微纳光电子材料与器件工艺原理

Doping 掺杂

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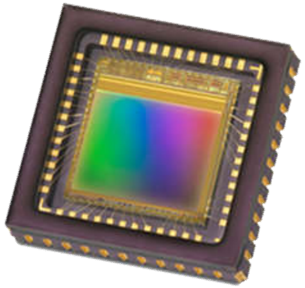
Semiconductor PN Junctions

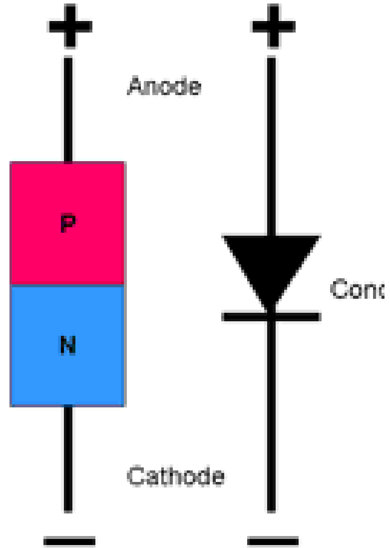
LEDs

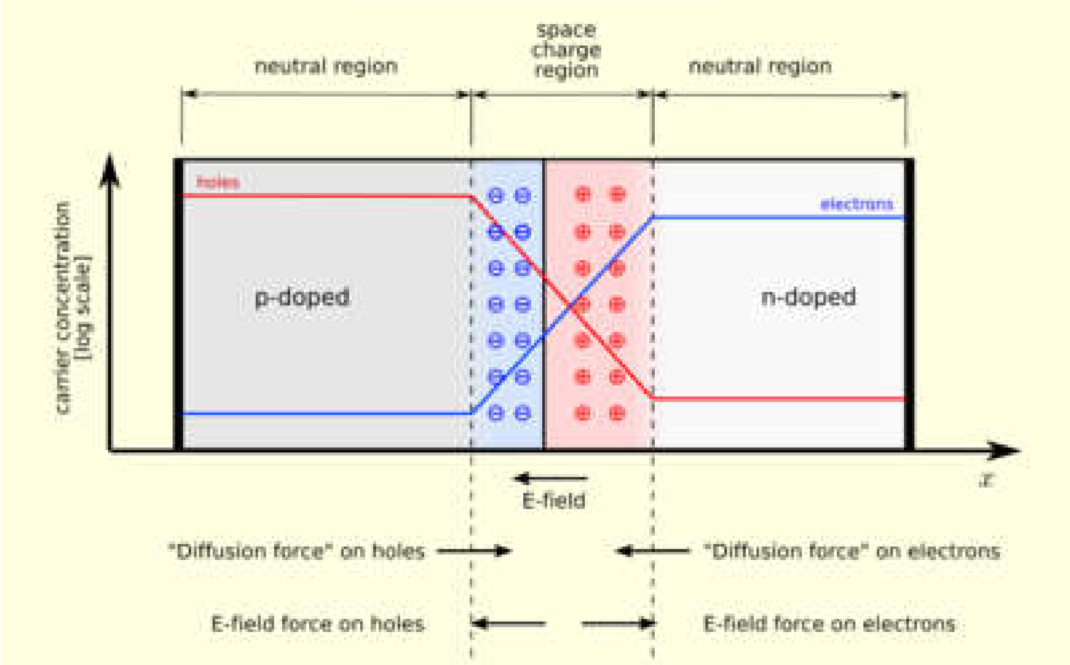
lasers



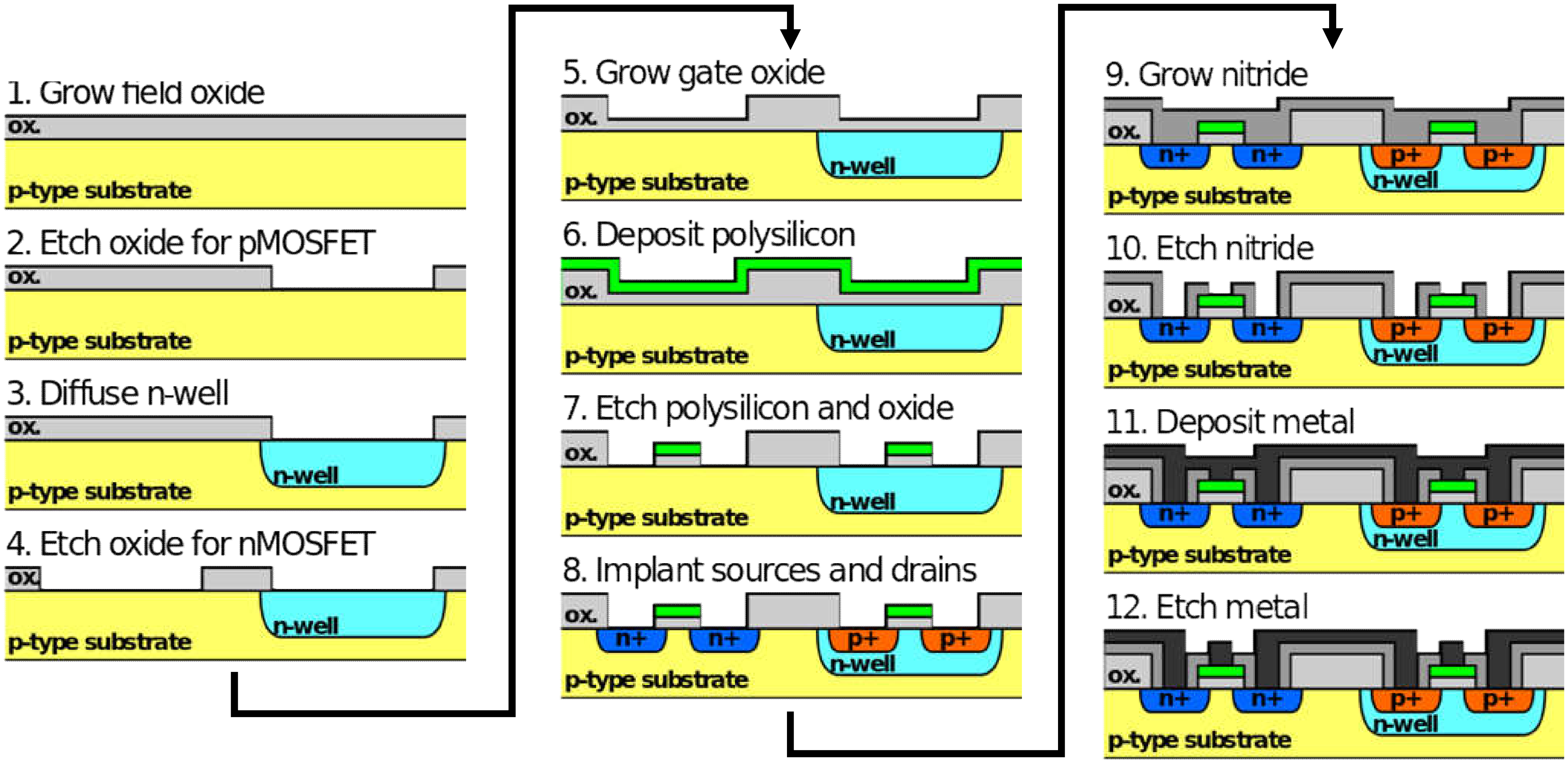
detectors

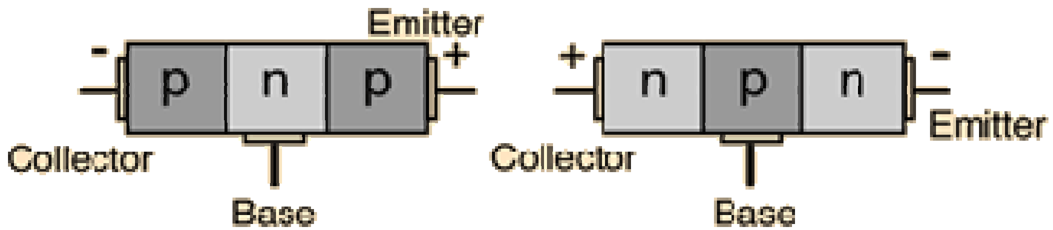
solar cells



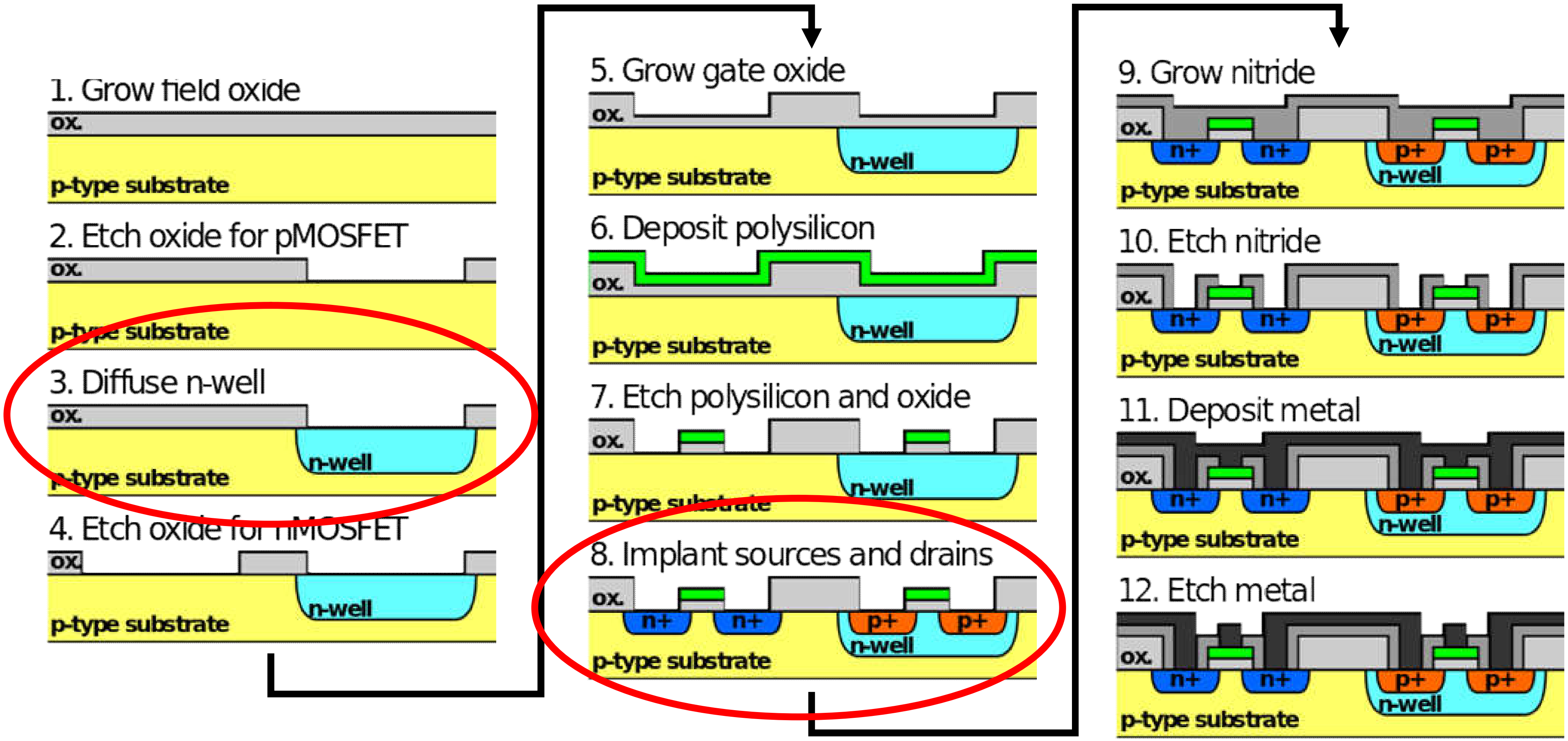


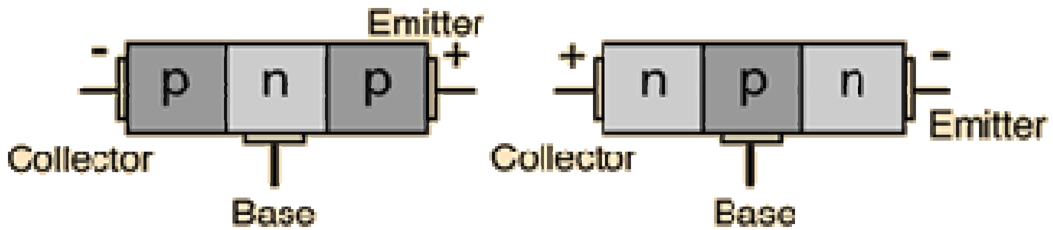
CMOS Transistors





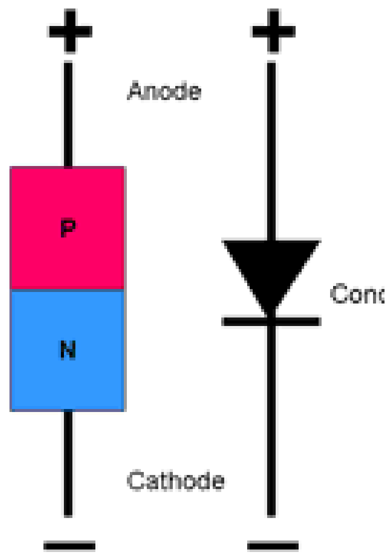
CMOS Transistors

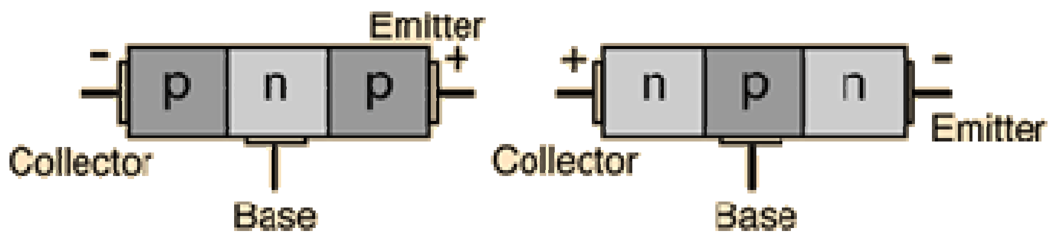




Doping

ingots and wafers





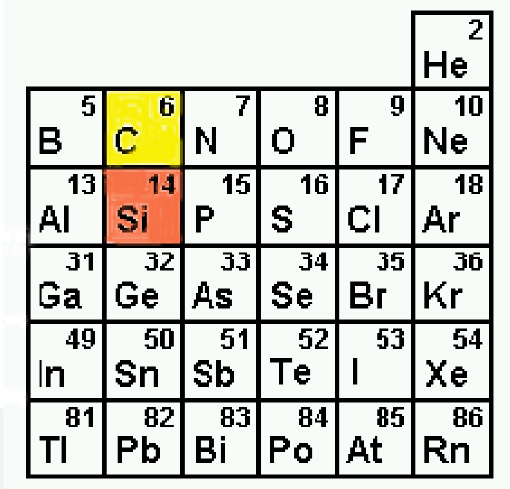
Doping in Silicon

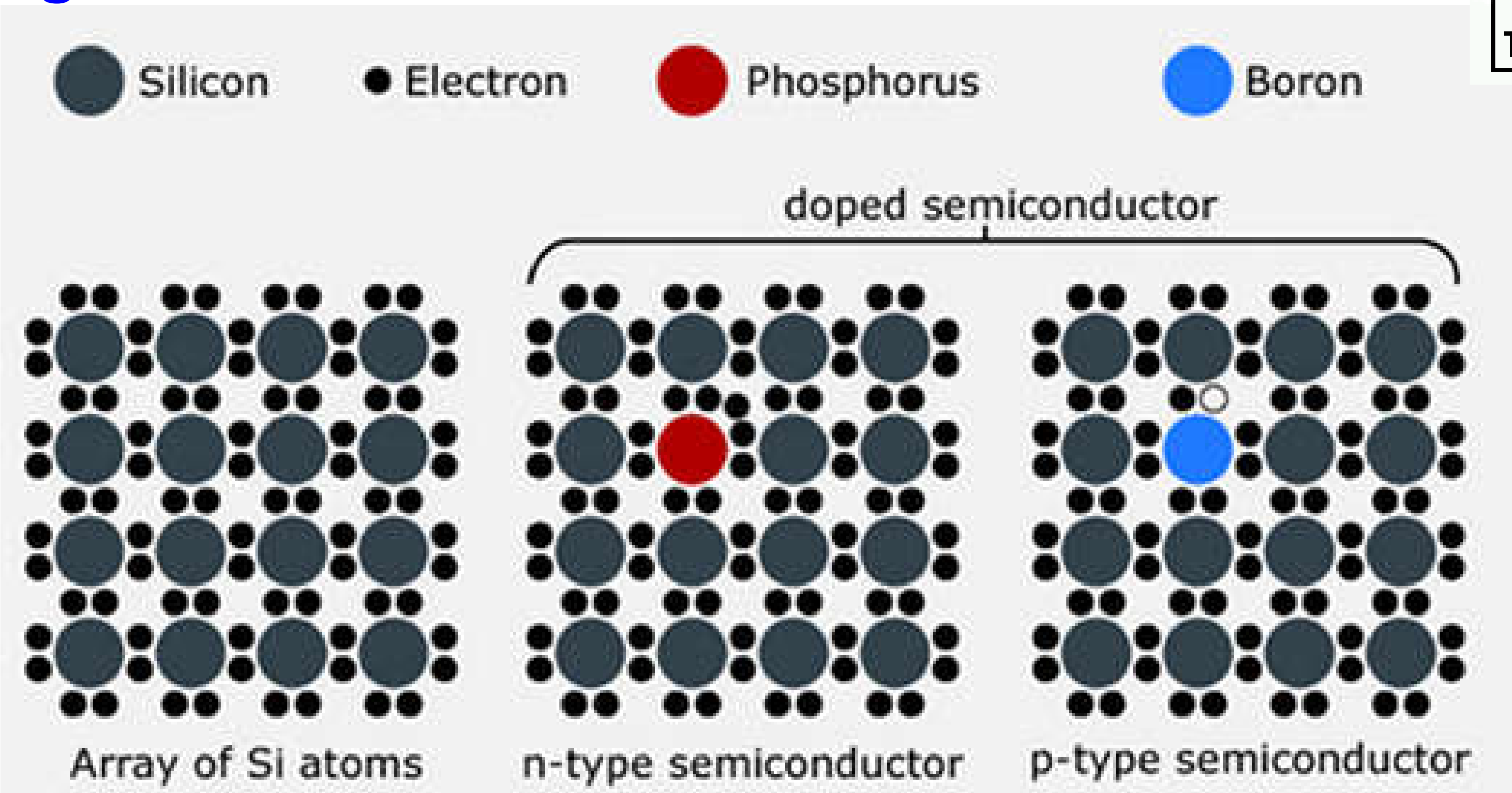
For silicon:

p dopant: **B, Al, Ga, ...**

n dopant: **P, As, Sb, ...**

germanium is similar to Si.





Doping in Silicon

For silicon:

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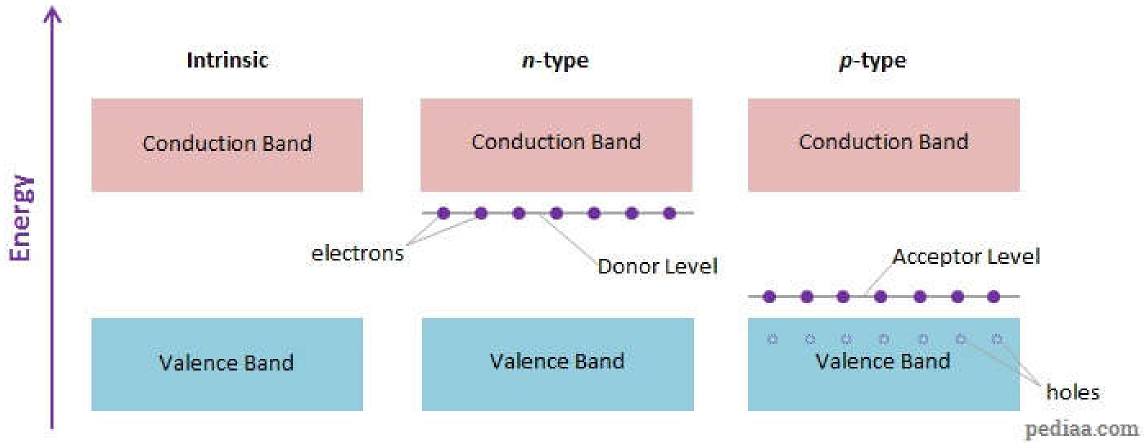
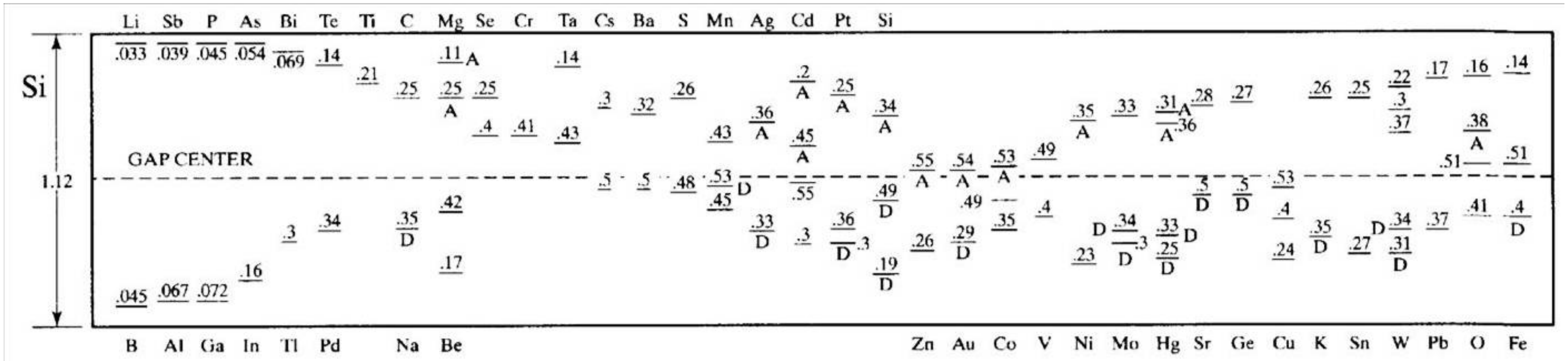
n dopant: P, As, Sb, ...





Doping in GaAs

For GaAs:

p dopant:

replace Ga: Mg, Zn, Be

replace As: C

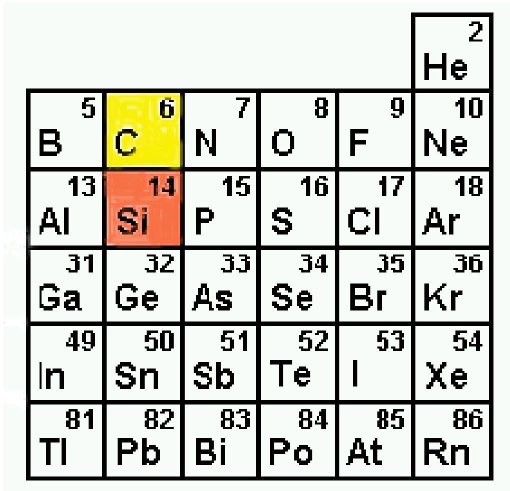
...

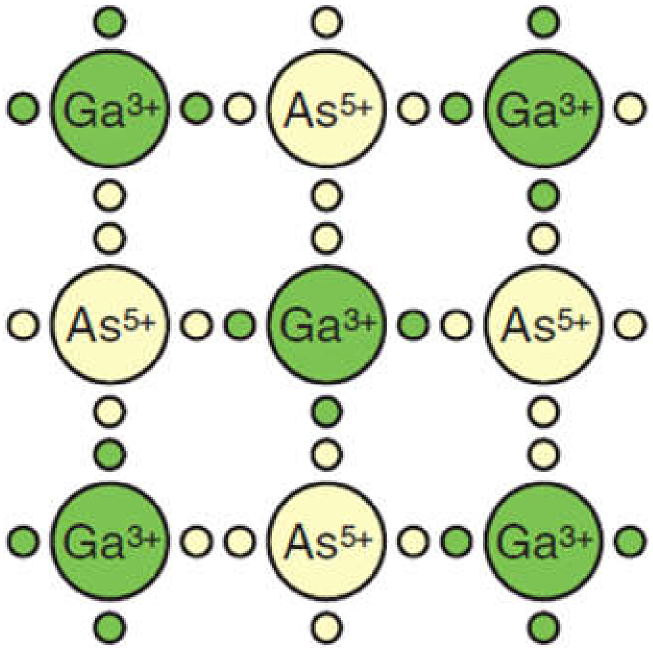
n dopant:

replace As: Se

replace Ga: Si, Ge

...





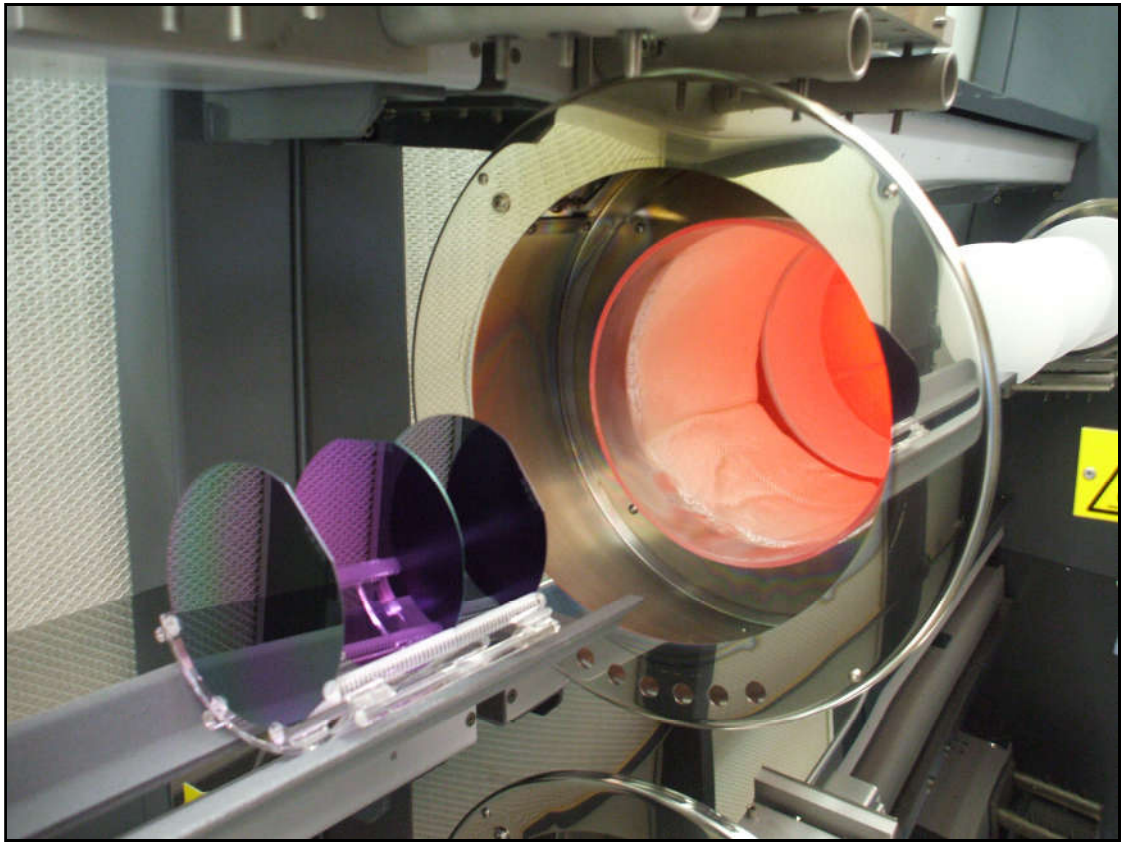
Doping Methods

- Thermal diffusion
- Ion implantation
- In situ growth

Thermal Diffusion - Silicon

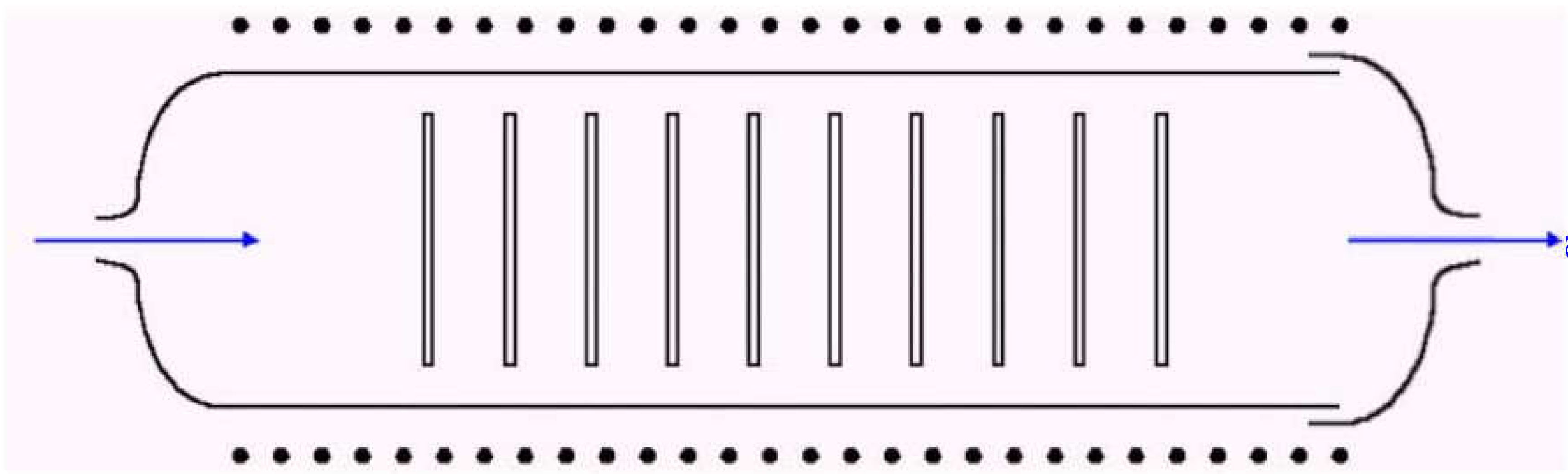
Sources

- **Phosphorus (P)**
  - Liquid - $POCl_3$
  - Gas - PH_3
- **Boron (B)**
  - Liquid - BBr_3
  - Solid - B_2O_3
  - Gas - B_2H_6
- **Arsenic (As)**
  - Solid - As_2O_3
  - Gas - AsH_3



Thermal Diffusion - Silicon

Gas Source Diffusion



$2PH_3\ (g) \rightarrow 2P\ (in\ Si) + 3H_2$

Thermal Diffusion - Silicon

Liquid Source Diffusion

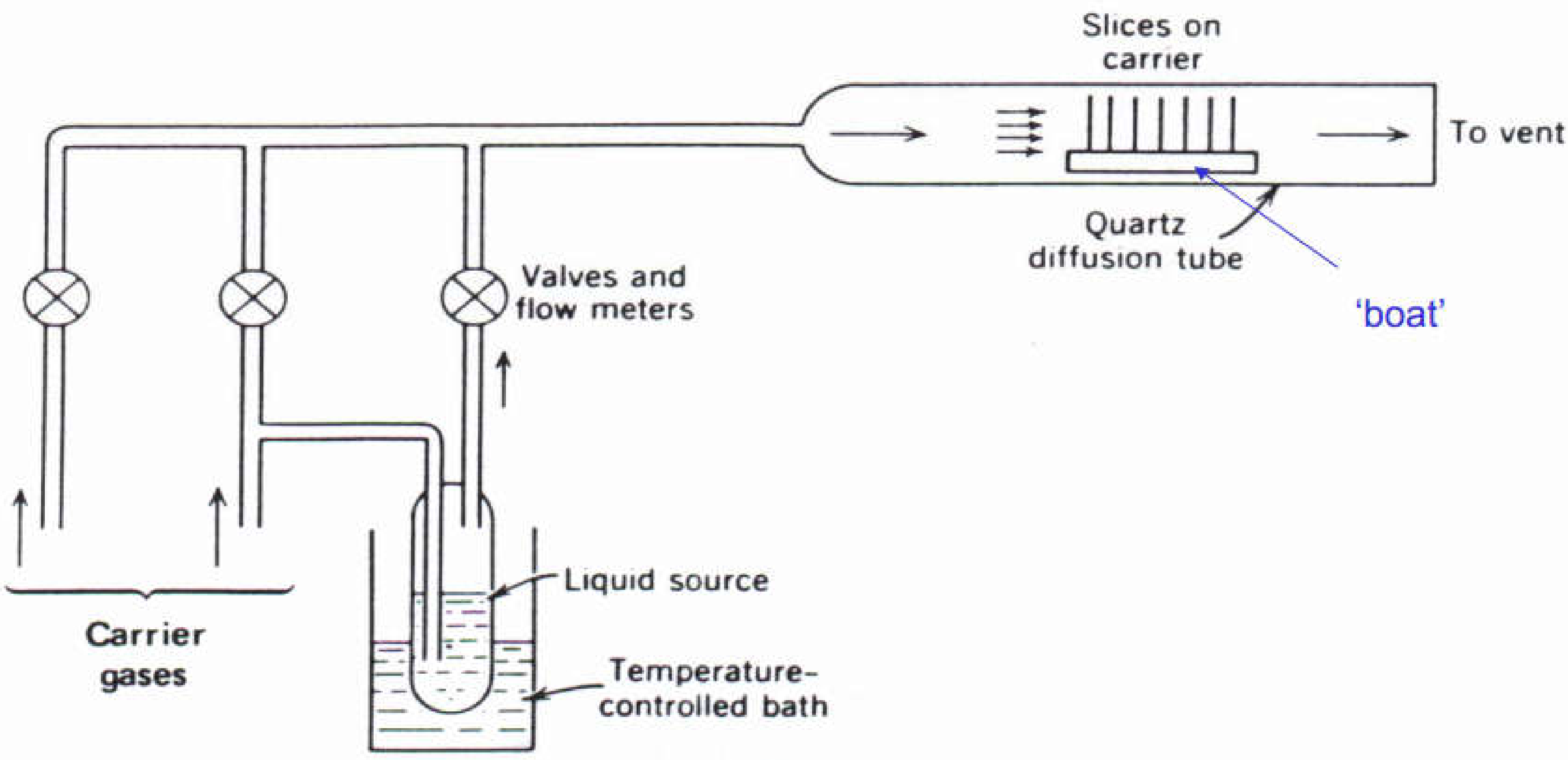


Fig. 4.27 Liquid-source diffusion system.

Thermal Diffusion - Silicon

Solid Source Diffusion

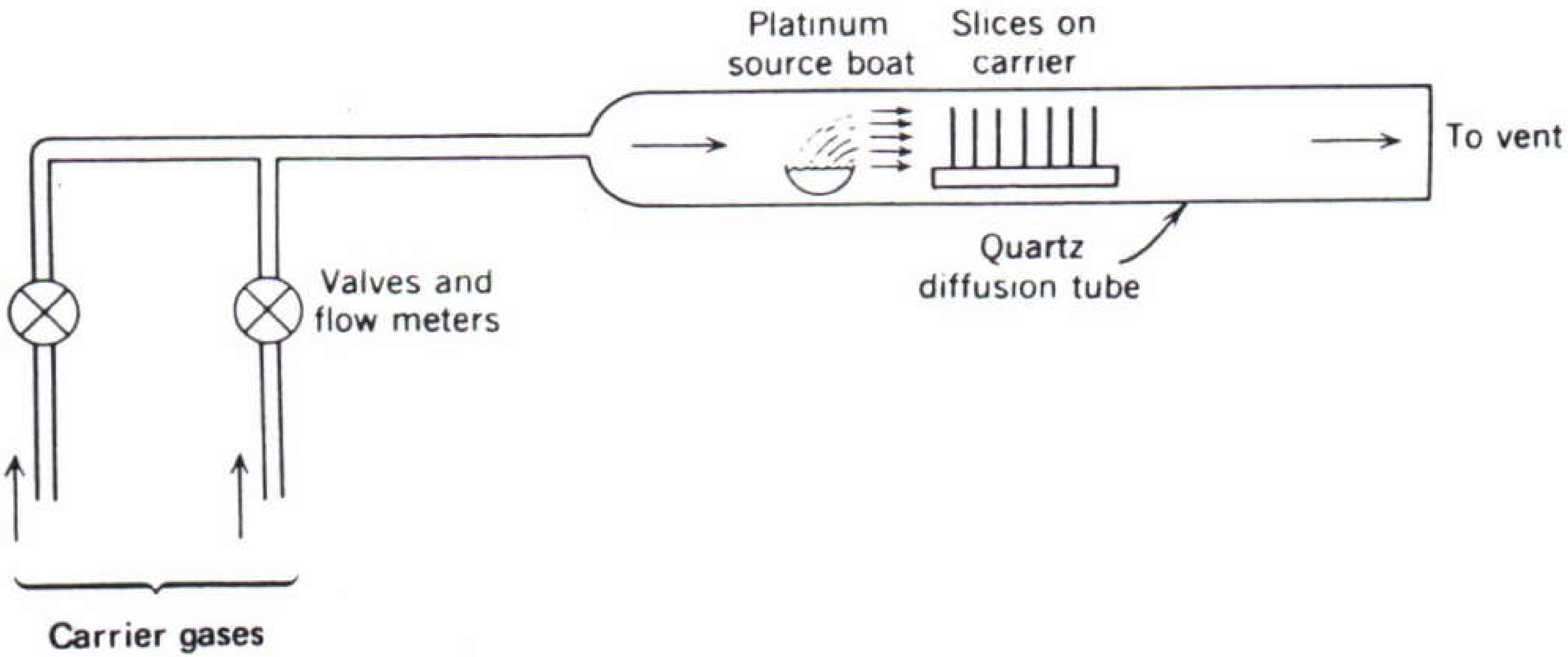
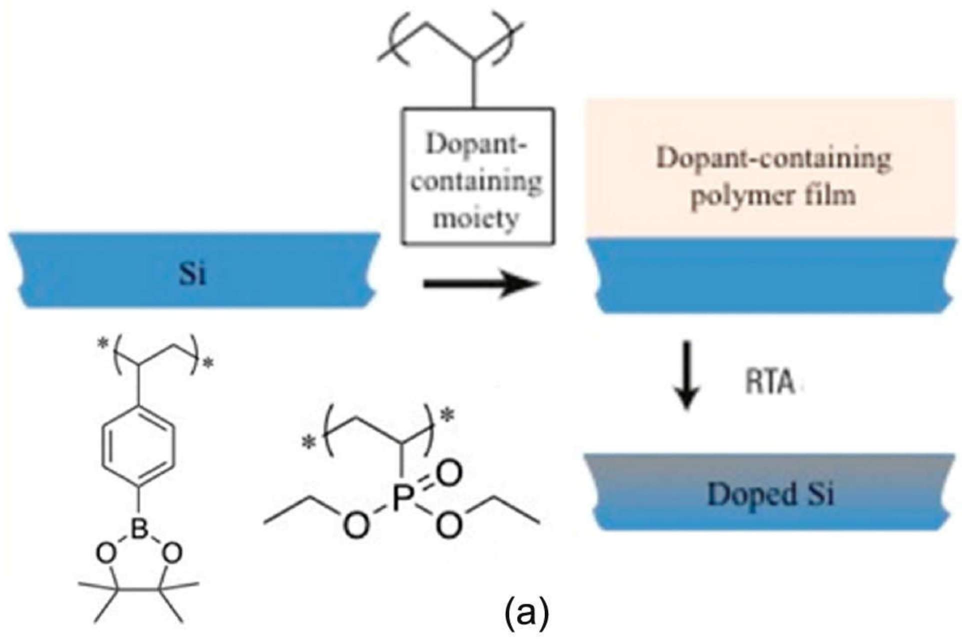
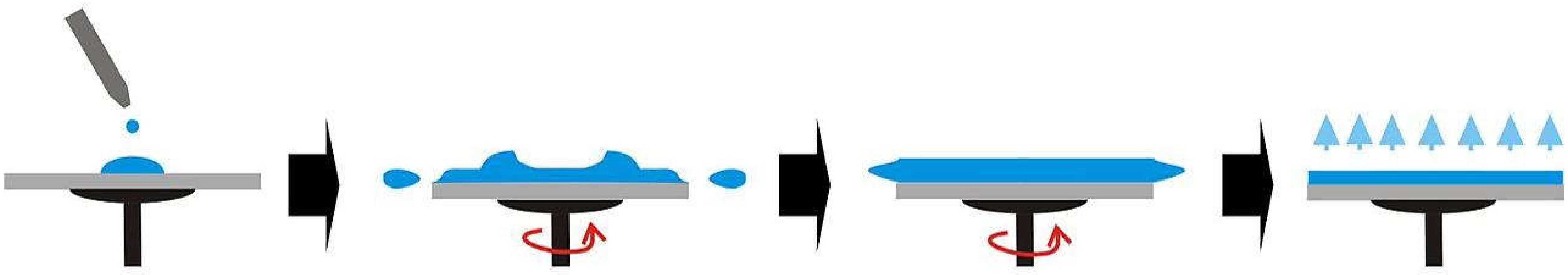


Fig. 4.26 Solid-source diffusion system.

Thermal Diffusion - Silicon

Spin-on doping

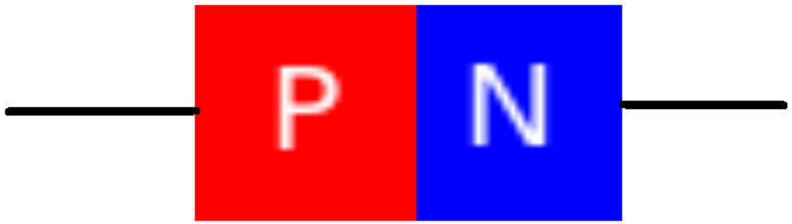


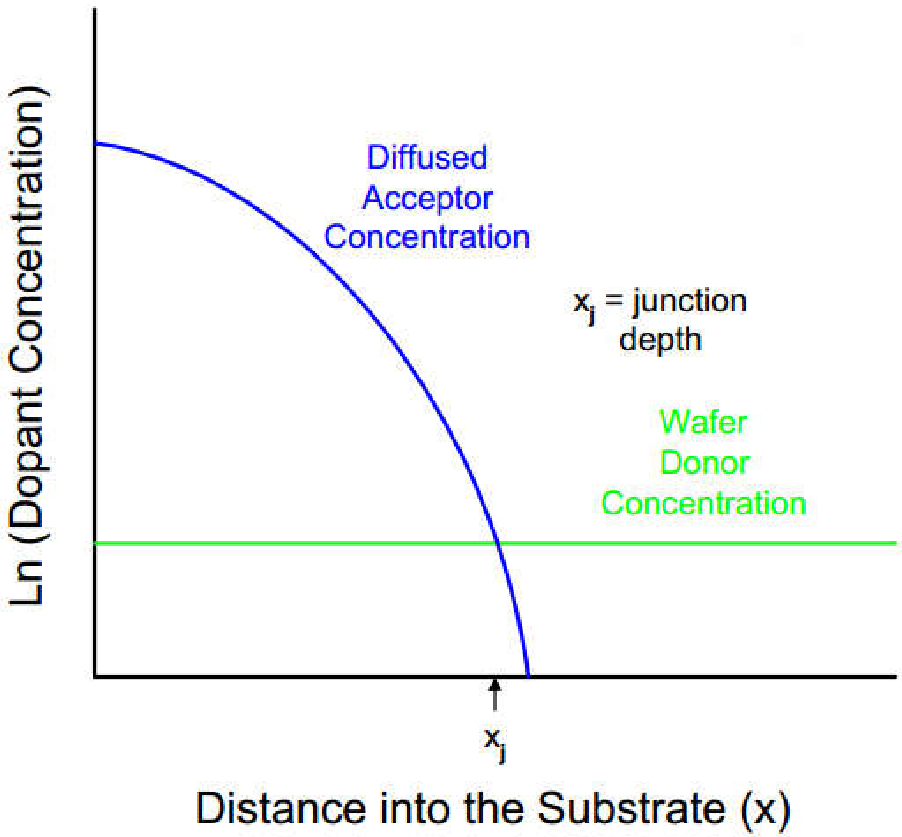


Thermal Diffusion

- **Process Parameters**
  - **Time**
  - **Temperature**
  - **Gas pressure**
  - **Gas flow rate**

- **Control Parameters**
  - **Junction depth**
  - **Doping concentration**
  - **Doping profile**

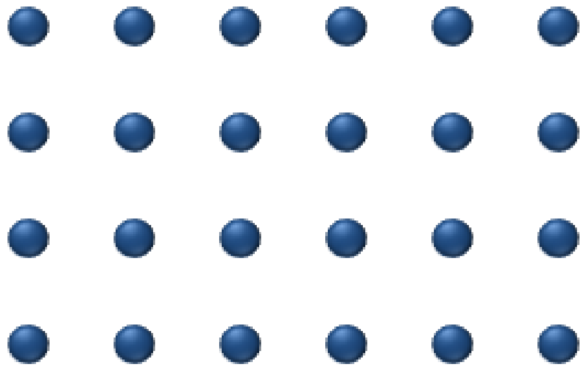




Diffusion Law

Liquid

Solid



C **concentration (mol/m^3)**

J **diffusion flux (mol/m^2/s)**

D **diffusivity (m^2/s)**

Diffusion Law

- **Fick's first law**

1D $$J = -D\frac{\partial C}{\partial x}$$

3D $$\mathbf{J} = -\mathbf{D}\nabla\mathbf{C}$$

- **Fick's second law**

1D $$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

3D $$\frac{\partial \mathbf{C}}{\partial t} = \mathbf{D}\nabla^2\mathbf{C}$$

***J*: mol/m^2/s** **_D_: m^2/s** **_C_: mol/m^3**

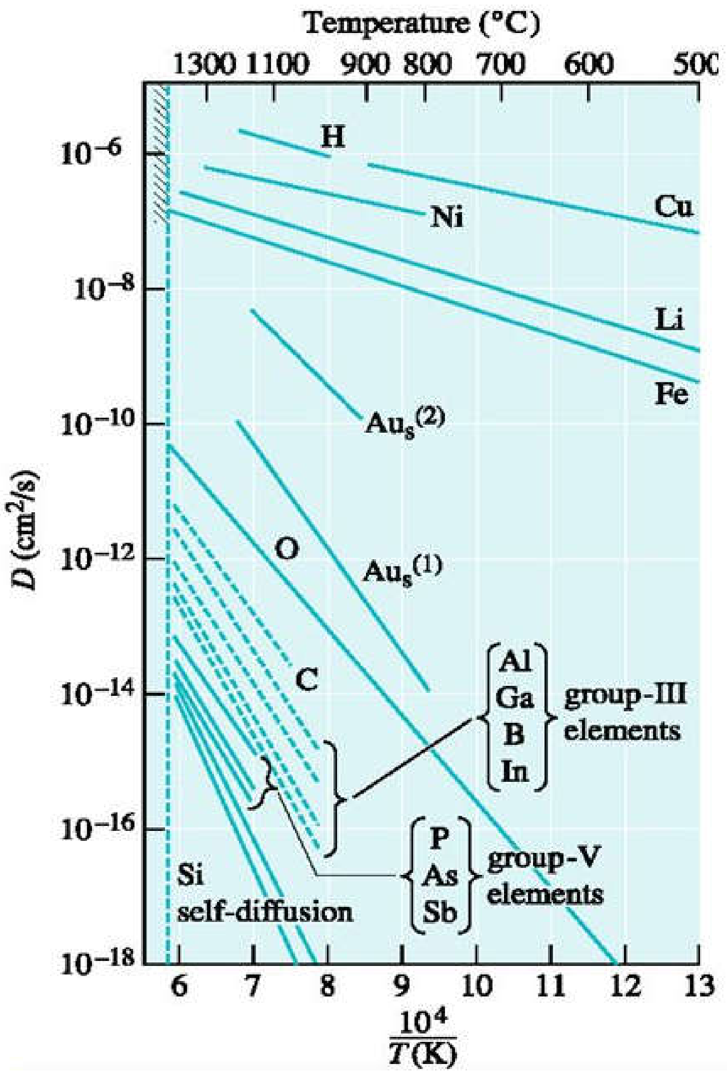
Dopant Diffusivity in Silicon

- **Diffusivity (扩散系数) *D***
  - rate of spread
  - unit: cm^2/s

$$D = D_0 \exp\left(-\frac{E_A}{kT}\right)$$

- **Diffusion length *L***

$$L = \sqrt{Dt}$$

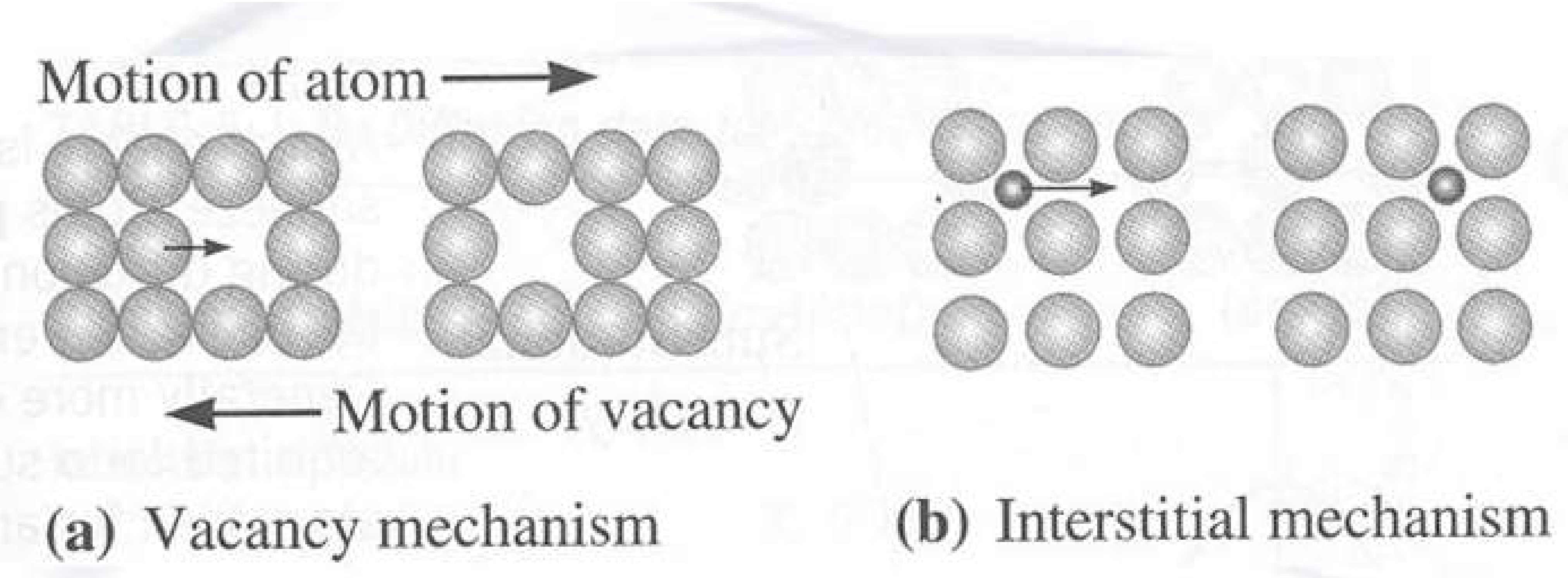


fast

slow

diffusivity of defects in Si

Dopant Diffusivity in Silicon

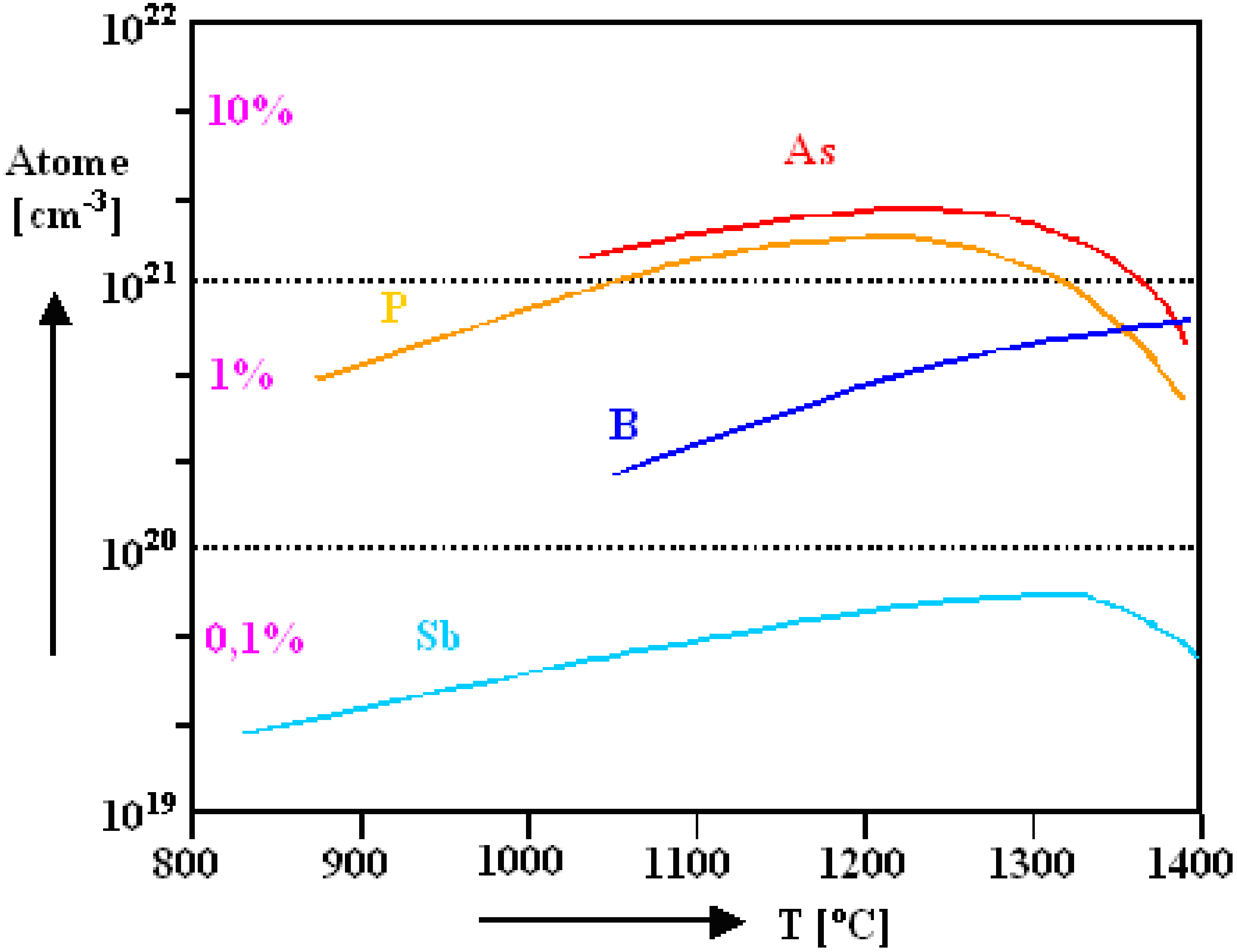


B, P, As, Sb, Si, ...

Cu, Fe, Li, H, Au, ...

Dopant Solubility in Silicon

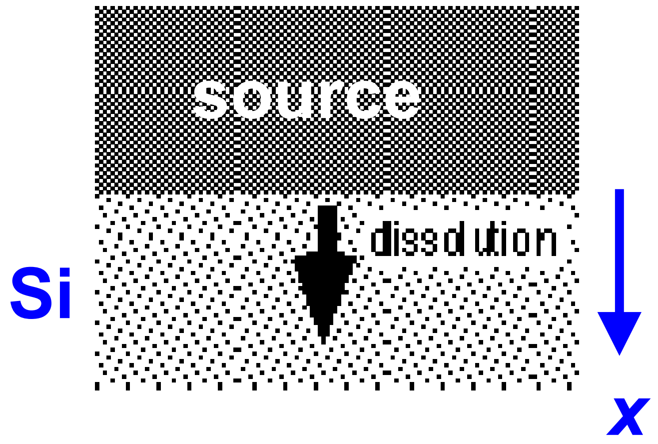
maximum dopant amount in silicon



Dopant Diffusion in Silicon

when the source is semi-infinite,
and the surface is at the solubility limit C_{ss}

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$



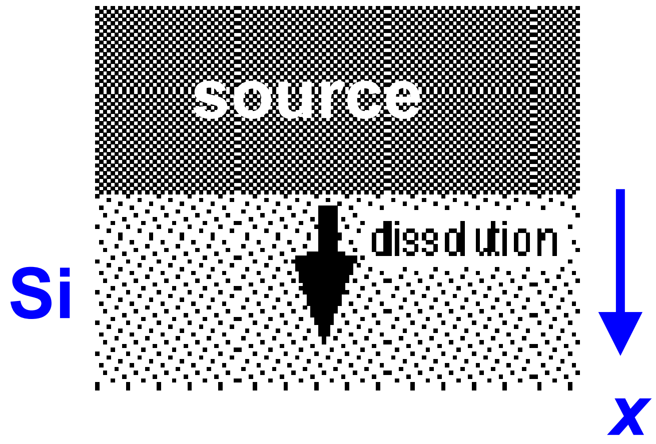
$$\boxed{\begin{aligned} &C(x>0, t=0) = 0 \\ &C(x=+\infty, t>0) = 0 \\ &C(x=0, t>0) = C_{ss} \end{aligned}}$$

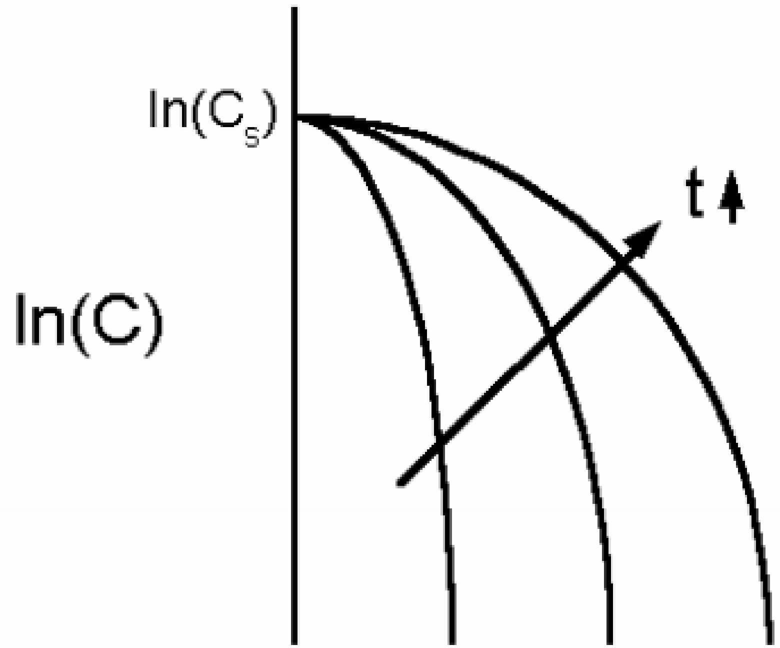
$$\Rightarrow \quad C(x,t) = C_{ss} \cdot \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Error Function

Dopant Diffusion in Silicon

when the source is semi-infinite,
and the surface is at the solubility limit C_{ss}



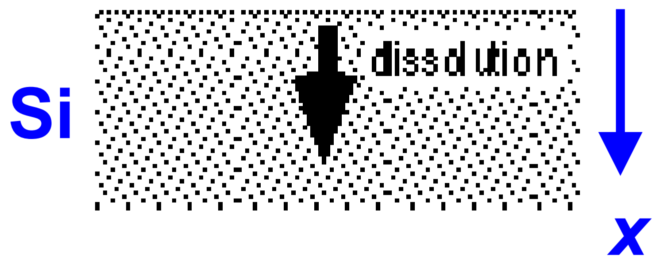


$$C(x,t) = C_{ss} \cdot \mathrm{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Dopant Diffusion in Silicon

when the source is limited,

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$



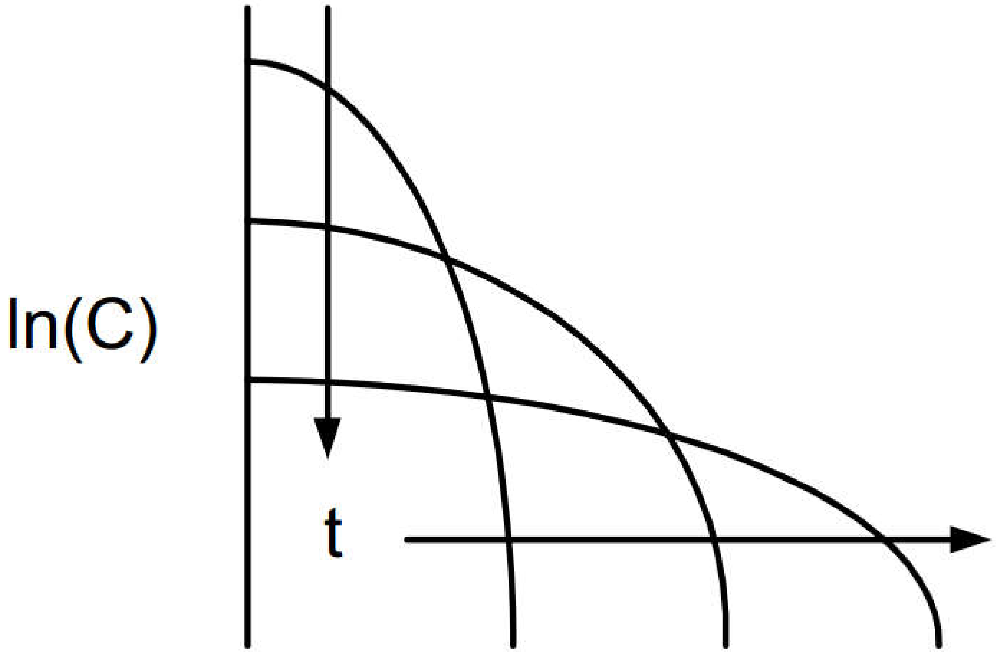
$$\boxed{\begin{aligned} &C(x=0, t=0) = Q \\ &C(x>0, t=0) = 0 \\ &C(x=+\infty, t>0) = 0 \end{aligned}}$$

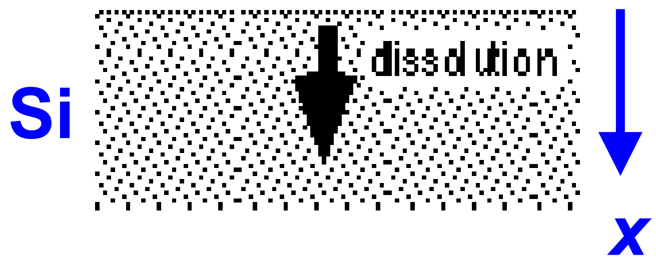
$$\rightarrow C(x,t) = \frac{Q}{\sqrt{\pi D t}} \cdot \exp\left(-\frac{x^2}{4Dt}\right)$$

Gaussian Function

Dopant Diffusion in Silicon

when the source is limited,





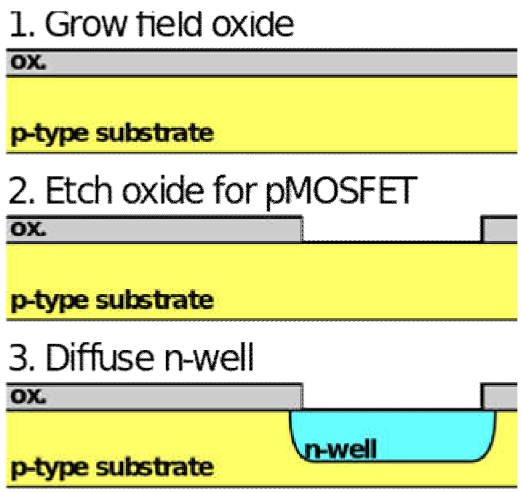
$$C(x,t)=\frac{Q}{\sqrt{\pi Dt}}\cdot\exp\left(-\frac{x^2}{4Dt}\right)$$

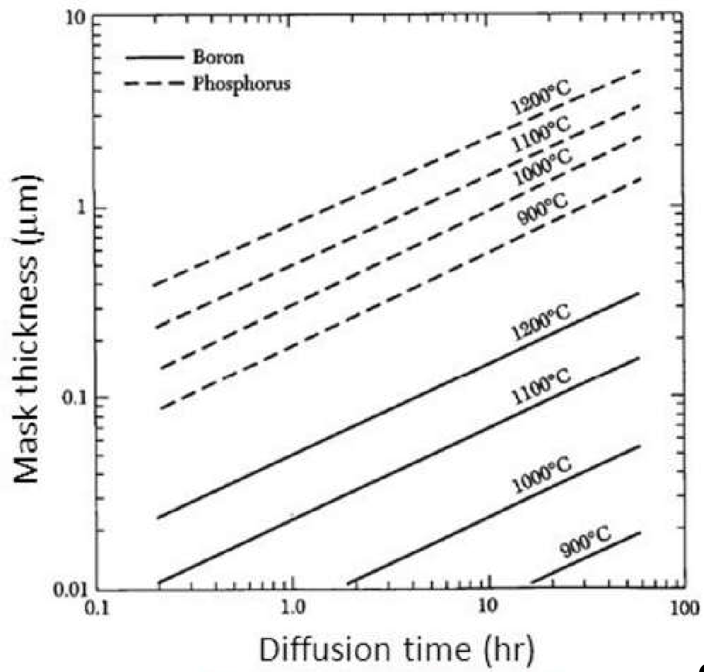
Gaussian Function

Diffusion Masks

SiO_2 can provide a selective mask against diffusion at high temperatures. ($D_{SiO2} << D_{Si}$)
Oxides used for masking are ~0.5-1μm thick.

Dopants	Diffusion Constants at 1100 °C (cm^2/s)
B	$3.4 \times 10^{-17} - 2.0 \times 10^{-14}$
Ga	5.3×10^{-11} (not good for Ga)
P	$2.9 \times 10^{-16} - 2.0 \times 10^{-13}$
As	$1.2 \times 10^{-16} - 3.5 \times 10^{-15}$
Sb	9.9×10^{-17}

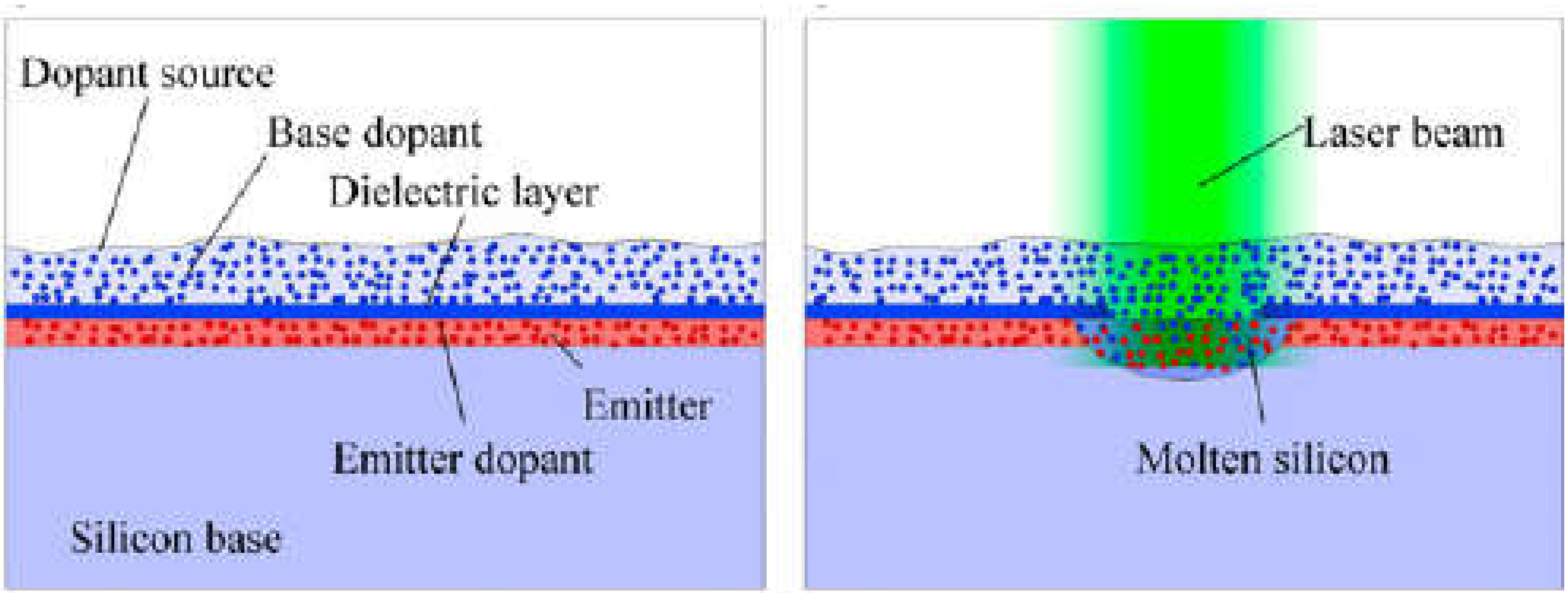




SiO_2 masks for B and P

Q: why not photoresist?

Laser Assisted Annealing

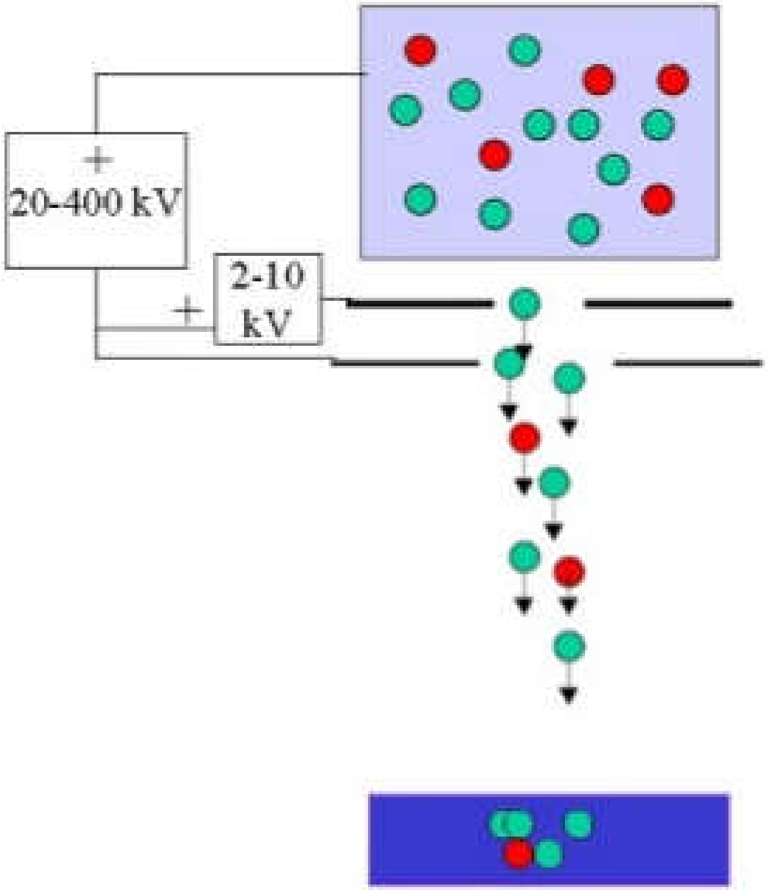


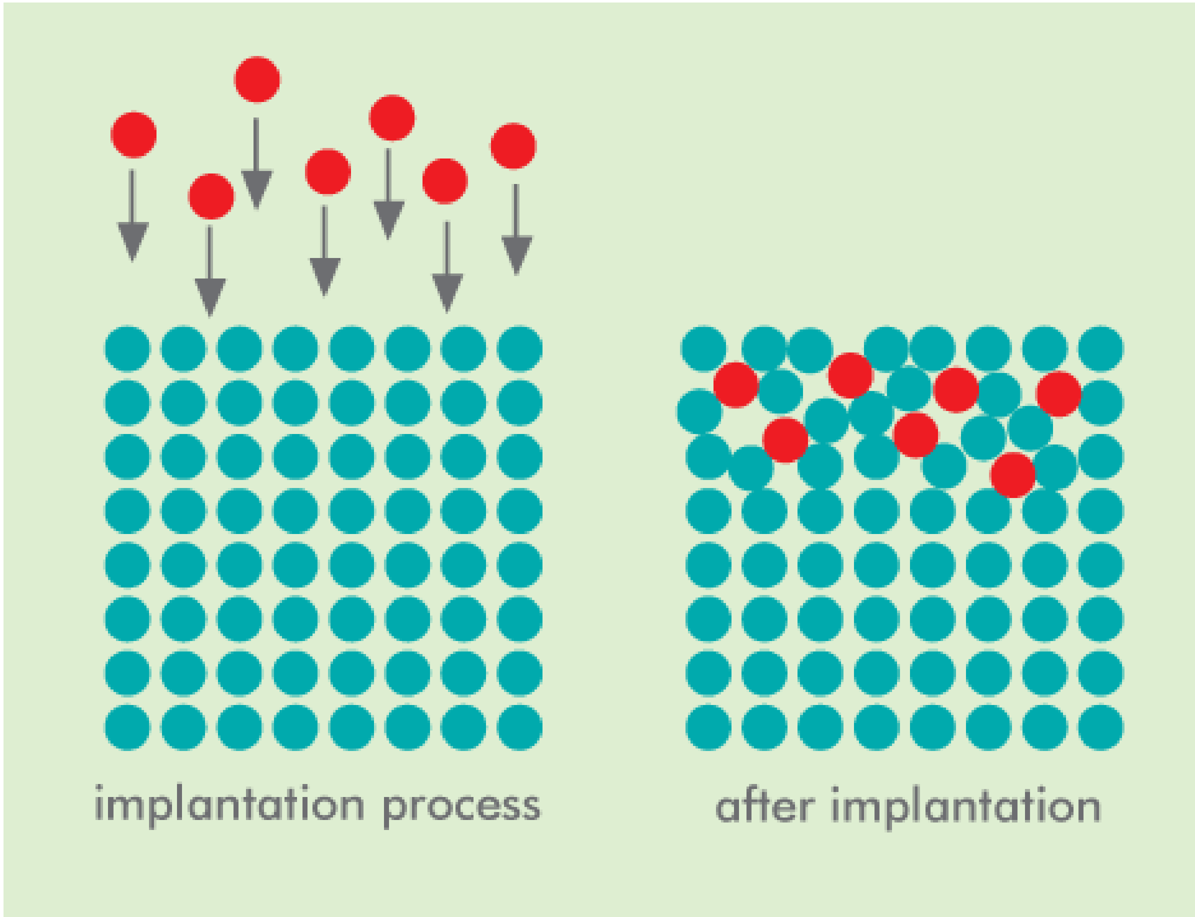
local heating

Doping Methods

- Thermal diffusion
- Ion implantation
- In situ growth

Ion Implantation (离子注入)



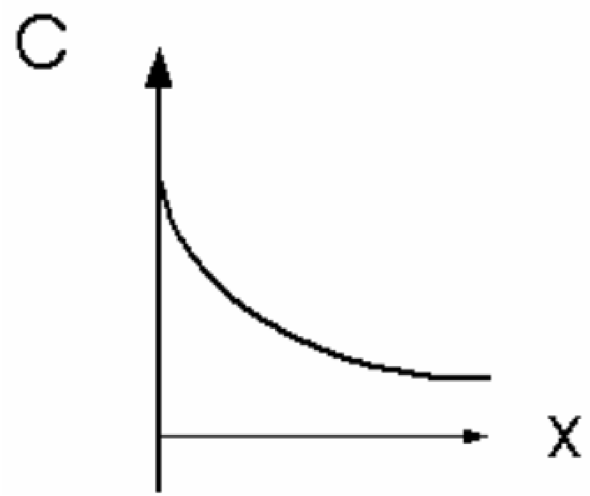


Ion Implantation - Advantages

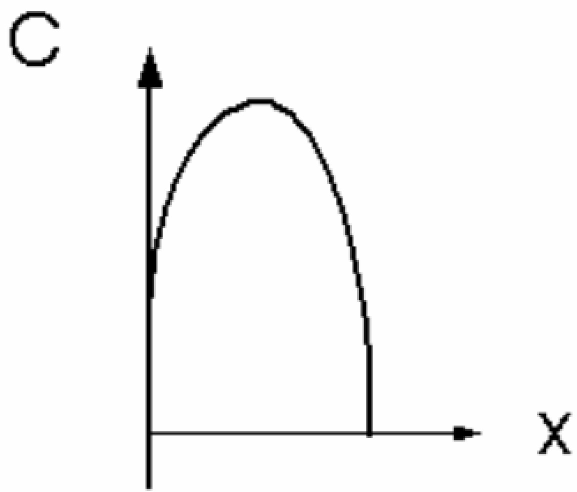
- Precise control of dose, depth and profile
- Low temperature process
- Tailor lateral distribution
- Wide selection of dopants

Ion Implantation - Advantages

- **Precise control of dose, depth and profile**



vs.

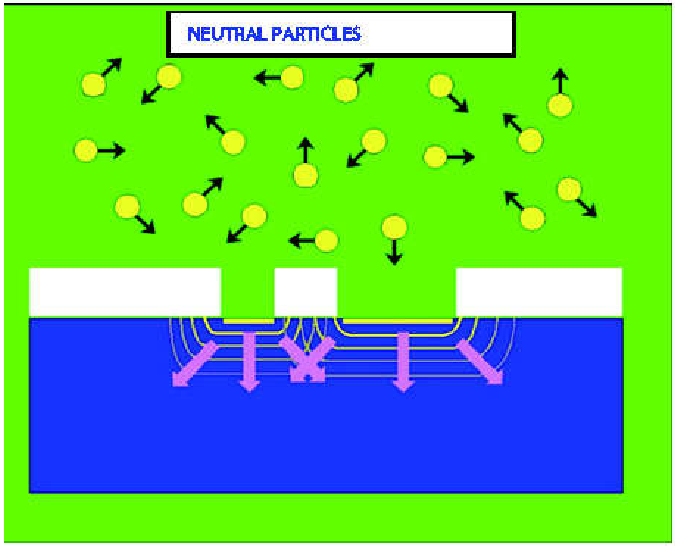


Thermal diffusion **Ion implantation**

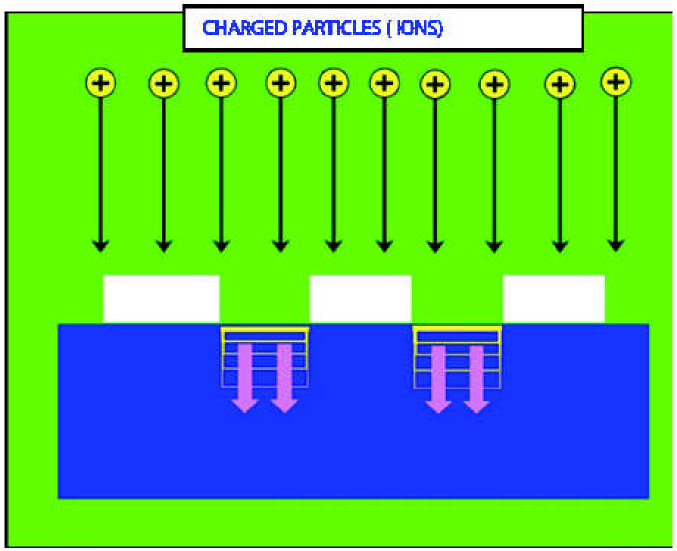
Ion Implantation - Advantages

- **Low temperature process**
  - **implantation at room temperature**
  - **mask materials: photoresist, SiO_2, metal, ...**

- **Lateral distribution**



Thermal diffusion



Ion implantation

Ion Implantation - Advantages

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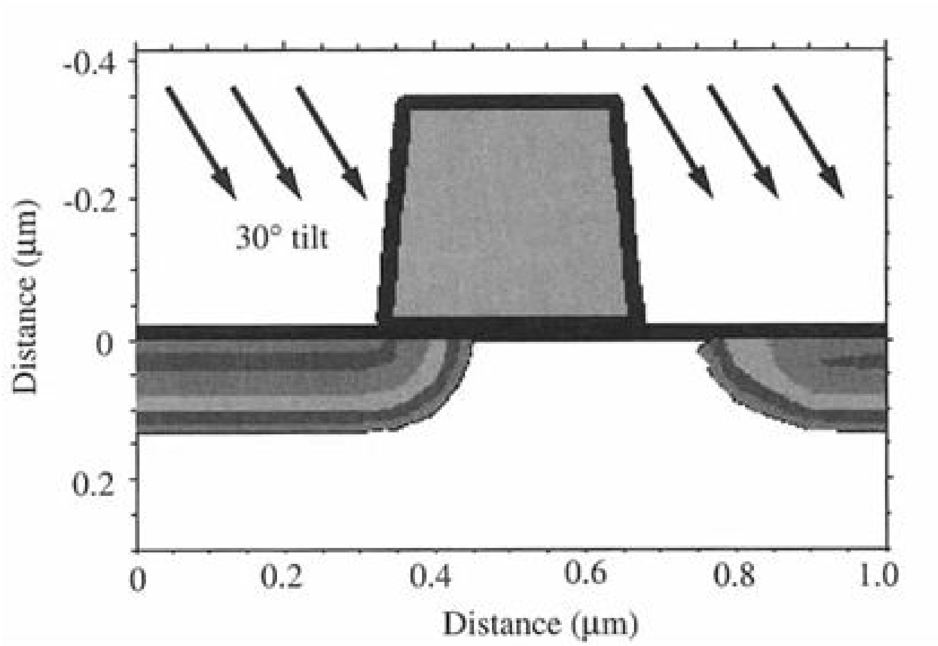
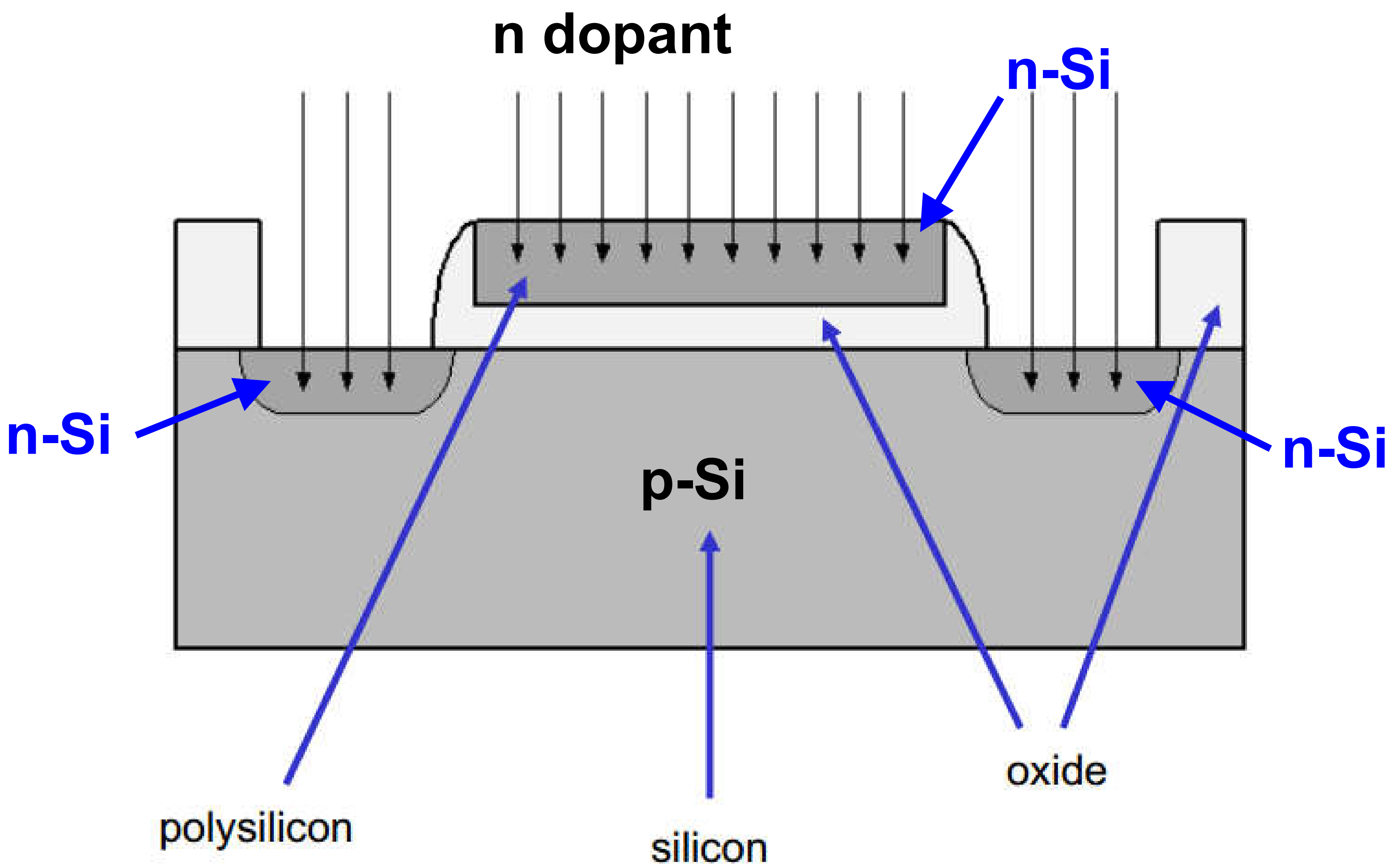
- **Lateral distribution**



shadow effect

Self Alignment



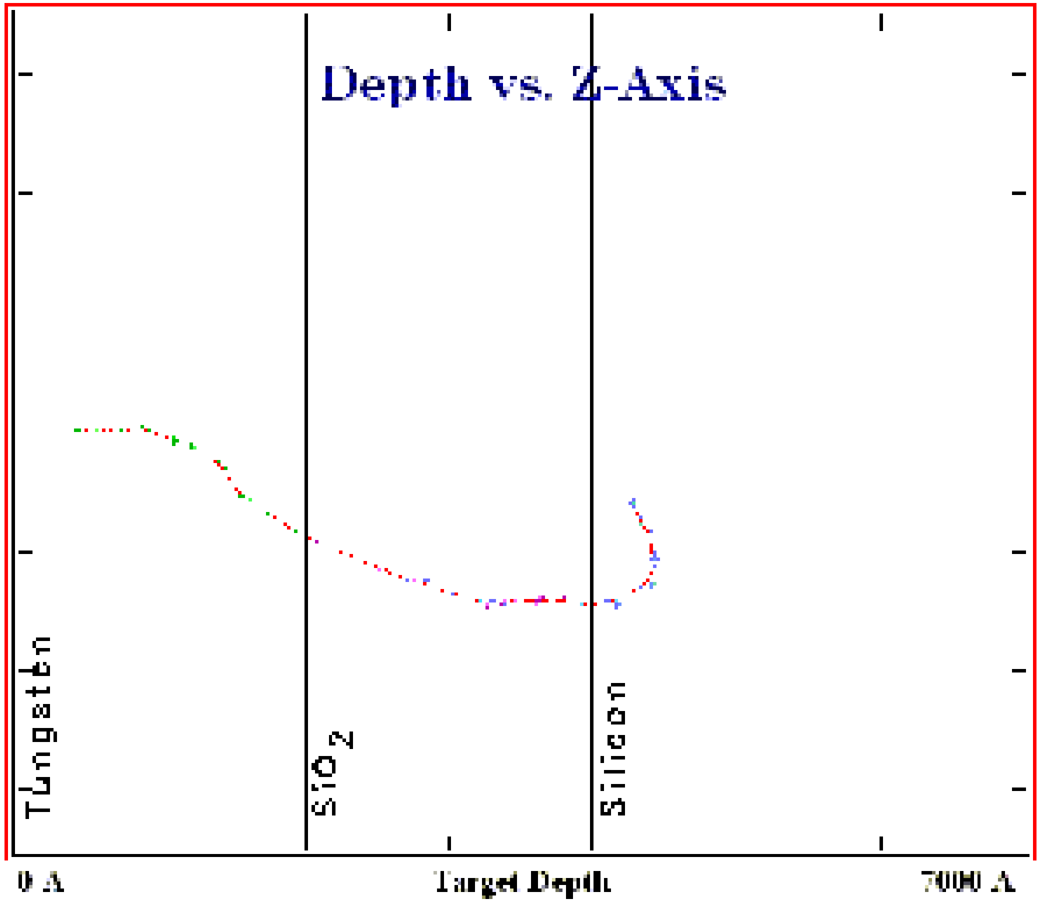
Dopant Distribution

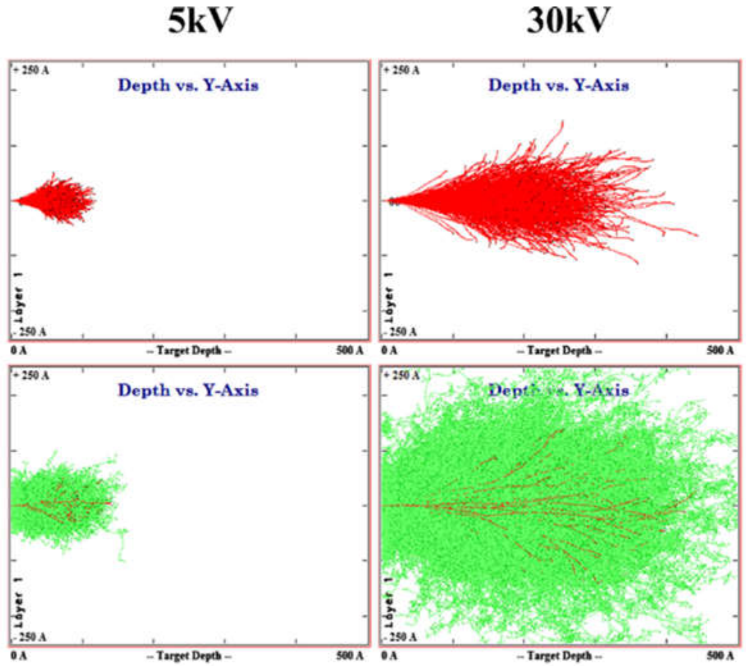
- **Process Parameters**
  - dopant type (B, P, As, Sb, ...)
  - implantation dose (# /cm^2)
  - energy (eV)
  - substrate orientation
  - anneal time, temperature

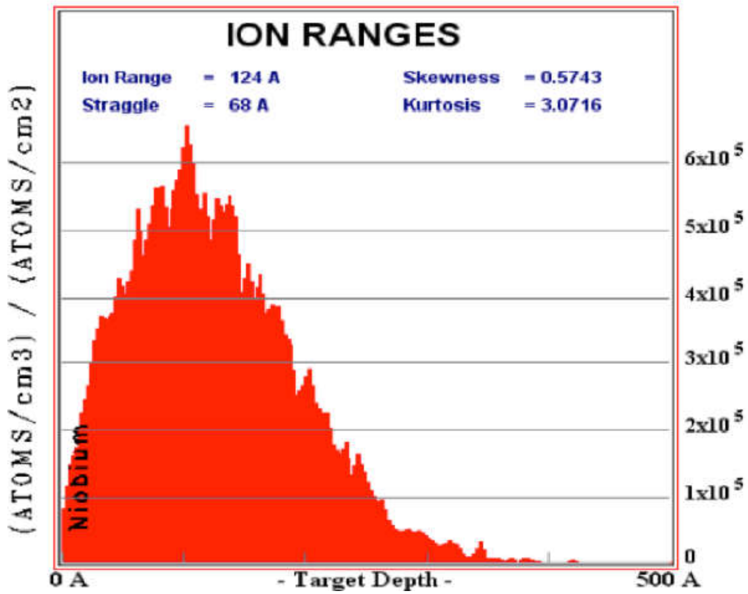
- **Control Parameters**
  - Junction depth
  - Doping concentration
  - Doping profile

Simulation Software - SRIM

http://www.srim.org

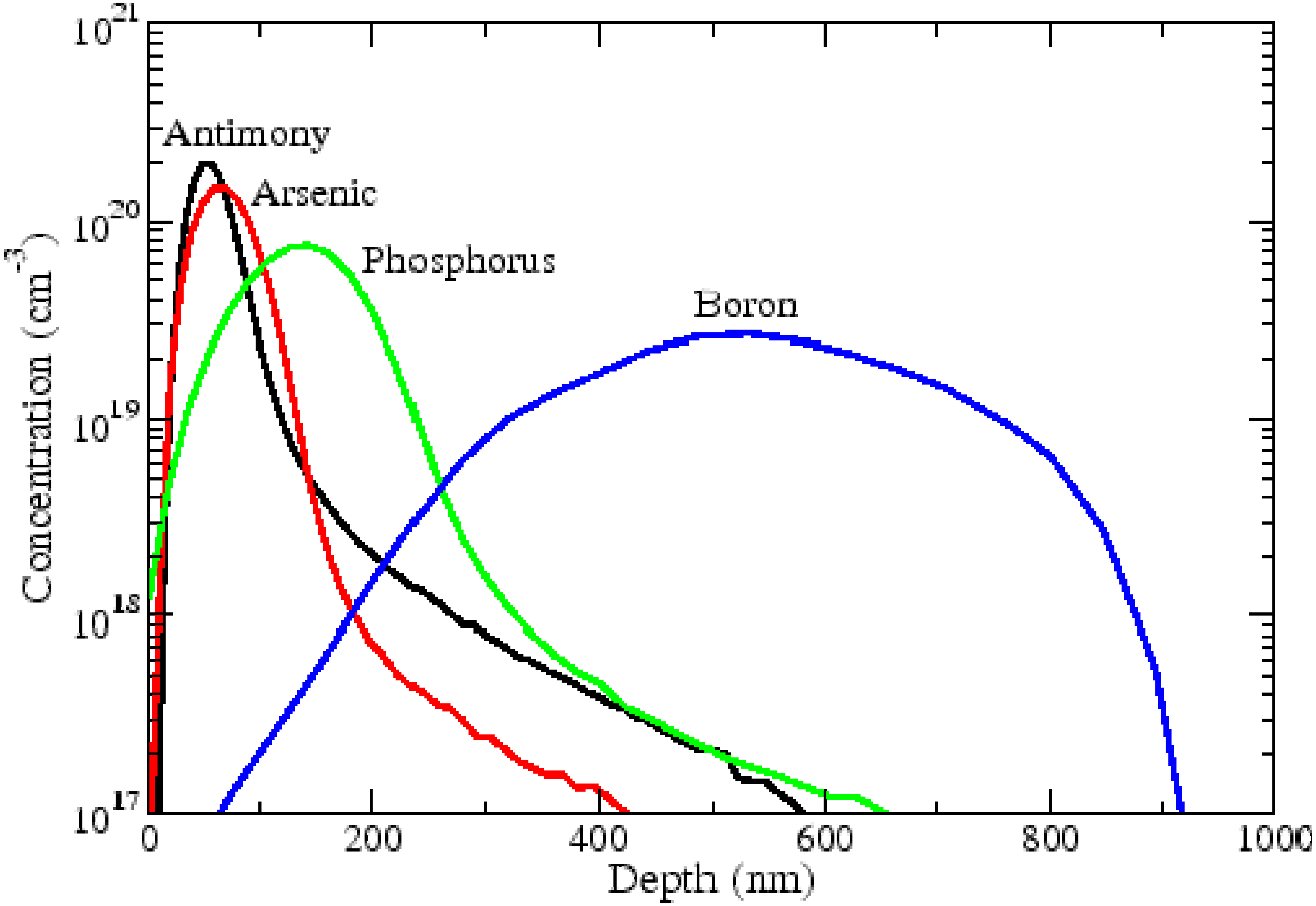






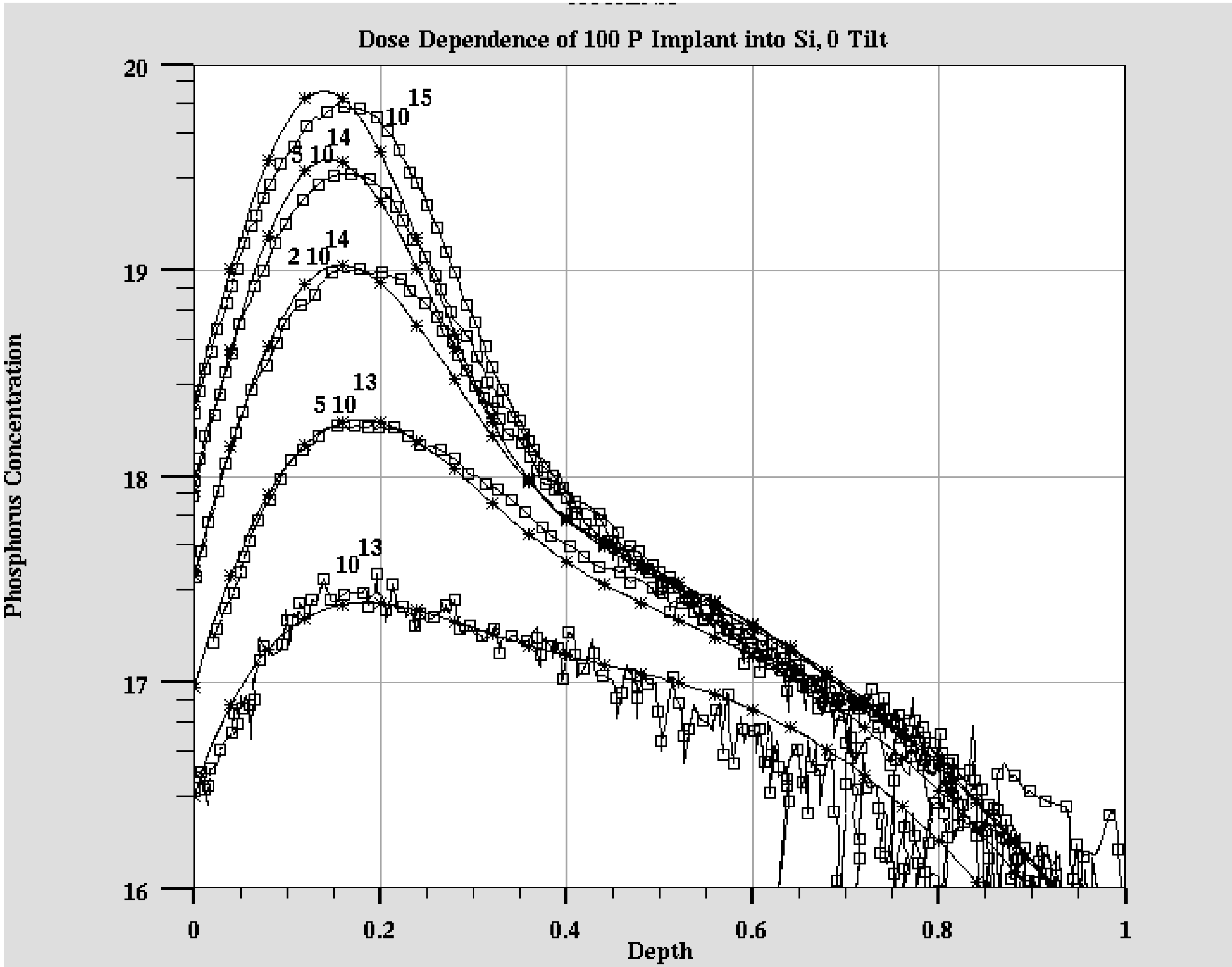
Dopant Distribution

dopant type



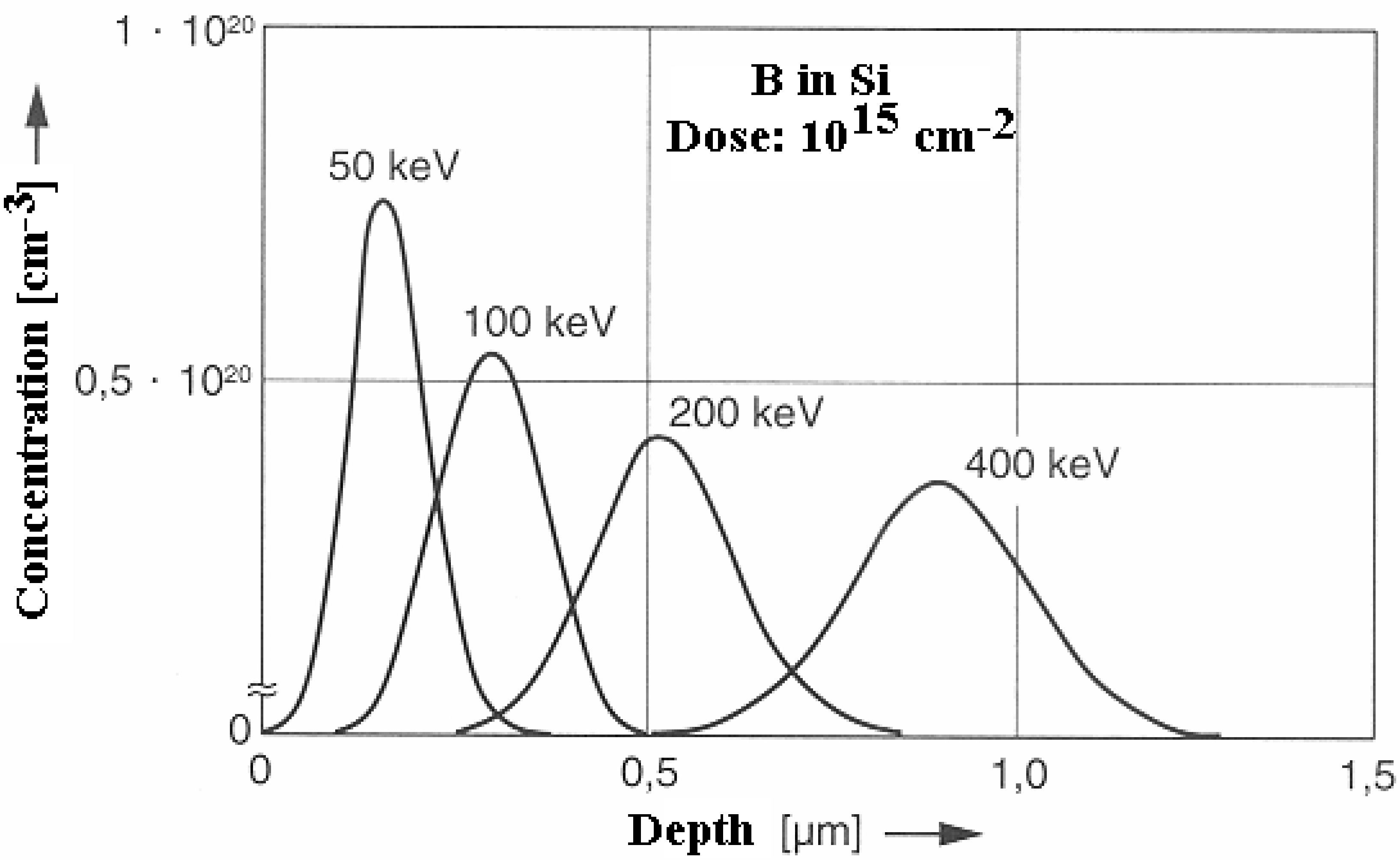
Dopant Distribution

dose



Dopant Distribution

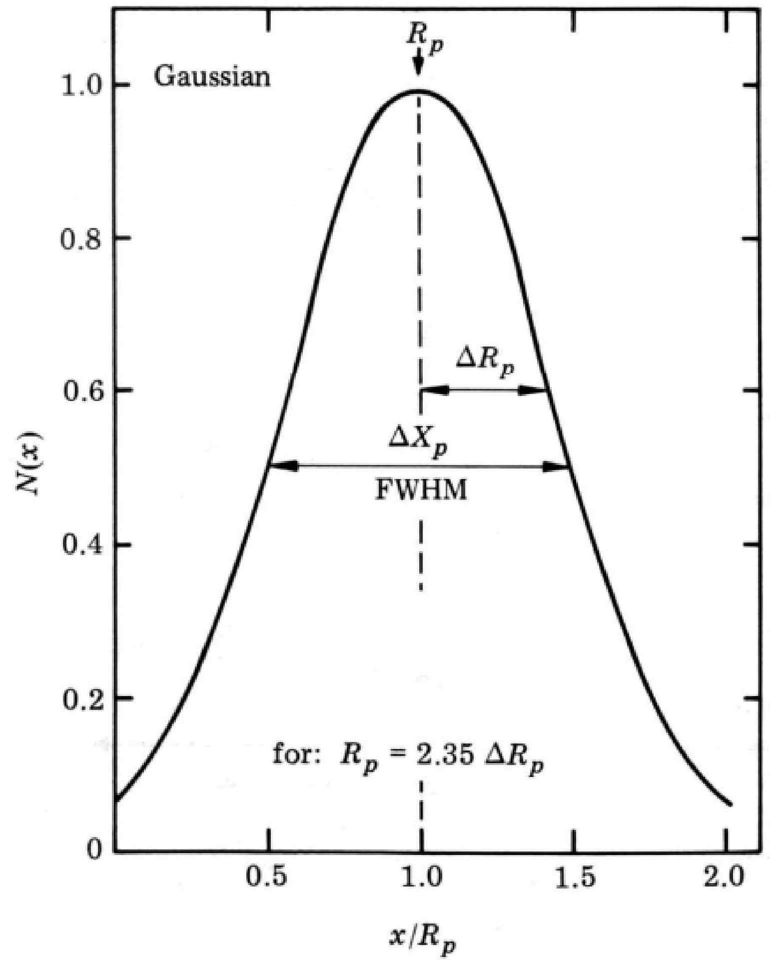
energy



Dopant Distribution

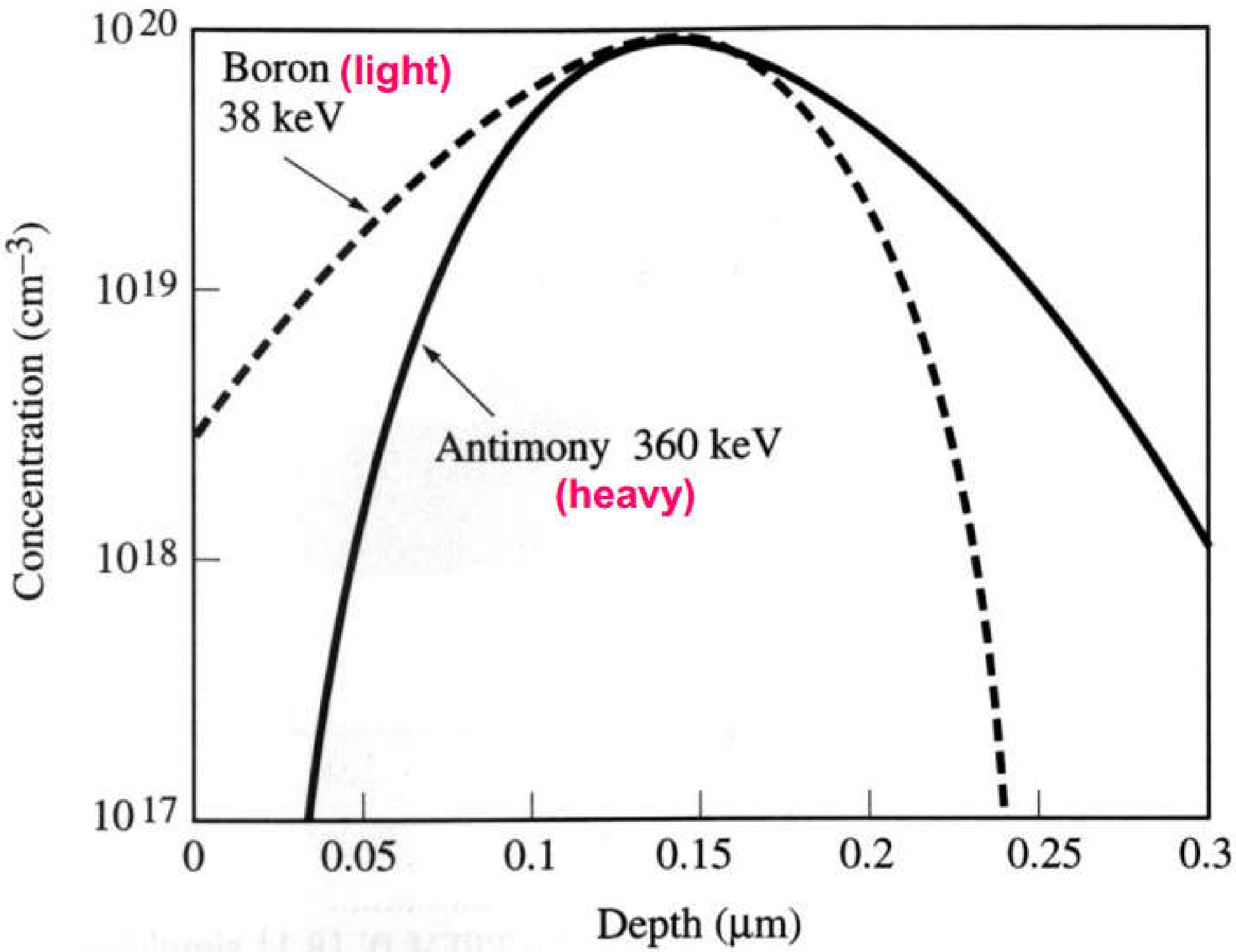
Ideal case: Gaussian profile

$$N(x) = \exp\left[-\frac{1}{2}\left(\frac{x - R_p}{\Delta R_p}\right)^2\right]$$



Dopant Distribution

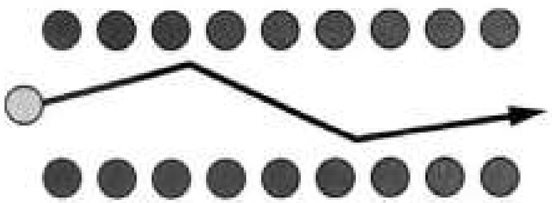
Light atoms (e.g. B): back scattering
Heavy atoms (e.g. Sb): forward scattering



Dopant Distribution

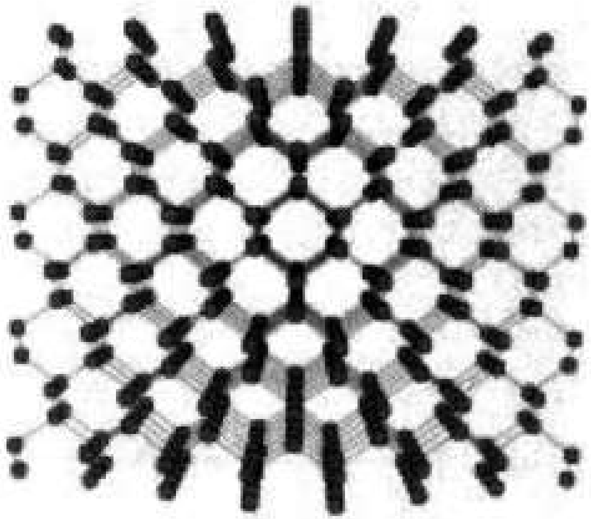
Ion Channeling

(沟道效应)

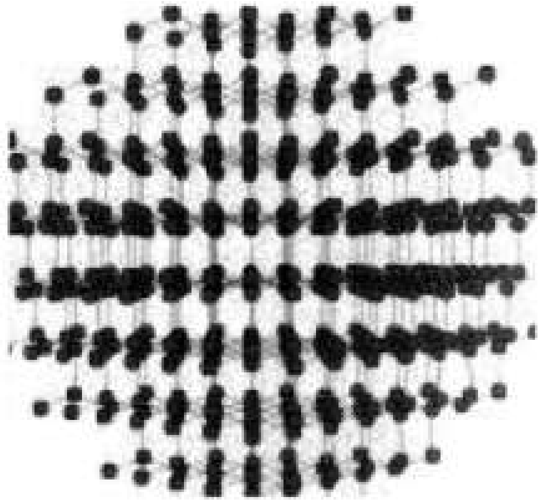


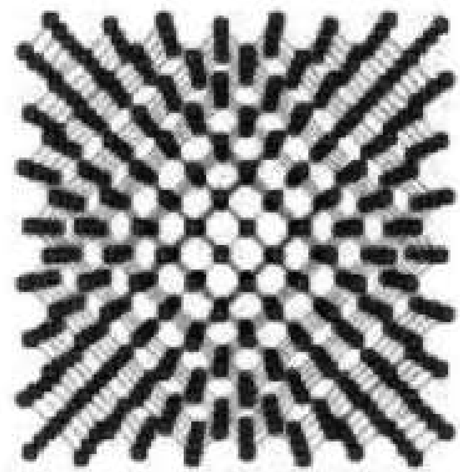
implantation is generally carried out with wafers tilted a few degrees relative to the beam

(110) axial

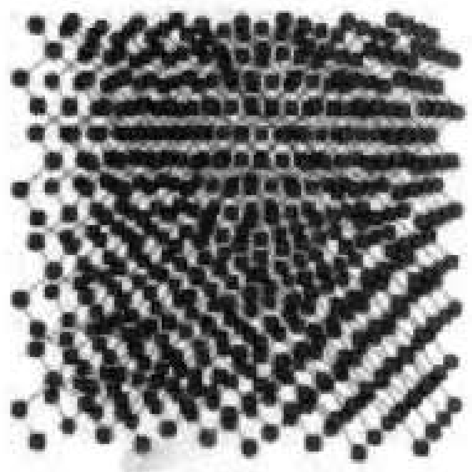


(111) planar



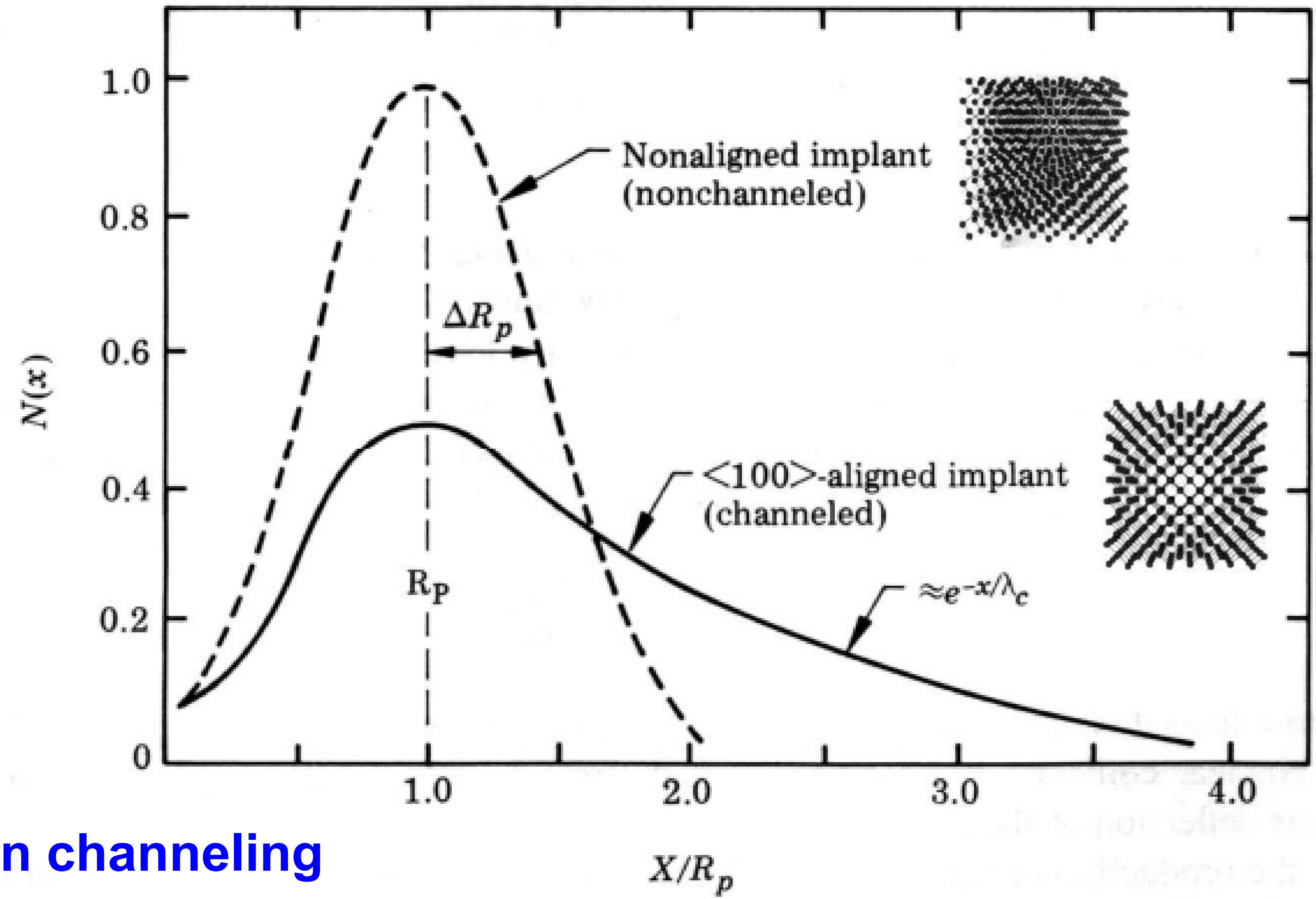


(100) axial



random

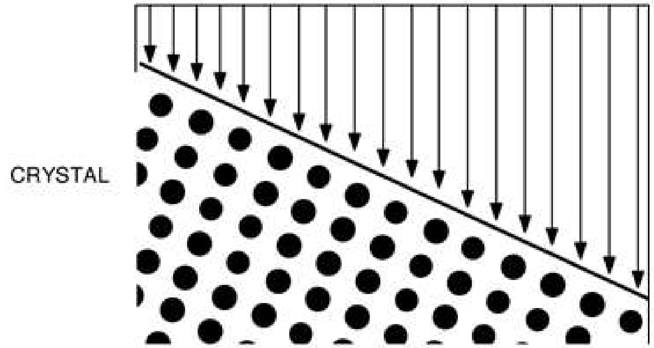
Dopant Distribution



ion channeling

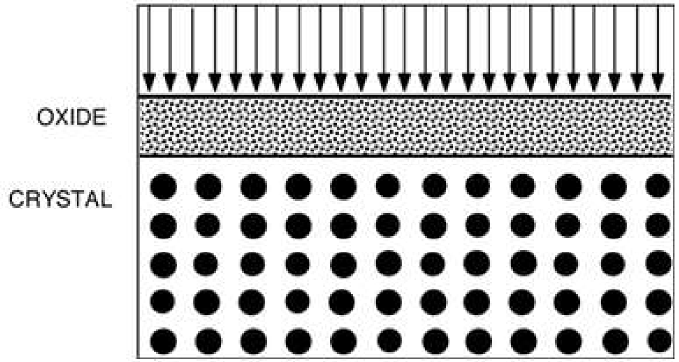
Reduce Channeling Effects

tilt the crystal



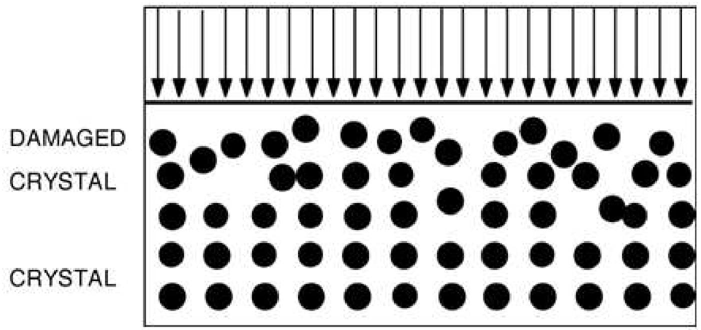
a

form a thin oxide layer



b

damage the surface by implantation

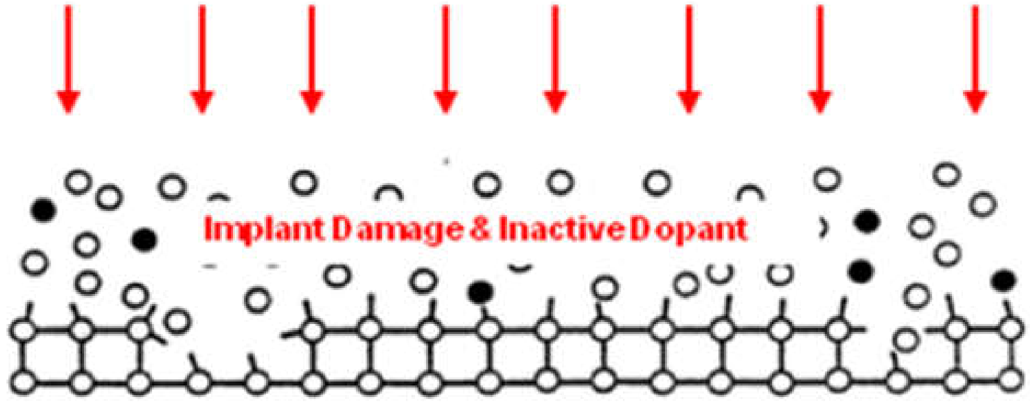


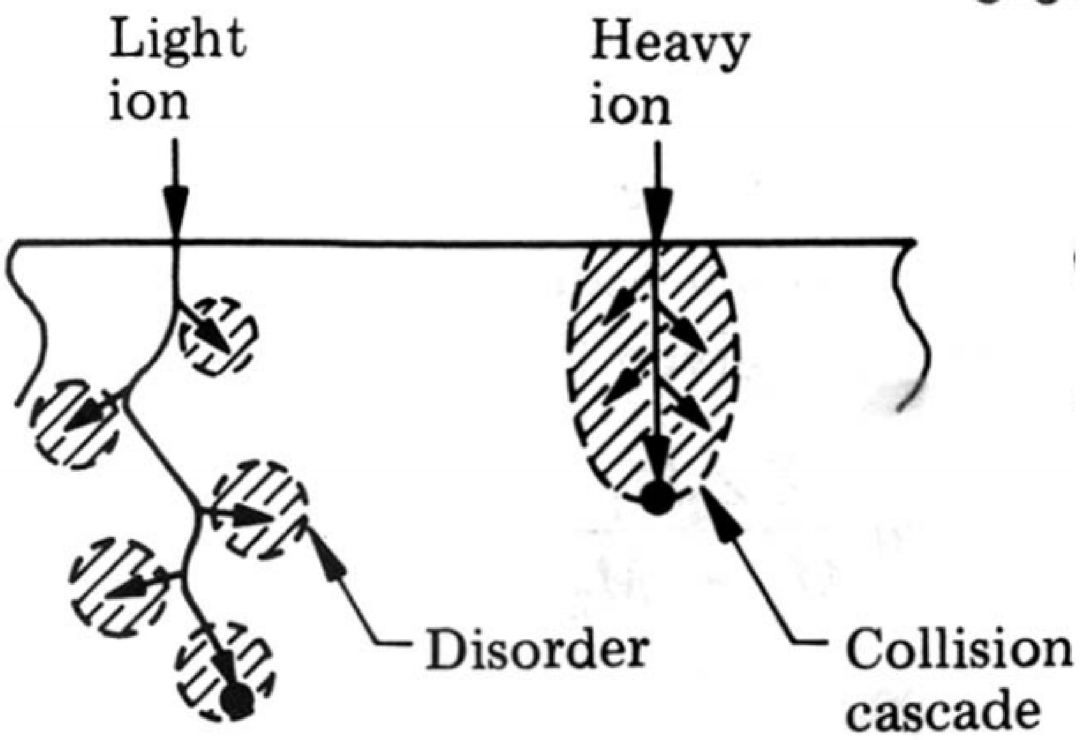
c

Implantation Damage

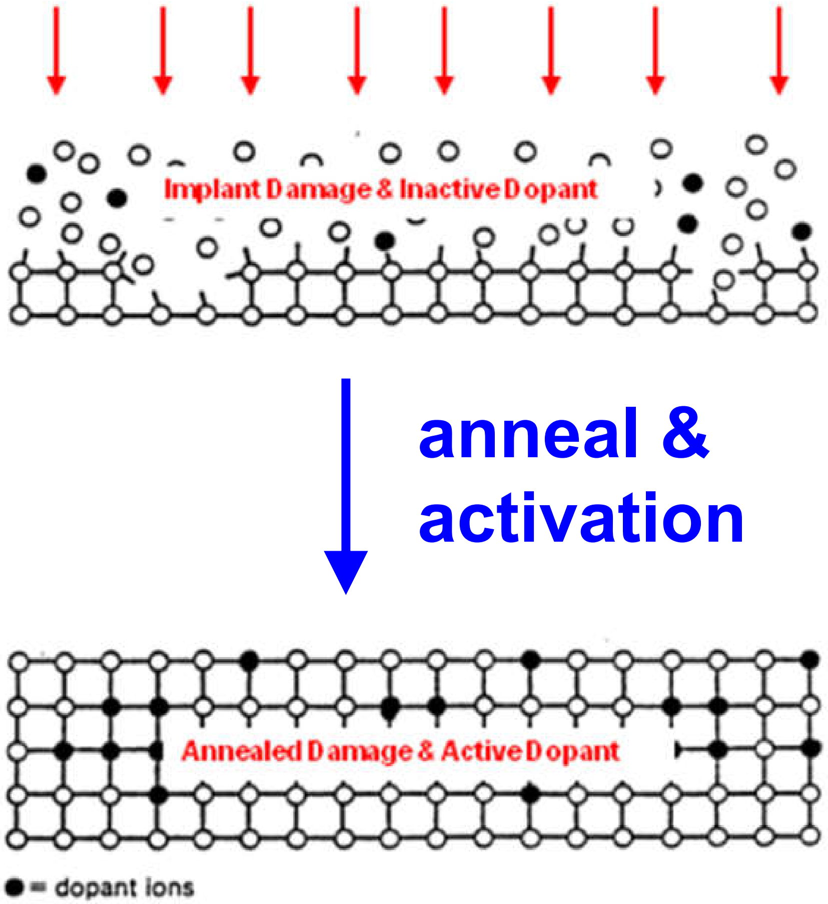
Video: Bullet in gel

amorphous





Implantation Damage



anneal & activation

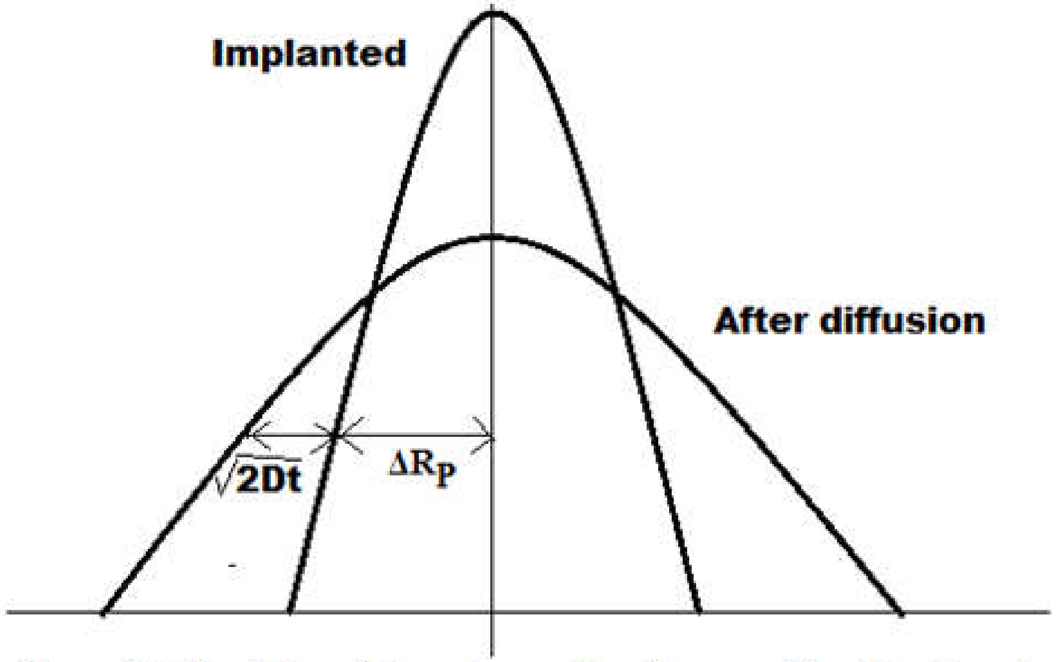


Figure 6.43 Evolution of Gaussian profile after annealing. The Gaussian preserves its shape as it diffuses in an infinite medium.

Effect of Annealing

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2}$$

$$\boxed{\begin{aligned} &C(x, t=0) = C_0(x) \\ &C(x=+\infty, t>0) = 0 \end{aligned}}$$

$$\Downarrow$$

$$C(x,t) = C_0(x)\cdot\exp\left(-\frac{x^2}{4Dt}\right)$$

$$N(x) = \exp\left[-\frac{1}{2}\left(\frac{x - R_p}{\Delta R_p}\right)^2\right]$$

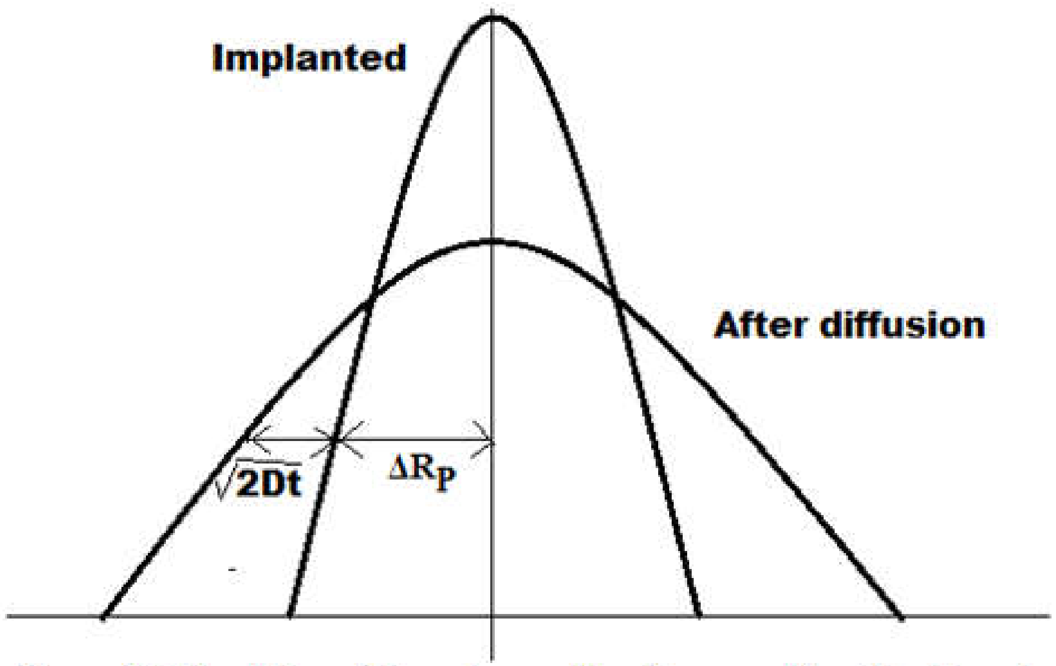
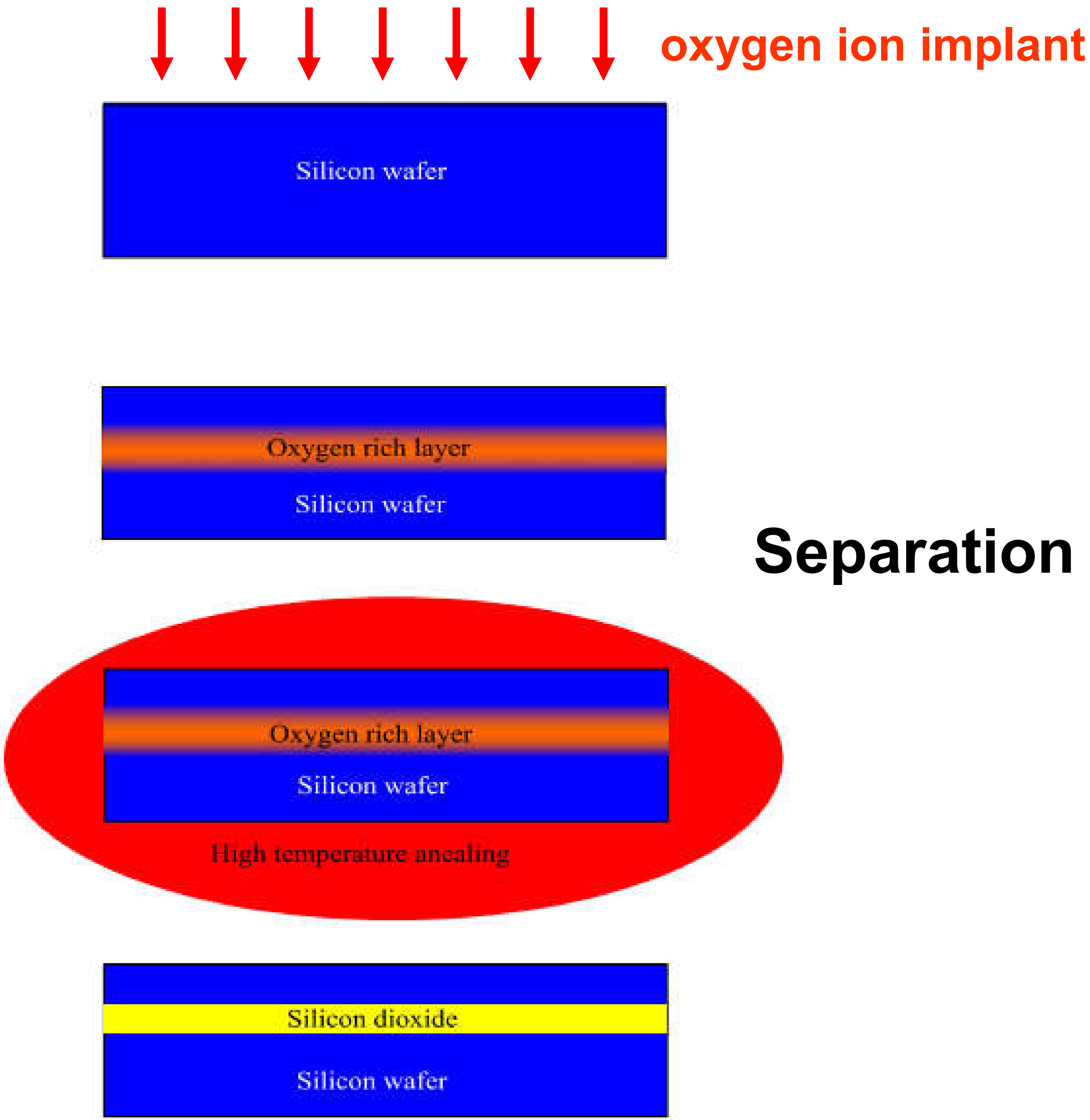


Figure 6.43 Evolution of Gaussian profile after annealing. The Gaussian preserves its shape as it diffuses in an infinite medium.

Make Silicon-on-Insulator (SOI)



'SIMOX'

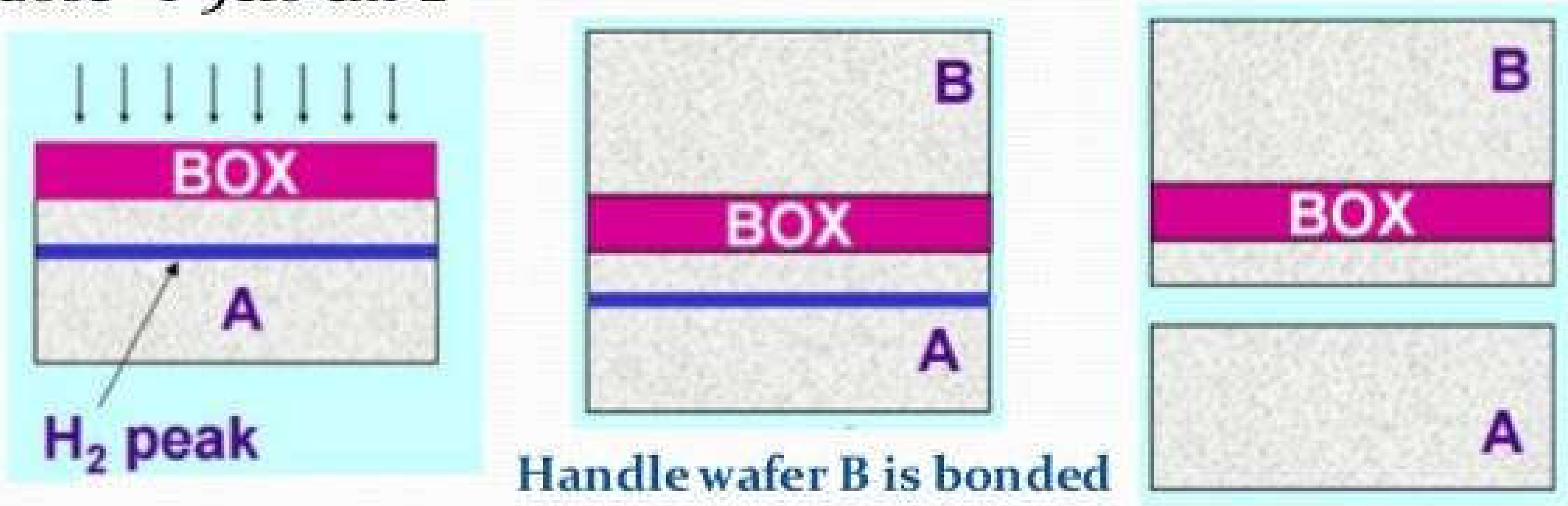
Separation by IMplanted OXygen

Make Silicon-on-Insulator (SOI)

'Smart-Cut'

Hydrogen implantation
through thermal oxide
dose ~1-5e16 cm-2

At ~400-600°C wafer
A separates from B
at H2 peak



After low temperature splitting, SOI wafer (B) is annealed ~1100°C to strengthen the bond, whereas wafer A is reused. SOI film thickness set by H2 implant energy and BOX thickness

Doping Methods

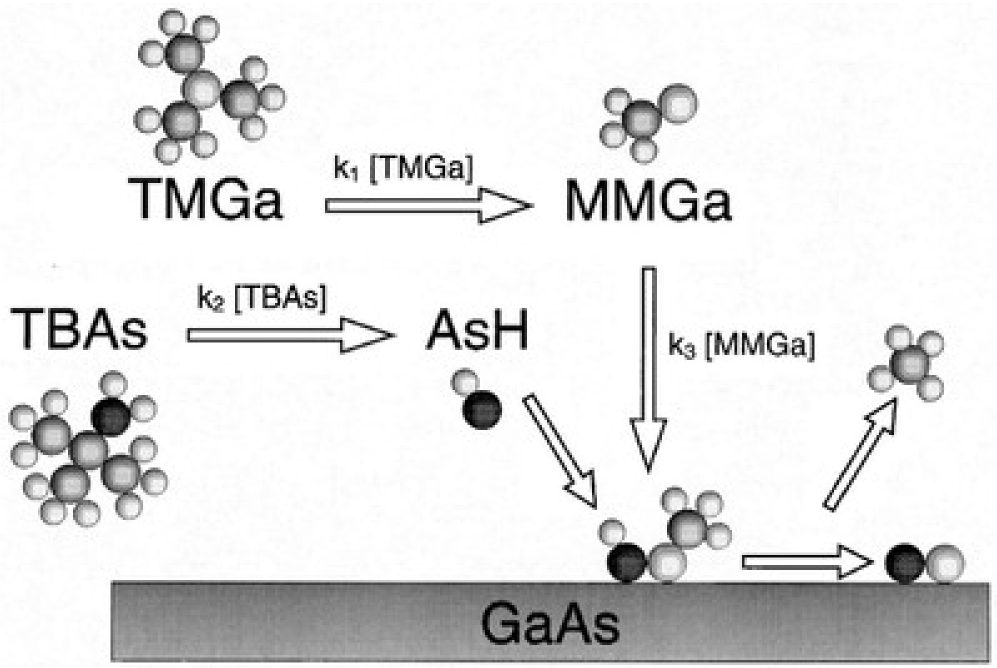
- Thermal diffusion

- Ion implantation

- In situ growth

Doping of Gallium Arsenide (GaAs)

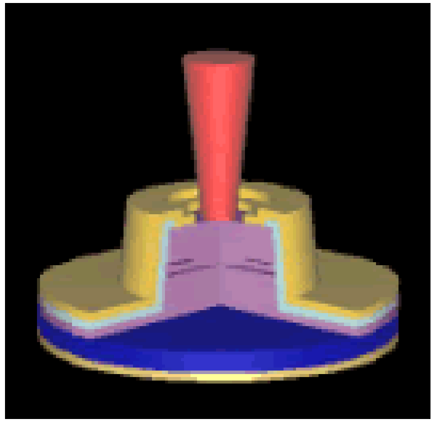
- **GaAs growth**
  - **MOCVD: $Ga(CH_3)_3 + AsH_3 \rightarrow GaAs + 3CH_4$**
  - **add dopant gas: SiH_4, Mg, Zn, ...**
  - **vertical structures with high quality thin-films**



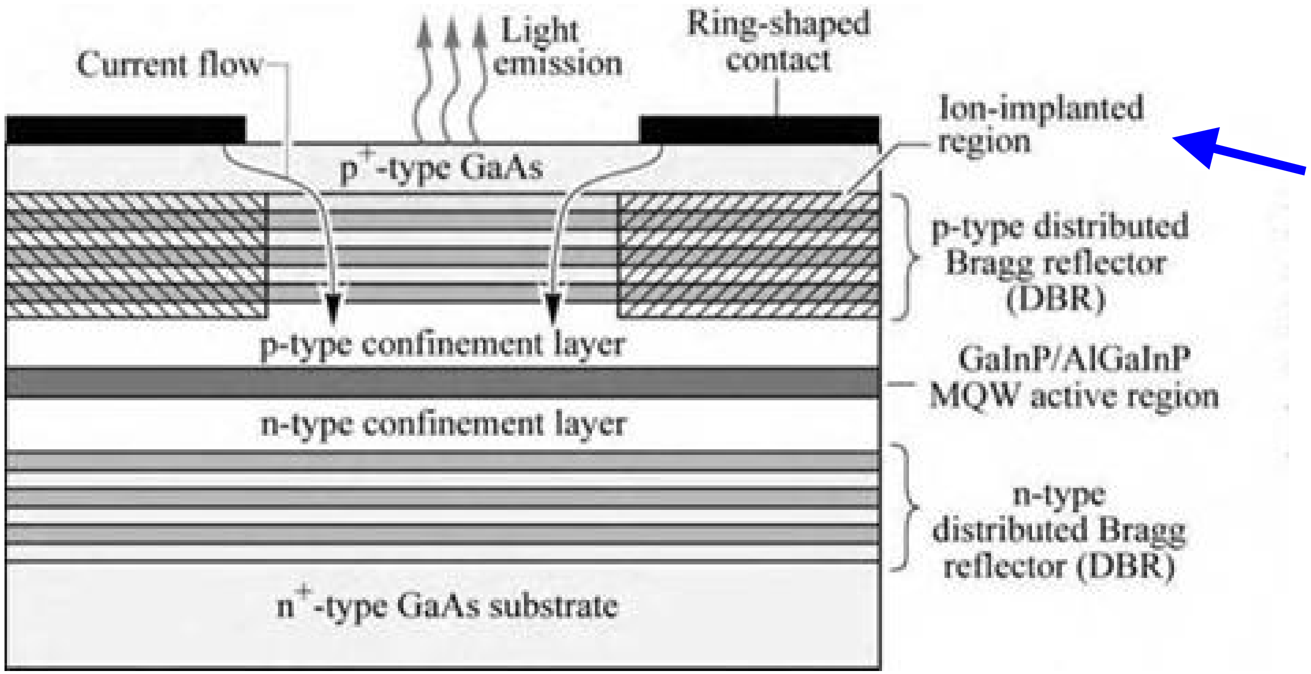
materials	thickness (nm)	doping (cm^{-3})	dopant
n+ GaAs contact	200	6e18	Si
n+ InGaP window	30	2e18	Si
n+ GaAs emitter	100	2e18	Si
p- GaAs base	2500	1e17	Zn
p+ $Al_{0.3}Ga_{0.7}As$ BSF	100	5e18	Mg
p+ GaAs substrate	-	5e18	Mg

Example: GaAs solar cell

GaAs VCSEL



- **Vertical Cavity Surface Emitting Laser**
  - **growth with in situ doping**
  - **isolation by ion implantation**

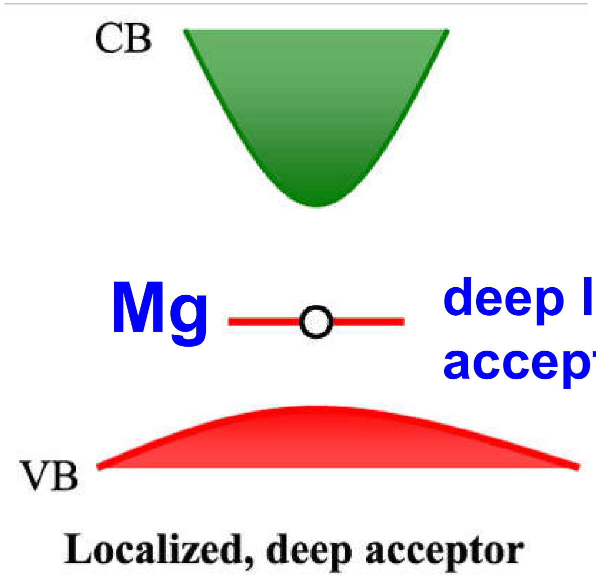


ion implanted (H^+, O^-, ...) region for isolation

highly damaged and resistive region

Doping of Gallium Nitride (GaN)

- n-GaN is easy
  - use Si to replace Ga
- p-GaN is very difficult
  - use Mg to replace Ga, but ...

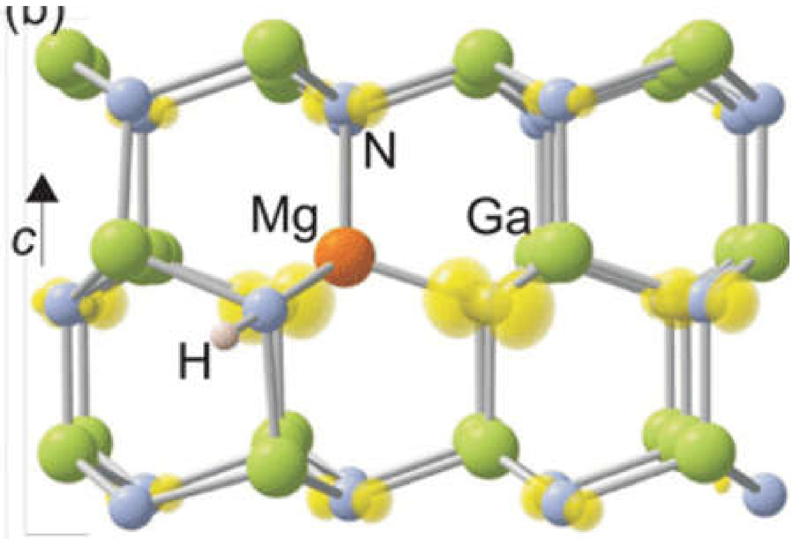


H. Amano, *et al.*, *Jpn. J. Appl. Phys.* **28,** L2112 (1989)
S. Nakamura, *et al.*, *Appl. Phys. Lett.* **64,** 1687 (1994)



I. Akasaki H. Amano S. Nakamura

2014 Nobel Prize in Physics



hydrogen reduces distortion

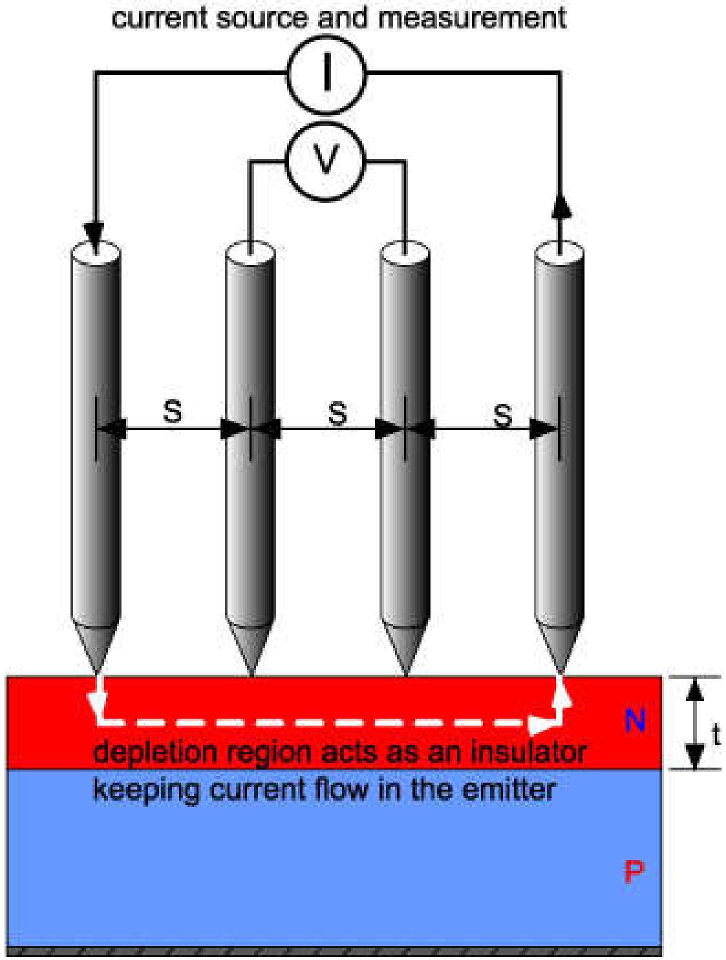
Doping Measurement

TABLE 4
Commonly used diffusion profile measurement techniques

Profile techniques	Characteristics
Capacitance-Voltage	Carrier concentration at the edge of the depletion layer of a pn junction. Maximum total dopants 2×10^{12} atoms/cm^2.
Differential conductance	Resistivity and Hall effect mobility of net electrically active species. Requires thin-layer removal, concentration range from 10^{20} to 10^{18} atoms/cm^3.
Spreading resistance	Resistance on angle-beveled sample. Good for comparison with known profiles and quick semi quantative evaluation. $x_j \geq 1 \mu m$.
SIMS	High sensitivity on many elements; for B and As detection limit is $5 \times 10^{15} cm^{-3}$. Capable of measuring total dopant profiles in 1000Å range. Needs standards.
Radioactive tracer analysis	Total concentration. Lower limit is $10^{15} cm^{-3}$. Limited to radioactive elements with suitable half-life times: P, As, Sb, Na Cu, Au, etc.
Rutherford backscattering	Applicable only for elements heavier than Si.
Nuclear reaction	Measures total boron through $^{10}B(n,{}^4He)^7Li$, or $^{11}B(p,\alpha)$. Needs Van de Graaff generator.

Resistivity

- **Four Point Probe Measurement**



conductivity

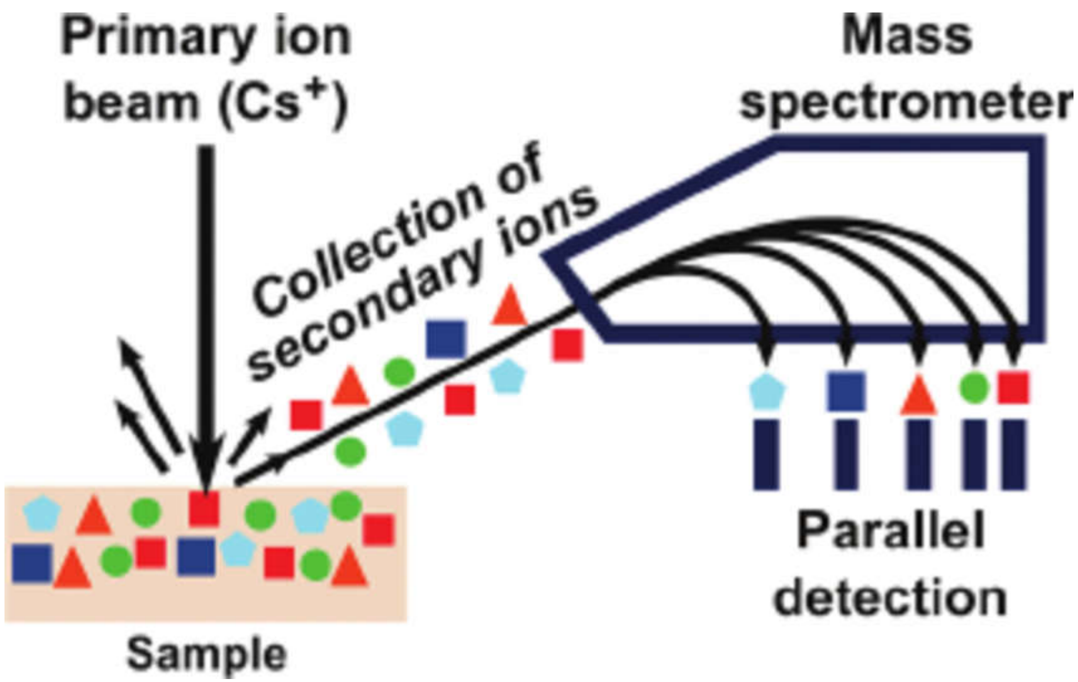
$$\sigma(x) = e \cdot \mu \cdot C(x) = \frac{1}{\rho(x)}$$

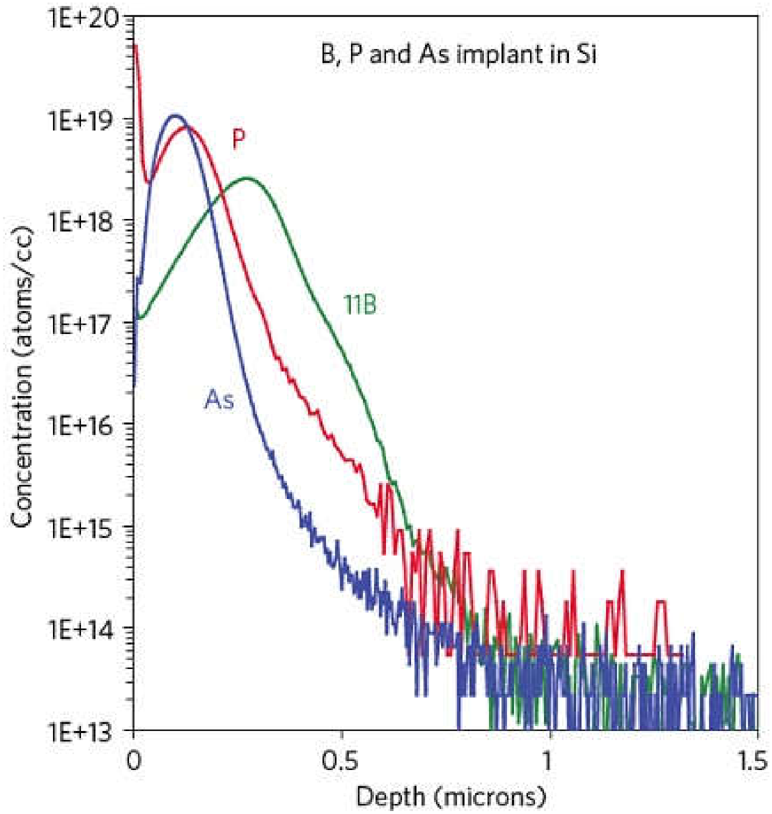
sheet resistance

$$R_s = \frac{\rho}{x} = \frac{1}{\int_0^t \sigma(x)dx}$$

SIMS

- **SIMS: Secondary Ion Mass Spectroscopy**
  - **equipment similar with ion implantation**





Thank you for your attention