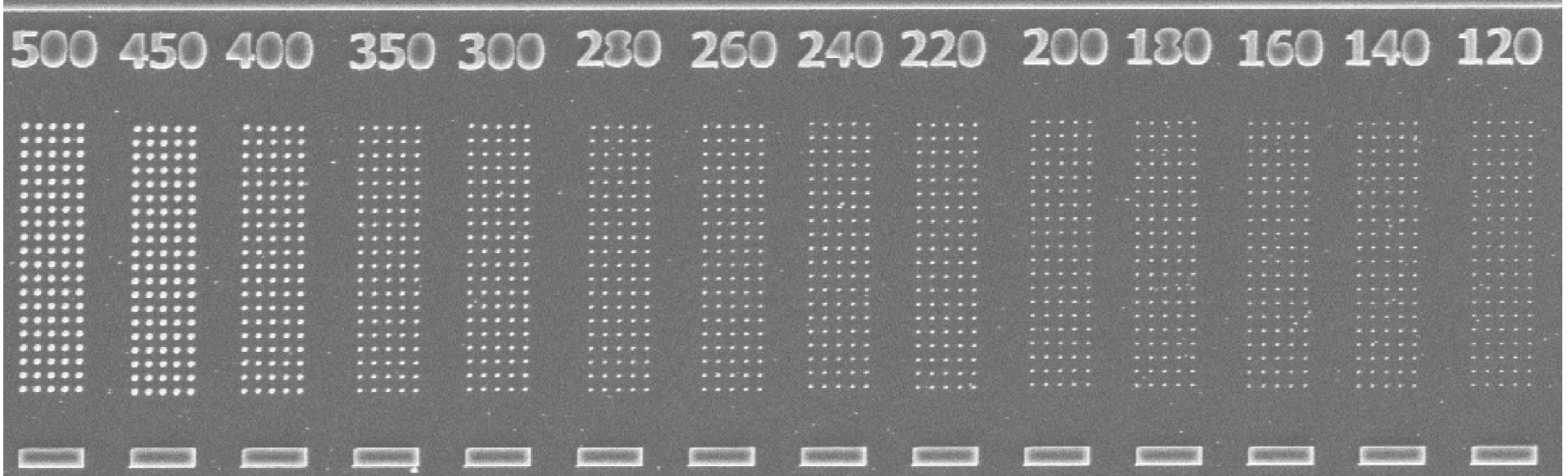
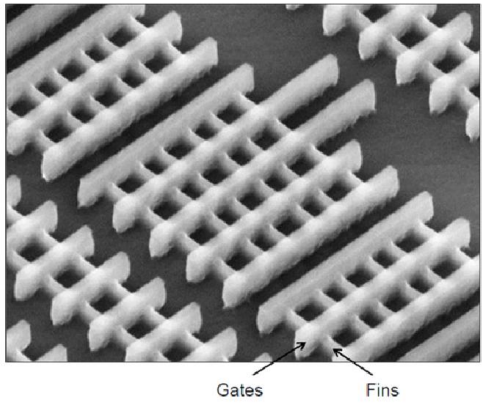
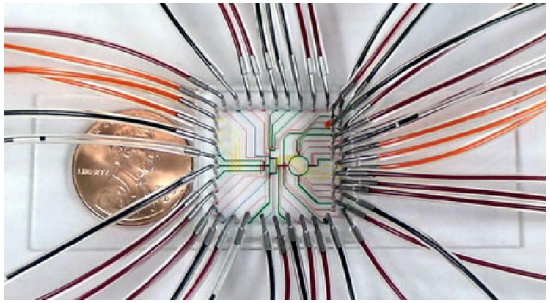
Semiconductor Processing: Crystal Growth

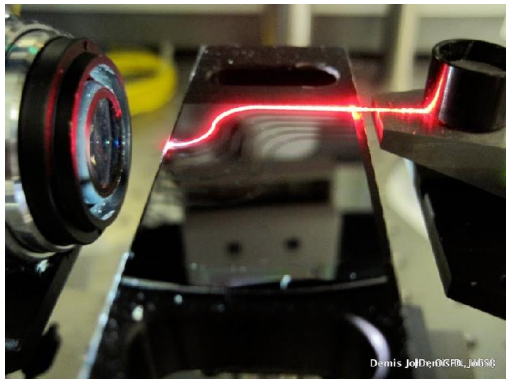


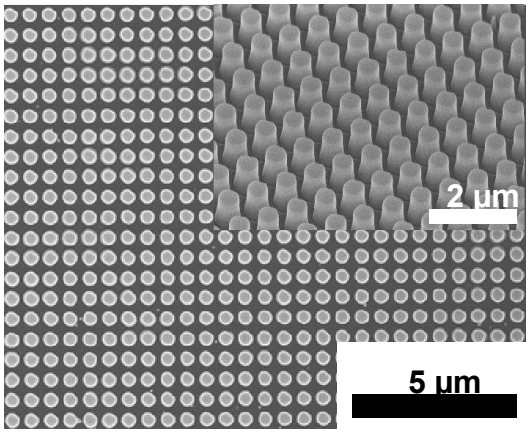
Professor Benjamín Alemán
Department of Physics
University of Oregon

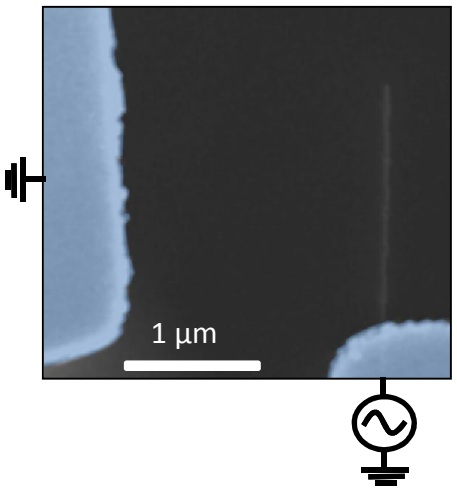
How do we make these useful and curious structures?

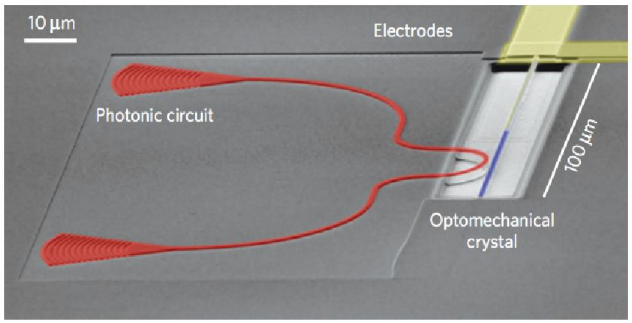




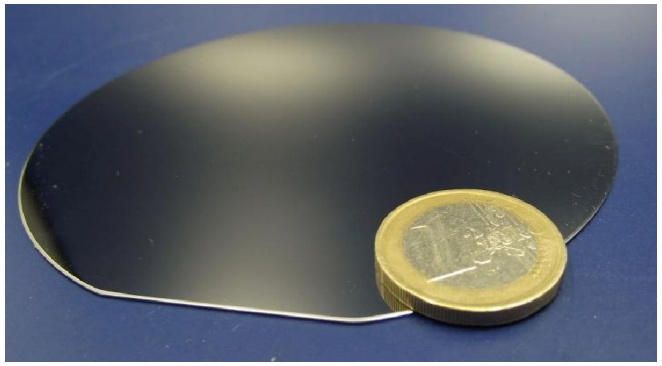


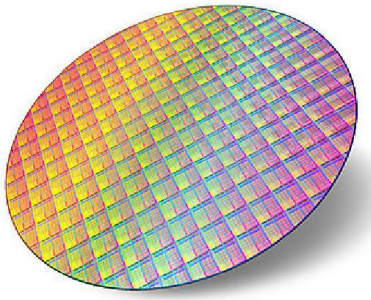


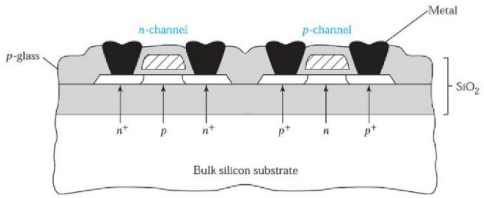




Planar Processing with Semiconductors (Silicon): Course Map



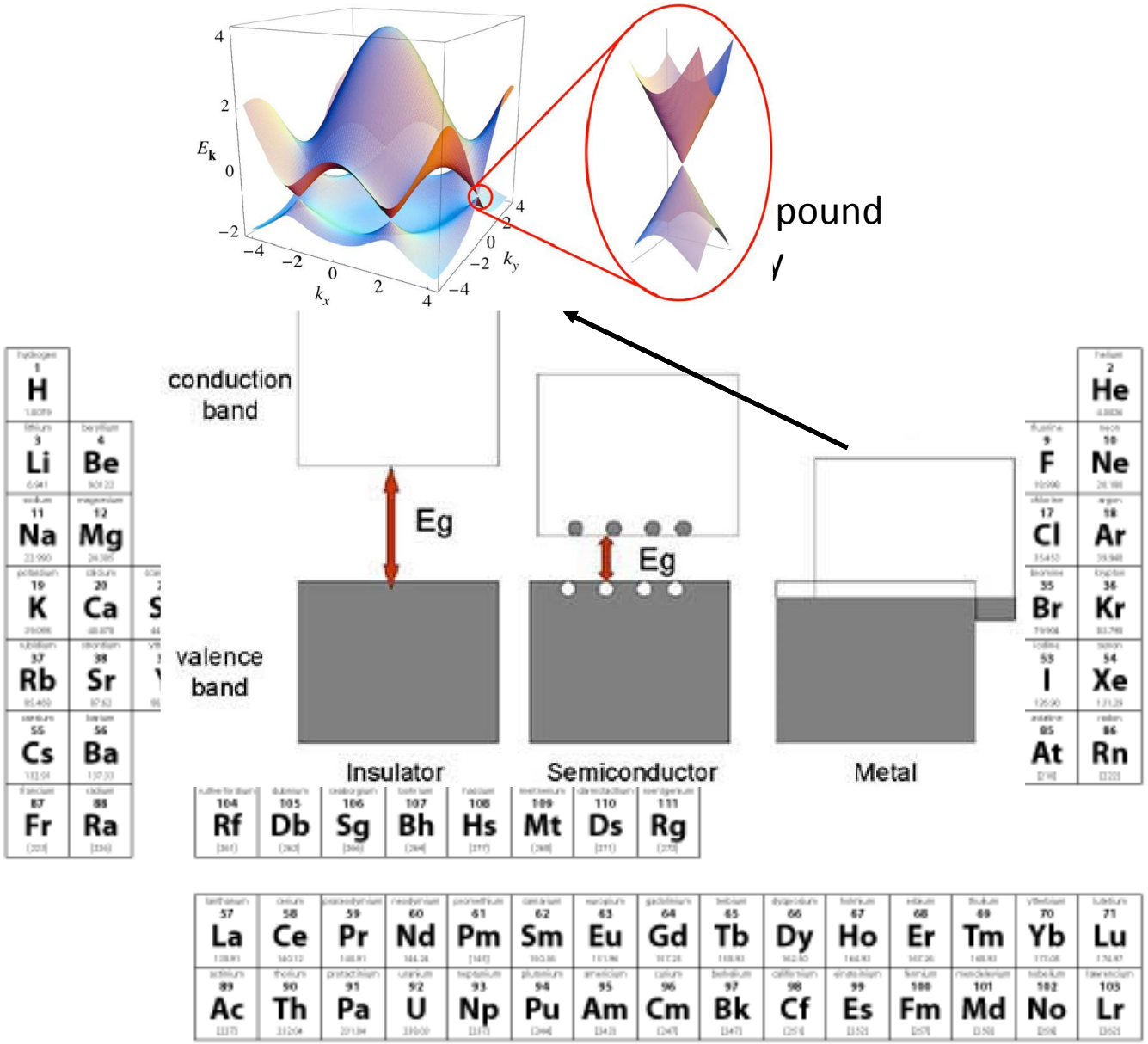




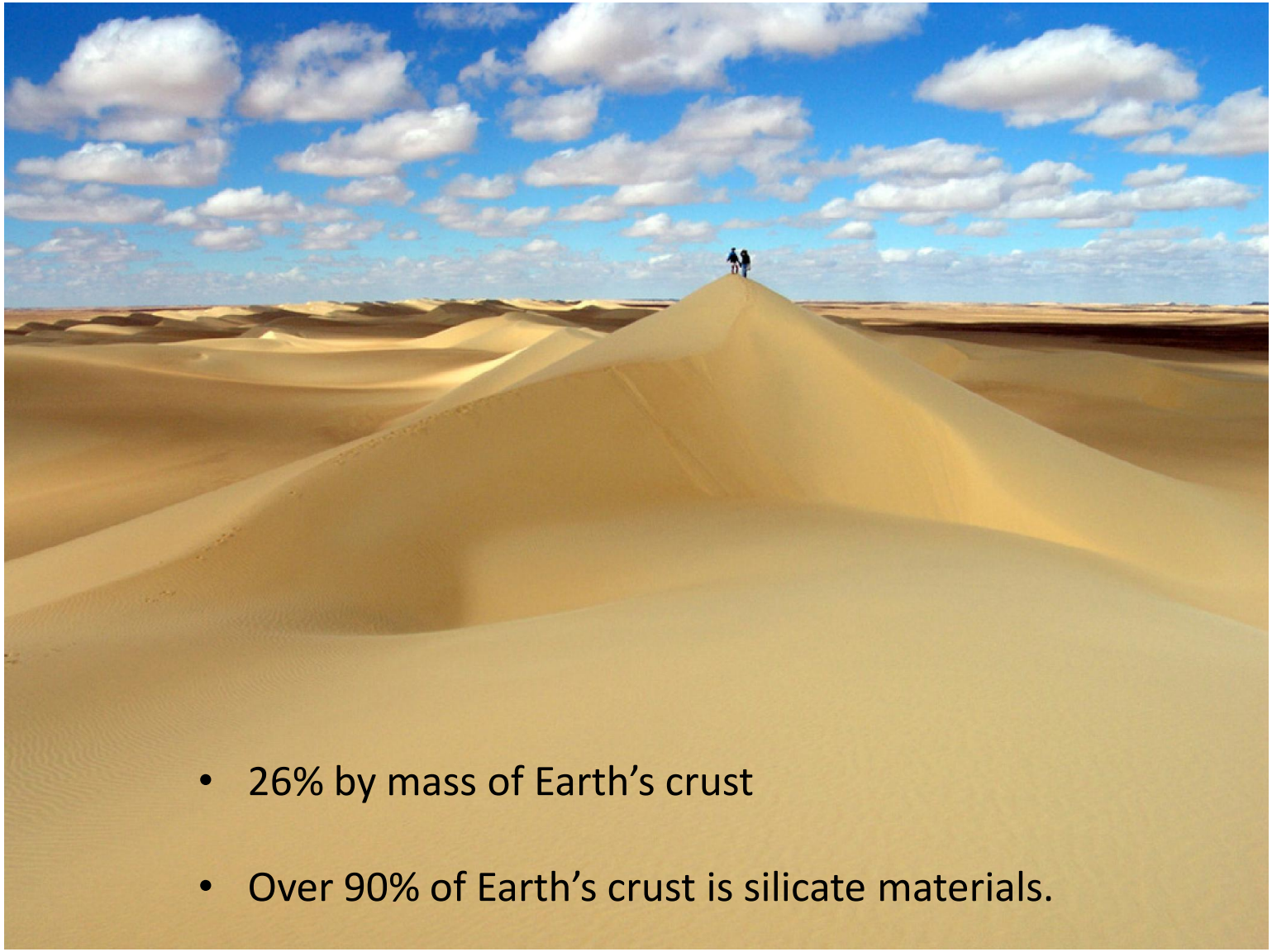
- Crystal growth (semiconductors)
- Wafer characteristics
- Wafer doping
- Defects and impurities
- (SiO_2 growth)

- (SiO_2 growth)
- Masked doping
- Lithography
- Vacuum Systems
- Thin Films: CVD, MBE, PVD, ALD
- Implantation
- Wet and Dry Etching
- Integration

Why are semiconductors useful?



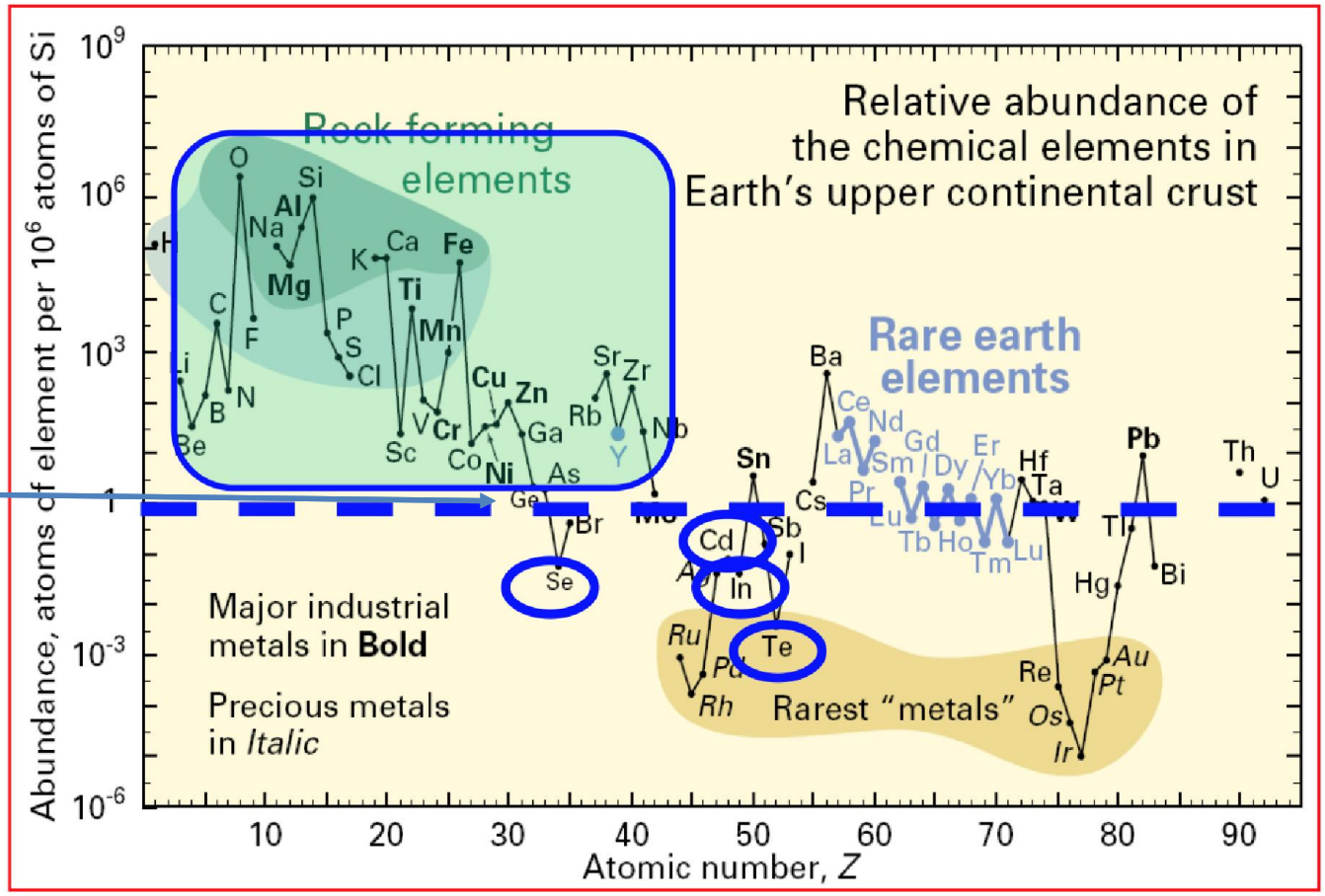
Why is Silicon an important semiconductor and why is it so popular in planar processing?



- 26% by mass of Earth's crust
- Over 90% of Earth's crust is silicate materials.

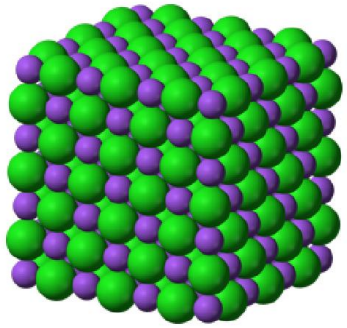
Silicon is abundant

Relative abundance of elements vs. atomic number*



from P.H. Stauffer et al, Rare Earth Elements - Critical Resources for High Technology, USGS (2002)

A brief introduction to crystal structure

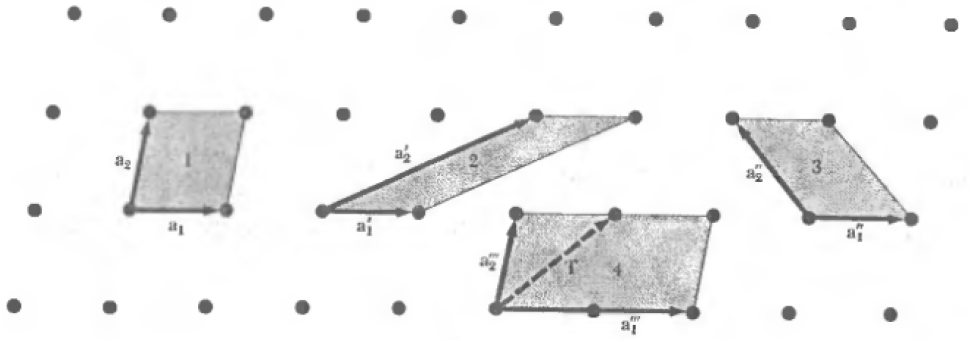


Crystal Structure = Lattice + Basis

A *lattice* is defined by a set of fundamental translation vectors $\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3$, such that the atomic arrangement looks the same from the perspective of both $\boldsymbol{r}$ and $\boldsymbol{r}'$, where

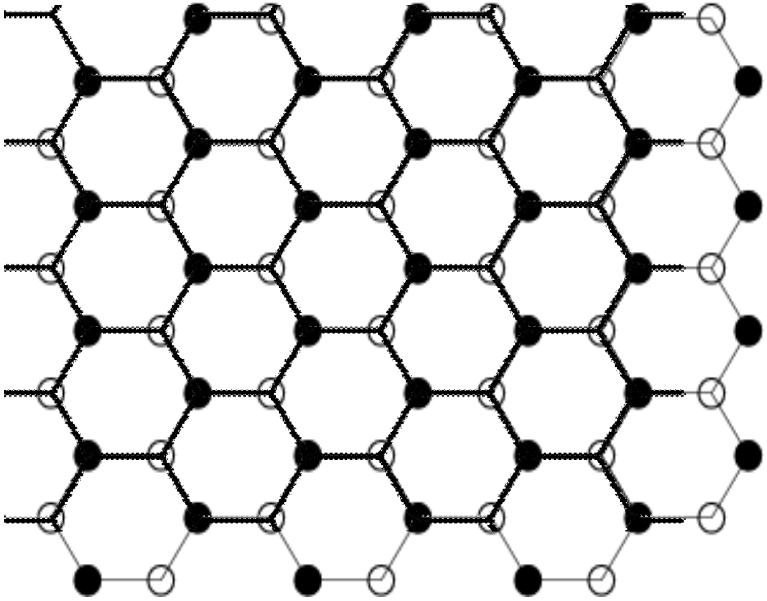
$$\boldsymbol{r}' = \boldsymbol{r} + u_1\boldsymbol{a}_1 + u_2\boldsymbol{a}_2 + u_3\boldsymbol{a}_3$$

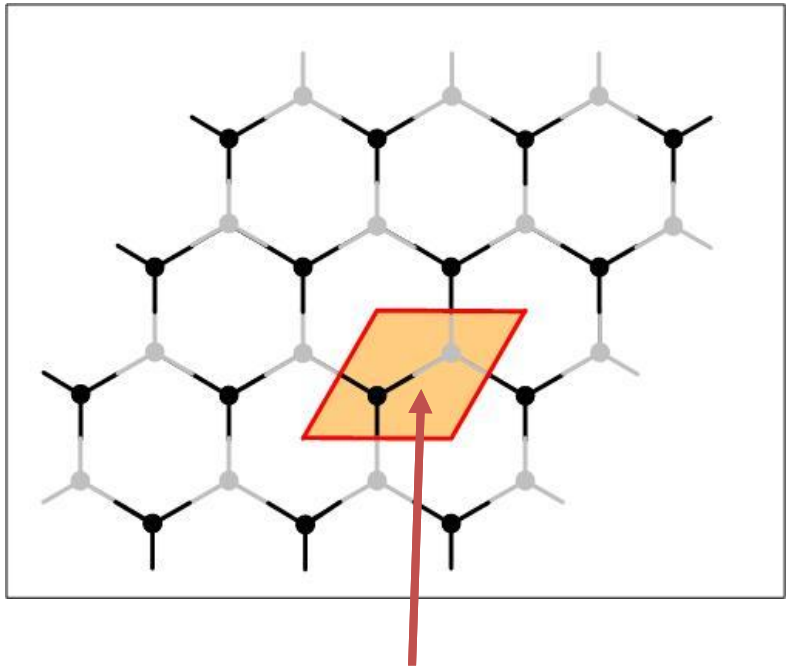
and u_1, u_2, u_3 are arbitrary integers.



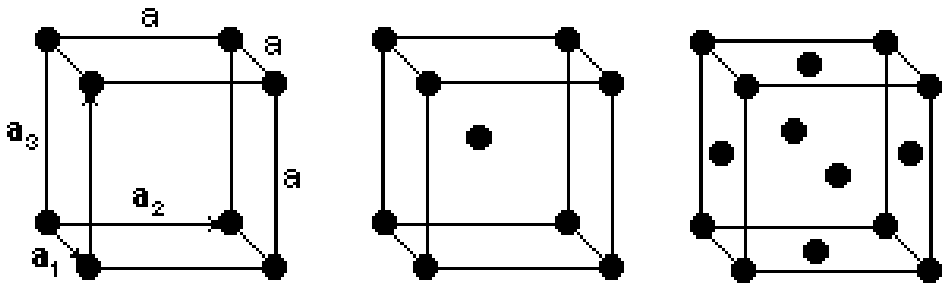
The basis

Lattice?





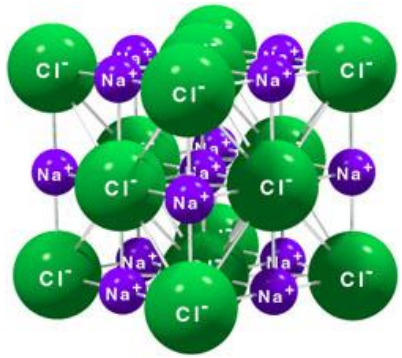
Cubic lattices



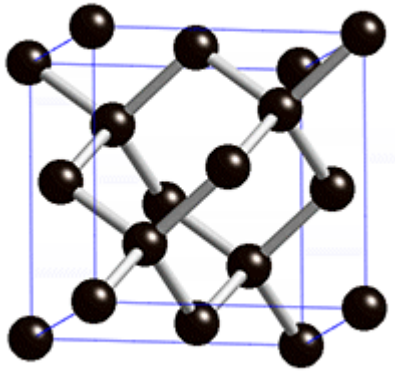
simple
n = 1

body-centered
n = 2

face-centered
n = 4



Salt is FCC with basis containing one Na and one Cl.



Diamond is FCC with two identical basis atoms:

All group IV elements can crystallize into diamond, including *C* and *Si*.

Index system for crystal planes

Crystal planes are identified using Miller indices in the following way:

1. Find the intersection of the axes in terms the basis of the fundamental translation vectors $\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3$.
2. Take the reciprocal and reduce to three integers having the same ratio, usually the smallest three integers. The result is enclosed in parentheses (hkl) and called the index of the plane. Negative integers are denoted with bars $(h\bar{k}l)$.

Also, planes equivalent by symmetry are denoted with braces $\{hkl\}$.

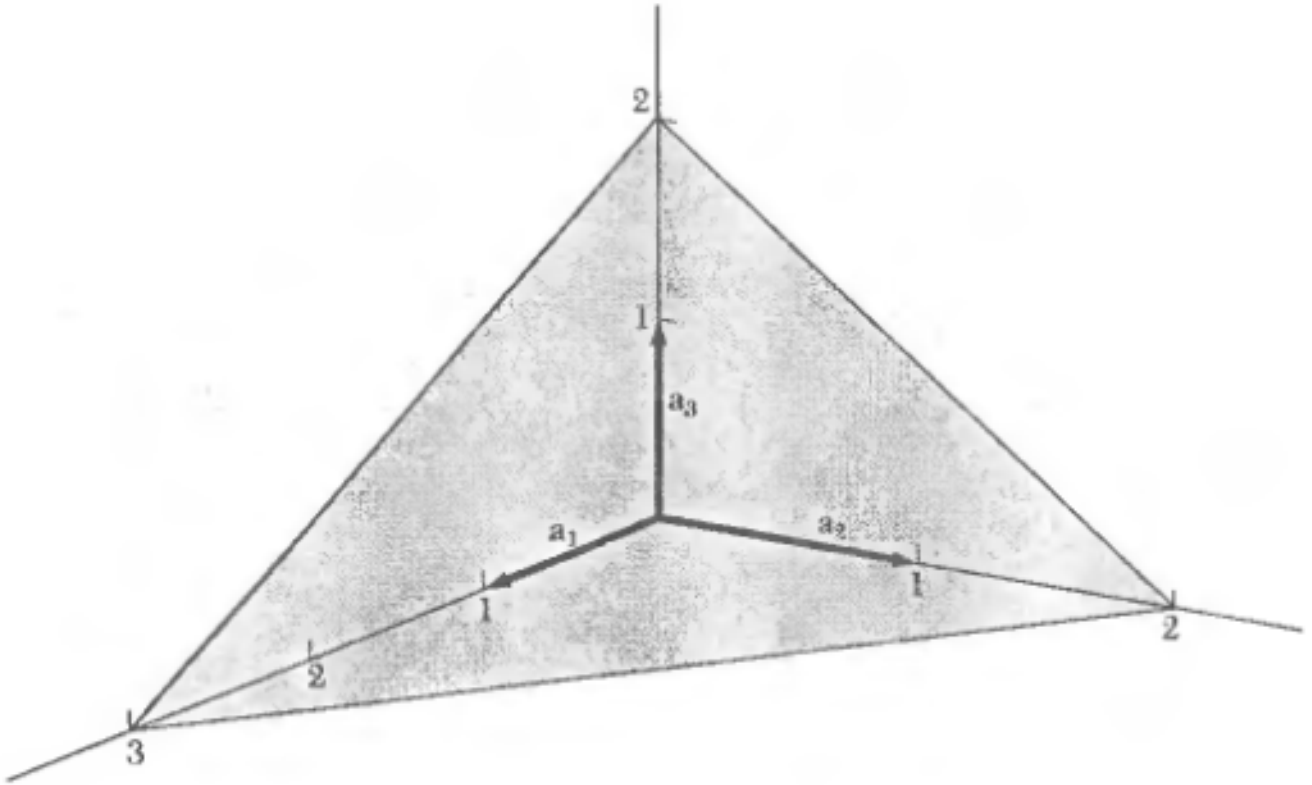
- The set of cube faces is $\{100\}$.

The indices $[uvw]$ of a direction in a crystal are the set of the smallest integers that have the ratio of the components of a vector in the desired direction.

- The $\boldsymbol{a}_1$ axis is the $[100]$ direction, the $-\boldsymbol{a}_2$ axis is the $[0\bar{1}0]$ direction.

- **NB**: In *cubic* crystals, the direction $[hkl]$ is perpendicular to the plane (hkl) having the same indices.

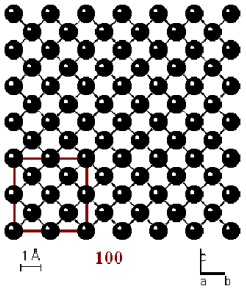
Index system for crystal planes

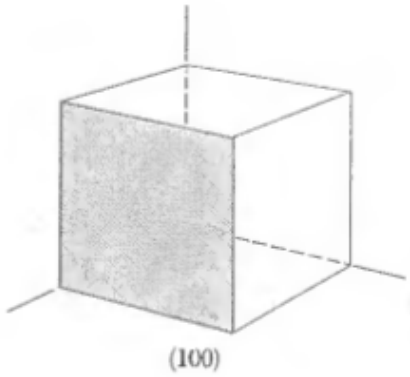


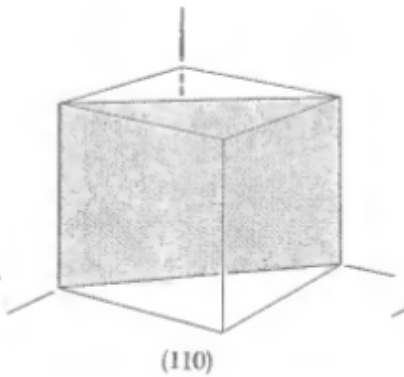
Plane intercepts the vectors $\boldsymbol{a}_1, \boldsymbol{a}_2, \boldsymbol{a}_3$ axes at $3\boldsymbol{a}_1, 2\boldsymbol{a}_2, 2\boldsymbol{a}_3$. Reciprocals of these numbers are $\frac{1}{3}, \frac{1}{2}, \frac{1}{2}$. Small integers having the same ratio are $2, 3, 3$, thus indices of the plane are (233).

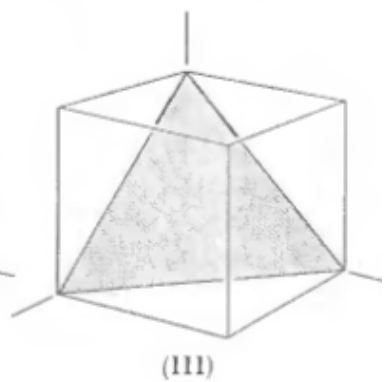
Examples of indexed crystal planes

Si (100)

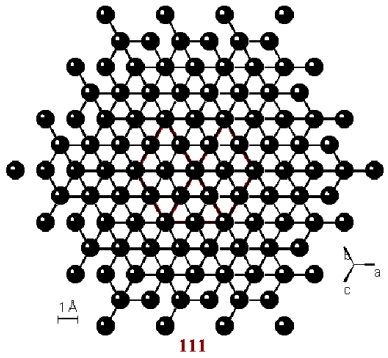


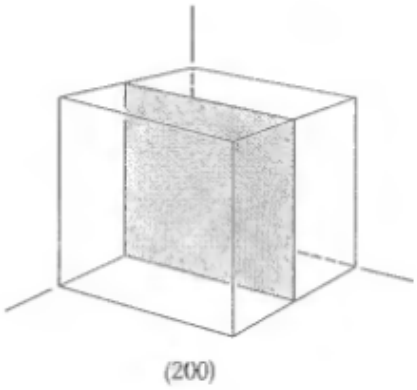


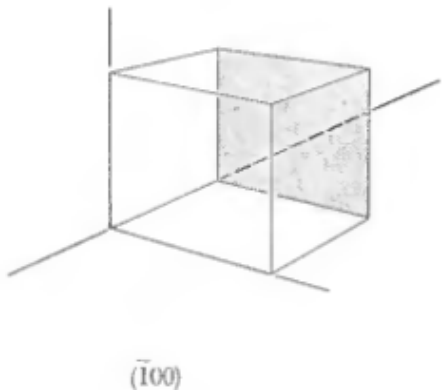




Si (111)







Crystal Growth: Silicon and Gallium Arsenide

Advantages of Si	Advantages of GaAs
• Cheaper • More stable and less defects, better for VLSI • Bigger wafers • SiO_2 • Pure element, easier to make • Higher hole mobility (for CMOS)	• Higher electron mobility • Higher saturation velocity • Good for MW electronics (250GHz) • Direct Band Gap: emits and absorbs efficiently; for LEDs, Lasers, and PVs • Can make AlxGa1-xAs which allow HEMTs.

- How we make single-crystal Si and GaAs?
- How we shape into wafers?
- Characteristics of wafers?

Manufacture of single-crystal Silicon requires high purity raw Silicon, made by the *Siemens Process*

Quarzite

+

Carbon

$$SiC\ (solid) + SiO_2\ (solid) \rightarrow Si\ (solid) + SiO\ (gas) + CO\ (gas)$$

98% pure MGS, which is then pulverized

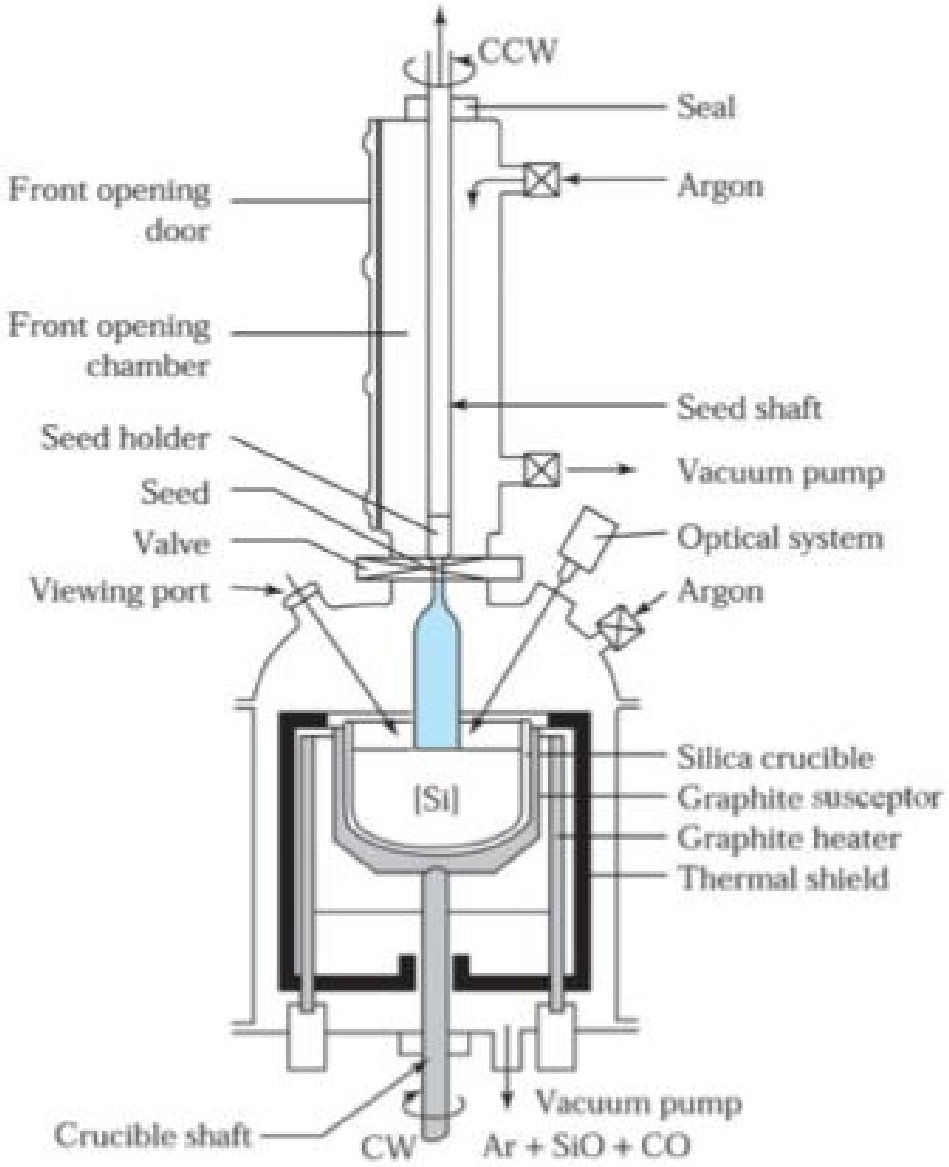
$$Si\ (solid) + 3HCl\ (gas) \xrightarrow{300^{o}C} SiHCl_3\ (gas) + H_2\ (gas)$$

Forms trichlorsilane (boils at 32 C), which is then distilled for hydrogen reduction

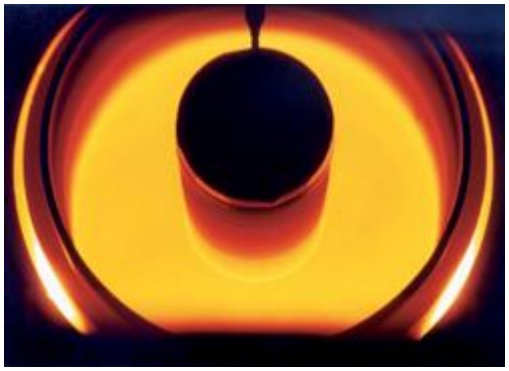
$$SiHCl_3\ (gas) + H_2\ (gas) \rightarrow Si\ (solid) + 3HCl\ (gas)$$

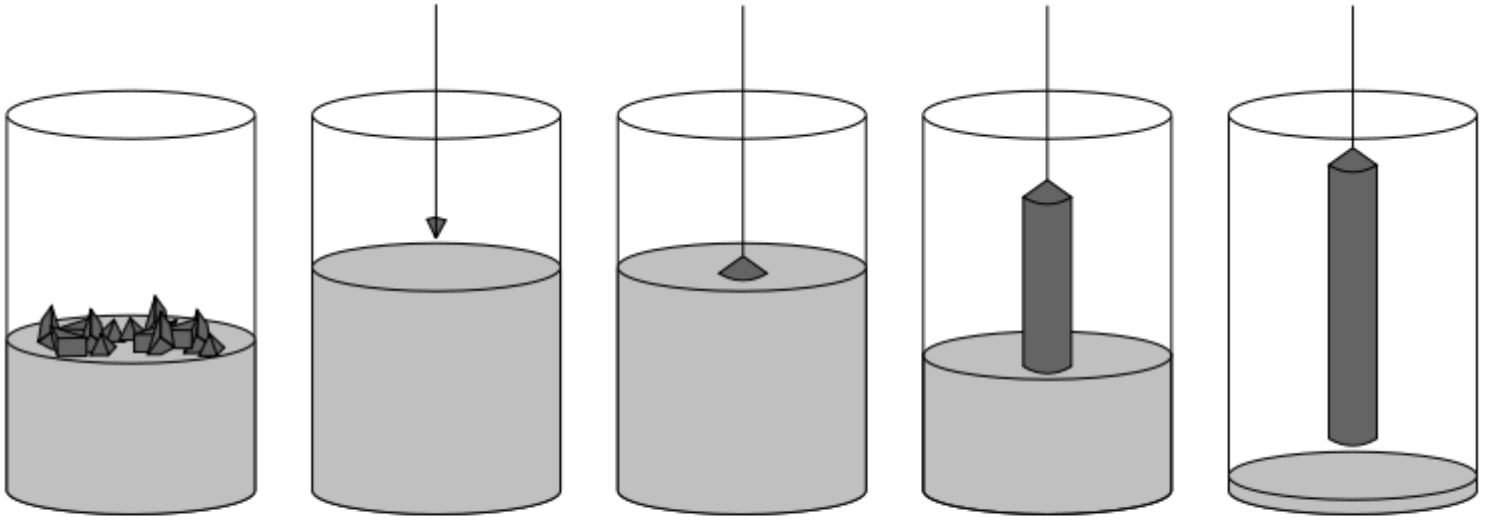
Produces very pure polycrystalline EGS on a heated Si rod in chamber.
Impurity range is in parts-per-billion (ppb).

The Czochralski (CZ) technique: the crystal puller



The CZ technique in pictures





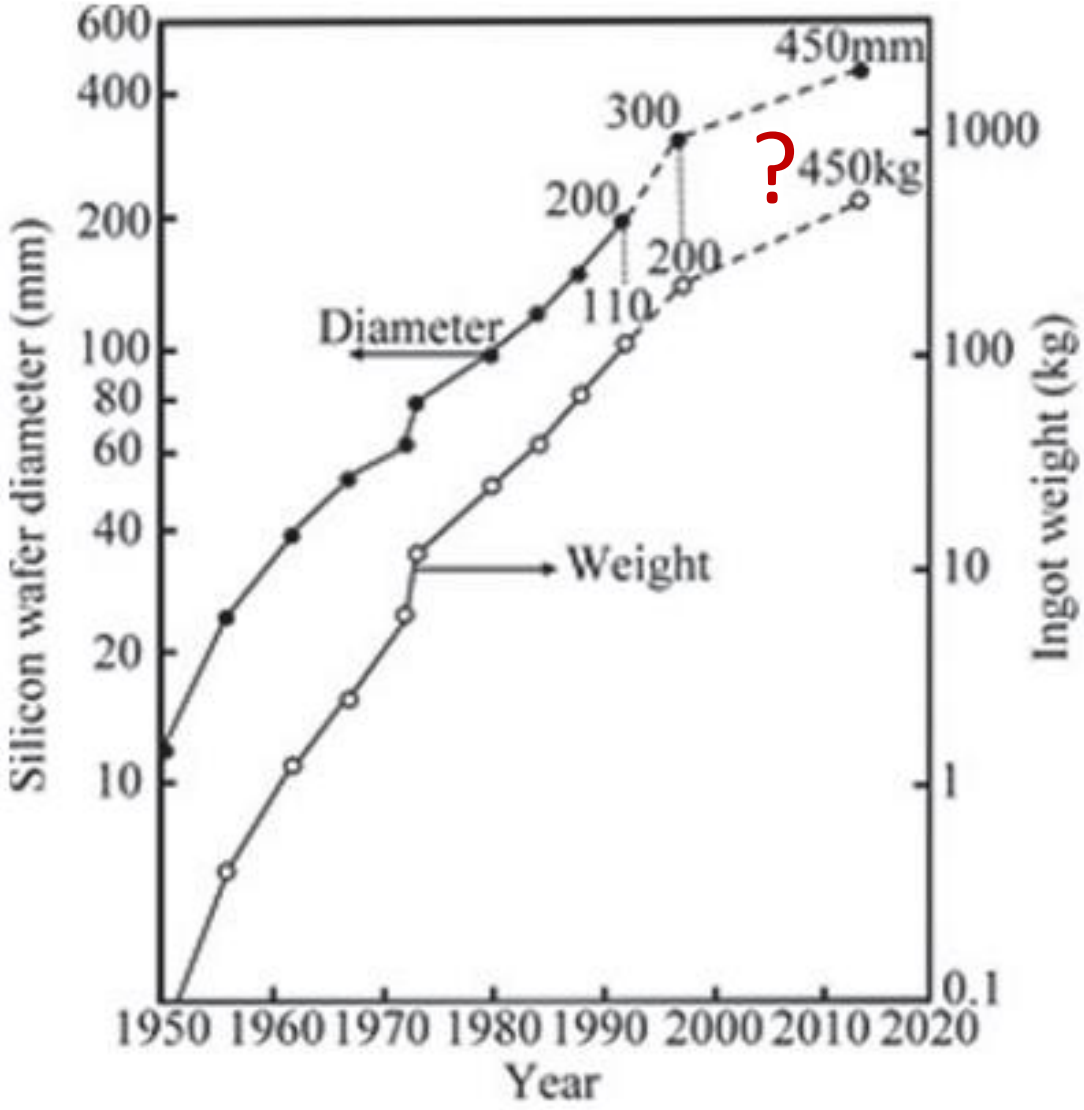
1412° C
Dopants
(*e.g.* B)

[111] or [100]

Molten Si freezes onto Si seed.

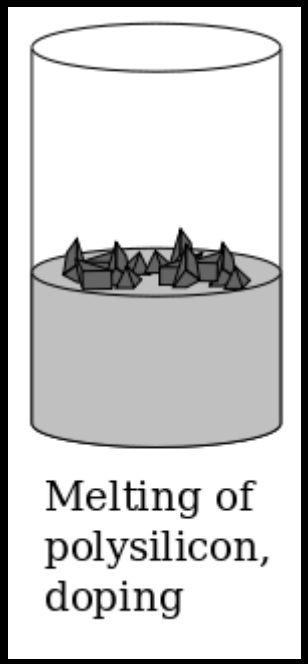
Si ingots are 200 kg in mass and 300 mm in diameter

Wafer size projections

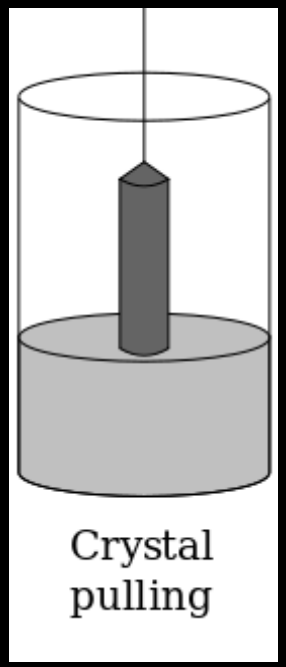


The bigger, the cheaper?

How is do we dope Silicon?



Melting of polysilicon, doping



Crystal pulling

Doping profiles of Silicon ingots

The concentration of dopant in liquid and solid phases of Si is not the same and changes during growth.

The *equilibrium segregation coefficient*:

$$k_0 = \mathrm{C_s}/\mathrm{C_l}$$

Equilibrium concentrations

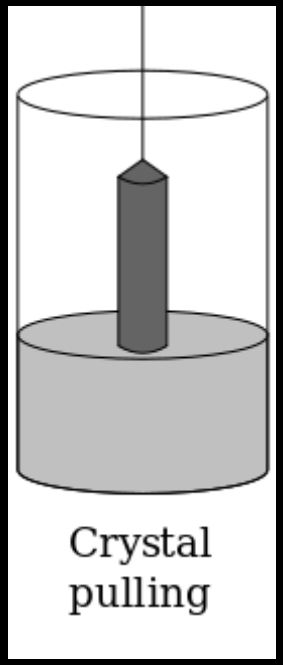
TABLE 1 EQUILIBRIUM SEGREGATION COEFFICIENTS FOR DOPANTS IN SI

Dopant	k_0	Type	Dopant	k_0	Type
B	8×10^{-1}	p	As	3.0×10^{-1}	n
Al	2×10^{-3}	p	Sb	2.3×10^{-2}	n
Ga	8×10^{-3}	p	Te	2.0×10^{-4}	n
In	4×10^{-4}	p	Li	1.0×10^{-2}	n
O	1.25	n	Cu	4.0×10^{-4}	—[a]
C	7×10^{-2}	n	Au	2.5×10^{-5}	—[a]
P	0.35	n			

[a]Deep-lying impurity level.

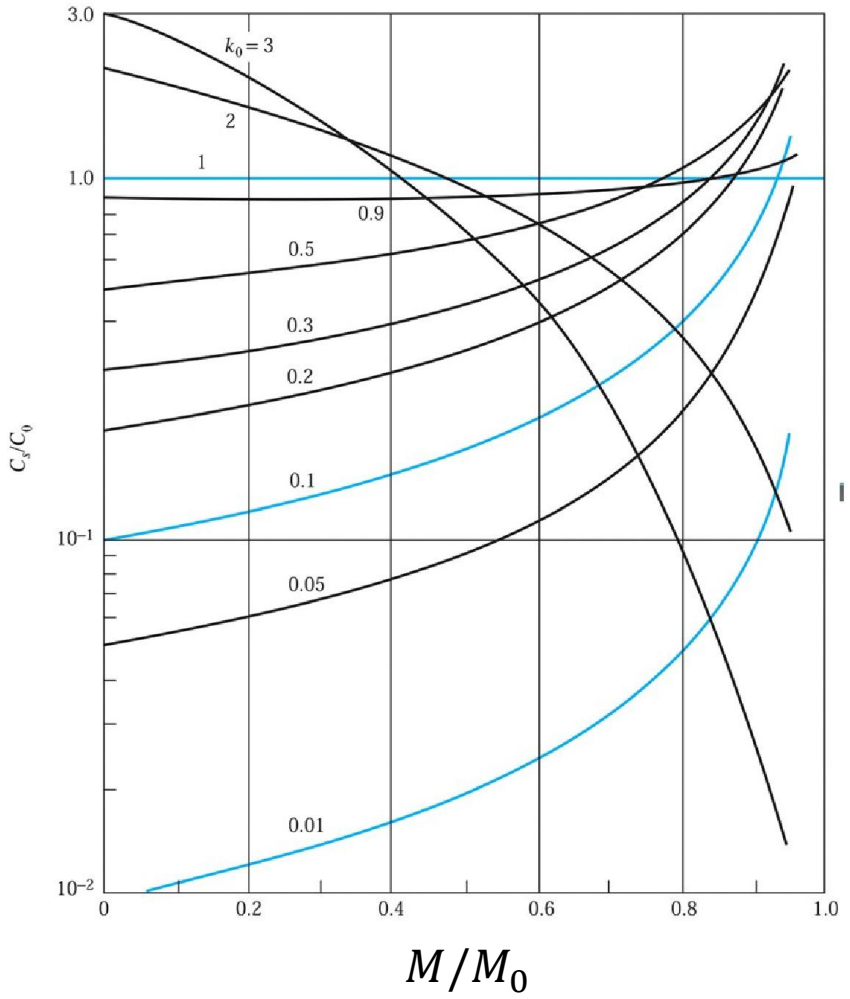
$k_0 < 1$ means dopants are rejected by solid Si into the melt, so concentration in melt increases during growth. Also, if C_l increase, then C_s will too.

How does an increasing/decreasing dopant concentration in the liquid (C_l) affect the dopant concentration (C_s) in a growing Si crystal?



Doping distribution of Silicon ingots during growth

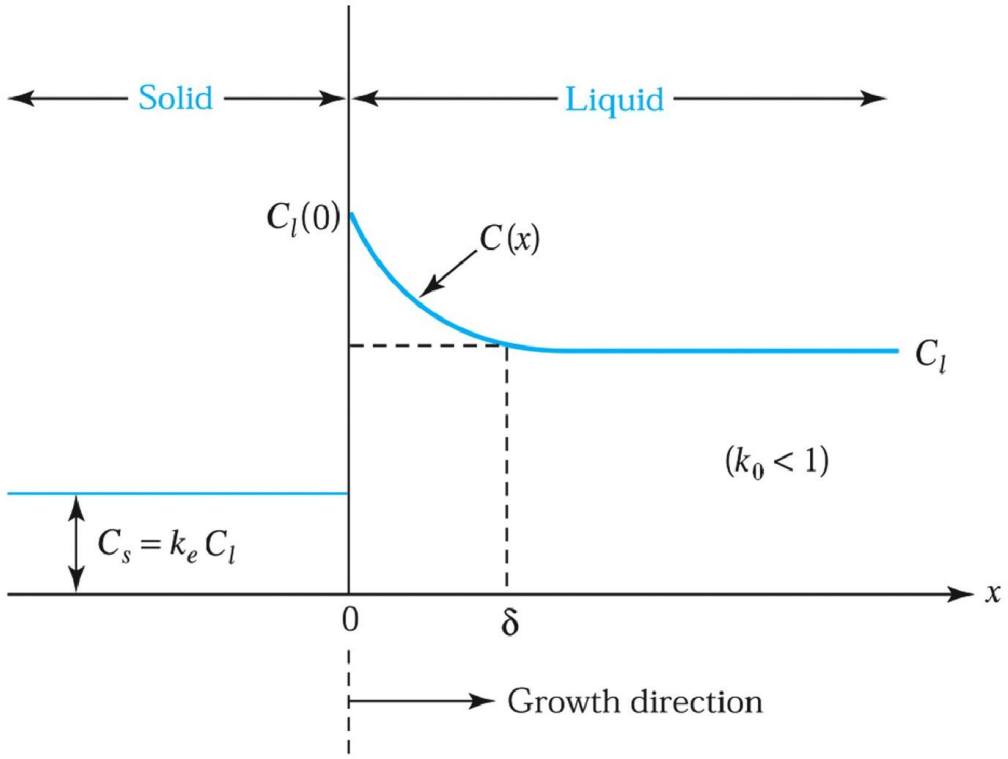
$$C_s = k_0 C_0 \left(1 - \frac{M}{M_0}\right)^{k_0 - 1}.$$



- Example

Effective Segregation Coefficient

During crystal growth, the dopant can accumulate near the liquid-solid interface and cause a dopant concentration gradient ($k_0 < 1$):



How can we model the system to account for the stagnant layer?

Mass transport by diffusion and drift