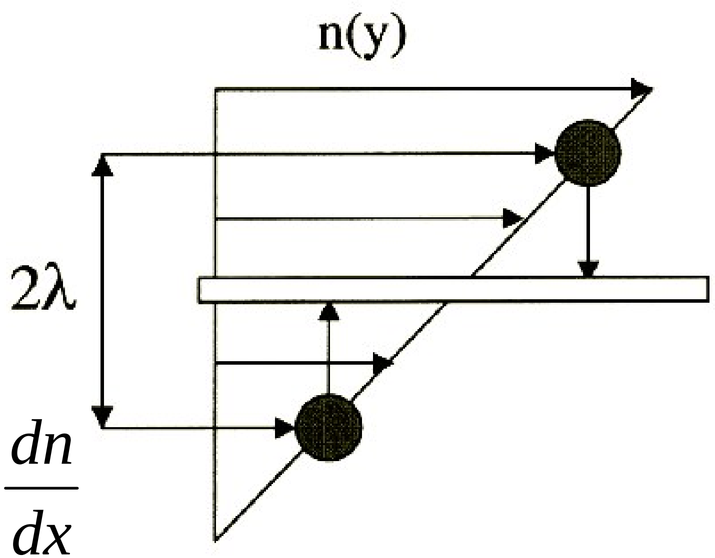
Diffusion & Oxidation
Doping

Diffusion



- 1st Fick's law

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

$$J = -D\frac{dn}{dx}$$

Fick's First Law is used in steady state diffusion, i.e., when the concentration within the diffusion volume does not change with respect to time.

$$D = D_0 \exp\left(-\frac{E_{diff}}{k_B T}\right)$$

E_{diff}: activation energy for diffusion

Diffusion

- 2nd Fick's law

$$J = -D\frac{dn}{dx}$$

Fick's Second Law is used in non-steady state diffusion,i.e., when the concentration within the diffusion volume changes in time.

Continuity :

$$dN = \left[J(x) - J(x+\Delta x)\right]Sdt = -\frac{dJ}{dx}dtdV$$

$$\frac{dn}{dt} = -\frac{dJ}{dx} \Rightarrow \boxed{\frac{dn}{dt} = D\frac{\partial^2 n}{\partial x^2}}$$

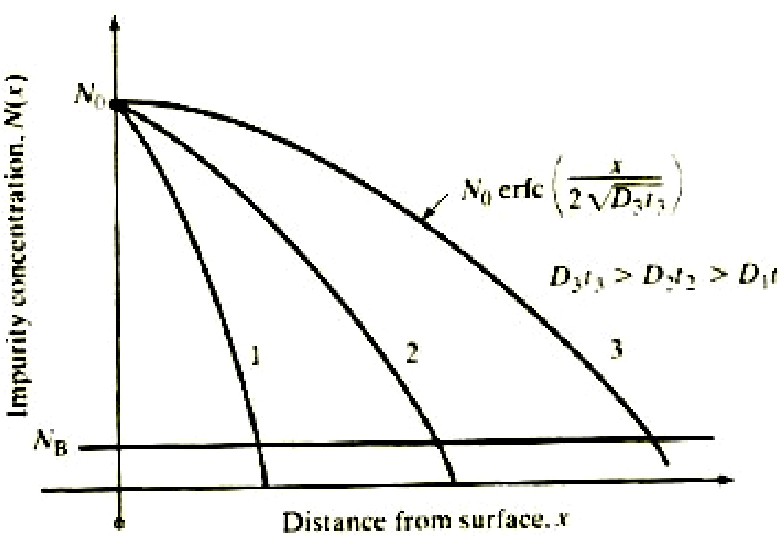
Diffusion

Constant source diffusion
"pre-deposition"

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

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

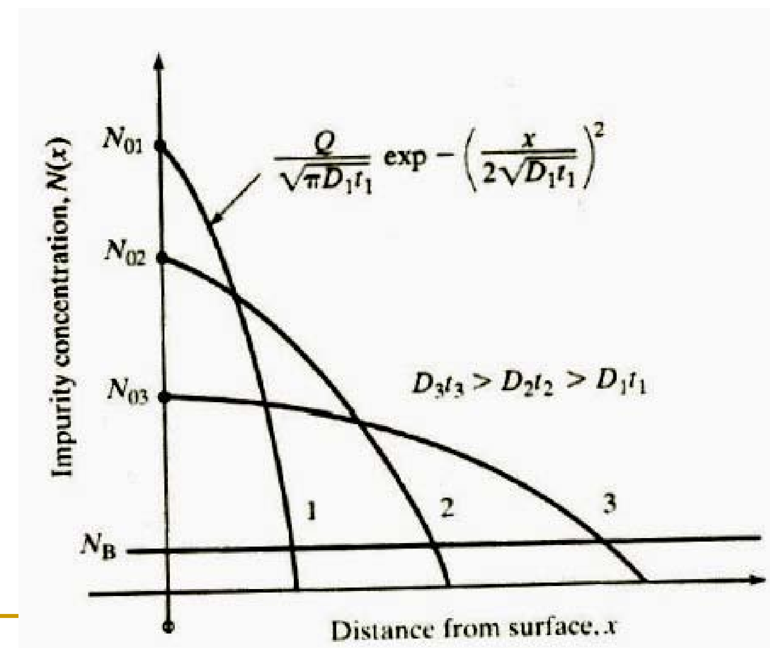
(complimentary error function)



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

Limited source diffusion
"drive-in"

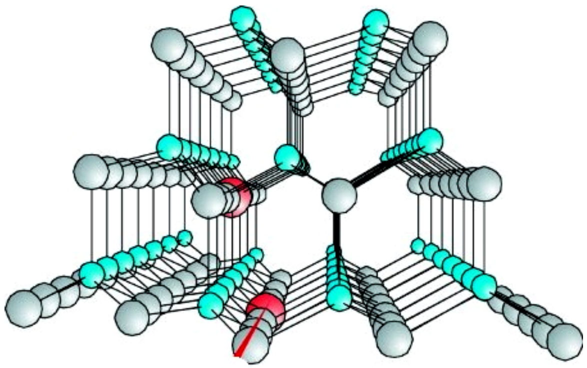
$$n(x,t) = \frac{Q}{\sqrt{\pi Dt}} \exp\left(\frac{x}{2\sqrt{Dt}}\right)^2$$

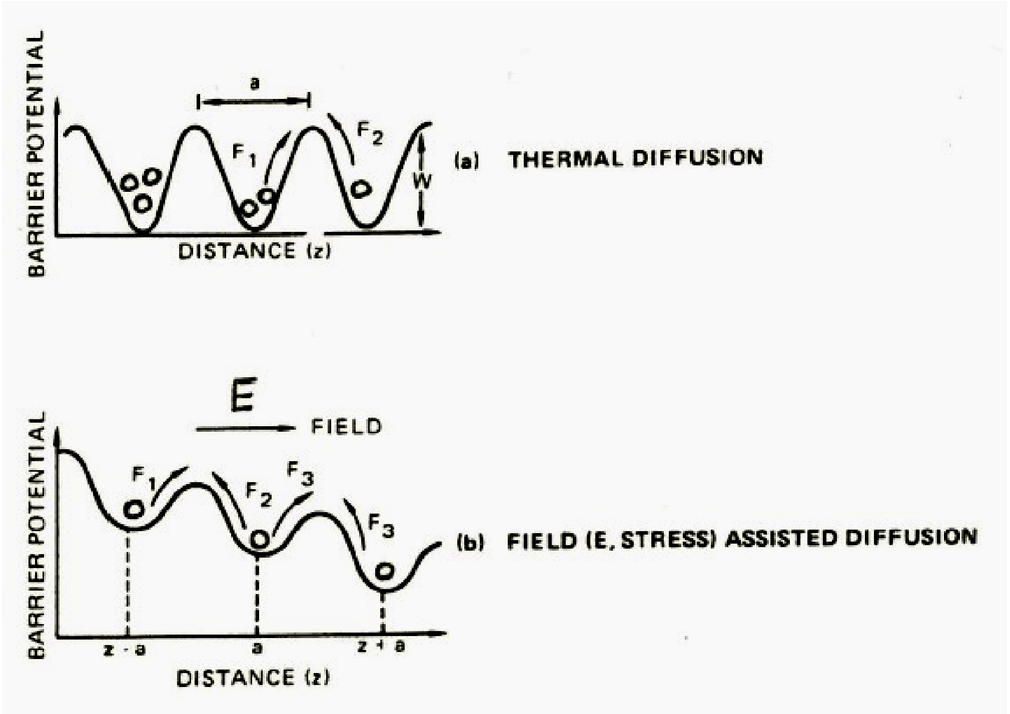


Diffusion

Parameters that affect diffusion:
- Temperature
- Pressure
- Crystal direction (channeling)

Enhanced diffusion:
- Stress, electric field
- Ionization
- Grain boundaries (defects)





Probability to escape in thermal activation process:

$$P = \omega \cdot an \cdot \exp\left(-\frac{W - eaE/2}{k_B T}\right)$$

w- attempt frequency

Diffusion

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

	D [cm²/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:

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

$$u = BF$$

Mobility *B*, force *F*, drift velocity *u* of ions

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

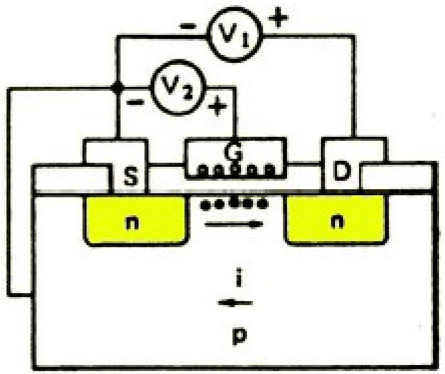
$$D = k_B T\, B$$

Einstein's equation

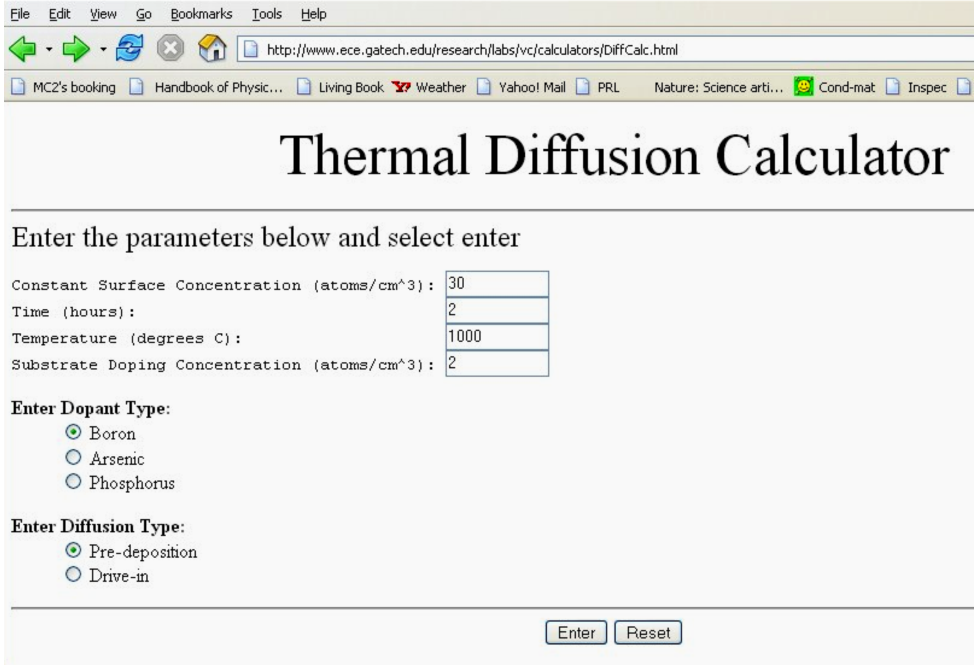
L

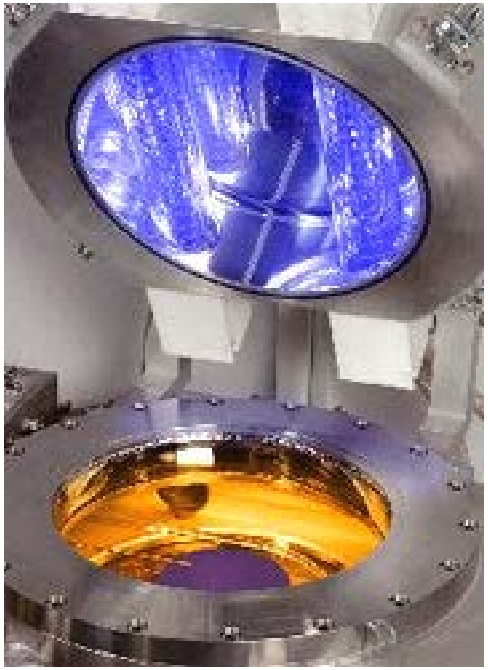
Doping

n-p and p-n junctions

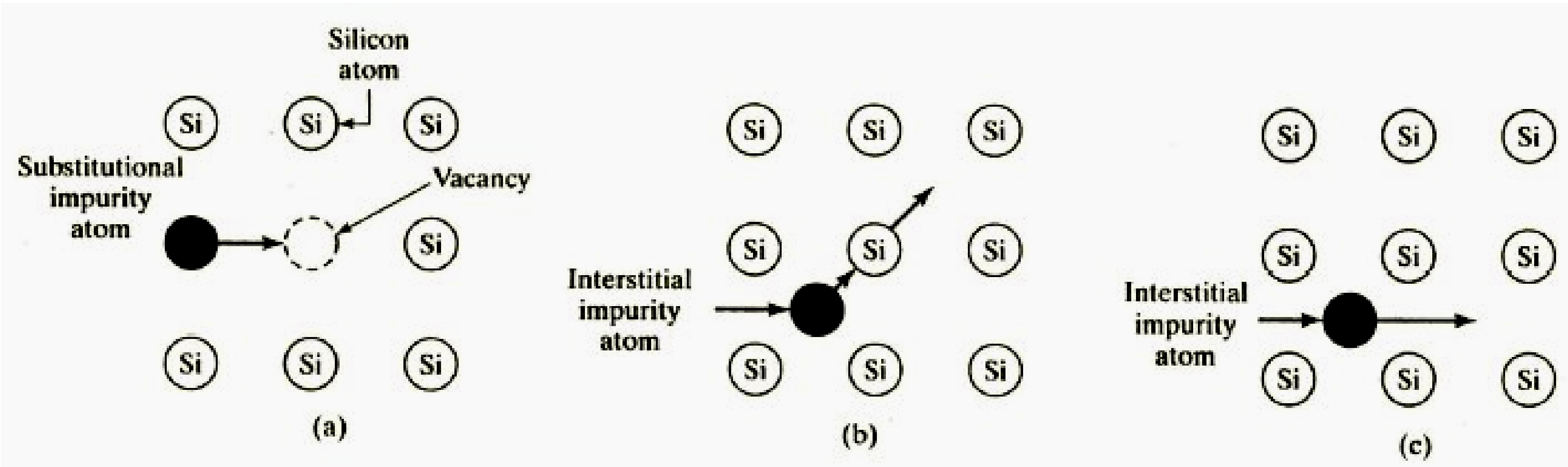


n – TYPE ENHANCEMENT-MODE MOS TRANSISTOR





Mechanism of Diffusion



a) substitutional diffusion
b) impurity atom replaces Si atom
c) impurity atom does not replace Si atom

Doping

Uniformity on Wafers

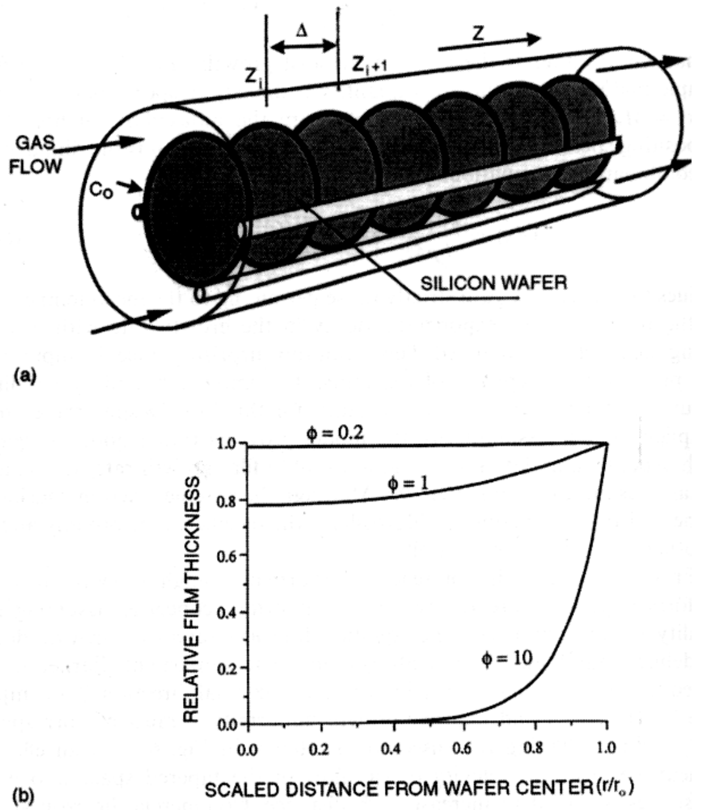


Figure 6-11 (a) Schematic representation of hot-wall, multiple wafer LPCVD reactor geometry with gas flow boundary conditions. (b) Film thickness variation as a function of the scaled radial distance along the wafer for different values of ϕ. (From *Chemical Vapor Deposition*, edited by M. L. Hitchman and K. F. Jensen. Reprinted with the permission of Academic Press, Ltd., and Professor K. F. Jensen, MIT.)

$$2B_2O_3 + 3Si \rightarrow 4B + 3SiO_2$$

$$4BBr_3 + 3O_2 \rightarrow 2B_2O_3 + 6Br_2$$

$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$$

$$2P_2O_5 + 5Si \rightarrow 4P + 5SiO_2$$

$$4POCl_3 + 3O_2 \rightarrow 2P_2O_5 + 6Cl_2$$

$$2PH_3 + 4O_2 \rightarrow P_2O_5 + 3H_2O$$

$$\frac{d(r/r_0)}{d(1)} = \frac{C(r)}{C_0} = \frac{I_0\left(\sqrt{\frac{2r_0k}{\Delta D}}\frac{r}{r_0}\right)}{I_0\left(\sqrt{\frac{2r_0k}{\Delta D}}\right)}$$

φ

Doping

- by thermal diffusion

Tool #433
Rapid Thermal Processor (RTP) AG Heatpulse 610

a PC-controlled halogen lamp furnace.
It accommodates 2", 3", and 4" wafers, or small pieces placed on a wafer.

It is typically used for alloying of ohmic contacts on III-V semiconductors.
No other substrates than III-V are allowed.

Specifications:
Protecting gas: N2
Wafer size: pieces, 2", 3", 4“
Max temperature:1000°C
Heating rate: 120°C/sec
Temperature sensor: Thermocouple / Pyrometer

Diffusion

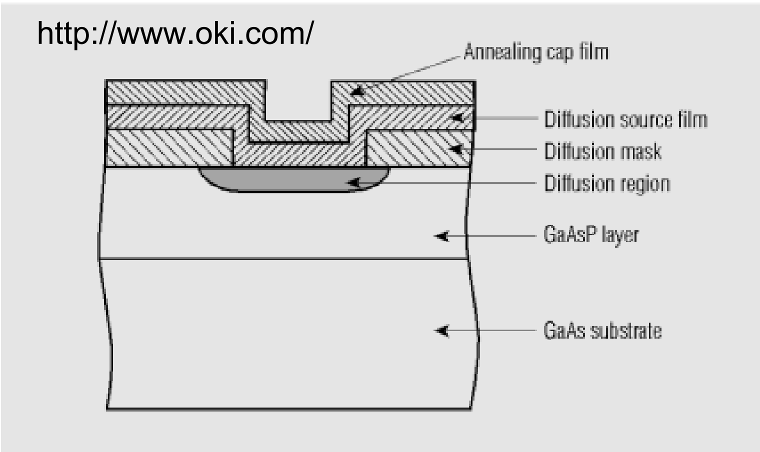
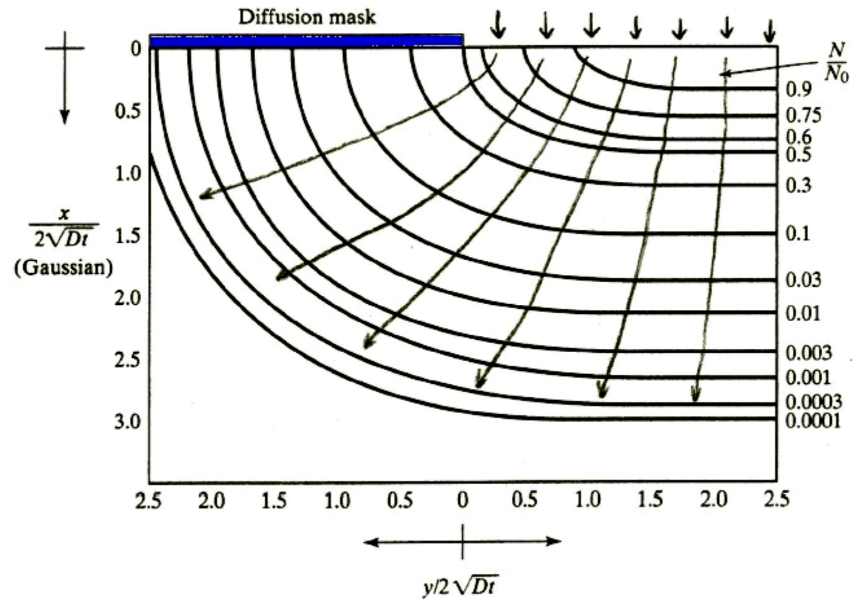


Figure 3: Schematic drawing of the wafer in solid-phase diffusion

Lateral Diffusion



diffusion of dopant atoms in the direction parallel to the surface of semiconductor; undesired in device manufacturing as it causes distortion of the device geometry.

Thermal Oxidation of Si

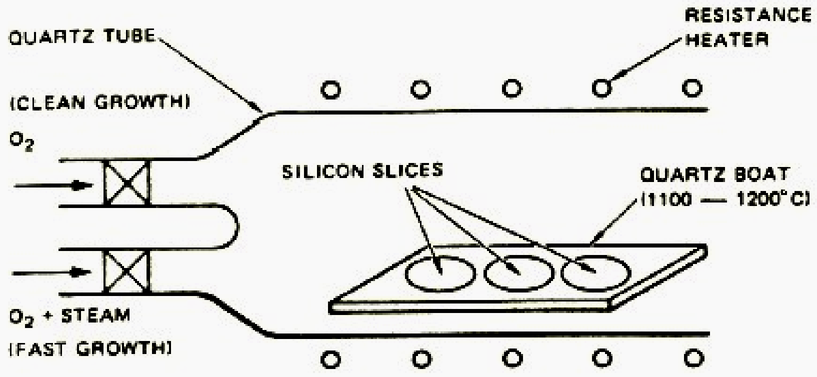


FIGURE 1.12. Thermal oxidation of SiO_2 layer. From Ref. 30.

$$Si + O_2 \rightarrow SiO_2$$

$$Si + 2H_2O \rightarrow SiO_2 + 2H_2$$

1. Oxygen is transported from the bulk of the gas phase to the gas-oxide interface
2. Oxygen diffuses through the growing solid oxide film
3. When oxygen reaches the Si/SiO_2 interface, it chemically reacts with Si and forms SiO_2

Interface Reaction Kinetics

$$J_{gs} = h_g (C_g - C_s) \qquad J_s = k_s C_s$$

$$C_s = \frac{C_g}{1 + k_s / h_g} \quad \text{for } J_{gs} = J_s$$

$$k_s \propto \exp\left(-\frac{E}{RT}\right)$$

$k_s >> h_g$: mass transfer

$k_s << h_g$: surface reaction

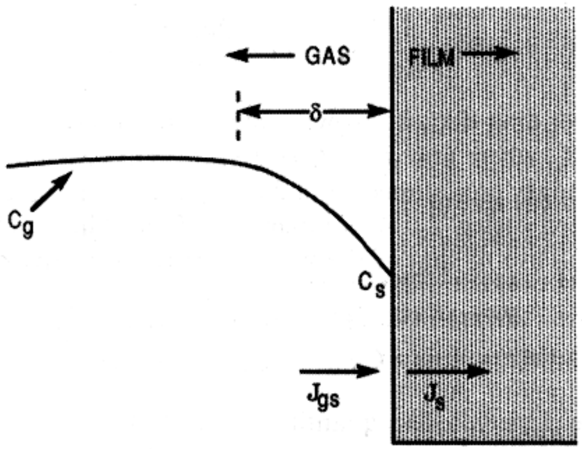


Figure 6-12 Model of CVD growth process. Gas flows normal to plane of paper. (From Ref. 26. Reprinted with permission from John Wiley & Sons, copyright © 1967.)

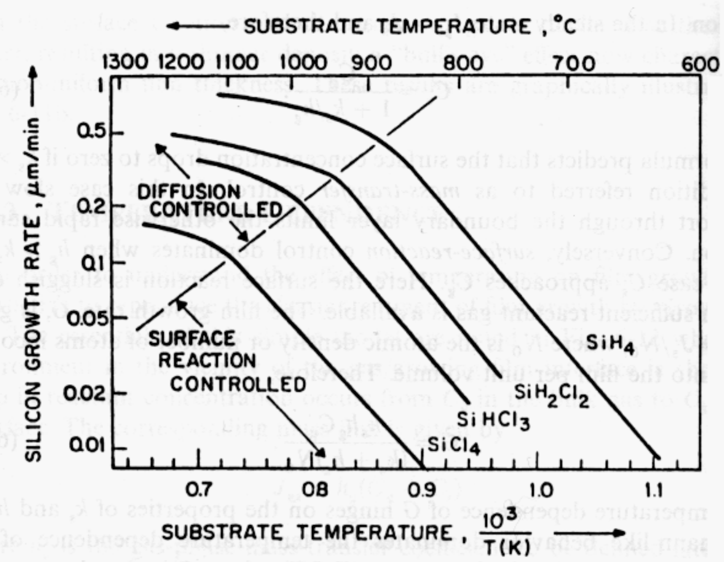


Figure 6-13 Deposition rate of Si from four different precursor gases as a function of temperature. (From W. Kern, in *Microelectronic Materials and Processes*, ed. R. A. Levy, reprinted with permission of Kluwer Academic Publishers, 1989.)

Interface Reaction Kinetics

$$J_1 = h_g \left(C_g - C_0 \right)$$

$$J_2 = \frac{D\left(C_0 - C_i \right)}{d_0}$$

$$J_3 = k_S C_i$$

C_g – concentration of oxygen in the gas

C_i – concentration of oxygen at the gas/SiO_2 interface

C_0 – concentration of oxygen at the SiO_2 / Si interface

h_g – mass transport coefficient

D – diff. coeff. of oxygen in SiO_2

k_S – chemical reaction rate constant

$$J_1 = J_2 = J_3 \ \text{(steady-state growth)}$$

$$C_0 = \frac{C_g \left(1 + \frac{k_S d_0}{D} \right)}{1 + \frac{k_S}{h_g} + \frac{k_S d_0}{D}}$$

$$C_i = \frac{C_g}{1 + \frac{k_S}{h_g} + \frac{k_S d_0}{D}}$$

Interface Reaction Kinetics

$$C_0 = \frac{C_g\left(1+\frac{k_S\, d_0}{D}\right)}{1+\frac{k_S}{h_g}+\frac{k_S\, d_0}{D}} \qquad C_i = \frac{C_g}{1+\frac{k_S}{h_g}+\frac{k_S\, d_0}{D}}$$

$$C_i \approx C_0 = \frac{C_g}{1+\frac{k_S}{h_G}} \text{ reaction limited } \left(D >> k_S\, d_0\right)$$

$$C_0 \approx C_g ; C_i \approx 0 : \text{diffusion limited } \left(D << k_S\, d_0\right)$$

the actual growth depends on J3:

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

$$d_0^2 + A d_0 = B(t+\tau)$$

Interface Reaction Kinetics

the actual growth depends on J3:

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

$$d_0^2 + Ad_0 = B(t+\tau)$$

$$N_0 = 2.2\times10^{22}\ \text{(dry)}\ 4.4\times10^{22}\ \text{(wet)}\ \left[\text{cm}^{-3}\right]$$

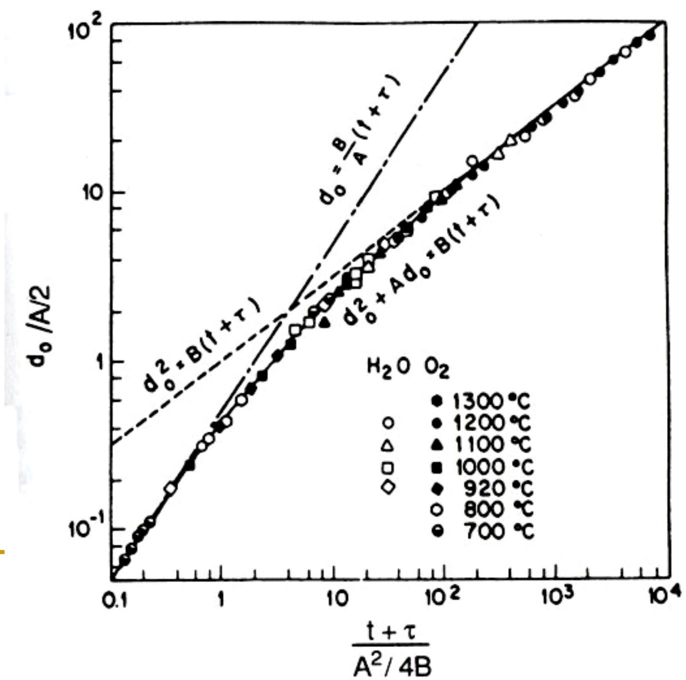
$$A = 2D(h_g^{-1} + k_S^{-1});\quad B = 2DC_g / N_0;\quad \tau = \left(d_i^2 + Ad_i\right)/B$$

d_i – initial oxide thickness (if any)

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

$$d_0(t) \cong Bt,\quad t >> A^2/4B$$

$$d_0(t) \cong \frac{B}{A}(t+\tau),\quad t+\tau << A^2/4B$$



Oxide Expansion

- Cracks – lower breakdown voltage (5-10 MV/cm
- Leakage
- Trapped charges

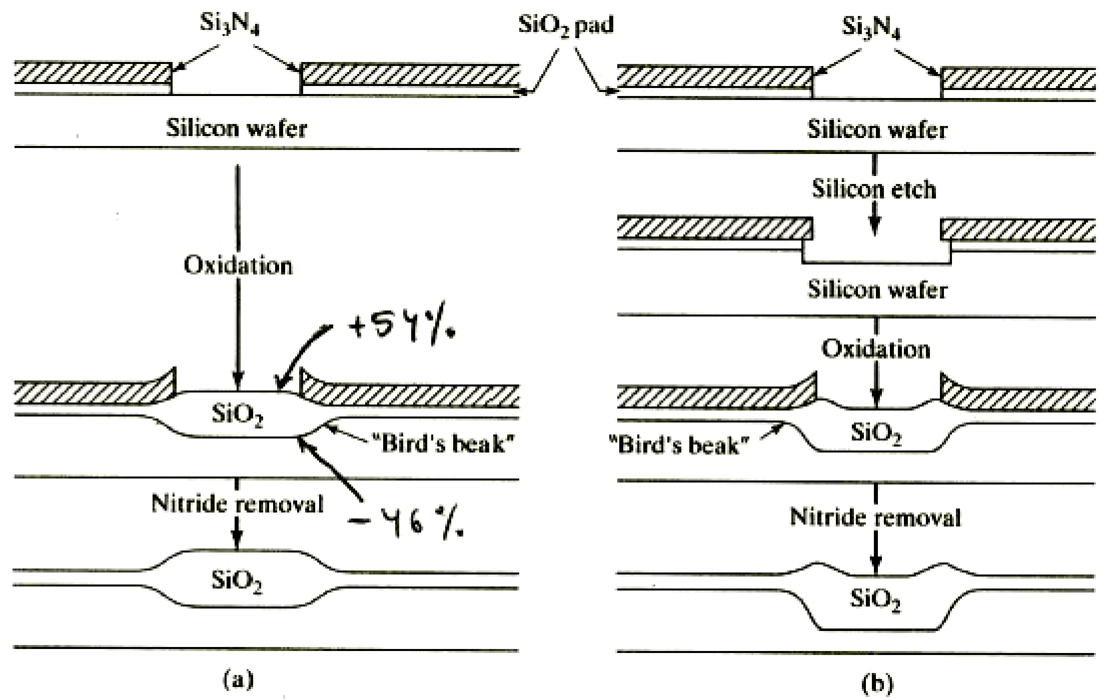


FIGURE 3.12

Cross section depicting process sequence for local oxidation of silicon (LOCOS): (a) semirecessed and (b) fully recessed structures.

Mechanical Relaxation Effects

during oxide growth (expansion)

Stress relaxation:

$$\varepsilon_T = \varepsilon_1 + \varepsilon_2$$

$$\varepsilon_1 = \frac{\sigma_x}{Y};\ \ \dot{\varepsilon}_2 = \frac{\sigma_x}{\eta}$$

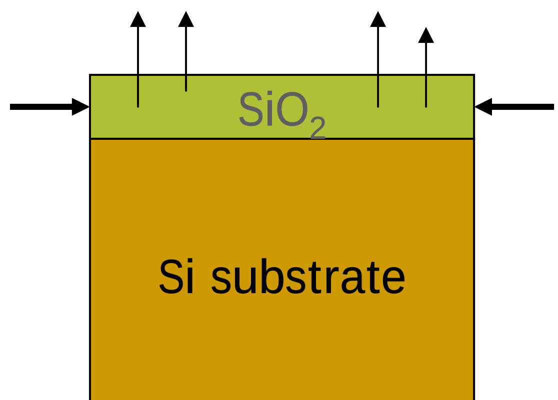
$$\dot{\varepsilon}_1 = -\dot{\varepsilon}_2 \text{ (constant strain)}$$

$$\sigma_x = \sigma_0 \exp(-Yt/\eta)$$

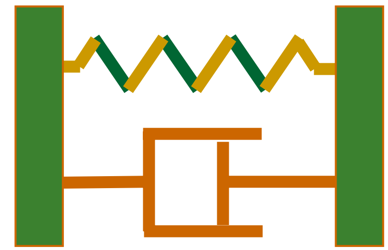
$$\text{for } Y = 6.6\cdot 10^{11} \text{ dyn/cm}^2$$

$$\eta = 2.8\cdot 10^{12} \text{ dyn}\cdot\text{s/cm}^2$$

$\tau \sim 4$ sec



Strain relaxation:



$$\varepsilon = \frac{\sigma_0}{Y}\left[1 - \exp(-Yt/\eta)\right]$$

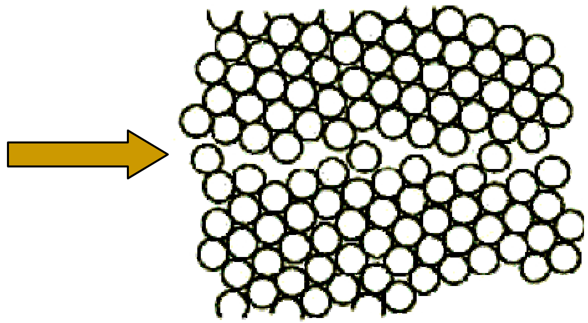
Usually a mixture of strain and stress relaxations

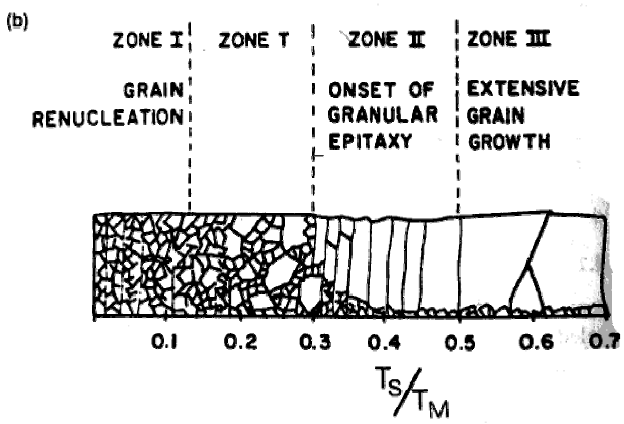
A volume change of ~200%!

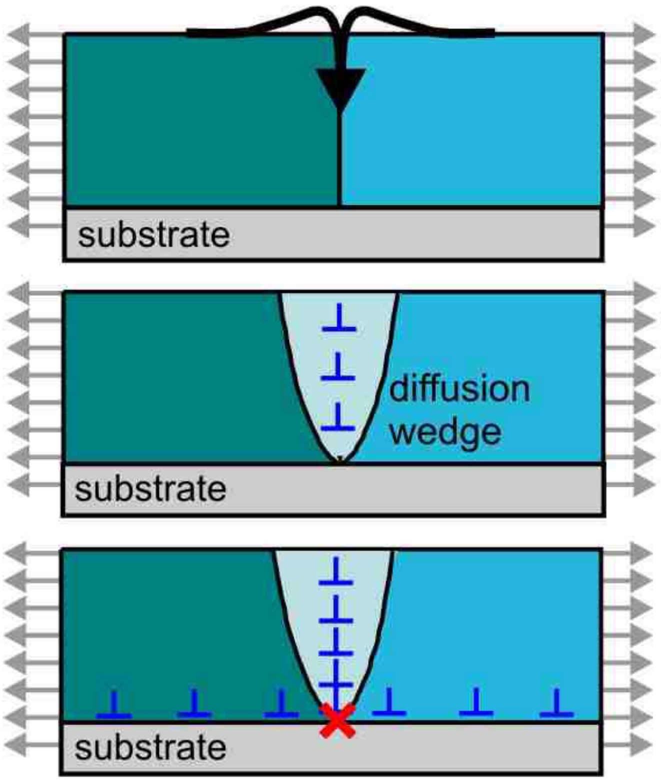
Diffusion Along Grain Boundaries

- Stress
- Defects

easier diffusion along grain boundaries

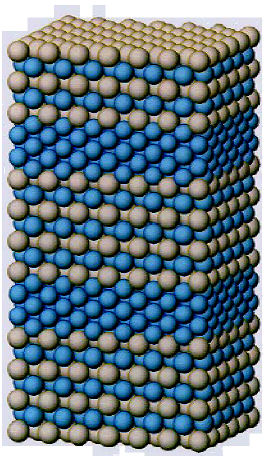






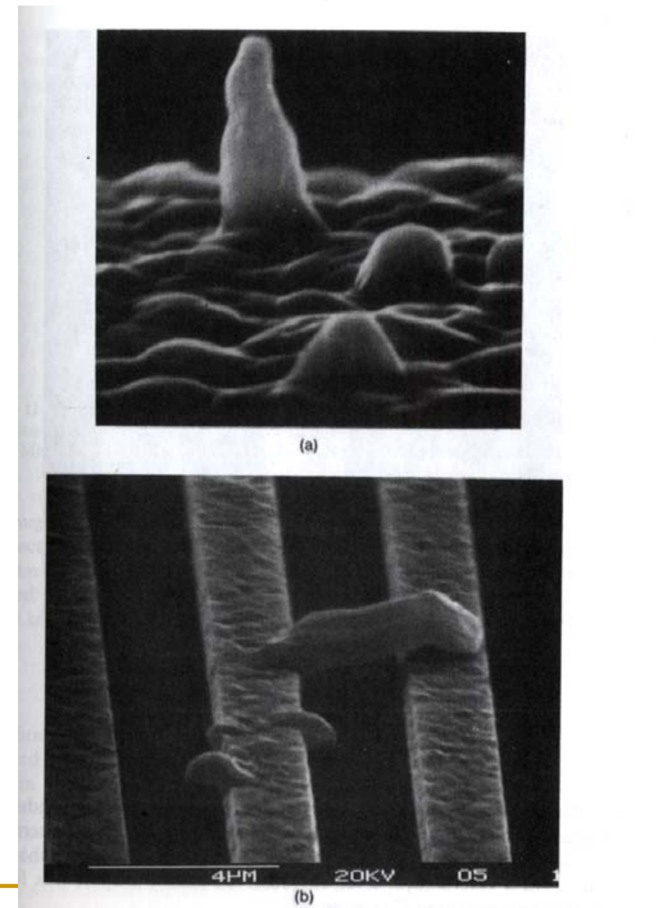
http://shasta.mpi-stuttgart.mpg.de/research/thinfilmcnt/thinfilms.htm

Interdiffusion & Transformations in Thin Films

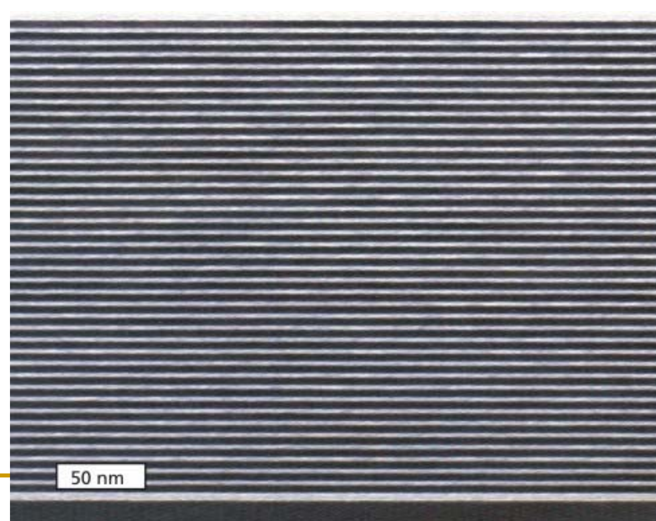


Interdiffusion is crucial in multilayers

Electro-migration



MoSi multilayers



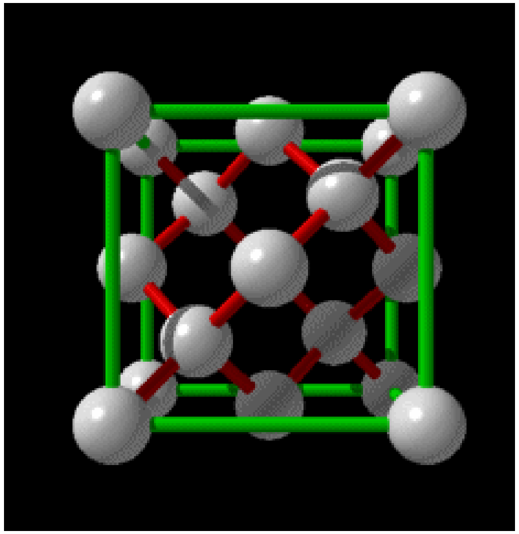
- EUV lithography
- EUV metrology
- EUV microscopy
- synchrotron optics
- x-ray astronomy
- soft x-ray lasers
- element analysis
- plasma physics

http://www.iof.fraunhofer.de/departments/optical-coatings/

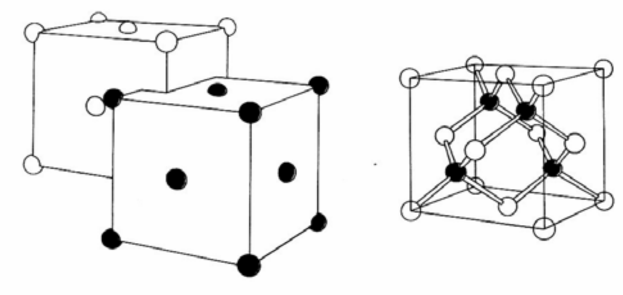
M. Ohring: Materials Science of thin films

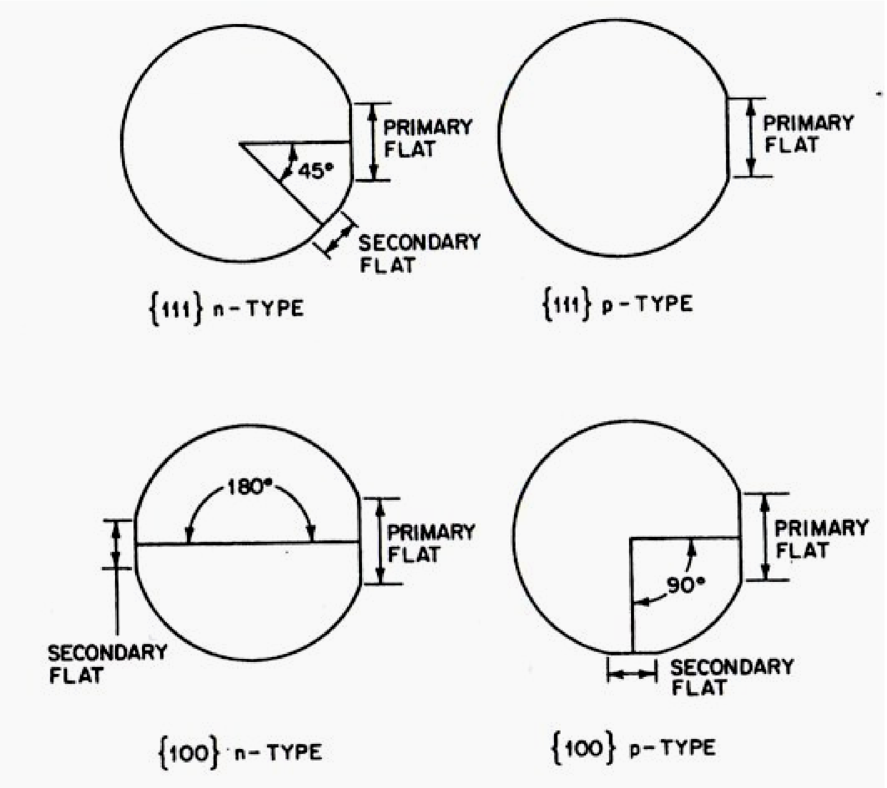
Si Crystal Structure

diamond structure



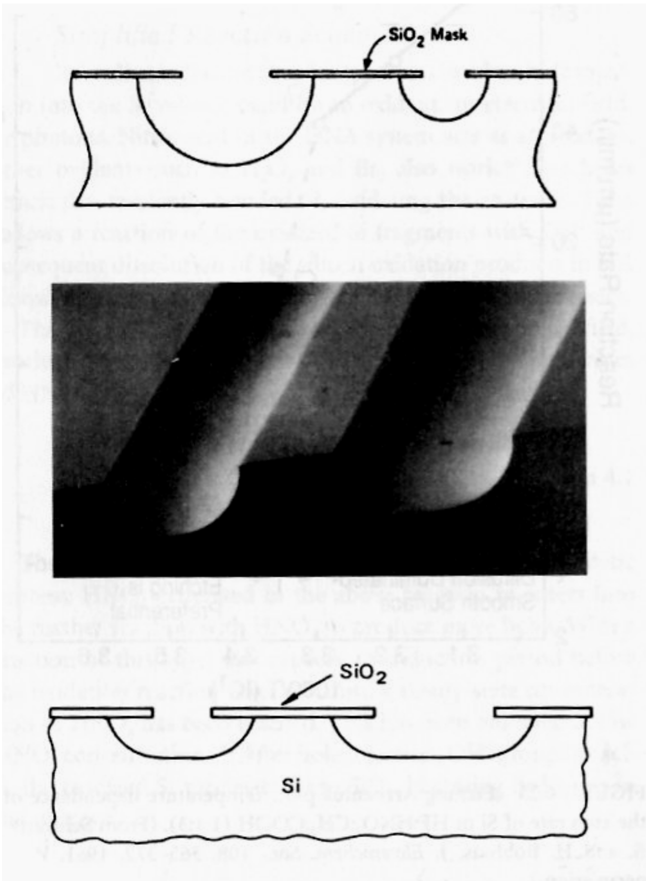
Two interleaving FCC cells offset by 1/4 of the cube diagonal



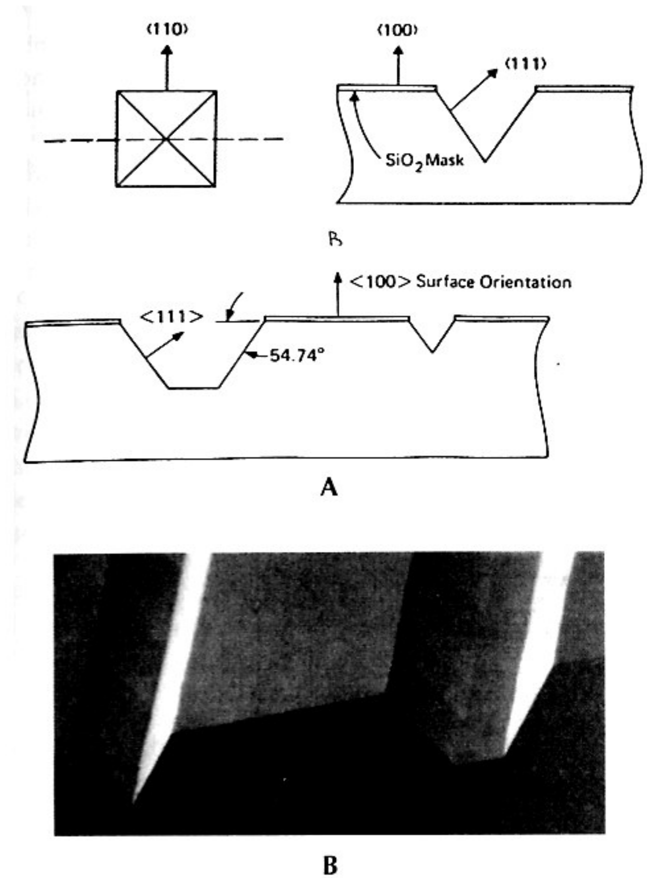


Primary and secondary flats on silicon wafers.

Isotropic vs Anisotropic Wet Etching



Isotropic etching of Si with (A) and without (B) etchant solution agitation.



Chemicals

Isotropic

$HF:HNO_3:CH_3COOH:H_20$

HF

$HF:NH_4F$

Masking Materials

Photoresist (Acids Only)

Si_3N_4

SiO_2

Anisotropic

KOH

EDP (Ethylenediamine Pyrocatechol)

CsOH

NaOH

N_2H_4-H_20 **(Hydrazine)**

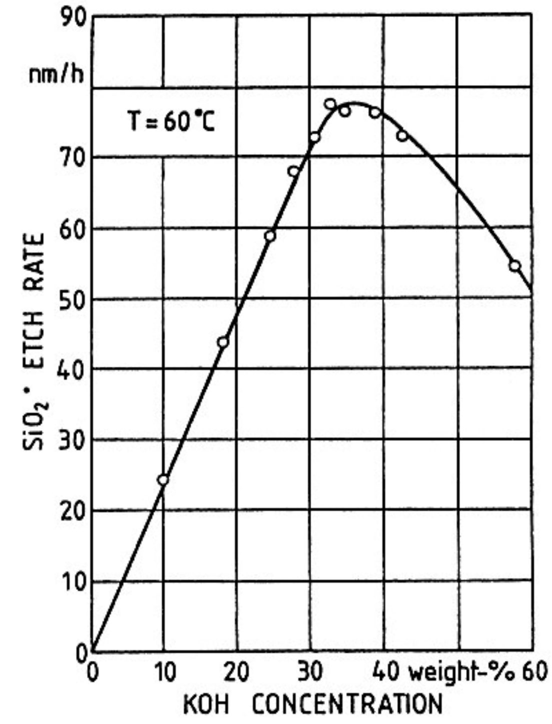
Chemicals

KOH Etching

Etch rate

(110) > (100) > (111)
(111) > (110) > (111) w/ IPA

Varies with *T* and concentration

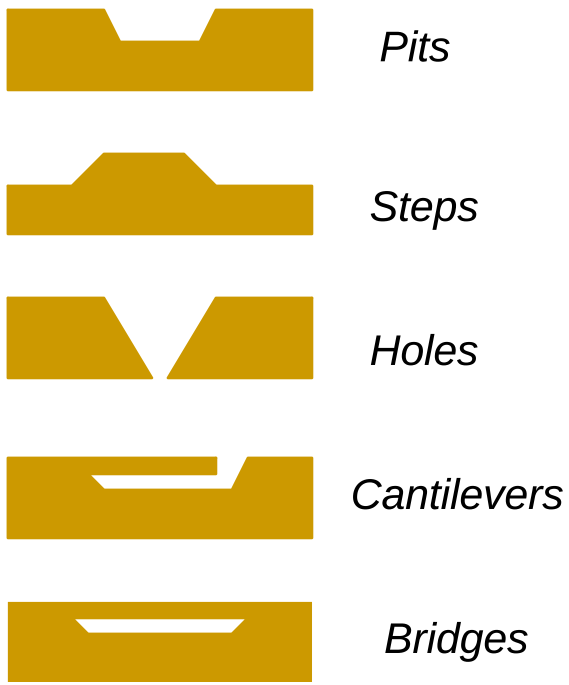


The SiO_2 etch rate in nm/hr as a function of KOH concentration at 60°C. (From Seidel, H. et al., *J. Electrochem. Soc.*, 137, 3612–3626, 1990. With permission.)

Masks

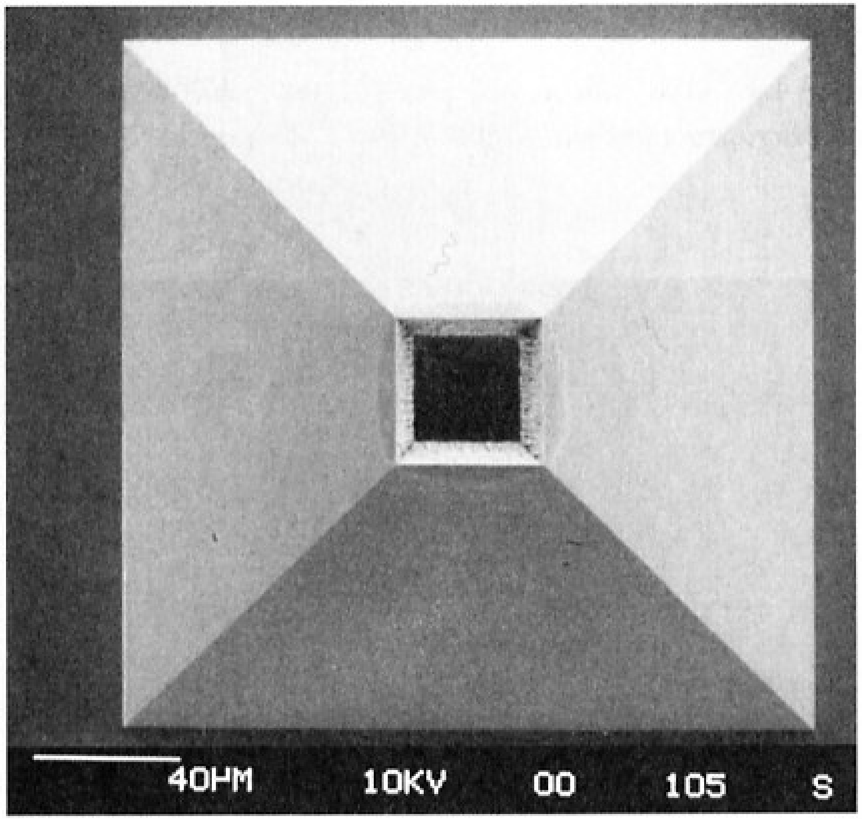
Si_3N_4: is the best, very slow etch rate, selectivity > 1000
SiO_2 :selectivity >> 100

Application of Anisotropic Etch



Micromachining

Orifice (A via through Si wafer)

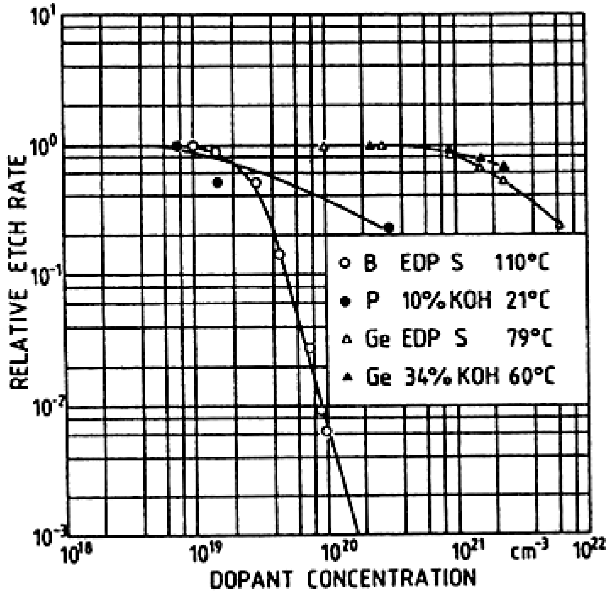


M. Madou "Fundamentals of microfabrication"

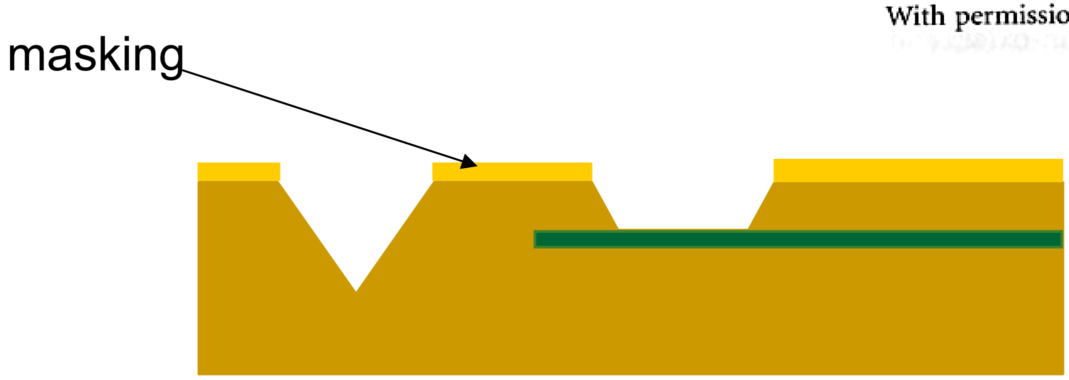
Etch Stop Layers

Boron Stops Etching

$\sim 10^{20}$ cm^{-3} reduces etch rate 1000 times

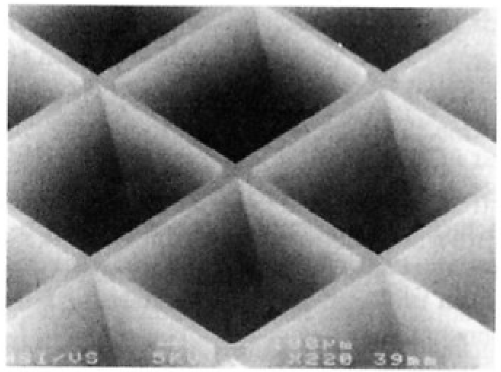


Relative etch rate for (100) Si in EDP and KOH solutions as a function of concentration of boron, phosphorus, and germanium. (From Seidel, H. et al., *J. Electrochem. Soc.*, 137, 3626–3632, 1990. With permission.)

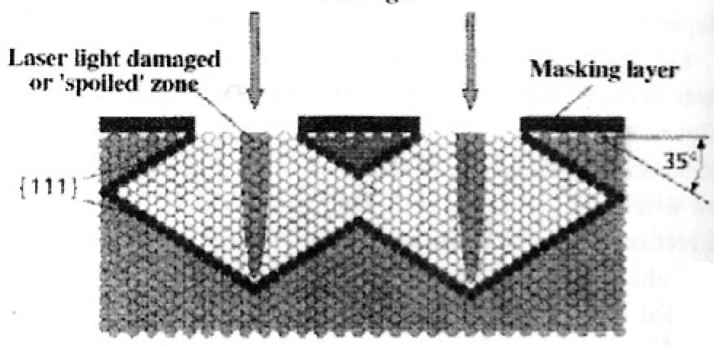


Laser-Assisted Wet Etching

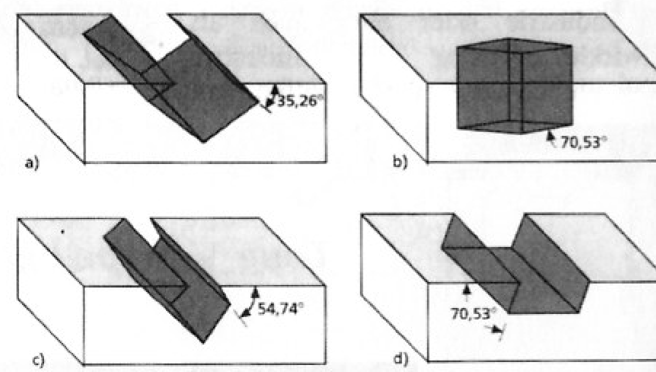
Fundamentals of Microfabrication



A



B

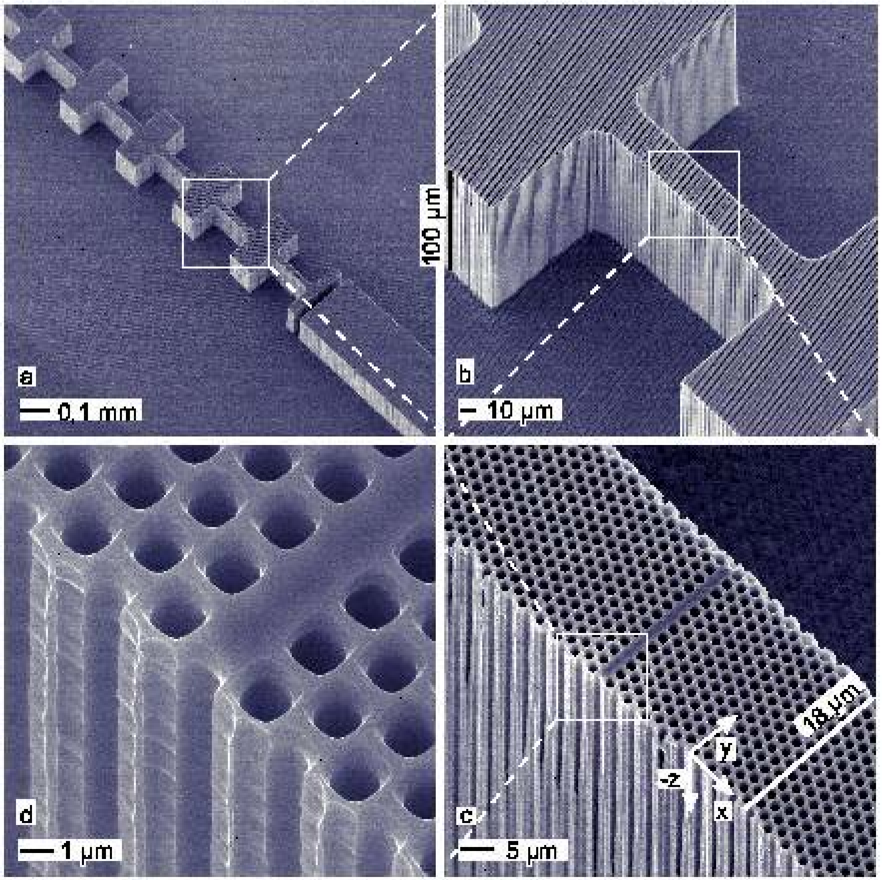


C

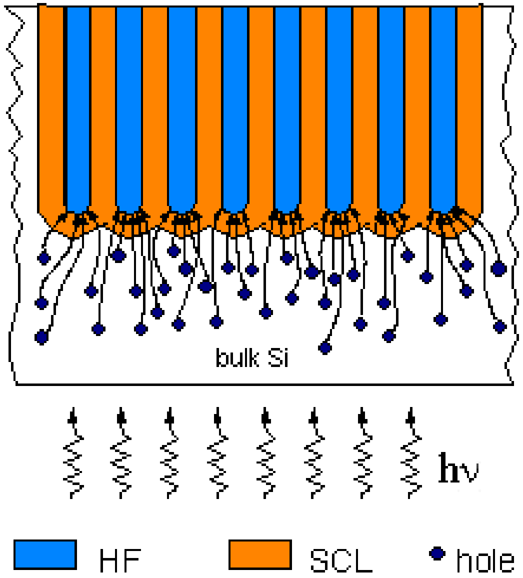
M. Madou, Fundamentals of Microfabrication

Macroporous Si

http://www.macroporous-silicon.com/



www-tkm.physik.uni-karlsruhe.de/



Photogenerated minority carriers (in the case of n-type Si this means "holes") diffuse from the back side of the sample to the pore (etch) pits and promote dissolution there, because of the enhanced electrical field in the space charge layer (SCL).