

Difusão

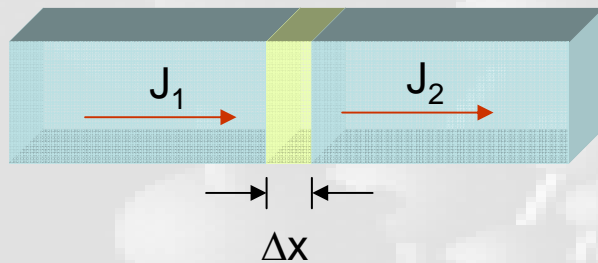
Leitura: S. M. Hu e S. Schmidt, *Phys. Rev.*, **107** (1957) 392
L. J. van der Pauw, *Philips Res. Rep.* **13** (1958) 1

EEL6760 - Processamento de Materiais Eletrônicos

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EEL/CTC/UFSC

1. Leis de Fick



$$[C] = \text{mol/m}^3$$

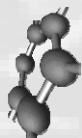
$$[J] = \text{mol/m}^2 \text{ s}$$

$$J = -D \frac{\partial C}{\partial x} \quad (1^{\text{a}} \text{ Lei})$$

$$J_2 - J_1 = -\Delta x \frac{\partial J}{\partial x}$$

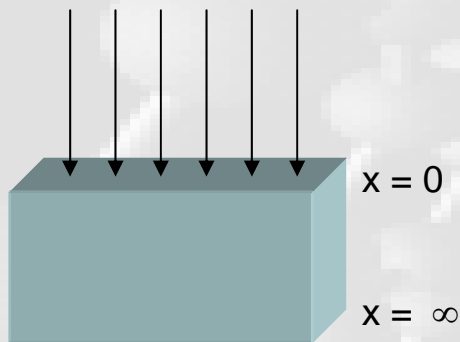
$$\frac{\partial C}{\partial t} = \frac{J_2 - J_1}{\Delta x} = -\frac{\partial J}{\partial x}$$

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2^{\text{a}} \text{ Lei})$$



2. Pré-deposição

Fonte tem suprimento constante de dopantes!



(Difusão lateral ~75%-85%)

$C(x,0) = 0$ Inicialmente puro.

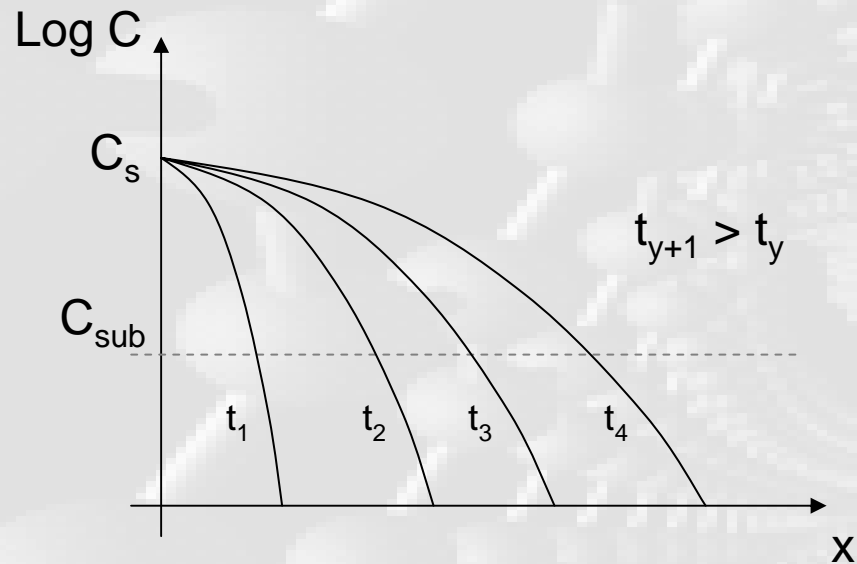
$C(0,t) = C_s$ Dopagem constante na superfície durante todo processo.

$C(\infty,t) = 0$ Nunca atinge o fundo.

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

Distância de difusão

3. Junção pn / Pré-dep.



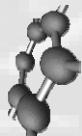
$$C(x,t) = C_s \cdot \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Faz $C(x,t) = C$ do substrato C_{sub} :

$$x_j = 2\sqrt{Dt} \cdot \operatorname{erfc}^{-1}\left(\frac{C_{\text{sub}}}{C_s}\right)$$

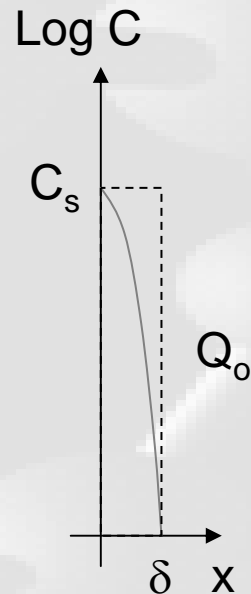
Carga total depositada:

$$Q_o = \int_{-\infty}^{\infty} C(x,t) dx = \int_{-\infty}^{\infty} C_s \cdot \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) dx = \frac{2}{\sqrt{\pi}} C_s \sqrt{Dt}$$



4. Difusão de redistribuição

(Drive-in diffusion)



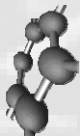
$$C(x,0) = 0 \quad \text{Para } x > \delta$$

$$\int_0^{\infty} C(x,t) dx = Q_0 \quad \text{Dopagem constante na superfície durante todo processo.}$$

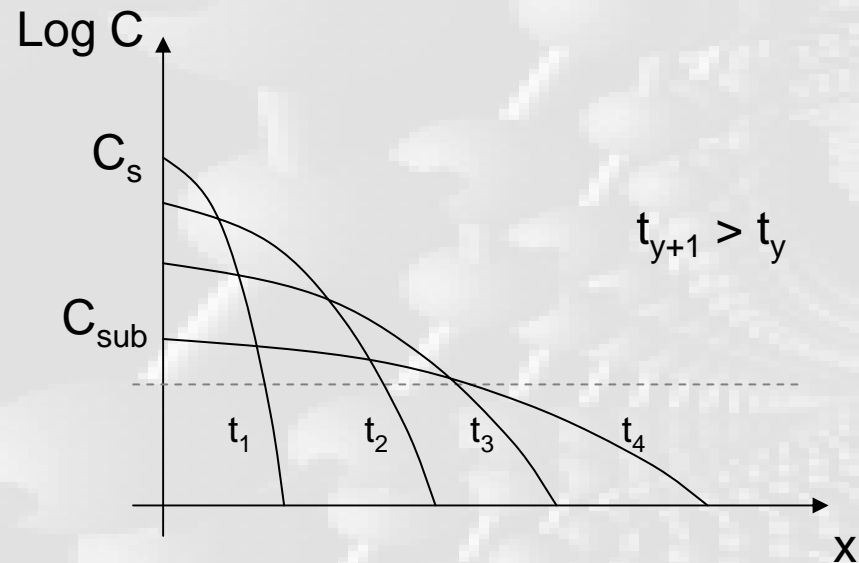
$$C(\infty,t) = 0 \quad \text{Nunca atinge o fundo.}$$

$$C(x,t) = \frac{Q_0}{\sqrt{\pi Dt}} \cdot e^{-\frac{x^2}{4Dt}}$$

(Difusão lateral ~65%-70%)



5. Junção pn / Drive-in



$$C(x,t) = \frac{Q_o}{\sqrt{\pi Dt}} \cdot e^{-\frac{x^2}{4Dt}}$$

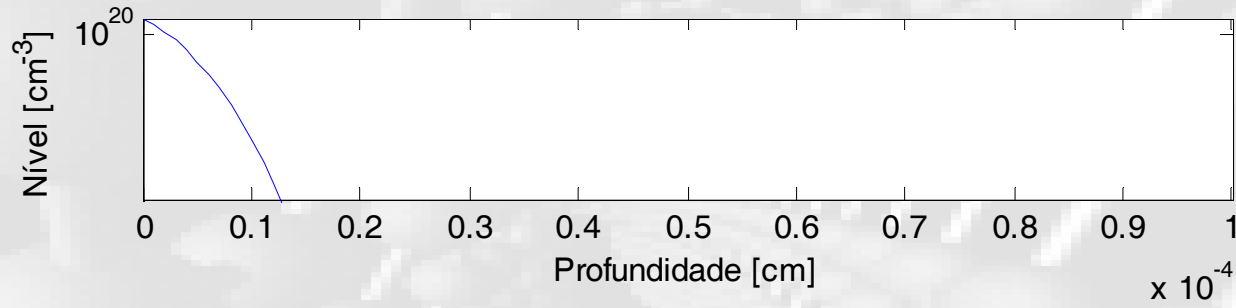
$$C_s = C(0,t) = \frac{Q_o}{\sqrt{\pi Dt}}$$

Carga total não muda!

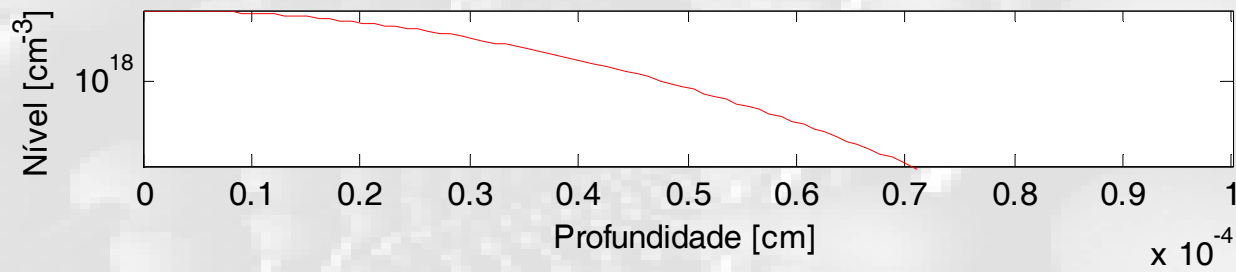
$$x_j = 2\sqrt{Dt} \left[\ln \left(\frac{Q_o}{C_{sub} \sqrt{\pi Dt}} \right) \right]^{1/2}$$

1º Trabalho

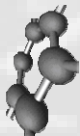
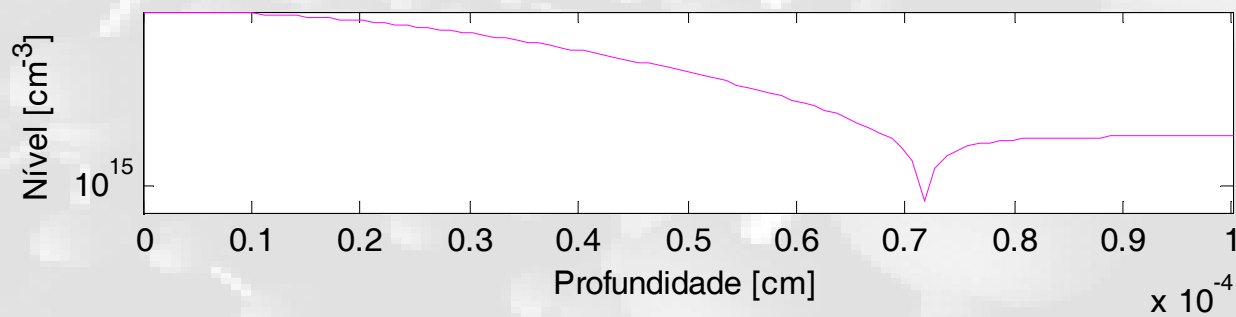
Pré-deposição



Redistribuição



Total



6. Difusão intrínseca e extrínseca

$$n_i = p_i = \sqrt{N_V N_C} e^{-\frac{E_g(T)}{2k_B T}}$$

> C: intrínseca
< C: extrínseca

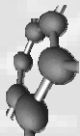
$$E_g(T) = E_g(0) - bT$$

p/ Si: $E_g(0) = 1.46 \text{ eV}$, $b = 2.97 \text{E-}4 \text{ eV/K}$

Entre 800 °C e 1100 °C

$$\cancel{\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}} \rightarrow \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) = \frac{\partial D}{\partial x} \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2}$$

Boltzmann-Matano



7. Difusão intrínseca

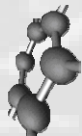
$$D_A = D_{A0} e^{-\frac{Q_A}{k_B T}}$$

(Relação de Arrhenius)

Doadores	Q_A [eV]	Aceitadores	Q_A [eV]
P	3.51 – 3.67	B	3.25 – 3.87
As	4.05 – 4.34	Al	3.36
Sb	3.8 – 4.05	Ga	3.75
		In	3.60

Difusores rápidos em Si: Na, K, Cu, Au, Ag, Pt, Fe, Ni, O₂ e H₂

$$D = D^0 + D^- \left(\frac{n}{n_i} \right) + D^{2-} \left(\frac{n}{n_i} \right)^2 + D^+ \left(\frac{n_i}{n} \right) \quad \rightarrow \quad D = D^0 + D^- + D^{2-} + D^+$$



7.1. Difusão intrínseca de dopantes

$$D = D^0 + D^- + D^{2-} + D^+$$

	D^0	D^-	D^{2-}	D^+
B	$0.037e^{-\frac{3.46}{k_B T}}$			$0.72e^{-\frac{3.46}{k_B T}}$
As	$0.066e^{-\frac{3.44}{k_B T}}$	$12.0e^{-\frac{4.05}{k_B T}}$		
P	$3.85e^{-\frac{3.66}{k_B T}}$			
Sb	$0.214e^{-\frac{3.65}{k_B T}}$	$13e^{-\frac{4.08}{k_B T}}$		

(*) Energias em eV, D's em cm²/s

8. Difusão assistida

- Gradiente de íons difundindo criam campo elétrico:

$$J = -D \frac{\partial C}{\partial x} \rightarrow J_{AX} = -D_{AX} \frac{\partial C}{\partial x} + \underset{\substack{\text{mobilidade} \\ \downarrow}}{Z_{AX} \mu_{AX}} C_{AX} E$$

↑
carga

- Boltzmann + Rel. Einstein:

$$D_A = h \left[D_{A^+X^0} + D_{A^+X^-} \left(\frac{n}{n_i} \right) + D_{A^+X^{-2}} \left(\frac{n}{n_i} \right)^2 \right]$$

$$h = 1 + \frac{C_A}{2n_i} \left[\left(\frac{C_A}{2n_i} \right)^2 + 1 \right]^{-1/2}$$

Também ocorre com ambientes oxidantes:

$$OED \propto \left(\frac{\partial x_{ox}}{\partial t} \right)^n$$

9. Reações para Boro

Boro: $2\text{B}_2\text{O}_3 + 3\text{Si} \leftrightarrow 4\text{B} + 3\text{SiO}_2$ (alta solubilidade, cuidado com pele, $> T_{\text{fusão do Si}}$)

TMB: $2(\text{CH}_3\text{O})_3\text{B} + 9\text{O}_2 + 900^\circ\text{C} \rightarrow \text{B}_2\text{O}_3 + \text{CO}_2 + 9\text{H}_2\text{O}$ (sólido)

BTB: $4\text{BBr}_3 + 3\text{O}_2 \rightarrow 2\text{B}_2\text{O}_3 + 6\text{Br}_2$ (líquido, Br funciona como getter)

DB: $\text{B}_2\text{H}_6 + 3\text{O}_2 + 300^\circ\text{C} \rightarrow \text{B}_2\text{O}_3 + 2\text{H}_2\text{O}$ (gás explosivo e letal, dilui em Ar ou N)

DB: $\text{B}_2\text{H}_6 + 6\text{CO}_2 \rightarrow \text{B}_2\text{O}_3 + 6\text{CO} + 3\text{H}_2\text{O}$ (gás explosivo e letal, dilui em Ar ou N)

Diborano: *life threatening exposure* = 160 ppm / 15 min

10. Reações para P, As e Sb

Fósforo: $2P_2O_5 + 5Si \leftrightarrow 4P + 5SiO_2$ (altíssima solubilidade)

Alternativas: $NH_4H_2PO_4$ (monofosfato de amônia) e $(NH_4)_2H_2PO_4$ (difosfato de amônia)

POC: $4POCl_3 + 3O_2 \rightarrow 2P_2O_5 + 6Cl_2$ (líquido, precisa de *bubbler*, Cl_2 funciona como *getter*)

PH₃: $2PH_3 + 4O_2 \rightarrow 2P_2O_5 + 3H_2O$ (gás explosivo e letal, dilui em Ar ou N 99.9%)

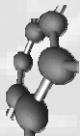
Arsênico: $2As_2O_3 + 3Si \leftrightarrow 3SiO_2 + 4As$ (altíssima solubilidade, LETAL implantação)

Sb: $2Sb_2O_3 + 3Si + \sim 650^\circ C \leftrightarrow 3SiO_2 + 4Sb$

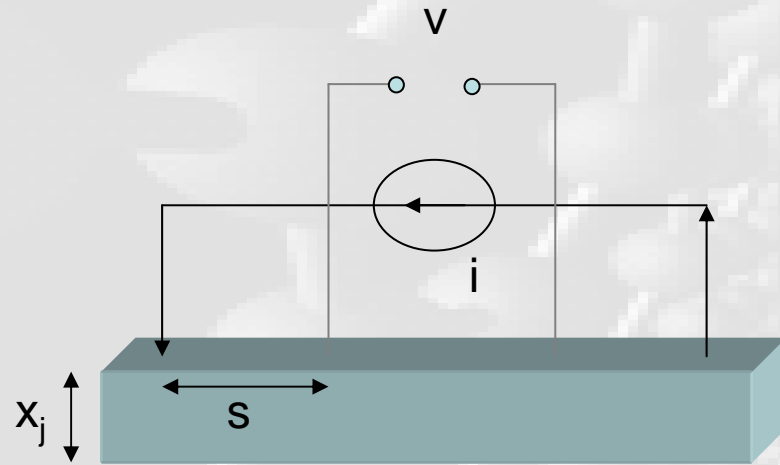
Alternativas: Sb_3Cl_5 (pentacloreto de antimônio - líquido)

Fosfina: *life threatening exposure* = 400 ppm / 30 min

Arsina: *life threatening exposure* = 6-15 ppm / 30 min



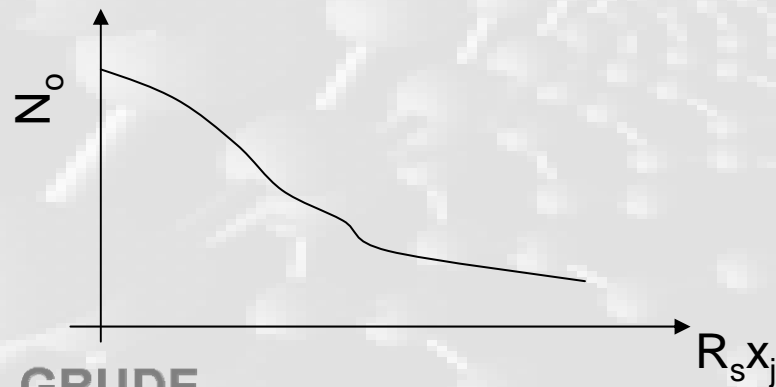
11. Medidas Van der Pauw



$$R_s [\Omega/\square] = \rho [\text{ohm-cm}] / x_j [\text{cm}]$$

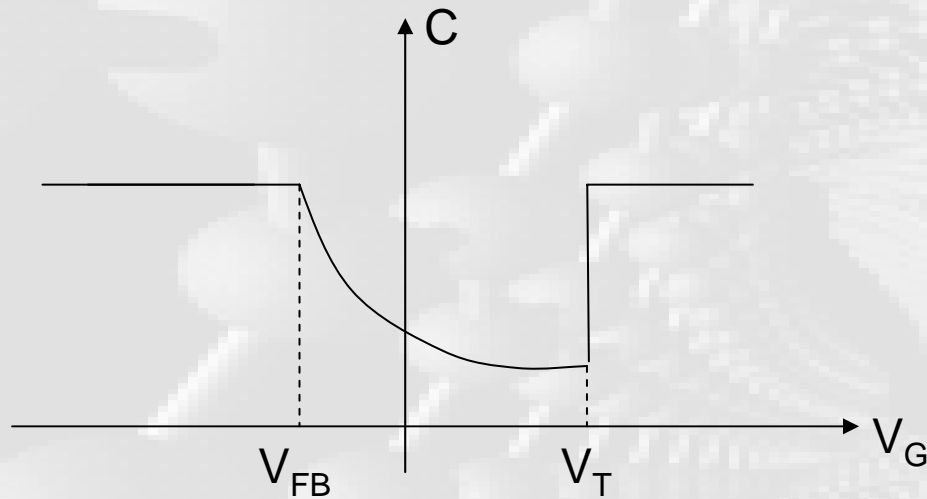
$$\rho = \left[q \int_0^{x_j} \mu(C_A) C_A(x) dx \right]^{-1}$$

Curva de Irvin



$$R_s = 2\pi s F\left(\frac{v}{i}\right) \longrightarrow R_s = 4.532\left(\frac{v}{i}\right)$$

12. C-V



$$W = \sqrt{\frac{2\varepsilon}{qN} \left(V_{bi} - V - \frac{k_B T}{q} \right)} = \frac{\varepsilon}{C(V)}$$

$$x_j = \sqrt{\frac{2\varepsilon}{qN} \left(V_{bi} - \frac{k_B T}{q} \right)} = \frac{\varepsilon}{C_o}$$

$$N = -\frac{2}{q\varepsilon} \left[\frac{dC^{-2}}{dV} \right]^{-1}$$

$$C^{-2} = \frac{2(V_{bi} - V - k_B T)}{q\varepsilon N}$$

$V_{bi} = V$ que torna $C^{-2} = 0$

