Xtal Growth

Main techniques

Growth/solidification mechanism

Introduction of defects during xtal growth

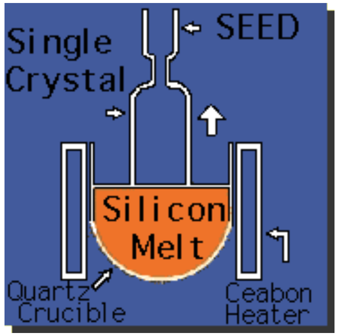
Impurities during xtal growth

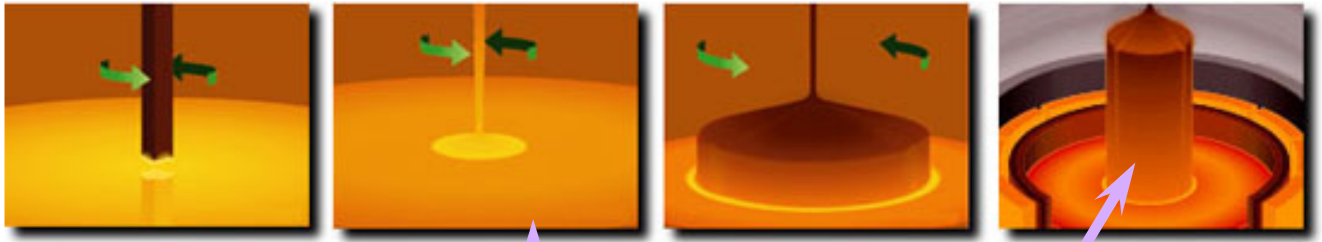
- Phase diagrams, Solubility, Segregation

Zone refining

Main techniques

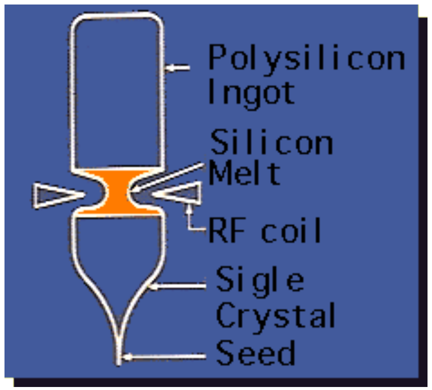
Czochralski CZ an Floatzone FZ



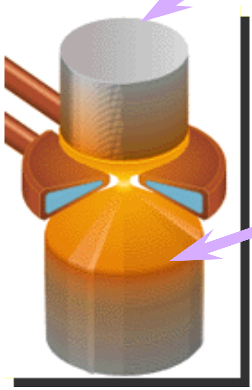


CZ

Poly-Si

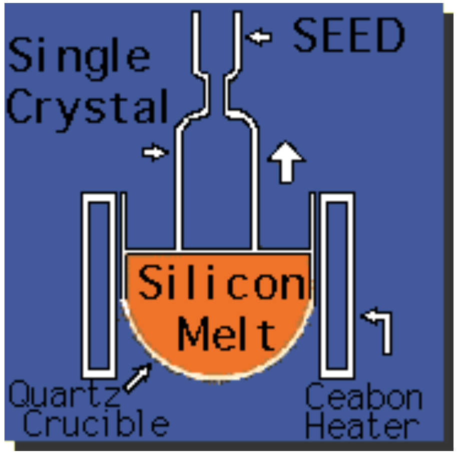


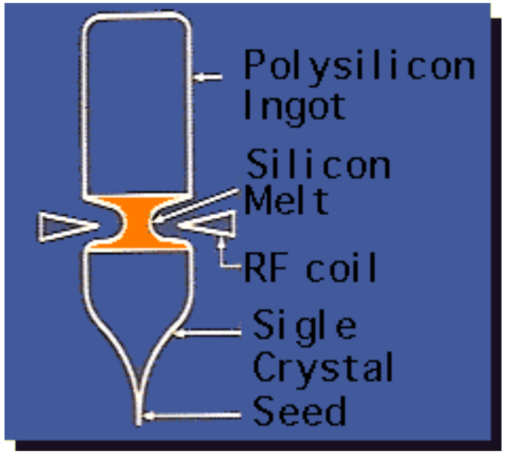
FZ



Single crystal Si

Comparison CZ and FZ





Most widely used,MOS	Much less, detectors, discretes
Contain O ~1E18cm^{-3}	Can be very pure, little O
Large diam 12 (18) inch	Smaller 6 inch common
Cheaper	

Phase diagrams

Important for equilibrium solid-liquid, so important Xtal growth
CZ and FZ Xtal growth = solidification with sofistication

Important for impurity incorporation
Important for impurity segregation

Important for reaction between metal and 1/2cond.
metal contacts and Schottky barriers

Phase diagrams: Example Si Ge

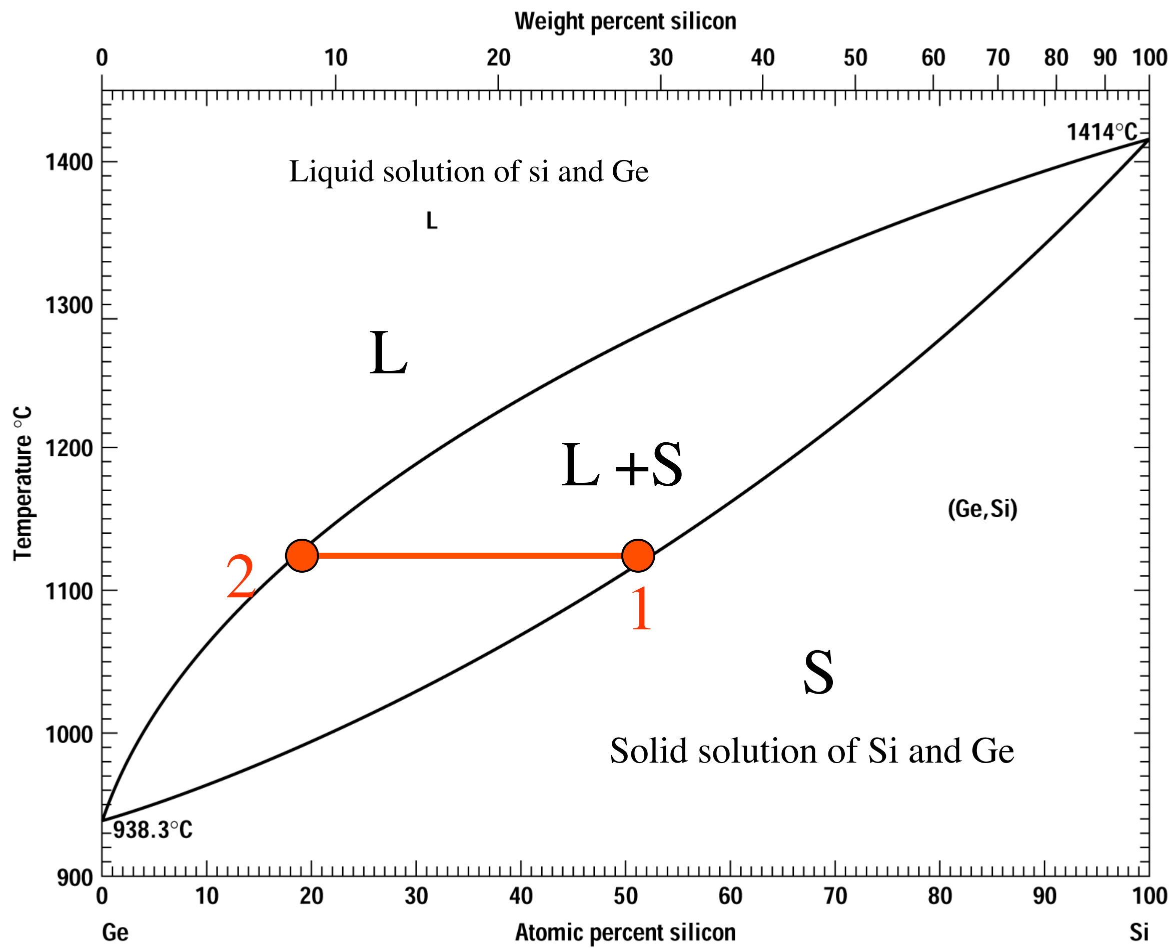


Figure 2.1 Phase diagram of Ge–Si. thermodynamic equilibrium *(courtesy*

Why is Solid w conc 1 equilib w liquid conc 2?

Phase diagrams: Example Si -As

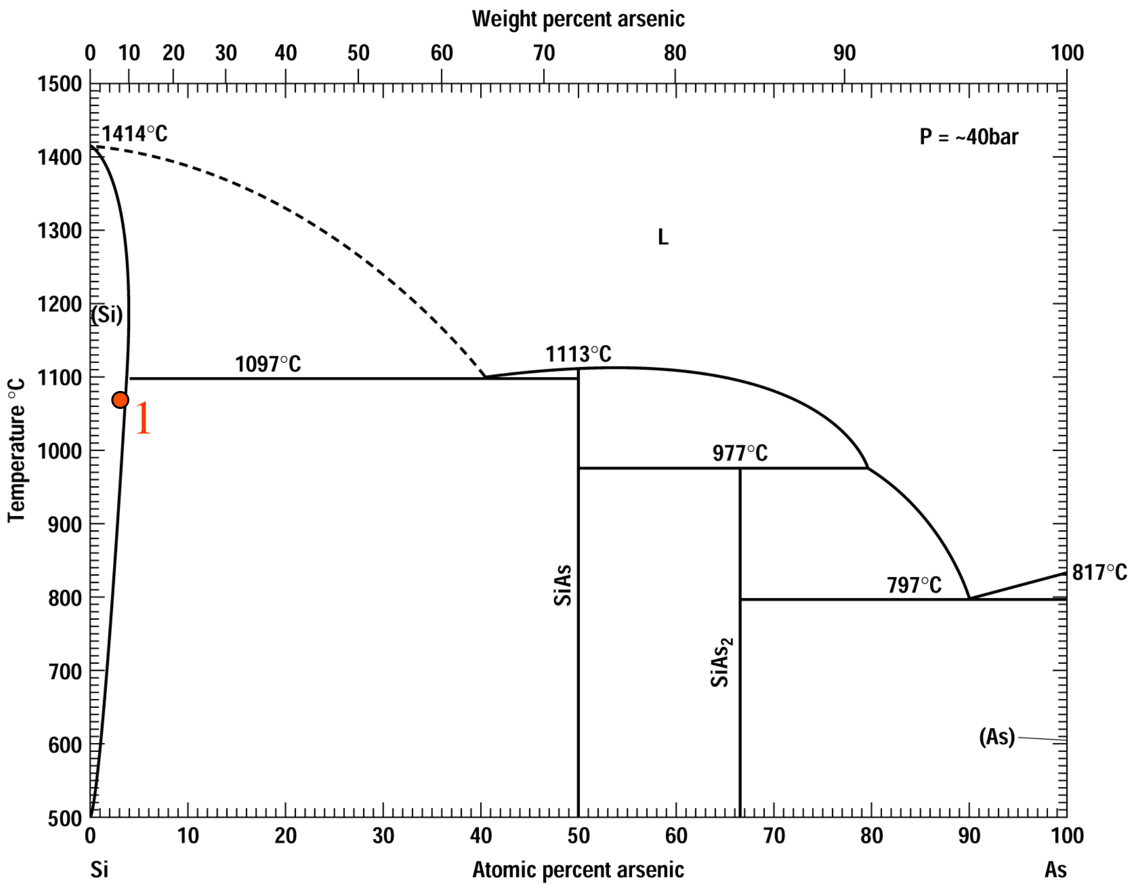


Figure 2.3 Phase diagram for As–Si *(courtesy of ASM International)*.

Why is there a limit to the solubility 1
Why is there an increase in elastic energy?
What is 'Fermi-effect'?
Why free energy of binary SiAs > Si(As) ?

Solid solubility in Si

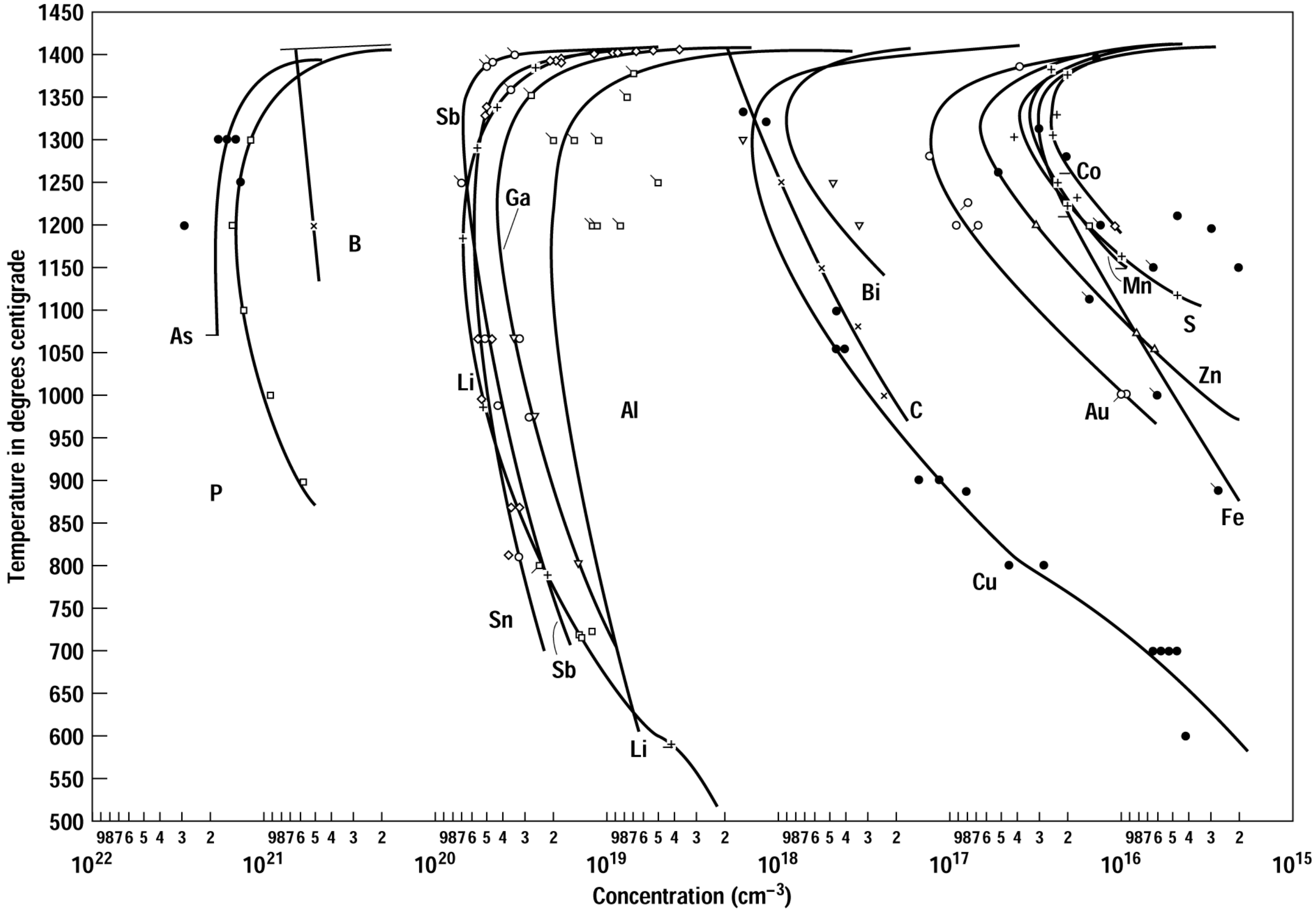


Figure 2.4 Solid solubility of common silicon impurities *(all rights reserved, reprinted with permission, © 1960 AT & T).*

What is the fracional concentration?
Which of these are dopants in Si?

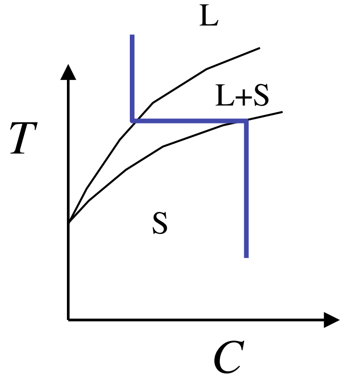
Segregation

In equilibrium, the concentration in liquid state is different from that in the solid state. How come?

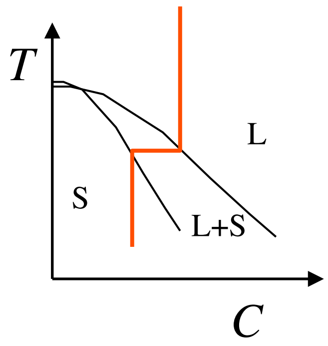
$$k_0 \equiv \frac{C_s}{C_l}$$

C_s Equilibrium conc. in solid .

C_l Equilibrium conc. in liquid.



$k_0 > 1$



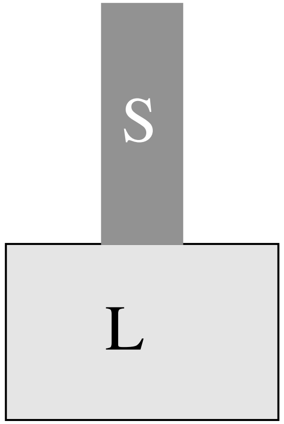
$k_0 < 1$

Values in Si

element	Al	As	B	C	Cu	Fe	O	P	Sb	Si
k_0	0.002	0.3	0.8	0.07	4e-7	8e-6	0.25	0.35	0.023	1

Purification by melting and segregation

$$k_0 \equiv \frac{C_s}{C_l}$$ $k_0<1$



Equation 2.13

$$C_s = kC_0(1-X)^{k-1}$$

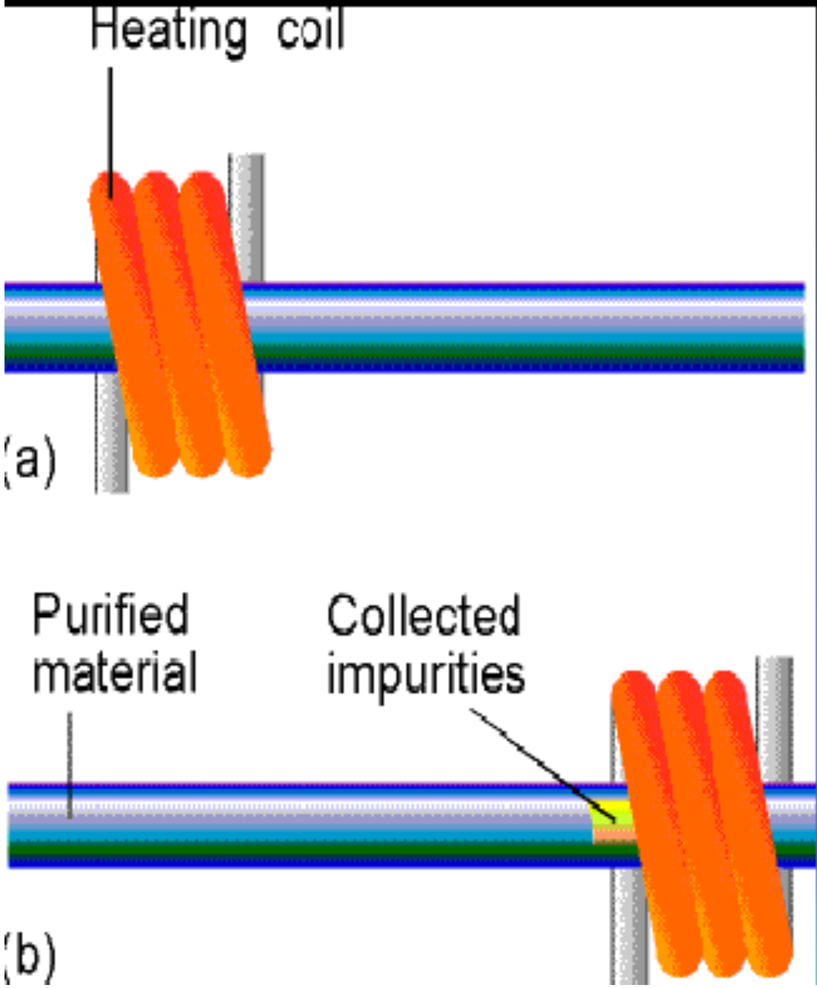
X: fraction of melt solidified

Homework- derive it

digression

Zone refining

Zone Refining



- In zone refining, a heater melts a small region at a time.
- After a molten zone is passed along the rod from left to right, the impurities are more concentrated at the right.
- In practice, a series of molten zones are passed along the rod.

Purity, achievable doping concentrations

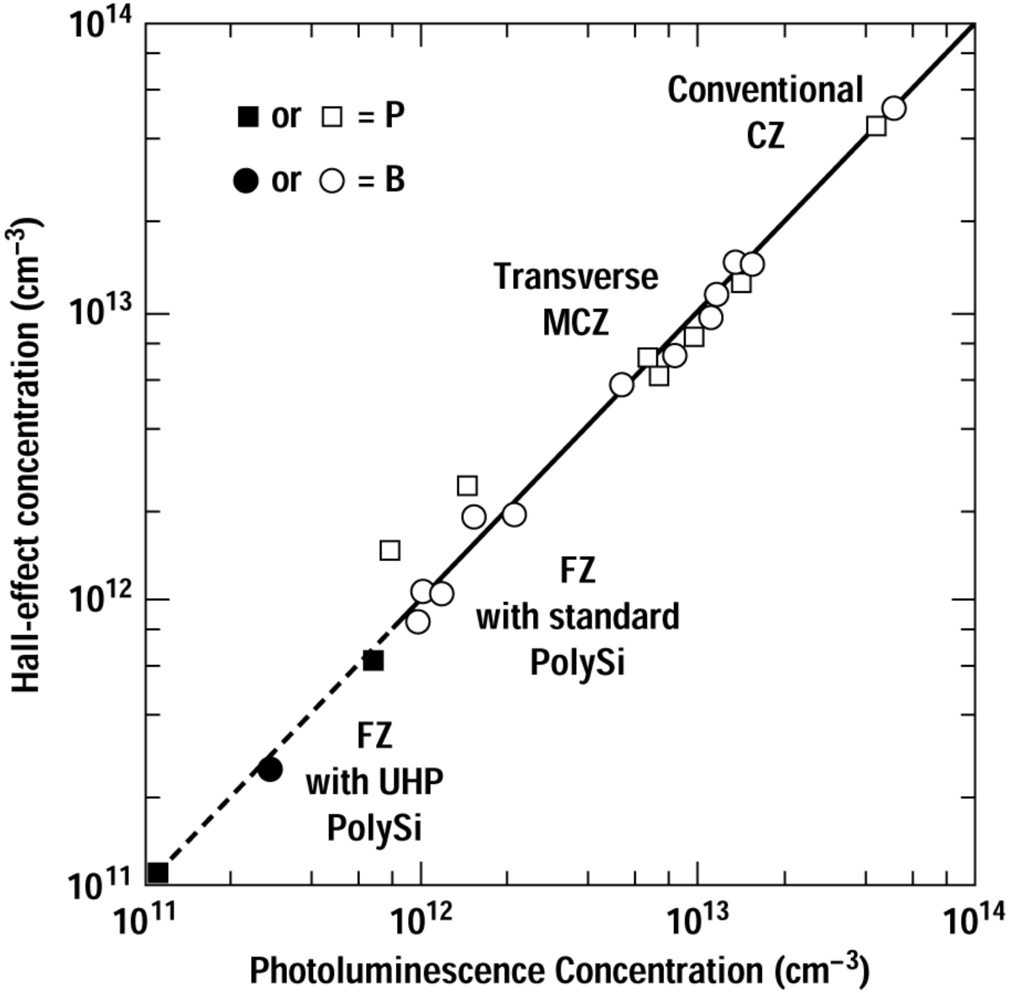
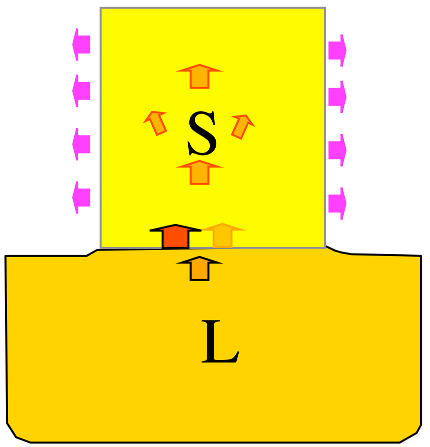


Figure 2.20 Minimum achievable carrier concentration for various growth technologies *(Thomas et al.)*.

Heat transfer in xtal pulling



$$\left(-k_L A \frac{\mathrm{d}T}{\mathrm{d}x}\bigg|_L\right) - \left(-k_S A \frac{\mathrm{d}T}{\mathrm{d}x}\bigg|_S\right) = L_m \frac{\mathrm{d}m}{\mathrm{d}t}$$

Maximum pulling rate

$$v_{\max} = \frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k_S A}{L_m}\frac{\mathrm{d}T}{\mathrm{d}m} = \frac{k_S}{\rho_m L_m}\frac{\mathrm{d}T}{\mathrm{d}x}\bigg|_S$$

k: thermal conductivity
L_m: heat of fusion
m: mass; ρ_m: mass density
T: temperature, A: area

$$\left.\begin{array}{l} \propto r^2 \\ \propto r \end{array}\right\} \Rightarrow \boxed{r \nearrow \Rightarrow v_{\max} \searrow}$$

$$v_{\max} = \frac{1}{\rho_m L_m}\sqrt{\frac{2\sigma\varepsilon k_m T_m^5}{3r}}$$

Problem 200-17

Si Xtal pulling Czochralski: Some typical numbers

Si boule dimensions
1200 mm long Si
300 mm diameter
neck diam 3 mm
seed diam 6 mm

Crucible charge
250 kg electronic grade Si
boule rotation up to 30 rpm
growth speed up to 8 mm/min

Power consumption 1 MW
- 66% of this goes to magnetic convection damping (w.o supercond magnet)

Cooling water 760 liter/min
Ar gas flow 400 liters/min

1 m crystal
1.5 h growth time,
500 kWh power,
68000 liter water,
36 000 liter Ar

X20

A factory room with 20 xtal pullers

Introduction of defects in xtal growth

Si xtal growt is very refined and sophisticated

Vacancies can not be avoided   Dislocations can, in principle

Mechanisms for dislocation introduction

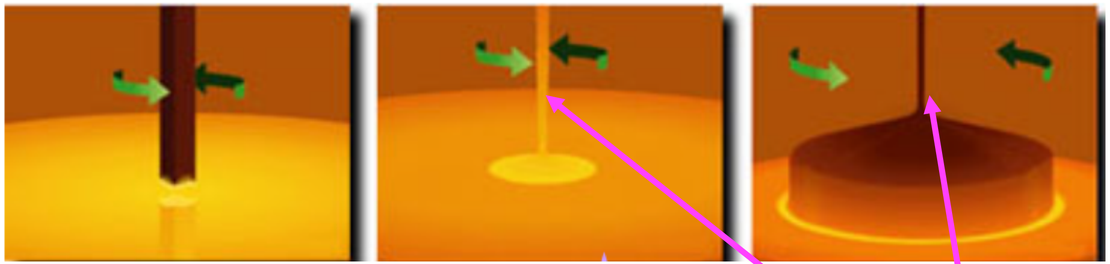
Thermal stress, -> elastic stress -> slip ; For Si eliminated by necking rapid
Impurities (induced stacking disorder)
Point defect super-saturation, nucleation, [V] [I] interplay, different D, balance

Striations , whirls

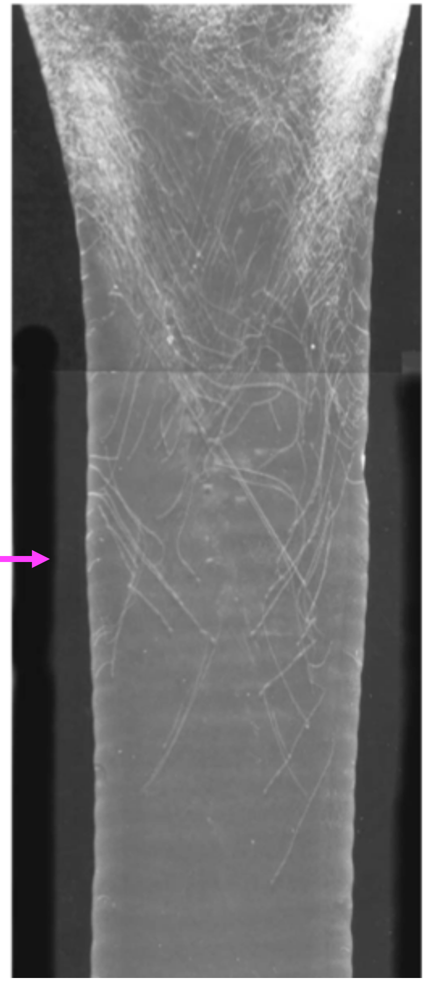
Introduction of defects in xtal growth

Mechanisms for dislocation introduction

Thermal stress, -> elastic stress -> slip ; For Si eliminated by **necking**

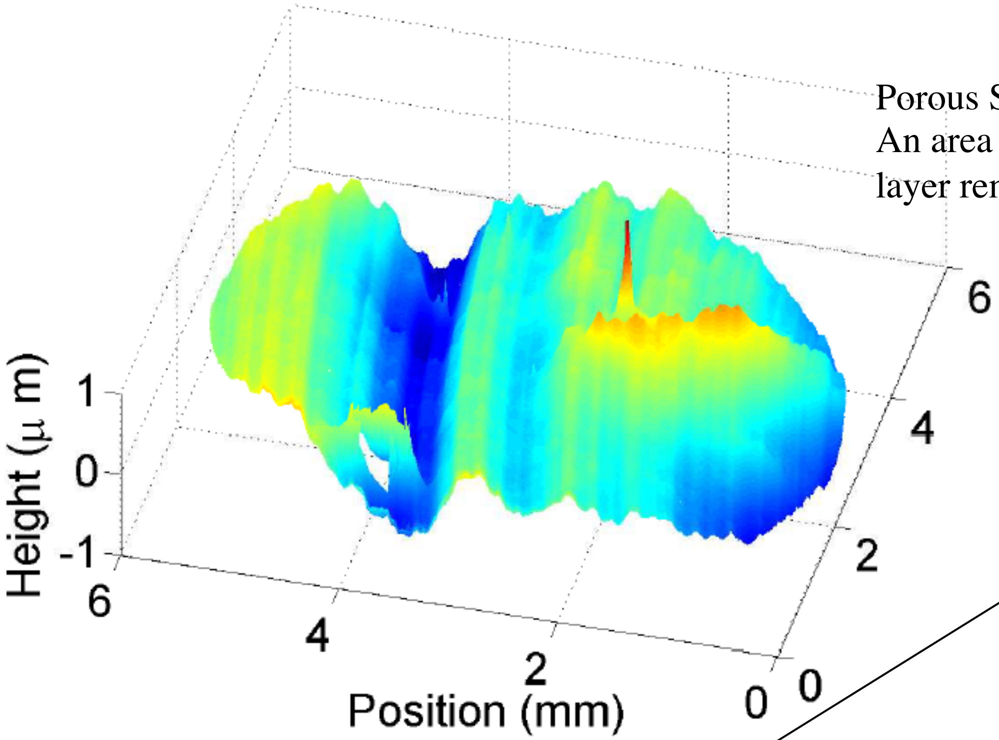


neck



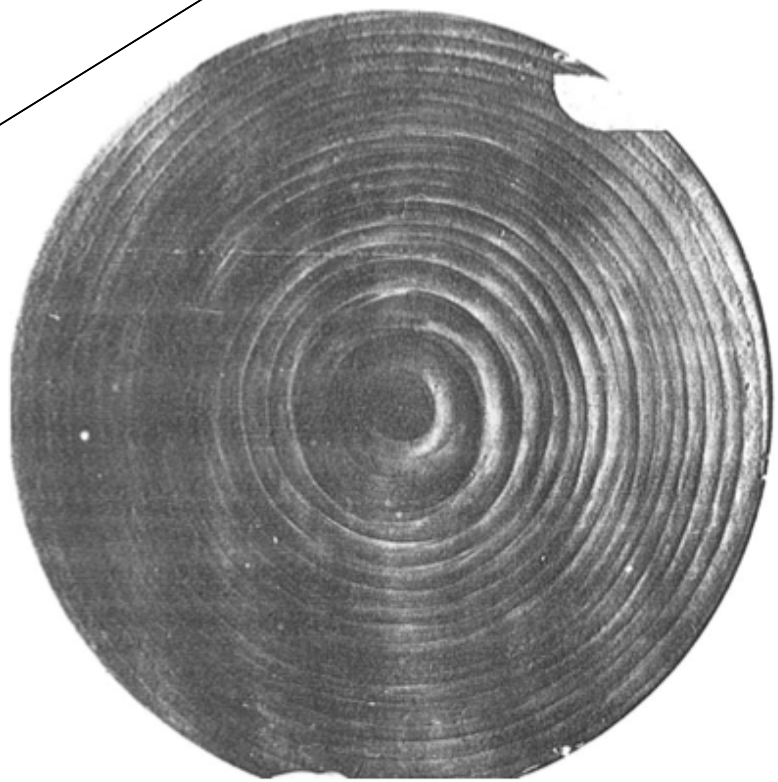
Elimination of slip dislocations by necking.
Dislocations does not propagate through the neck,
creates a stronger xtal allowing larger area to be grown
without slip

Striations



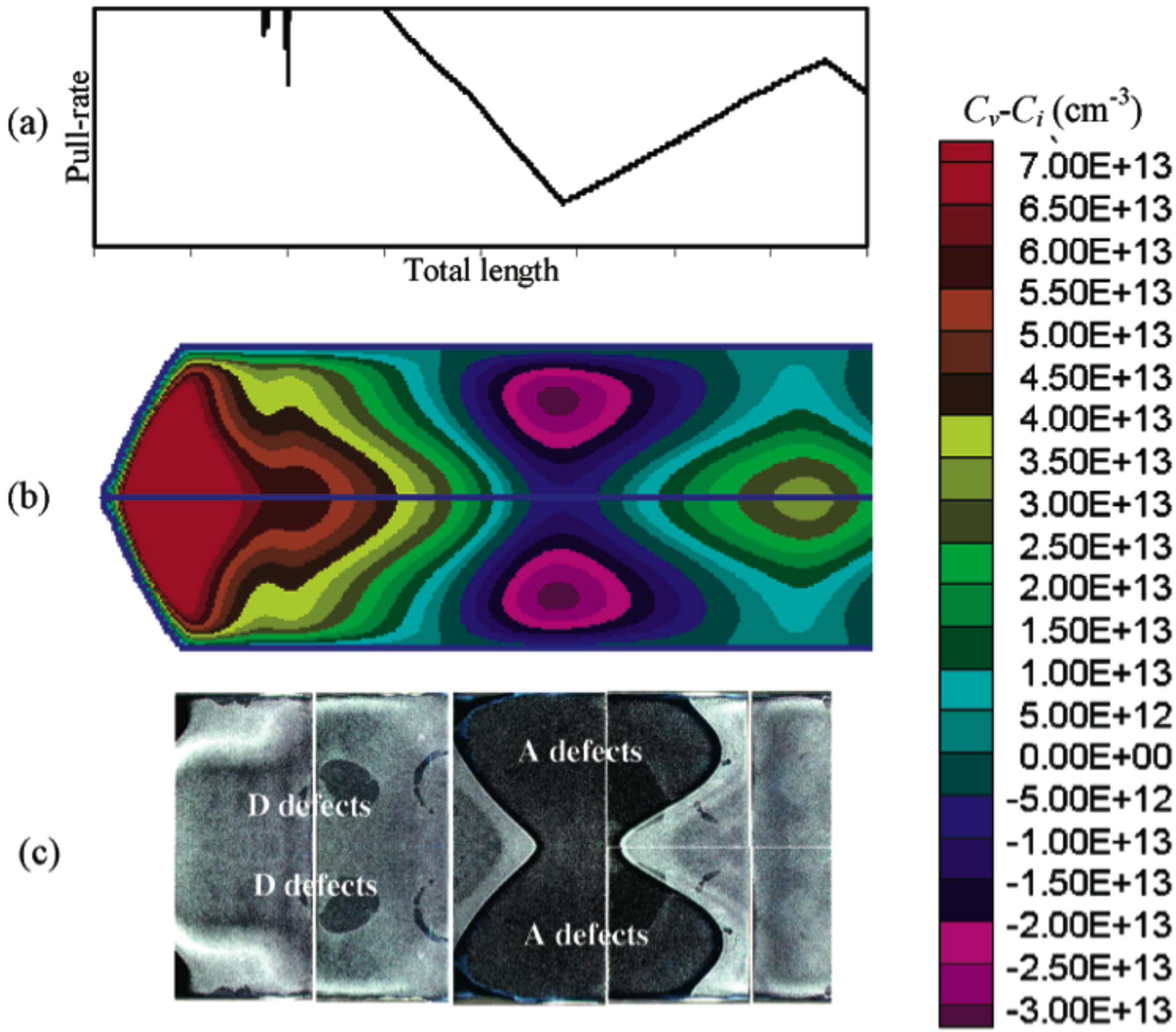
Porous Si formation depend upon local carrier conc
An area of wafer made porous over an earea. The porous layer removed, thus the fig shows variation in PS

X-ray topograph of a Si wafer



Point defect injection

Ind. Eng. Chem. Res., Vol. 44, No. 16, 2005



The effect of oxygen in Si

solubility $C_{ox} = 2\times10^{21}\,\frac{\text{at.}}{\text{cm}^3}\exp\left(\frac{-1.032\text{eV}}{kT}\right)$

Typical O conc. (CZ: $[O_i]$ 1e^{18}, FZ: $[O_i]$ <1e^{16})
(So process/cooldown temperature<1150C gives 3D defects)

Rapid cooling yields O supersaturation

O_i is electrical neutral bond centered

O_i is stable at RT, low diffusivity

Subsequent anneal >650 C -> rod like precipitates <110>
anneal 800 C square precipitates on (100) plane

SiO_2 cluster precipitates at high T

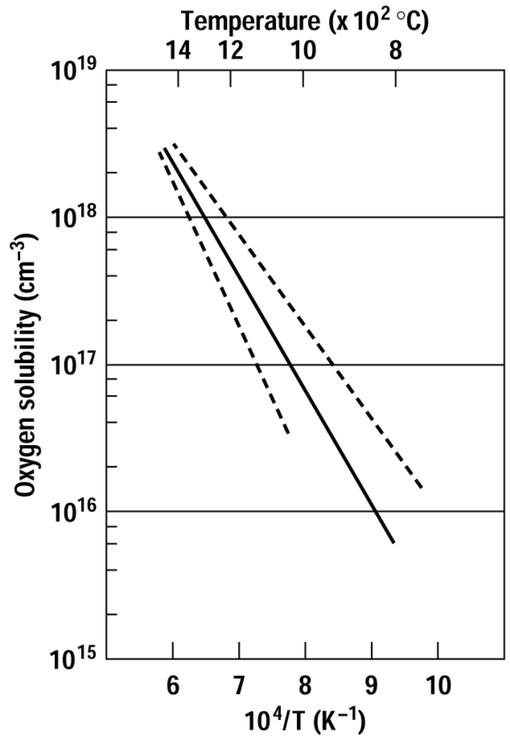


Figure 2.10 The solubility of oxygen in silicon. The dashed lines correspond to the highest and lowest variations *(after Shimura)*.

The effect of oxygen in Si

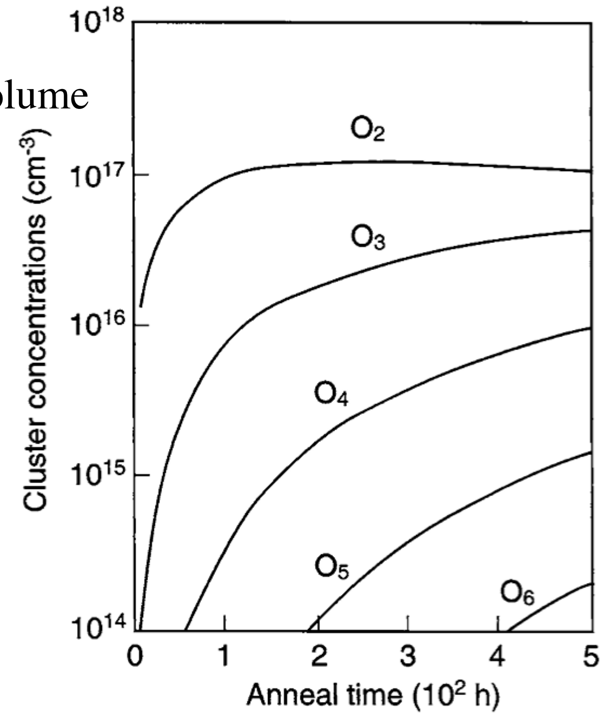
(So process/cool down temperature<1150C gives 3D defects)

Rapid cooling yields O supersaturation

SiO_2 clusters (SiO_4 chains) precipitates at high T anneal
traps for metals Fe, Cu (1e11 cm-3) , gettering

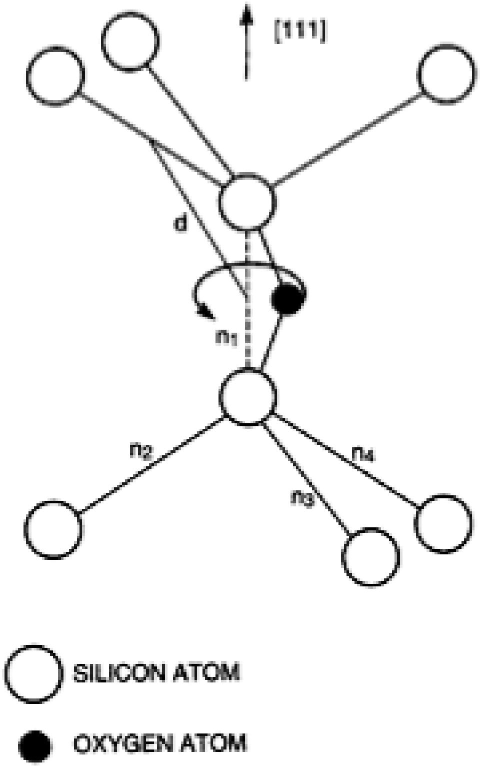
Accompanied by I =Si_i,
On average 1 I required to accomodate local increase in volume
for every 2 O_i growing to SiO_2
Thus O_i diffusion and I diffusion

Thermal donors TD low temp
Undoped Si becomes n-type
At low T, low diff rate Oi :
1st state of aggregation attributable to dimers
The thermal donor zoo family
TDN (N) N=1,2,3…
STDH(N) Shallow thermal donor w. H
STDAl(N) Shallow thermal donor w. Al
STDX(N) Shallow thermal donor w. X, X= V, N,..?



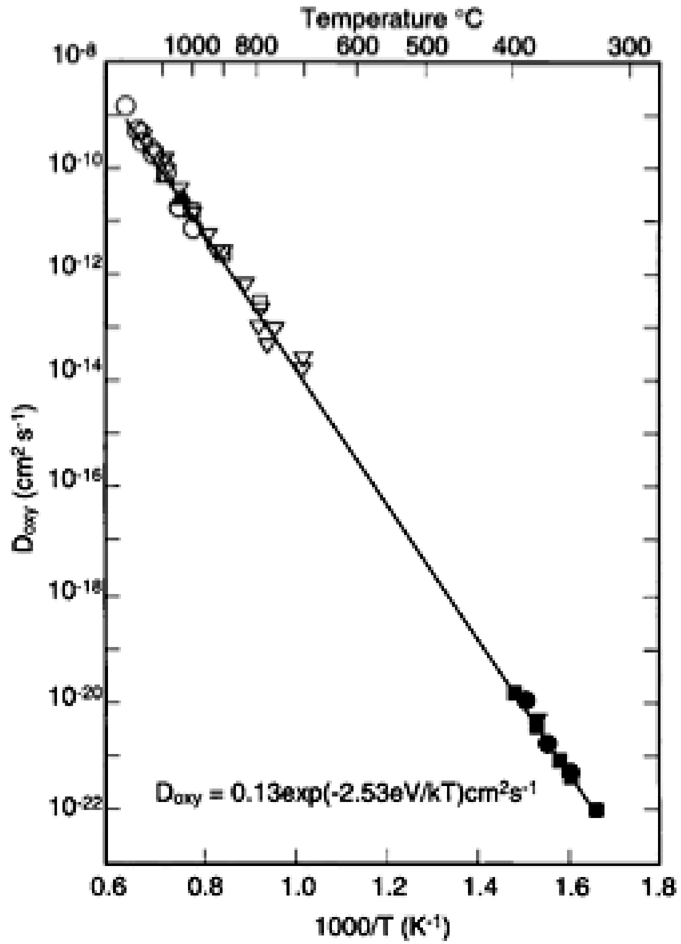
Oxygen in Si- O_i

O_i is electrical neutral bond centered



Geometry of a bond-centred interstitial oxygen impurity in silicon showing a small displacement from a 111 axis and the diffusion jump distance *d*. O_i may be located at any of the 4 nonequivalent bonds (under uniaxial stress)

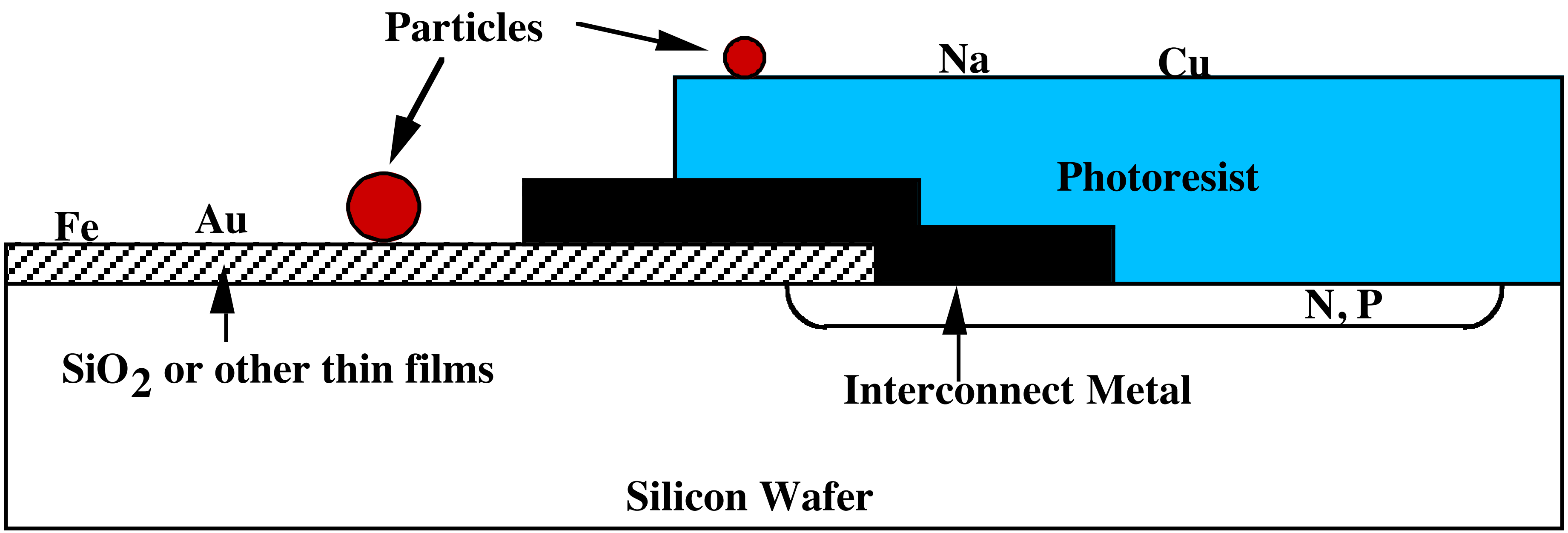
Oxygen diffusivity



Gettering, Denuded zone

Type of contaminants

Contaminants may consist of particles, organic films photoresist), heavy metals or alkali ions.



Modern IC factories employ a three tiered approach to controlling unwanted impurities:

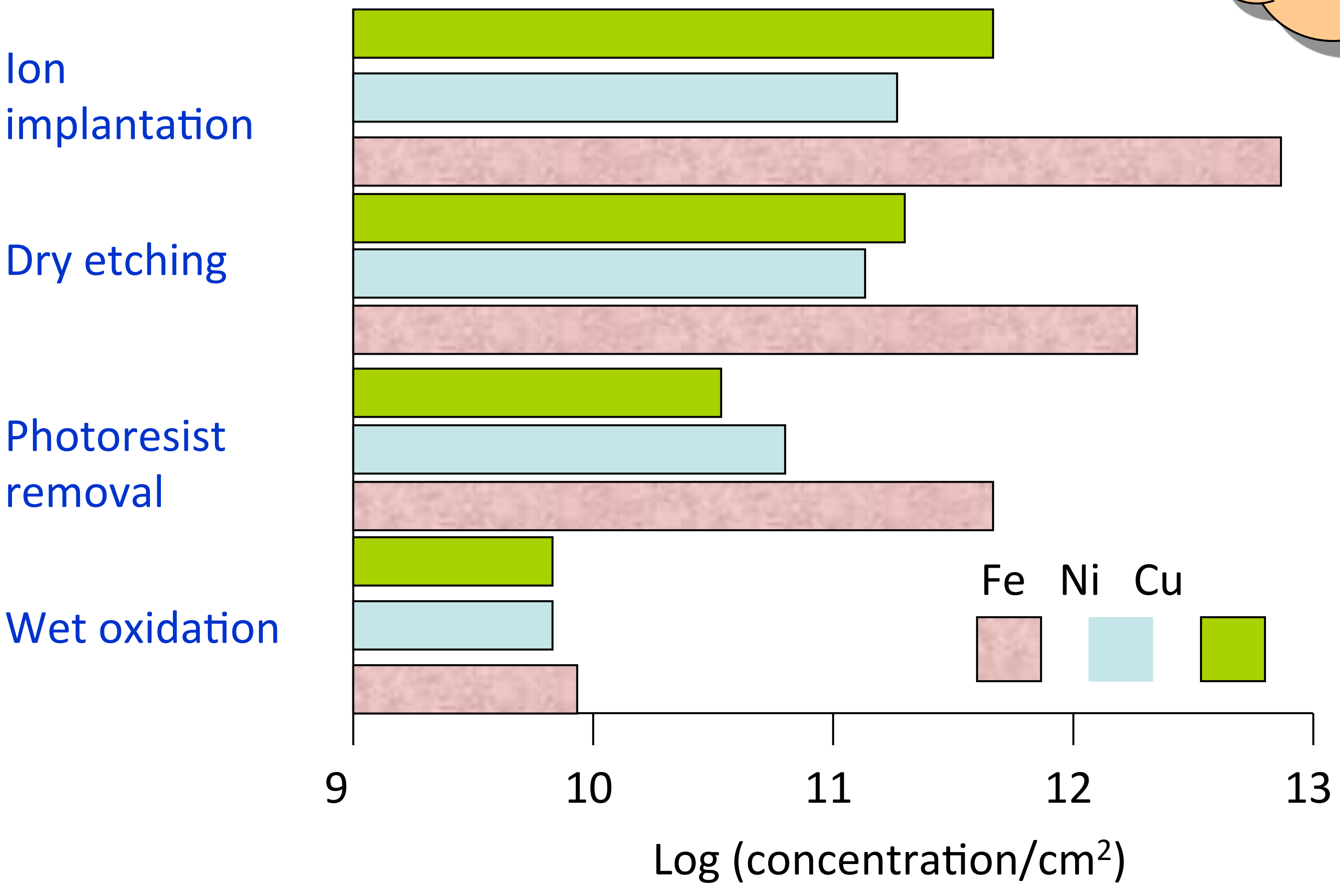
1. clean factories
2. wafer cleaning
3. gettering

Metal contamination

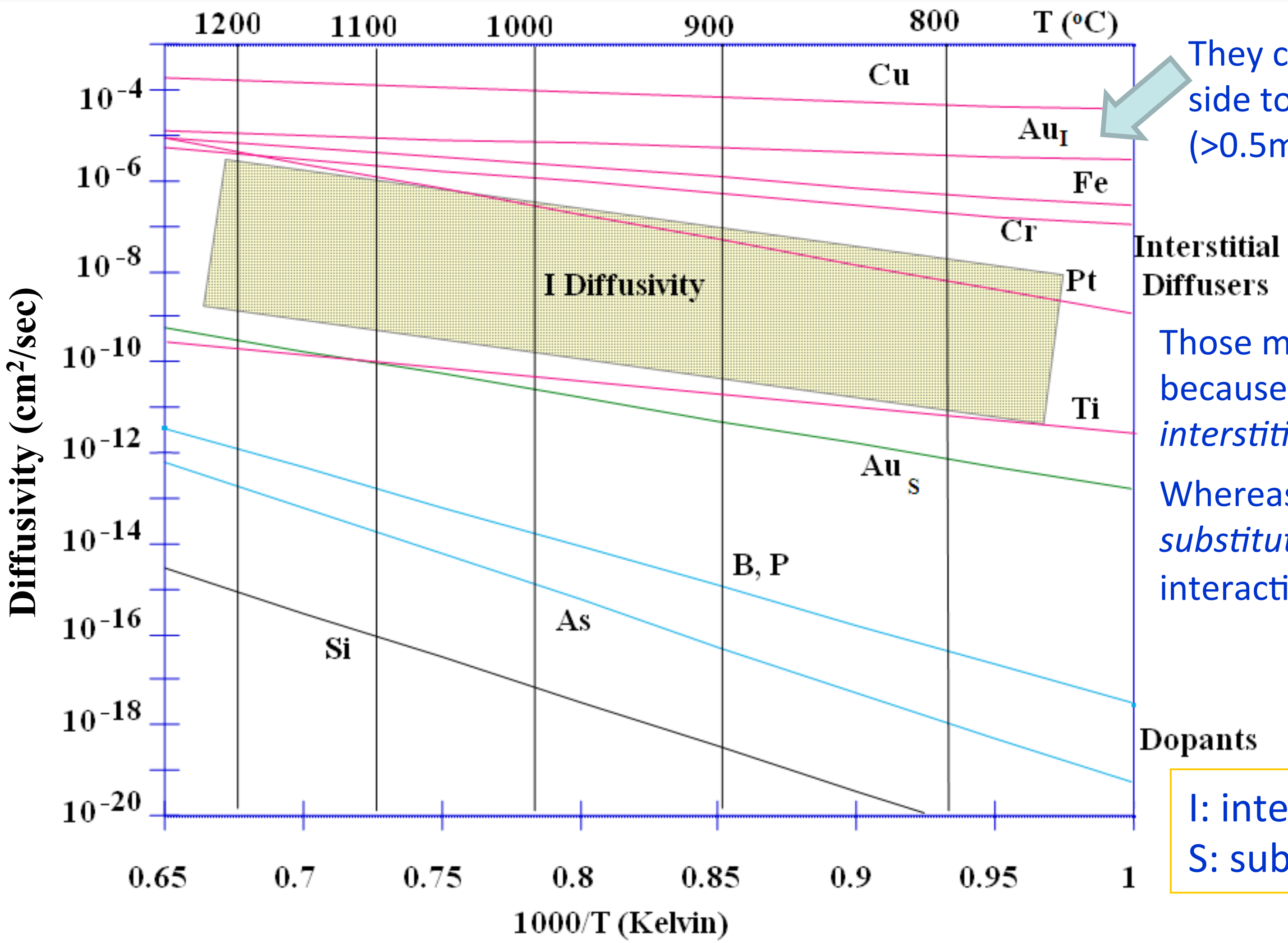
Sources: chemicals, ion implantation, reactive ion etching, resist removal, oxidation.

Effects: defects at interface degrade device; leads to leak current of p-n junction, reduces minority carrier life time.

Fe, Cu, Ni,
Cr, W, Ti…
Na, K, Li…



Fast diffusion of various impurities



They can diffuse from front-side to backside of the wafer (>0.5mm distance)

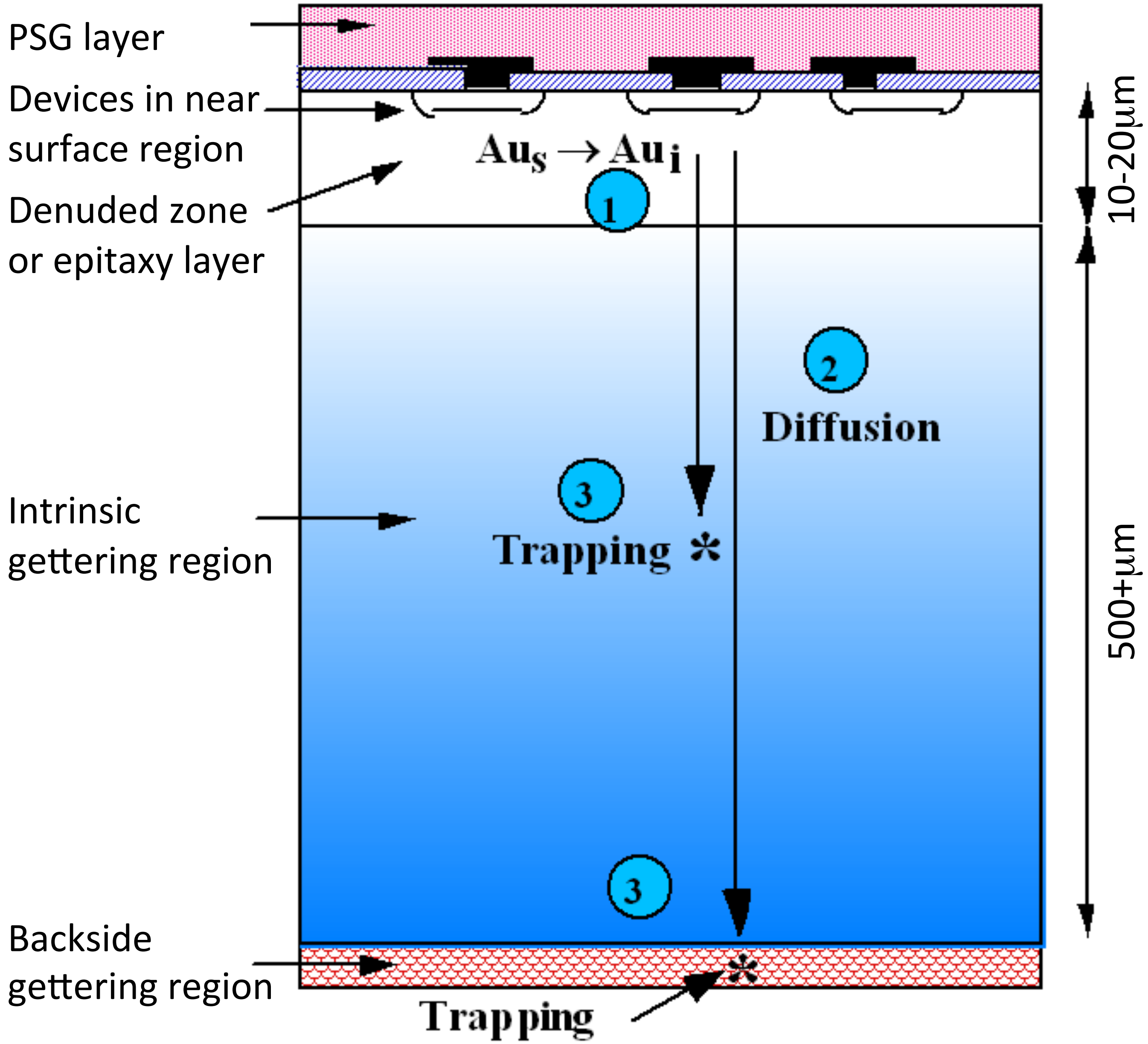
Those metal diffuses fast because they do so as *interstitials*.

Whereas dopants are *substitutional* and diffuse by interacting with point defects.

I: interstitial
S: substitutional

Heavy metal gettering relies on metal's very high diffusivity (when in interstitial sites) in silicon, and its preference to segregate to "trap" sites.

Gettering mechanism



Intrinsic gettering

Precipitates (size) grow @ high T

Density of nucleation sites grow @ low T

Therefore, low T to increase density, and high T to grow its size.

Oxygen diffusivity:

$$D_0 = 0.13 \exp\left(\frac{-2.53}{kT}\right) cm^2 \sec^{-1}$$

$D_0 >> D_{dopants}$ but $D_0 << D_{metals}$

In intrinsic gettering, the metal atoms segregate to dislocations (formed because of volume mismatch of SiO_2 and host Si lattice) around SiO_2 precipitates.

15 to 20 ppm oxygen wafers are required:

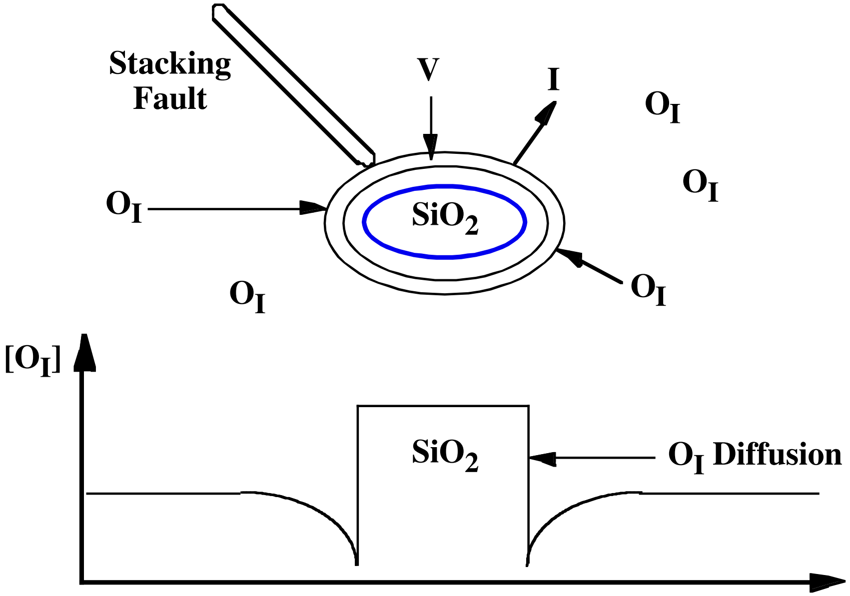
<10 ppm - precipitate density is too sparse to be an effective getterer.

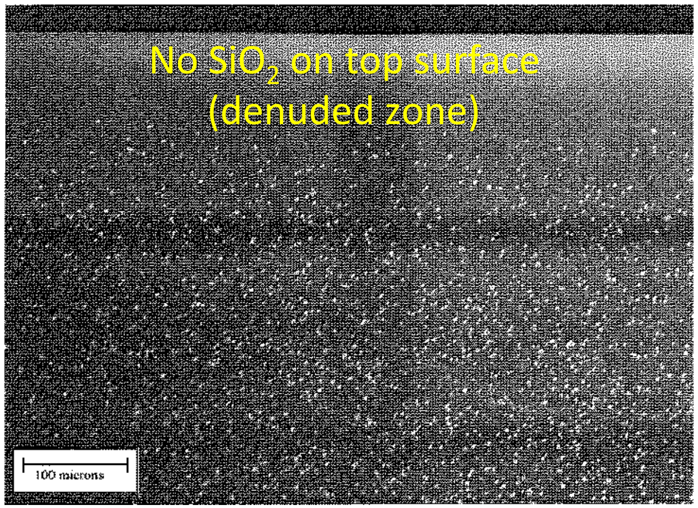
>20 ppm - wafers tend to warp during the high temperature process.

Note: devices that use the entire wafer as the active region (solar cells, thyristors, power diodes, etc...) can not use this technique, but can use extrinsic gettering.

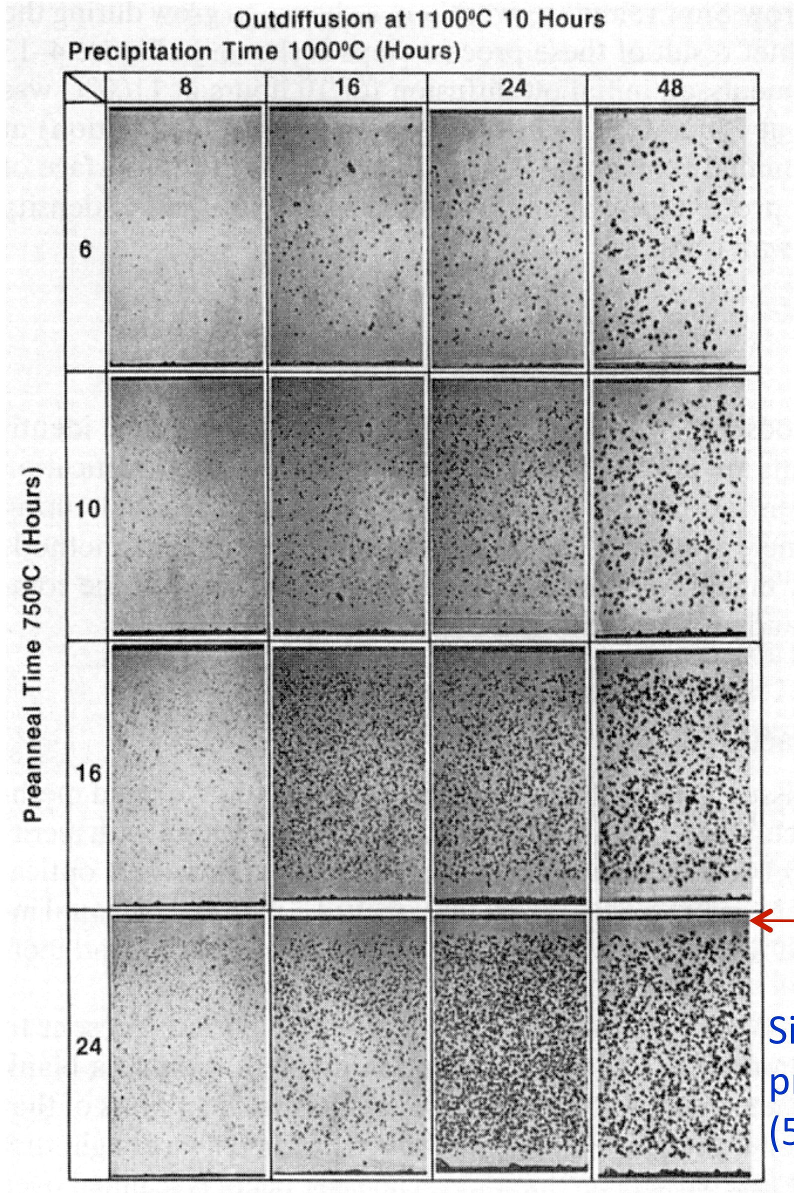
Today, most wafer manufactures perform this intrinsic gettering task that is better controlled.

Intrinsic Gettering: SiO_2 precipitates





SiO_2 precipitates (white dots) in bulk Si

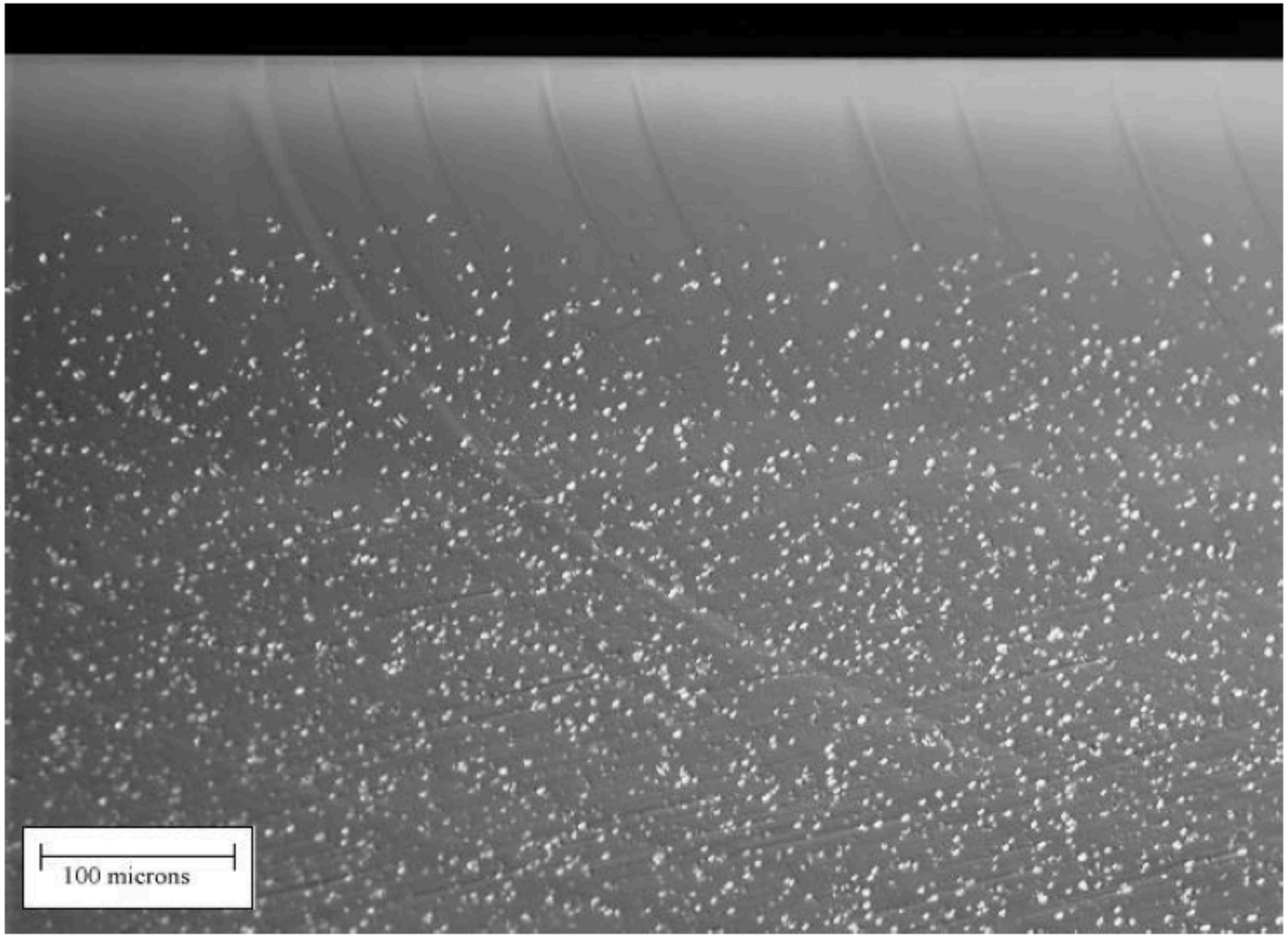


no SiO_2

SiO_2 precipitates (50-100nm)

Figure 4-13

Intrinsic Gettering: SiO_2 precipitates



denuded zone

An etched cross section of a silicon wafer with an ideal distribution of oxygen precipitates for internal gettering purposes. It has a denuded zone of about 80 microns and a bulk precipitate density of about 5×10^{9} cm^{-3}.