Atom Diffusion in Solids

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Outline

- ➢ Total energy of solids
  - ➲ Stability and equilibrium
  - ➲ Kinetic model

- ➢ Diffusion flux and diffusion equation
  - ➲ Solution of the diffusion equation

- ➢ "The" coefficient of diffusion

- ➢ Diffusion mechanisms

- ➢ Diffusion paths

- ➢ Diffusion coefficient measurements

- ➢ Special issues
  - ➲ Influence of impurities
  - ➲ Pressure effect
  - ➲ Nanometric-size effect
  - ➲ Grain boundary motion
  - ➲ Electromigration

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Total energy of solids I
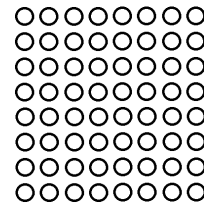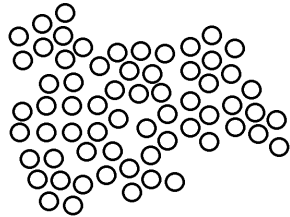
structural periodicity
bcc, fcc, hcp, *diamond* cubic

System = collection of atoms $\Rightarrow$ crystals

Conditions (of diffusion) = constant pressure + constant temperature

Atom interactions

Temperature effect

Total energy (eV)
(Gibbs free energy)

$$G = H - TS$$

Total energy at 0K (eV)
(enthalpy) = internal energy
- atomic pair interactions
- semi-empirical potentials
- ...

Temperature (K)

Config. with higher disorder
$\Rightarrow$ higher S
$\Rightarrow$ lower G

Entropy
$S \propto$ disorder (configuration)
$S = k_B \ln\Omega$ (eV/K)
$\hookrightarrow$ probability of existence

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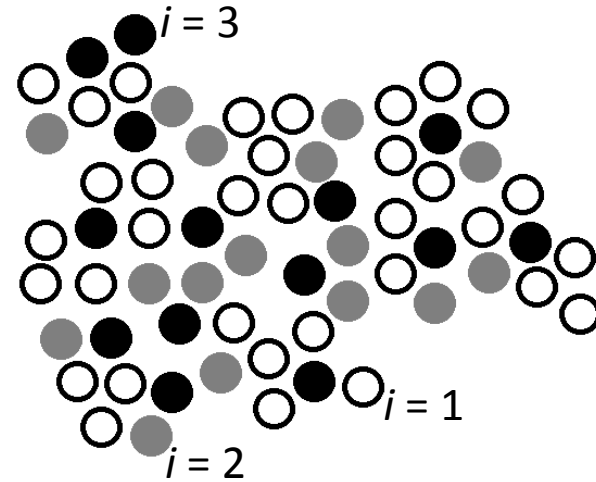# Total energy of solids II

$(n, T, P = \text{const})$

at equilibrium

$$G = \sum_i n_i \, \mu_i$$

Total energy (eV)
(Gibbs free energy)

Nbr of atoms of type i

Chemical potential of atoms of type i (eV)

$i = 3$

$i = 1$

$i = 2$

$$\left(\frac{\partial G}{\partial n_i} \right)_{P,T} = \mu_i$$ Energy per atom of type i in the system having a total energy G at equilibrium (otherwise μ_i^j atom of type i on site $j \neq \text{const}$)

$dG = \mu_i dn_i$ = work to add an atom of type i in the system at equilibrium

Total energy of solids II

$\mu_i = k_B T \ln(a_i) = k_B T \ln(\gamma_i C_i)$ with a_i activity, $\gamma_i \leq 1$ activity coefficient and $0 \leq C_i \leq 1$ concentration of element i in the system

Activity a_i = concentration of active atoms of type i in the system
➢ When an atom is put with other atoms, its chemical activity ("power of reaction") decreases due to its interactions with the other atoms

Ideal case
The atom do not experience any interactions (neither attractive nor repulsive)
Its activity does not decrease when its concentration increases
$\Rightarrow a_i = C_i$ and $\gamma_i = a_i/C_i = 1$ (Raoult's law)

Pure elements
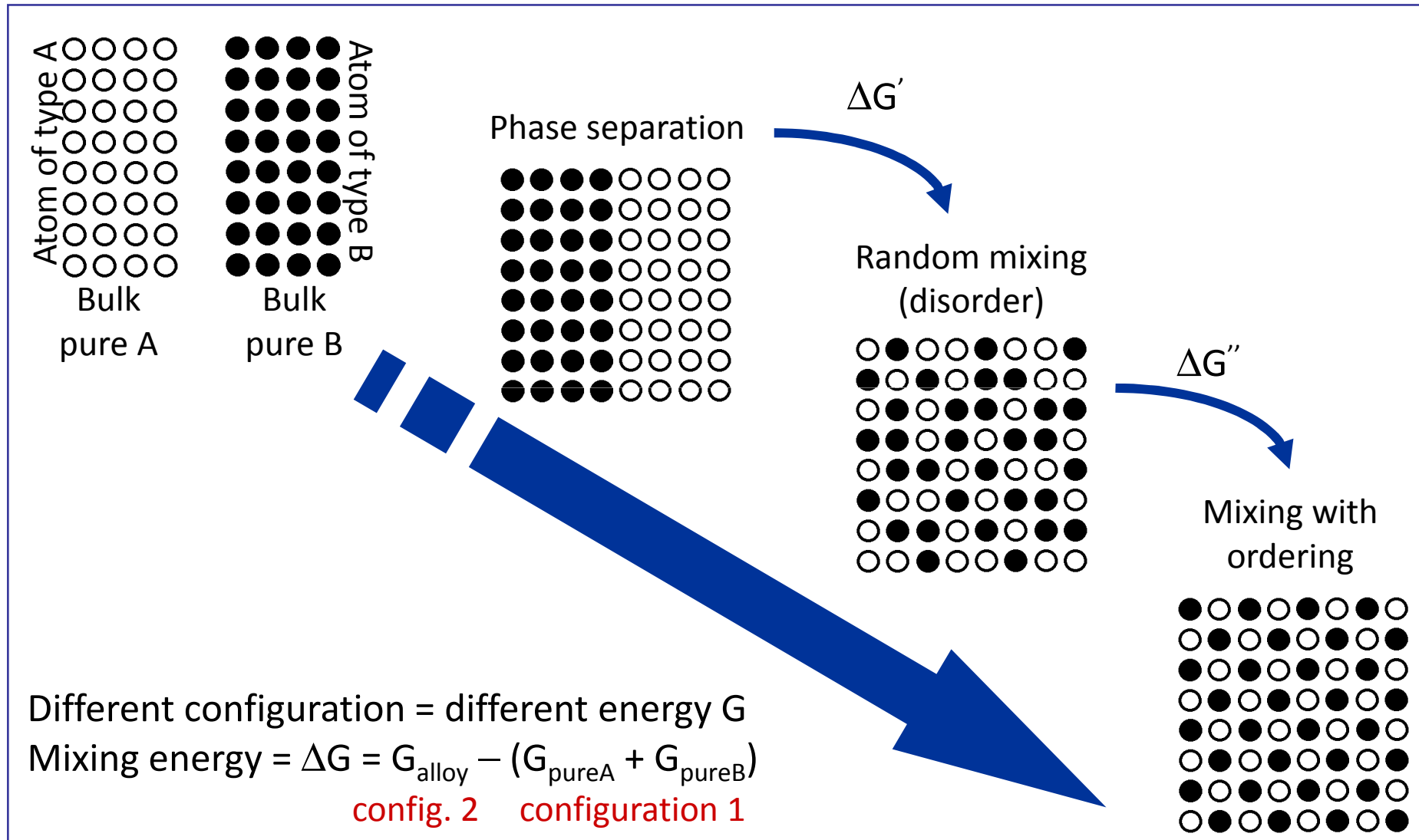$\Rightarrow a_i = 1$

Strong dilution (not ideal)
A given solute atom has no interactions with other solute atoms
The variation of its activity is linear with its concentration ($C_i \ll 1$)
$\Rightarrow a_i = \gamma_i C_i$ and γ_i = constant (Henry's law)

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Mixing energy

Atom of type A

Atom of type B

Bulk pure A

Bulk pure B

Phase separation

$\Delta G'$

Random mixing (disorder)

$\Delta G''$

Mixing with ordering

Different configuration = different energy G

Mixing energy = $\Delta G = G_{alloy} - (G_{pureA} + G_{pureB})$

config. 2   configuration 1

Stability and equilibrium

(n, T, P = const $\Rightarrow$ evolution of the system versus time)

The next configuration is more stable if

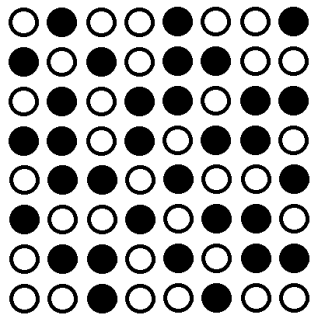$$dG = dH - TdS = \sum_i n_i d\mu_i < 0$$

The configuration is stable if the equilibrium configuration has been reached:

$$dG = dH - TdS = \sum_i n_i d\mu_i = 0$$

The condition $d\mu_i = 0$ can be also applied versus dr (distance) meaning that all the atoms of same type i exhibit the same μ_i everywhere in the system at equilibrium

Mixing energy

Random mixing
(disorder)

$$\Delta G = \Delta H - T\Delta S$$

Internal energy = Ising model

> rigid lattice
> pair interactions
> first neighbors

$$H = \frac{1}{2} \sum_{\substack{n,m \neq n \\ i,j}} p_i^n p_j^m \varepsilon_{ij}^{nm}$$

+

$$\Delta H = H_{alloy} - (H_{pureA} + H_{pureB})$$

$$\begin{cases} \Delta H = -\dfrac{1}{2} NZ C_A C_B V \\ V = \varepsilon_{AA} + \varepsilon_{BB} - 2\varepsilon_{AB} \end{cases}$$

$N = n_A + n_B$, Z nbr 1st neighbors , $\varepsilon_{ij} < 0$ atomic pair energy between i and j

Random distribution stable only if $V = 0$ (no difference of interactions $\varepsilon_{AA} + \varepsilon_{BB} = \varepsilon_{AB}$)
$\Rightarrow$ ideal case $\Delta H = 0$

Uniform distribution (random) = most probable state = Largest $\Omega \Rightarrow$ highest $S = k_B \ln\Omega$

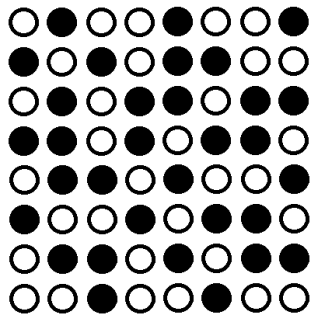$$\Delta S = S_{alloy} - (S_{pureA} + S_{pureB})$$

$$\Delta S = -Nk_B \left(C_A \ln C_A + C_B \ln C_B \right)$$

$$\Delta G = Nk_B T \left(C_A \ln C_A + C_B \ln C_B \right)$$

Energy minimization ($\Delta G < 0$) controlled by maximum entropy

Mixing energy

Random mixing
(disorder)

$$(n, T, P = \text{const}) \Rightarrow dG = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i$$

$$\Delta G = \sum_i n_i \Delta \mu_i$$

Energy minimization ($\Delta G < 0$) controlled by minimum chemical potential

$$\Delta G = n_A \Delta \mu_A + n_B \Delta \mu_B = n_A (\mu_A^{alloy} - \mu_A^{pure}) + n_B (\mu_B^{alloy} - \mu_B^{pure})$$
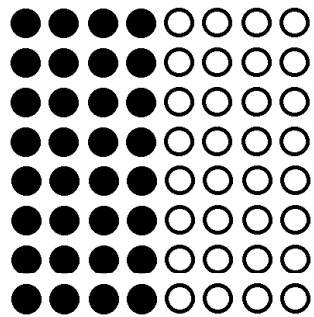
$\mu_i = k_B T \ln(a_i)$, and random mixing = no interactions between atoms ($V = 0$)
$\Rightarrow$ ideal case $a_i = C_i$

$$\Delta G = n_A k_B T \ln C_A + n_B k_B T \ln C_B \qquad \blacksquare\!\!\longrightarrow \qquad \boxed{\Delta G = N k_B T (C_A \ln C_A + C_B \ln C_B)}$$

Stable random solution = ideal solution $\Rightarrow V = 0$, $\Delta H = 0$, $dG = 0$ if $S = \text{Max}$ or $\mu_i = \text{Min}$
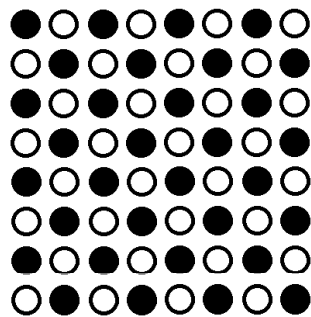
Mixing energy

Diffusion = under solubility ~ dilution

Phase separation

Mixing with ordering

Solute $\mu_B = k_B T \ln(\gamma_B C_B)$ with γ_B = const.
Matrix $\mu_A = k_B T \ln(C_A)$, $\gamma_A = 1$

$V < 0$, $\Delta H > 0$ $V > 0$, $\Delta H < 0$

$\mu_i = k_B T \ln(\gamma_i C_i)$ with $\gamma_i = f(C_i)$

$\Delta G'$
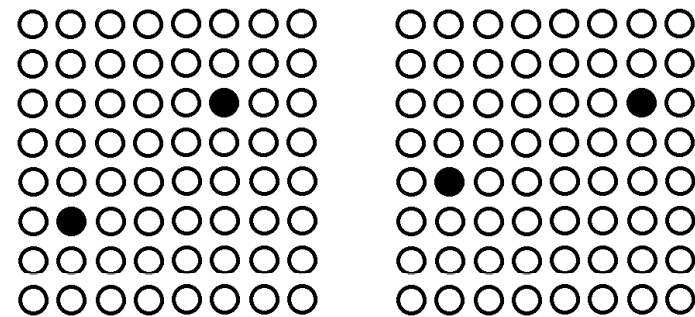
No interactions between diluted atoms $\approx$ random distribution (ideal solution)
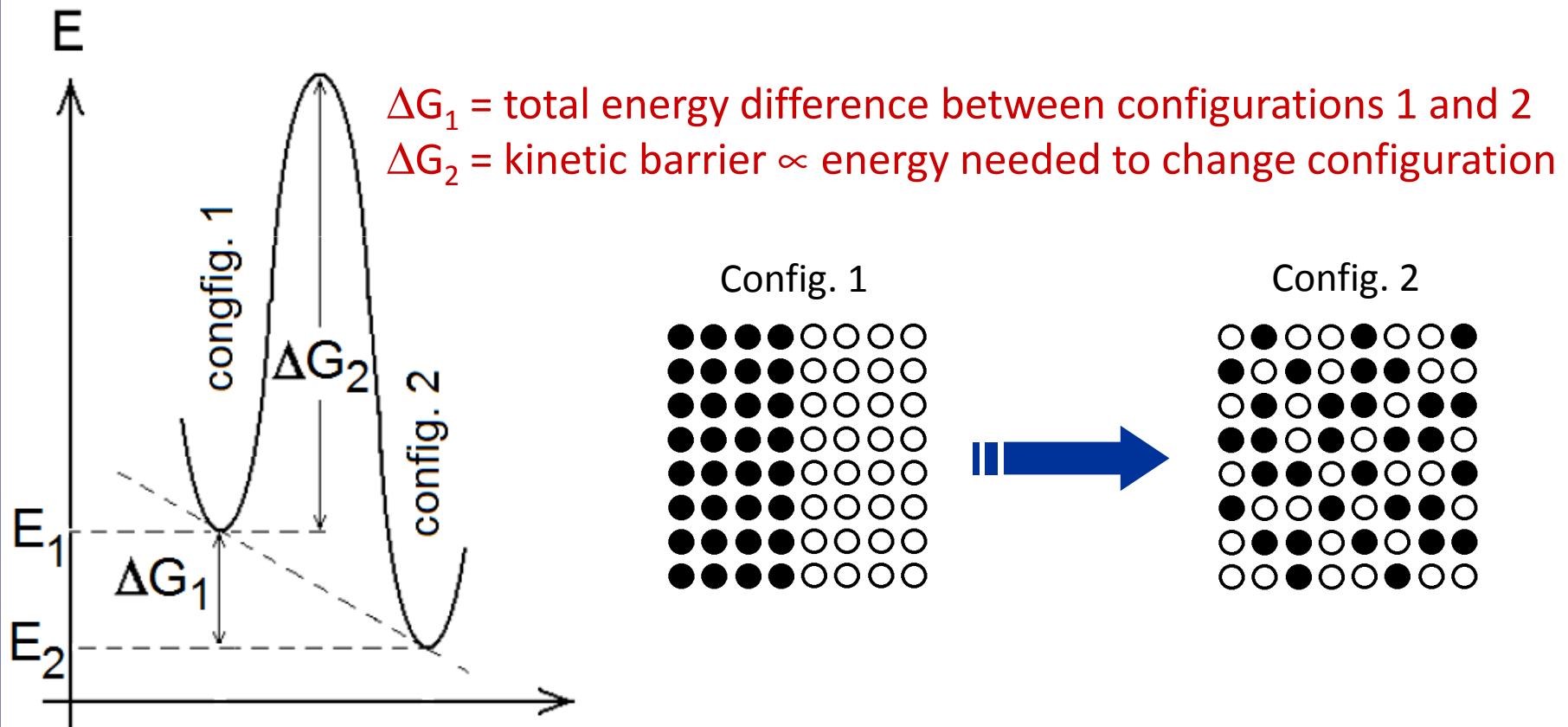
$\Rightarrow V \neq 0$ but $\Delta H' = 0$

$\Rightarrow dG = 0$ if S = Max or $\mu_i = k_B T \ln(\gamma_i C_i)$ = Min with γ_i = const

$\Rightarrow d\mu_i = 0 \Rightarrow d(\ln C_i) = 0 \approx$ ideal case with $\mu_i = k_B T \ln(C_i)$

Kinetic model

Effective change of configuration: configuration 1 $\rightarrow$ configuration 2

Depends on the driving force ($\Delta G_1 < 0$) and of the kinetics (ΔG_2)

ΔG_1 = total energy difference between configurations 1 and 2

ΔG_2 = kinetic barrier $\propto$ energy needed to change configuration

Minimum energy = driving force

Diffusion definition = "long distance" atomic transport $\Rightarrow$ atomic flux

➢ Diffusion because the early configuration is not the equilibrium configuration (at T, P, n)

➢ Different driving force "names" (maximum S, minimum μ) but same goal that is a minimum $G \Rightarrow$ same kinetics for different changes of configurations (if point defect concentrations at equilibrium) as surface segregation, phase formation...
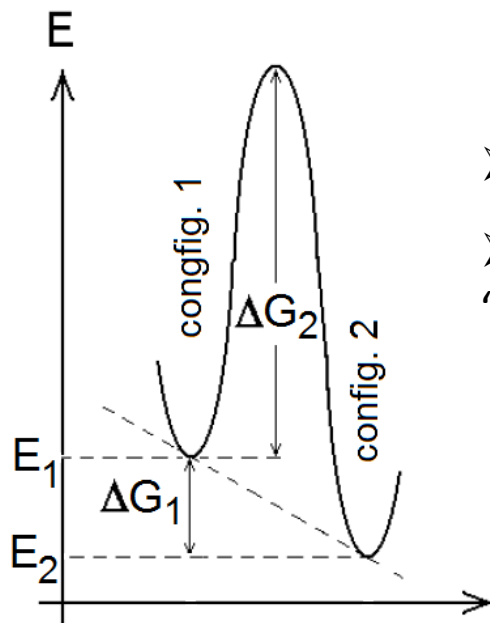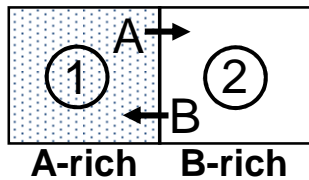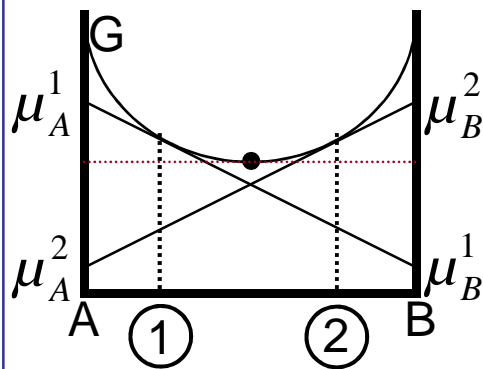
The driving force is very important

➢ No driving force = no diffusion (whatever the kinetics)

➢ Need to know the driving force in order to correctly extract the "coefficient of diffusion" from the measurement of flux

$E_2 < E_1 \Rightarrow$ config. 2 more stable than config. 1
ΔG_1 = driving force to go to config. 2

Minimum energy = driving force
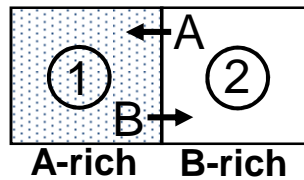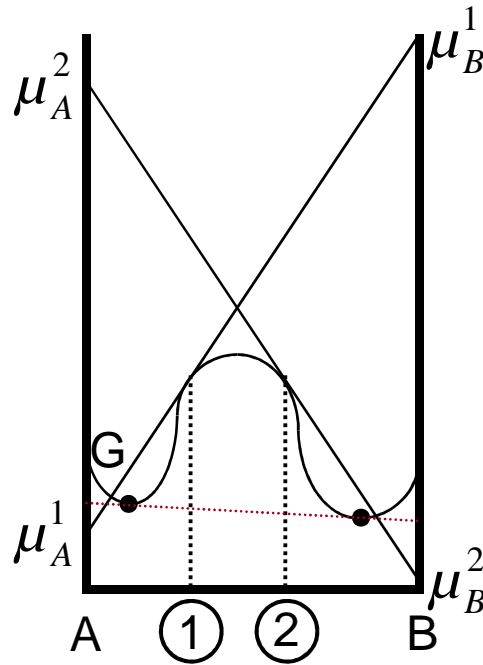
$$dG = \sum_i n_i d\mu_i = 0$$

$$d\mu_i = 0$$

μ_A in A-rich phase = μ_A in B-rich phase
μ_B in A-rich phase = μ_B in B-rich phase

mixing   demixing

Atomistic mechanism = kinetics

➢ ΔG_2 depends on the "path" used to go from config. 1 to config. 2
➢ Several "paths" or "mechanisms" with different ΔG_2 can allow to change configuration
➢ The mechanism the most probable (the fastest) is the one exhibiting the lowest ΔG_2
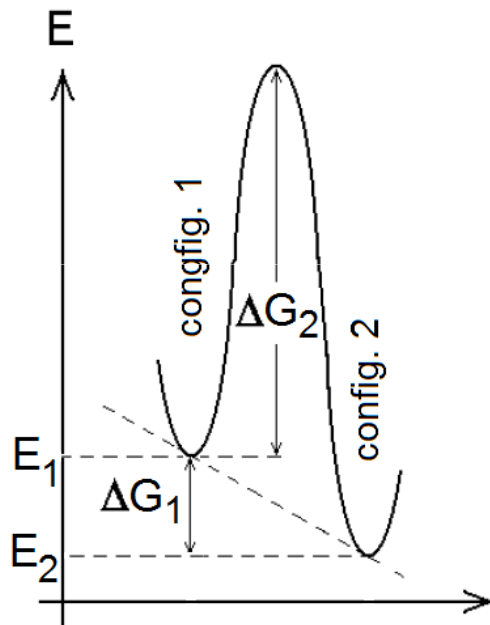
During diffusion
Main energy source = Temperature $\Rightarrow E \approx 3/2\ k_BT$ per atom

$20°C \Rightarrow k_BT \sim 0.025$ eV
$500°C \Rightarrow k_BT \sim 0.067$ eV
$1000°C \Rightarrow k_BT \sim 0.11$ eV

Probability of configuration change $\propto$ Exp[$-(\Delta G_1 + \Delta G_2)\ /k_BT$]
(Boltzmann distribution, k_B = Boltzmann constant)

Diffusion flux and diffusion equation

J (at s^{-1}): particle flux = number of particles that are going through a surface unit (section) per time unit

$$J = \sum_i C M_i F_i$$

J proportional to the number of particles and to their velocity

C: particle concentration in the matrix, F: flux driving force

$i \Rightarrow$ same type of particles can use in a same matrix several different paths or mechanisms exhibiting different mobility, and can experience different driving forces

$$M = \frac{D}{k_B T}$$

M: mobility of uncharged particles in a given matrix ,
1/M: friction coefficient, $M{\times}F$ = particles' velocity (m s^{-1})

D (m^2 s^{-1}): diffusion coefficient

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Diffusion flux and diffusion equation

Mass conservation (equation of continuity) $\Rightarrow$ $\dfrac{dC}{dt} = -(\nabla \cdot J)$

$\nabla = e_x d/dx + e_y d/dy + e_z d/dz$

Diffusion equation

Allows the prediction (from initial conditions) of particle concentration variations versus time everywhere in the matrix

$$\frac{dC}{dt} = -\frac{1}{k_B T} \frac{d}{dx}\left(\sum_i C D_i F_i \right)$$

Single type of atoms in a single spatial direction (x)

Diffusion flux and diffusion equation

Driving force = minimum chemical potential $\Rightarrow$ $F = -\dfrac{d\mu}{dx}$

"$-$" $\Rightarrow$ atoms diffuse in the direction of decreasing chemical potential

$$J = -\frac{CD}{k_B T}\frac{d\mu}{dx}$$ Nernst-Einstein equation

Assuming D = constant (point defect concentration at equilibrium)
and considering that $\mu = k_B T \ln(\gamma C)$

$$\frac{dC}{dt} = D\frac{d}{dx}\left(C\frac{d}{dx}\ln(\gamma C)\right) = D\frac{d}{dx}\left(\frac{dC}{dx}\left(1 + \frac{C}{\gamma}\frac{d\gamma}{dC}\right)\right)$$

Ideal solution (or non-ideal diluted solution) $\Rightarrow$ $\gamma = 1$, $\mu = k_B T \ln(C)$

$$\frac{dC}{dt} = D\frac{d^2 C}{dx^2}$$ Fick's equation = random motion
diffusion depends only on concentration

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Diffusion flux and diffusion equation

Δx: averaged distance of atoms during random motion
Δt: diffusion time

$$D = \frac{\Delta x^2}{2\Delta t}$$

Einstein's equation (one dimension)

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2}$$

Fick's equation cannot be used for all case (ideal or diluted solutions), however it is easier to use than the Nernst-Einstein equation, since the atom concentration is easy to measure in the samples, while the knowledge of atom chemical potential is not straight forward

For non-ideal solution, instead of to use the Nernst-Einstein equation, we can use the Fick equation with the addition of driving forces (included in the chemical potential) exhibiting a field easily measured or predictable in samples

$$\frac{dC}{dt} = D\frac{d^2C}{dx^2} - \frac{d}{dx}\left(\sum_i CM_iF_i\right)$$

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Diffusion flux and diffusion equation

Example: chemical potential expressed versus pressure or stress

$$\mu = \frac{dF^H}{dN} = \frac{dF^H}{d\left(V/\Omega\right)} = \Omega \frac{dF^H}{dV} = -\Omega\, p$$

p: pressure
Ω: atomic volume
$F^H = U - TS$: Helmholtz's free enthalpy

Driving force = stress gradient ("−" for compression, "+" for tension), strain can be measured experimentally to deduce the stress field and thus to model diffusion

$$\frac{d\mu}{dx} = \pm\Omega \frac{d\sigma}{dx} \qquad\Longrightarrow\qquad \frac{dC}{dt} = D\frac{d^2 C}{dx^2} \mp \frac{CD\Omega}{k_B T}\frac{d^2\sigma}{dx^2}$$

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Diffusion flux and diffusion equation

Example: dopant-induced electric field for dopant diffusion in semiconductors

Dopants are ionized when substitutionally dissolved in semiconductors $\Rightarrow$ modify the Fermi level E_F of semiconductors $\Rightarrow$ internal electric field that varies with dopant concentration (and thus with diffusion time)

For n-type dopants (single positive charge), the electric field and driving force F is

$$F = \frac{d}{dx}\left(\frac{E_F^i - E_F}{q}\right) = -\frac{k_B T}{q}\frac{d}{dx}\left(\ln\frac{n}{n_i}\right)$$

E_F^i: intrinsic Fermi level
q: charge of the dopant
n: free electron concentration
n_i: intrinsic free electron concentration

Dopant mobility in the electric field $\Rightarrow$ $M = \dfrac{qD}{k_B T}$

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Diffusion flux and diffusion equation

Example: dopant-induced electric field for dopant diffusion in semiconductors

Flux for *n*-type dopants (single positive charge):

$$J = -D\frac{dC}{dx} - CD\frac{d}{dx}\left(\ln\frac{n}{n_i}\right) = -CD\frac{d}{dx}\left(\ln\left(C\frac{n}{n_i}\right)\right)$$

Diffusion equation for *n*-type dopants (single positive charge):

$$\frac{dC}{dt} = CD\frac{d^2}{dx^2}\left(\ln\left(C\frac{n}{n_i}\right)\right)$$

Solution of the diffusion equation

In some cases (given geometry and given limit conditions) the diffusion equation can be solved analytically

➤ Diffusion can be predicted using the analytical solution of the diffusion equation (exact solution)

➤ Often solutions considers the Fick equation in a given geometry (microstructure)

$$\frac{dC}{dt} = D \frac{d^2 C}{dx^2}$$

For more complex diffusion cases (not at equilibrium, complex geometry, diffusion coefficient varying with time…) without analytical solution, diffusion is predicted using numerical simulations (approached solution)

For more analytical solutions, see: Y. Adda and J. Philibert, La Diffusion dans les Solides (bibliothèque des Sciences et Techniques Nucléaires, Saclay, Presses Universitaires de France, Paris, 1966),Tome 1

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Solution of the diffusion equation

Limit conditions

C → 0   as   t → 0   for   x > 0

C → ∞   as   t → 0   for   x = 0

$$\int_{-\infty}^{+\infty} C(x,t)\,dx = Q \quad = \text{Total amount}$$

at/cm^2

Solution of Fick's second law $\dfrac{dC}{dt} = D\dfrac{d^2C}{dx^2}$

$$C(x,t) = \frac{Q}{2\sqrt{\pi Dt}}\exp\left(-\frac{x^2}{4Dt}\right) = C(0,t)\exp\left(-\frac{x^2}{4Dt}\right)$$

➤ Peak concentration decreases as 1/√t and is given by C(0,t)

➤ When the distance from origin (x = 0) is x = 2√Dt the concentration has fallen by 1/e

➤ A Gaussian solution remains Gaussian when more diffusion time is added (profiles of atoms implanted in the sample)

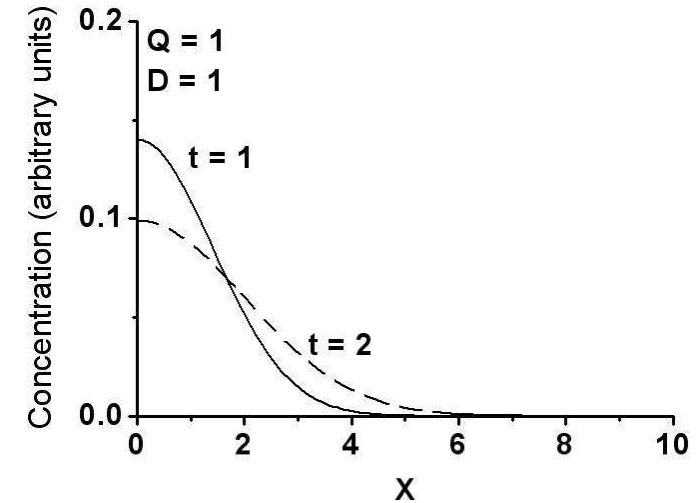# Solution of the diffusion equation

Limit conditions

C → 0   as   t → 0   for   x > 0

C → ∞   as   t → 0   for   x = 0

$$\int_{-\infty}^{+\infty} C(x,t)\,dx = Q \quad = \text{Total amount}$$

at/cm²

Gaussian solution near the surface

Solution of Fick's second law $\dfrac{dC}{dt} = D\dfrac{d^2C}{dx^2}$

$$C(x,t) = \frac{Q}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right) = C(0,t)\exp\left(-\frac{x^2}{4Dt}\right) \text{ at/cm}^3$$

➤ Peak concentration decreases as 1/√t and is given by C(0,t)
➤ When the distance from origin (x = 0) is x = 2√Dt the concentration has fallen by 1/e
➤ A Gaussian solution remains Gaussian when more diffusion time is added (profiles of atoms deposited on the surface of the sample)

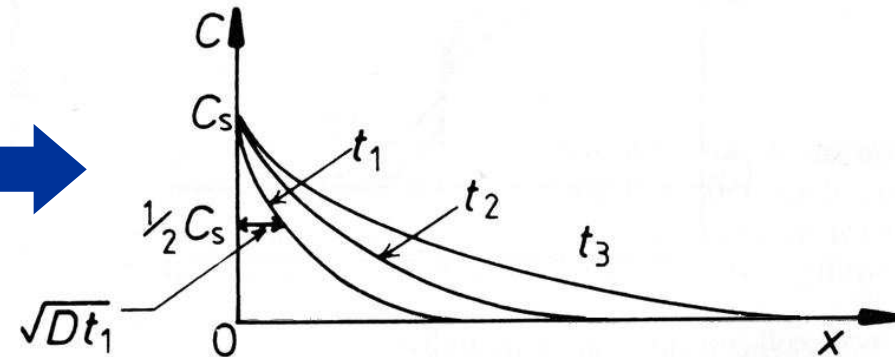# Solution of the diffusion equation

Limit conditions

$C = 0$ at $t = 0$ for $x > 0$

$C = C_S$ at $\begin{cases} t = 0 \\ \text{and } t = \infty \end{cases}$ for $x = 0$

Infinite source of atoms near the surface

Solution of Fick's 2nd law $\quad \dfrac{dC}{dt} = D\dfrac{d^2C}{dx^2}$

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

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

$$Q = \frac{2C_S}{\sqrt{\pi}}\sqrt{Dt} = \text{Amount diffused in the material}$$

➢ Quantity of atoms in the sample bulk increases with time
➢ Diffusion from vapor: C_s = constant amount of adsorbed atoms at a given temperature
➢ Diffusion from a film (dissolution): C_s = solubility limit of atoms at a given temperature

Solution of the diffusion equation

Important law to remember

Einstein's equation (one dimension)

$$\Delta x \propto \sqrt{Dt}$$

Average diffusion length
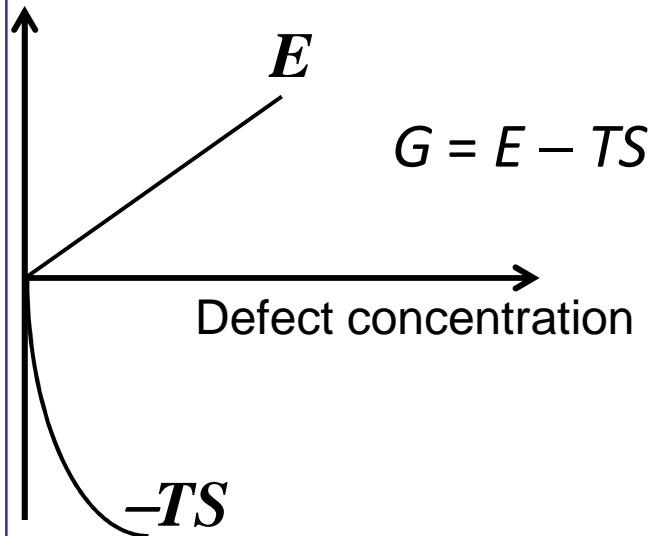
Coefficient of diffusion

Diffusion time

$$2 \; \Delta x \equiv 4 \; \Delta t$$

"The" coefficient of diffusion

Introduction of a defect in the solid

➢ Increase of the system internal energy (formation energy of the defect ΔG_f)

➢ Increase of the system entropy (configuration: for the same energy G, defects can occupy different locations in the crystal)

E

$G = E - TS$

Defect concentration

$-TS$

Random distribution of point defects in a pure crystal

$$G = NC\Delta G_f + Nk_B T\left[C \ln C + (1-C)\ln(1-C)\right]$$

G: total energy of the crystal (single type of atoms)

n: total number of defects in the crystal

N: total number of sites in the crystal

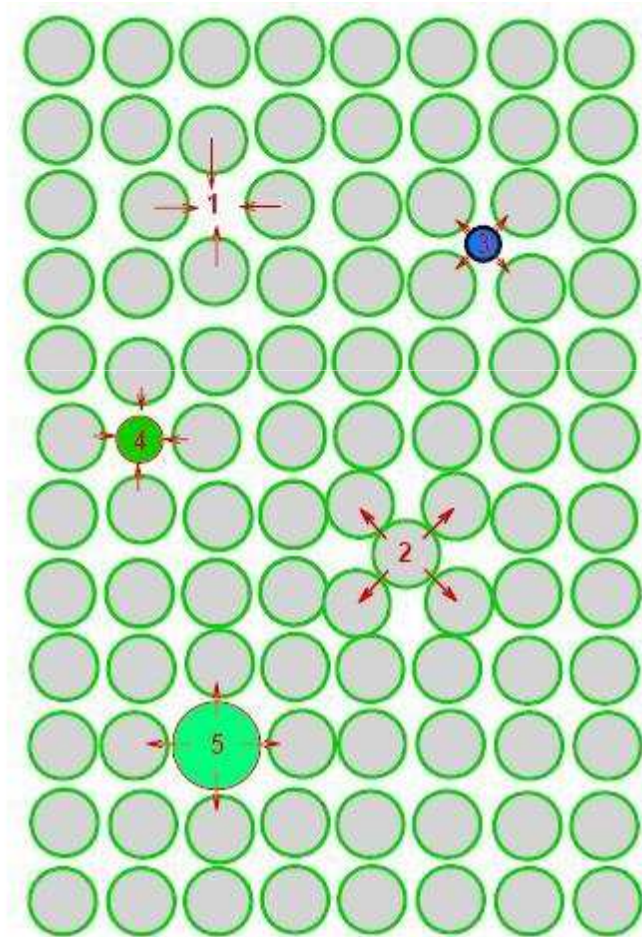$C = n/N$: defect concentration

$(1 - C)$: atom concentration

In equilibrium conditions, solids always possess point defects

Equilibrium concentration (T, p)

$$\frac{dG}{dC} = 0 \Rightarrow \frac{C}{1-C} = \exp\left(\frac{-\Delta G_f}{k_B T}\right)$$

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"The" coefficient of diffusion

Examples of point defects

(1) Vacancy $\Rightarrow$ V

(2) Self-interstitial $\Rightarrow$ I

(3) Interstitial impurity $\Rightarrow A_i$

(4), (5) substitutional impurity $\Rightarrow A_s$

Arrows show the local stress introduced by the point defects

"The" coefficient of diffusion

Metals

➢ E_F in the middle of the conduction band, only one type of charged carriers = electrons (holes are not considered)

➢ A lot of electronic states close to the Fermi level (E_F) $\Rightarrow$ small variations of the electron concentration due to the occurrence of a defect do not change significantly the position of the Fermi level

➢ AB initio calculations show that usually:

❶ the electron density varies in the vicinity of a defect

❷ the density of states changes in the vicinity of a defect

❸ the filling of the electronic states close to the defect keeps the neutrality of charges

$\Rightarrow$ Generally, defects are not charged in metals (elastic interactions)

Semiconductors / dielectrics

➢ E_F in the middle of the gap, considers two types of charged carriers: the electrons (negative) in the conduction band and the holes (positive) in the valence band

➢ Quasi-no states close to E_F $\Rightarrow$ small variations of the electron concentration due to the occurrence of a defect can change significantly the position of the Fermi level

$\Rightarrow$ Generally, defects are charged in semiconductors (elastic and coulombic interactions)

"The" coefficient of diffusion

➢ In crystals, atoms move using point defects: vacancy-mediated or interstitial-mediated mechanisms

➢ The signature of the atomic mechanism used by atoms to move in crystals is contained in the diffusion coefficient

General expression of the equilibrium concentration of an uncharged point defect X^0

$$C_{X^0}^{eq} = \theta_{X^0} \, C_{XS} \exp\left(\frac{-\Delta G_{X^0}^{f}}{k_B T}\right)$$

ΔG_x^f: the defect formation energy

θ_x: number of internal freedom degrees of the defect

C_{XS}: density of possible sites for the defect in the lattice (substitutionals, interstitials…)

Example: in metals the defects are not charged, and the density of self-interstitials is negligible. The principal diffusion mechanism is the direct vacancy mechanism (vacancies diffuse in the opposite direction to atom diffusion).

"The" coefficient of diffusion

General expression of the equilibrium concentration of a point defect X having a charge j

$$C^{eq}_{X^j} = \theta_{X^j}\, C_{XS}\, \exp\left(-\frac{\Delta G^f_{X^j} - z_j E_F}{k_B T}\right) = C^{eq}_{X^0}\, \delta_{X^j}\left(\frac{n}{n_i}\right)^{z_j}$$

n: local concentration of electrons

n_i: intrinsic concentration of electrons

z_j: number of electrons associated to each charged state of the defect δ_X: intrinsic relative concentration of defect X^j compared to the same uncharged defect X^0 (δ_{X0} = 1, δ_{Xj} = $f(T)$)

The expression on the right is obtained assuming that in intrinsic condition E_F is located close to the middle of the gap between the valence and the conduction bands of the solid

➤ The concentration of uncharged defects is independent of E_F
⇒ E_F variations lead to the change of the total point defect concentration (≠ proportion)

Example: in semiconductors, uncharged and charged defects are coexisting, and the density of self-interstitials can be as important as the concentration of vacancies

"The" coefficient of diffusion

Example: equilibrium concentration of a defect *X* exhibiting a single negative charge (X^{-1}) or a double negative charge (X^{-2}) in semiconductors

$$C^{eq}_{X^{-1}} = C^{eq}_{X^0} \frac{\theta_{X^{-1}}}{\theta_{X^0}} exp\left(-\frac{E_{X^{-1}} - E_F}{k_B T}\right) = \delta_{X^{-1}} \frac{n}{n_i}$$

E_{X-1} and E_{X-2}: the energy of the defects X^{-1} and X^{-2} in the gap of the semiconductor

$$C^{eq}_{X^{-2}} = C^{eq}_{X^0} \frac{\theta_{X^{-2}}}{\theta_{X^0}} exp\left(-\frac{E_{X^{-2}} + E_{X^{-1}} - 2E_F}{k_B T}\right) = \delta_{X^{-2}} \left(\frac{n}{n_i}\right)^2$$

Example: equilibrium concentration of a defect *X* exhibiting a single positive charge X^{+1} or a double positive charge X^{+2} in semiconductors

$$C^{eq}_{X^{+1}} = \delta_{X^{+1}} \frac{p}{n_i} \qquad C^{eq}_{X^{+2}} = \delta_{X^{+2}} \left(\frac{p}{n_i}\right)^2 \qquad \frac{n_i}{p} = \frac{n}{n_i} = \exp\left(\frac{-\Delta E_F}{k_B T}\right)$$

n: local concentration of electrons
p: local concentration of holes

"The" coefficient of diffusion

➤ Point defects can interact together, as well as with charge carriers

⇒ Reactions (particularly important for out-of-equilibrium conditions for which point defect concentrations vary during material ageing)

Defect/charged carrier interactions ⇒ change of charge state

$$X^j + p_t^i \Leftrightarrow X^{j+i}$$
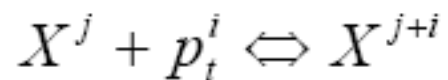
X^j: defect X with the charge j
p_t^i: an electron ($i = -1$) or a hole ($i = +1$)

However, in general, reactions between point defects and charged carriers are neglected, since their kinetics are very fast compared to atom or ion reactions (instantaneous equilibrium of charged carrier distributions)

Reactions between point defects cannot be neglected
⇒ Example: formation and annihilation of point defects allowing to reach point defect equilibrium concentrations

"The" coefficient of diffusion

In a perfect crystal without extended defects (dislocations, grain boundaries…) equilibrium defect concentrations can be obtained following two mechanisms:

➤ bulk mechanism (Frenkel)
➤ surface mechanism (Schottky)

Frenkel's process: an atom of the lattice leave its substitutional site to occupy an interstitial site, creating simultaneously a self-interstitial (I) and a vacancy (V)

$$I + V \Leftrightarrow \langle 0 \rangle$$
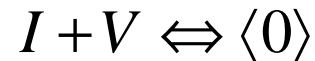
➤ Despite that this reaction takes place in the bulk, the vacancy and self-interstitial concentrations are not always the same, as defects can diffuse to the surface of the crystal and can be annihilated in order to decrease the system energy

➤ Frenkel's process corresponds to an important activation barrier

"The" coefficient of diffusion

Schottky process: vacancies and self-interstitials can be produced independently at the surface of the crystal $\Rightarrow$ a substitutional atom on the surface can create a self-interstitial by jumping in an interstitial site, or a vacancy by jumping on another surface site
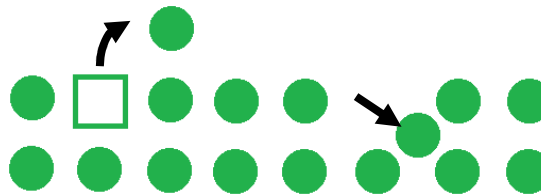

➢ Lower activation energy than the Frenkel process

➢ at a given temperature, point defects can diffuse from the surface toward the bulk of the crystal in order to reach the bulk equilibrium concentration of defects
➢ due to the bulk recombination process (Frenkel process), a flux of point defects exists between the surface and the bulk of the crystal ($\Rightarrow$ stationary conditions)

$$J_X = v_X \left(C_X - C_X^{eq} \right)$$

v_X: velocity of the point defect X
C_X^{eq}: equilibrium concentration of X at the considered temperature

"The" coefficient of diffusion
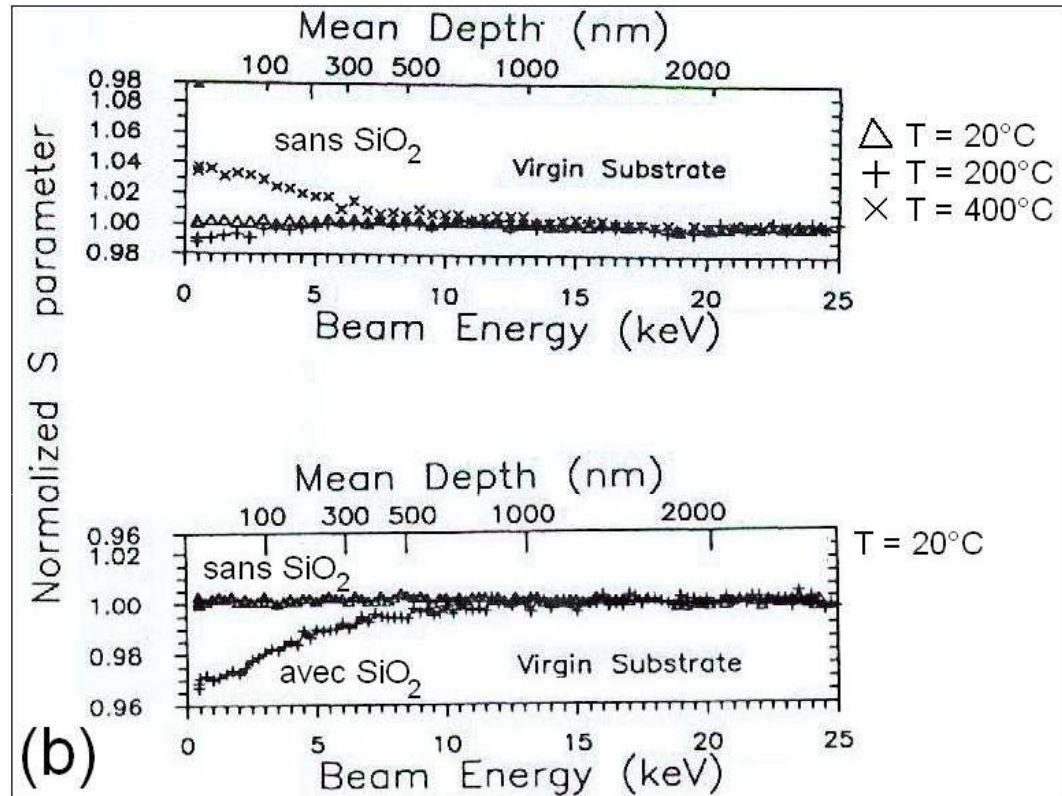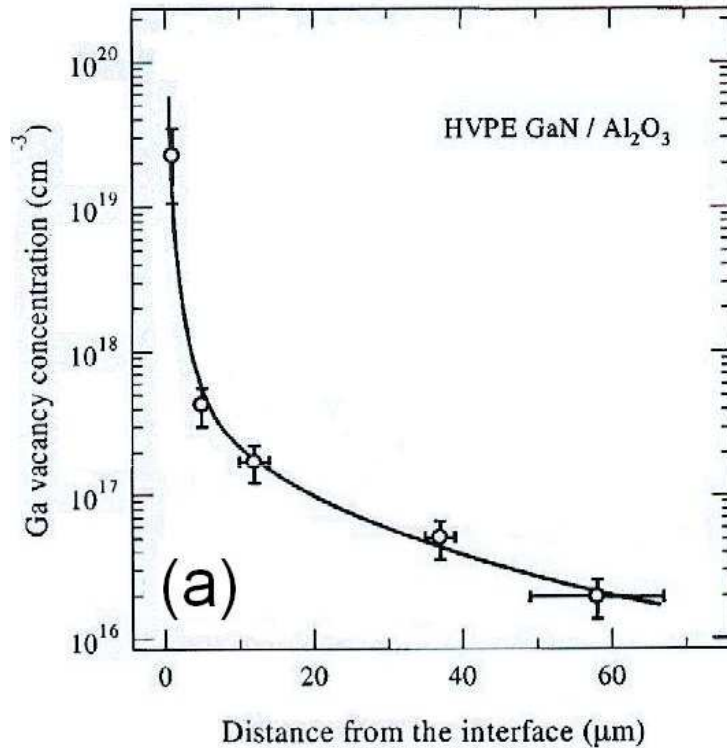
Proportion of vacancies measured by positron annihilation: (a) vacancy concentration in a GaN film versus thickness [J. Oila et al., Applied Physics Letters 82 (2003) p. 3433], (b) vacancy proportion versus depth in a Si substrate with or without native oxide [P. Asoka-Kumar et al., Physical Review B 48 (1993) p. 5345]

"The" coefficient of diffusion
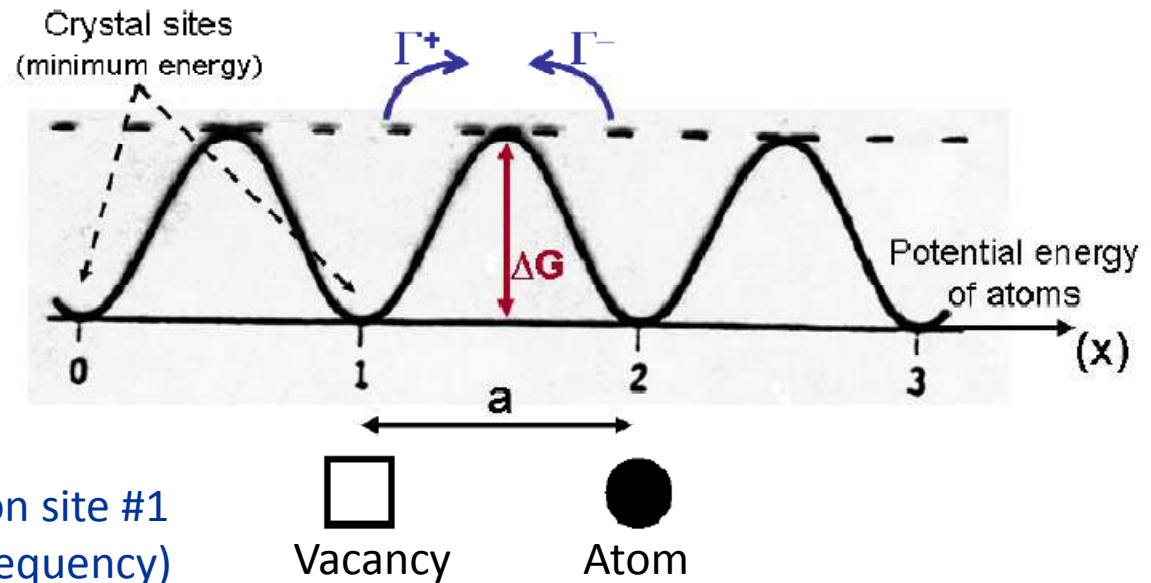
Direct vacancy
mechanism
random motion

Γ: jump frequency
ν: Jump probability
f: correlation factor
η: probability to find the defect on site #1
ν_0: exchange frequency (Debye frequency)

Crystal sites
(minimum energy)

Γ^+ Γ^-

ΔG

Potential energy
of atoms

(x)

0   1   2   3

a

Vacancy   Atom

$$\Gamma = f\eta\nu \quad \text{with} \quad \eta = \exp\left(\frac{-\Delta G_f}{k_B T}\right) \quad \text{and} \quad \nu = \nu_0 \exp\left(\frac{-\Delta G_m}{k_B T}\right)$$

ΔG_f: defect formation energy
ΔG_m: migration energy of the defect

$$\Gamma = \Gamma^- = \Gamma^+ = f\nu_0 \exp\left(\frac{-\Delta G}{k_B T}\right) \quad \text{with} \quad \Delta G = \Delta G_f + \Delta G_m$$

"The" coefficient of diffusion

$$\langle X^2 \rangle = f \langle X^2 \rangle_{rd}$$

$$\langle X^2 \rangle = \sum_{i=1}^{n} \langle x_i^2 \rangle + 2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \langle x_i x_j \rangle$$

X: distance performed in the direction x (diff. length)

n ($\rightarrow \infty$): number of atomic jump

Random motion (two successive jumps are independent) $\Rightarrow \sum\sum\langle x_i x_j \rangle = 0$ since for each $x_i x_j$ couple, one can find for an other atom, a same couple but exhibiting the opposite sign

$$\langle X^2 \rangle_{rd} = \sum \langle x_i^2 \rangle \quad \text{and} \quad f = 1$$

Correlated jumps (two successive jumps are not independent) $\Rightarrow \sum\sum\langle x_i x_j \rangle \neq 0$ and $f < 1$ (*case of a vacancy in a matrix made of two types of atoms*)

$$f = \frac{\langle X^2 \rangle}{\langle X^2 \rangle_{rd}} = 1 + \frac{2 \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} \langle x_i x_j \rangle}{\sum_{i=1}^{n} \langle x_i^2 \rangle}$$

Direct vacancy mechanism in 3D cubic crystal

$$f = \frac{1 + \langle \cos\theta \rangle}{1 - \langle \cos\theta \rangle}$$

θ: angle between the ith jump and the $(i+1)^{\text{th}}$ jump = const

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"The" coefficient of diffusion

$$\langle X^2 \rangle_{rd} = \sum \langle x_i^2 \rangle = \langle n_1 \rangle x_1^2 + \ldots + \langle n_i \rangle x_i^2 = \tau \Gamma_1 x_1^2 + \ldots + \tau \Gamma_i x_i^2 = \tau \sum_i \Gamma_i x_i^2$$

$\langle n_i \rangle$: averaged number of jumps of type i performed during the time τ for the total diffusion length X in the direction x

Einstein's equation (one dimension) $\Rightarrow$ $\quad D_x = \dfrac{\langle X^2 \rangle_{rd}}{2\tau} = \dfrac{1}{2} \sum_i \Gamma_i x_i^2$

Single type of jumps (= a the lattice parameter) in the x direction $\Rightarrow i = 1 \Rightarrow$ $\underline{D_x = \Gamma a^2}$

General expression of the diffusion coefficient

$$D = f \eta v a^2 = C_X D_X \qquad D = D_0 \exp\left(\dfrac{-(\Delta H_f + \Delta H_m)}{k_B T}\right) = D_0 \exp\left(\dfrac{-E_a}{k_B T}\right)$$

C_X: point defect concentration
D_X: point defect diffusion coefficient

$$D_0 = a^2 g f v_0 \exp\left(\dfrac{\Delta S_f + \Delta S_m}{k_B}\right)$$

"The" coefficient of diffusion

Remark 1: the activation energy can be found written in different ways, it always takes into account the energy of formation and migration of the point defect involved in the diffusion mechanism

$$D = D_0 \exp\left(\frac{-\Delta G}{k_B T}\right)_{T,p} = D_0 \exp\left(\frac{-\Delta F^H}{k_B T}\right)_{T,V} = D_0 \exp\left(\frac{-E_a}{k_B T}\right)$$

$$dF^H = -SdT - pdV + \sum_i \mu_i dn_i + \sum_i n_i d\mu_i \quad \text{Helmholtz free energy } (T, V)$$

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i + \sum_i n_i d\mu_i \quad \text{Gibbs free energy } (T, p)$$

Example: diffusion at constant T, under constant hydrostatic pressure p

$$E_a^p = E_a - p\Delta V \quad \text{with} \quad \Delta V = \Delta V_f + \Delta V_m$$

ΔV_f: volume of formation of the defect
ΔV_m: volume of migration of the defect

Remark 2: "The" diffusion coefficient referrers actually to the diffusion coefficient observed when the point defects in the crystal are at equilibrium!

$$D = C_X^{eq} D_X \quad \text{at given } T$$

Rule of thumb

Empirical rules

For a given crystal structure and a given bond type
(for a given class of materials)

$D(T_m) \sim$ constant, $Q/RT_m \sim$ constant and $D_0 \sim$ constant

The diffusion coefficient of all materials with a given crystal structure and bond type will be approximately the same at the same fraction of their melting temperature
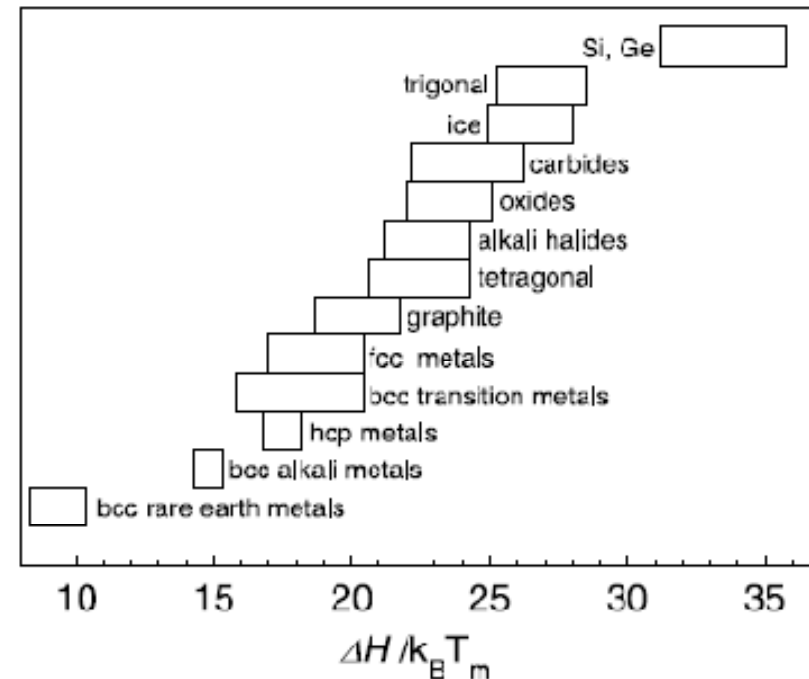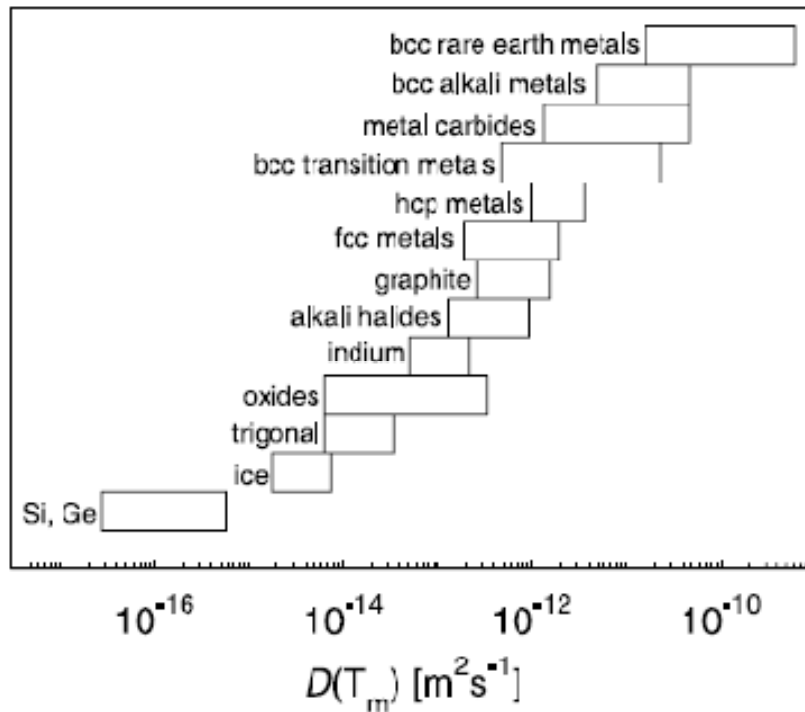
$$D\left(\frac{T}{T_m}\right) \sim \text{constant}$$

If melting temperature (T_m) ↗

➤ Bond strength ↗ (ΔH_m ↗)
➤ Formation energy of defect ↗ (ΔH_f ↗) = concentration of defects ↘
➤ Coefficient of diffusion ↘

Rule of thumb

Self-diffusion in different types of materials

$$D(T_m) = D^0 \exp\left(-\frac{\Delta H}{k_{\mathrm{B}} T_m}\right) = g f a^2 \nu^0 \exp\left(\frac{\Delta S}{k_{\mathrm{B}}}\right) \exp\left(-\frac{\Delta H}{k_{\mathrm{B}} T_m}\right)$$

Rule of thumb

Bulk Self Diffusion in pure metals

(fcc and hcp closed packed metals)

Diffusion mechanism: vacancy

<u>Empirical rules</u>

1-The diffusion coef. at the melting temp is roughly const.

$$D(T_m) \approx 10^{-8} \ cm^2/s$$

2-The activation energy scales with the melting T

$$Q / RT_m \approx 18$$

3 -The pre-exponential is roughly constant

$$D_0 \approx 1 \ cm^2/s$$

Bulk Self diffusion in Silicon

Diffusion mechanism: vacancy + interstitial

$$D(T_m) \approx 10^{-12} \ cm^2/s$$

$$Q / RT_m \approx 35$$

$$D_0 \approx 10^4 \ cm^2/s$$

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Diffusion mechanisms

➢ Several types of point defects (single vacancy, double vacancies,…)
➢ Proportion of each type of defect can vary with temperature

$\Rightarrow$ same type of atom can use simultaneously several types of mechanisms, exhibiting different diffusion coefficients

$$D_A^{eff} = \sum_X D_X \frac{C_X}{C_S}$$

X: a defect *X*

C_X: concentration of defect *X*
C_S: total concentration of atomic sites
D_A^{eff}: effective diffusion coefficient of atom *A*
C_X/D_X: probability to find a defect X close to an atom A
D_X: diffusion coefficient of defect *X* = probability of migration

Diffusion mechanisms

Atoms interstitially dissolved $\Rightarrow$ direct interstitial mechanism

Interstitial atom before diffusion

Interstitial atom after diffusion

A_i
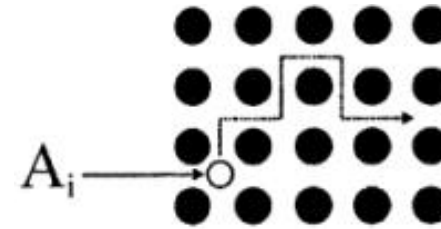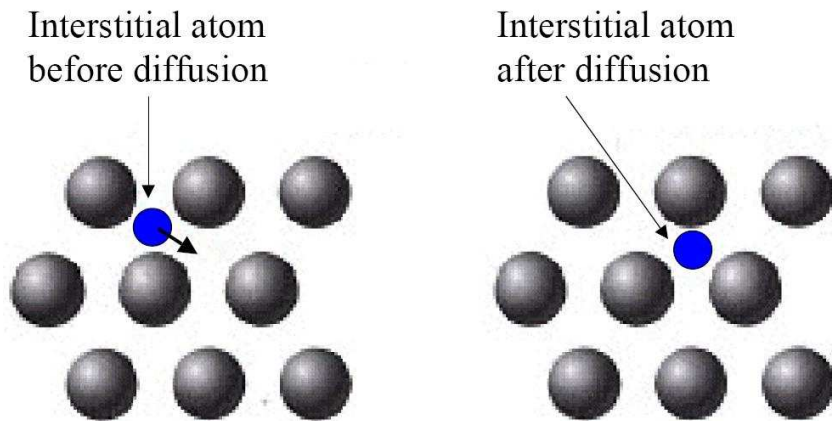
$$D_A = D_A^{A_i} = D_{A_i}$$

$$D_{A_i} = D_0 \exp\left(\frac{-\Delta H_m^{A_i}}{k_B T}\right)$$
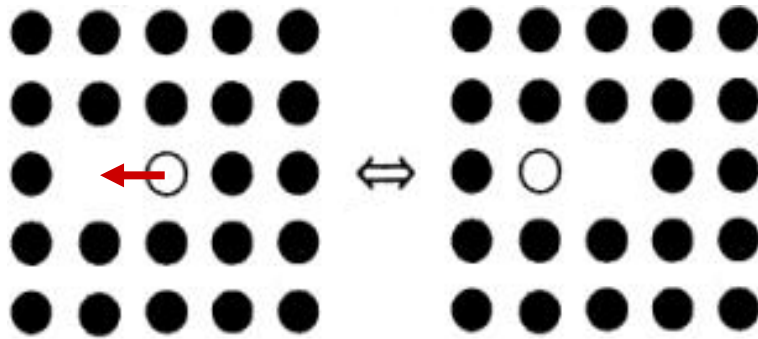
No need to create a defect ($\Delta H_f = 0$) since interstitial sites are already present in the crystal

$\Rightarrow$ Activation energy depends only on migration energy (ΔH_m)

$\Rightarrow$ Fastest bulk diffusion mechanism

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Diffusion mechanisms

Atoms substitutionally dissolved and direct vacancy mechanism
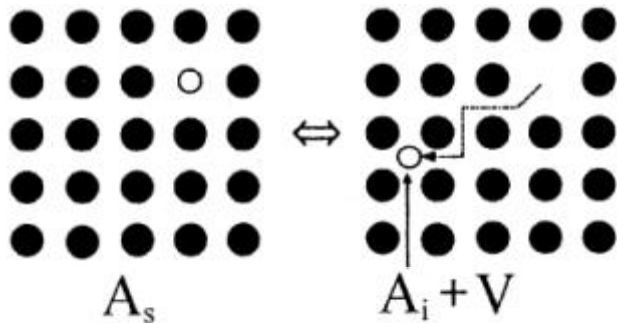
$$D_A = C_V D_V$$

$$D_A = D_0 \exp\left(\frac{-\left(\Delta H_f^V + \Delta H_m^V\right)}{k_B T}\right)$$

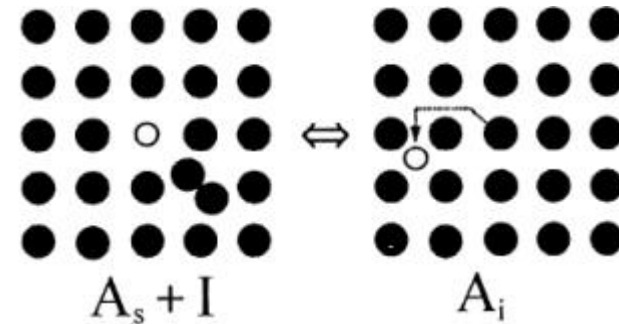Vacancies diffuse in the opposite direction to atoms

➢ Among the slower mechanisms (proportional to melting point)

Diffusion mechanisms

Atoms substitutionally dissolved and interstitial mechanism

$$A_i + V \Leftrightarrow A_s \qquad\qquad A_S + I \Leftrightarrow A_i$$
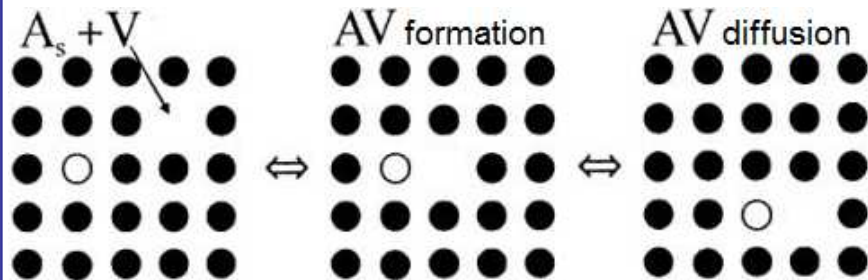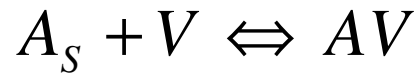

dissociation mechanism
or
Frank-Turnbull reaction

kick-out mechanism

$$D_A = D_A^{A_i} = \frac{C_{A_i}}{C_{A_S}} D_{A_i}$$

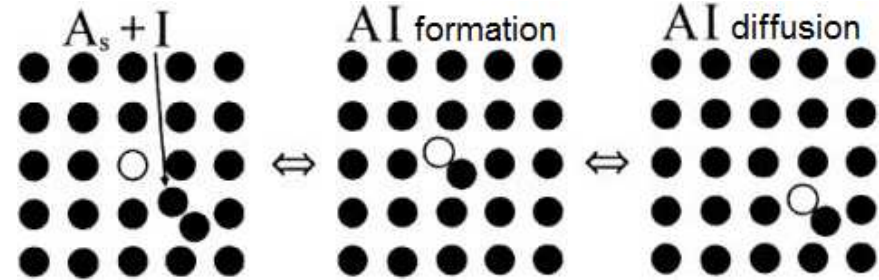➢ Substitutionally dissolved $\left(C_{A_s}^{eq} >> C_{A_i}^{eq}\right)$
➢ Move as interstitial defects
➢ Slower than direct interstitial mechanism, but faster than direct vacancy mechan.

Diffusion mechanisms

Atoms substitutionally dissolved & atom-defect pair mechanism

$$A_S + V \Leftrightarrow AV$$

$$A_S + I \Leftrightarrow AI$$

Vacancy mechanism
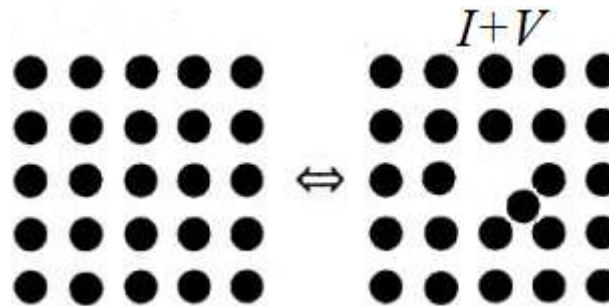(partially dissociated: 3rd neighbors)

Interstitialcy mechanism
(not dissociated)

$$D_A = D_A^{AV} + D_A^{AI} = \frac{C_{AV} D_{AV}}{C_{A_s}} + \frac{C_{AI} D_{AI}}{C_{A_s}}$$

➢ Substitutionally dissolved $\left(C_{A_s}^{eq} >> C_{AX}^{eq} \right)$
➢ Move as a pair atom-defect (= new point defect)
➢ Slow mechanism (~ direct vacancy mechanism)

Diffusion mechanisms

Self-diffusion

$$I + V \Longleftrightarrow \langle 0 \rangle$$ Frenkel's reaction

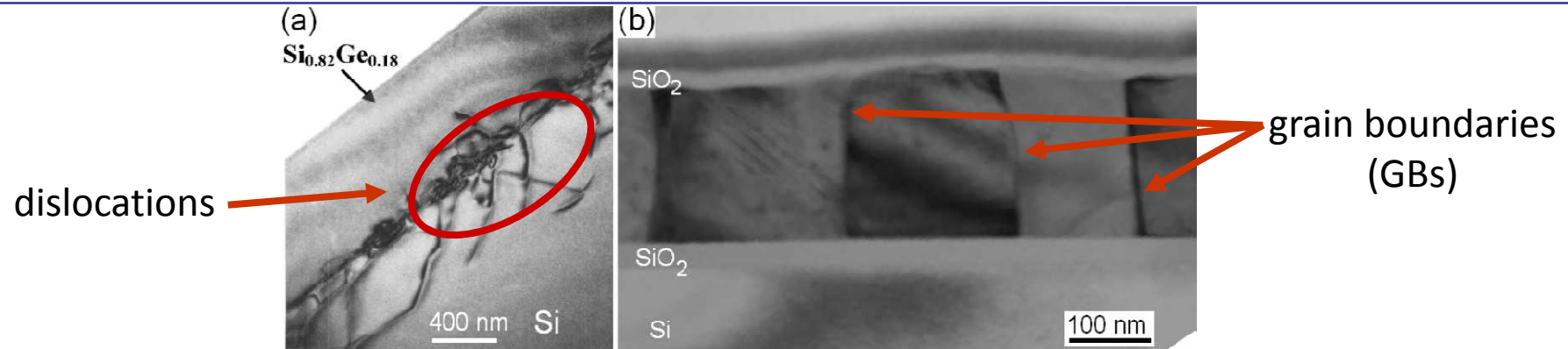$$D_A = D_A^I + D_A^V = C_I^{eq} D_I + C_V^{eq} D_V$$

Examples:

$$D_{Metal} = D_A^V = C_V^{eq} D_V$$

$$D_{Si} = D_{Si}^I + D_{Si}^V = C_I^{eq} D_I + C_V^{eq} D_V$$
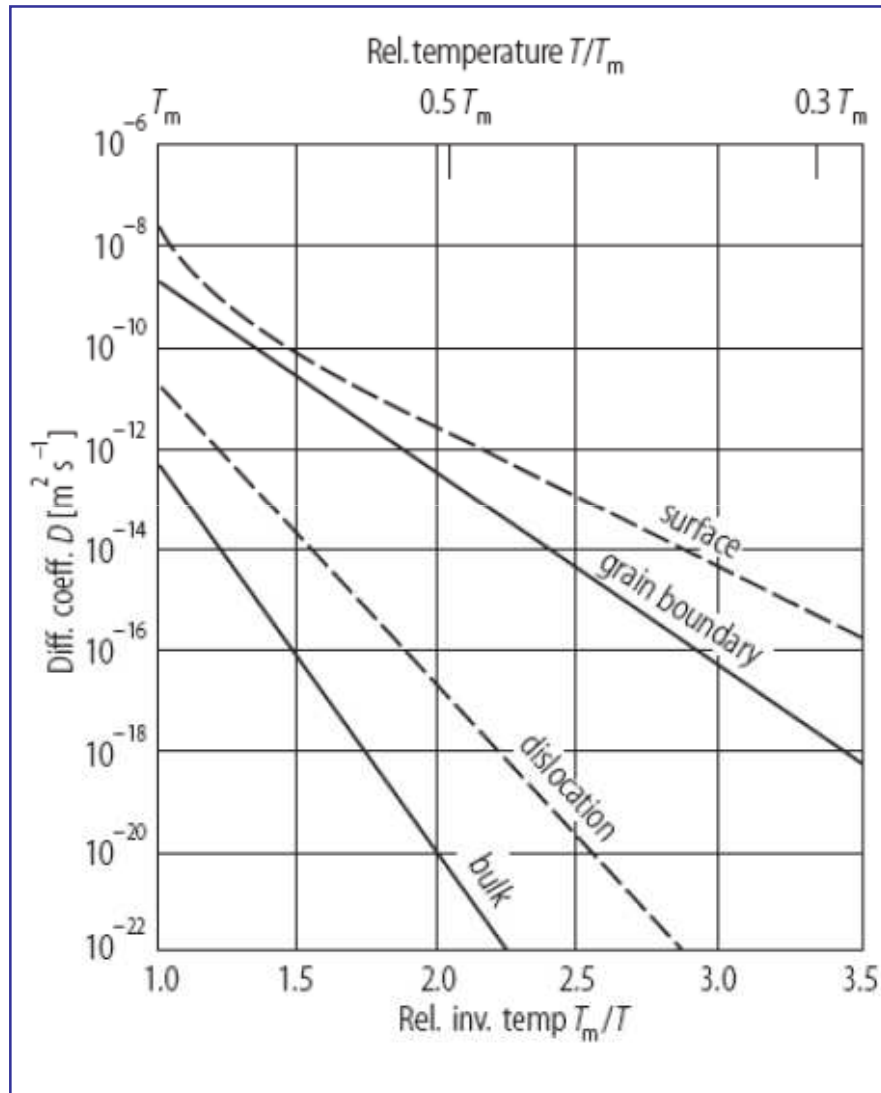
$$D_{Ge} = D_{Ge}^V = C_V^{eq} D_V$$

Diffusion paths

(a) Si$_{0.82}$Ge$_{0.18}$

dislocations

400 nm   Si

(b) SiO$_2$ SiO$_2$ Si   100 nm

grain boundaries (GBs)

Extended defects (dislocations, GBs, interfaces…) = fast diffusion paths

➢ generally, due to higher concentrations of point defects in or close to extended defects, diffusion is faster than in bulk $\Rightarrow$ diffusion "short circuits"

➢ same diffusion mechanisms than lattice (bulk) diffusion, as well as new mechanisms due to properties and geometry of extended defects

$\Rightarrow$ collective mechanisms (atomic chains) appear to be more important in GBs

$\Rightarrow$ on reconstructed surfaces diffusion can be strongly anisotropic and can use multi-mers

➢ point defect formation energy is smaller in extended defects than in crystal bulk, but can significantly change from site to site in the extended defects   ➢

in extended defects, the vacancy formation energy is close to the one of interstitial

$\Rightarrow$ the coexistence probability of vacancy and interstitial mechanisms is higher than in bulk (but the structure of extended defects can promote one mechanism versus the other)
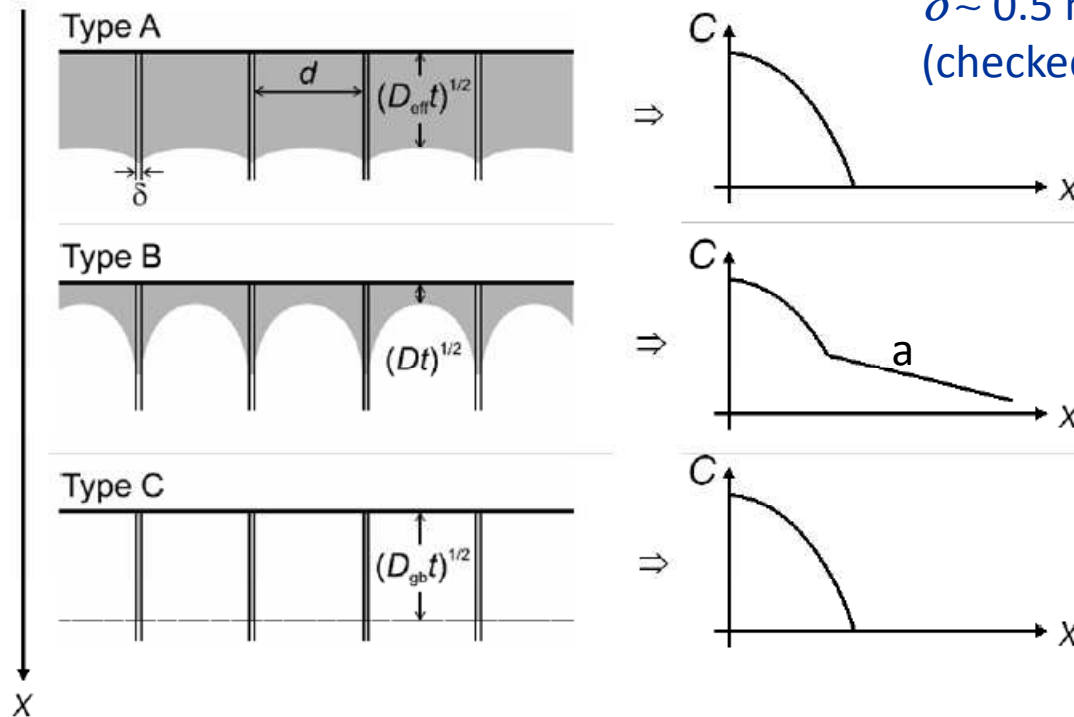
Diffusion paths

Self-diffusion in a metal with the melting temperature T_m

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Diffusion paths

Diffusion in poly-crystals

$\delta \sim 0.5$ nm
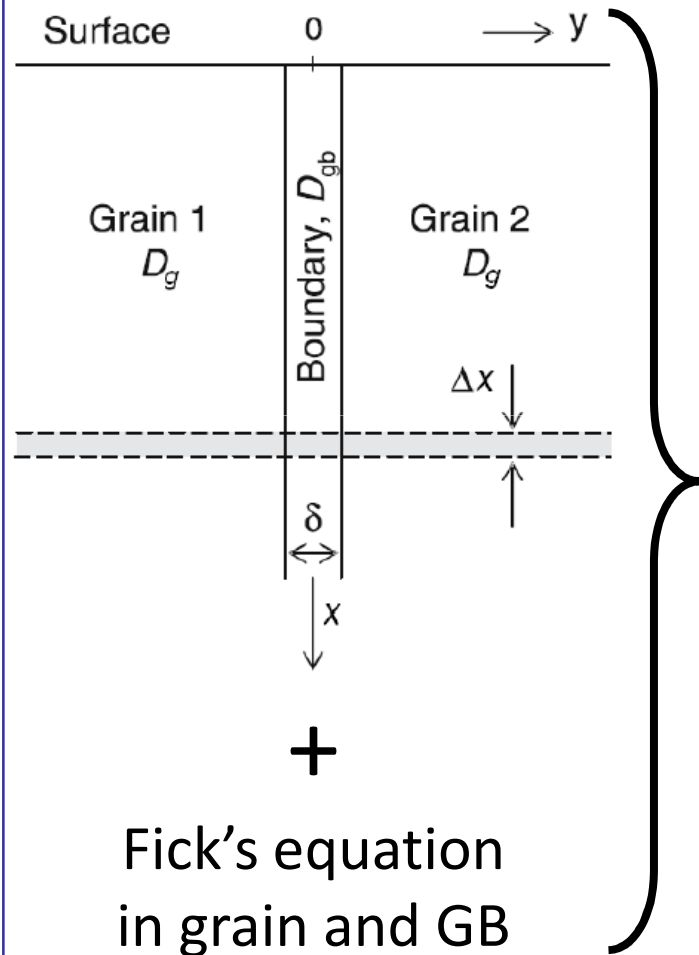(checked experimentally and theoretically)

Kinetic regimes from
Harrison

Kinetic regime "A" $\Rightarrow$ $(D_g\, t)^{1/2} \geq d\,/0.8$ ➡ $D^{\text{eff}} = \dfrac{g\delta}{d} D_{gb} + \left(1 - \dfrac{g\delta}{d}\right) D_g$

g: geometrical factor (= 1 parallel grains)

Kinetic regime "C" $\Rightarrow$ $(D_g\, t)^{1/2} \ll s\delta$

Henry segregation $C_{gb} = sC_g$

Diffusion paths

Diffusion in poly-crystals: kinetic regime "B"

$$s\delta << (D_g t)^{1/2} << d$$

+

Fick's equation
in grain and GB

constant source on the surface

$$sD_{gb}\delta = 1.322 \left(\frac{D_g}{t}\right)^{\frac{1}{2}} (-a)^{-\frac{5}{3}}$$

Instantaneous source on the surface

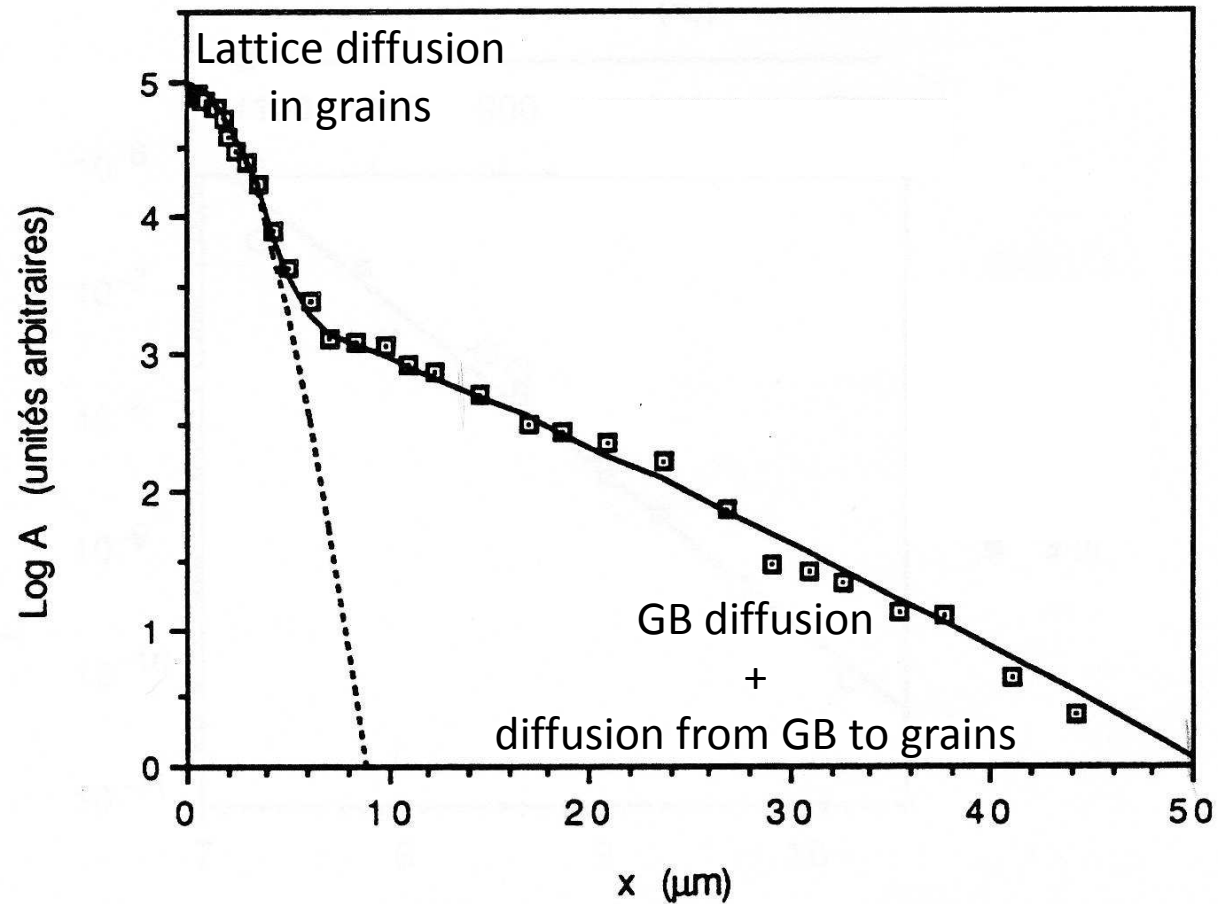$$sD_{gb}\delta = 1.308 \left(\frac{D_g}{t}\right)^{\frac{1}{2}} (-a)^{-\frac{5}{3}}$$

with $a = \dfrac{d \ln C}{dx^{6/5}}$

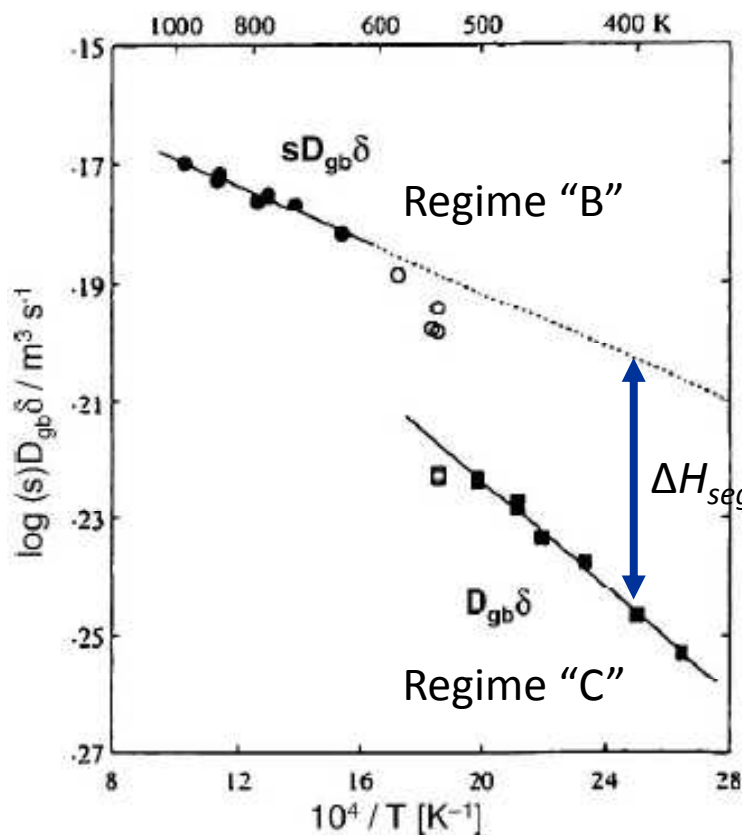s: segregation coefficient in the GB

Diffusion paths

Diffusion in poly-crystals: kinetic regime "B"

$$s\delta \ll (D_g t)^{1/2} \ll d$$

Diffusion paths

Diffusion in poly-crystals

Te diffusion in Ag grain boundaries according to Herzig et al.
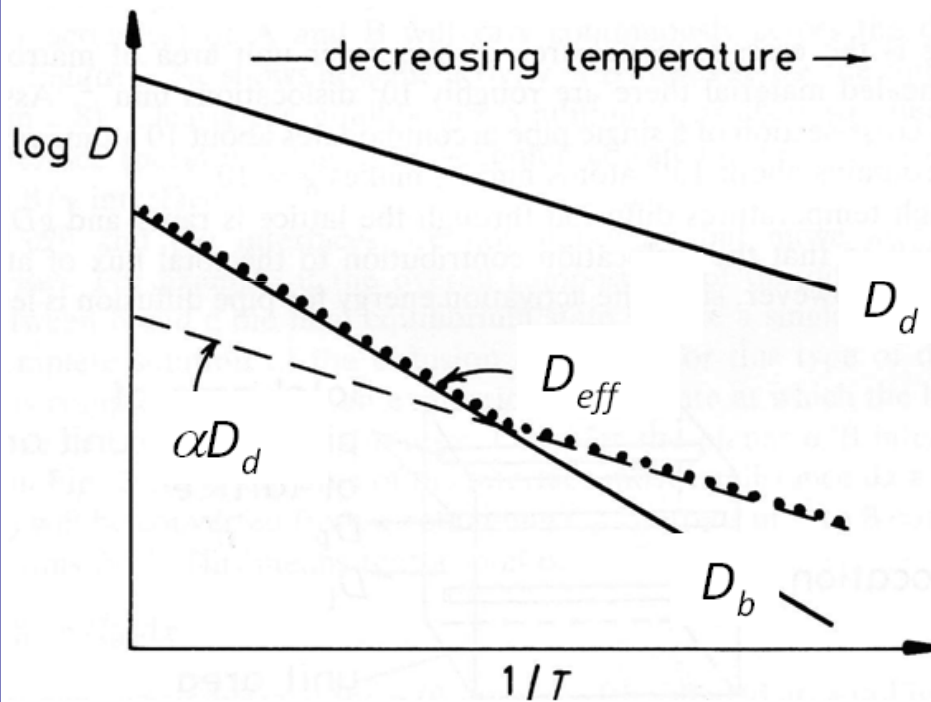
$\Delta H_{seg} = -0.45$ eV

$$C_{gb} = sC_g$$

Henry segregation

$$s = s_0 \exp\left(\frac{-\Delta H_{seg}}{k_B T}\right)$$

Diffusion paths

Diffusion in a crystal with dislocations

D_d: diffusion coefficient in dislocations
D_b: diffusion coefficient in bulk

Hart formula

$$D_{eff} = \alpha\, D_d + (1-\alpha)\, D_b$$

$\alpha = \delta/d$: proportion of sites in dislocations

Kinetic regime "A"

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Diffusion not at equilibrium

⮫ Industrial process ⟹ materials not at thermodynamic equilibrium!

➢ Point defect concentrations not at equilibrium

➢ Point defect reactions not at equilibrium   ➢

Strong influence of point defect sources and sinks

➢ Diffusion coefficients not constant (varies with t, C…)

⮫ Industrial process ⟹ Complex geometry (nanostructures with different types of interfaces, nano-crystalline…)

No analytical solution ⟹ numerical simulations

➢ Surface reactions can inject point defects in the bulk of the sample
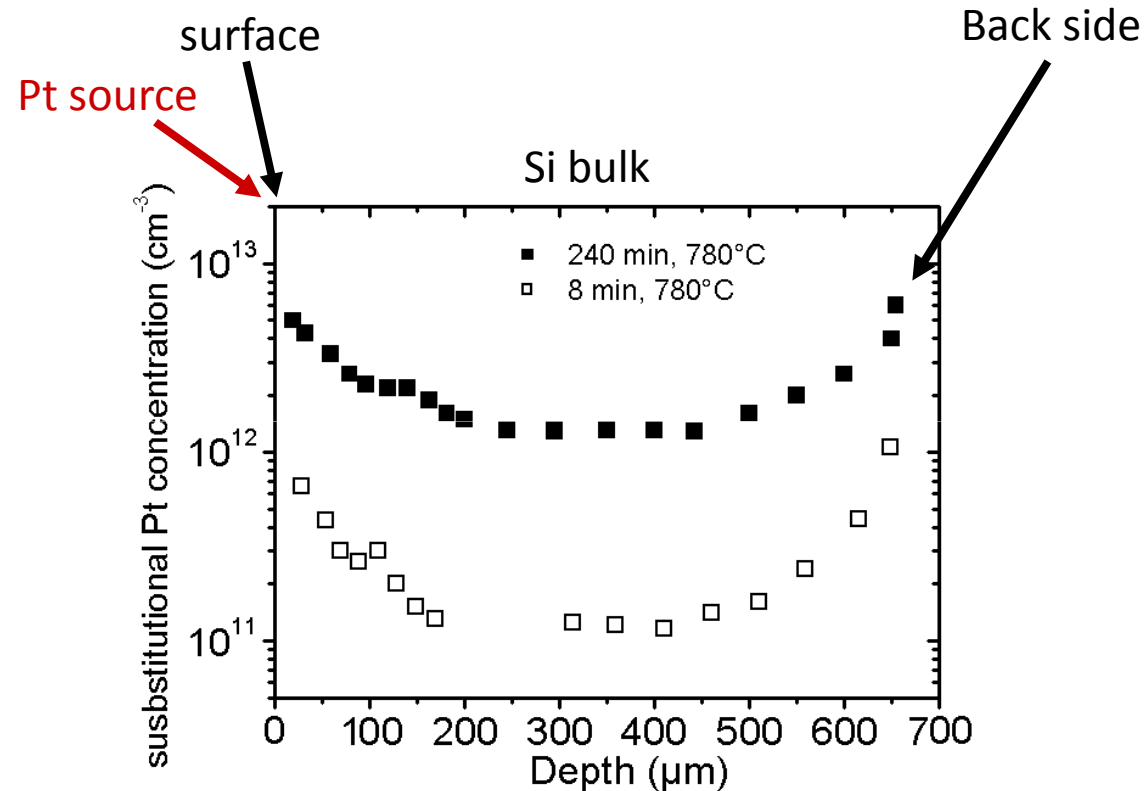
⟹ self-interstitial injection during Si oxidation

⟹ vacancy injection during Si nitridation

➢ Over-saturation of self-interstitials after atom implantation

➢ Irradiations

Source and sink influence

Example: simple case of Pt diffusion in mono-crystalline Si bulk

Asymmetric profiles (especially at short annealing times)
with a "U" shape
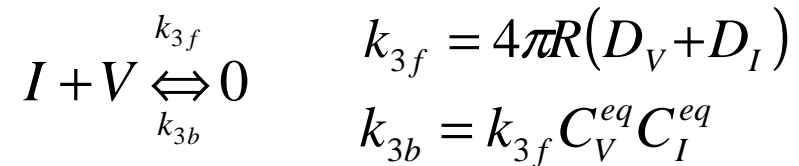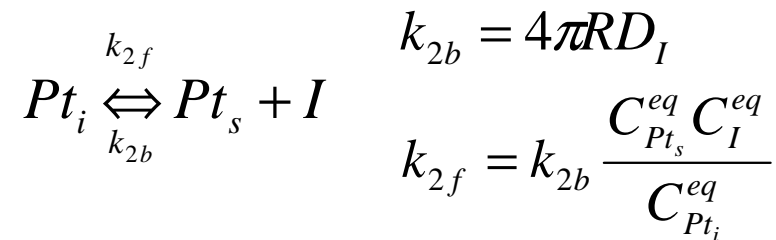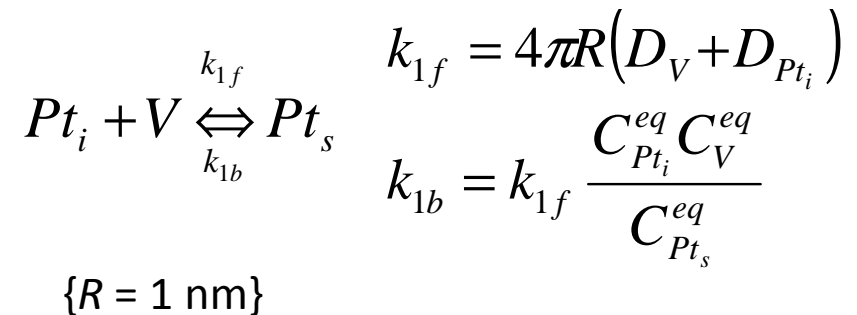
Source and sink influence

Three diffusing species

⮞ interstitial Pt
⮞ vacancies
⮞ Si self-interstitials

$$J_{Pt_i} = -D_{Pt_i} \frac{dC_{Pt_i}}{dx}$$

$$J_V = -D_V \frac{dC_V}{dx}$$

$$J_I = -D_I \frac{dC_I}{dx}$$

Diffusion limited reactions

$$Pt_i + V \underset{k_{1b}}{\overset{k_{1f}}{\Longleftrightarrow}} Pt_s$$

$$k_{1f} = 4\pi R \left(D_V + D_{Pt_i} \right)$$

$$k_{1b} = k_{1f} \frac{C_{Pt_i}^{eq} C_V^{eq}}{C_{Pt_s}^{eq}}$$

{R = 1 nm}

$$Pt_i \underset{k_{2b}}{\overset{k_{2f}}{\Longleftrightarrow}} Pt_s + I$$

$$k_{2b} = 4\pi R D_I$$

$$k_{2f} = k_{2b} \frac{C_{Pt_s}^{eq} C_I^{eq}}{C_{Pt_i}^{eq}}$$

$$I + V \underset{k_{3b}}{\overset{k_{3f}}{\Longleftrightarrow}} 0$$

$$k_{3f} = 4\pi R \left(D_V + D_I \right)$$

$$k_{3b} = k_{3f} C_V^{eq} C_I^{eq}$$

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Source and sink influence

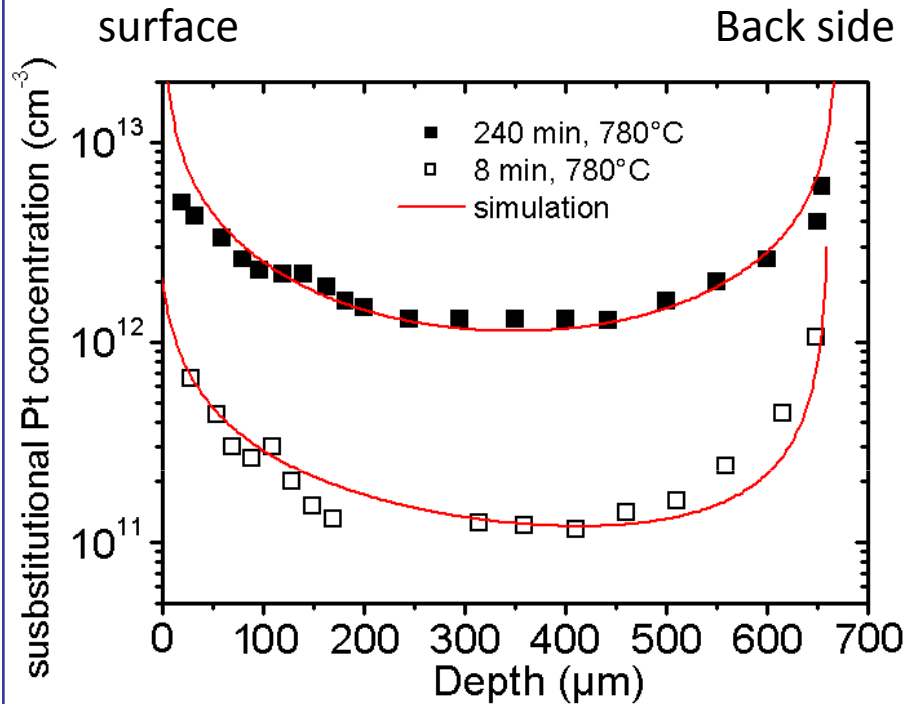Four different species: substitutional Pt, interstitial Pt, vacancies, and Si self-interstitials

$$\frac{dC_{Pt_s}}{dt} = k_{1f}C_{Pt_i}C_V - k_{1b}C_{Pt_s} + k_{2f}C_{Pt_i} - k_{2b}C_{Pt_s}C_I$$

$$\frac{dC_{Pt_i}}{dt} = k_{1b}C_{Pt_s} - k_{1f}C_{Pt_s}C_V + k_{2b}C_{Pt_s}C_I - k_{2f}C_{Pt_i} - \frac{dJ_{Pt_i}}{dx}$$

$$\frac{dC_I}{dt} = k_{2f}C_{Pt_i} - k_{2b}C_{Pt_s}C_I + k_{3b} - k_{3f}C_VC_I - k_{2f}C_{Pt_i} - \frac{dJ_I}{dx}$$

$$\frac{dC_V}{dt} = k_{1b}C_{Pt_s} - k_{1f}C_{Pt_i}C_V + k_{3b} - k_{3f}C_VC_I - \frac{dJ_V}{dx}$$

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Source and sink influence

surface   Back side

Initial conditions

$$C_V^{surf} = C_V^{bulk} = C_V^{eq}$$

$$C_I^{surf} = C_I^{bulk} = C_I^{eq}$$

Si at equilibrium

$$C_{Pt_s}^{surf} = C_{Pt_s}^{eq}$$

$$C_{Pt_i}^{surf} = C_{Pt_i}^{eq}$$

Pt solubility limit

$$C_{Pt_s}^{bulk} = C_{Pt_i}^{bulk} = 0 \quad \text{no Pt in bulk}$$

Boundary conditions

$$C_V^{surf} = C_V^{eq} \quad \text{Point defects at equilibrium}$$

$$C_I^{surf} = C_I^{eq} \quad \text{at the two surfaces}$$

$$C_{Pt_s}^{surf} = C_{Pt_s}^{eq} \quad \text{Diffusion under the Pt solubility}$$

$$C_{Pt_i}^{surf} = C_{Pt_i}^{eq} \quad \text{limit at the surface with Pt}$$

Unknown parameters

$$D_{Pt_i} \qquad C_{Pt_s}^{eq} \qquad \alpha = \frac{C_{Pt_i}^{eq}}{C_{Pt_s}^{eq}}$$

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Measurements of "the" diffusion coefficient

Diffusion coefficient measurements

$$D_A = C_X^{eq} D_X$$

⮑ Use materials as pure as possible (purification treatments)

⮑ Point defects need to be at equilibrium

⮑ Microstructure needs to be stable (no grain growth for poly-crystals for example)

⮑ The knowledge of the driving force is needed to use the correct diffusion equation allowing to extract the correct diffusion coefficient

⮑ If use an analytical solution: be sure to be in the correct conditions corresponding to the used solution (geometry + initial and boundary conditions)

$\Rightarrow$ choose as simple as possible experimental conditions (reduce diffusion equation complexity and parameters)

$\Rightarrow$ Perform a pre-annealing (stabilization of microstructure + point defect equilibrium)

$\Rightarrow$ Perform several measurements at same temperature but for different times in same sample: check that D is constant (equilibrium point defect concentration + stable microstructure)

$\Rightarrow$ Check microstructure before and after diffusion annealing

Influence of impurities
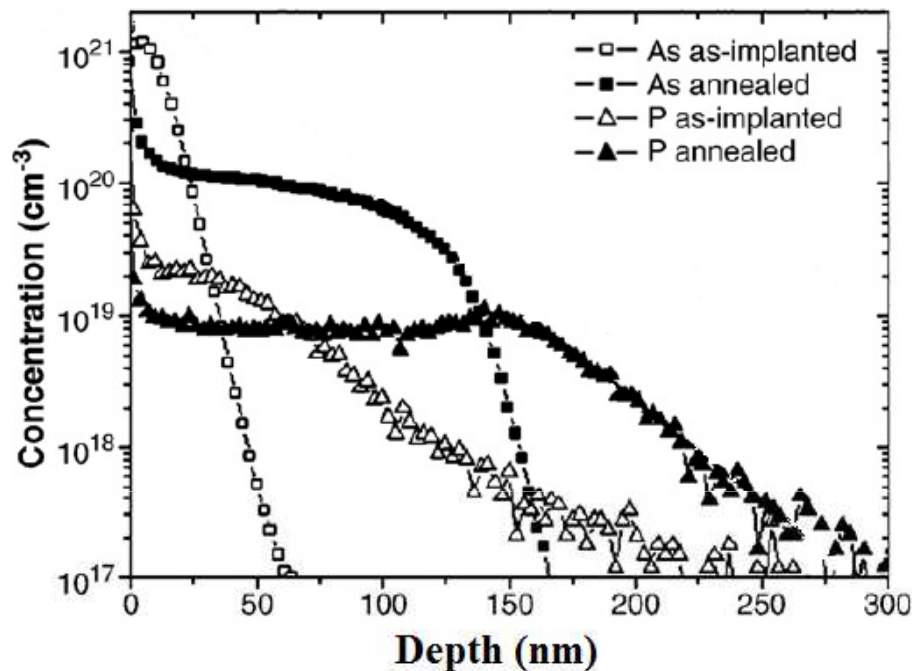
As (squares) and P (triangles) profiles measured in the as-implanted sample (open symbols) and after annealing at 950 °C for 900 s (solid symbols)
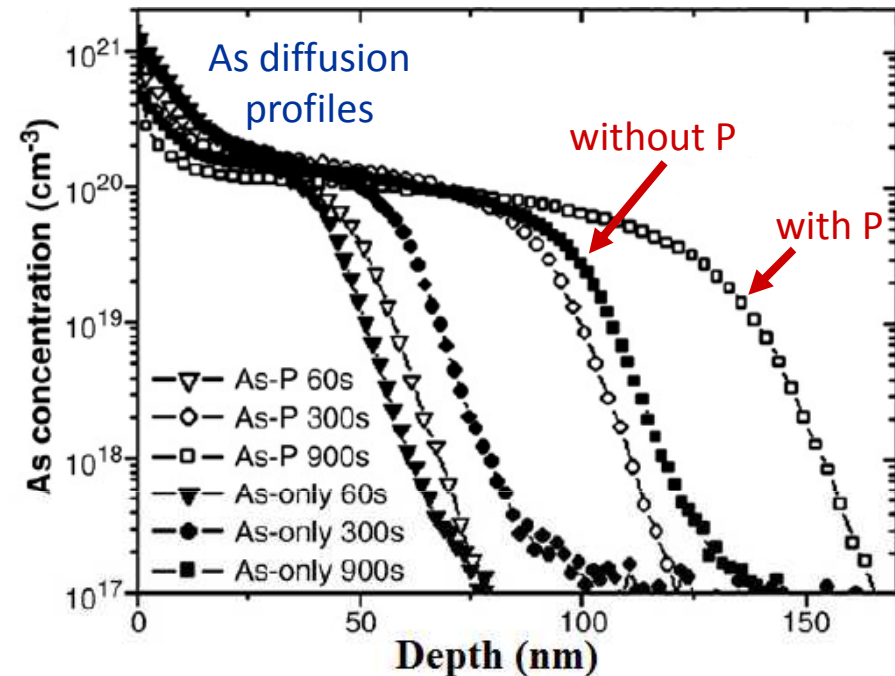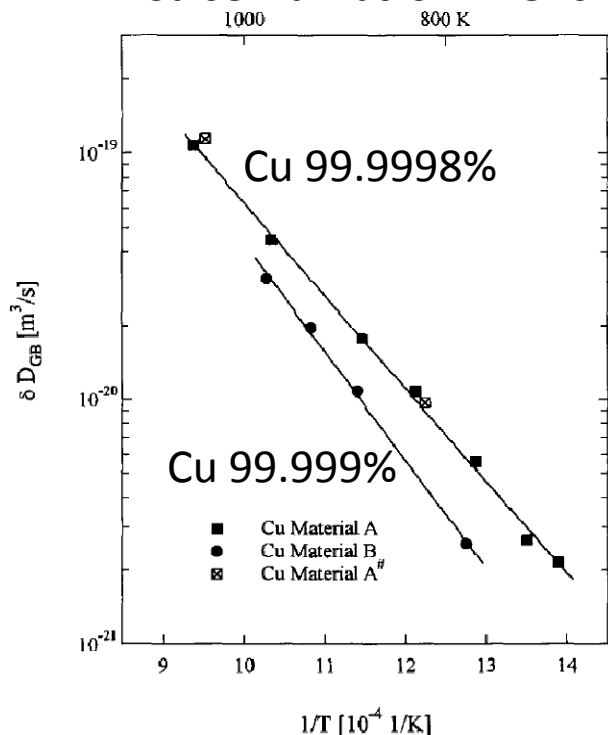
As profiles measured in As-only samples and in As–P samples

N. Rodriguez, A. Portavoce et al., Thin Solid Films 518 (2010) 5022

➲ During co-diffusion of several impurities, impurity-impurity interactions, as well as impurity-point defect interactions modify the diffusion kinetic
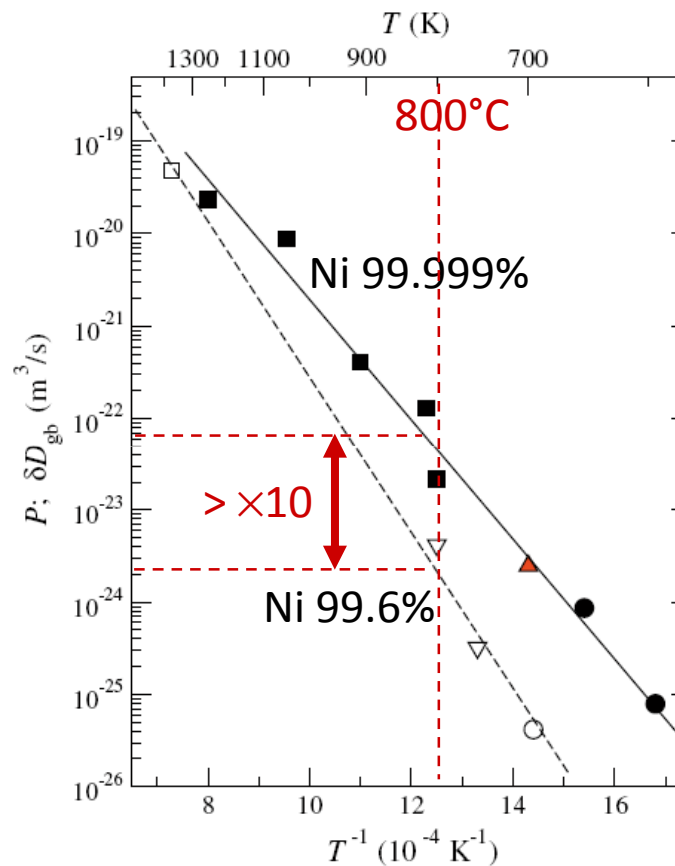
Influence of impurities

Cu self-diffusion in GBs

T. Surholt et al., Acta mater. 45 (1997) 3817

Table 2. Impurity content of Cu and material A (c_A) in relation to Cu material B (c_B) for some selected solutes

	C	N	O	F	Cl	As
c_A/c_B	0.5	19.7	1.4	0.8	0.01	0.4

Ni self-diffusion in GBs

S.V. Divinski et al., Acta Mater. 58 (2010) 386

➲ Impurities decrease GB diffusion coefficients

Pressure effect

Sb diffusion in Si
(vacancy-mediated)

$\Delta V^* = +0.07\Omega$

860°C
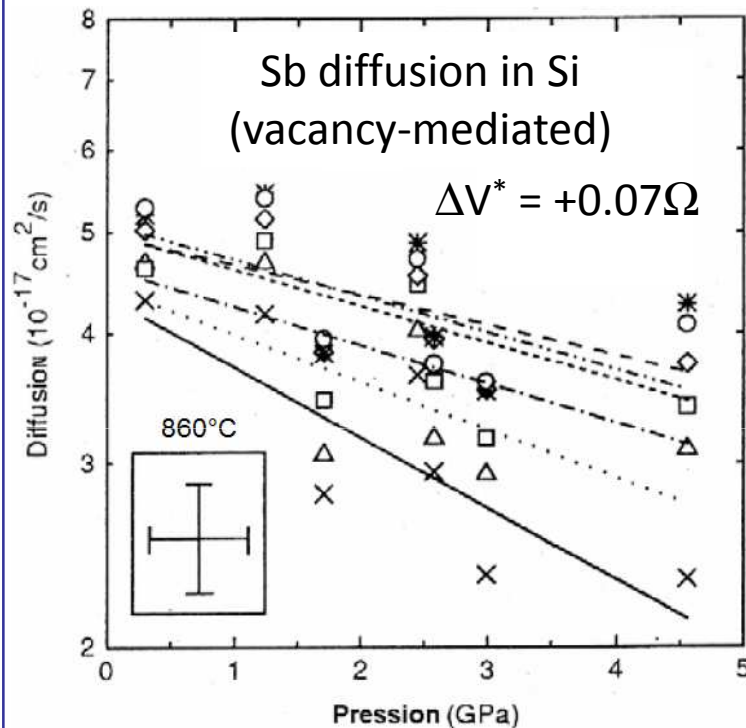
Y. Zhao et al., Appl. Phys. Lett. 75 (1999) 941

B diffusion in Si
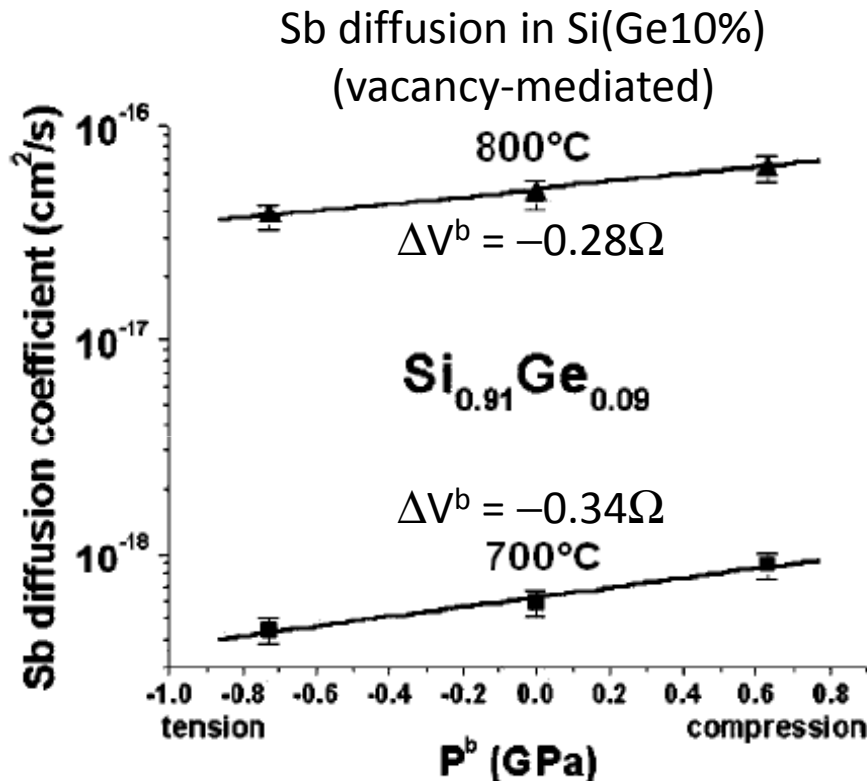(interstitial-mediated)

$\Delta V^* = -0.17\Omega$
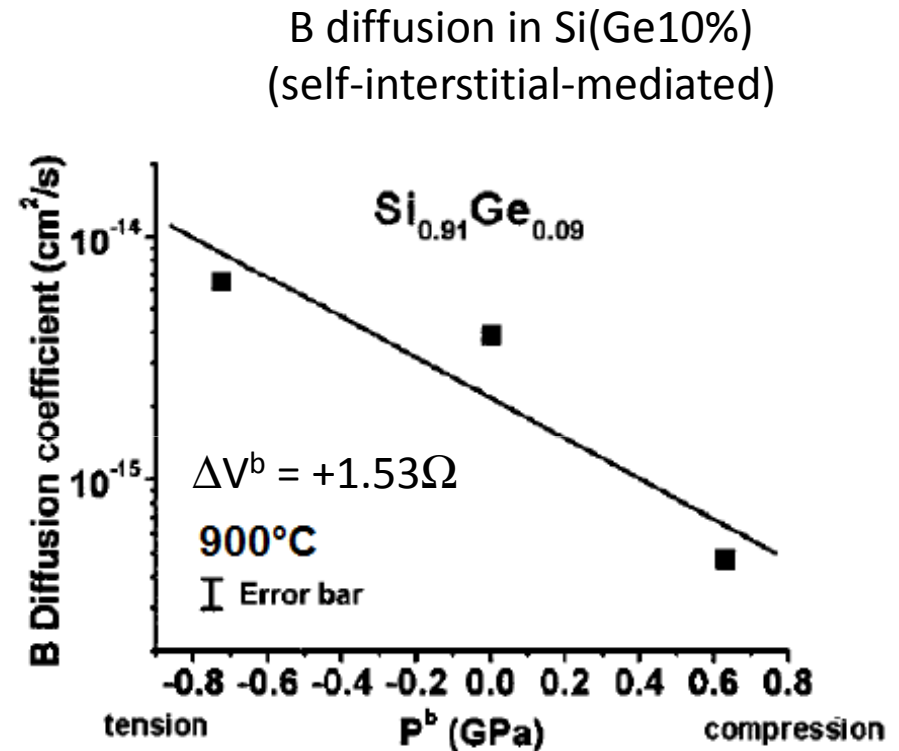
810°C
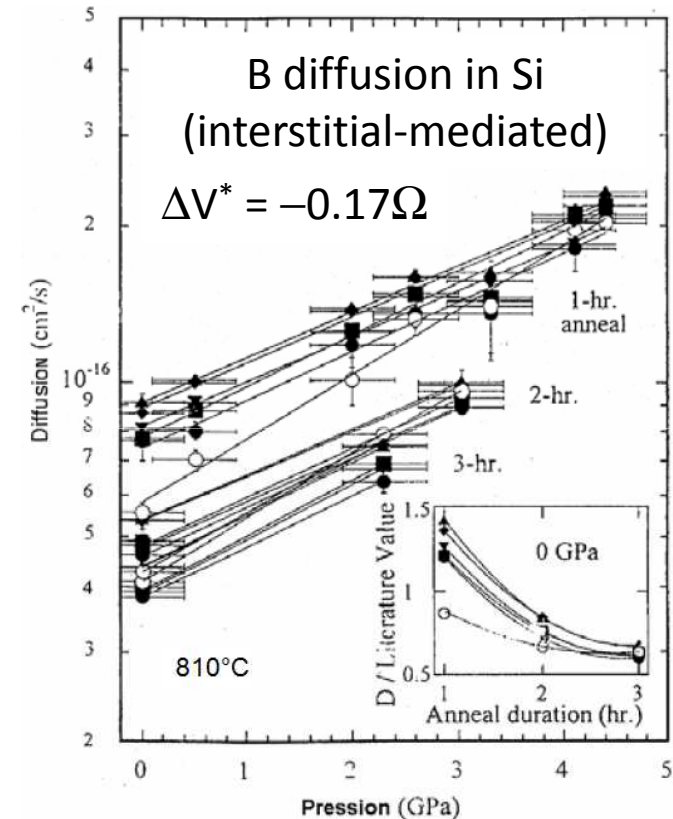
Y. Zhao et al., Appl. Phys. Lett. 74 (1999) 31

➲ Hydrostatic pressure decreases the diffusion coefficient of vacancy-mediated elements and increases the diffusion coefficient of interstitial-mediated elements

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Pressure effect

Biaxial pressure

Sb diffusion in Si(Ge10%)
(vacancy-mediated)

B diffusion in Si(Ge10%)
(self-interstitial-mediated)

A. Portavoce et al., Phys. Rev. B 69 (2004) 155415

A. Portavoce et al., J. Appl. Phys. 96 (2004) 3158

➲ Biaxial pressure increases the diffusion coefficient of vacancy-mediated elements and decreases the diffusion coefficient of interstitial-mediated elements

Nanometric-size effect

Table 1. Analysis of diffusion in nanocrystalline materials ➲ **GB diffusion faster in nano-crystalline layers?**

Metal (diffusant)	Reported data				
	d (nm)	T (K) T/T_M	D_{ig} (m^2 s^{-1})[a]	D_{gb} (m^2 s^{-1})[a]	
Cu (Cu) Self-diffusion	8	293 0.216	2.6×10^{-20} [6]	9.6×10^{-24} [28]	$D_{nano}/D_{gb} \sim 3 \times 10^3$
	8	353 0.260	2.0×10^{-18} [6]	1.2×10^{-20} [28]	$D_{nano}/D_{gb} \sim 1.7 \times 10^2$
	8	393 0.289	1.7×10^{-17} [6]	4.4×10^{-19} [28]	$D_{nano}/D_{gb} \sim 3 \times 10^3$
Cu (Ag) Impurity diffusion	8	303 0.223	3.0×10^{-19} [8]	2.6×10^{-22} [8]	$D_{nano}/D_{gb} \sim 10^3$
	8	353 0.260	3.1×10^{-18} [8]	1.4×10^{-20} [8]	$D_{nano}/D_{gb} \sim 2 \times 10^2$
	8	373 0.275	1.2×10^{-17} [8]	4.5×10^{-19} [8]	$D_{nano}/D_{gb} \sim 3 \times 10^1$
Cu (Bi) Impurity diffusion	11	293 0.216	5.0×10^{-23} [10]	3.4×10^{-29} [30]	$D_{nano}/D_{gb} \sim 3 \times 10^3$
	11	333 0.245	3.3×10^{-20} [10]	7.6×10^{-26} [30]	$D_{nano}/D_{gb} \sim 1.5 \times 10^6$
	11	373 0.275	2.3×10^{-19} [10]	3.2×10^{-23} [30]	$D_{nano}/D_{gb} \sim 7 \times 10^3$

Nanometric-size effect

Rel. inv. temp. T/T_m^{Si}

Ge Diff. coeff. D ($cm^2 s^{-1}$) in Si

(111) surface
Triple junction
Grain boundary
40nm-Lattice
Lattice

Rel. inv. temp. T_m^{Si}/T

Top view

Triple-junction

Grain

Grain boundary

A. Portavoce et al., J. Appl. Phys. 104 (2008) 104910
A. Portavoce et al., Appl. Phys. Lett. 96 (2010) 214102

⮚ Identical GB diffusion in micro- and nano-crystalline layers
⮚ Fast diffusion in nano-crystalline layers = fast diffusion in Triple Junctions + faster lattice diffusion in nano-crystal

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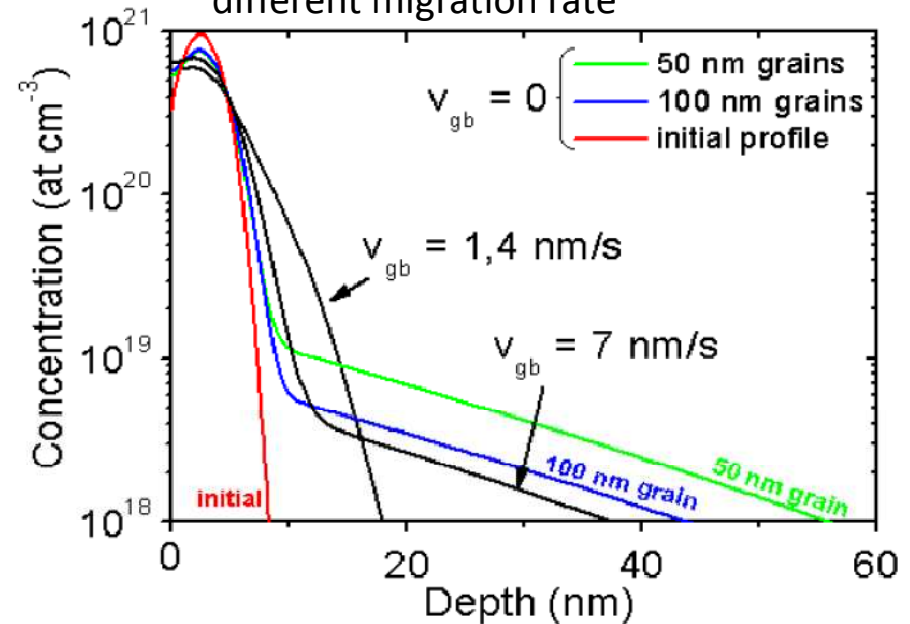
Grain boundary motion

Results of 2D simulations of diffusion during grain growth

migration rate = const,
different fraction of mobile GBs
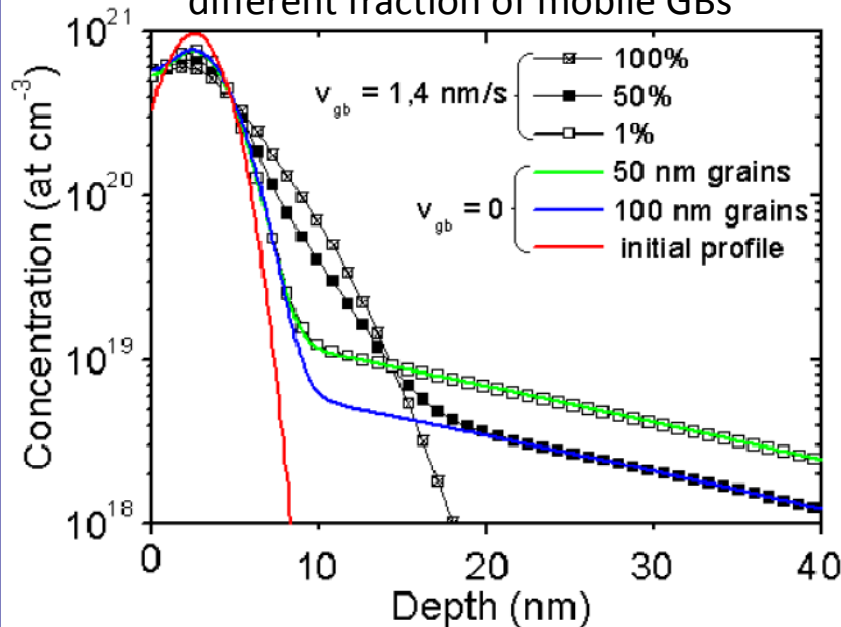
fraction of mobile GBs = const
different migration rate

⮞ Same diffusion coefficient in moving GBs and stationary GBs (P. Zieba, Interface Science 11 (2003) 51)

⮞ GB migration modifies significantly the diffusion profiles

⇒ for small fraction of mobile GBs, the GB diffusion coefficient can be extracted from the deepest part of the profile using usual solutions of the Fick equation (regime "B")

Electromigration

Electron scattering on ions $\Rightarrow$ electrical resistance

➤ Low current density: no displacement of ions
scattering from phonon vibrations generates Joule heating

➤ High current density (> 10^4 A/cm^2): transport of current can displace the ions and can influence atom transport in the crystal $\Rightarrow$ Electromigration

Electromigration = mass transport due to the electric field and the charged carriers $\Rightarrow$ void and extrusion formation

Example in microelectronics

a 5 μm wide line of Al of thickness 0.2 μm subjected to a current of 1 mA experiences a current density of 10^5 A/cm^2

line cross-section ↘ $\Rightarrow$ current density ↗

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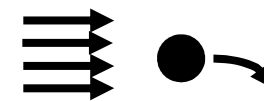
Electromigration

Fick's law $$J = -D\frac{\partial C}{\partial x} + CMF$$

Electromigration in pure metal
Electric field the only driving force $J = CMF$

⮑ Electromigration is due to the combination of thermal and electrical effects
⮑ Occurs at $T \sim 3T_m/4$ in bulk metal and at $T \sim T_m/2$ in a polycrystalline thin film
⇒ T at which a large number of atoms undergo a random walk process

Atom on a saddle point

➤ greater contribution to the resistance to the electric current than an atom on a lattice site
➤ greater electron scattering effect
➤ greater "electron wind force"

Atom in saddle point
electron wind force
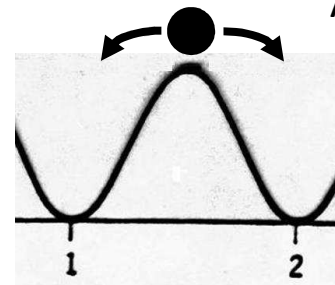
Atom in saddle point
random walk

Electromigration

1/ Electrostatic field effect on the diffusing atoms (= ions)
2/ Momentum exchange of the moving charge carriers with the diffusing atoms

$$F = Z^* e \varepsilon = [Z_{el}^* + Z_{wd}^*] \, e \varepsilon$$

ε: electric field
e: charge of an electron
Z*: effective charge number

Z^*_{el}: nominal valence of the diffusion ion in the metal without screening effect
Z^*_{wd}: charge number representing the momentum exchange effect = "electron wind force"

Good conductor: $Z^*_{wd} \sim 10$

Momentum exchange effect > electrostatic field effect in metals

Without grain boundaries

$$J^{em} = C < v > = CMF = C \frac{D}{k_B T} Z^* e \varepsilon$$

With grain boundaries

$$J_b^{em} = C_b \frac{D_b \delta}{k_B T d} Z_b^* e \varepsilon$$

Electromigration

➢ Electromigration is a reliability concern because it can lead to interconnect failure

➢ Where there is a net depletion of atoms, local stresses become increasingly tensile
⇨ voiding
Failure by open circuit + In the case of interconnects clad in refractory layers or liners, the electric current can shunt through these layers once a void has formed in the interconnect, which will lead to a resistance increase

➢ Where there is a net accumulation of atoms, the local stresses become increasingly compressive ⇨ extrusions
Failure by short circuit if the extruded metal touches a neighboring interconnect
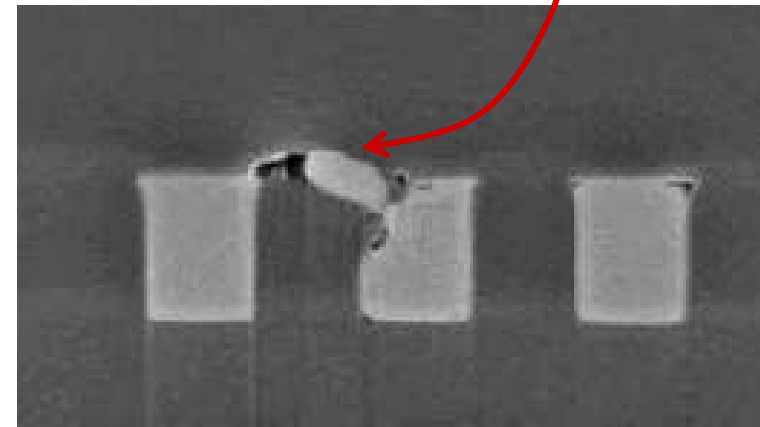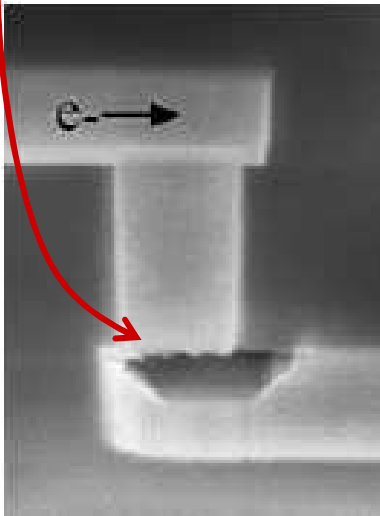
Electromigration

➢ In contrast to Al-based interconnects, microstructure does not play a dominant role in the electromigration of today's Cu-based interconnects

➢ The top surface/interface of Cu is the fastest diffusion path ($D_s \gg D_{gb}$)

➢ Differences in thermal coefficients of expansion (TCE) at interfaces support an enhanced void formation induced by electromigration due to mechanical stresses
⇨ The TCE ratio is 2.5 for Cu/Ta and 6.6 for Cu/Si$_3$N$_4$

Interlevel-diffusion barrier

Liner
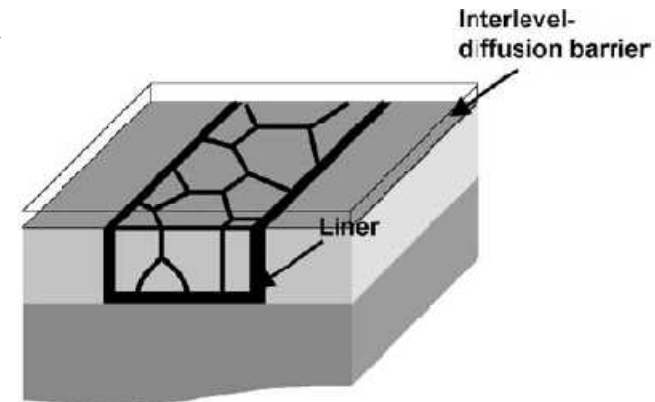
Diffusion coefficients at interfaces?
⇒ more and more important in nanotechnology (lots of different interfaces in a same structure)
⇒ today, no systematic studies
⇒ need new experimental scheme to measure interface diffusion coefficients

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