

# Bulk crystal growth

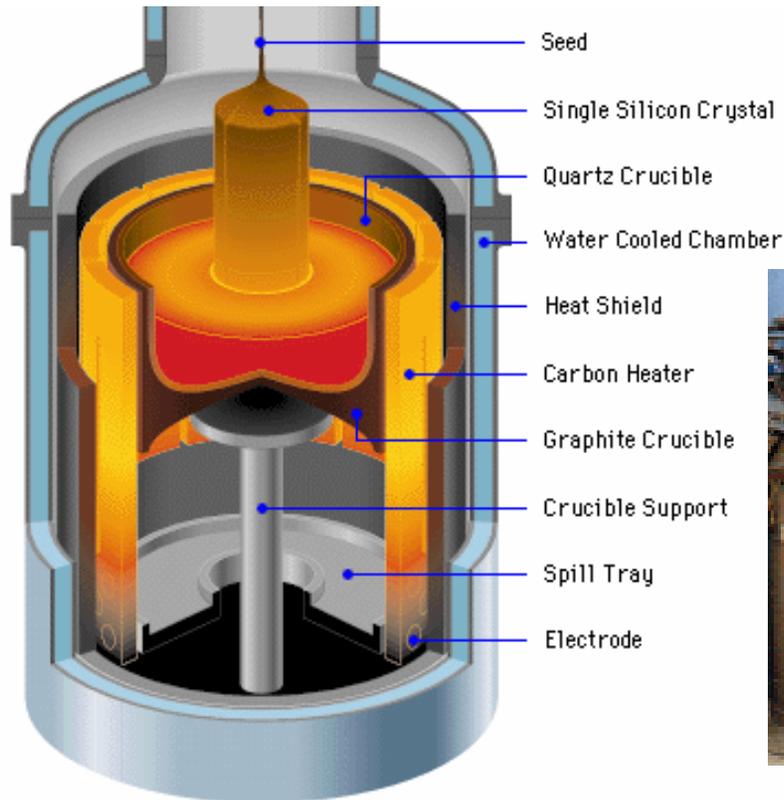
- **melting points**
  - silicon: 1420° C
  - GaAs: 1238° C
  - quartz: 1732° C
- **starting material: metallurgical-grade silicon**
  - by mixing with carbon, SiO<sub>2</sub> reduced in arc furnace
    - T > 1780° C:  
 $\text{SiC} + \text{SiO}_2 \rightarrow \text{Si} + \text{SiO} + \text{CO}$
  - **common impurities**
    - Al: 1600 ppm (1 ppm = 5 x 10<sup>16</sup> cm<sup>-3</sup>)
    - B: 40 ppm
    - Fe: 2000 ppm
    - P: 30 ppm
  - used mostly as an additive in steel

# Preparation of electronic-grade silicon

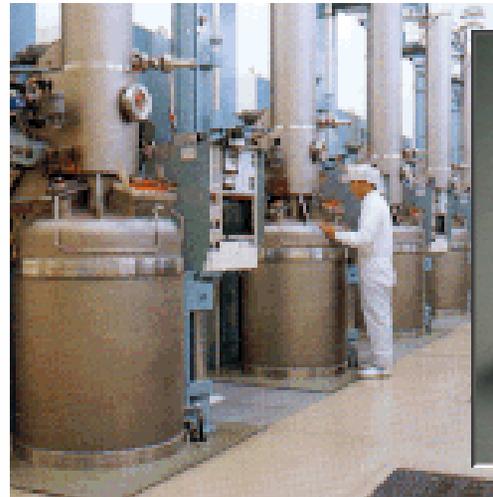
- **gas phase purification used to produce high purity silicon**
  - ~ 600°C
  - **crud + Si + HCl →**
    - SiCl<sub>4</sub> (silicon tetrachloride)
    - SiCl<sub>3</sub>H (trichlorosilane)
    - SiCl<sub>2</sub>H<sub>2</sub> (dichlorosilane)
    - chlorides of impurities
  - trichlorosilane (liquid at rm temp), further purification via fractional distillation
- **now reverse reaction**
  - **2SiHCl<sub>3</sub> + 2H<sub>2</sub> (heat) → 2Si + 6HCl**
  - **after purification get**
    - Al: below detection
    - B: < 1 ppb (1 ppb = 5 x 10<sup>13</sup> cm<sup>-3</sup>)
    - Fe: 4 ppm
    - P: < 2 ppb
    - Sb: 1 ppb
    - Au: 0.1 ppb

# Czochralski crystal growth

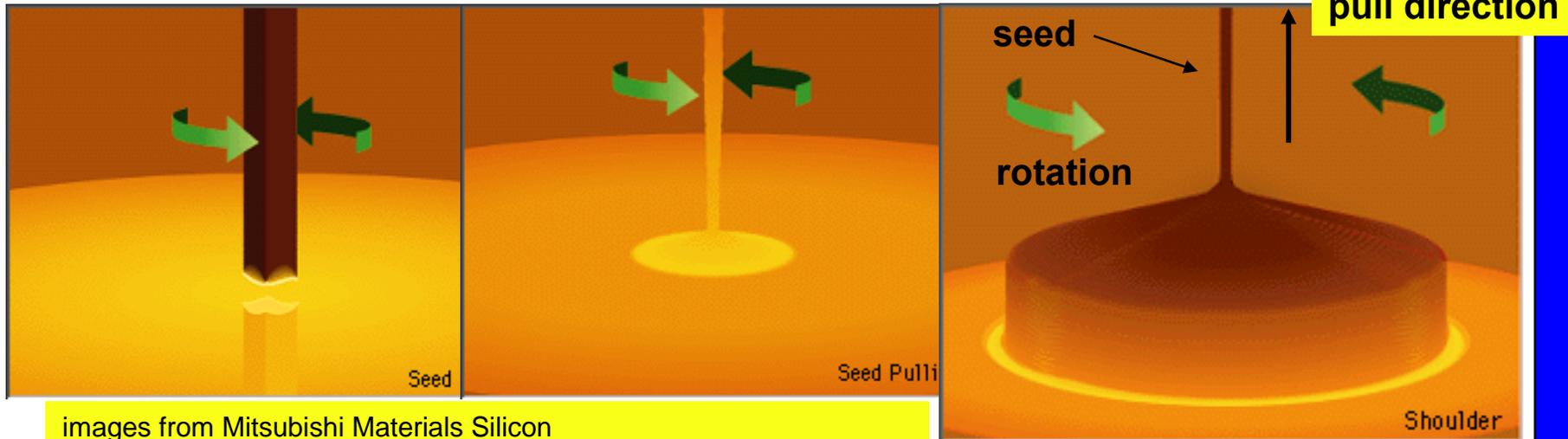
- silicon expands upon freezing (just like water)
  - if solidify in a container will induce large stress
- CZ growth is “container-less”



images from Mitsubishi Materials  
Silicon  
<http://www.egg.or.jp/MSIL/english/msilhist0-e.html>



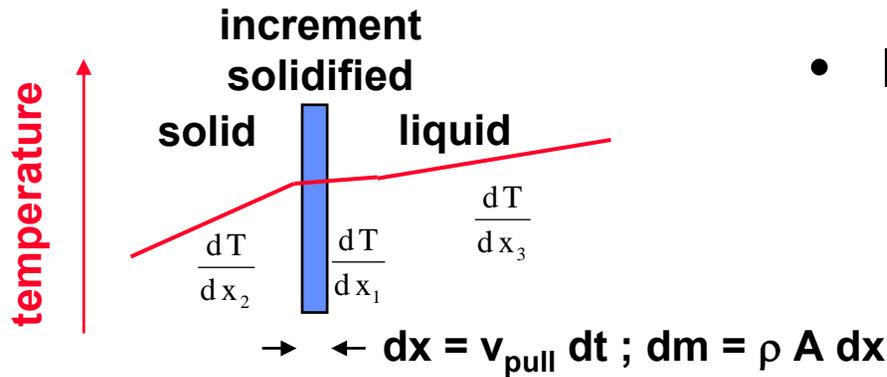
# Diameter control during CZ growth



images from Mitsubishi Materials Silicon  
<http://www.egg.or.jp/MSIL/english/msilhist0-e.html>

- **critical factor is heat flow from liquid to solid**
  - interface between liquid and solid is an isotherm
    - temperature fluctuations cause problems!
  - already grown crystal is the heat sink
    - balance latent heat of fusion, solidification rate, pull rate, diameter, temperature gradient, heat flow
    - diameter **inversely proportional** to pull rate (typically ~ mm/min)

# Diameter control during CZ growth



- latent heat of fusion
    - heat flux (power) released is
- $$L \cdot \frac{dm}{dt} = L \cdot \frac{\rho A dx}{dt} = (L \rho A) v_{\text{pull}}$$

- critical factor is heat flow from liquid to solid

- heat flux (power) balance

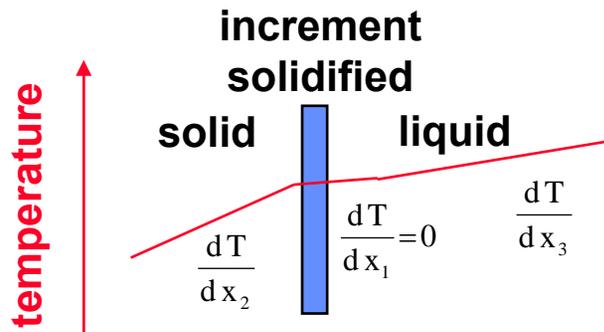
heat released as solidifies + thermal diffusion in liquid from hot liquid towards solidification interface = thermal diffusion in solid from solidification interface towards cooler sides/end of boule

$$(L \rho A) \cdot v_{\text{pull}} + \kappa_{\text{liquid}} \cdot A \cdot \frac{dT}{dx_1} = \kappa_{\text{solid}} \cdot A \cdot \frac{dT}{dx_2}$$

- interface between liquid and solid should be an isotherm

- temperature fluctuations cause problems!  $\frac{dT}{dx_1} = 0$

# Diameter control during CZ growth



- heat flow balance becomes

$$(L \rho A) \cdot v_{pull} = \underbrace{\kappa_{solid} \cdot A \cdot \frac{dT}{dx_2}}_{\text{thermal current}}$$

– or

$$\frac{dT}{dx_2} = \frac{L \rho}{\kappa_{solid}} \cdot v_{pull}$$

- so critical factor is relation between temperature gradient in boule and boules size

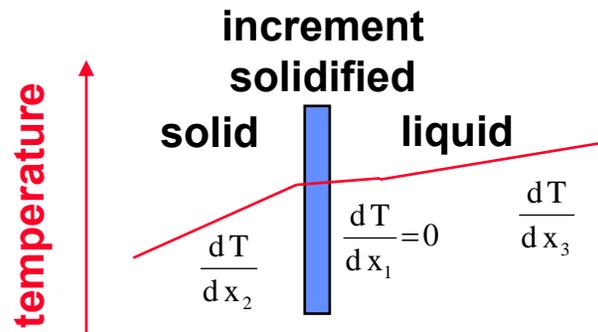
- thermal current proportional to cross sectional area  $A$  and  $v_{pull}$
- if the only heat sink were at the end of the boules:
  - thermal resistance inversely proportional to  $A$ , directly proportional to length of boules  $l$
- temperature change (“voltage”) =  $I_{thermal} R_{thermal}$

$$\Delta T = [(L \rho A) \cdot v_{pull}] \cdot \left[ \frac{l}{\kappa_{solid} \cdot A} \right] = l \cdot \frac{L \rho}{\kappa_{solid}} \cdot v_{pull} \rightarrow \frac{dT}{dx} \approx \frac{\Delta T}{l} = \frac{L \rho}{\kappa_{solid}} \cdot v_{pull}$$

➔ net effect: just what we got above!

➔  $dT/dx$  independent of diameter ➔ diameter doesn't appear!!!

# Diameter control during CZ growth



$$v_{\text{pull}} = \frac{\kappa_{\text{solid}}}{L\rho} \cdot \frac{dT}{dx_2}$$

- but most of the heat is lost via radiation from the **SIDES** of the boules!
  - thermal current still proportional to cross sectional area  $A \propto (\text{diameter})^2$  and  $v_{\text{pull}}$
  - if the heat sink is from sides of boules:
    - thermal resistance inversely proportional to perimeter  $\propto$  diameter,
    - temperature change (“voltage”) =  $I_{\text{thermal}} R_{\text{thermal}}$

$$\Delta T = \left[ \text{constant} \cdot (\text{diam})^2 \cdot v_{\text{pull}} \right] \cdot \left[ \frac{\text{constant}}{\text{diam}} \right] \propto \text{diam} \cdot v_{\text{pull}} \quad \rightarrow \quad \text{diam} \propto (v_{\text{pull}})^{-1} \cdot \Delta T$$

➡ net effect: diameter is inversely proportional to pull rate

# Impurities in Czochralski Grown Silicon

- **choice of crucible material is crucial:**
  - must be stable at high temperatures (~1500° C)
  - carbon: saturates solution and causes poly growth
  - refractories: too much metal in materials
  - quartz: in exclusive use for silicon growth
- **dissolution of quartz crucibles into melt is major concern:**
  - function of relative velocity between melt & crucible
  - almost all oxygen present in silicon melt is due to the dissolution of the SiO<sub>2</sub> crucible
  - most of this oxygen evaporates in the form of SiO

# Doping and segregation effects during crystal growth

- when two dissimilar materials / phases are in contact, the concentration of an impurity across the interface is **NOT NECESSARILY CONTINUOUS**
  - segregation (distribution) coefficient

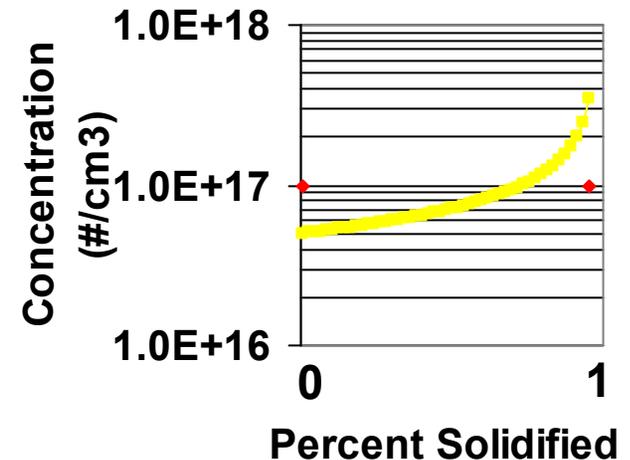
$$k = \frac{C_s}{C_L}$$

element	Al	As	B	O	P	Sb
$C_{\text{solid}}/C_{\text{liquid}}$	0.002	0.3	0.8	1.25	0.35	0.023

- when a volume of liquid freezes, if  $k < 1$ , what is concentration in solid?
  - must be less than in liquid
  - what happens to extra impurities?
    - rejected into melt  $\rightarrow$  increased [impurity] in melt
- if  $C_0$  is initial melt concentration, and  $X$  is fraction solidified

$$C_S = k \cdot C_0 \cdot (1 - X)^{k-1}$$

$k = 0.5, C_{\text{liquid}} = 1e17$

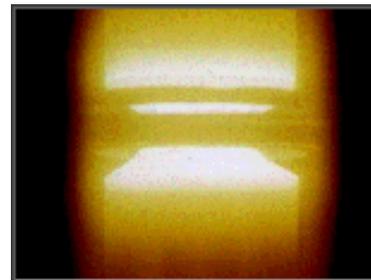
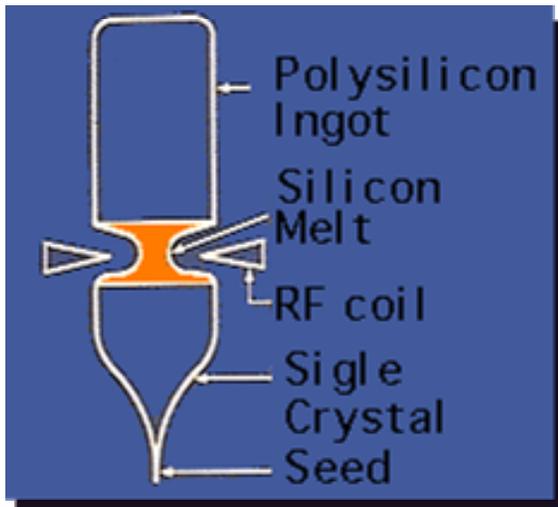


# Doping and segregation effects during crystal growth

- segregation effects can be used intentionally to purify semiconductor material
  - zone refining consists of repeated passes through the solid by a liquid zone

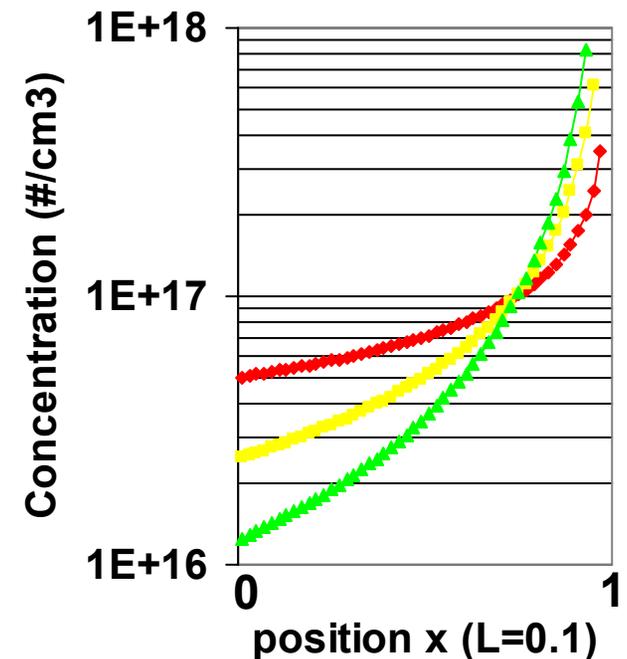
$$C_{n+1}(x) = C_n(x) \cdot [1 - (1-k) \cdot e^{-k \cdot x/L}]$$

- float zone silicon used for high resistivity



images from Mitsubishi Materials Silicon  
<http://www.egg.or.jp/MSIL/english/msilhist0-e.html>

Zone Refining  $k = 0.5$



# Oxygen in CZ Silicon

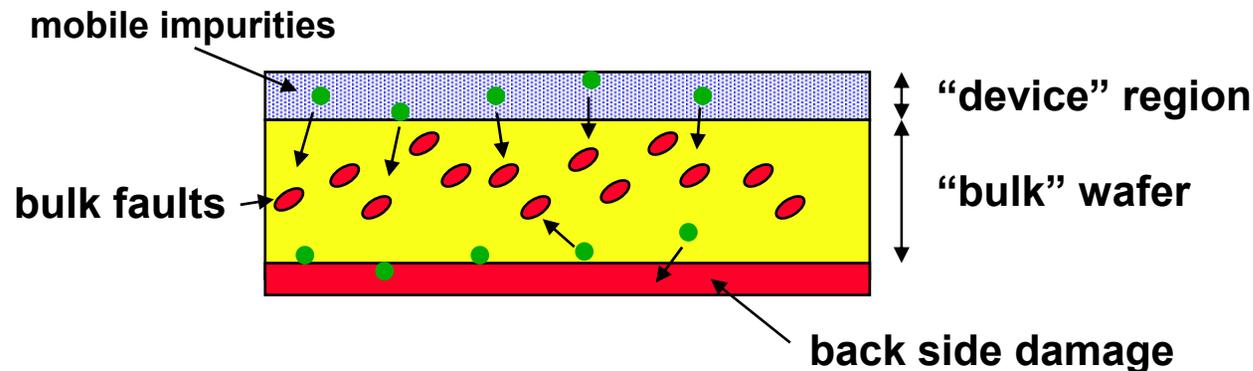
- **concentrations typically in  $10^{16}$  -  $10^{18}$  cm<sup>-3</sup> range**
  - segregation coefficient  $k \sim 1.25$ 
    - more in solid than liquid
  - contact area between crucible and melt decreases as growth proceeds
  - oxygen content decreases from seed to tang end
- **effects of oxygen in silicon**
  - ~ 95% interstitial; increases yield strength of silicon via "solution hardening" effect
  - as-grown crystal is usually supersaturated (occurs above about  $6 \times 10^{17}$ )

# Oxygen complexes in silicon

- usually donor-like
- two classes of complexes:
  - "old thermal donors"
    - very small silicon-oxygen atom clusters
    - very rapid formation rates in 400-500° C range ( $\geq 10^{10}/\text{cm}^3\text{sec}$ )
  - "new thermal donors"
    - slow formation rate above 500° C
    - slow dissolution rate at high temperature
      - $\sim 10^{13} \text{ cm}^{-3}$  @ 2 hours, 900° C
      - $\sim 10^{11} \text{ cm}^{-3}$  @ 2 hours, 1150° C
    - donor behavior possibly due to surface states of large  $\text{SiO}_x$  complexes

# Gettering in Silicon Wafers

- devices fabricated only in the top five or ten microns of the wafer: use gettering to provide a sink for unwanted defects in the bulk of the wafer
  - gettering sites provide sinks for impurities generated during the processing



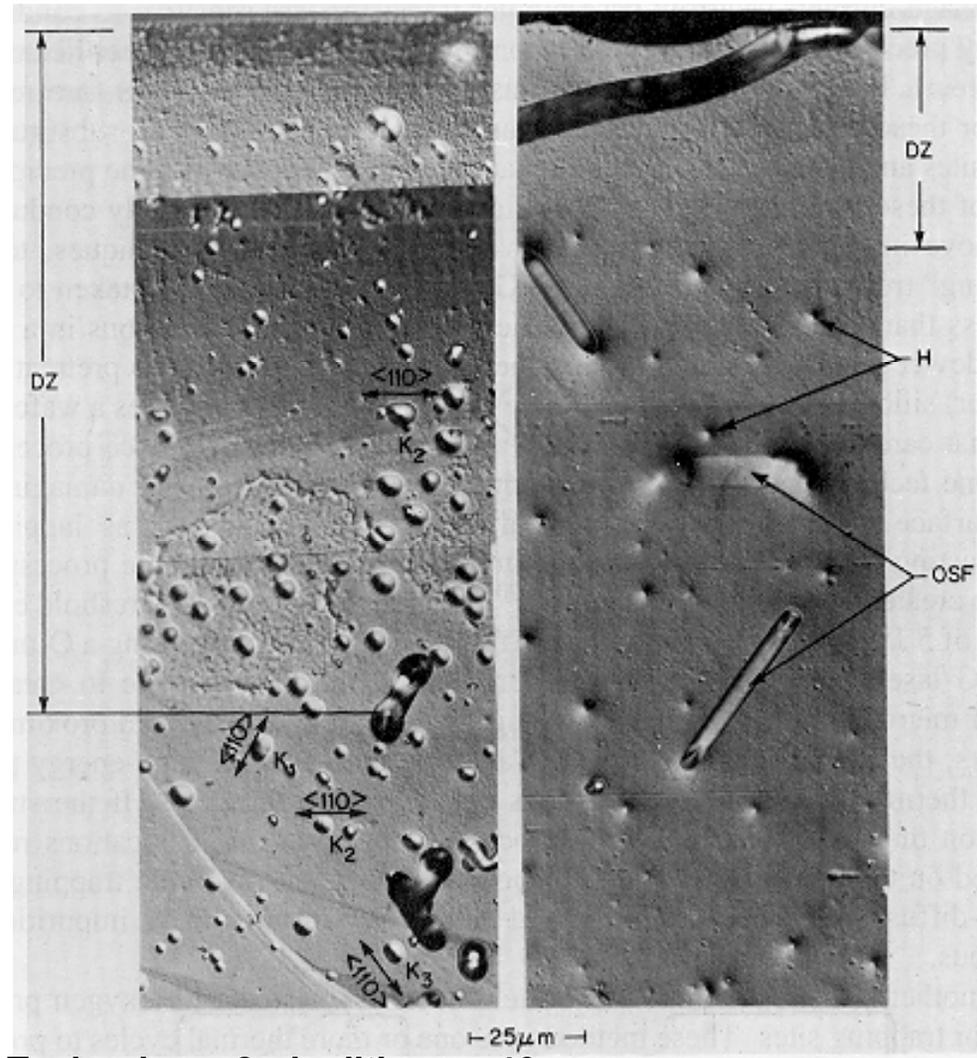
- backside damage: (pre-gettering)
  - mechanical damage produces high strain regions
  - impurities nucleate on dislocations; if wafer stresses are kept small during subsequent processing dislocations will remain localized on back

# Intrinsic Gettering and Oxygen Precipitates

- **wafer starting material:**
  - initial oxygen content between  $\sim 3.5$  and  $\sim 8 \times 10^{17} \text{ cm}^{-3}$
- **denuded zone formation:**
  - high temperature step ( $1050^\circ \text{ C}$ ) reduces interstitial oxygen content via diffusion of O to surface
  - formation of internal gettering sites:
    - low temp step ( $500\text{-}600^\circ \text{ C}$ ) creates large reserve of small, stable oxygen precipitates
    - higher temperature step ( $700\text{-}900^\circ \text{ C}$ ) causes growth of larger  $\text{SiO}_x$  complexes
    - subsequent thermal processing creates dislocation loops associated with  $\text{SiO}_x$  complexes
  - actual starting material oxygen concentration and process determined by trial device fab and performance evaluation.

# Denuded zone

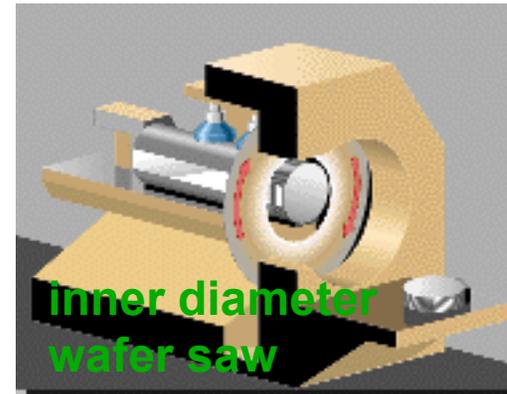
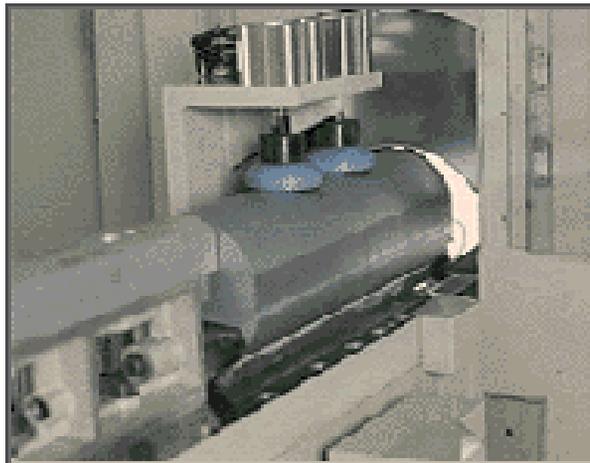
- preferential (decorating) etch used to reveal stacking faults and precipitates
  - OSF: oxidation induced stacking faults



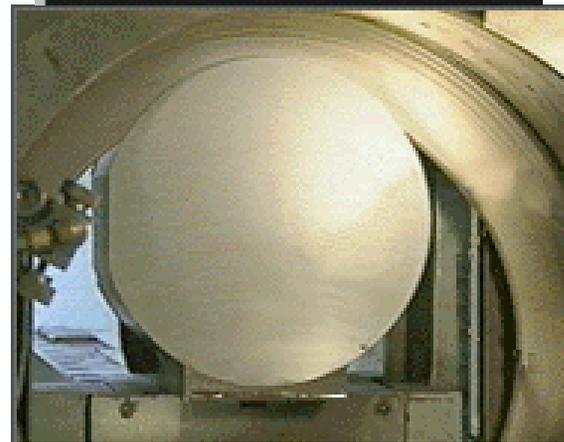
from: Sze, VLSI Technology, 2nd edition, p. 46.

# Wafer preparation

- boule forming, orientation measurement
  - old standard: “flat” perpendicular to  $\langle 110 \rangle$  direction;
  - on large diameter “notch” used instead



- wafer slicing
  - $\langle 100 \rangle$  typically within  $\pm 0.5^\circ$
  - $\langle 111 \rangle$ ,  $2^\circ - 5^\circ$  off axis



images from Mitsubishi Materials Silicon  
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# Wafer prep (cont.)

- **lapping**
  - grind both sides, flatness  $\sim 2\text{-}3\ \mu\text{m}$ 
    - $\sim 20\ \mu\text{m}$  per side removed
- **edge profiling**
- **etching**
  - chemical etch to remove surface damaged layer
    - $\sim 20\ \mu\text{m}$  per side removed
- **polishing**
  - chemi-mechanical polish,  $\text{SiO}_2$  / NaOH slurry
    - $\sim 25\ \mu\text{m}$  per polished side removed
  - gives wafers a “mirror” finish
- **cleaning and inspection**

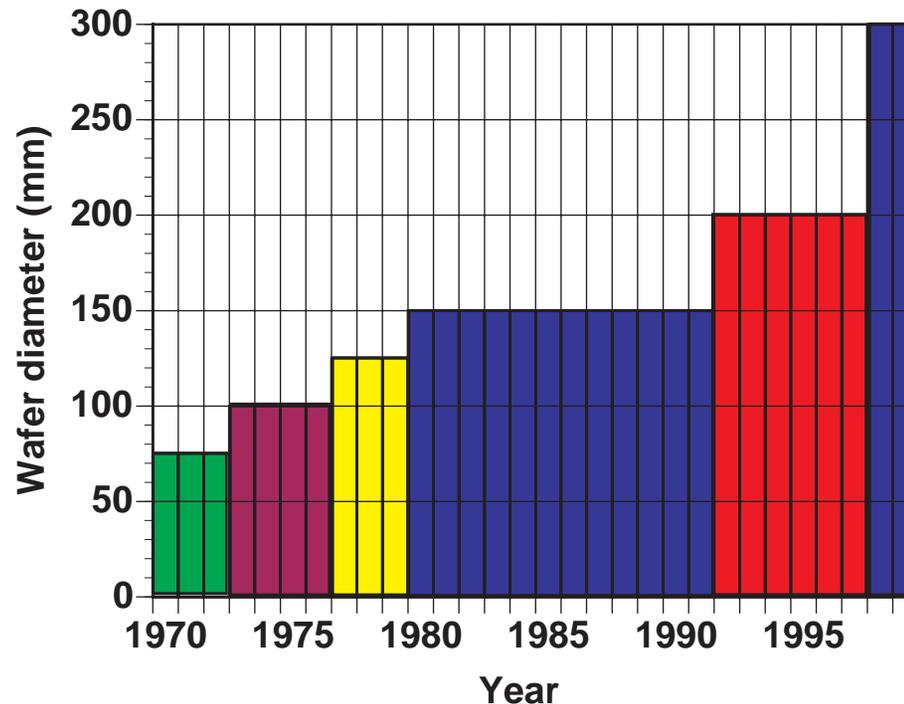
# Wafer specifications

wafer diam.	thickness	thickness variation	bow	warp
150 mm ± 0.5mm	675 $\mu$ m ± 25 $\mu$ m	50 $\mu$ m	60 $\mu$ m	
200 mm ±				
300 mm ± 0.2mm	775 $\mu$ m ± 25 $\mu$ m	= 10 $\mu$ m		= 100 $\mu$ m

- **warp: distance between highest and lowest points relative to reference plane**
- **bow: concave or convex deformation**

# Wafer diameter trends

- desire is to keep number of chips (die) per wafer high, even as die size increases



- challenge: thermal nonuniformities, convection currents become more significant as diameter grows



# Silicon wafer production

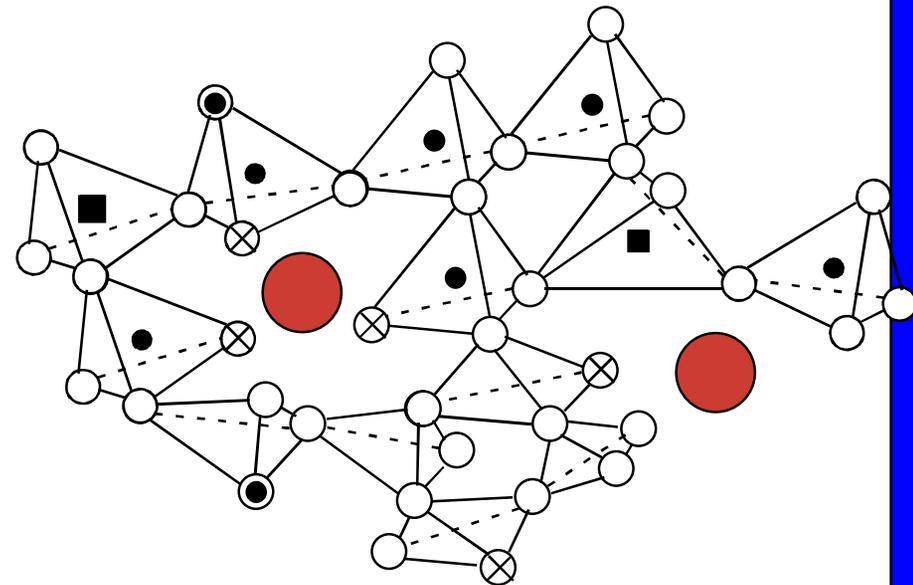
- **1999: 4.263 billion square inches, \$5.883 billion**
  - \$1.38 per square inch, \$0.21 per square cm
  - 100mm, 150mm: 2.808 billion square inches (65.9% of total)
  - 200mm: 1.441 billion square inches (33.8%)
  - 300mm: 0.014 billion square inches of silicon (0.3%)
- **2000, expected: 4.692 billion square inches, \$6.475 billion**
- **2001, expected: 5.204 billion square inches**
- **2003, expected:**
  - 200mm: 2.892 billion square inches
  - 300mm: 0.112 billion square inches
- **from EE Times, “Advanced silicon substrates prices rise as wafer glut eases” by J.Robert Lineback [Semiconductor Business News](#) (01/12/00, 2:04 p.m. EST)**

# Volume Silicon processing costs

- 2001 processing cost date
  - reference: ICKnowledge, [http://www.icknowledge.com/economics/wafer\\_costs.html](http://www.icknowledge.com/economics/wafer_costs.html)
- advanced CMOS process, ~0.13 micron, 300mm wafers, ~25 mask levels:
  - about \$5 per cm<sup>2</sup>
  - reference: ICKnowledge, <http://www.icknowledge.com>
  - model assumes a 30,000 300mm wafer per month fab running at 90% of capacity
    - that's about 21 million cm<sup>2</sup> / month!
    - about 40 wafer starts per hour
  - 2001 world-wide wafer starts, 8" (200mm) equivalent: ~5 million wafers per month (~1.5billion sq. cm per month)
    - from [http://www.semichips.org/downloads/SICAS\\_Q4\\_01.pdf](http://www.semichips.org/downloads/SICAS_Q4_01.pdf)
- MOSIS (ref <http://www.mosis.org/Orders/Prices/price-list-domestic.htm>)
  - 1.5 micron cmos ~\$200 per square mm, 5 to 20 parts per lot ⇒ cost ~\$4K- \$1K per cm<sup>2</sup>
  - 0.18 micron ~\$1-2K per square mm for 40 parts ⇒ cost > ~\$2.5K per cm<sup>2</sup>

# Silicon Oxides: SiO<sub>2</sub>

- **Uses:**
  - diffusion masks
  - surface passivation
  - gate insulator (MOSFET)
  - isolation, insulation
- **Formation:**
  - grown / “native”
    - thermal: “highest” quality
    - anodization
  - deposited:
    - C V D, evaporate, sputter
- **amorphous silica: material is a GLASS** under “normal” circumstances
  - can also find “crystal quartz” in nature
- **m.p. 1732° C; glass is “unstable” below 1710° C**
  - BUT devitrification rate (i.e. crystallization) below 1000° C negligible



- bridging oxygen
- ⊗ non-bridging oxygen
- silicon
- network modifier
- network former
- ⊙ hydroxyl group