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SPRING COLLEGE IN MATERIALS SCIENCE ON
"NUCLEATION, GROWTH AND SEGREGATION IN MATERIALS
SCIENCE AND ENGINEERING"
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TRANSPORT PROCESSES
(INCLUDING RADIATION ENHANCED DIFFUSION)
Part II

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Radiation-Induced and
Radiation-Enhanced Diffusion,
and Related Phenomena

Thermally Activated Diffusion in Solids

Diffusion in Thermal Equilibrium

Direct diffusion:

$$D = \underbrace{g a^2 \nu_0 \exp(S^M/k)}_{D_0} \exp(-H^M/kT)$$

Indirect diffusion via vehicles v ($= V$ or I):

$$D_v^s = f_v D_v C_v^{eq}$$

$$D_v = D_{v,0} \exp\left(-H_v^M/kT\right)$$

$$C_v^{eq} = \exp(S^F/k)\exp(-H^F/kT)$$

Diffusion under Non-Equilibrium Conditions

I. Mobility-enhanced/retarded diffusion (e.g., radiation-induced diffusion)

Direct diffusion: $D \rightarrow D^*$ $\quad (H^M, D_0 \rightarrow H^{M*}, D_0^*)$

Indirect diffusion: $D_v^s \rightarrow D_v^{s*}$ $\quad (H_v^M, D_{v,0} \rightarrow H_v^{M*}, D_{v,0}^*)$

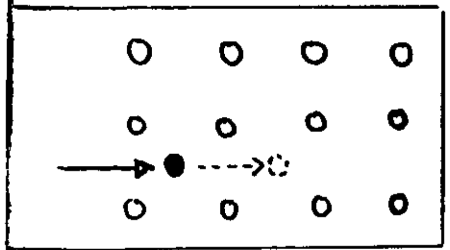
II. Concentration-enhanced/retarded diffusion (e.g., radiation-enhanced diffusion)

Only possible for indirect diffusion: $C_v^{eq} \rightarrow C_v^*$

Mechanisms of Mobility-Enhanced* Diffusion

1. Collision-enhanced mobility

1.1. Direct collision displacement

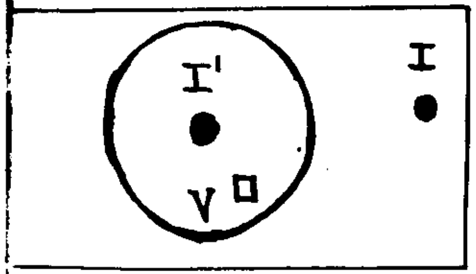


a) very unlikely

b) practically T-independent

c) strongly dependent on crystallographic direction

1.2. Indirect collision displacement



a) seeming displacement of self-interstial ($I' \rightarrow I$)

b) fairly effective, since spontaneous recombination volume $\simeq 10^4$ at. vol.

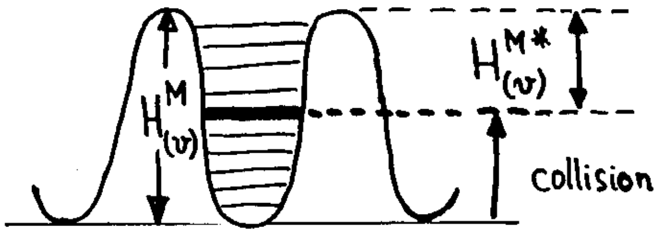
c) works also for subthreshold displacements

d) works also for vacancies or foreign atoms

e) T-dependent via recombination volume

*"Enhancement" includes "retardation" (negative enhancement)

1.3. Thermally assisted collision displacement via excited states of vibration



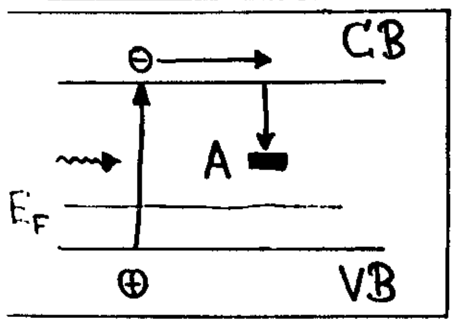
a) T-dependent

b) Example: low-T-irradiation-induced recombination of V–I pairs

1.4. Mobility enhancement by local irradiation heating

Example: low-T-irradiation-induced recombination of V–I pairs

2. Electronic-state-controlled mobility changes



a) restricted to non-metals (e.g., semiconductors)

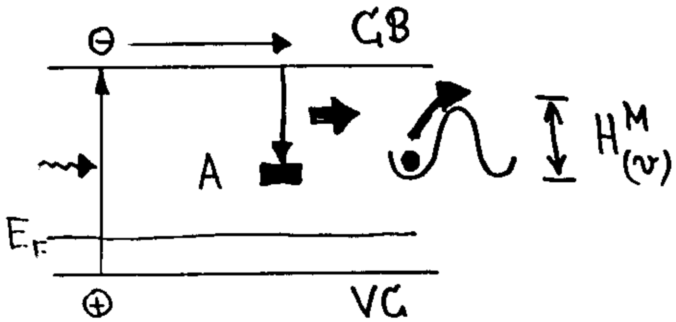
b) may arise from particle irradiation or illumination

c) may involve change of charge state [see left] and/or electronic excitation state and thus changes the defect size, the coupling to the matrix, and the geometrical

3. Mobility enhancement by electronic-energy release

(restricted to non-metals, e.g., semiconductors)

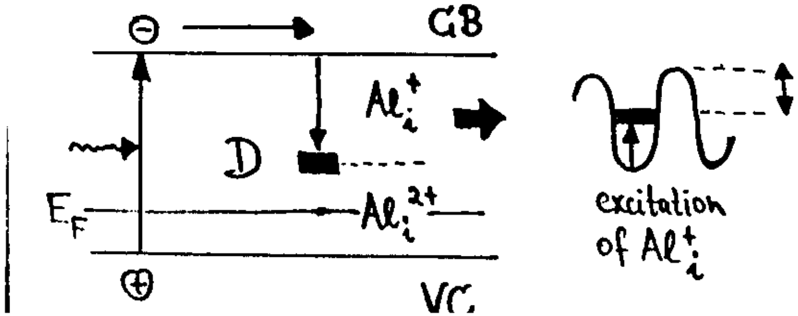
3.1. Direct energy-release mechanism



Examples: a) athermal migration of self-interstitials under irradiation or illumination in Si and Ge at ~0 K, indicated by $Al_s + I \rightarrow Al_i$

b) GaAs

3.2. Thermally assisted energy-release mechanism via excited states of vibration



$H^{M*}_{Al_i^+} = 0.27\,eV$

Compare:

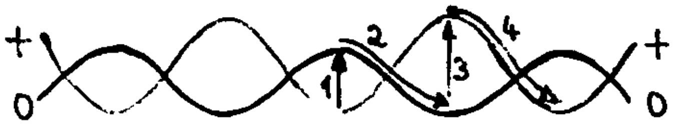
$H^{M}_{\ldots} = 1.2\,eV$

3.3. Bourgoin–Corbett-type mechanisms

Prerequisites:

a) coupling between charge state and geometrical configurations

b) configurations in different charge states are centred on crystallographically different sites



- irradiation or illumination → e^- in CB, h^+ in VB

1 : $D^+ + e^- \rightarrow D^0$

2 : D^0 moves to its equilibrium position

3 : $D^0 + h^+ \rightarrow D^+$

4 : D^+ moves to its equilibrium position

⇨ random walk as a result of repeated changes of charge state

Phenomena of Concentration – Enhanced Diffusion

1. Enhancement of the concentrations of intrinsic defects by irradiation

1.1. Spatially homogeneous defect concentrations

Enhancement of indirect diffusion (self-diffusion or diffusion of substitutional solutes):

$$D^S = f_V D_V C_V + f_I D_I C_I$$

Steady state $(D_V C_V = D_I C_I)$:

$$D^S = (f_V + f_I) D_V C_V = (f_V + f_I) D_I C_I$$

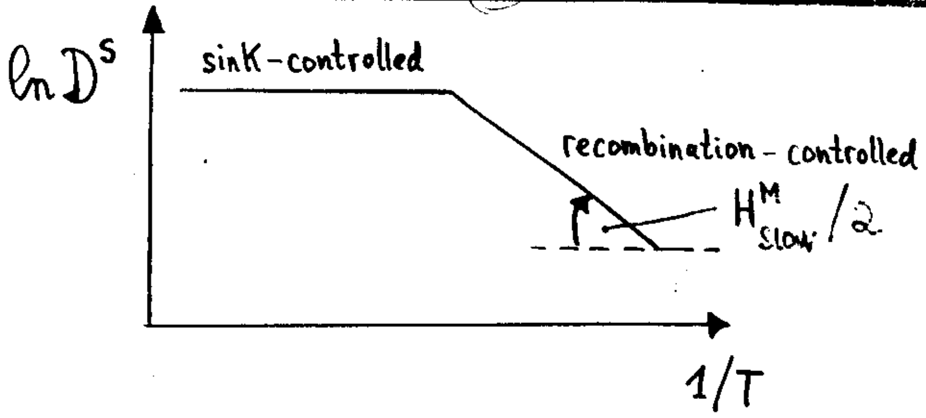
Major results of the Lomer–Dienes–Damask–Sizmann rate-equation treatment:

a) Sink-controlled case (high T, low $C_{V,I}$):

$$D^S \sim D_V C_V = D_I C_I \neq f(T)$$

b) Recombination-controlled case (low T, high $C_{V,I}$):

$$D^S \sim \exp\left(-H^M_{slow}/2kT\right)$$



1.2. Spatially inhomogeneous defect concentrations (redistribution of substitutional solutes)

Potential mechanisms:

1) Formation of rapid pairs

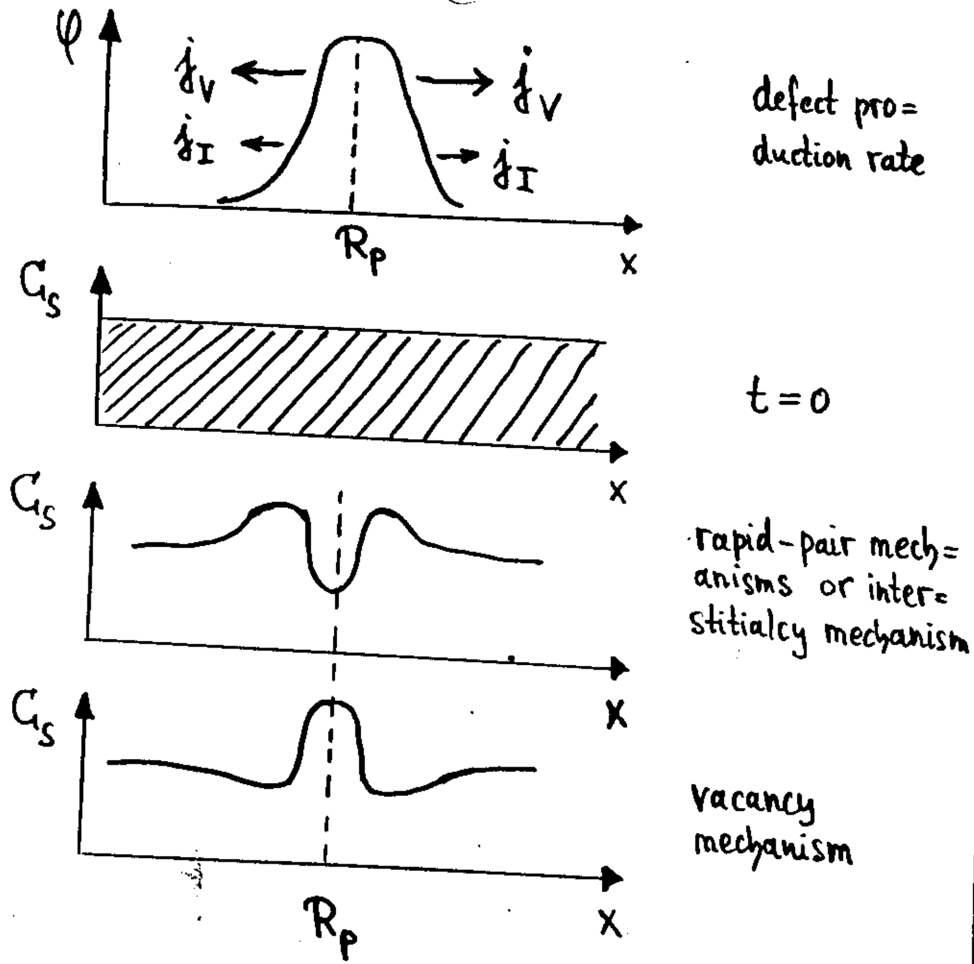
a) V–S pairs : $j_{V-S} = j_V = j_S$

b) I–S pairs : $j_{I-S} = j_I = j_S$

2) Inverse KirKendall effects

a) V as vehicles : $j_V = -(j_M + j_s)$

b) I as vehicles : $j_I = (j_M + j_s)$



Example: B and P in Si give to a dip at $x = R_p$

⇒ rapid-pair mechanism or interstitialcy mechanism

(for discrimination see below)

2. Enhancement of the concentrations of intrinsic defects by chemical surface reactions

Examples: a) self-interstitial injection in Si by surface oxidation (SO)

b) vacancy injection in Si by surface nitridation (SN)

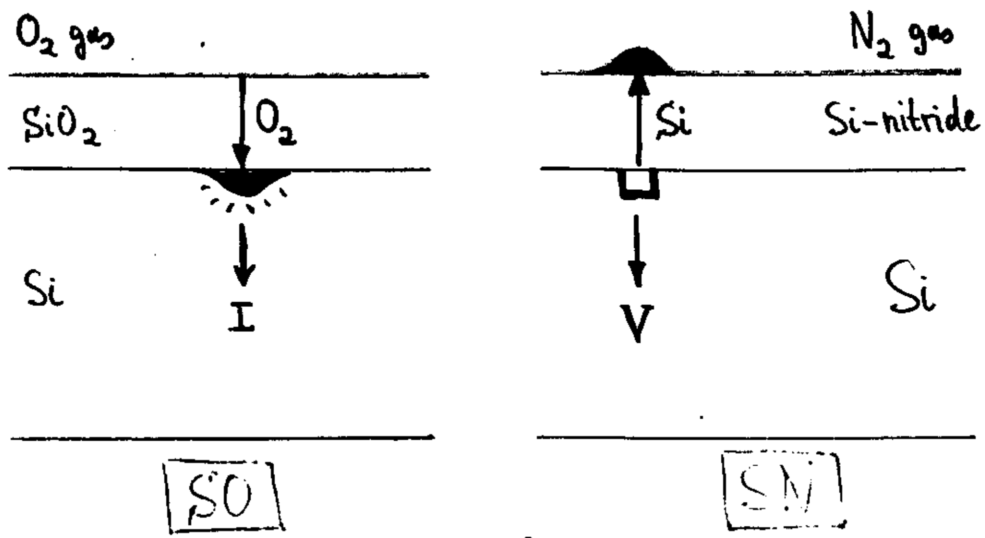
Experiments by Mizuo & Higuchi (≥ 1981) and by Fahey & Dutton (≥ 1986):

treatment	interstitial-type dislocation loops (TEM)	diffusion	
		B	Sb
SO	grow	enhanced	retarded
SN	shrink	retarded	enhanced

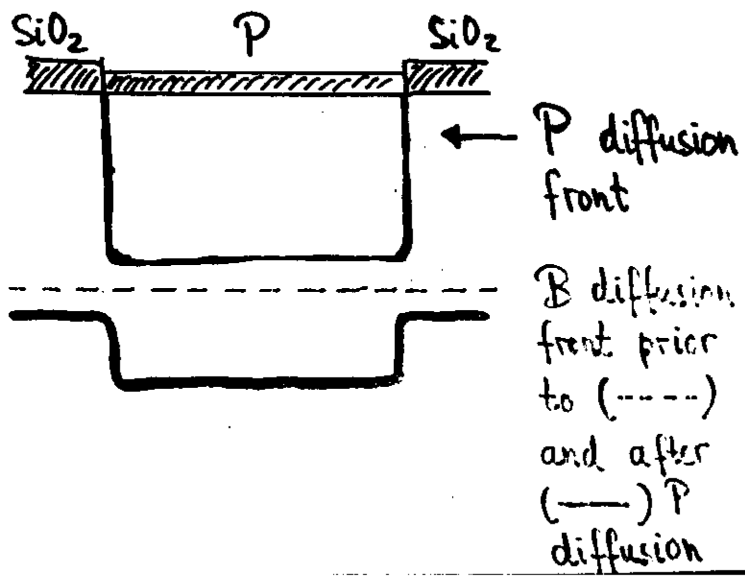
Requirements for compatibility of observations:

1) SO injects I
2) SN injects V
3) V & I coexist in thermal equilibrium
4) B diffuses via I
5) Sb diffuses via V

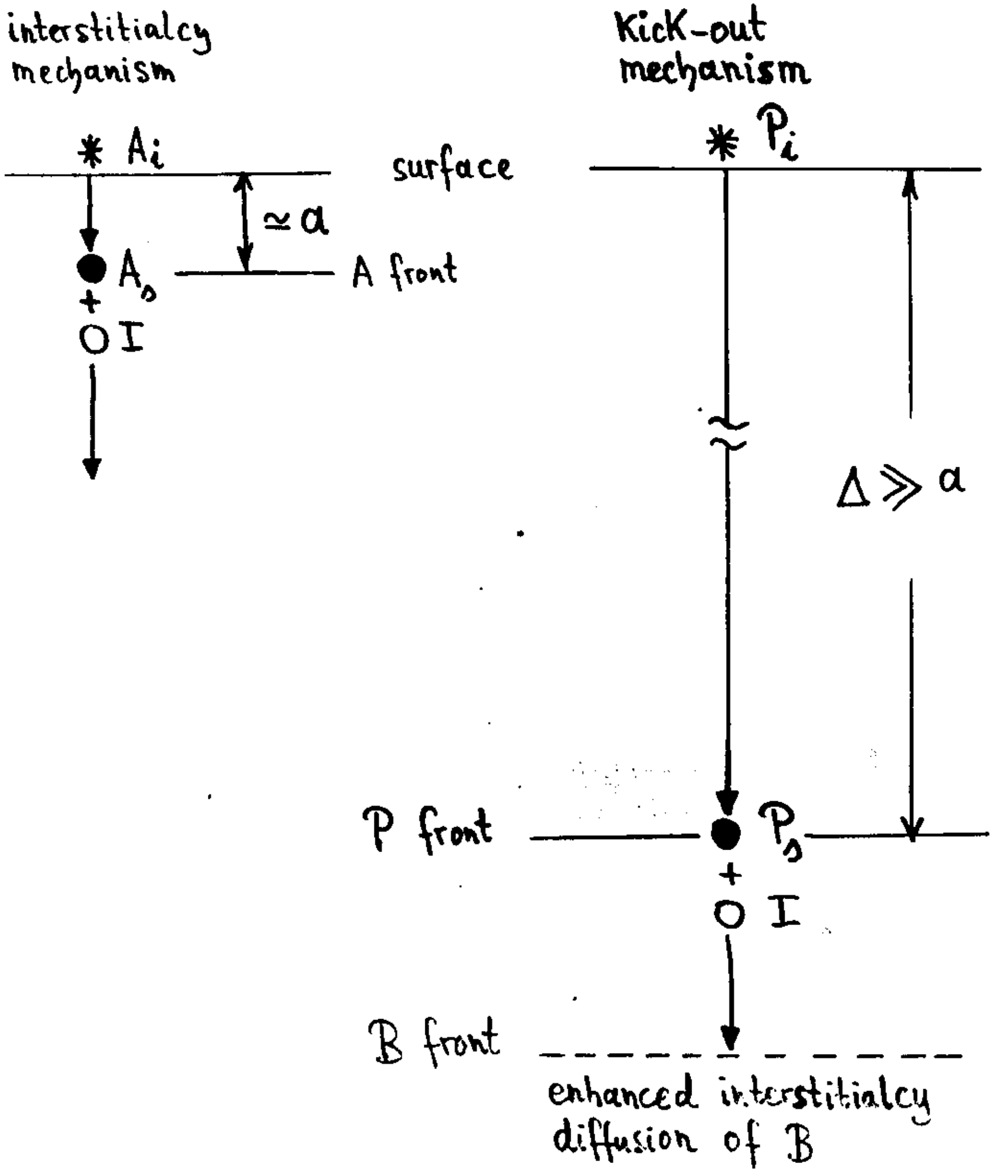
Mechanisms of SO and SN



3. Generation of a self-interstitial supersaturation in silicon by the in-diffusion of P ("emitter-push" effect)



Explanation



Kick-out diffusion is even more pronounced for Au in Si $[\Delta(Au_i) > \Delta(P_i)]$!