电子与电气工程系
Department of Electrical and Electronic Engineering

Diffusion

Lecturer: Mengyuan Hua

Outline

- Applications
- Methods & Equipment
  - Predeposition
  - Drive-in
- Diffusion mathematics
  - The transport equation
  - The continuity equation
  - Field enhanced diffusion
- Diffusion in solids
- Linear Diffusion
  - Predeposition
  - Drive-in
- Masking
- Segregation
- Diffusion & point defects
  - High doping effects
  - Enhanced/retarded diffusion
- Non-linear diffusion
  - Predeposition
  - Drive-in
- Evaluation
  - Chemical & electrical conc.
  - Sheet resistance
  - Junction depth

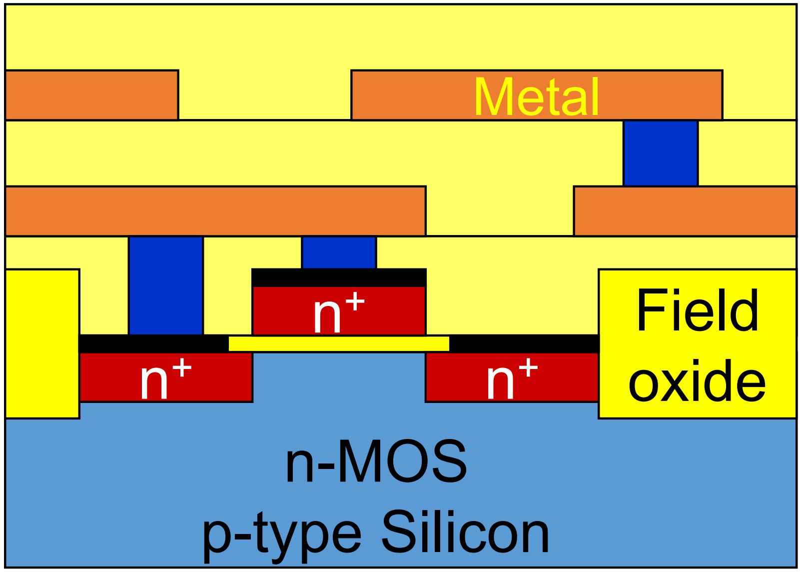
Applications of Diffusion

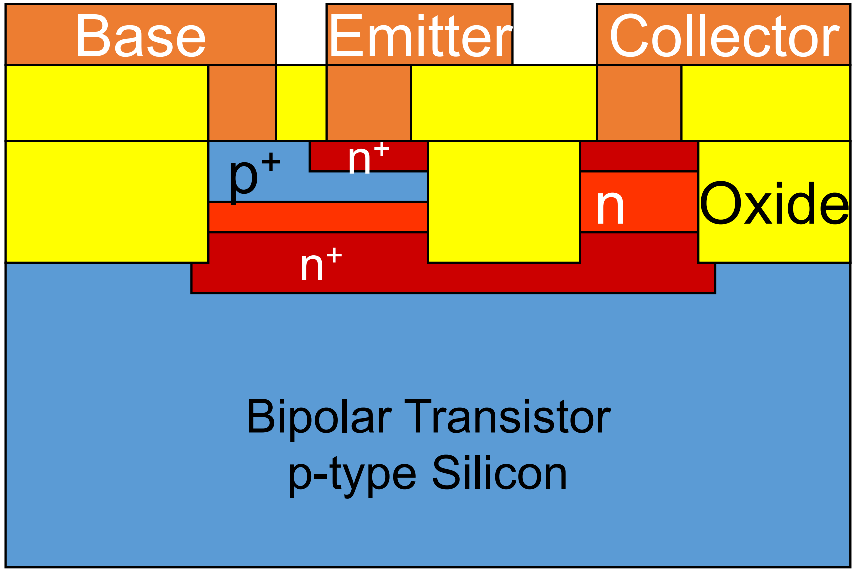
- Diffusion of dopants

  pn-junctions; MOST; BJT; Resistors, piezoresistors

- Diffusion of contaminants

  Gettering





Category of Main Semiconductor Devices

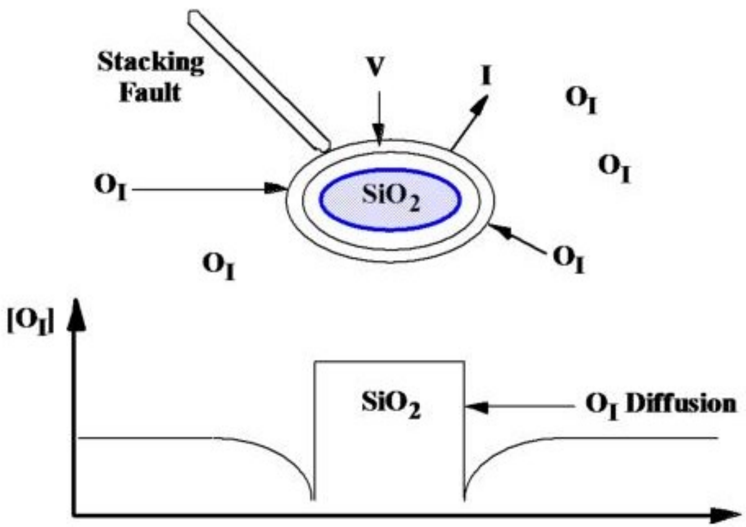
- **Semiconductor Devices**
  - **Rectifier**
    - PiN diode ”
    - SBD *
    - JBS *
  - **Switch**
    - **Transistor**
      - BJT ”
      - IGBT ”
      - MOSFET *
      - HEMT (GaN) *
    - **Thyristor**
      - SCR ”
      - GTO ”
      - IGCT ”
      - MCT ”

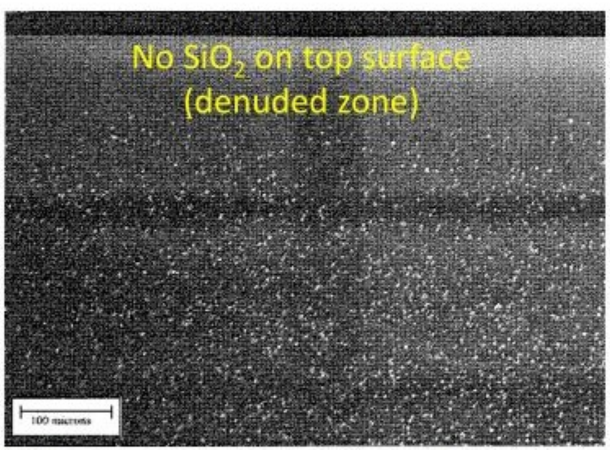
Bipolar device ”

Unipolar device *

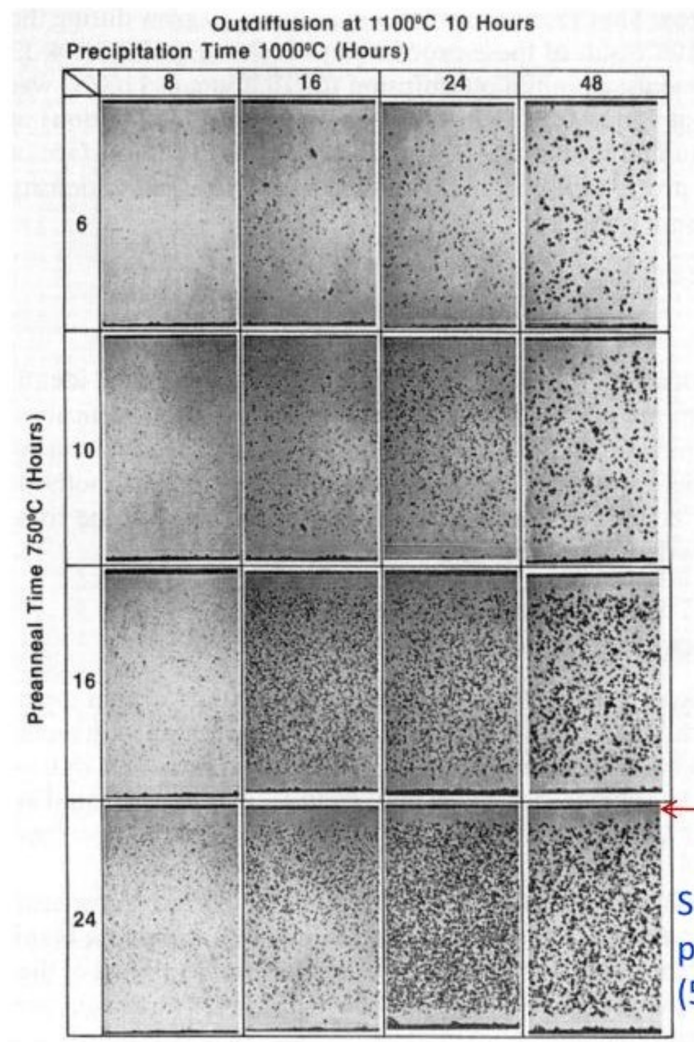
Applications of Diffusion

•Diffusion of contaminants → Gettering





SiO_2 precipitates (white dots) in bulk Si



no SiO_2

SiO_2 precipitates (50-100nm)

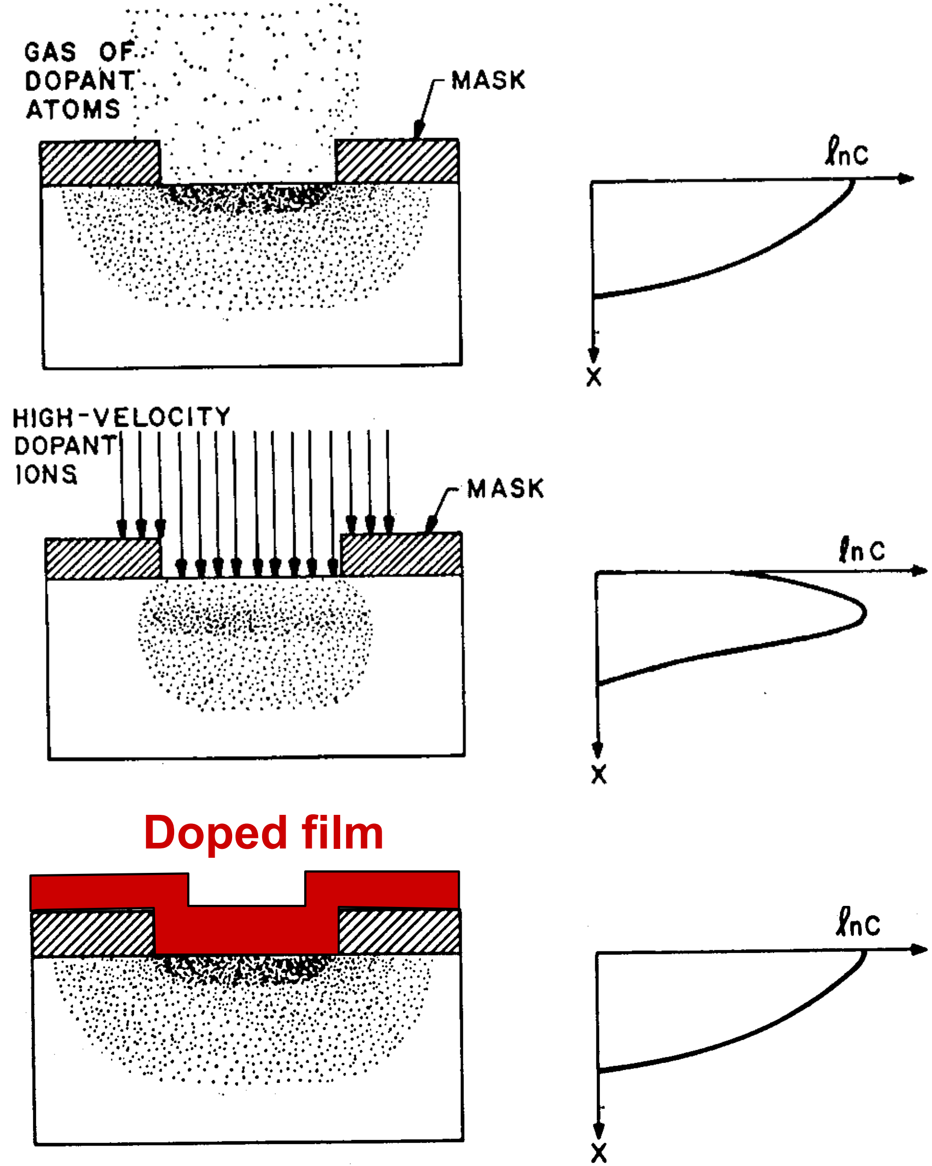
Doping of Semiconductors

Dopants in Silicon

- Donors (V): P, As, Sb
- Acceptors (III): B, Al, Ga, In

Doping a two step process:

1. Predeposition -
   Introduce dopants
   - Diffusion from gas-phase
   - Diffusion from thin films
   - Ion implantation
   - Grown-in dopants
2. Drive-in -
   Redistribute dopants
   - Furnace Anneal
   - Rapid Thermal Annealing



Predeposition: Gas Phase or Ion Implantation

Gas Phase / Doped Film:

Advantages

- Batch process
- No damage
- Low cost

Disadvantages

- Only SiO_2 masks
- Only moderate/high doses
- Only high surface conc.
  - $C < C_{sol}$

Ion Implantation:

Advantages

- All materials mask
- Precise Dose Control
- 10^{11}-10^{16}/cm^2 Doses
- Buried profiles

Disadvantages

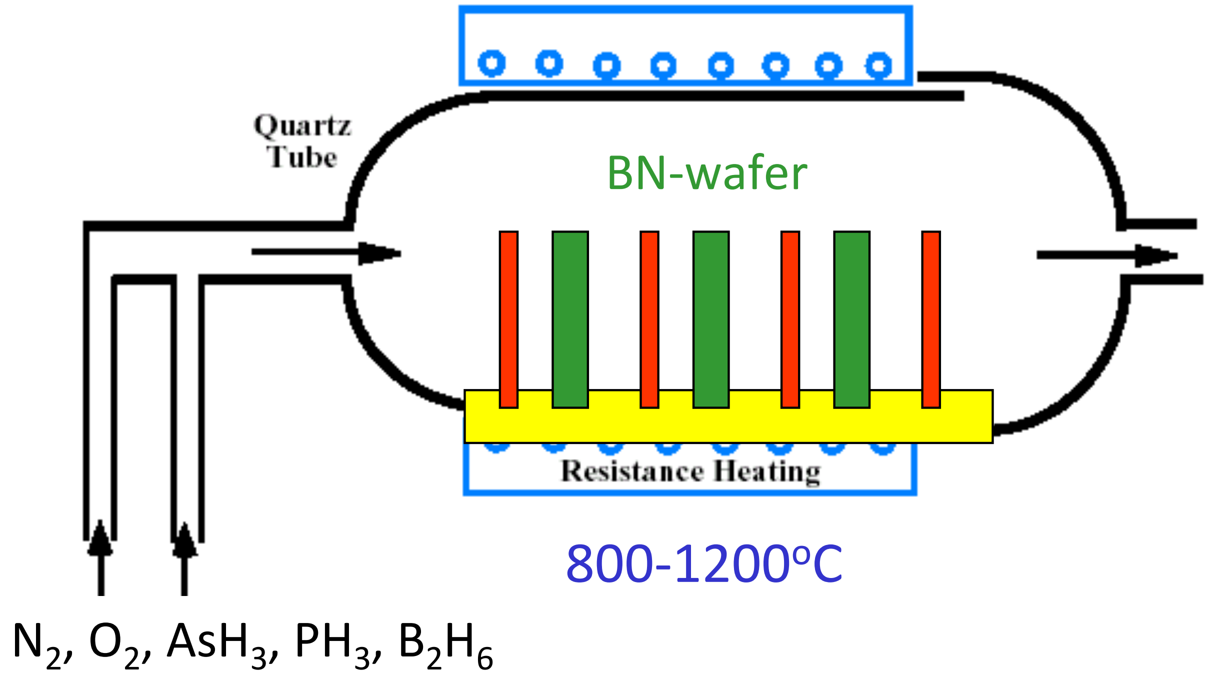
- High cost
- Damage causing:
  - Enhanced diffusion
  - Dislocations

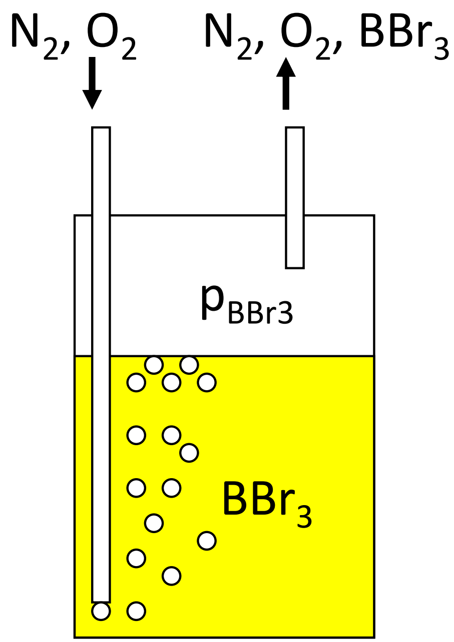
Gas Phase Predeposition

A furnace process similar to thermal oxidation.

Dopant sources: (The real source is always the oxide)

- Gas: AsH_3, PH_3, B_2H_6
- Vaporised liquid: $POCl_3$, BBr_3,
- Vapours of a solid: B_2O_3, P_2O_5, As_2O_5





Vaporiser: Controlled temperature

Sheet Resistance

Homogenous sample:

$$R = \rho\frac{L}{Wh} = \frac{\rho}{h}\frac{L}{W} = \frac{L}{W}R_{\mathbf{sh}}$$

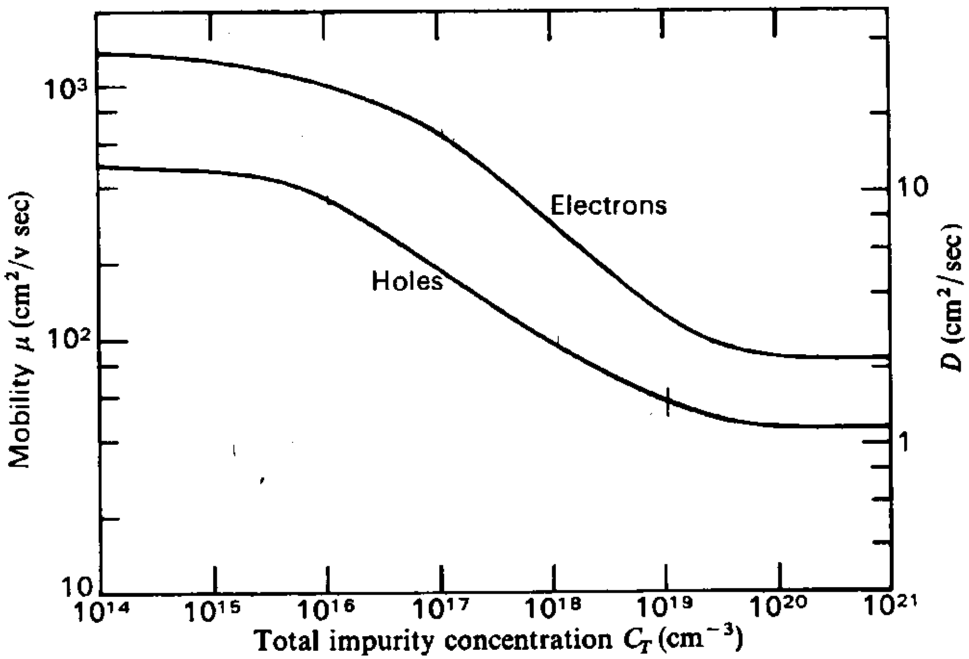
Sheet resistance: $\underline{R_{\mathbf{sh}} = \frac{\rho}{h}}$

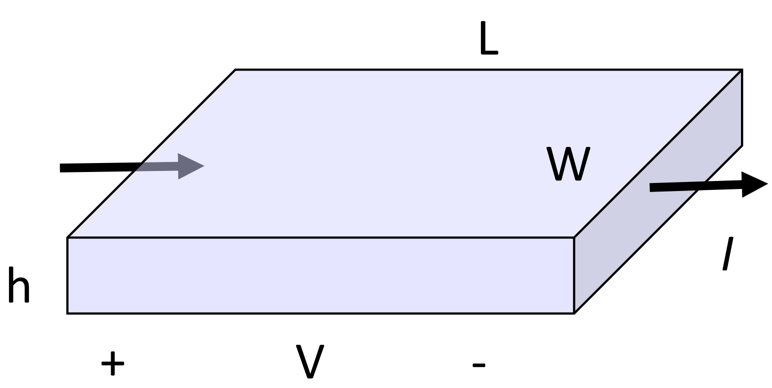
Inhomogenous:

Conductivity: $\sigma = q\mu_n n + q\mu_p p$

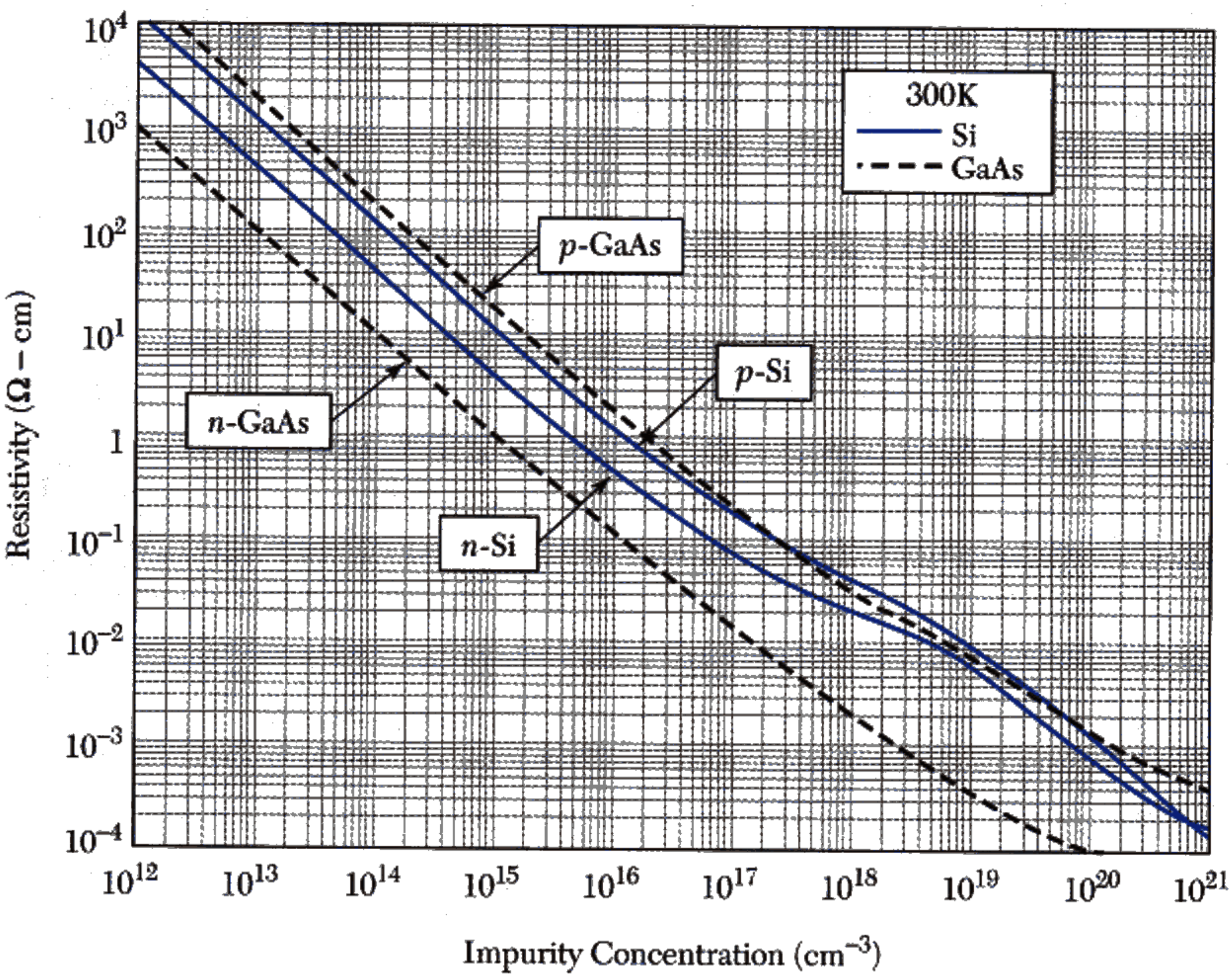
$$\frac{1}{R} \equiv \frac{W}{L}\int_0^h \sigma(x)dx \equiv \frac{W}{L}\frac{1}{R_{\mathbf{sh}}} \Rightarrow$$

$$\underline{R_{\mathbf{sh}} = \frac{1}{\int_0^h \sigma(x)\,dx}} \cong \frac{1}{\int_0^h q\mu_n n\,dx} \approx \frac{1}{q\overline{\mu_n}Q}$$





Resistivity of Doped Silicon



Dopants:

Donors: **P, As, Sb**

Acceptors: **B, Al, Ga**

$$\rho = \frac{1}{q\mu_n n + q\mu_p p}$$

$$\rho_n \approx \frac{1}{q\mu_n N_D}$$

$$\rho_p \approx \frac{1}{q\mu_p N_A}$$

Solid Solubility

Dopants are soluble in bulk silicon up to a maximum value before they precipitate into another phase

<u>Purpose:</u>

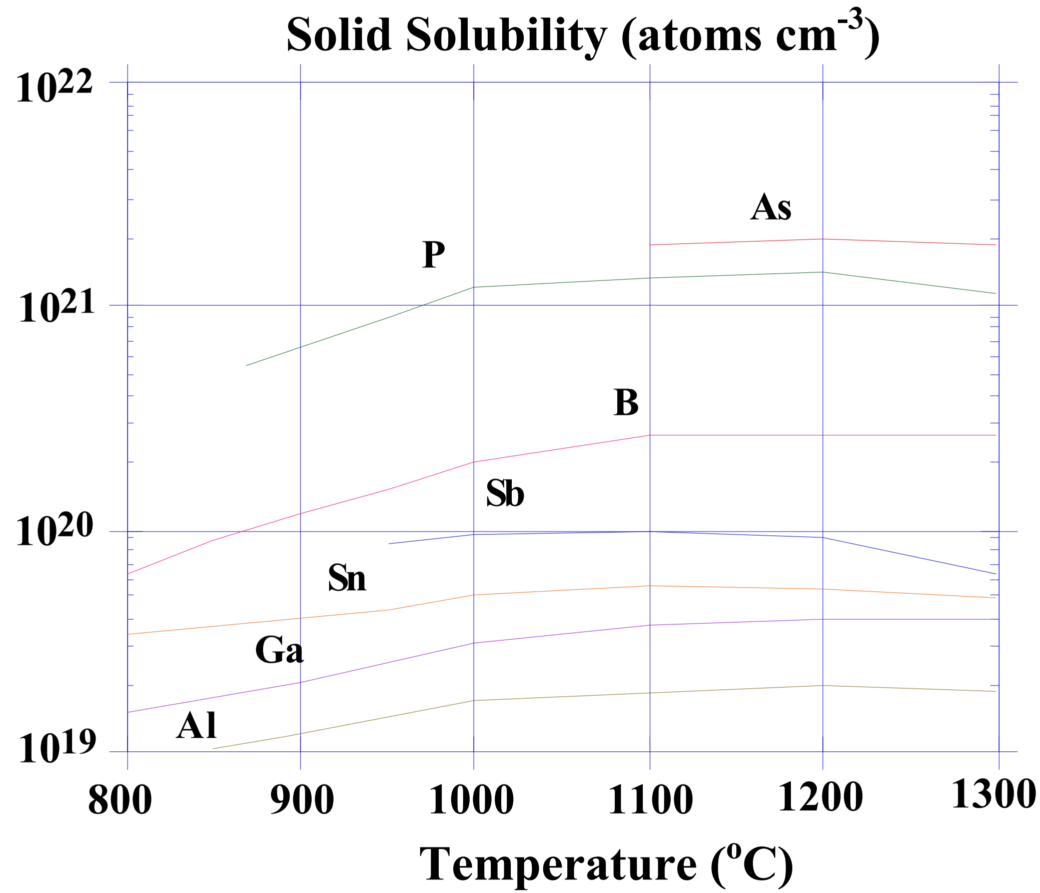
1. Change type
2. Change conductivity

- Concentration $\leq C_{sol}$
- Electrically active Concentration:

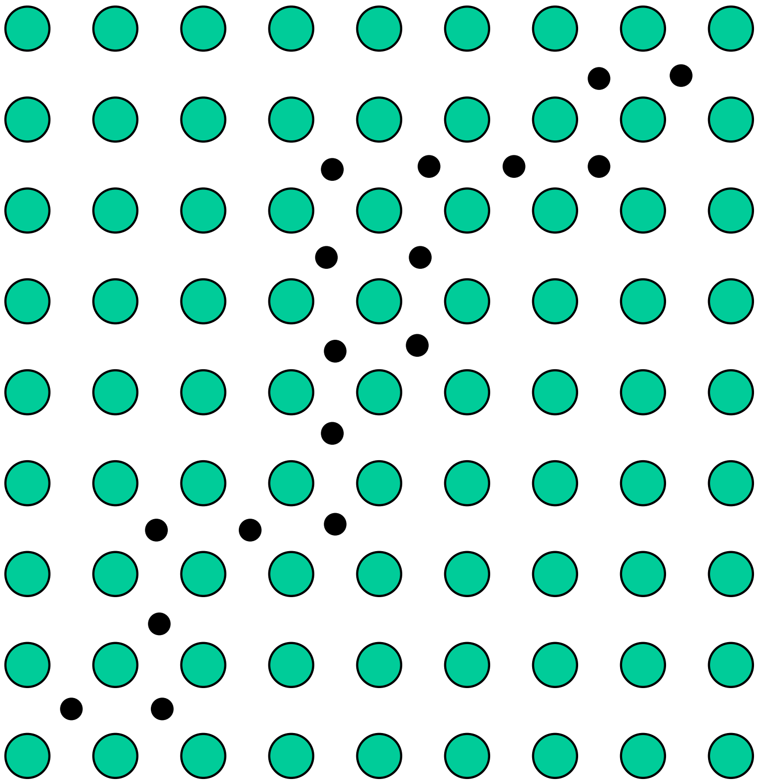
  $C_{elec} \leq C_{chem}$

Example: As-clustering

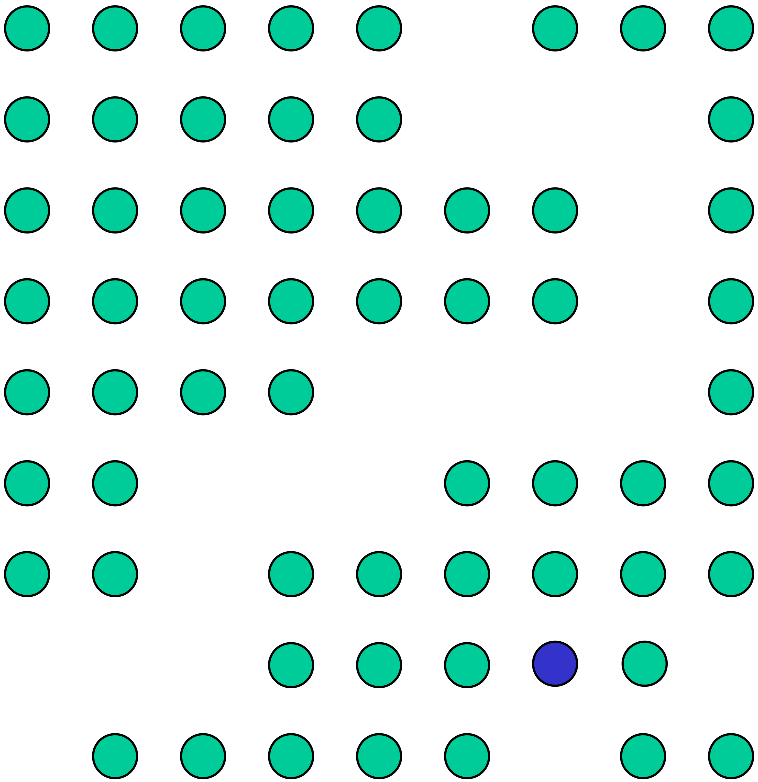
- As_4V
- $4As+V \leftrightarrow As_4V$
- $C_{cluster}=KC_{As}^4C_V$
- Important at high doping
  - $C_{chem} < 2*10^{21}/cm^3$
  - $C_{elec} < 2*10^{20}/cm^3$



Diffusion of Point Defects

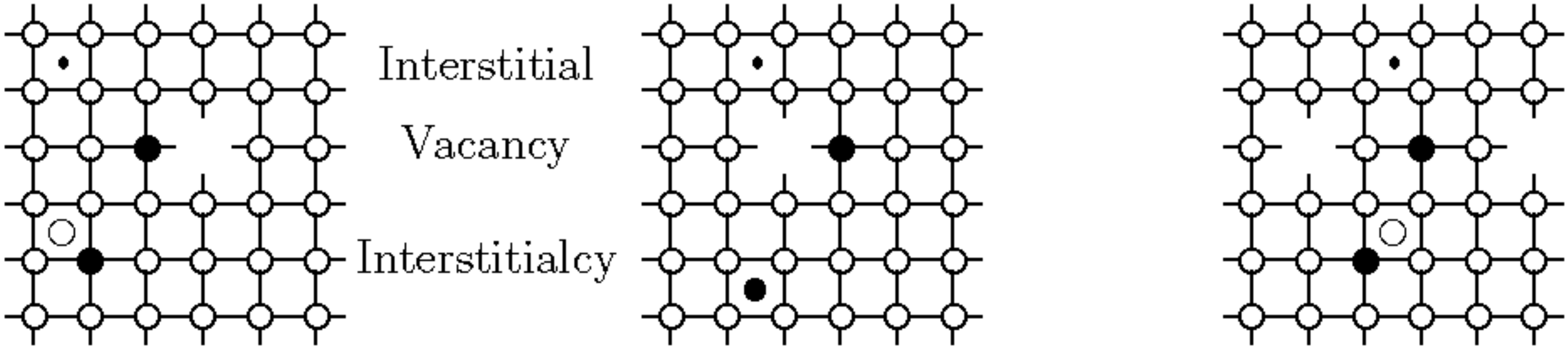


Interstitial diffusion
Self interstitials
Small foreign atoms



Vacancy diffusion
Substitutional atoms
Dopants

Point Defect Assisted Diffusion

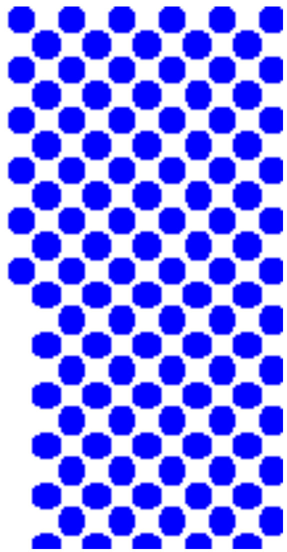


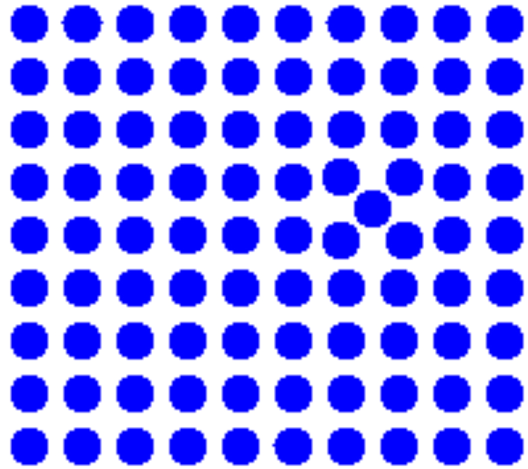
Diffusion of foreign atoms in Silicon can occur in several ways:

1. Direct Interstitial Diffusion: Small atoms, fast.
2. Vacancy assisted. Assumed for some dopants. Slow.
3. Interstitialcy – interstitial assisted diffusion. Slow.
   - Many different modes suggested.
   - Assumed for some dopants.

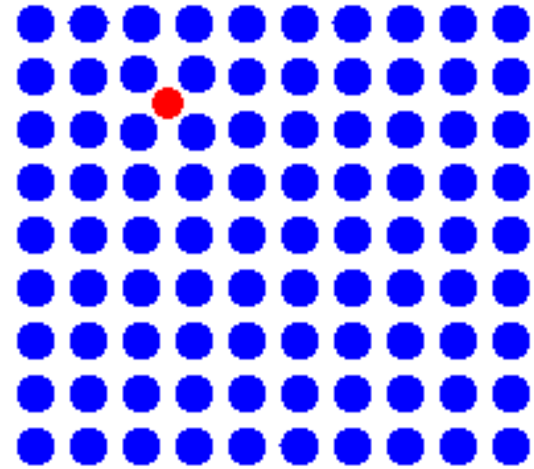
Point Defect Assisted Diffusion

Vacancy diffusion



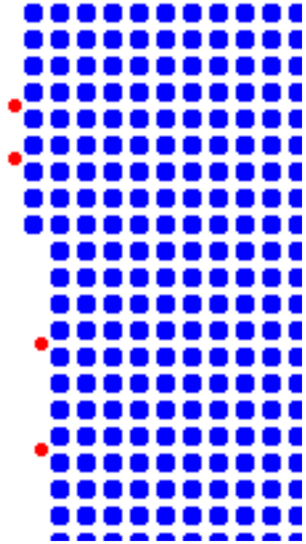


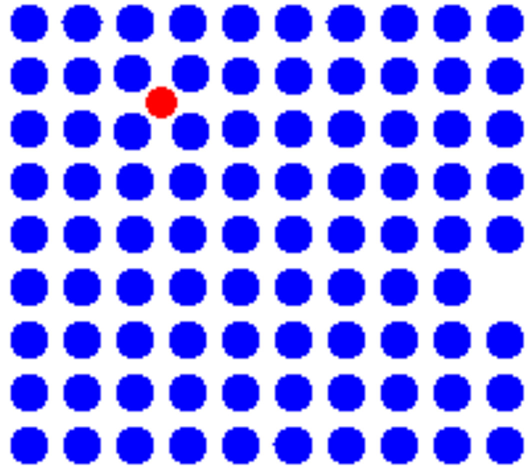
Indirect interstitial Mechanism



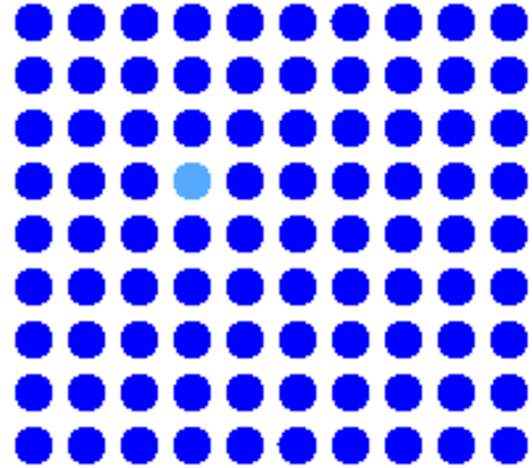
Kick-out mechanism

Direct interstitial mechanism





Frank Turnbull

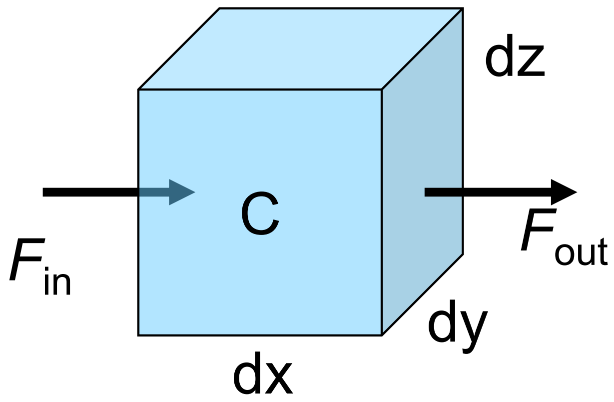


Exchange ”rotate”

Linear Predeposition - Model

<u>Purpose: a controlled dopant dose Q</u>

- Control surface concentration C_S
  - Obtain solid solubility C_{sol}
- Control temperature ($D=D(T)$)
- Control time t



1 D. Model, constant diffusivity:

Fick's 2. Law: $\dfrac{\partial C}{\partial t} = D\dfrac{\partial^2 C}{\partial x^2}$

Boundary conditions: $C(0,t) = C_S, \quad C(\infty,t) = 0$

Initial conditions: $C(x,0) = 0$

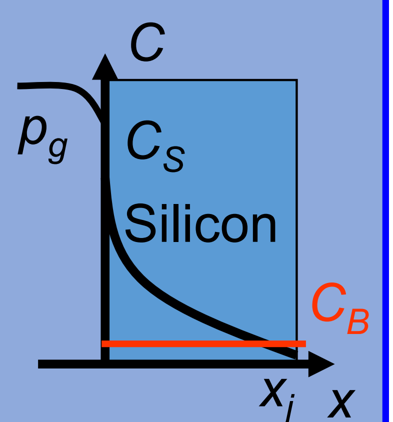
Solution: $\underline{C(x,t) = C_S \operatorname{erfc}\left(\dfrac{x}{2\sqrt{Dt}}\right)}$

Dose: $Q(t) = \int_0^\infty C(x,t)dx = \underline{\dfrac{2}{\sqrt{\pi}} C_S \sqrt{Dt}}$

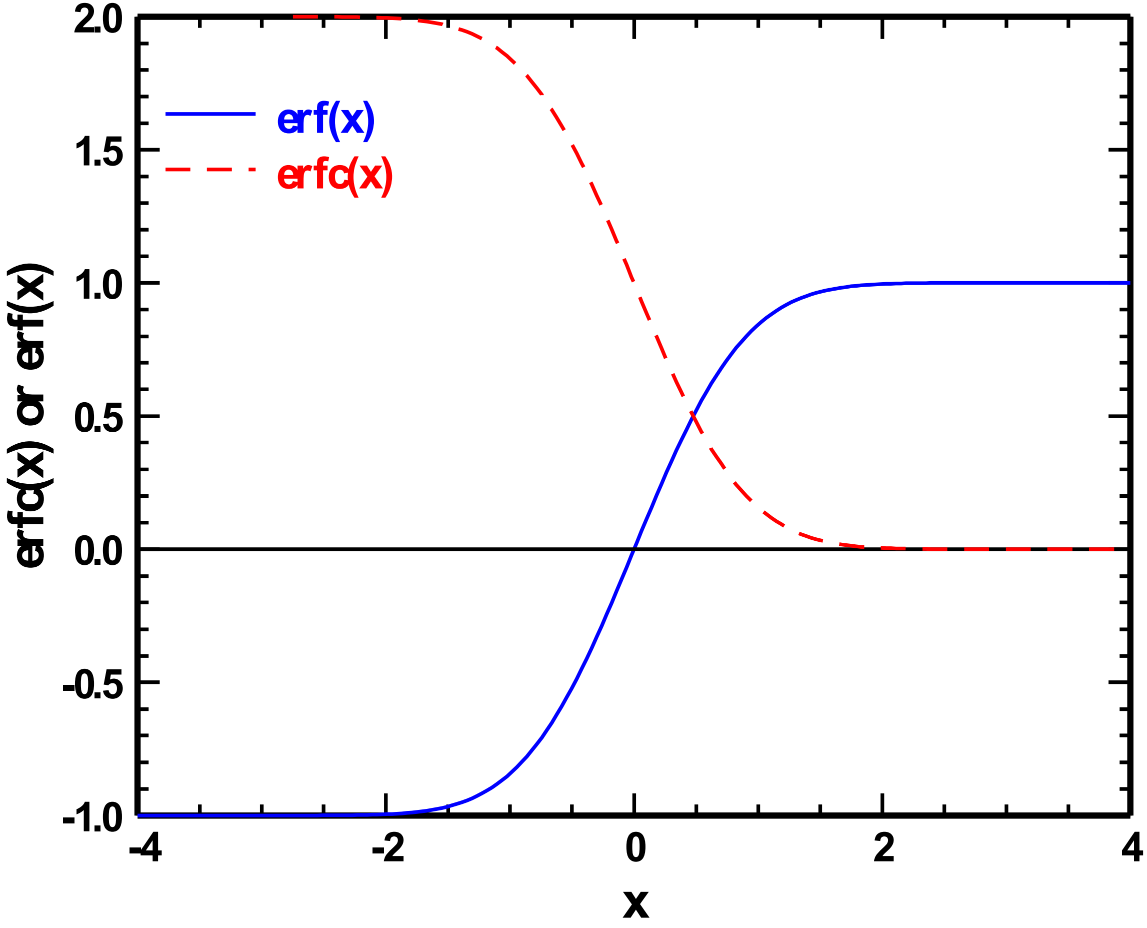
Fick's second law describes how the change in concentration in a volume element is determined by the fluxes in/out of the volume.

Junction depth :

$$C(x_j,t) = C_B \Rightarrow x_j = 2\sqrt{Dt}\operatorname{erfc}^{-1}\left(\frac{C_B}{C_S}\right)$$



Error Functions



$$\text{Definition}: \operatorname{erf}(x) \equiv \frac{2}{\sqrt{\pi}} \int_0^x \exp\left(-u^2\right) du$$

$$\text{Definition}: \operatorname{erfc}(x) \equiv 1 - \operatorname{erf}(x)$$

$$\operatorname{erf}(\pm\infty) = \pm 1, \quad \operatorname{erf}(0) = 0$$

$$\operatorname{erfc}(\infty) = 0, \quad \operatorname{erfc}(0) = 1, \quad \operatorname{erfc}(-\infty) = 2$$

$$\operatorname{erf}(x) \approx \frac{2}{\sqrt{\pi}} x, \text{for} \quad x << 1$$

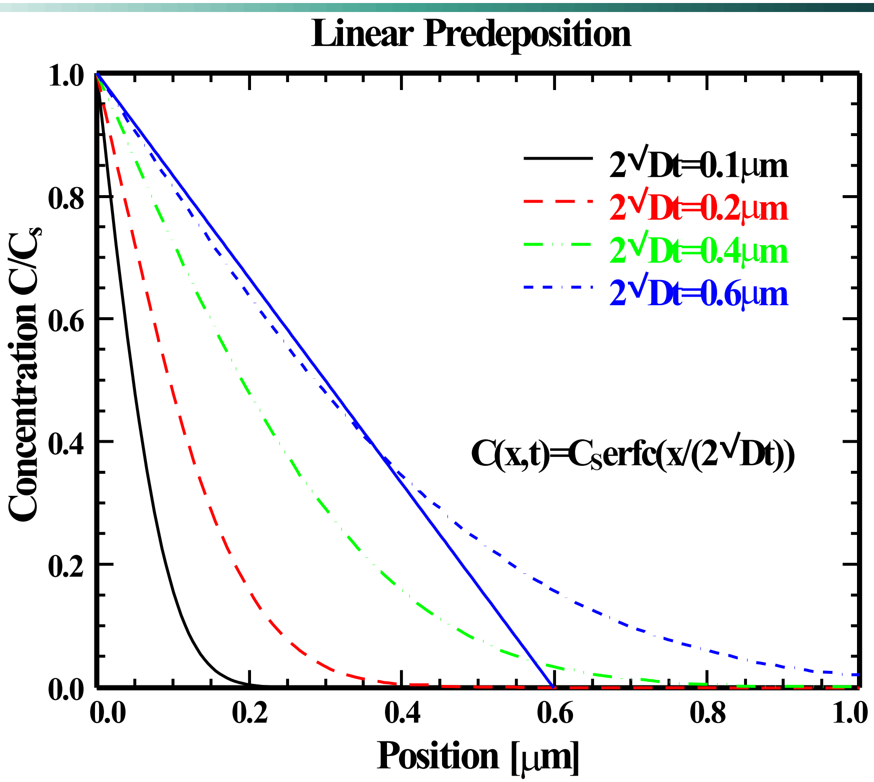
$$\operatorname{erfc}(x) \approx \frac{1}{\sqrt{\pi}} \frac{\exp\left(-x^2\right)}{x}, \text{for} \quad x >> 1$$

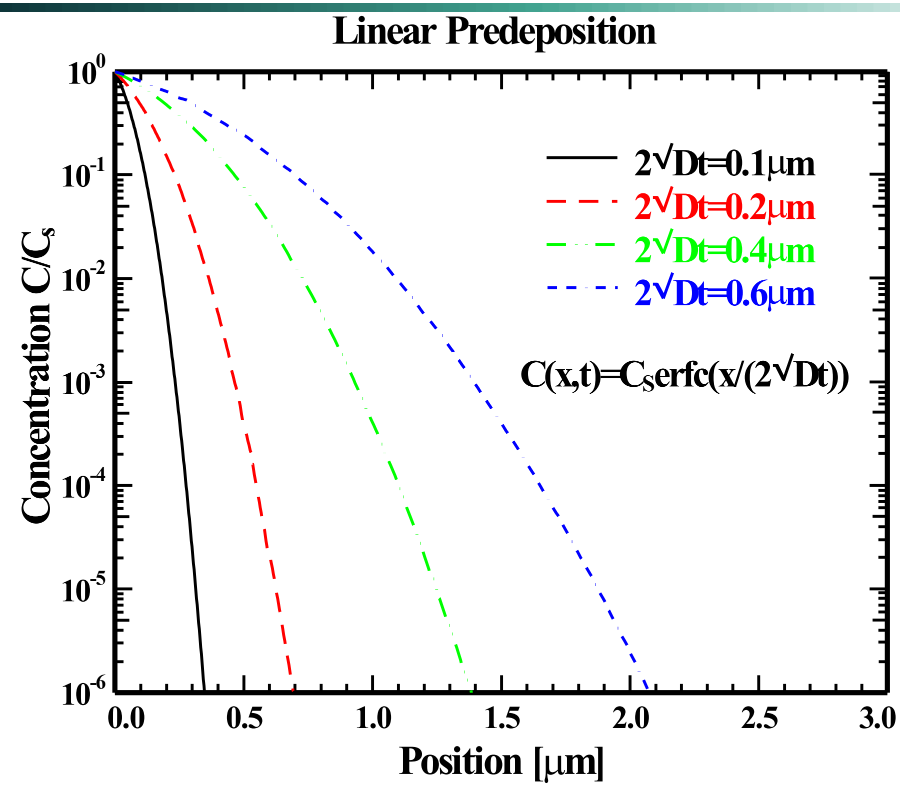
$$\frac{\partial \operatorname{erf}(x)}{\partial x} = \frac{2}{\sqrt{\pi}} \exp\left(-x^2\right)$$

$$\int_0^x \operatorname{erfc}(x')\, dx' = x \operatorname{erfc}(x) + \frac{1 - \exp\left(-x^2\right)}{\sqrt{\pi}}$$

$$\int_0^\infty \operatorname{erfc}(x)\, dx = \frac{1}{\sqrt{\pi}}$$

Predeposition Profiles – constant C_s





Almost triangular profile:

Dose: $\underline{Q = \frac{2}{\sqrt{\pi}} C_S \sqrt{Dt}} \approx C_S \sqrt{Dt}$

Surface gradient: $\underline{\frac{\partial C(0,t)}{\partial x} = \frac{C_S}{\sqrt{\pi Dt}}} \approx \frac{C_S}{2\sqrt{Dt}}$

Gradient: $\underline{\frac{\partial C(0,t)}{\partial x} = \frac{C_S}{\sqrt{\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)}$

Rapidly decaying tail:

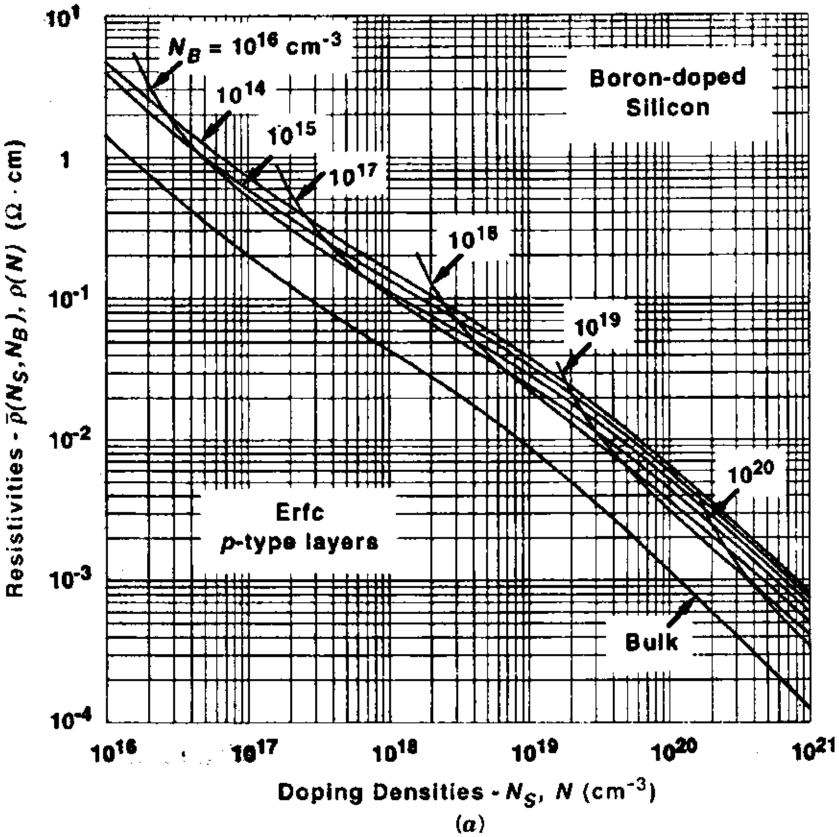
$$C(x,t) = C_S \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$

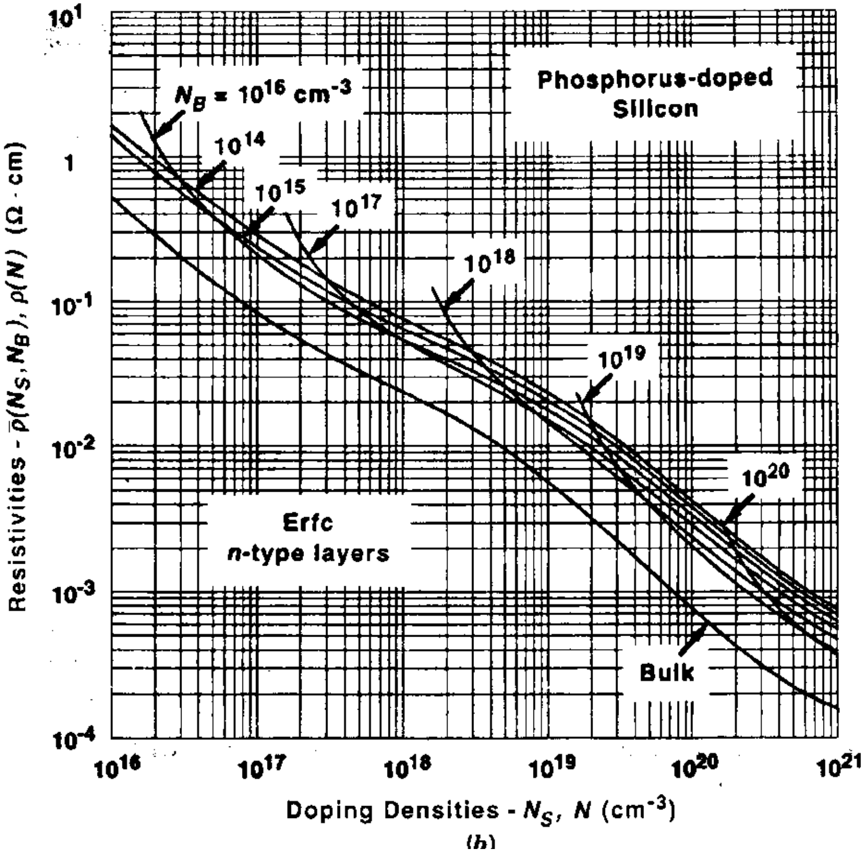
$$C(x,t) \approx C_S \frac{2\sqrt{Dt}}{\sqrt{\pi}x} \exp\left(-\frac{x^2}{4Dt}\right), \quad x >> 2\sqrt{Dt}$$

Definition: $\operatorname{erfc}(x) \equiv 1 - \frac{2}{\sqrt{\pi}} \int_0^x \exp\left(-u^2\right) du$

Average Resistivity, Predep

Irvins Graphs





$$\boxed{\bar{\sigma} = \frac{1}{\bar{\rho}} = \frac{1}{x_j}\int_0^{x_j} \sigma\, dx \Rightarrow R_{\mathbf{sh}} = \frac{\bar{\rho}}{x_j} = \frac{1}{\bar{\sigma} x_j}}$$

Linear Drive-in Model

Purpose: Redistribute a fixed dose Q

- Heat treatment with closed surface (oxide covered)
- Control temperature *T*, (*D=D(T)*)
- Control time *t*

1 D. Model, constant diffusivity:

Fick's 2. Law: $\dfrac{\partial C}{\partial t} = D\dfrac{\partial^2 C}{\partial x^2}$

Boundary conditions: $\dfrac{\partial C(0,t)}{\partial x} = 0, \quad C(\infty,t) = 0$

Initial conditions: $C(x,0) = C_{\text{Predep}}(x) \approx Q\,\delta(x)$

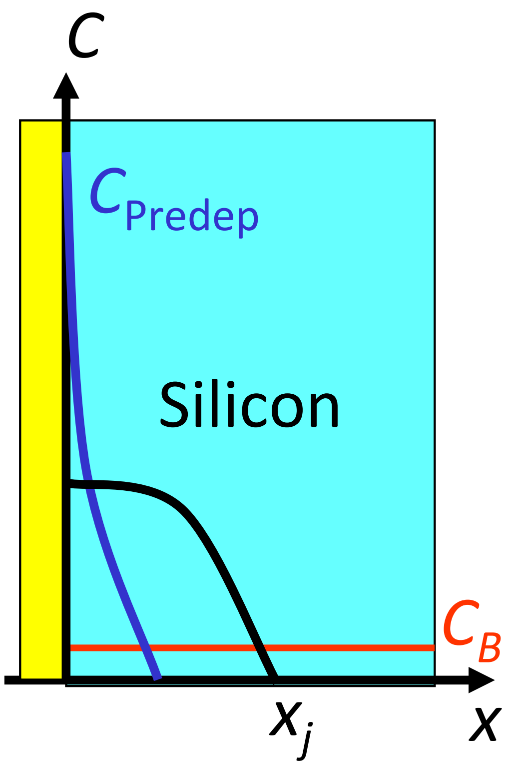
Solution, a Gaussian: $\underline{C(x,t) = \dfrac{Q}{\sqrt{\pi D t}}\exp\left(-\dfrac{x^2}{4Dt}\right)}$

Surface concentration: $\underline{C_S(t) = \dfrac{Q}{\sqrt{\pi D t}}}$

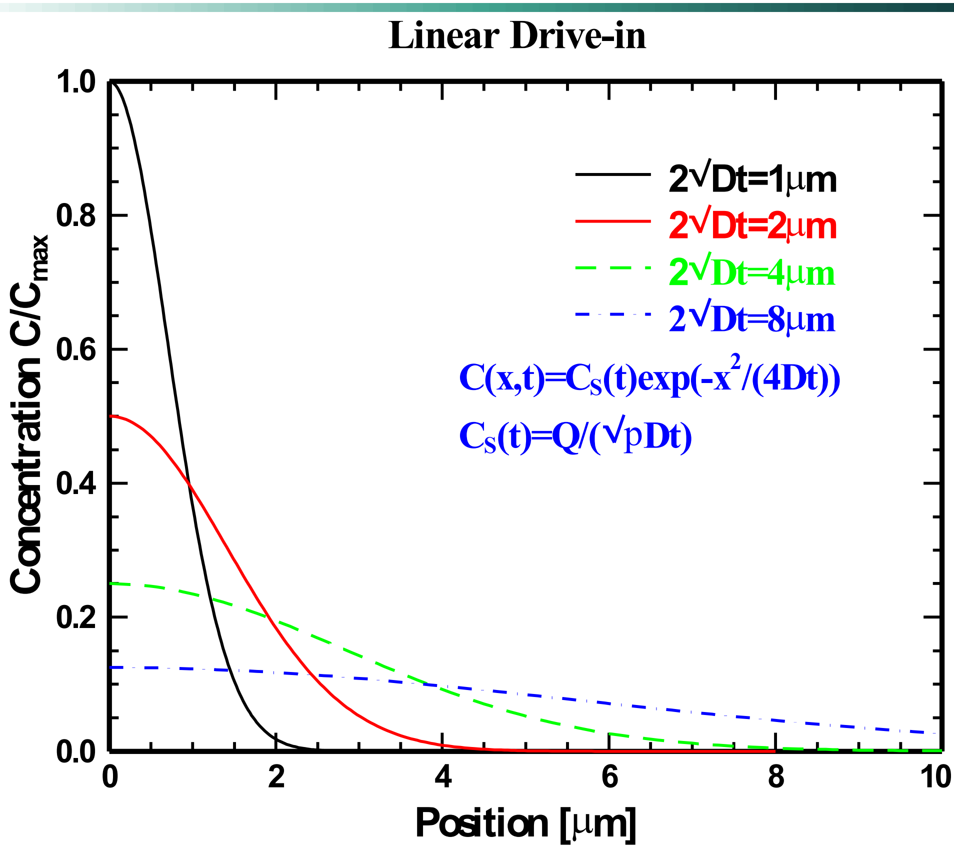
Junction depth: $C(x_j,t) = C_B \Rightarrow x_j = 2\sqrt{Dt}\sqrt{\ln\left(\dfrac{C_S(t)}{C_B}\right)}$

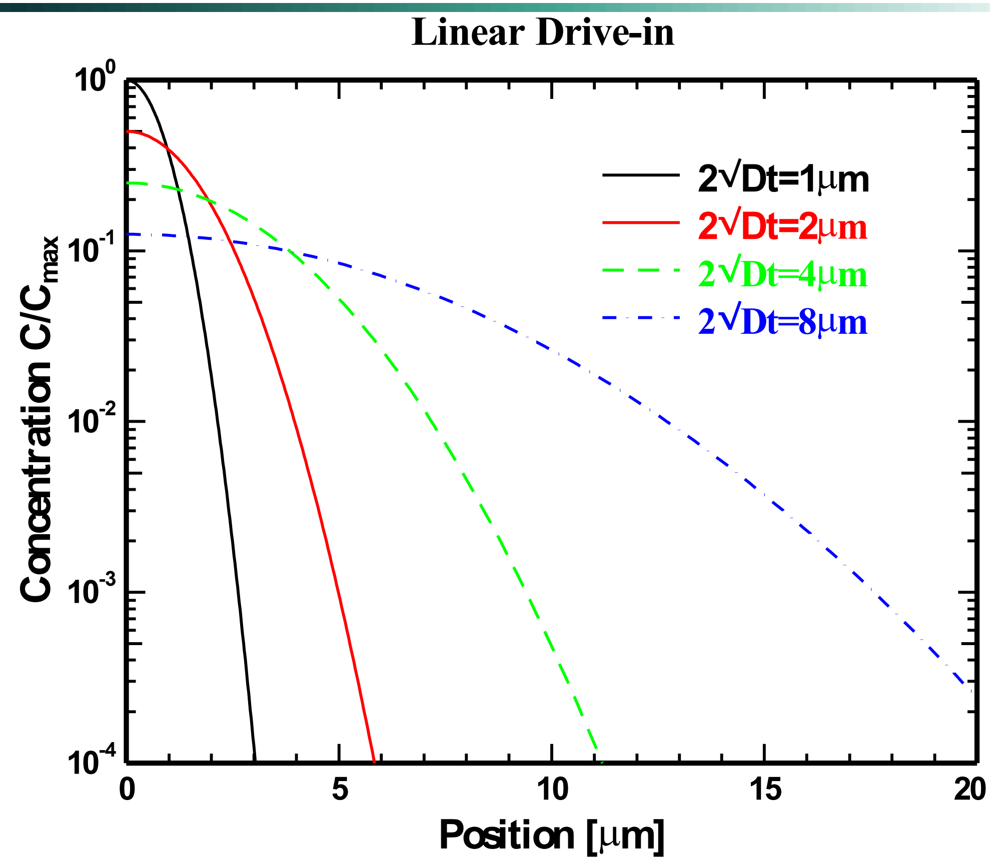
Repeated Drive-in's

$$(Dt)_{\text{eff}} = \sum Dt = \int D\,dt$$



Drive-in Profiles: constant Q_T

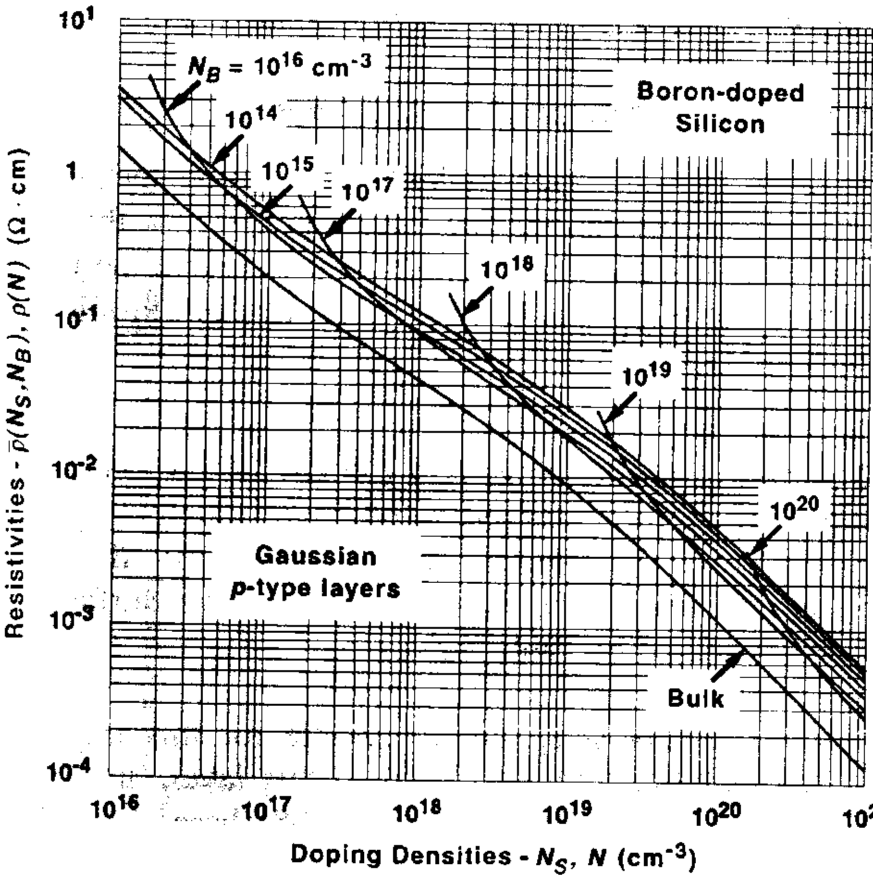




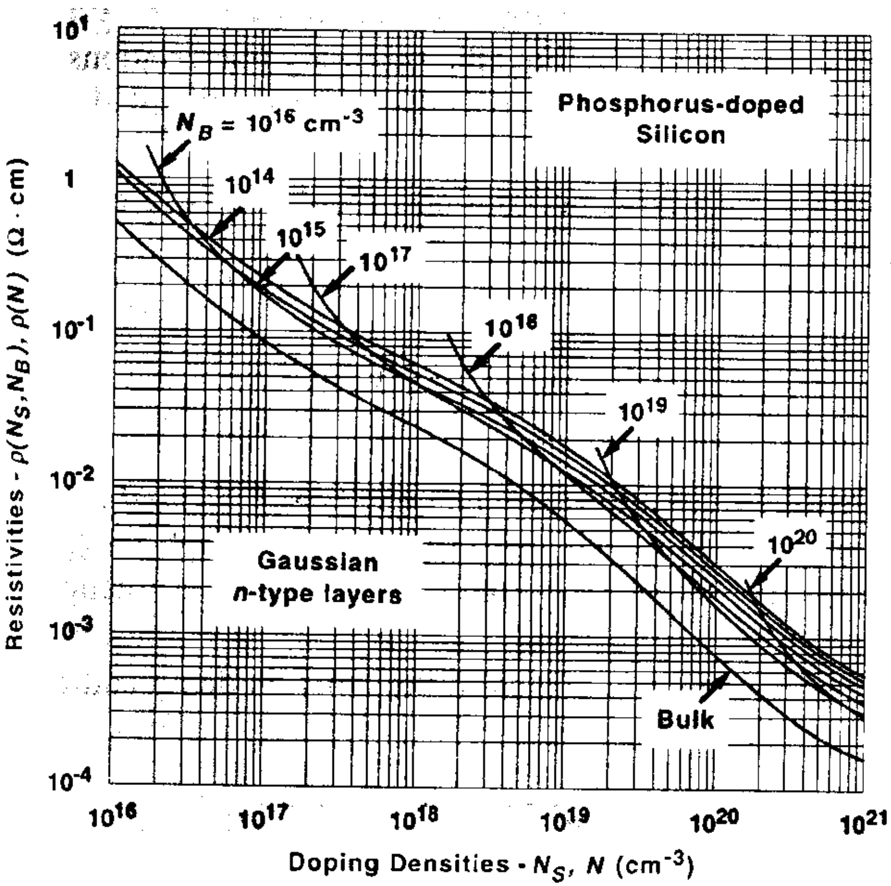
- Zero gradient at the surface
- Time decaying surface concentration
- Rapidly decaying tail

Average Resistivity, Drive-in

Irvins Graphs



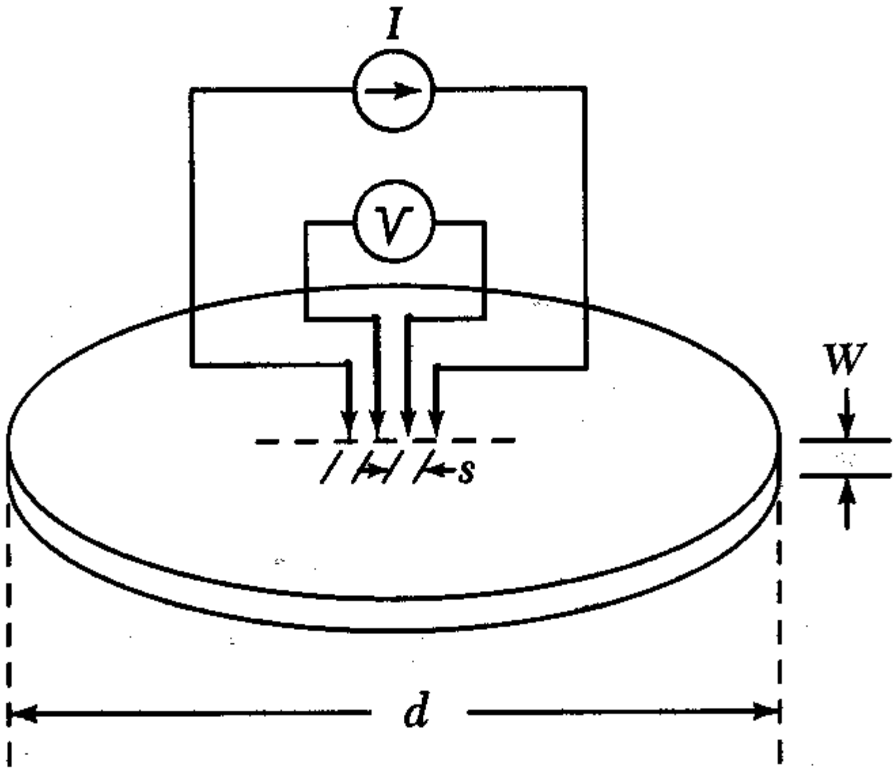
(a)

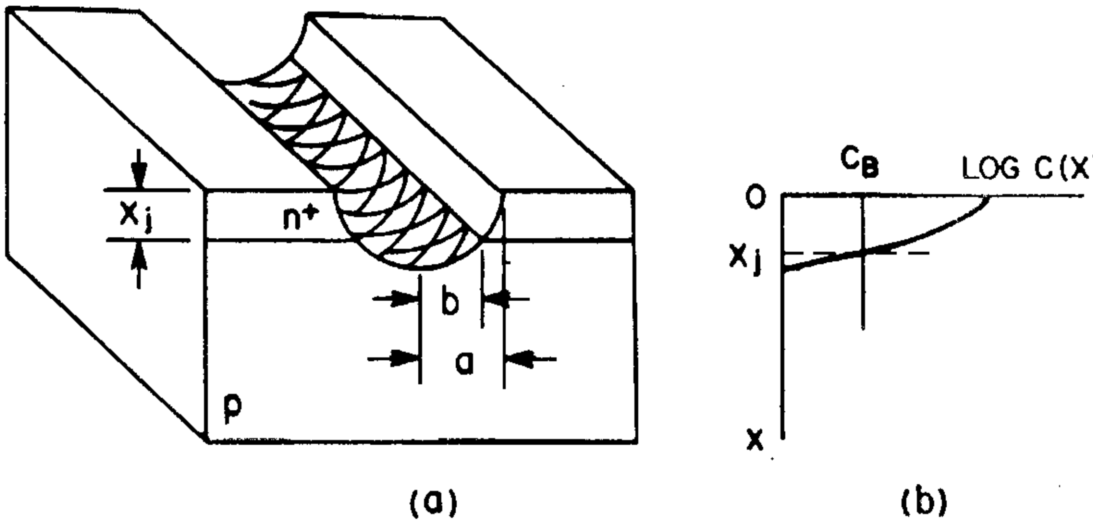


(b)

$$\bar{\sigma} = \frac{1}{\bar{\rho}} = \frac{1}{x_j}\int_0^{x_j} \sigma\, dx \Rightarrow R_{\mathbf{sh}} = \frac{\bar{\rho}}{x_j} = \frac{1}{\bar{\sigma} x_j}$$

Evaluation of Diffused Layers



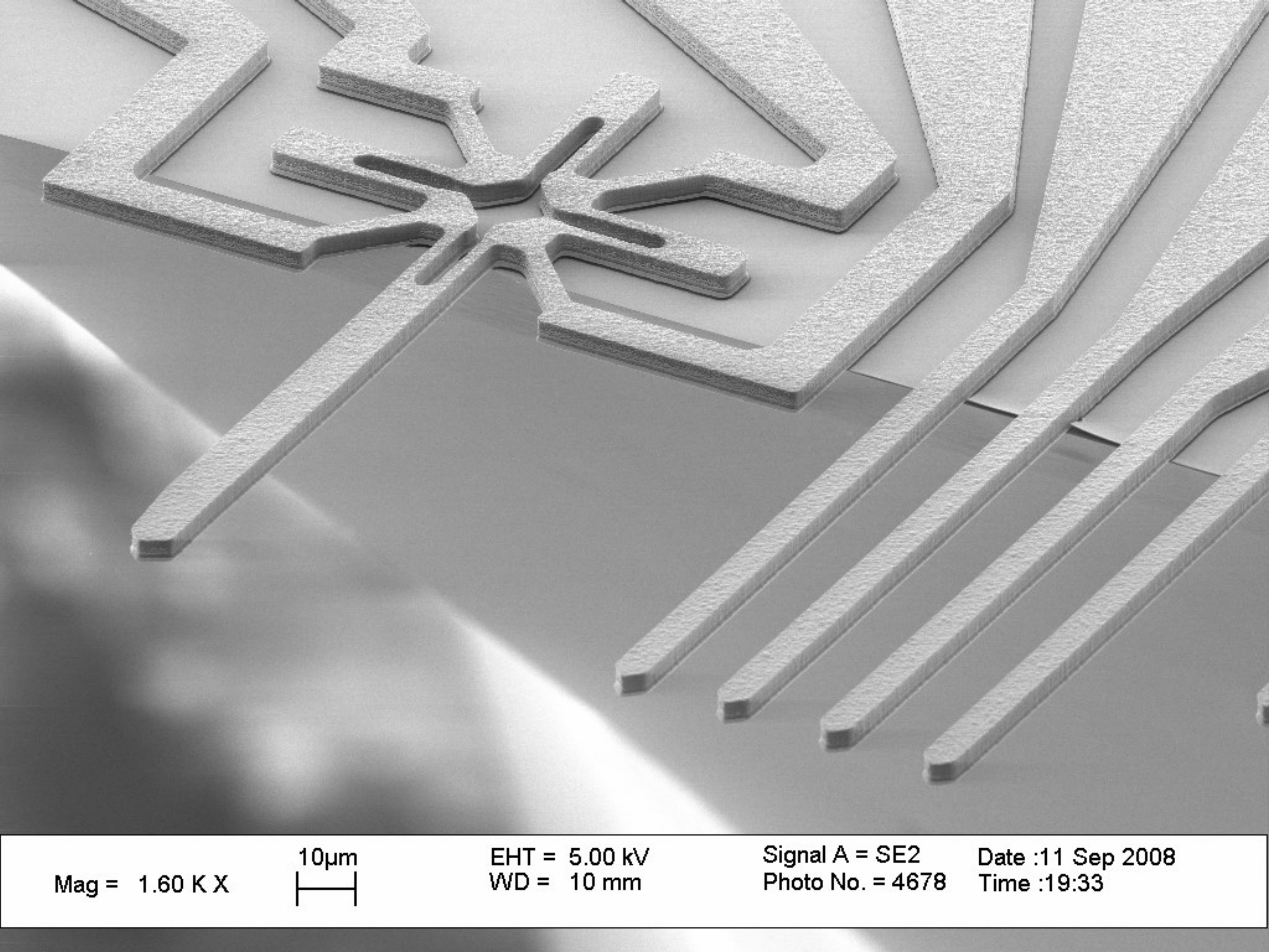


Junction depth measurement.
Groove, mechanical grinding.
Stain p-region (HNO_3+HF+hv)

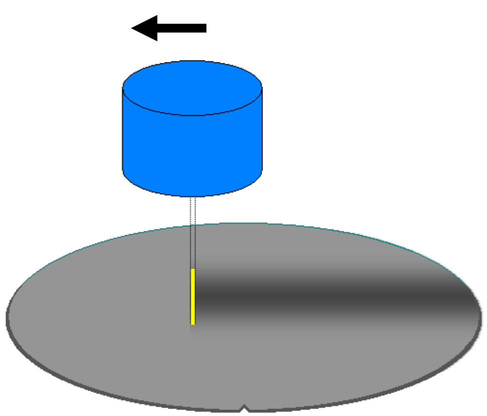
Four Point Probe:

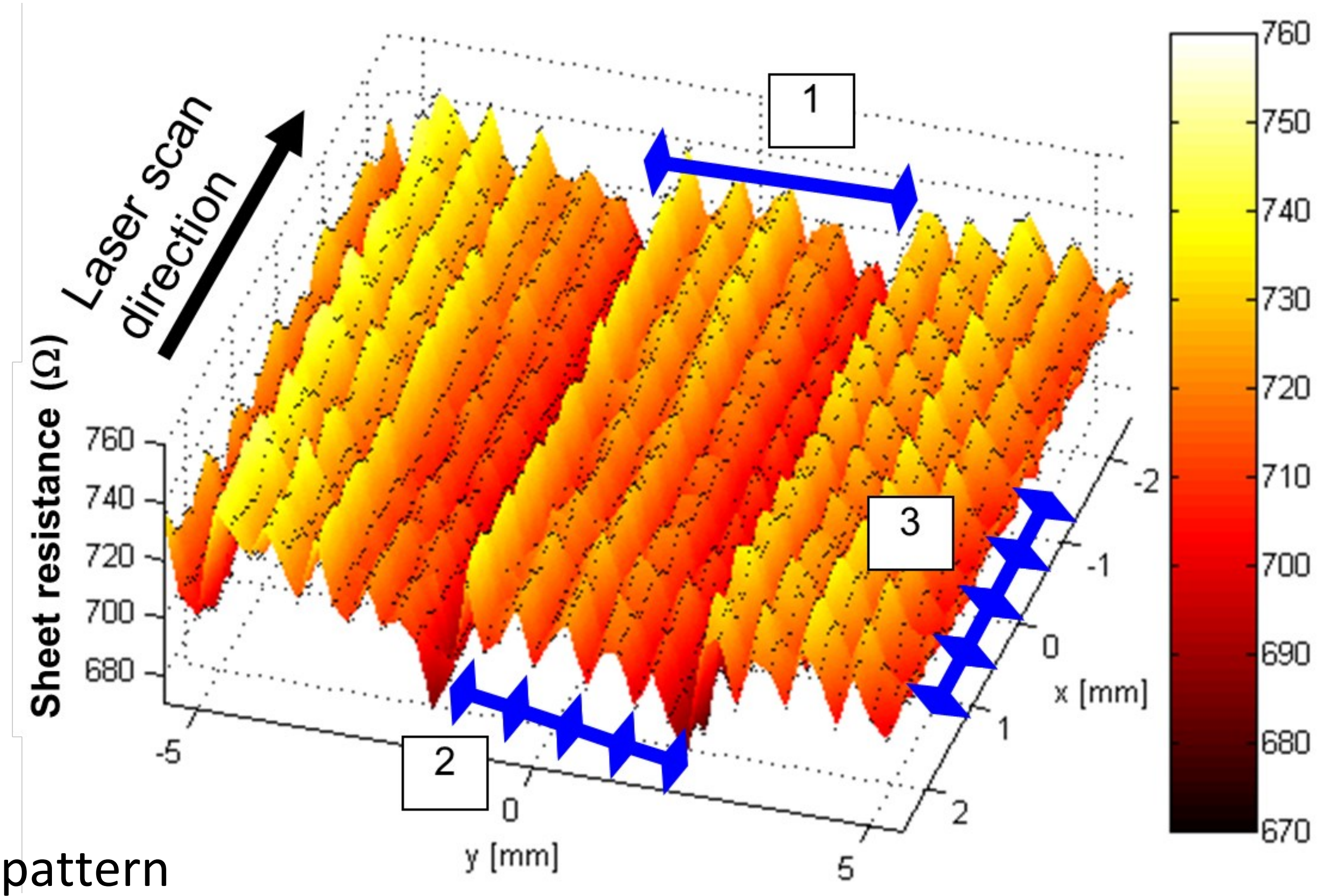
$$R_{\mathrm{sh}} = \frac{\pi}{\ln 2}\frac{V}{I} = 4.532\frac{V}{I}$$

Simple low-tech measurements
Four point probe a routine check.
Groove & stain useful for large x_j.


Mag = 1.60 K X
10µm
EHT = 5.00 kV
WD = 10 mm
Signal A = SE2
Photo No. = 4678
Date :11 Sep 2008
Time :19:33

Laser annealed USJ: Sheet resistance





1. Stitching pattern
2. Spatial laser power density varitions
3. Temporal laser power fluctuations

D. H. Petersen *et al*. JVST B **26**, 362 (2008).
W. Vandervorst *et al.* MRS 2008 Spring meeting (2008).

Temperature Effect

Intrinsic diffusion coefficient increases as temperature increases

$$\boxed{D = D_o \exp\left(-\frac{E_a}{kT}\right)}$$

• E_a for interstitial diffusion is the energy required for dopants to move from one intersitial site to another (around 0.5 to 2 eV)

• E_a for vacancy diffusion is related to the energies of dopant motion and vacancy formation (around 3 to 5 eV)

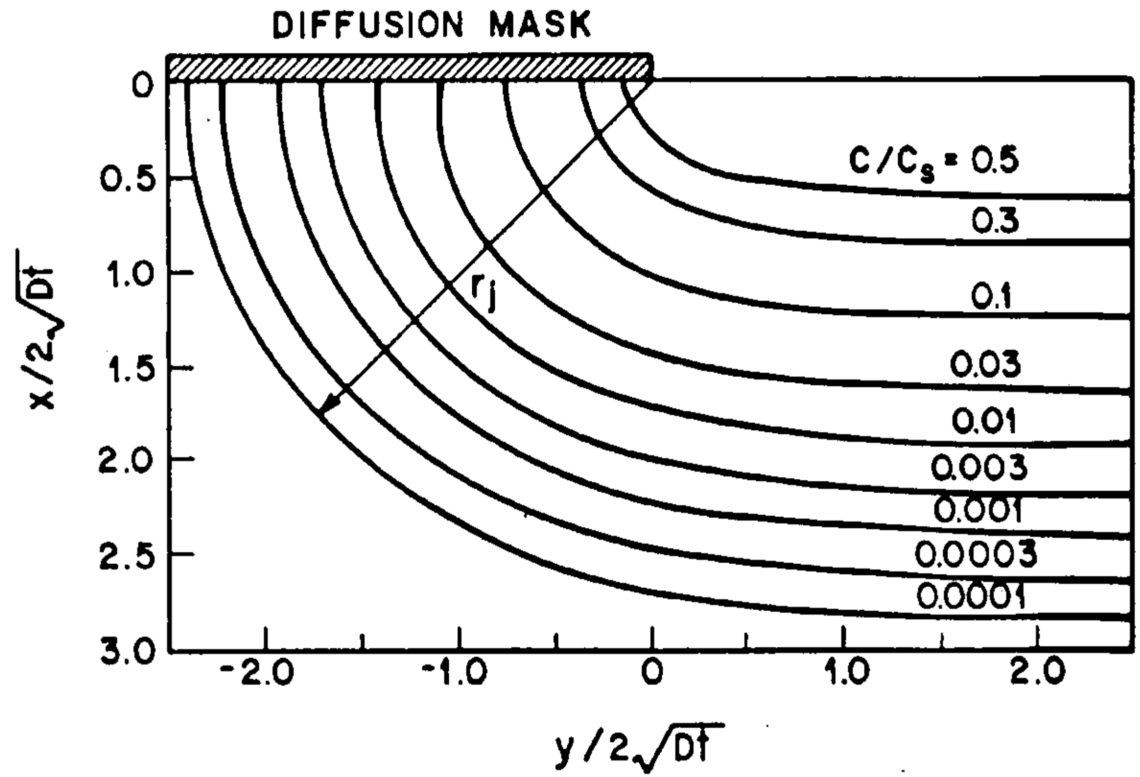
	Si	B	In	As	Sb	P	Units
D^0	560	1.0	1.2	9.17	4.58	4.70	$cm^2\ sec^{-1}$
E_A	4.76	3.5	3.5	3.99	3.88	3.68	eV

• Note that n_i is very large at process temperatures, so "intrinsic" actually applies under many conditions.

• Note the "slow" and "fast" diffusers. Solubility is also an issue in choosing a particular dopant.

Masking

- Required Mask Thickness in Predeposition?
- Dopant Profile after Predeposition & Drive-in? A 2D / 3D problem.



Dopant iso-concentration contours after a masked **Predeposition**. Lateral junction depth ~ 80% of vertical junction depth .

Required Mask Thickness

Constant surface concentration
& Interface segregation
Diffusion problem: Make x_j=0

$$\text{Fick's 2. Law: } \frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i$$

$$\text{Initial: } C(x,0) = 0$$

$$\text{Boundary: } C(\infty,t) = 0, \quad C(-x_{ox},t) = C_0$$

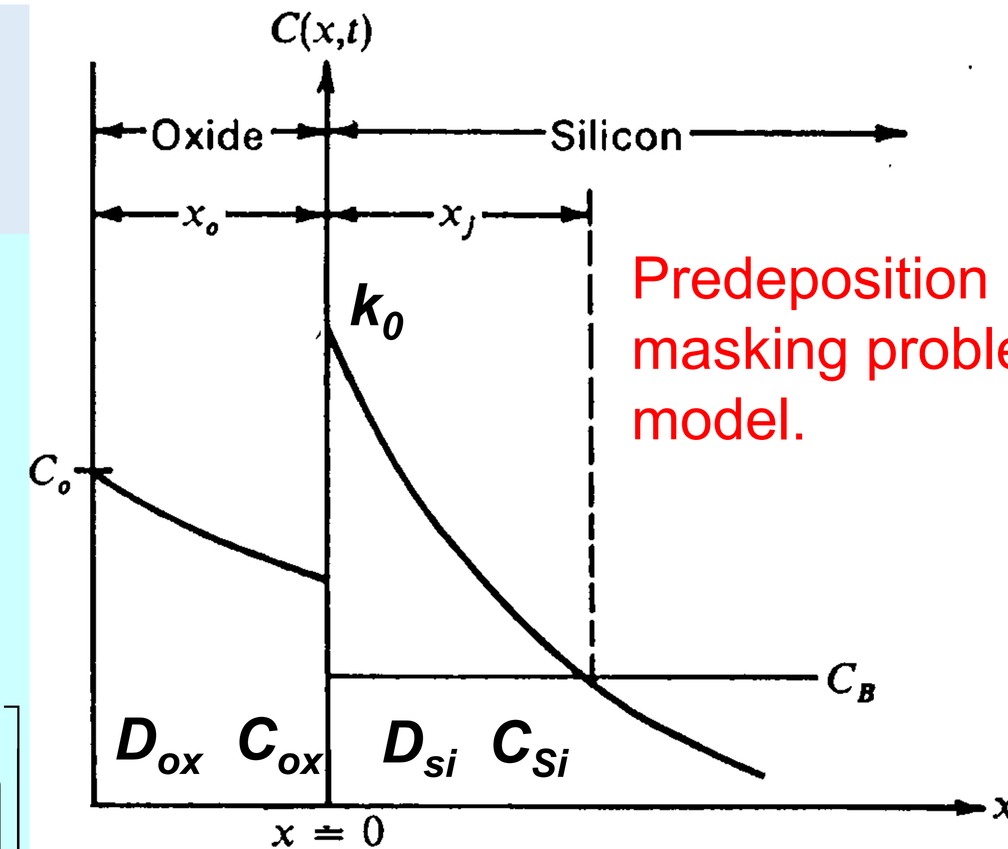
$$\text{Interface segregation: } C_{Si}(0,t) = k_0 C_{ox}(0,t)$$

$$\text{Continuous flux: } D_{ox}\nabla C_{ox} = D_{Si}\nabla C_{Si}$$

Approximate solution:

$$C_{Ox} \approx C_0 \left[\operatorname{erfc}\left(\frac{x_{ox}+x}{2\sqrt{D_{ox}t}}\right) - \frac{k_0 - \frac{D_{ox}}{D_{Si}}}{k_0 + \frac{D_{ox}}{D_{Si}}} \operatorname{erfc}\left(\frac{x_{ox}-x}{2\sqrt{D_{ox}t}}\right) \right]$$

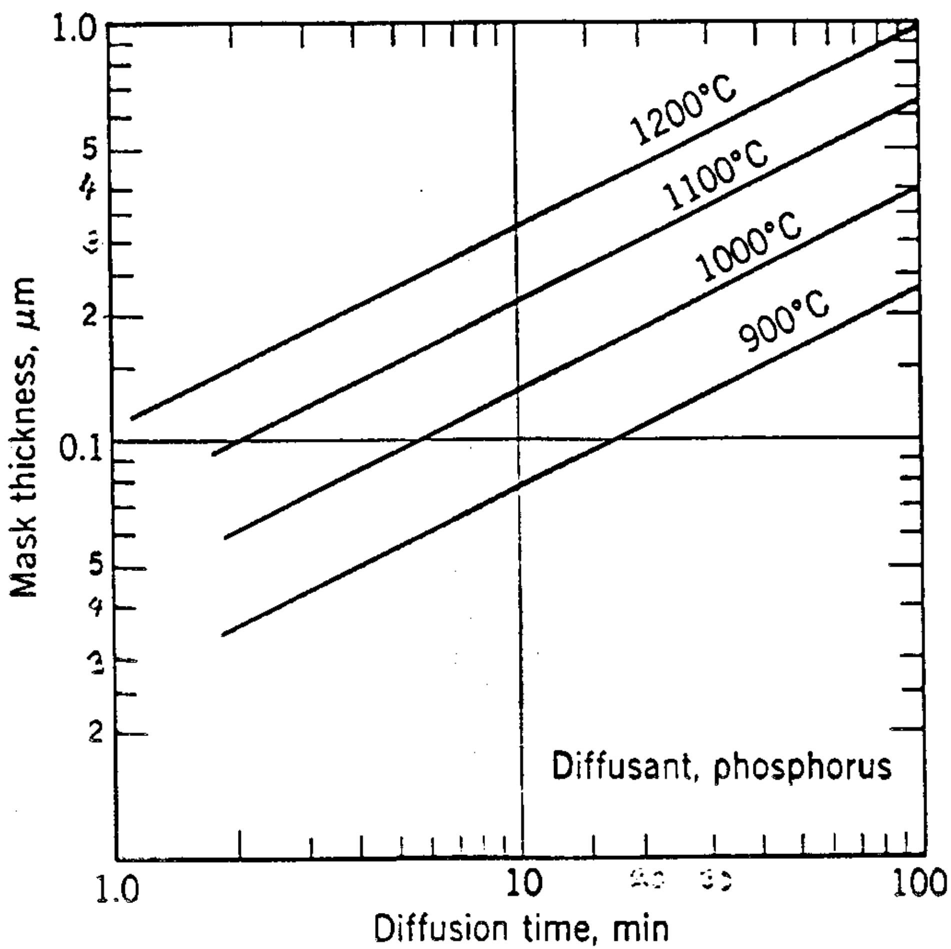
$$C_{Si} \approx C_0 \frac{2k_0 \frac{D_{ox}}{D_{Si}}}{k_0 + \frac{D_{ox}}{D_{Si}}} \operatorname{erfc}\left(\frac{x_{ox}}{2\sqrt{D_{ox}t}} + \frac{x}{2\sqrt{D_{Si}t}}\right)$$

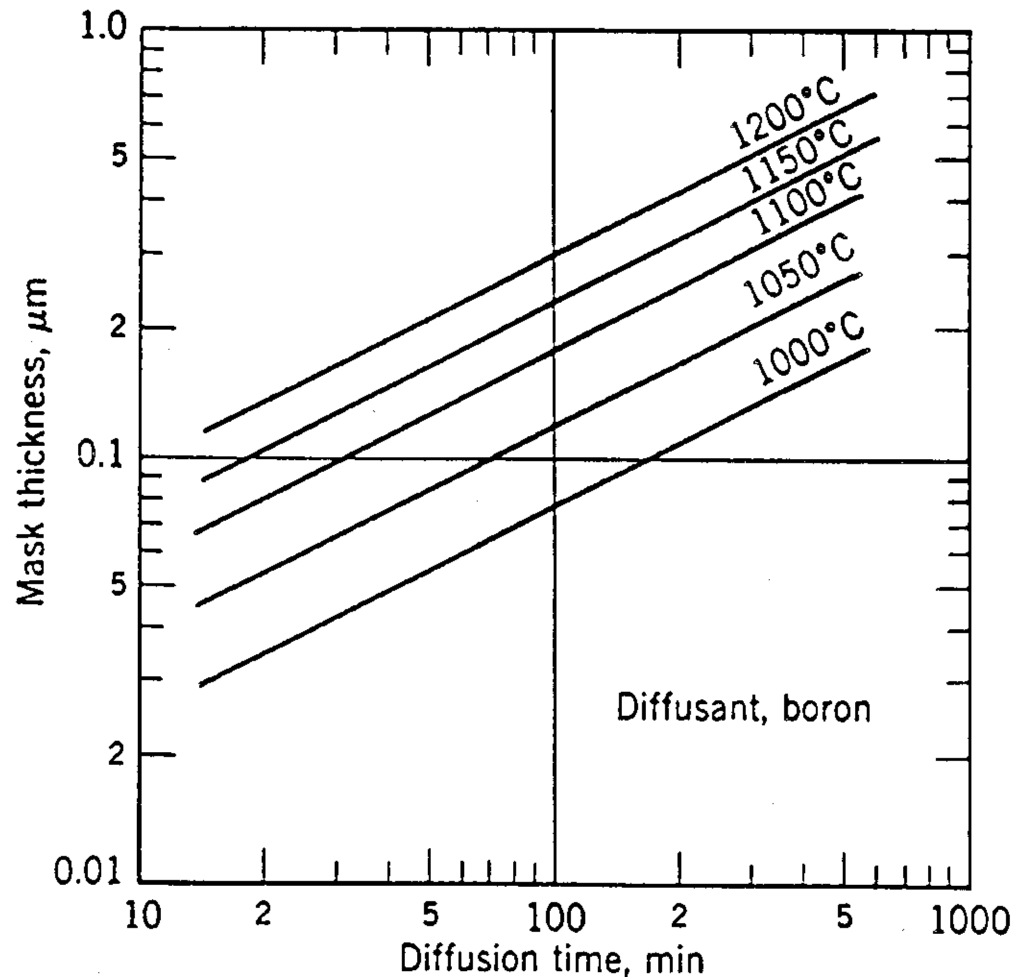


Predeposition masking problem model.

$$x_{ox} > 2\sqrt{D_{ox}t}\ \operatorname{argerfc}\left(\frac{C_B}{C_0} \frac{k_0 + \frac{D_{ox}}{D_{Si}}}{2k_0 \frac{D_{ox}}{D_{Si}}} \right)$$

Required Mask Thickness

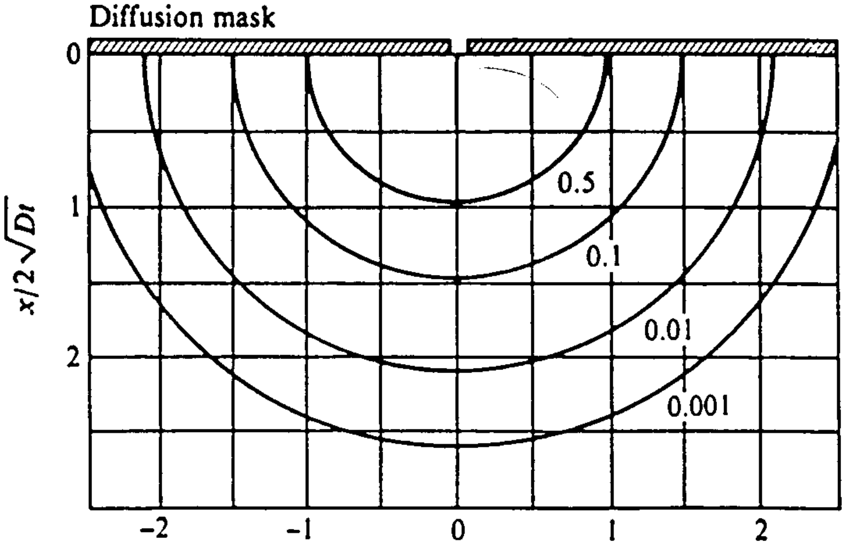




Thick masks due to high diffusivity and $\boldsymbol{k_0=10}$.

Thin masks due to low Diffusivity and $\boldsymbol{k_0=0.3}$.
Note, most graphs are wrong!

Drive-in Profiles



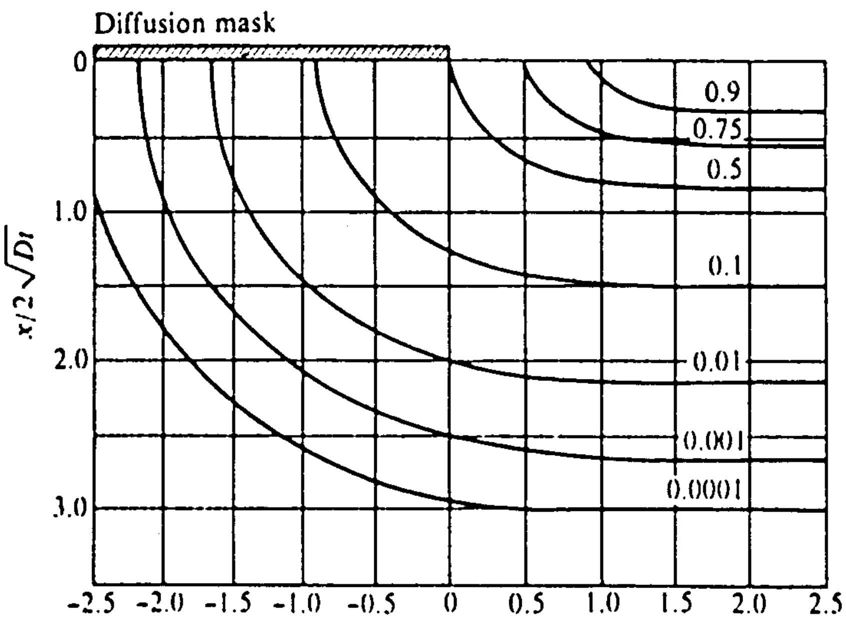
Drive - in : Line source

Fick's 2. Law : $\frac{\partial C}{\partial t} = D\nabla^2 C = D\left(\frac{\partial^2 C}{\partial r^2} + \frac{\partial C}{r\partial r}\right)$

Initial : $C(x,y,0) = Q'\delta(x)\delta(y)$

Boundary : $C(r \to \infty, t) = 0, \quad \frac{\partial C(0,y,t)}{\partial x} = 0$

Gaussian Solution : $C(r,t) = \frac{Q'}{2\pi Dt}\exp\left(-\frac{r^2}{4Dt}\right)$



Drive-in: Half plane source

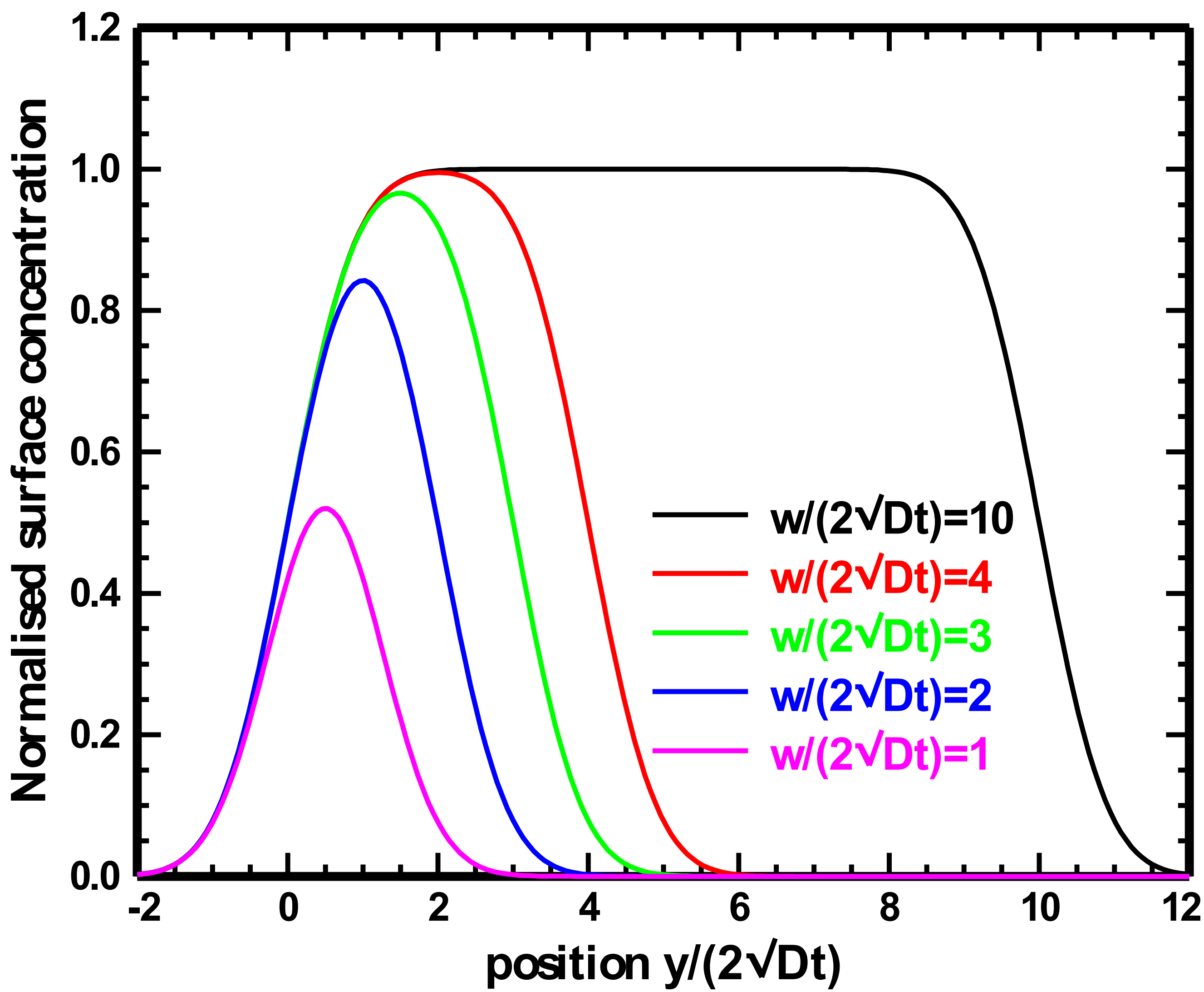
Fick' s 2. Law: $\frac{\partial C}{\partial t} = D\nabla^2 C = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right)$

Initial: $C(x,y,0) = Q\delta(x)h(y)$

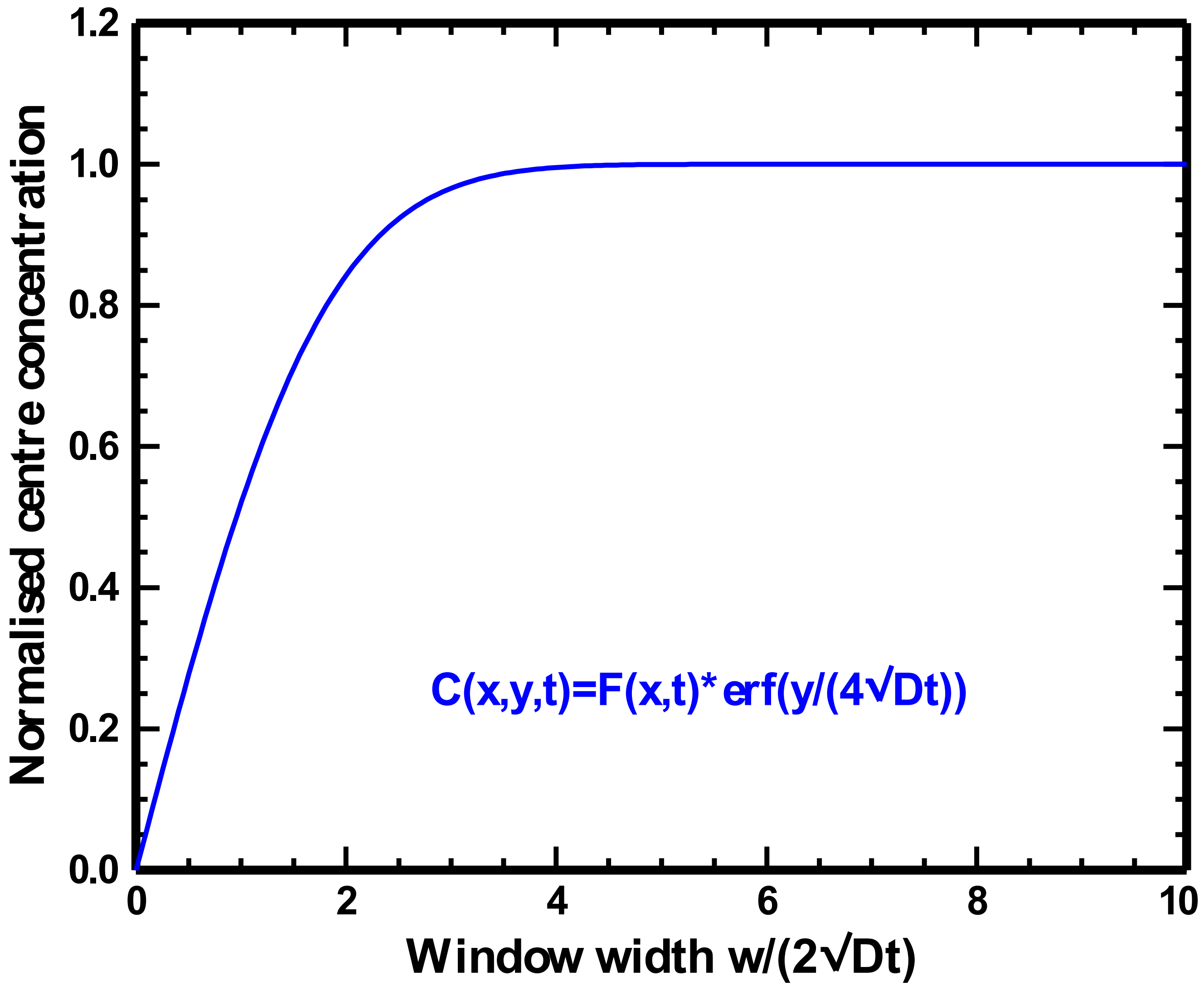
Boundary: $C(x \to \infty, y, t) = 0, \quad \frac{\partial C(0,y,t)}{\partial x} = 0$

Solution: $C(x,y,t) = \frac{Q}{\sqrt{\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right)\frac{\mathrm{erfc}\left(\frac{-y}{2\sqrt{Dt}}\right)}{2}$

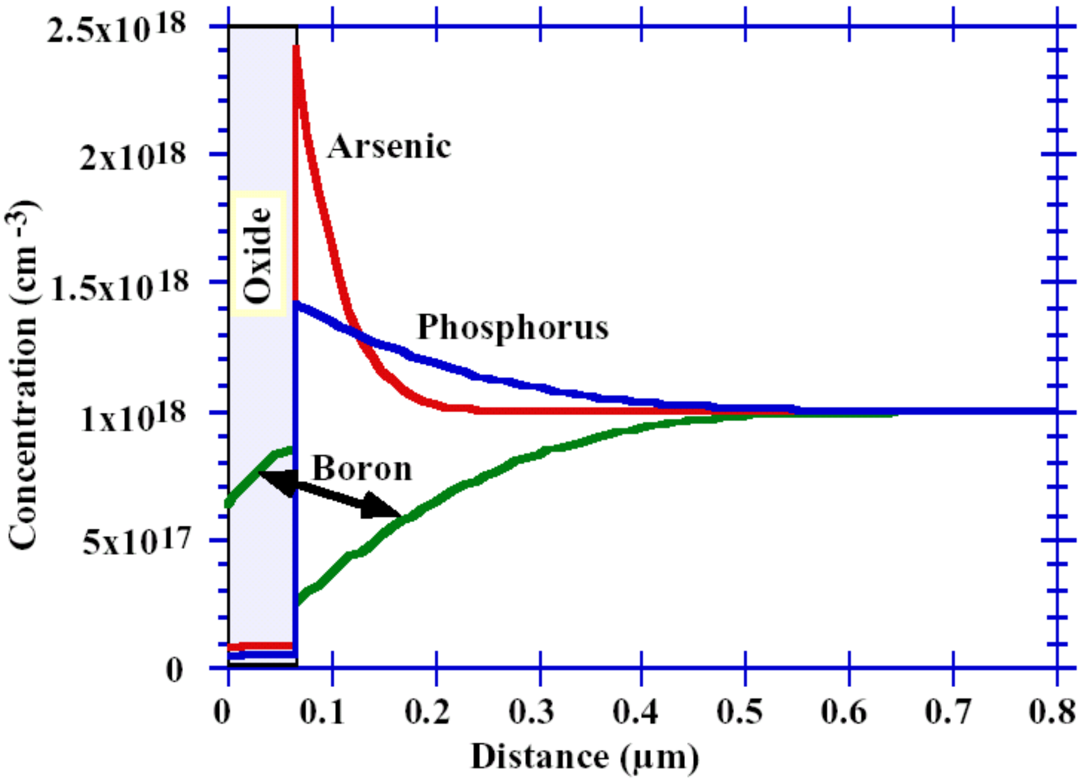
Masked Drive-in Diffusion

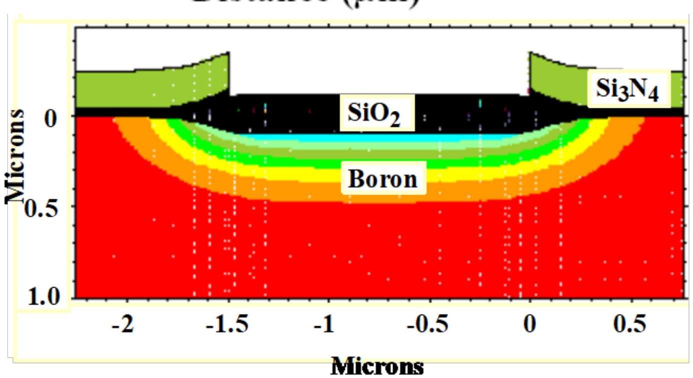


Masked Drive-in Diffusion



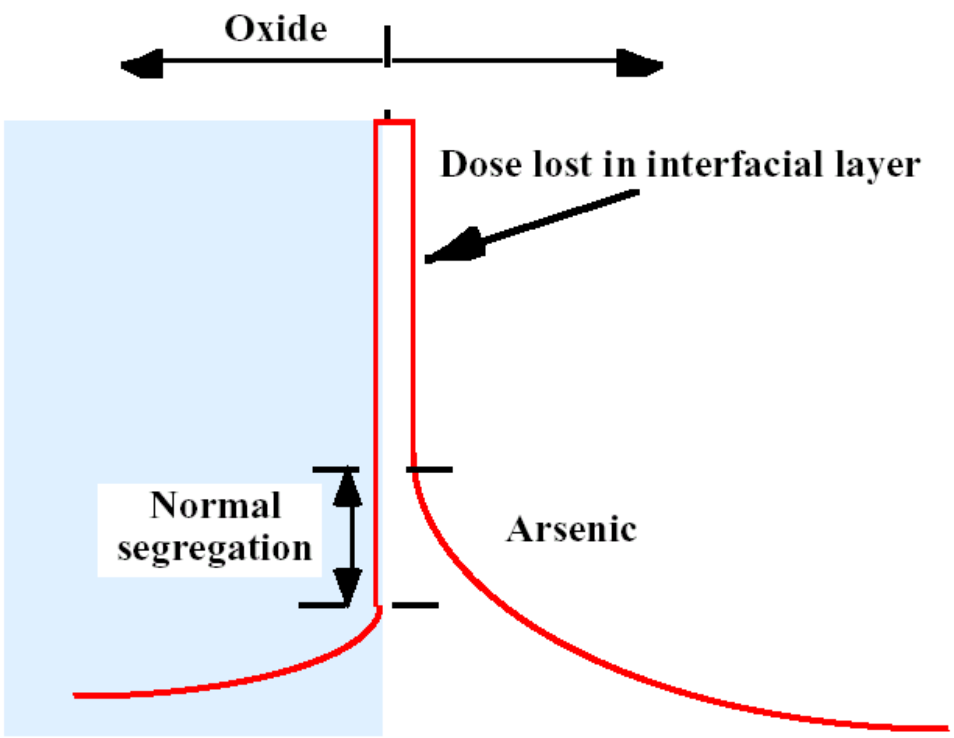
Dopant Segregation

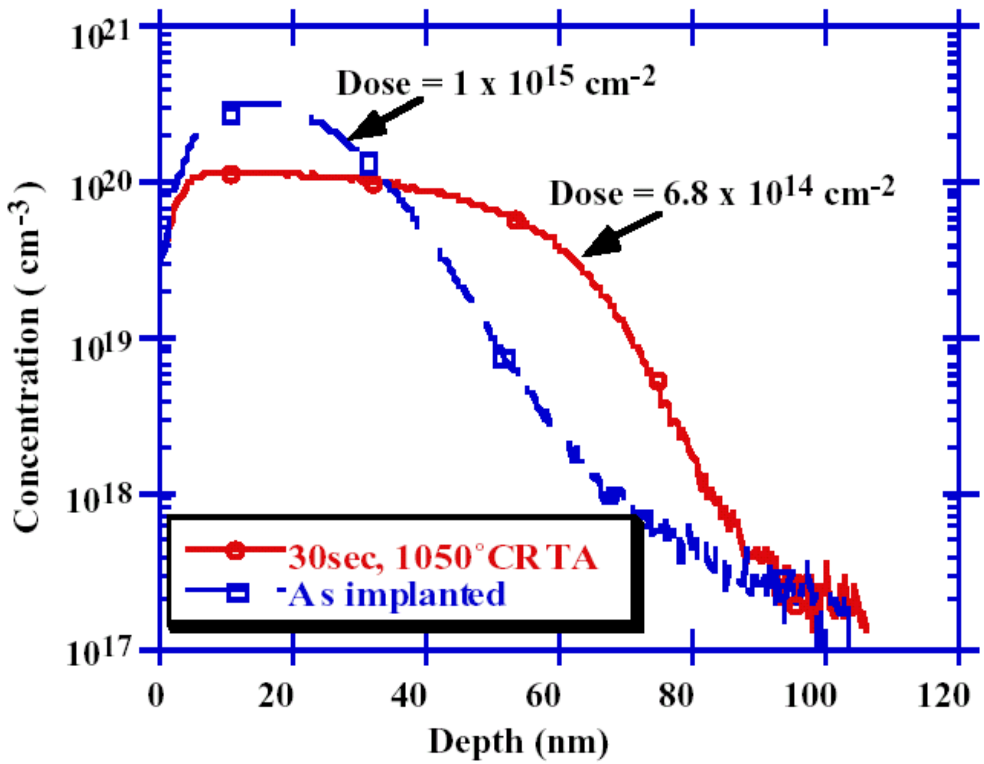




- **Solubility in oxide and silicon different, (2 Phases):**
  - **Equilibrium: $C_{Si}=k_0C_{Ox}$**
  - **k_0: Segregation coefficient**
  - **B: $k_0 \approx 0.3$**
  - **P, As, Sb: $k_0 \approx 10$**
- **Diffusivity in oxide and silicon different**
  - **Mostly: $D_{Si} >> D_{Ox}$**
  - **Dopant redistribution during oxidation**
  - **Complicated moving boundary condition @ interface**

Interfacial Dopant Pile Up

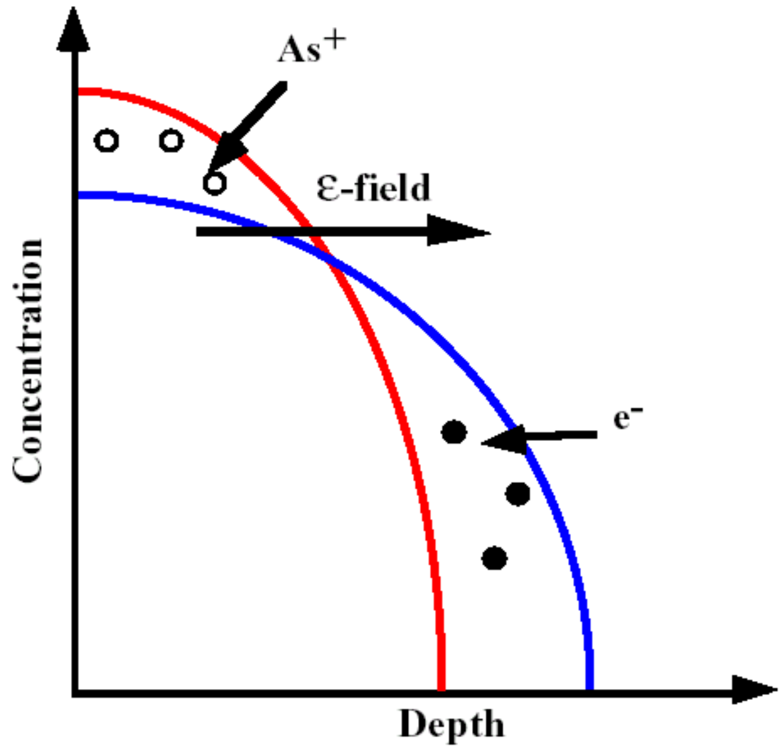


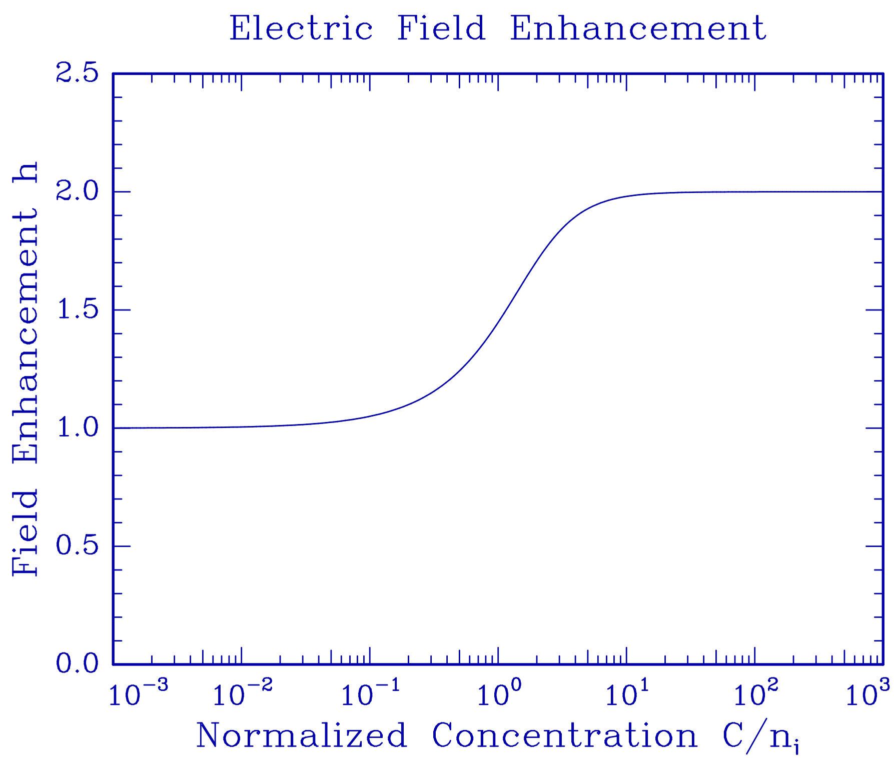


The surface is really a separate phase.
A very different solubility might apply.
Inactive dopant may accumulate ~ 0.5ML.

Experiment: Implanted annealed As
Dopant loss during anneal ~30%
Important for group V elements.

Electric Field Effects





Ionised Dopants, Dopant Gradients & Fast Electrons:

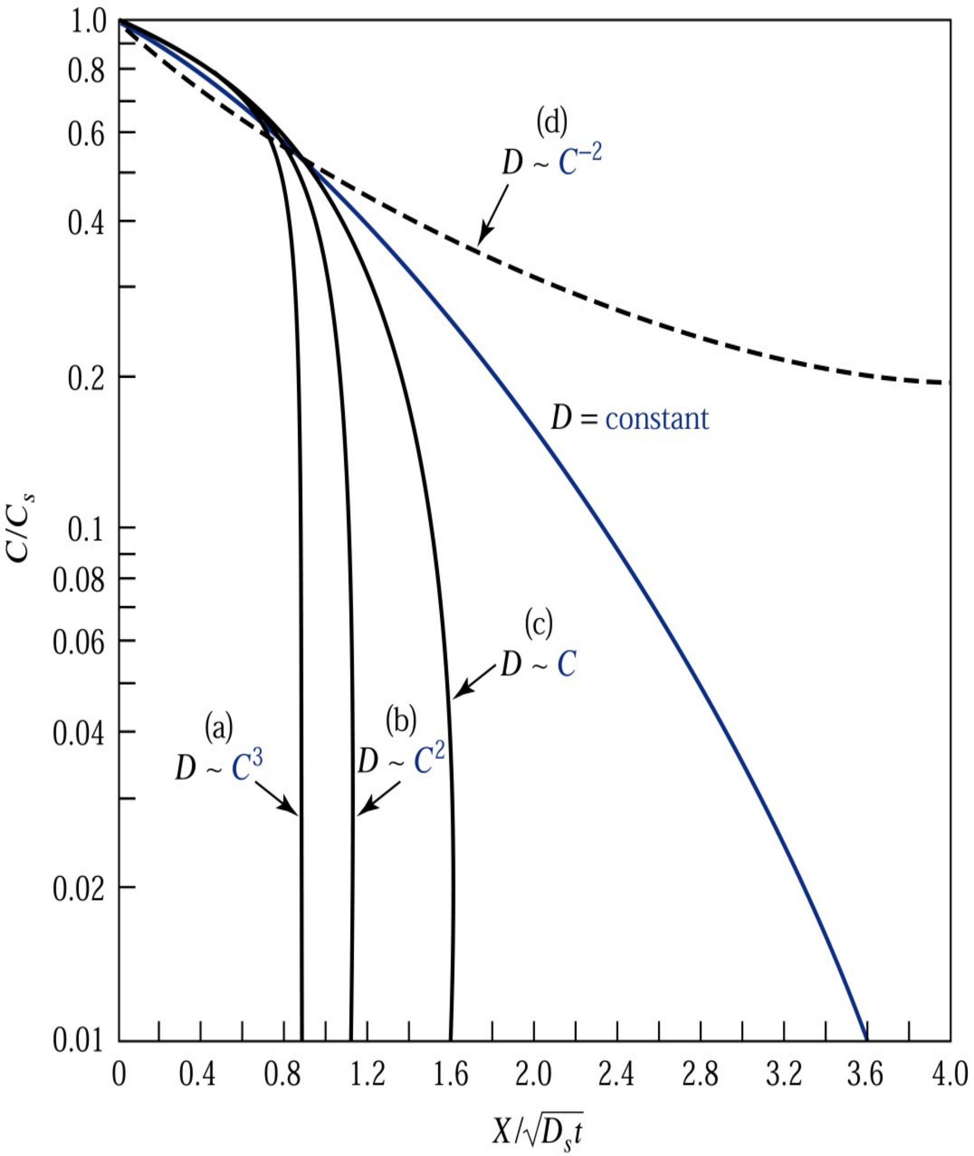
Built in electric field: $\vec{\mathbf{E}} = -\frac{kT}{q}\nabla \ln \frac{n}{n_i}$, **from** $\vec{J_n} = 0$

$$F = -D\nabla C + \frac{qD}{kT}\vec{\mathbf{E}}C = -D_{\text{eff}}\nabla C = \underline{-hD\nabla C}$$

Field enhancement factor: $h \cong 1 + \frac{C}{\sqrt{C^2 + 4n_i^2}}$

Important at high doping:
Criterion: $C > n_i \Rightarrow h \approx 2$
$C < n_i \Rightarrow h \approx 1$

Concentration Dependent Diffusivity



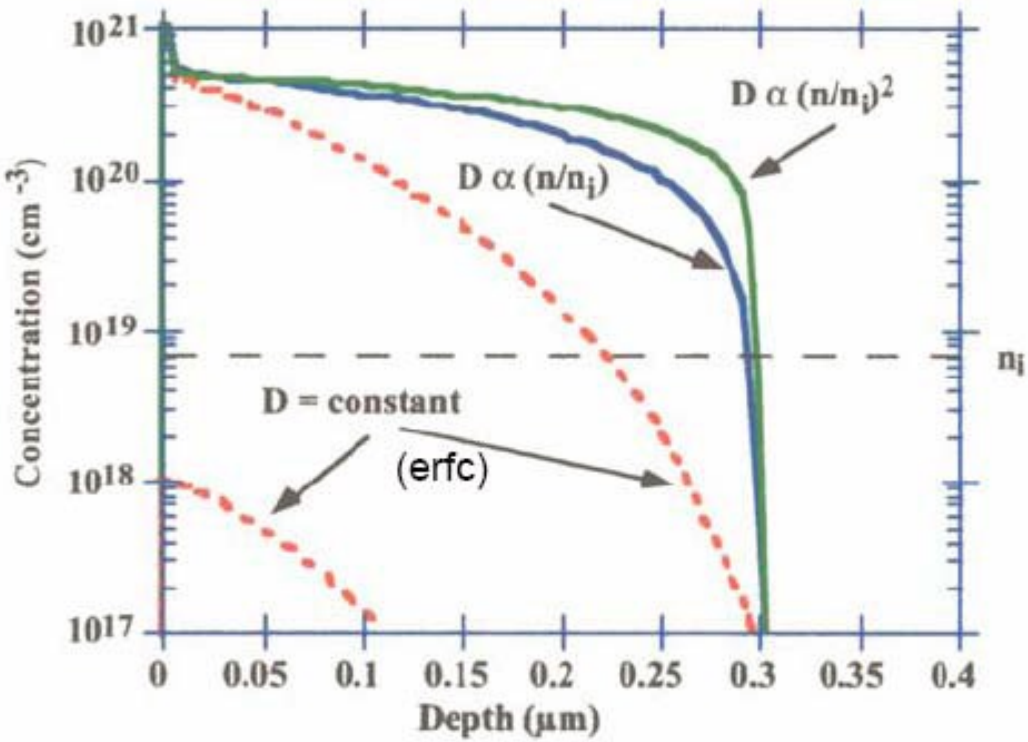
Constant-Surface-Concentration Diffusion

$$D = D_s \left(\frac{C}{C_s} \right)^{\gamma}$$

D_s: diffusion coefficient at the surface
C_s: the surface concentration

- for $\gamma > 0$ (B or As in Si, Zn in GaAs), the diffusion coefficient decreases as concentration drops
- due to sharp drop of the dopant concentration, abrupt junction is formed for $\gamma > 0$ with wide range of background doping (good for devices)
- for $\gamma < 0$ (Au and Pt), dopant can penetrate deep into substrate due to increased diffusion coefficient

Concentration Dependent Diffusivity



$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D_A^{eff} \frac{\partial C}{\partial x} \right)$$

Assumed reaction schemes:

$V^0 + e^- \leftrightarrow V^-$ $\quad I^0 + e^- \leftrightarrow I^-$

$V^0 + 2e^- \leftrightarrow V^=$ $\quad I^0 + 2e^- \leftrightarrow I^=$

$V^0 + e^+ \leftrightarrow V^+$ $\quad I^0 + e^+ \leftrightarrow I^+$

All point defect charge states are contributing:

$$D = D_{i0} + D_{i-}\left(\frac{n}{n_i}\right) + D_{i=}\left(\frac{n}{n_i}\right)^2 \quad \text{for N type dopants}$$

$$D = D_{i0} + D_{i+}\left(\frac{p}{n_i}\right) + D_{i++}\left(\frac{p}{n_i}\right)^2 \quad \text{for P type dopants}$$

At low doping densities: $n = n_i$

$$\underline{D_i = D_{i0} + D_{i-} + D_{i=}}$$

$$\underline{D = D.0 \exp\left(-\frac{D.E}{kT}\right)}$$

Experimental Diffusivities

	Si	B	In	As	Sb	P
D_{00} [cm^2/s]	560	0.05	0.6	0.011	0.214	3.85
E_{A0} [eV]	4.76	3.5	3.5	3.44	3.65	3.66
D_{0+} [cm^2/s]		0.95	0.6			
E_{A+} [eV]		3.5	3.5			
D_{0-} [cm^2/s]				31.0	15.0	4.44
E_{A-} [eV]				4.15	4.08	4.0
D_{0--} [cm^2/s]						44.2
E_{A--} [eV]						4.37

HW

Calculate the effective diffusion coefficient at 1000 ºC for two different box shaped arsenic profiles grown by silicon epitaxy, one doped $1 \times 10^{18} cm^{-3}$, and the other doped at $1 \times 10^{20} cm^{-3}$.