

Interdiffusion, Reactions, and Transformations in Thin Films

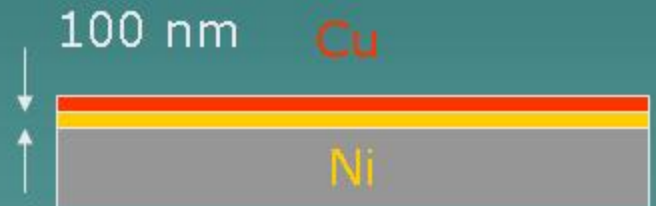
can be quite different as
compared to bulk material

An example

$$t \sim L^2 / 4D \quad D - \text{diffusivity, [cm}^2 / \text{s]}$$

Consider Cu-Ni film couple at 300 °C. $D = 3.8 \cdot 10^{-24} \text{ cm}^2/\text{s}$

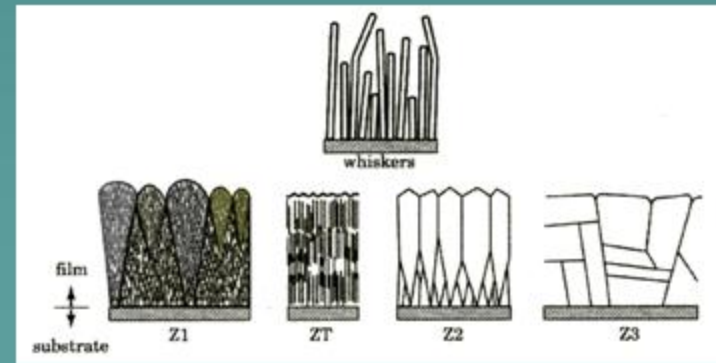
$$t \sim L^2 / 4D = (10^{-5})^2 / 4 \cdot 3.8 \cdot 10^{-24} = 6.6 \cdot 10^{12} \text{ s} = 200\,000 \text{ years}$$



In reality however, it takes about an hour

Answer: granularity.

The material can easily diffuse along the grain boundaries



Fundamentals of Diffusion

$$j = -D \frac{dc}{dx} \quad [D] = \frac{\text{cm}^2}{\text{s}}$$

	D [cm ² /s]
H ₂ in O ₂	0.7
CO ₂ in air	0.14
O ₂ in O ₂	0.18
sugar in water	3e-6

In gases:

$$D \sim vl \sim \frac{v}{n\sigma} \sim \frac{v k_B T}{P \sigma}$$

Time of equalization $t \sim \frac{L^2}{4D}$

$$u = BF$$

Mobility B , force F , drift velocity u of ions

$$D = k_B T B$$

Einstein's equation

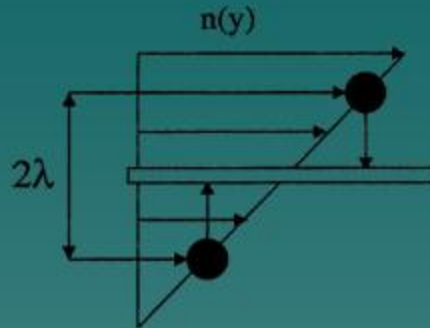


Diffusion

$$\frac{dN}{Sdt} = -\frac{\langle v \rangle}{6} (n(+\lambda) - n(-\lambda)) = -\frac{\langle v \rangle \lambda}{3} \frac{dn}{dx}$$

$$D = \frac{\langle v \rangle \lambda}{3}$$

$$\langle \Delta r \rangle = \sqrt{2Dt}$$



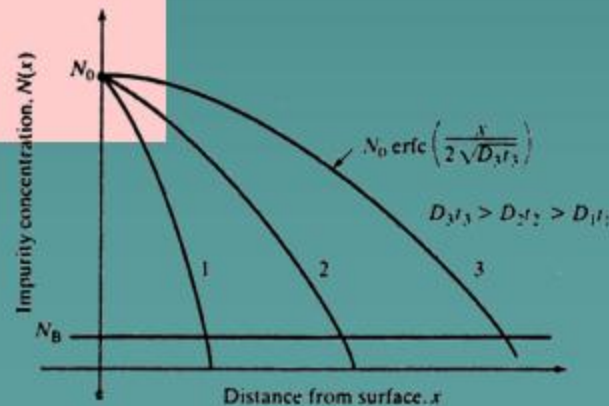
1-st Fick's law: $J = -D \frac{dn}{dx};$

Continuity:

$$dN = [J(x) - J(x + \Delta x)]Sdt = -\frac{dJ}{dx} dt dV$$

$$\frac{dn}{dt} = -\frac{dJ}{dx};$$

2-nd Fick's law: $\frac{dn}{dt} = D \frac{\partial^2 n}{\partial x^2}$



Constant source diffusion (predeposition):

$$n(x, t) = n_0 \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$

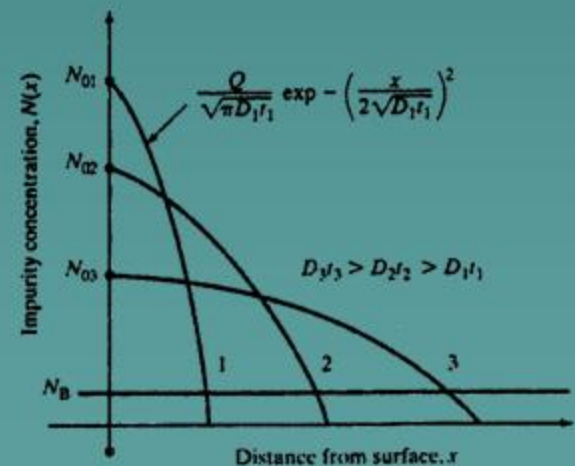
$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-x^2} dx$$

Dose (atoms/cm²):

$$Q = \frac{N}{S} = \int_0^\infty n(x, t) dx = \frac{2}{\sqrt{3}} n_0 \sqrt{Dt}$$

Limited source diffusion (Drive-in):

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

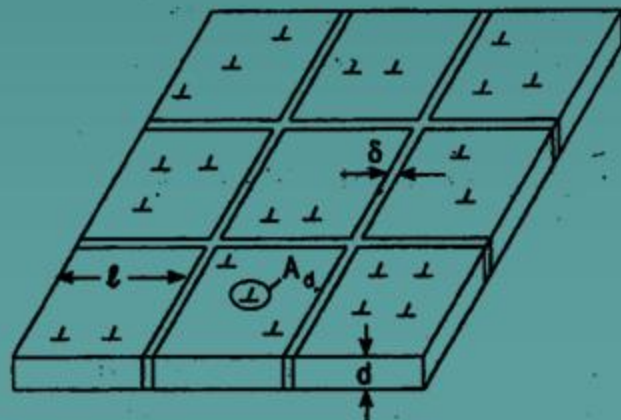


Diffusion Mechanisms

$$D = D_0 \exp(-E / k_B T)$$

(activation mechanism for diffusion)

- ◆ Lattice:
 $D_L \approx 0.5 \exp(-17T_m / T) \text{ [cm}^2/\text{s]}$
- ◆ Grain boundary:
 $\delta D_{GB} \approx 1.5 \cdot 10^{-8} \exp(-8.9T_m / T) \text{ [cm}^3/\text{s]}$
- ◆ Dislocations:
 $A_D D_d \approx 5.3 \cdot 10^{-15} \exp(-12.5T_m / T) \text{ [cm}^4/\text{s]}$
- ◆ Surface:
 $D_S \approx 0.014 \exp(-6.5T_m / T) \text{ [cm}^2/\text{s]}; T_m/T > 1.3$



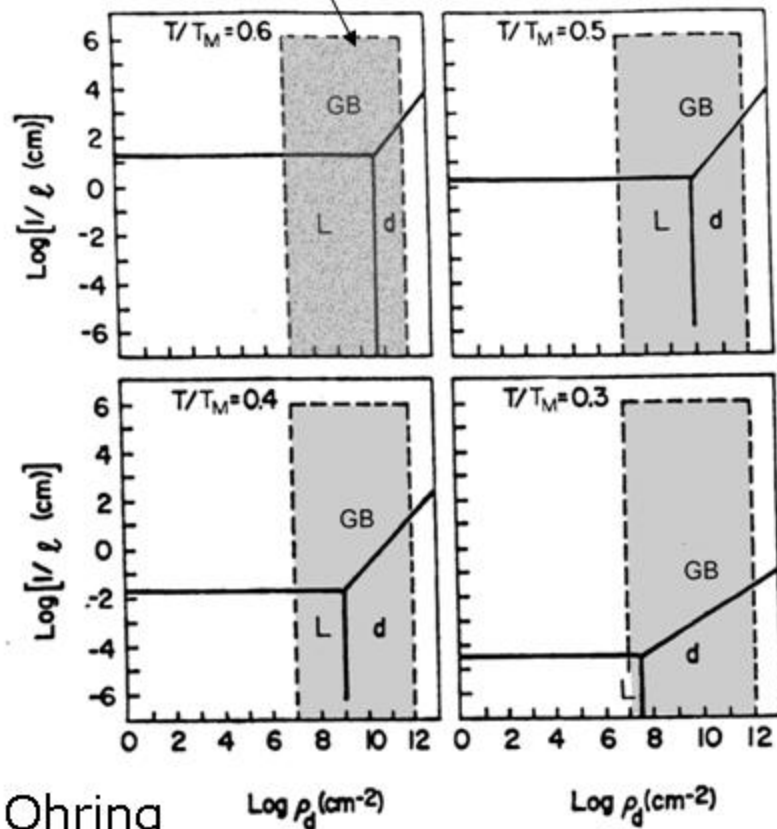
$$\dot{n}_L = D_L l^2 (dC / dx)$$

$$\dot{n}_{GB} = \delta D_{GB} l (dC / dx)$$

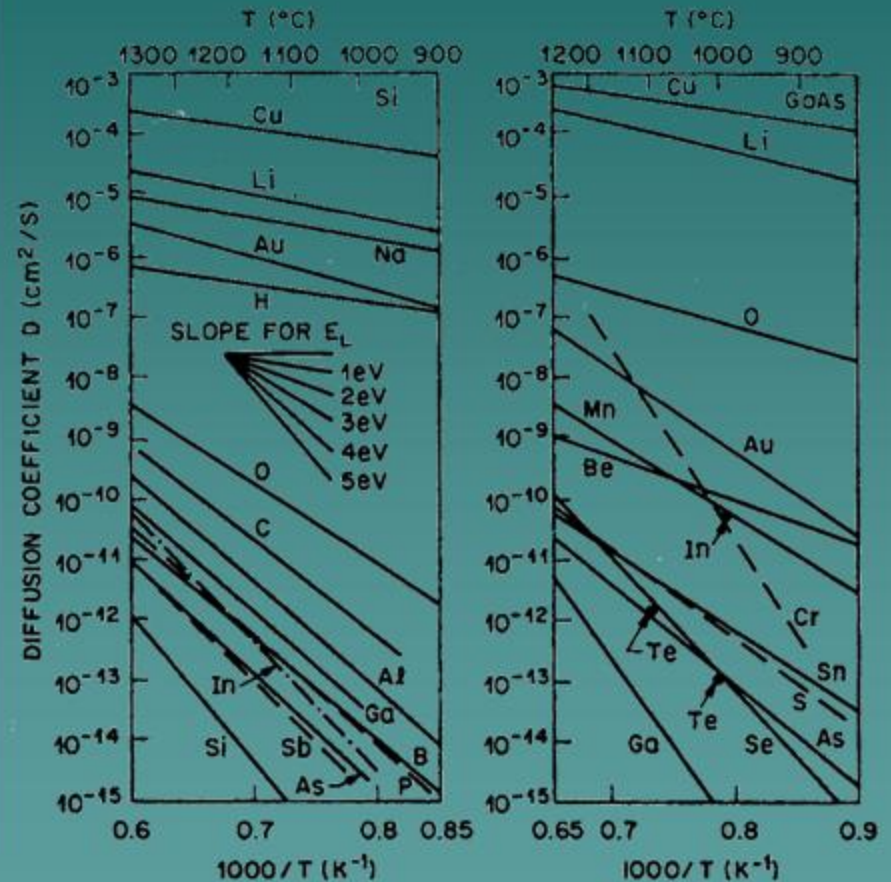
$$\dot{n}_d = A_d D_d l^2 \rho_d (dC / dx)$$

Comparison

occurs in practice

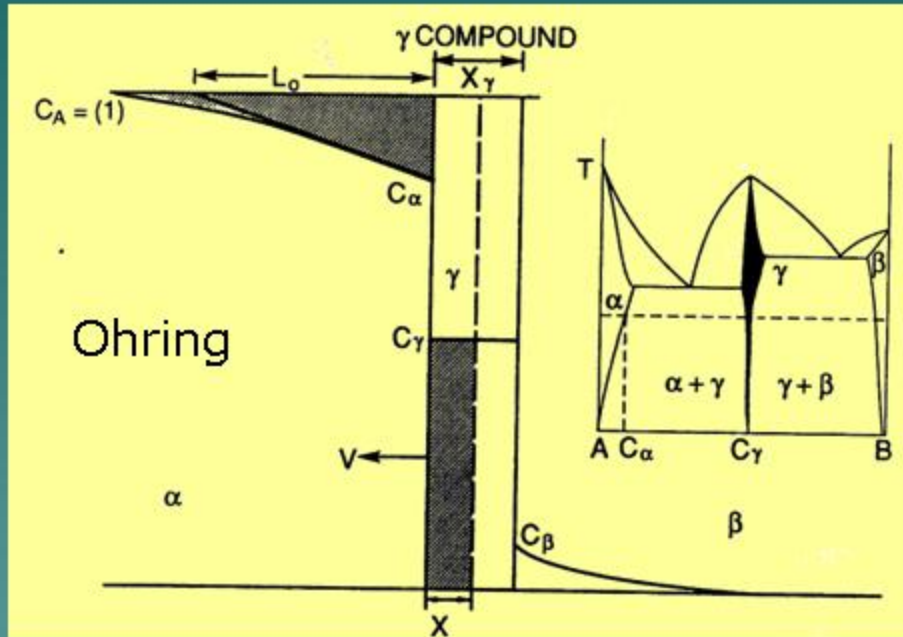


Ohring



Diffusion due to GB

Compound Formation



Flux into interface = $C_\alpha v - D_\alpha (dC_\alpha/dx)_{\text{int}}$

Flux away from interface = $C_\gamma v$.

$$v = \frac{dX}{dt} = \frac{D_\alpha \frac{dC_\alpha}{dx}}{C_\alpha - C_\gamma}$$

$$\frac{dX}{dt} = \frac{D_\alpha (C_A - C_\alpha)^2}{2X(C_\alpha - C_\gamma)C_\gamma}$$

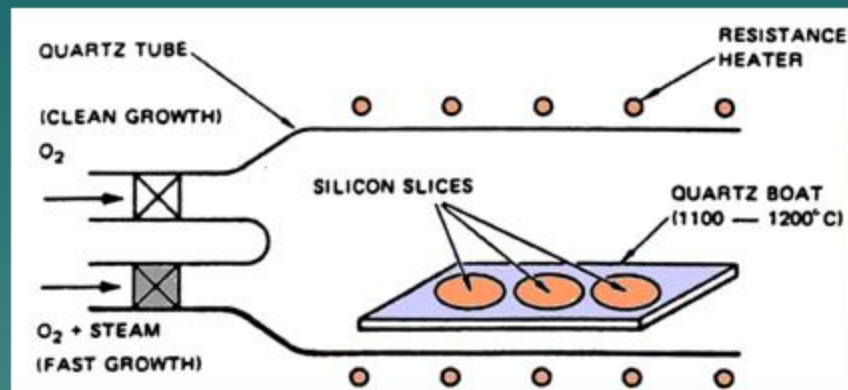
$$X = \frac{[D_\alpha (C_A - C_\alpha)^2]^{1/2} t^{1/2}}{[(C_\alpha - C_\gamma)C_\gamma]^{1/2}} \quad \text{after integration}$$

$$X_\gamma \sim a \sqrt{t} \exp\left(-\frac{E_p}{RT}\right)$$

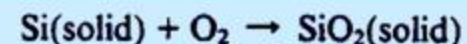
diffusion-limited growth
can be also chemical-reaction-limited $\sim t$

Thermal Oxidation of Si

(gate-oxide dielectric for field-effect transistors)



Dry oxidation:



Steam oxidation:



Oxidation involves:

- transport from the gas
- diffusion of O_2 through the growing solid oxide film
- chemical reaction at the oxide-Si interface

$$\begin{aligned} J_1 &= h_G(C_G - C_0) \\ J_2 &= D(C_G - C_0)/d_0 \\ J_3 &= k_s C_i \end{aligned}$$

Oxygen

C_G : in the gas

C_0 : gas/ SiO_2

C_i : SiO_2/Si

from condition $J_1 = J_2 = J_3$:

$$C_i = \frac{C_G}{(1 + k_s/h_G + k_s d_0/D)}$$

$$\frac{d(d_0)}{dt} = \frac{k_s C_i}{N_0}$$

h_G : mass-transport
 D : diffusion through SiO_2
 k_s : reaction rate
 d_0 : thickness of oxide

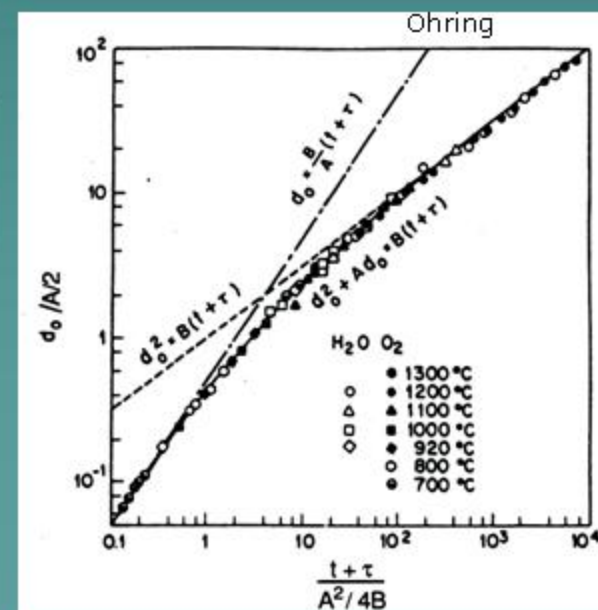
$$\frac{d_0}{A/2} = \sqrt{1 + \frac{t + \tau}{A^2/4B}} - 1$$

$$A = 2D(1/h_G + 1/k_s)$$

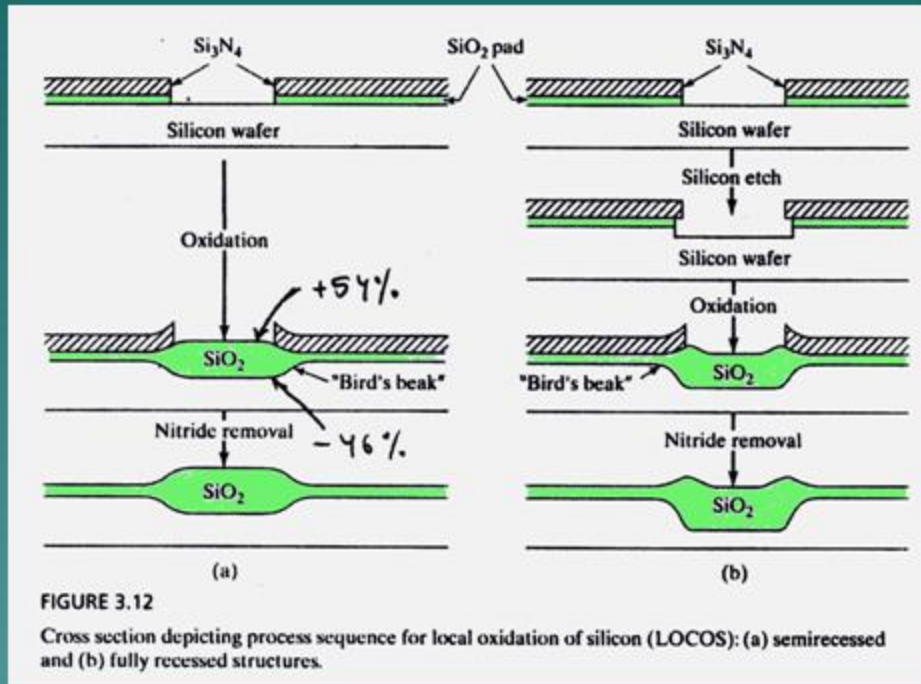
$$B = 2DC_G/N_0$$

$$\tau = (d_i^2 + A d_i)/B$$

d_i if initial oxide existed



Si Oxidation Problems

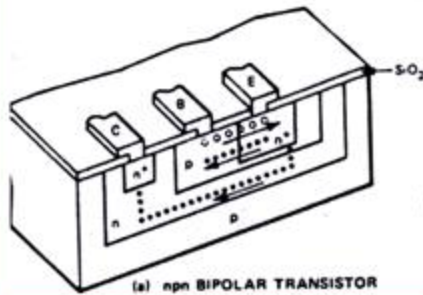


Oxide expansion

Oxide quality issues:

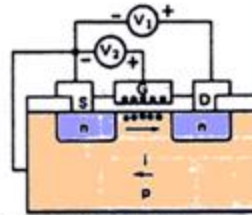
- Breakdown voltage 5-10 MV/cm
- Leakage
- Trapped charges

Doping

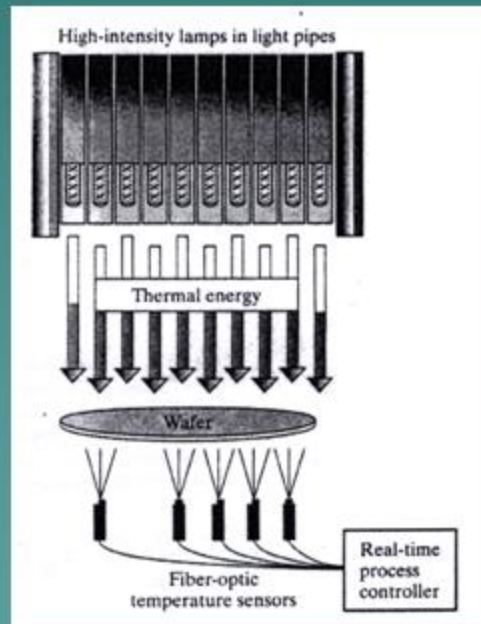
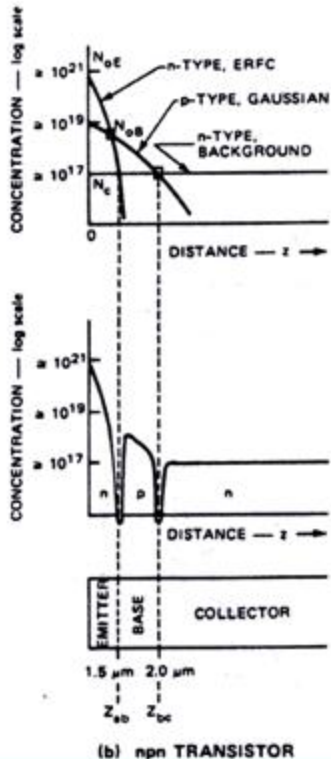


n-p and p-n
junctions

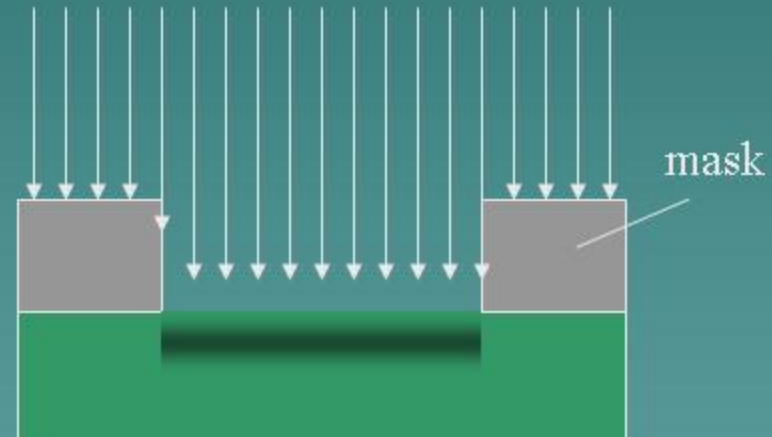
n - TYPE ENHANCEMENT-MODE MOS TRANSISTOR



By thermal diffusion



By ion implantation

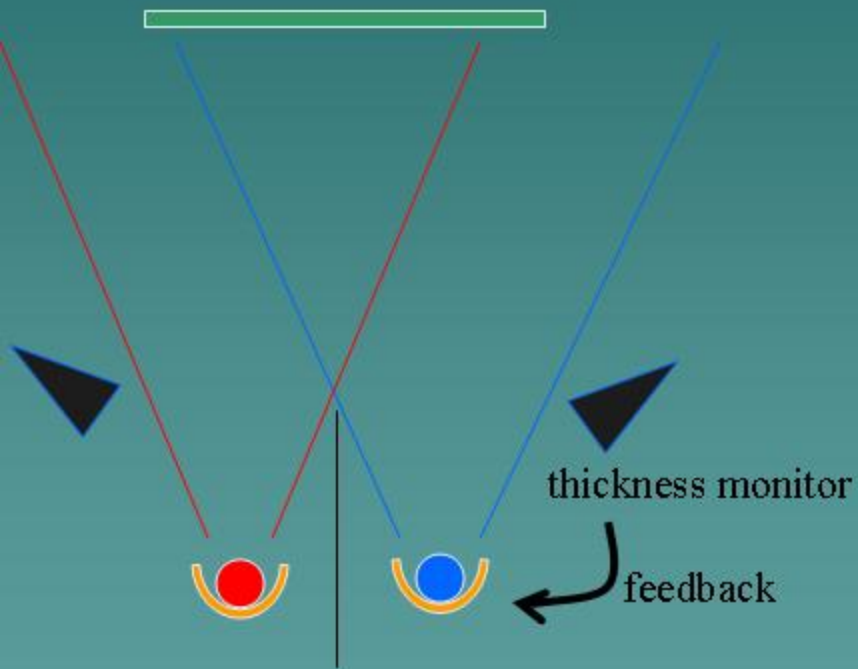


By neutron transmutation



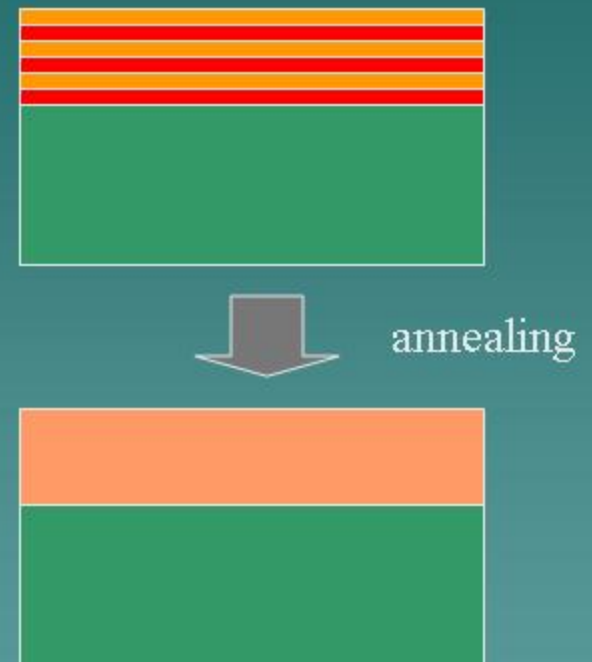
Mixing Materials

Co-evaporation



- requires accurate control over individual non-constant deposition rates (unless expensive Knudsen cells in MBE)

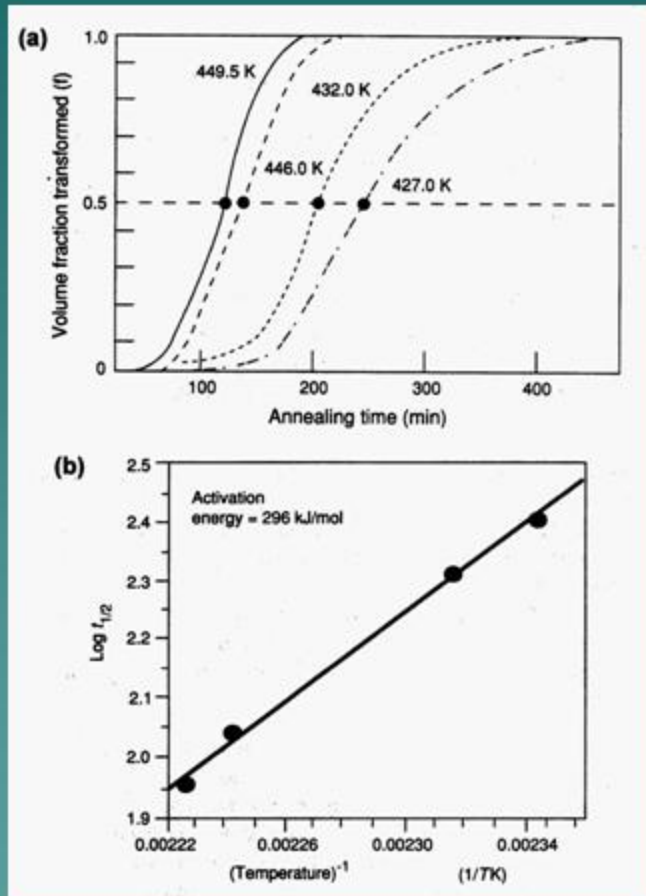
Multilayers + annealing



- + simple & cheap
- time consuming

Phase Transformations

Amorphous phase \rightarrow crystalline



cobalt disilicide CoSi_2

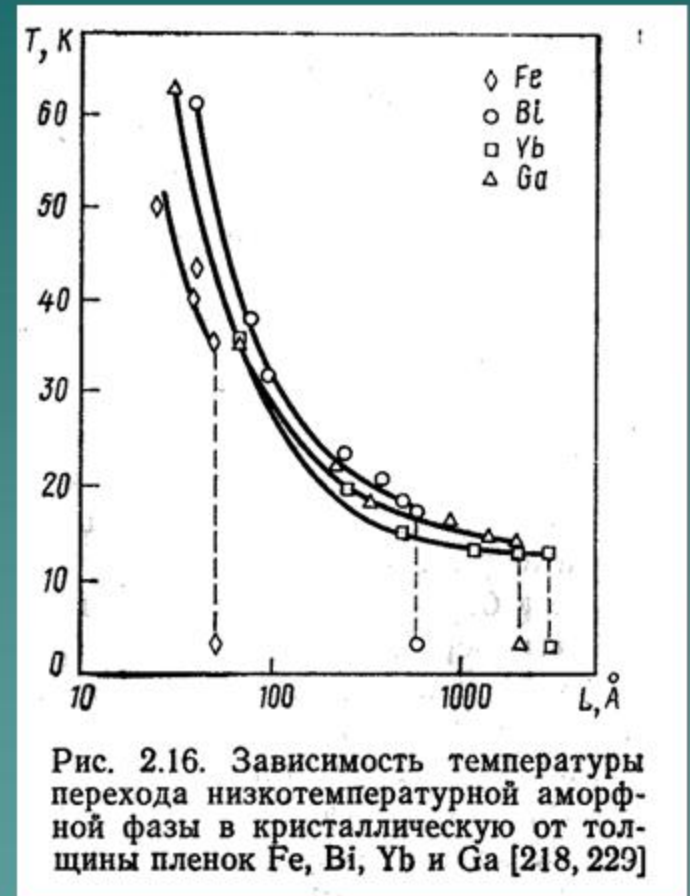
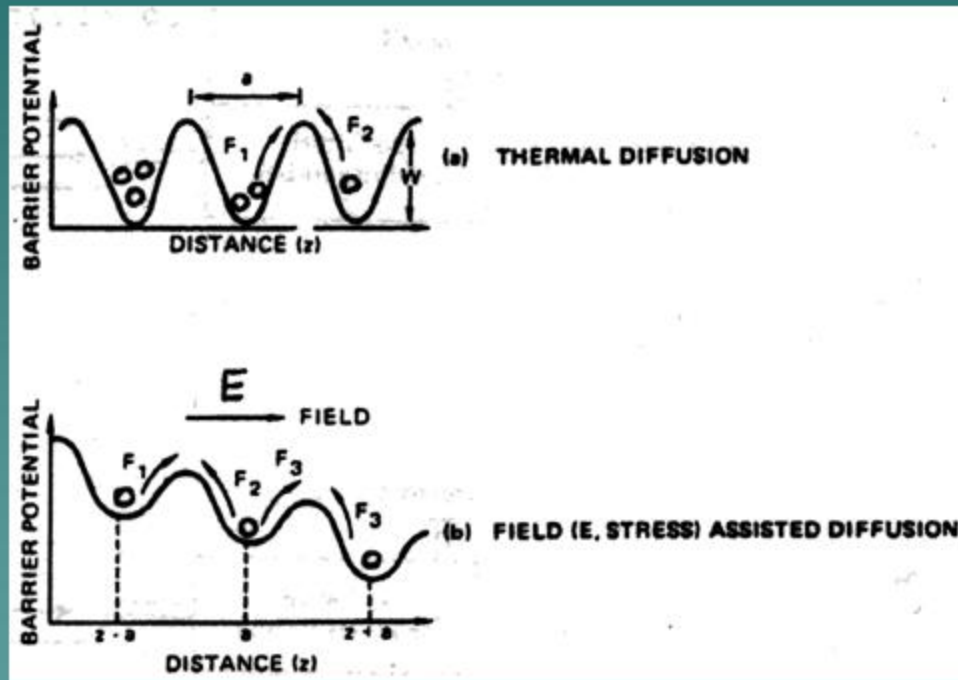


Рис. 2.16. Зависимость температуры перехода низкотемпературной аморфной фазы в кристаллическую от толщины пленок Fe, Bi, Yb и Ga [218, 229]

Mass Transport Under Driving Forces



Probability to escape via thermal activation:

$$P = \omega a n \exp \left(- \frac{W - \frac{eaE}{2}}{kT} \right)$$

attempt frequency

Electro-migration

gradual displacement of the metal atoms of a conductor as a result of the current flowing through that conductor.

Concerns: circuitry failure

- open circuit where voids appear
- short circuit where hillocks are built
- failures take time to develop, and are therefore very difficult to detect until it happens.

$$\tau \sim \frac{C}{j^n} \exp\left(-\frac{E_a}{kT}\right), \quad E_a \sim 1 \text{ eV}$$

mean lifetime of a line subject to electro-migration
Black's equation; $n=2$

Electro-migration can be prevented by:

- 1) proper design of the device such that the current densities in all parts of the circuit are limited;
- 2) increasing of the grain sizes of the metal lines such that these become comparable to their widths
- 3) deposition of thin films placed over the metal lines to suppress extrusions caused by electro-migration.

