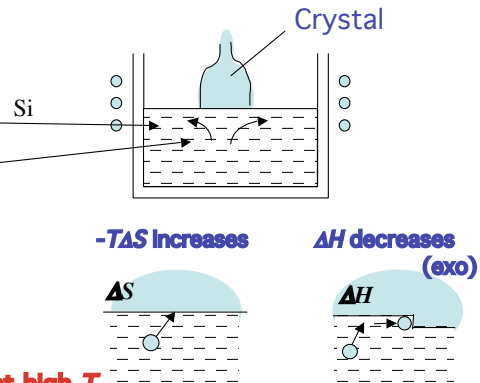# CRYSTAL GROWTH

6.12J / 3.155J Microelectronic processing

CRYSTAL GROWTH steps and questions

Crystal

Si

1. **Reactants in molten form**
2. **Transport to S/L interface**
3. **Adsorbtion:** entropy decreases

$-T\Delta S$ increases ΔH decreases (exo)

ΔS ΔH

4. **Critical nucleus size**
5. **Growth**
6. **Impurities, defects more stable at high T**
   ; how grow pure crystal?
7. **Segregation solid vs. liquid**
   What do we need to know prior to crystal growth?

1

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Defects and crystal growth

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- Defects
  impurities, vacancies, dislocations... T dependence

- Crystal growth techniques:
  float zone, Bridgman, Czochralski

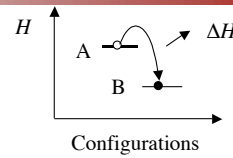- Segregation during growth
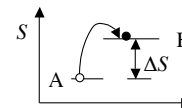 Segregation coefficients

2

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Thermodynamics and phase diagrams

$H_B - H_A = \Delta H$ = heat of formation
of B from A

Do all reactions that give off heat proceed?

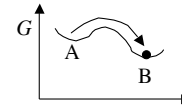
$S_B - S_A = \Delta S$ = Entropy (disorder) change
from A to B

Do all reactions that increase disorder proceed?

Answer in Gibbs free energy:

$G = H - TS$

$G_B - G_A = \Delta G = \Delta H - T\Delta S$

G must decrease if reaction is to proceed.
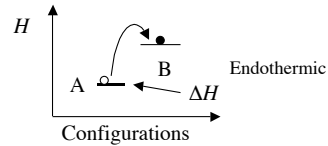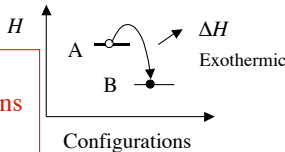(From equilibrium, all changes increase G).

3

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Thermodynamics and phase diagrams

ΔH = of B from A

Do all
exothermal reactions
proceed?

Exothermic

Endothermic

ΔS =from A to B

$\Delta S < 0$

B more
ordered

$\Delta S > 0$

B more
disordered
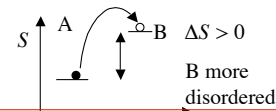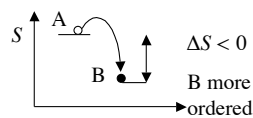
Does disorder always increase
in reactions?

$\Delta G = \Delta H - T\Delta S$

Will not go
above $T = \Delta H / \Delta S$
freezing of water

Will not go
below $T = \Delta H / \Delta S$
melting of copper

Examples:

4

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Under what conditions will Si melt crystallize?

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T

T_m

Liquid Si
$T = T_m{}^+$
$\begin{cases} \text{high } S \\ \text{high } H \end{cases}$

$T = T_m{}^-$
Crystal Si
$\begin{cases} \text{low } S \\ \text{low } H \end{cases}$
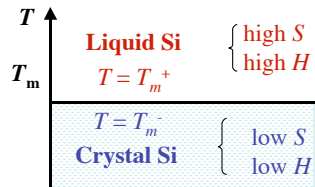
For solidification:

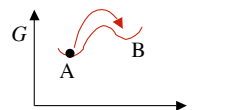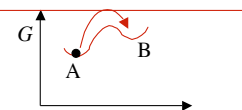$$\Delta S = S\left(T^-\right)_{final} - S\left(T^+\right)_{initial} < 0$$

$$\Delta H = H\left(T^-\right) - H\left(T^+\right) < 0$$

$$\boxed{\Delta G = \Delta H \underbrace{- T_m \Delta S}}$$

$\qquad < 0 \qquad > 0$

$T\Delta S$ must have smaller
magnitude than ΔH
for solidification;
this defines solidification temp.

5

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Note the relatively large solid solubility of As in Si

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....then decreases
on approaching T_{melt}

Arsenic solubility
in Si
increases with T

Whereas
this field
is As + SiAs$_2$

6

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1-dimensional defects: We saw soluble impurities in Si.

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1.0

T/T_m

B   As
P

From
Phase
diagram

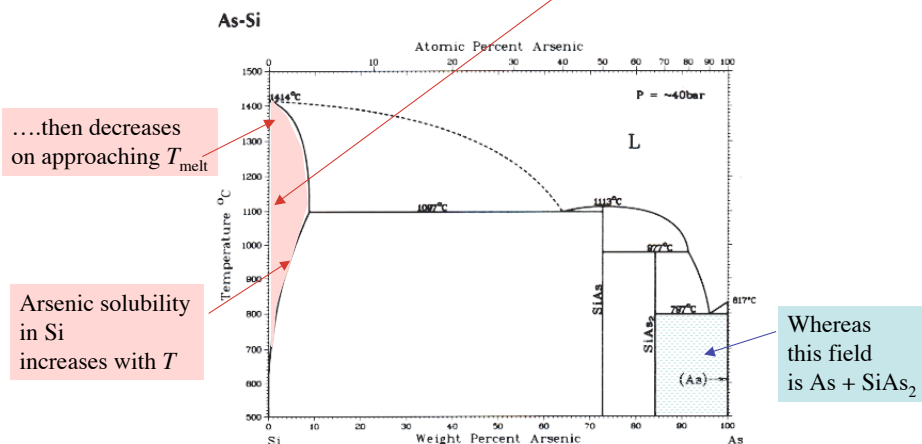10^{20} 10^{21}
Impurity content (cm^{-3})

S^{mix}

Si   Impurity

$-TS^{mix}$

Si   Impurity

7
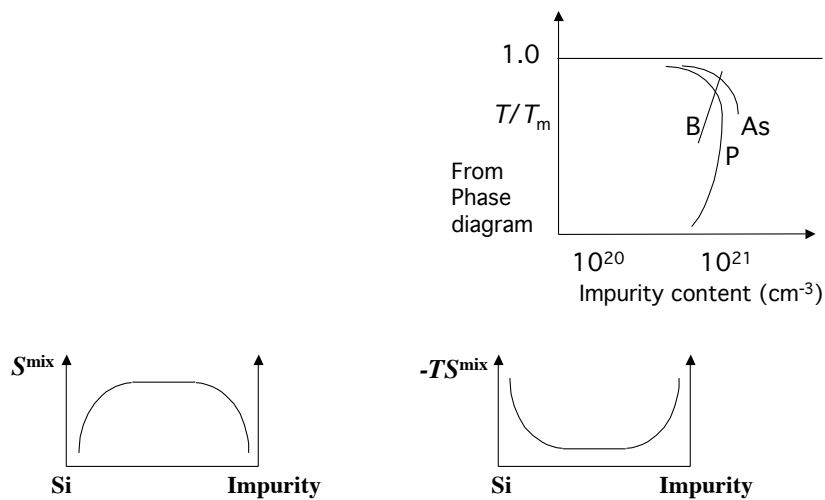
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1-dimensional defects: More point defects

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Vacancy

Interstitial
impurity

V-I pair =
Frankel defect

Self
interstitial

Substitutional
impurity

Strain field of vacancy...   interstitial

Strain and surface energy
  can be reduced
    by agglomeration:
Vacancy => void,
Interstitial => precipitate

...when concentration > equilibrium

8
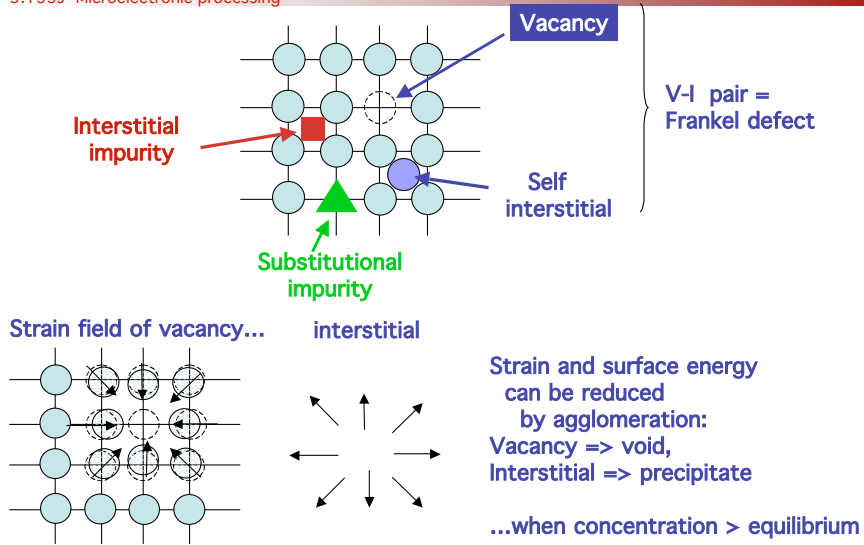
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Bonding-antibonding orbital energy separation

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Gp IV atom | Semicon crystal | Gp IV atom

E

s-p^3 anti-bonding

s^2p^2 ——   —— s^2p^2

Conduction band

s-p^3 bonding

bonding/antibonding => energy gaps in semiconductors, insulators

Valence band

Free Electrons

E_C

E E_G Gap

Intrinsic Carrier Generation

Hole

E_V

Bound Electrons
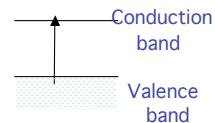
Band Model

Bond Model
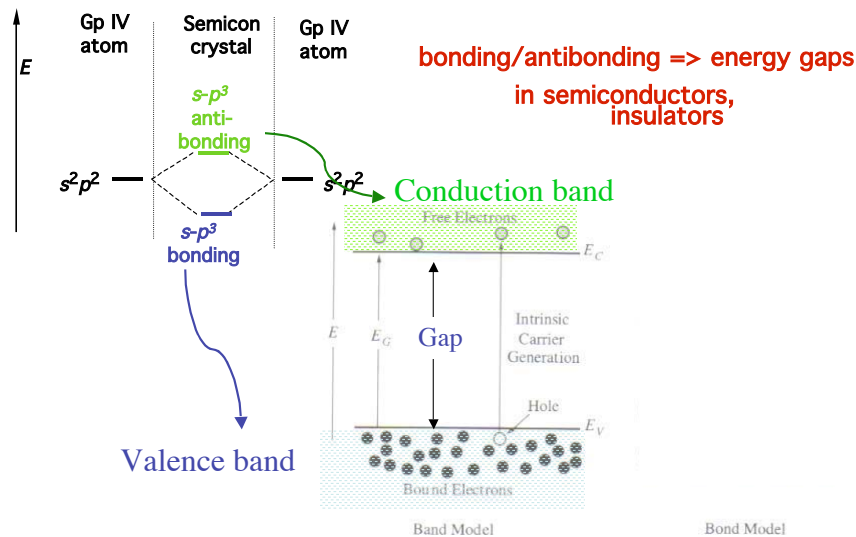
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Vacancy concentration: Vacancy requires breaking 4 bonds

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$$n_{vac} = n_0 \exp\left[-E_g / k_B T\right]$$

E_g = 1.12 eV

Conduction band

Valence band

Empirical:

$$n_{vac} = 5 \times 10^{22} \exp\left[-2.6 \ eV / k_B T\right]$$

$$\ln\left(\frac{n_{vac}}{n_0}\right) = -E_a / k_B T$$

$\ln\left(\frac{n_{vac}}{n_0}\right)$

E_a

Arrhenius plot

$1000 / k_B T$
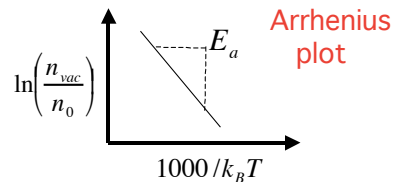
Equilibrium vacancy concentration:

At RT: n_{vac} = 3.4 x 10^{-23}/cm^3 (≈ 300 km between vacancies)

At 1273 K: n_{vac} = 2.6 x 10^{12}/cm^3 (≈ 700 nm between vacancies)

Vacancies abundant at high temperature

10

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Oxygen impurities in Si: Observed to follow Arrhenius

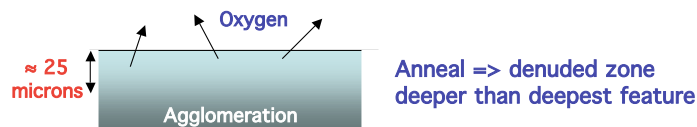6.12J / 3.155J Microelectronic processing

$$C_{oxy} = 2 \times 10^{22} \exp\left[-1.03 eV / k_B T\right]$$

C_{oxy} (ppm)

40 — } Agglomeration =>
      warpage, stress, dislocations

20 — } Optimal

0 — } No agglomeration
    (many isolated O^{2-} ions)

1414 —

High C_{oxy}

T (^{0}C)

1200 — 3 hr anneal
      => 15 ppm
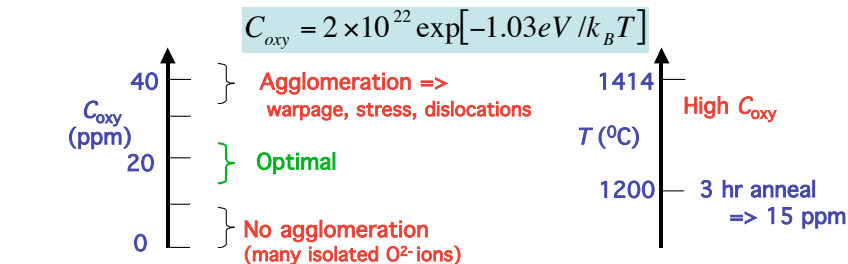
Want about 10 - 30 ppm (7 x 10^{17}/cm^3)... which occurs at $T \approx 1250^0$C

Oxygen

≈ 25 microns

Agglomeration

Anneal => denuded zone
deeper than deepest feature

	Oxygen	E_g	Vacancy	Interstitial
Activation energies (eV):	1.03	1.12	2.6	4.5

11

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Dopants, impurities (substitutional, interstitial)

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At RT number of *intrinsic* carriers:

$n_i = (n_e n_h)^{1/2} = n_0 \exp(-E_g/2k_B T)$ => $n_i = 2 \times 10^{10}$/cm^3

$\underbrace{5 \times 10^{22}}$

So doping at 1 ppm => $10^{-6} = n_{D,A}/(5 \times 10^{22}/\text{cm}^3)$

$n_{D,A} = 5 \times 10^{16}$/cm^3

Very small doping concentration
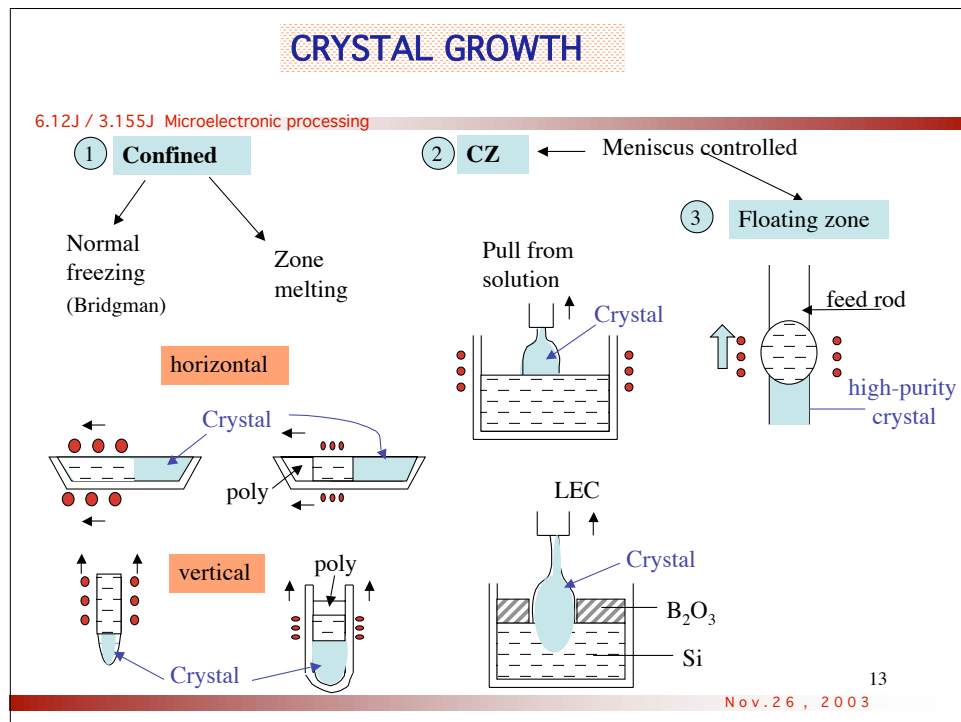   => large increase in carrier concentration

What do dopants do?

$$\sigma = \frac{ne^2\tau}{m*} \qquad J = \sigma E = ne <v>$$

$$\mu = \frac{\langle v \rangle}{E} = \frac{\sigma}{ne} = \frac{e\tau}{m*}$$

12

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CRYSTAL GROWTH

6.12J / 3.155J Microelectronic processing

① **Confined**   ② **CZ** ← Meniscus controlled

③ Floating zone

Normal freezing (Bridgman)   Zone melting

Pull from solution — Crystal

feed rod

high-purity crystal

horizontal

Crystal

poly

LEC — Crystal

B₂O₃

vertical   poly

Crystal   Crystal

Si

13

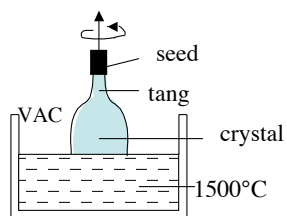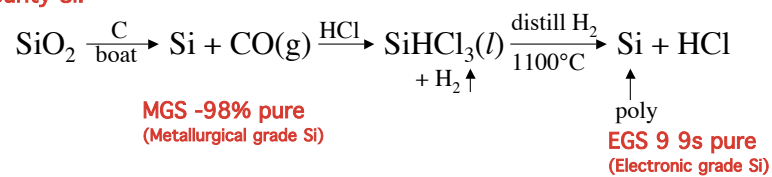## 1) Reactants: first need high-purity Si

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**Making
high-purity Si:**

$$SiO_2 \xrightarrow[\text{boat}]{C} Si + CO(g) \xrightarrow{HCl} SiHCl_3(l) \xrightarrow[1100°C]{\text{distill } H_2} Si + HCl$$

$+ H_2 \uparrow$

**MGS ~98% pure
(Metallurgical grade Si)**

poly

**EGS 9 9s pure
(Electronic grade Si)**

seed

tang

VAC

crystal

1500°C

16

Growth rate $\propto G_s - G_L \equiv \Delta G$

6.12J / 3.155J Microelectronic processing

Crystal

$\Delta G = 0 \Rightarrow$ Equilibrium at $\quad \Delta H = T\Delta S,$

$$\Delta S = \Delta H / T_{eq.}$$

$\Delta G = \Delta H - T\Delta S$

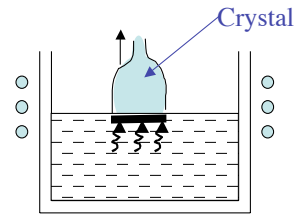$$\Delta G = \Delta H \left[\frac{T_{eq} - T}{T_{eq}} \right]$$

$\underbrace{\Delta H < 0}_{H_s - H_L} \qquad \therefore T_{interface} < T_{eq}$

Must decrease
for
solidification
to occur

larger
(latent) heat
content

17

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---

1) Pulling crystal from melt

6.12J / 3.155J Microelectronic processing

seed

tang

VAC

crystal

z

1500°C

T

Q

At S-L interface:
$$k_S A \frac{\partial T}{\partial z} \bigg)_S = k_L A \frac{\partial T}{\partial z} \bigg)_L + L \frac{\partial m}{\partial t} \qquad \frac{\partial m}{\partial t} = vA\rho_m$$

Thermal
conductivities
$k_s \approx 1.5 \; W/(cm - C)$

0

Heat of fusion Liquid →Solid
$L \approx 340 \;\; cal / mole$
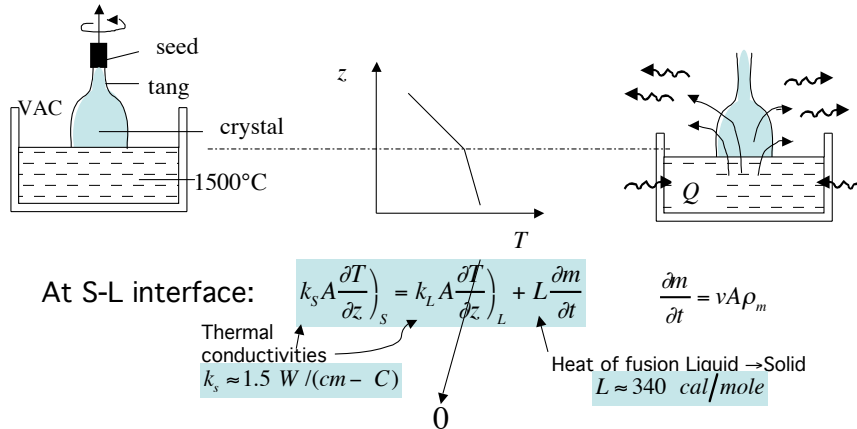
**If growth velocity too large,
solid cannot dissipate heat
(Typical v = 1 mm / min.)**

$$v_{max} = \frac{k_s}{L\rho_m} \frac{\partial T}{\partial z} \bigg]_{solid}$$
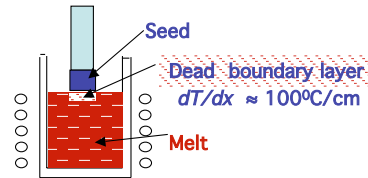
If $\;\; T(z)' \bigg|_S \;\;$ **too large
$\Rightarrow$ thermal stress**

18

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Czochralski growth of single crystals: stress, dislocations

6.12J / 3.155J Microelectronic processing

Seed

Dead   boundary layer
$dT/dx \approx 100^0C/cm$

Melt

For large temperature gradients,
e.g. $dT/dx \approx 100^0C/cm.$, and given $\alpha = 2.6 \times 10^{-6}/^0C$,
then $\Delta l/l = \alpha \Delta T \Rightarrow$ strains of 0.6%,
 which exceeds the yield stress of Si, $\Rightarrow$ dislocations
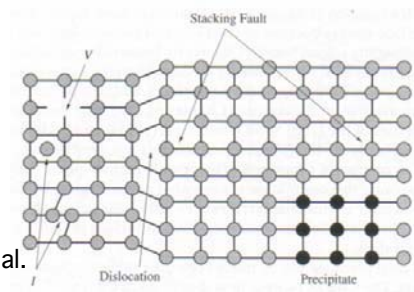
19
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Line defects: dislocations

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Dislocations originate in shear strains,
mostly induced by
thermal gradients
during growth.

Stacking Fault

Dislocation   Precipitate

A couple of dislocations/wafer is typical.
Why so few?
1) "Tang" (neck at beginning of xtl)
allows dislocations to move to surface
2) Large number of atoms are involved in a dislocation,
$\Rightarrow$ high energy, U
Dislocation has low entropy (most atoms are in unique place)
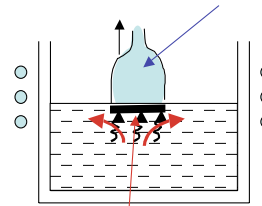
$G = H - TS$ is very positive
large   small

20
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Czochralski growth of single crystals: impurities

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**Boundary layer keeps impurities
away from solid-liquid interface**

Impurities

must diffuse across

still boundary layer.

B field suppresses convection of ions (reactive)
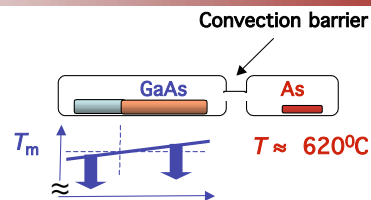deflecting them from interface

21

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Bridgman growth of GaAs
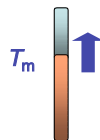
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Convection barrier

GaAs in quartz ampule:

GaAs   As

T_m $T \approx 620^0C$

dT/dx < 10⁰C/cm =>
dislocation density < $10^3/cm^2$
but melt-ampule contact =>
lower resistivity.

Vertical Bridgman

To correct contact problems,
use *vertical* Bridgman

**GaAs in
BN ampule:** T_m $v \approx$ mm/hr.

$\rho \approx$ 10 MΩcm

2 - 5 x 10^3 dislocations /cm²

22

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Liquid encapsulated CZ or Bridgman growth

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...because

	Ga	As
vapor pressure at T_m = 1238⁰C:	0.001	10 atmospheres.
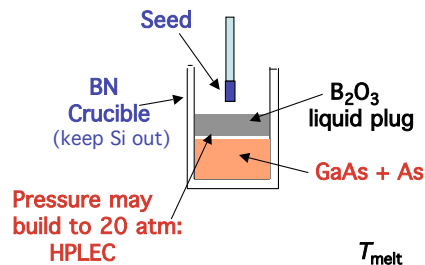
B_2O_3 minimizes loss of As;
$v \approx 1$ cm/hr.

Seed

BN
Crucible
(keep Si out)

B_2O_3
liquid plug

GaAs + As

$\rho \approx 100$ MΩcm
10^4 defects/cm^2
100+ dislocations /cm^2

Pressure may
build to 20 atm:
HPLEC

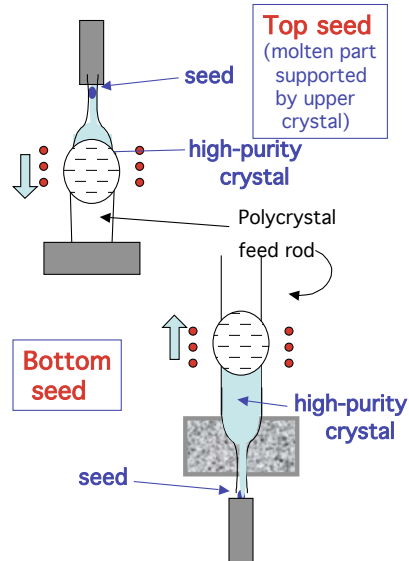|	T_{melt}	κ	Crit. resolved shear stress
Si	1414	0.21	1.85
Ge	960	0.17	0.70
GaAs	1238	0.07	0.4

GaAs cannot dissipate heat;
grow slowly

GaAs cannot take stress;
grow slowly

23

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Floating zone   For very high purity Si (not used for GaAs)

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seed

Top seed
(molten part
supported
by upper
crystal)

high-purity
crystal

Polycrystal
feed rod

Bottom
seed

high-purity
crystal

seed

24

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CRYSTAL GROWTH reviewed

6.12J / 3.155J Microelectronic processing

(1) **Confined**

(2) **CZ** ← Meniscus controlled

Largest crystals:
300 mm diameter

(3) Floating zone

Normal freezing (Bridgman)

Zone melting

Pull from solution

Crystal

feed rod

horizontal

Crystal

poly

LEC

Crystal

vertical

poly

Crystal

Crystal

Crystal

B₂O₃

Si

highest-purity crystal; Larger radial variations than CZ

25

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Introduction of dopants via melt

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Different dopants have different solubilities in solid
Define *segregation coefficient, k,*
as ratio of dopant concentrations solid/melt: $k = \dfrac{C_s}{C_l}$

	Al	As	B	O	P	Sb
$k =$	0.002	0.3	0.8	0.25	0.35	0.023

k < 1 implies only a small fraction of dopant moves into solid;
concentration builds up in melt
as S/L interface advances…
This in turn drives up amount transferred to solid…

We can calculate the dopant/impurity concentration
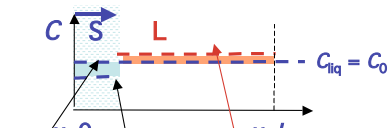as a function of position in crystal
(let *x* = fraction solidified)…

26

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Dopant or impurity concentration vs. Position
assumptions: no solid state diffusion, perfect liquid mixing

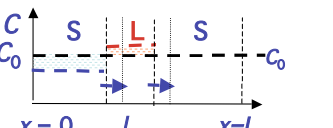6.12J / 3.155J Microelectronic processing

CZ growth

C S L

$C_{liq} = C_0$

$x=0$ $x=L$

$$\left[C_L(x) - C_S(x)\right]dx = dC_L(x)\left[L - x\right]$$

$$C_L(x)\left[1 - k\right]dx = dC_L(x)\left[L - x\right]$$

$$\left[1 - k\right]\int_0^x \frac{dx}{L - x} = \int_{C_0}^{C_L(x)} \frac{dC_L(x)}{C_L(x)}$$

$$C_L(x) = C_0\left[\frac{L}{L - x}\right]^{1-k}$$

$$C_S(x) = kC_0\left[\frac{L}{L - x}\right]^{1-k}$$

Float zone growth

C
C_0 C_0
S   L   S

$x = 0$ l_0 $x=L$

$$\left[C_0 - kC_L(x)\right]dx = dC_L(x)l_0$$

$$\int_0^x \frac{dx}{l_0} = \int_{C_0}^{C_L(x)} \frac{dC_L(x)}{C_0 - kC_L(x)}$$

$$\frac{x}{l_0} = -\frac{1}{k}\left[C_0 - kC_L(x)\right]_{C_0}^{C_L(x)}$$

$$-\frac{kx}{l_0} = \ln\left[\frac{C_0 - kC_L(x)}{C_0(1 - k)}\right]_{C_0}^{C_L(x)}$$

$$C_S(x) = C_0\left[1 - (1 - k)\exp(-kx/l_0)\right]$$

27

Dopant/inpurity concentration vs. Position
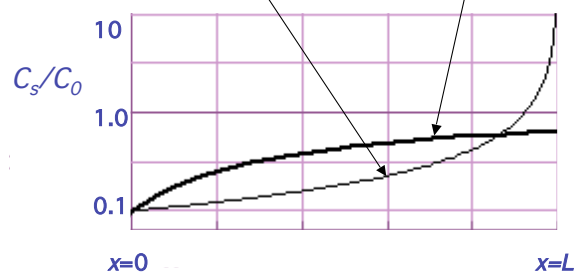
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$$C_S(x) = kC_0\left[\frac{L}{L - x}\right]^{1-k}$$

$$C_S(x) = C_0\left[1 - (1 - k)\exp(-kx/l_0)\right]$$

CZ growth
$k = 0.1, L = 1$

Float zone growth
$k = 0.1, l = 0.1L$

C_S/C_0

10

1.0

0.1

$x=0$ $x=L$

28