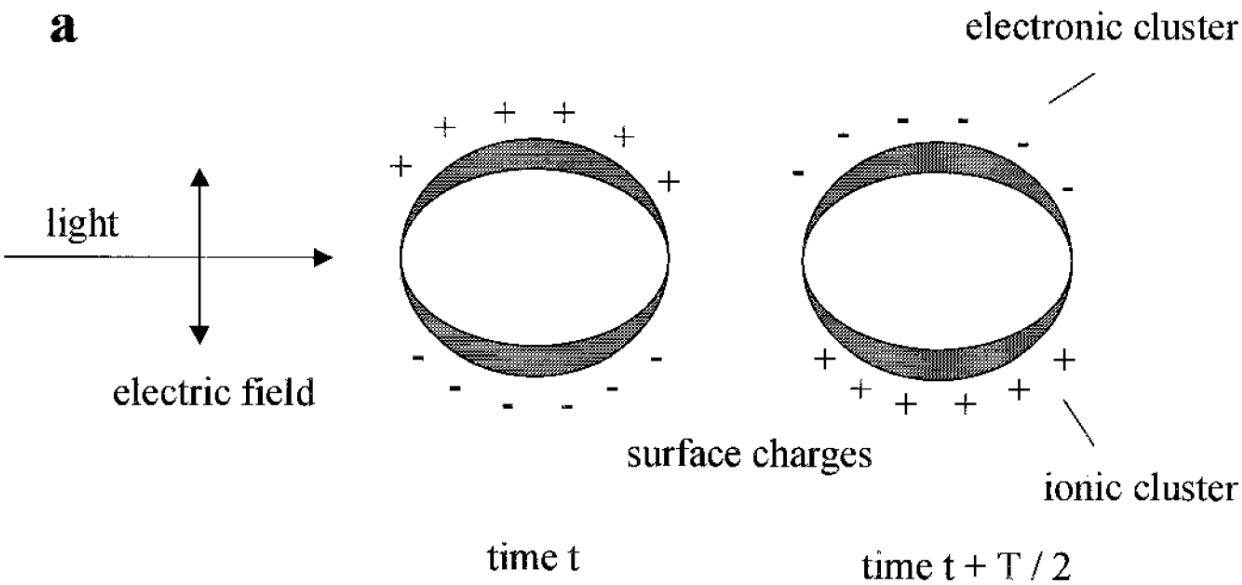
Plasmon: Coulombic attraction between ionic and electronic cluster



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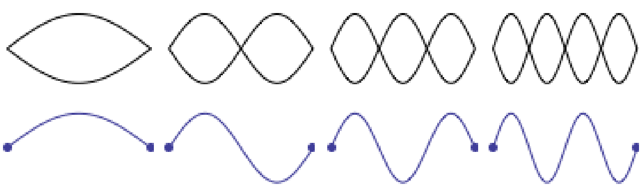
Result is a standing wave in the plasmonic particle that can be resonant with light



Standing waves have quantized energies: E_1, E_2, E_3, E_4

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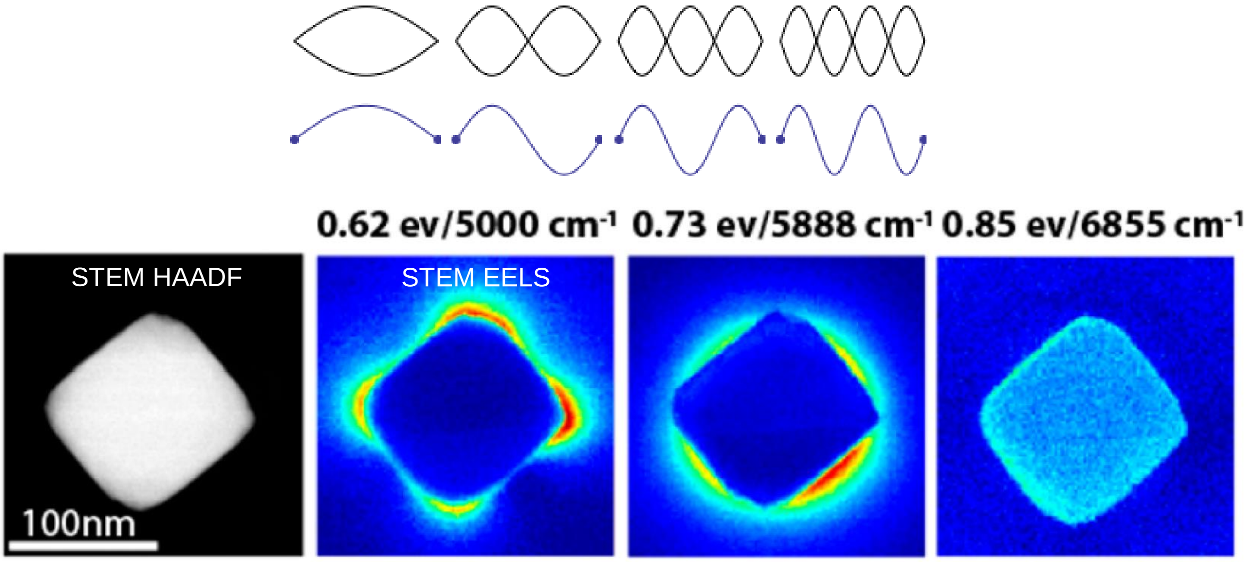
Result is a standing wave in the plasmonic particle



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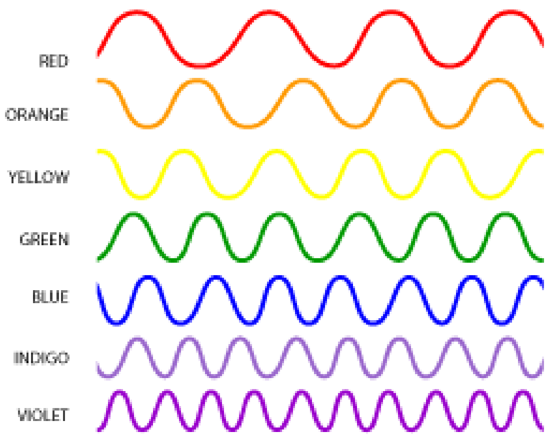
Resonance



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In contrast to bulk, plasmonic particles appear colored due to surface plasmon resonance

When an oscillatory field (EM, sound, etc.) is applied to an object capable of facilitating a standing wave

Certain frequencies (i.e. wavelengths) are amplified by each new oscillation of the incoming field

The repeated application of energy at this resonant frequency causes amplification of the standing wave

E.g., a surface plasmon that resonates at the frequency of red light appears bright red because it is amplifying photons with the frequency of red light

Au nanoparticles with varying plasmon resonance frequencies

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Metallic nanoparticle color can vary with size

In nanoparticles, plasmons are confined to a small surface instead of the bulk

This defines the possible wavelengths (i.e. frequencies of oscillation) of surface plasmons

Not all wavelengths (frequencies) are possible as in bulk case

Incident light can be resonant with the available frequencies, leading to strong scattering of that color of light

Au nanoparticles with varying plasmon resonance frequencies

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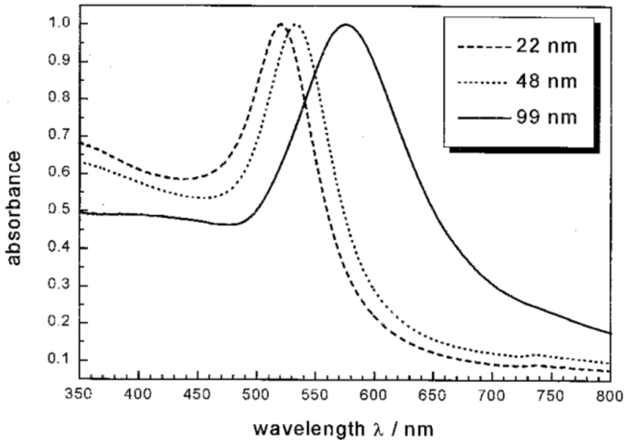
Visible light wavelength is much larger than nanoparticle size

Nanoparticles will absorb strongly at resonant frequencies

If light is in tune with resonant frequency of surface plasmon, the particle will absorb strongly

Absorption is therefore a key property of nanoparticles, because they re-emit the energy as light



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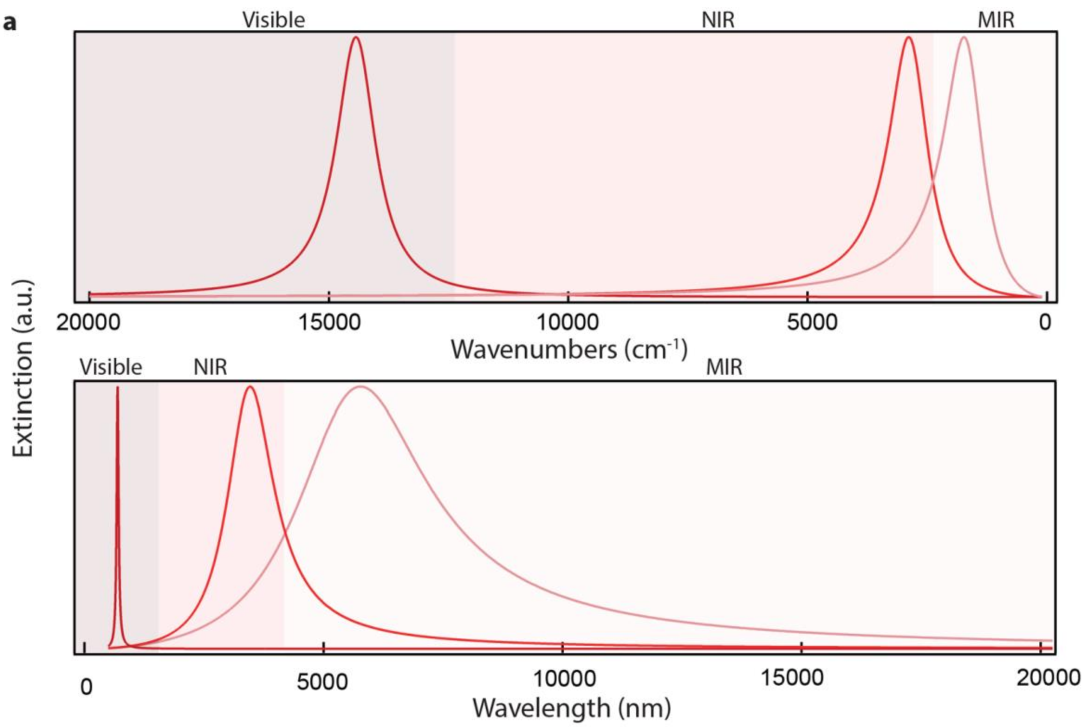

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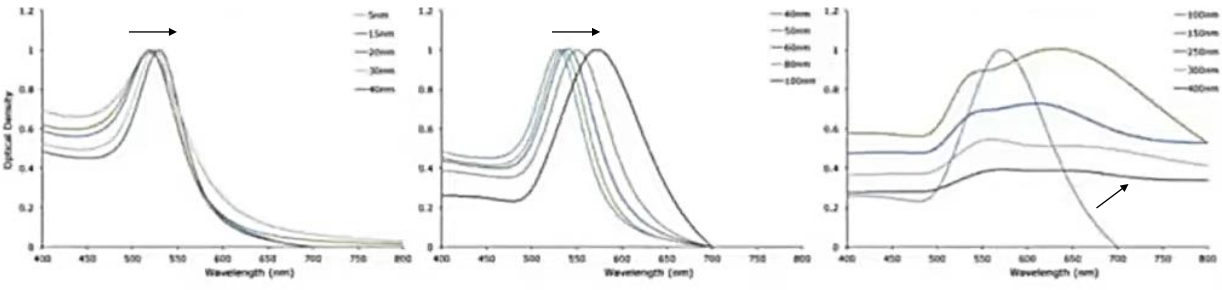
Particle size affects absorbance via excitation of plasmon resonance

Increasing particle size redshifts the peak absorption to longer wavelengths.
Surface plasmon resonance frequency is decreasing

At 400 nm, particles absorb across all wavelengths, like bulk conductor.

5 – 40 nm　　　40 – 100 nm　　　100 – 400 nm



Au nanoparticles

Wavelength of incident light (nm)

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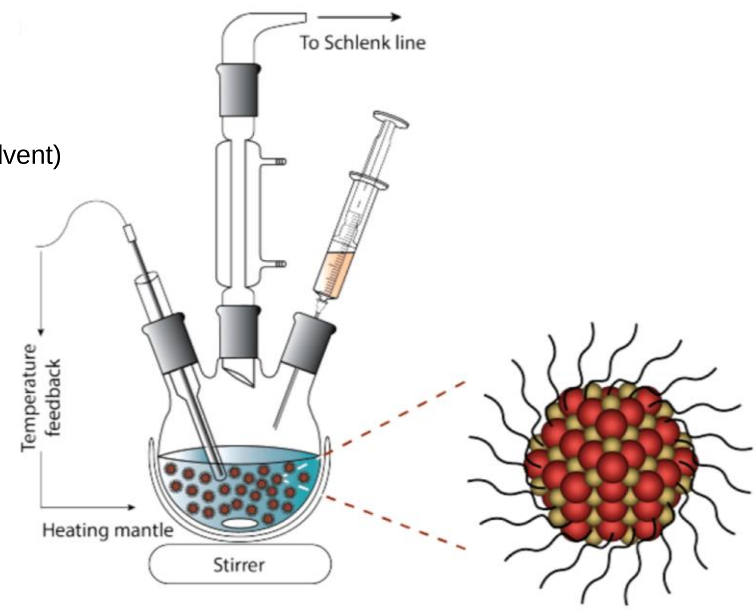
Three major components comprise a typical synthetic system

Metal precursors

Organic surfactants

Solvents (surfactant can also be the solvent)



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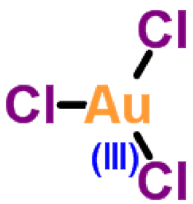
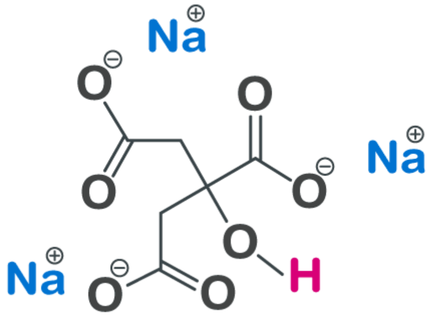
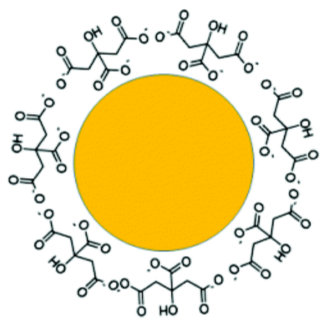
Metal salt dissolves to metal ion, which is reduced by citrate ion to metal NP







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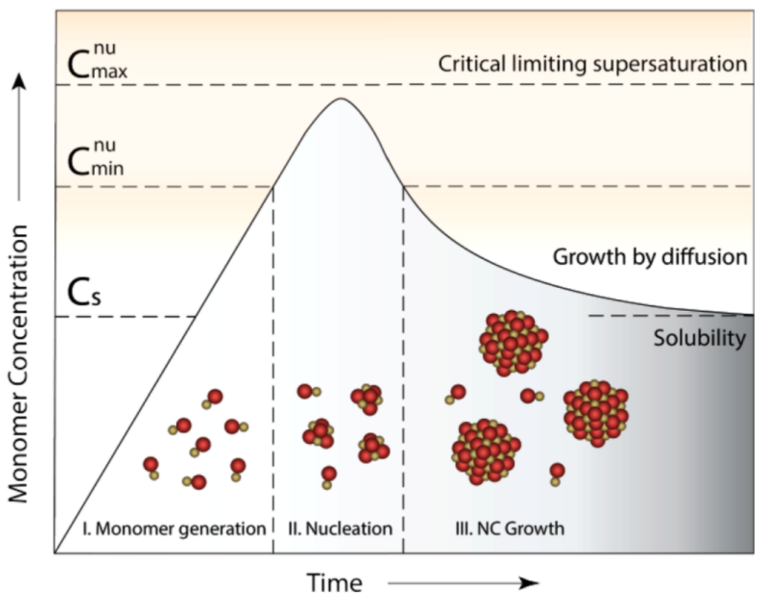
Nucleation and growth mechanism

Stage I. Monomer generation
- Rate depends on rxn rate & T
- increases concentration above saturation limit, Cs
- nucleation suppressed by energy barrier of nucleation



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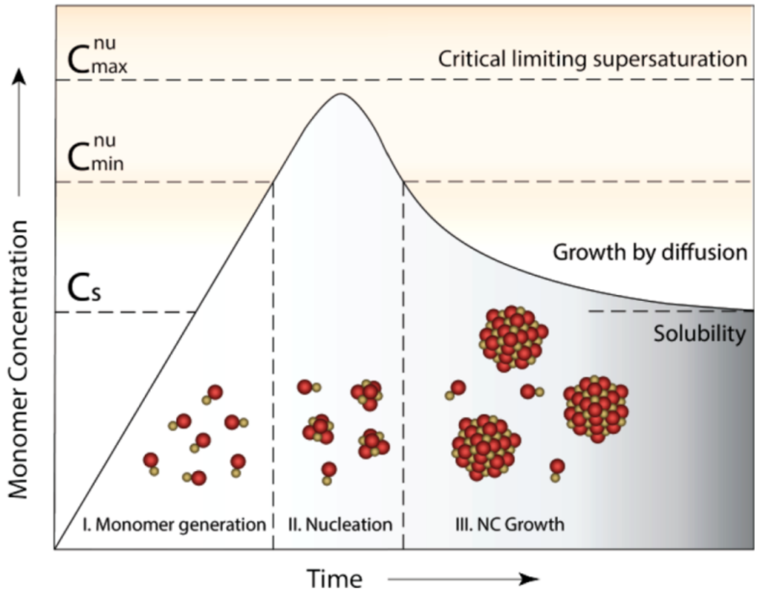
Stage II. Nucleation
- monomers rapidly consumed causing drop in concentration



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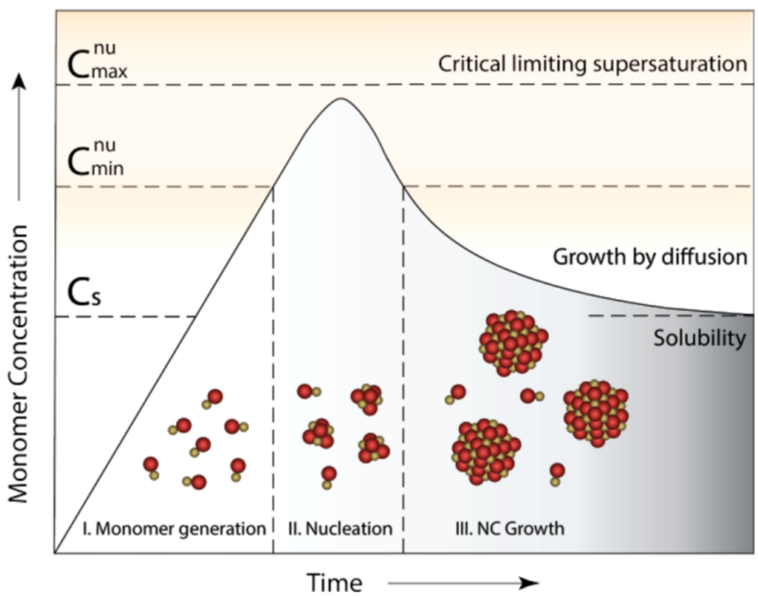
Stage III. Growth
- Nuclei grow by assimilation of monomers



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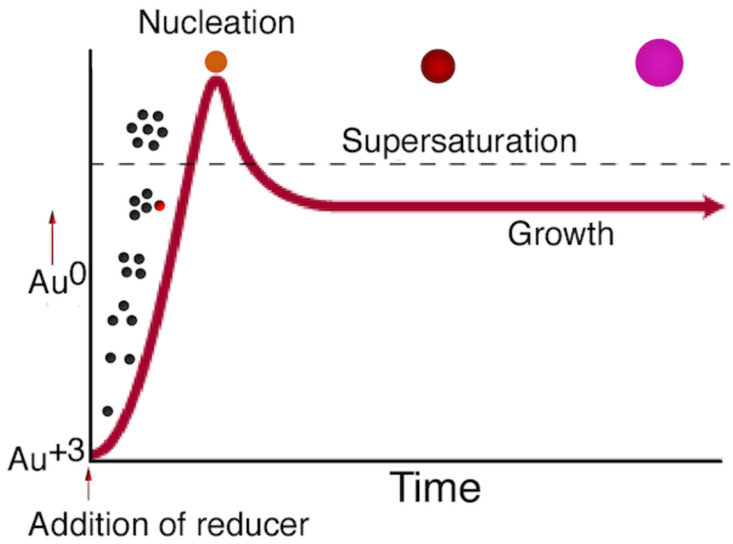

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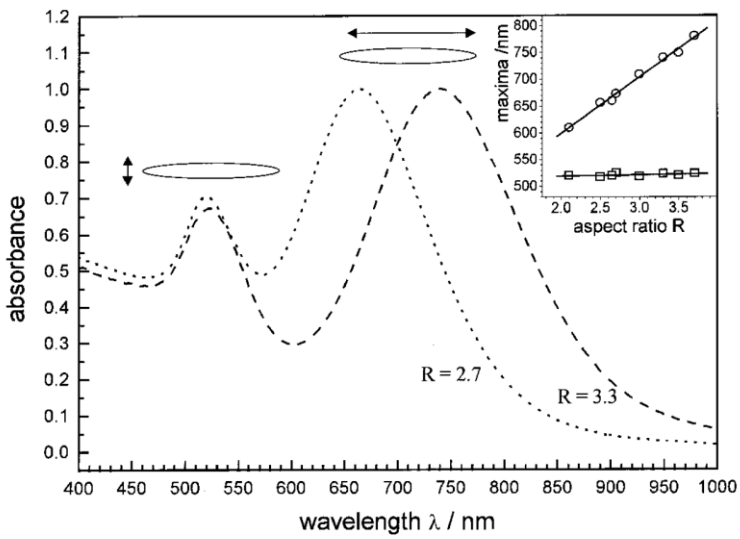
Aspect ratio affects resonance frequency of plasmon

Short-wavelength absorption band is due to the oscillation of the electrons perpendicular to the major axis of the nanorod

Long-wavelength band is caused by the oscillation along the major axis.

The absorption bands are transverse and longitudinal surface plasmon resonances, respectively.



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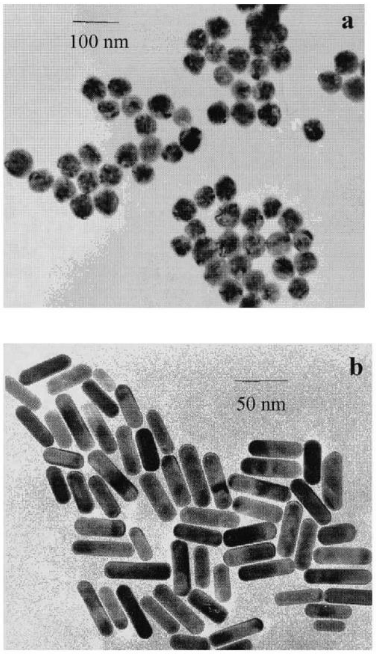
Aspect ratio



TEM images of (*a*) spherical gold nanoparticles with an average diameter of 48 nm and (*b*) gold nanorods with a mean aspect ratio of 3·3.

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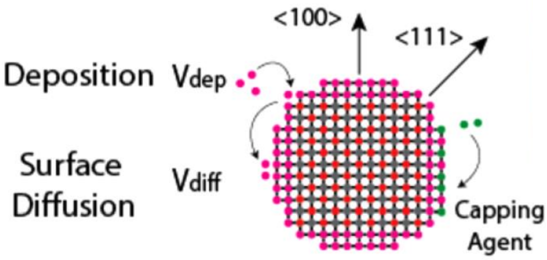
Shape control is governed by the relative rates of deposition and diffusion (V_dep, V_diff)



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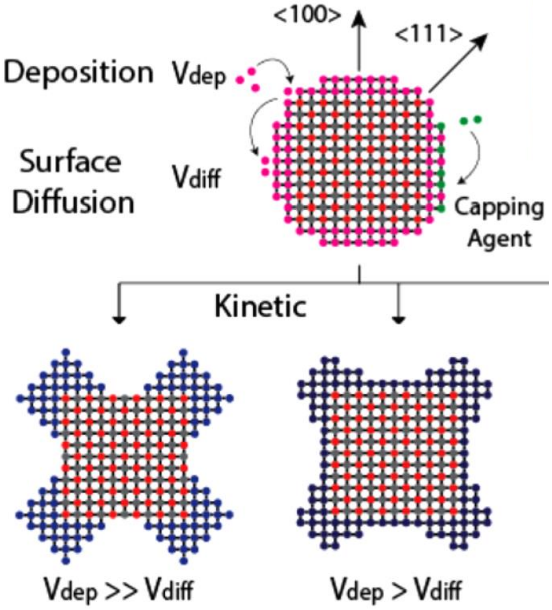

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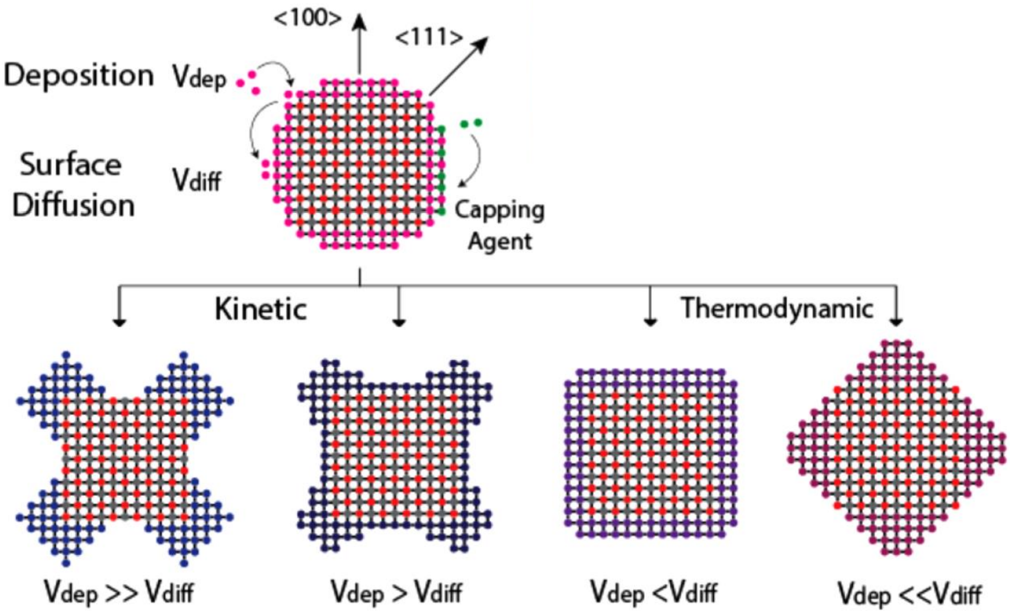

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Classical equation of plasmon resonance frequency predicts composition effect

Change in the number of electrons in a material will change the resonance frequency.

Nanoparticles of different elements have different color despite same geometry.

E.g. Au and Ag

Number density of electrons

Electron charge

Plamson resonance frequency

$$\omega_p{}^2 = \frac{Ne^2}{m\epsilon_o}$$

Electron mass

Permittivity of free space

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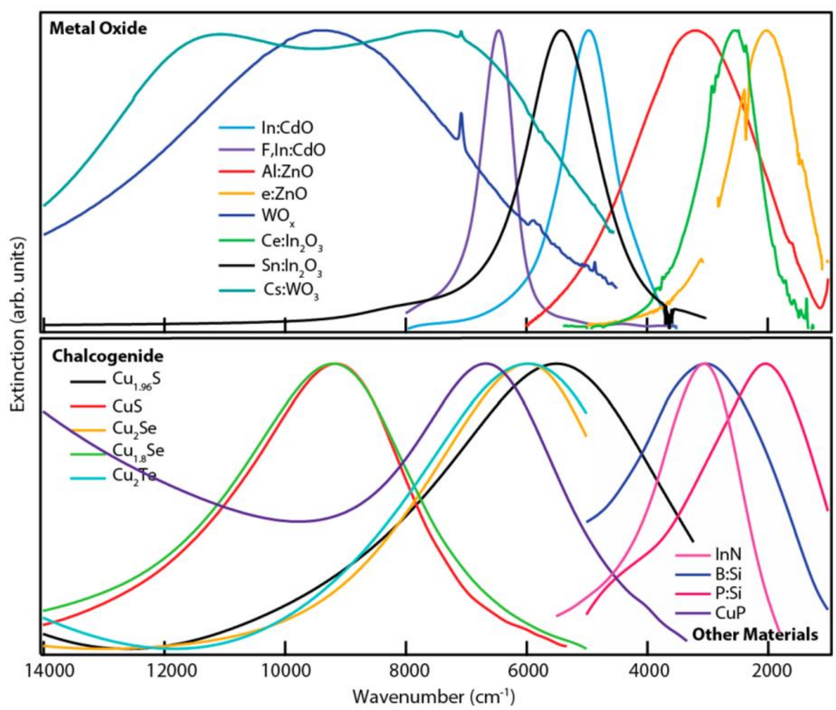
Chemical composition affects resonance



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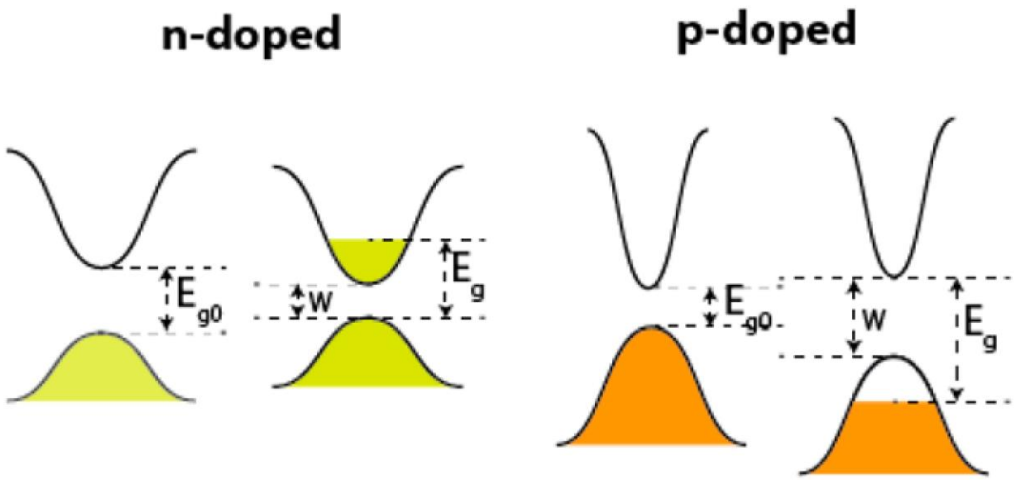
Doping changes the electronic structure, affecting plasmon resonance and absorbance



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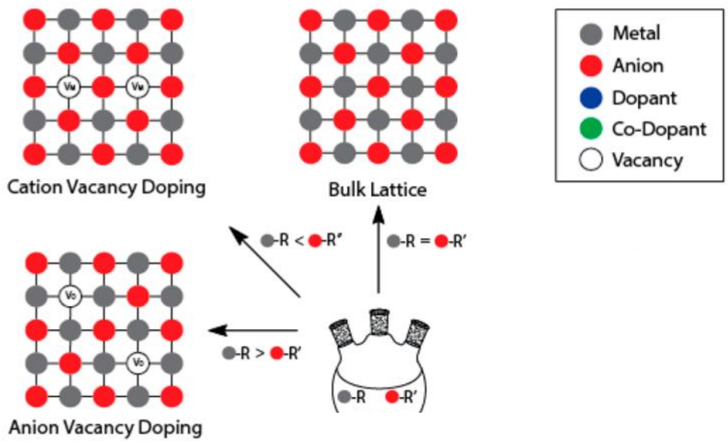
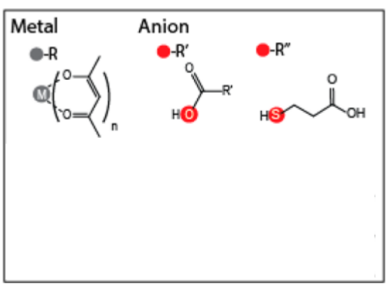
Dopant control through synthesis





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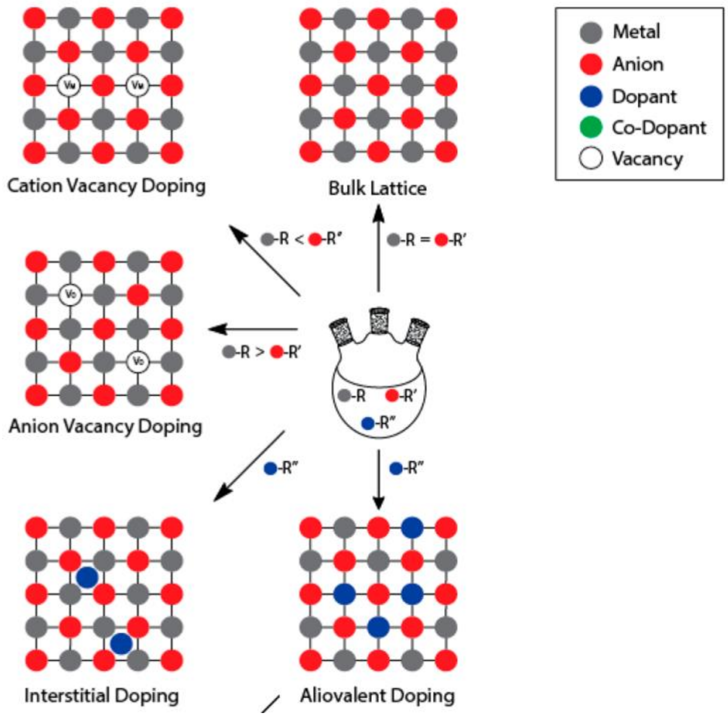
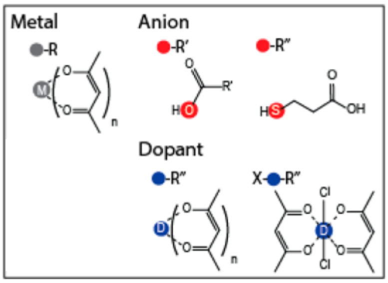
Dopant control through synthesis





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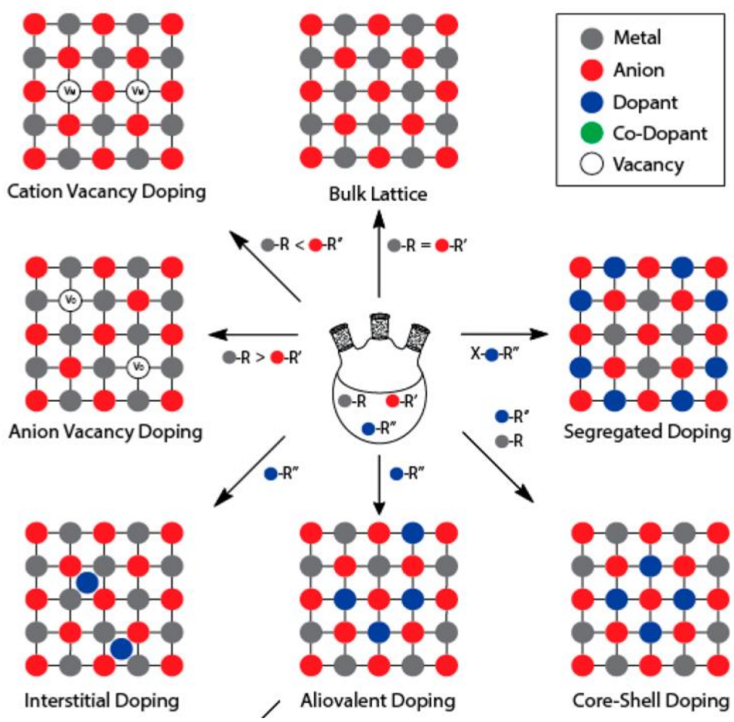
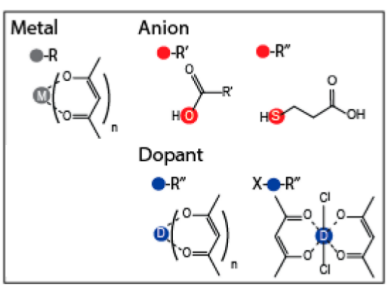
Dopant control through synthesis





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Outline

- Semiconductor physics
- Plasmonic nanocrystal synthesis
- Silicon wafer synthesis

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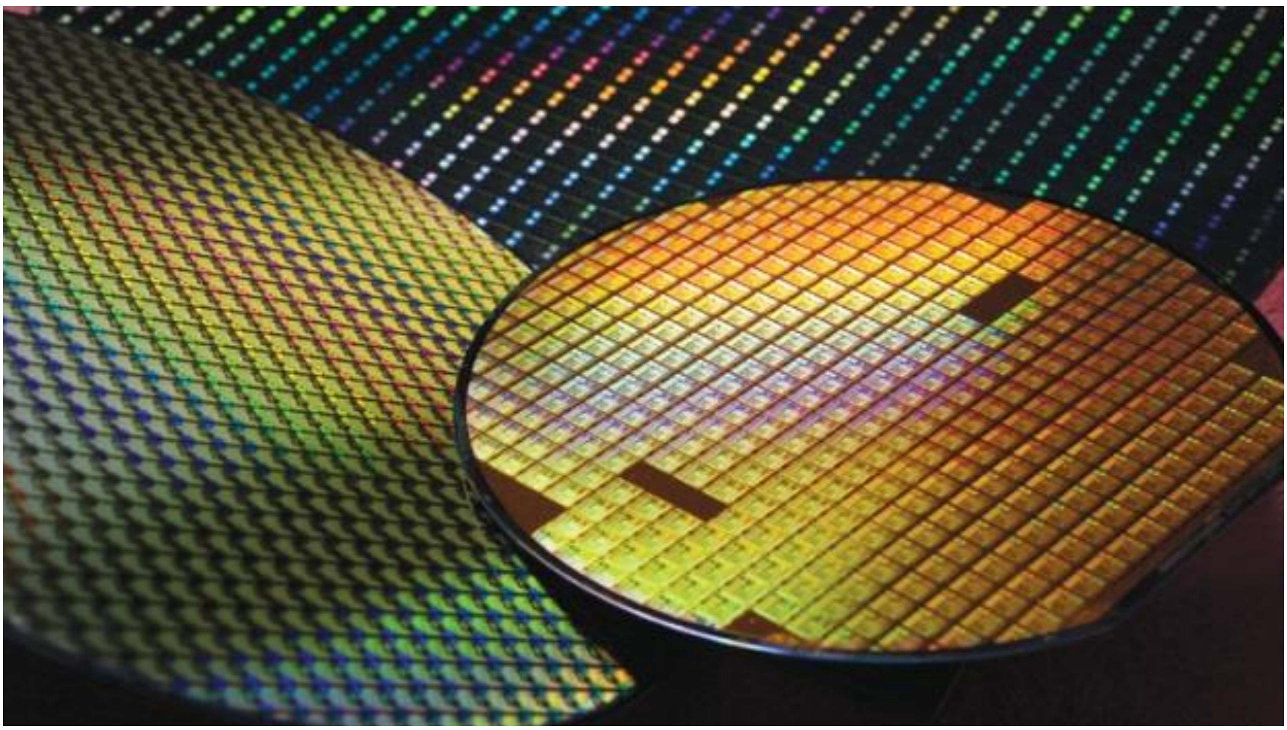

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Modern computers use single crystal Si wafer substrates

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Modern computers use single crystal Si wafer substrates

Why is Si black?

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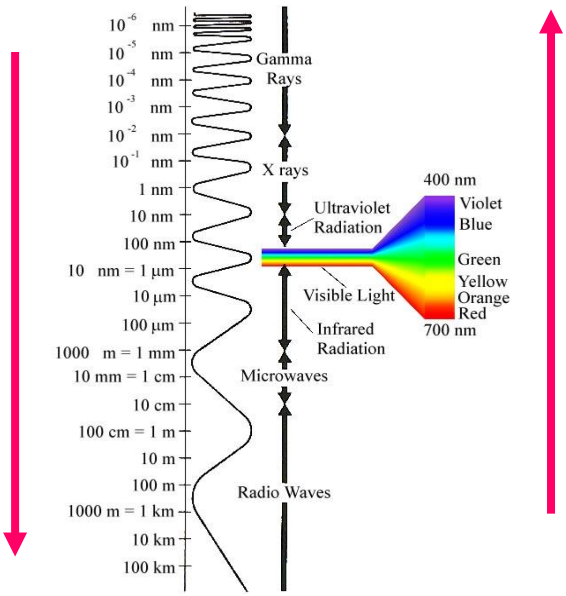
Semiconductors can have bandgap in the visible range

Increasing wavelength (m)



Increasing Photon Energy (eV)

Color & Energy
Violet ~ 3.17eV
Blue ~ 2.73eV
Green ~ 2.52eV
Yellow ~ 2.15eV
Orange ~ 2.08eV
Red ~ 1.62eV

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Home » Science & Innovation » Energy Sources » Solar

The tremendous growth in the U.S. solar industry is helping to pave the way to a cleaner, more sustainable energy future. Over the past few years, the cost of a solar energy system has dropped significantly -- helping to give more American families and business access to affordable, clean energy.

Through a portfolio of R&D efforts, the Energy Department remains committed to leveraging America's abundant solar energy resources -- driving research, manufacturing and market solutions to support widespread expansion of the nation's solar market.

Solar Energy Technologies Office

Solar Energy Technologies Office Homepage

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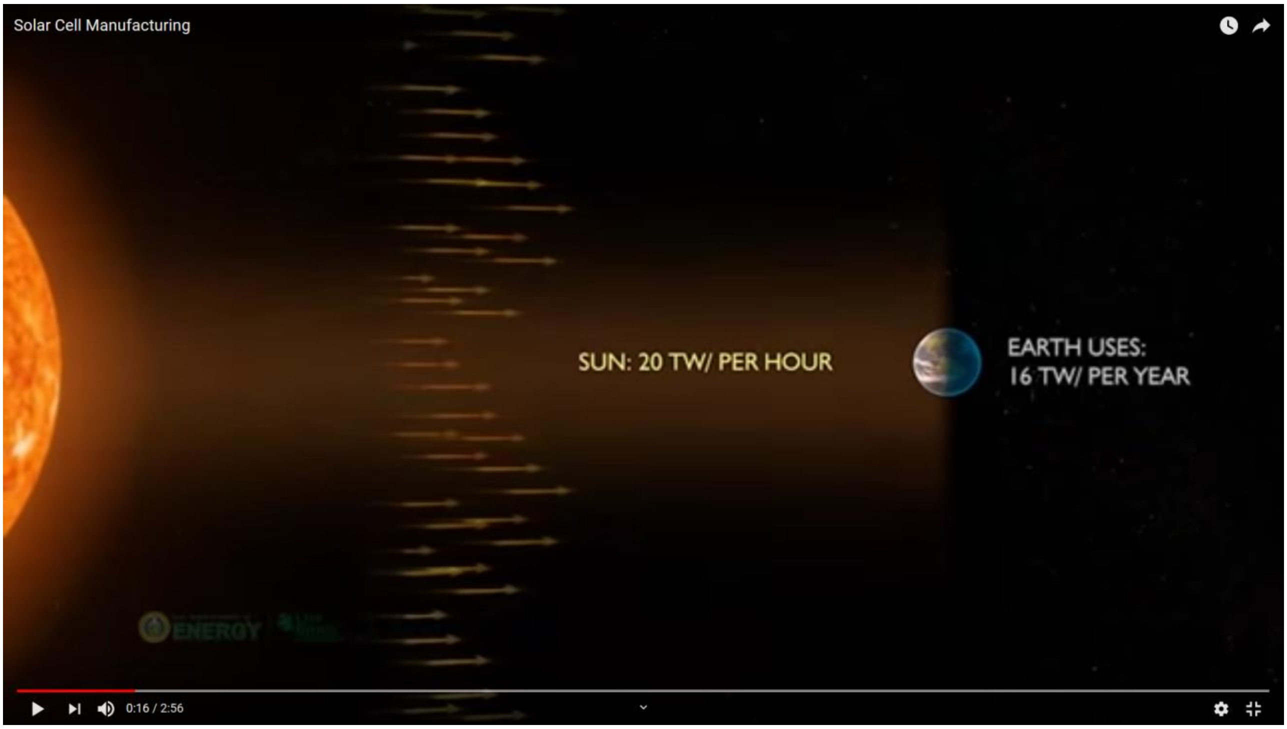

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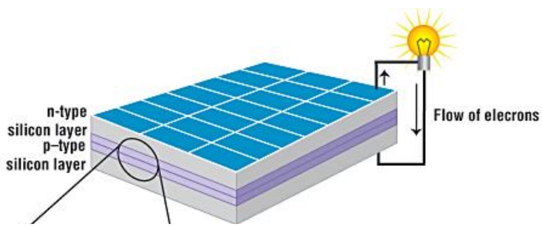
A photovoltaic cell is a p-n junction



Anthony Fernandez "How a Solar Cell Works"
American Chemical Society, acs.org

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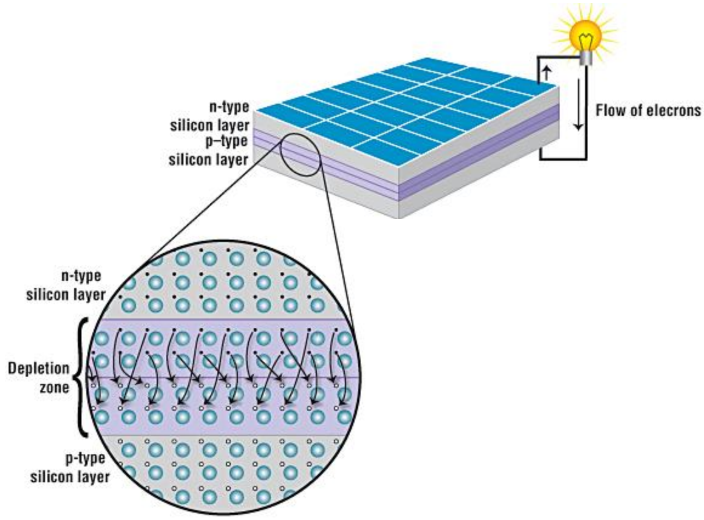
A photovoltaic cell is a p-n junction



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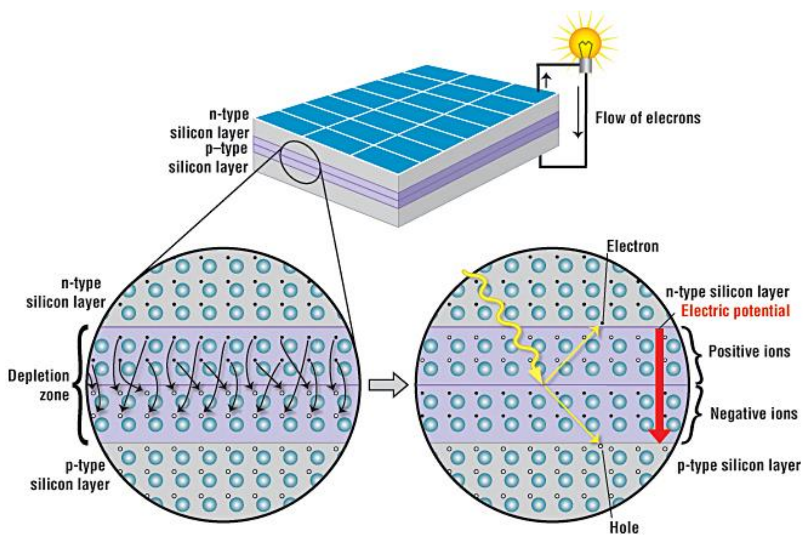

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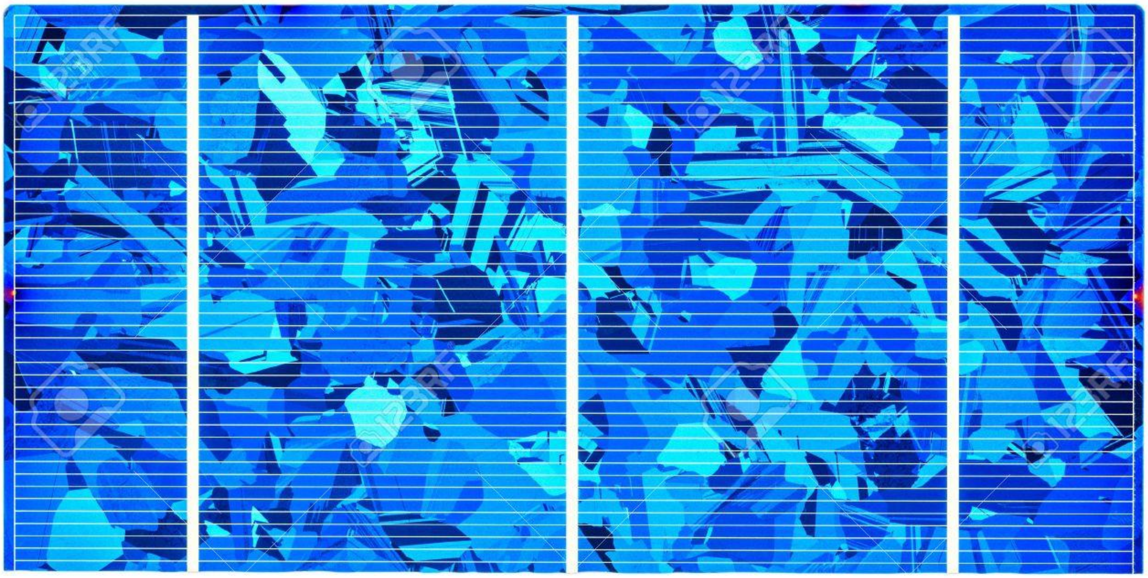

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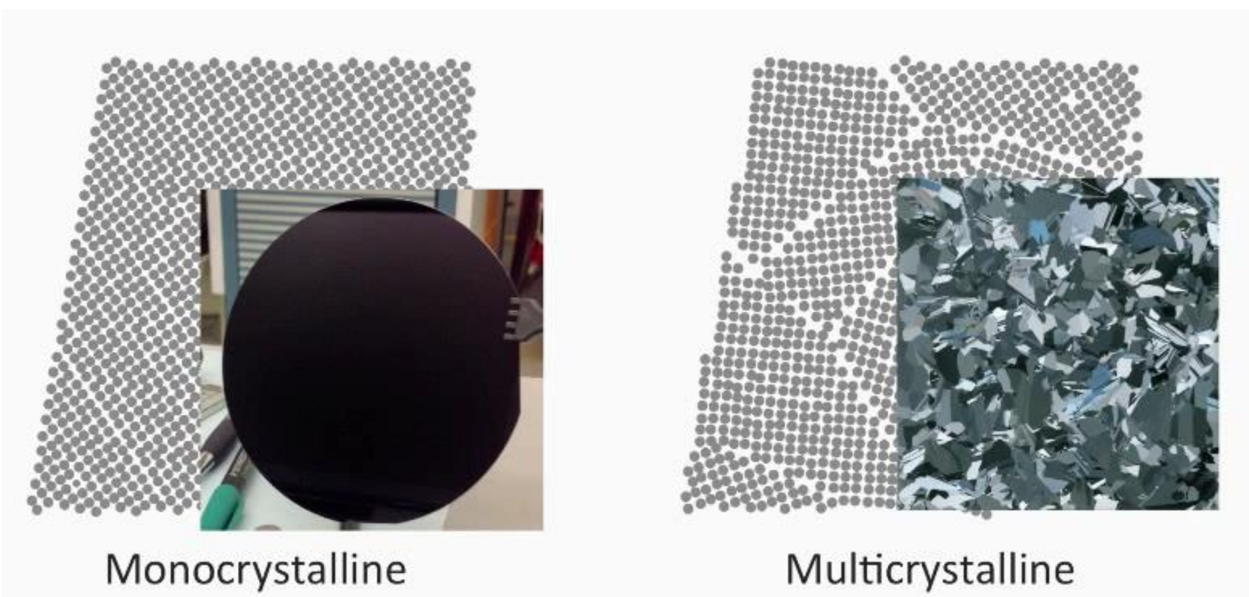

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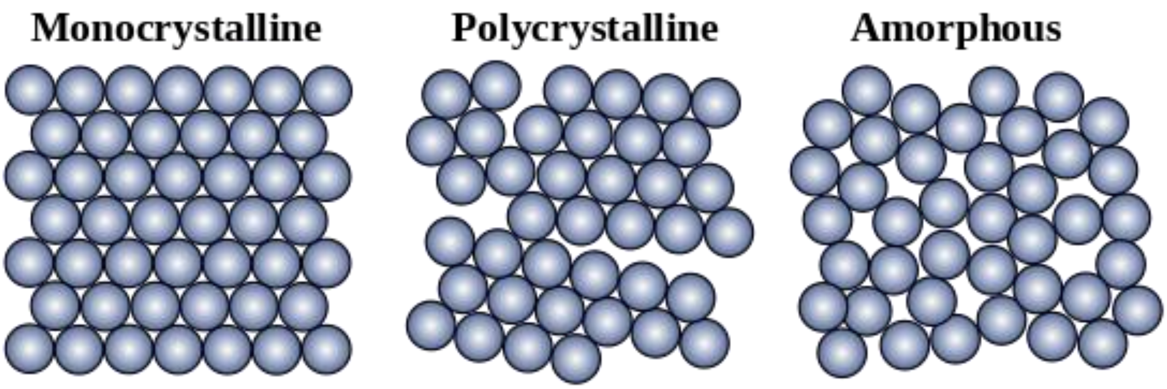

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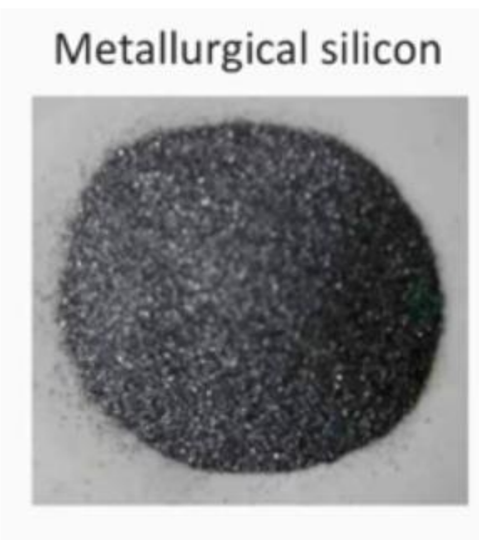
Si manufacturing is grounded in materials synthesis



70% of mg-si is for Al alloying for automotive.
30% for other Si for e.g. silicones.
1% for poly and mono Si

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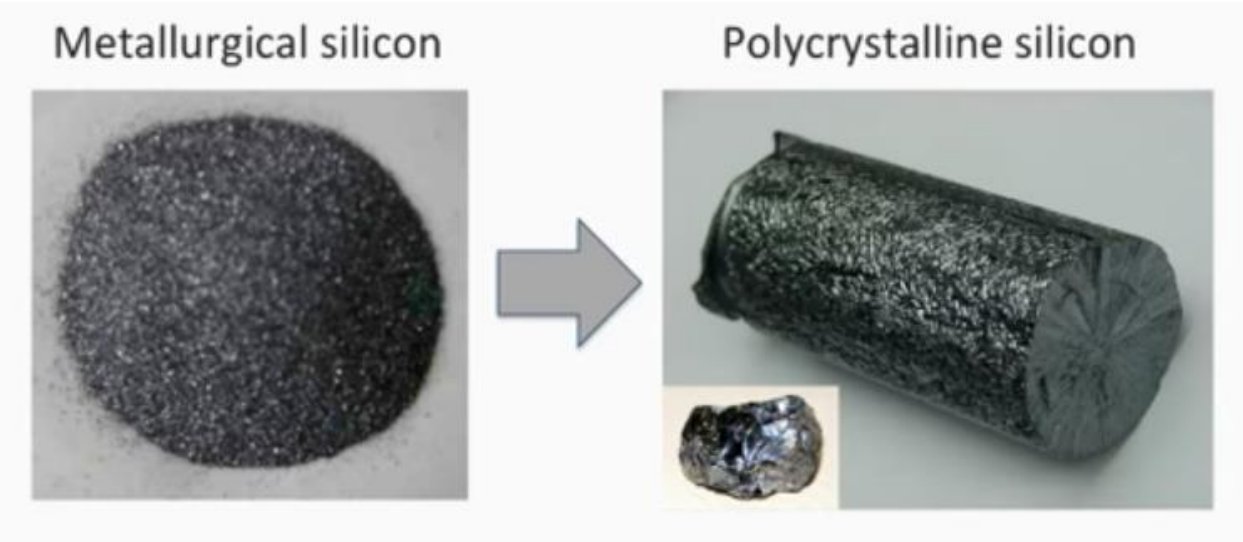
Si manufacturing is grounded in materials synthesis



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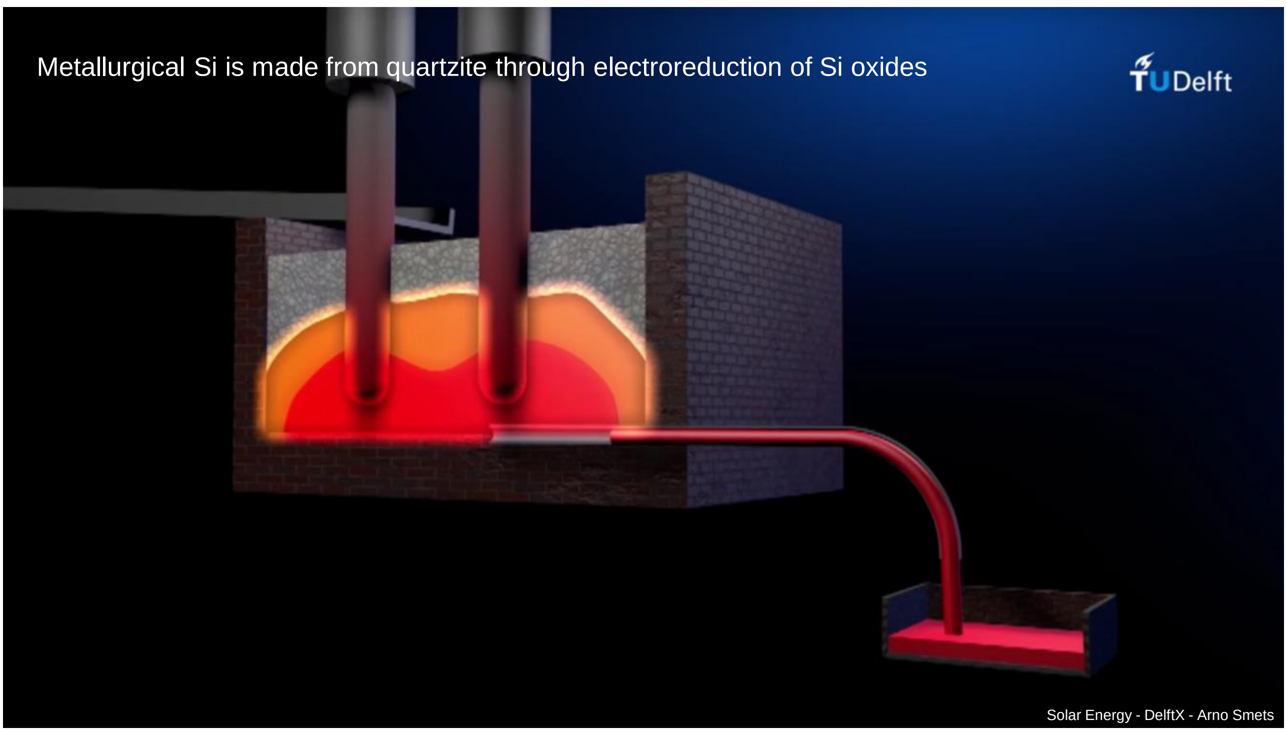

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Metallurgical Si is reacted with HCl gas to form tri-chloro-silane, 1 ppm impure

75

Polycrystalline Si (1 ppm) is made from metallurgical Si by chemical vapor deposition

Doping via gas phase borane or phosphane

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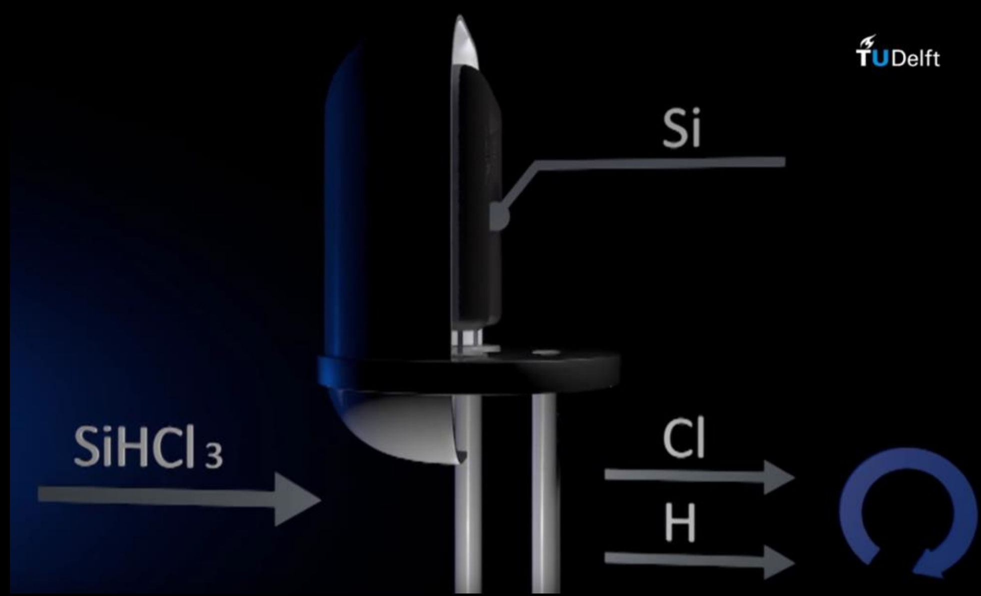
Polycrystalline Si (1 ppm) is made from metallurgical Si by chemical vapor deposition



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Modern computers use single crystal Si wafer substrates

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Si ingot is prepared from poly Si

https://www.youtube.com/watch?v=8QKzS_w_Ko0&t=320s

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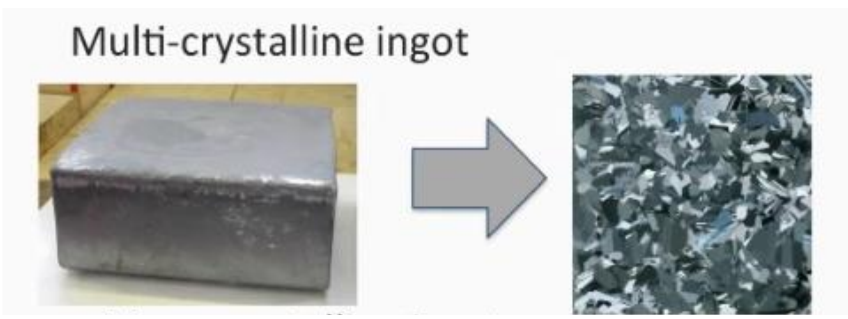
Multicrystalline ingot is also produced from melt by directional solidification



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Multicrystalline ingot is produced from melt

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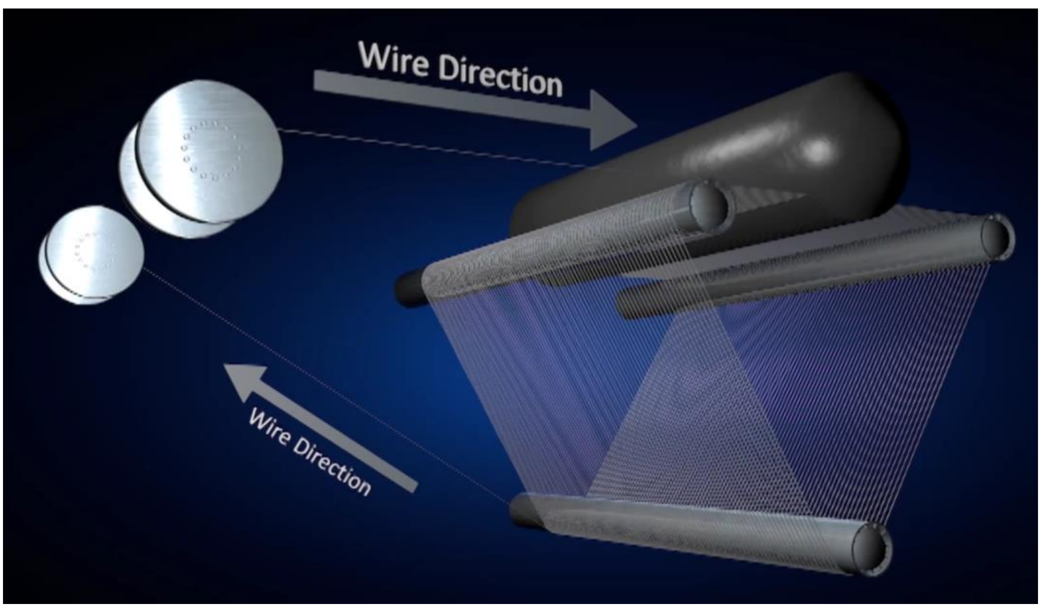
Wafers are created from ingot via sawing to ~150 μm



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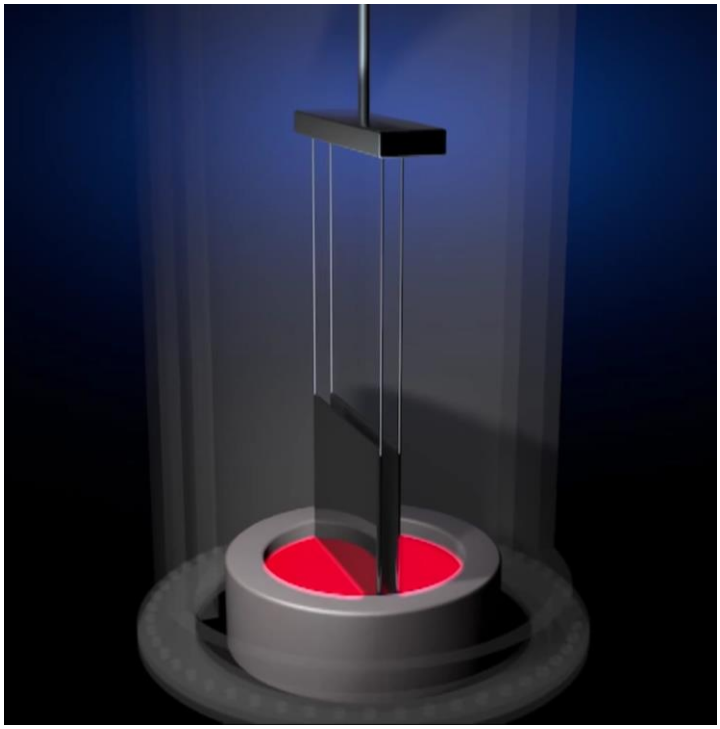
Wafers are created from Si ribbon



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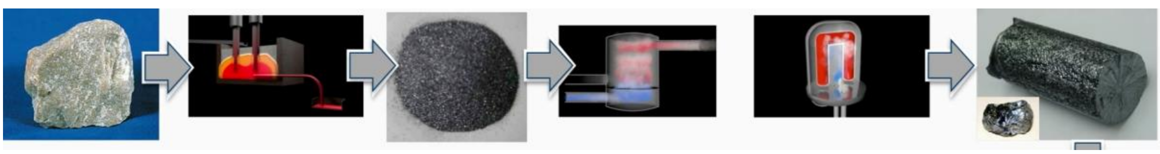
Si manufacturing is grounded in materials synthesis



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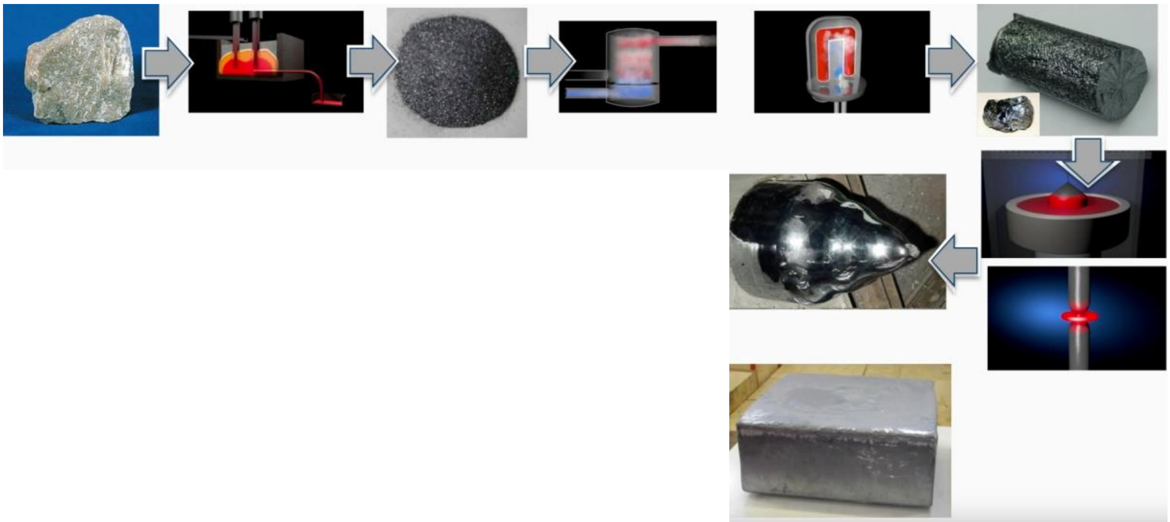

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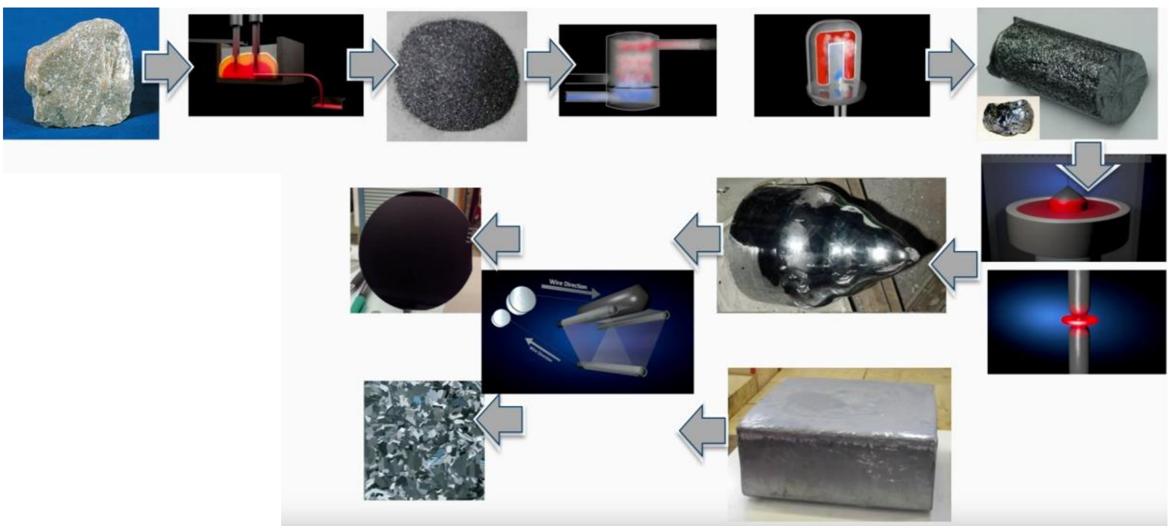

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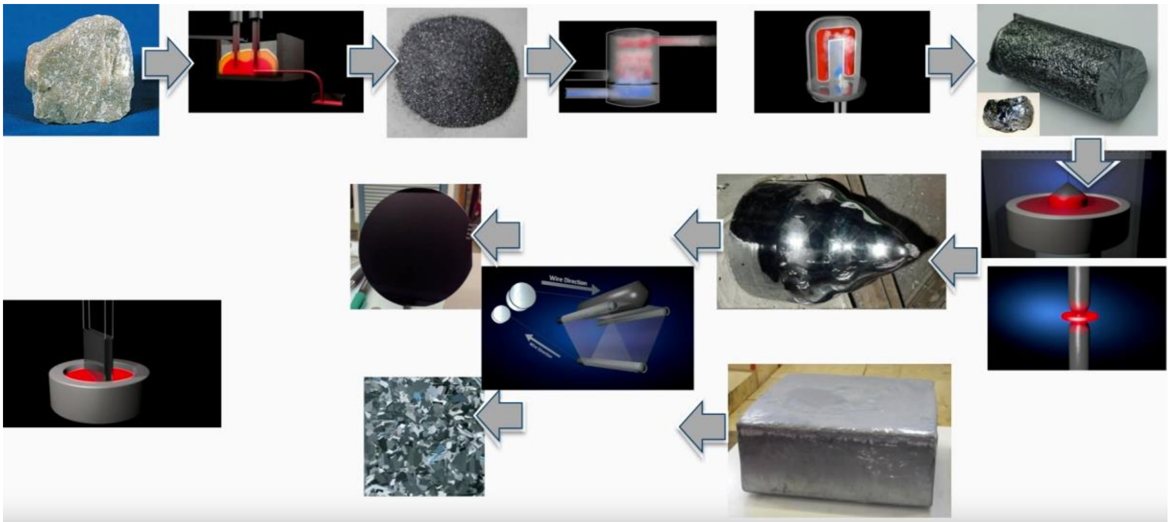

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Silicon wafer synthesis

Throughout

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