

# 電子材料與元件技術特論

## SPECIAL TOPICS IN ELECTRONIC MATERIALS AND DEVICES

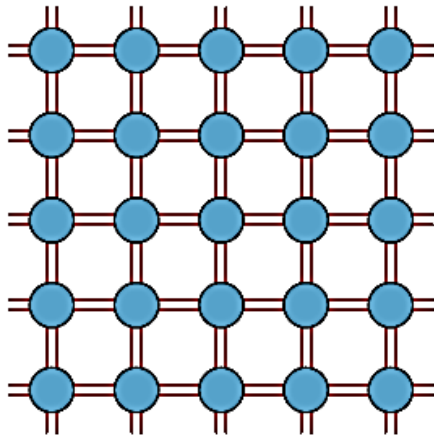
### *Elementary Materials Science Concepts-Part 2*

# Outline

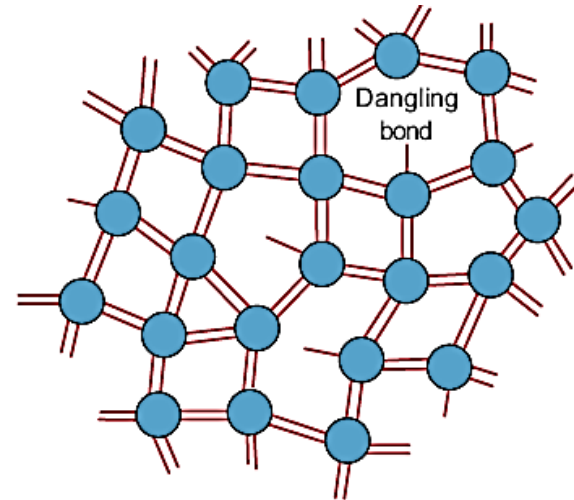
- **Si Crystallinity**
- Thermally Activated Processes
- Crystal Defects
- Crystal Surface and Its Properties

# Si Crystallinity

- Si can be grown as **single crystal** or **amorphous** film. Each line represents an electron in a band. A covalent bond has two lines.



(a) Two dimensional schematic representation of a silicon crystal

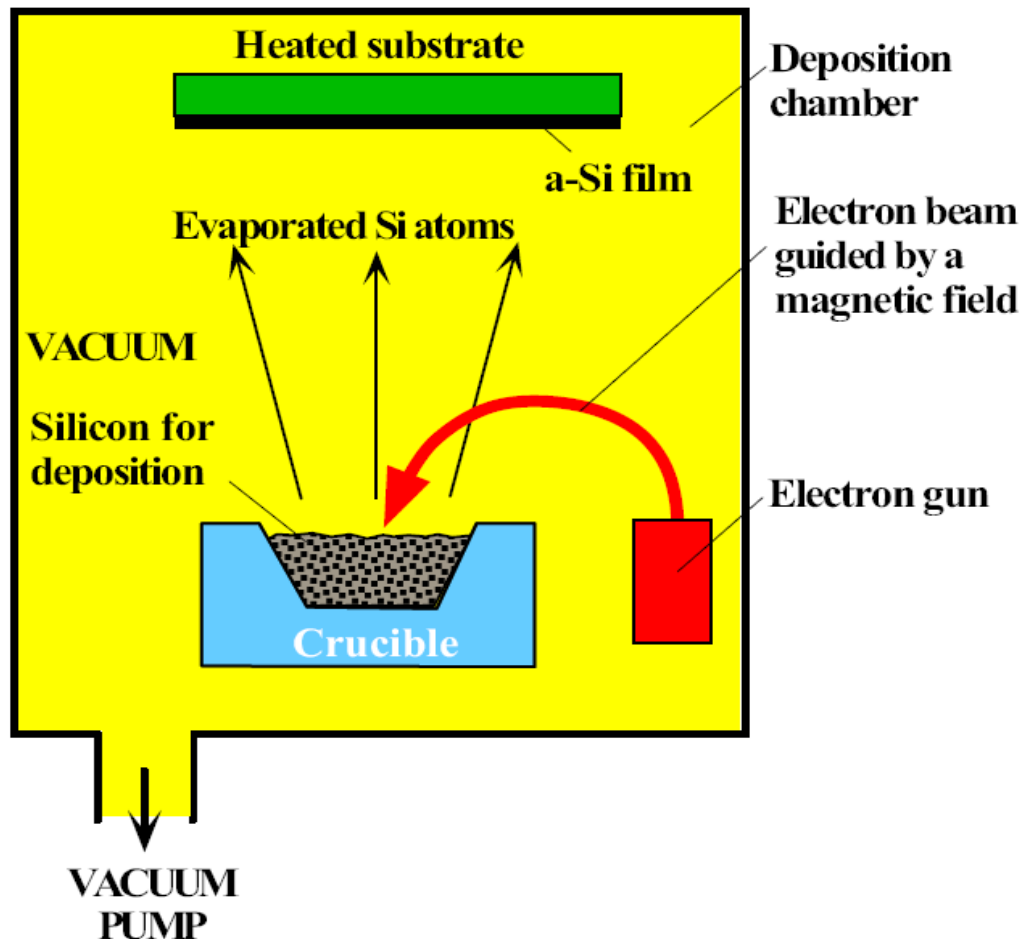


$\alpha$ -Si

(b) Two dimensional schematic representation of the structure of amorphous silicon. The structure has voids and dangling bonds and there is no long range order.

# Physical Vapor Deposition (PVD)

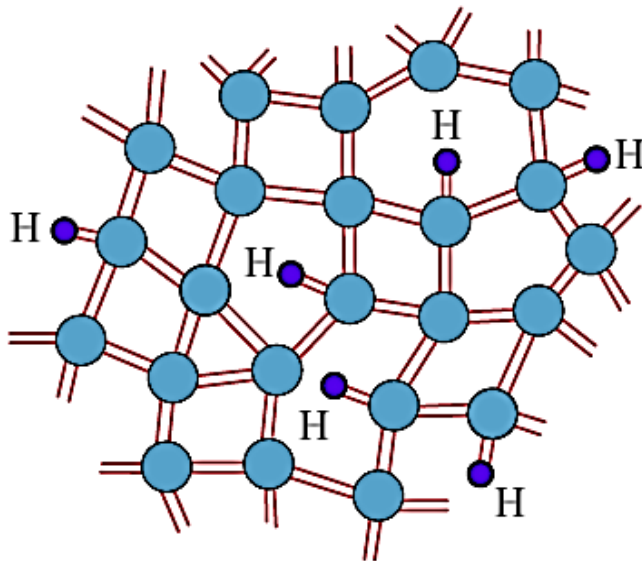
## E-gun Deposition



- Amorphous silicon,  $\alpha$ -Si, can be prepared by an electron beam evaporation of silicon.
- Si has a high melting temperature so that an energetic electron beam is used to melt the crystal in the crucible locally and thereby vaporize Si atoms.
- Si atoms condense on a substrate placed above the crucible to form a film of  $\alpha$ -Si.

# Si Crystallinity

- One way to **reduce the density of dangling bond** is simply to terminate a dangling bond using **hydrogen**.
- Since hydrogen has one e-, it can attach itself to the dangling bond, that is, **passive the dangling bond**.
- Therefore, the **carrier mobility** can be enhanced.



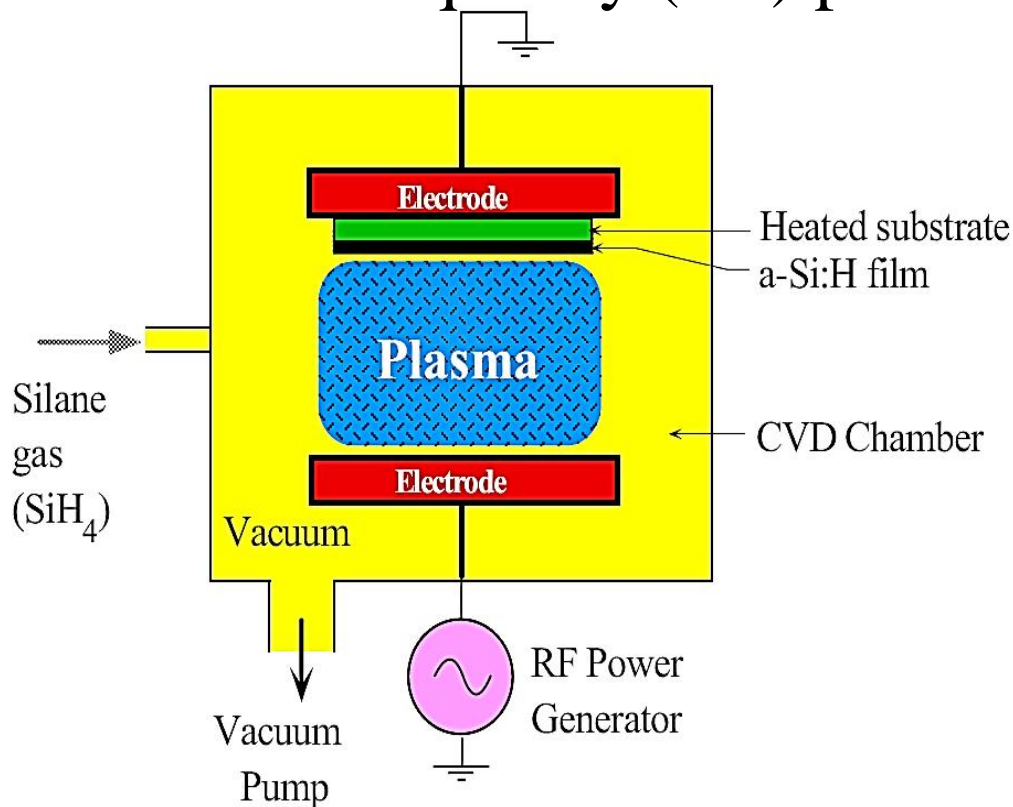
## **$\alpha$ -Si:H**

(c) Two dimensional schematic representation of the structure of hydrogenated amorphous silicon. The number of hydrogen atoms shown is exaggerated.

# Chemical Vapor Deposition (CVD)

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- Hydrogenated amorphous silicon,  $\alpha$ -Si:H, is generally prepared by the decomposition of silane ( $\text{SiH}_4$ ) molecules in a radio frequency (RF) plasma discharge.



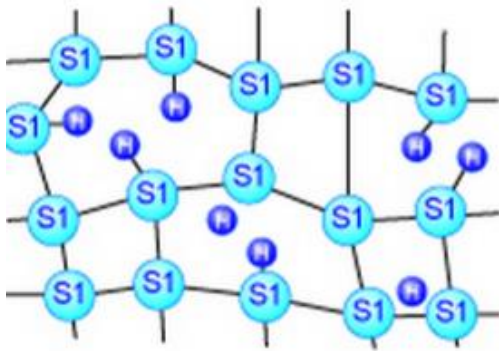
Si and H atoms condense on a substrate to form a film of  $\alpha$ -Si:H.

It's called plasma-enhanced chemical vapor deposition (**PECVD**).

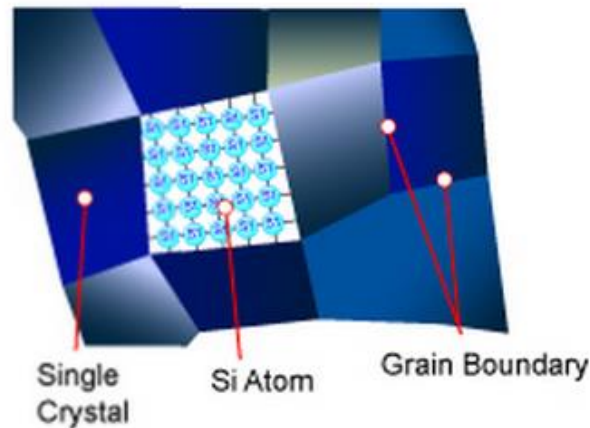
# Crystallinity of Si Channel

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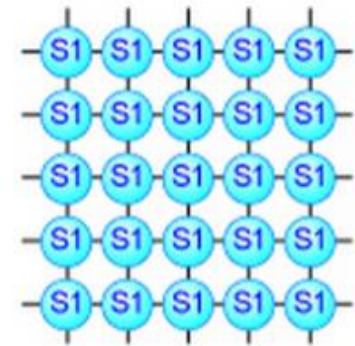
Amorphous Silicon



Poly-silicon



Single Crystal Silicon



**Mobility: Low**



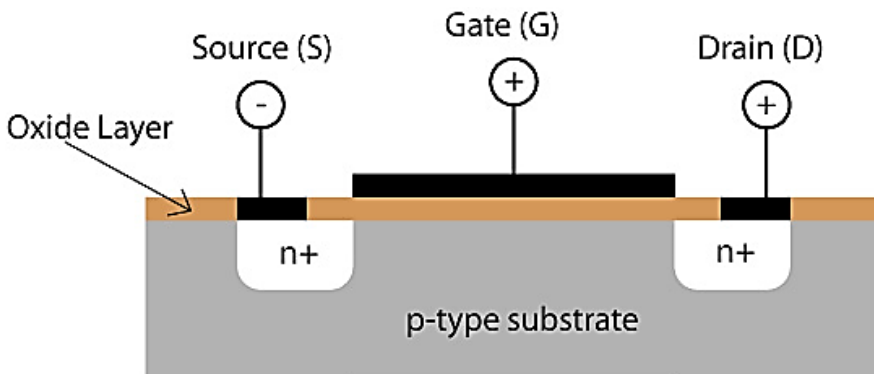
**Mobility: Medium**



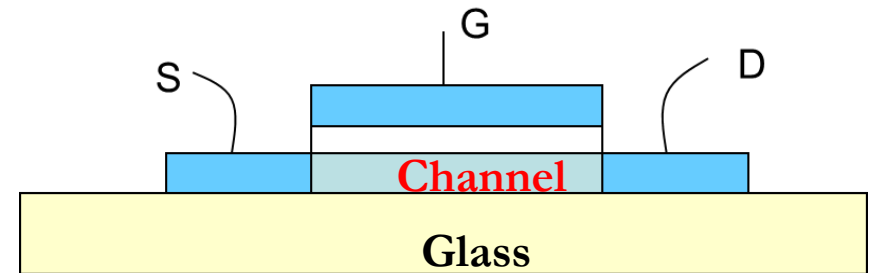
**Mobility: High**

# Crystallinity of Si Channel

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**MOSFET**



**Thin Film Transistor (TFT)**

Device	MOSFET	LTPS TFT	a-Si TFT
Base material	Crystal Si	Polycrystalline -Si	Amorphous -Si
Mobility	650	20-500	0.5
Design rule	0.09 um	2 um	4 um
Frequency	1GHz	10MHz	100KHz
Substrate	Si wafer	Glass	Glass

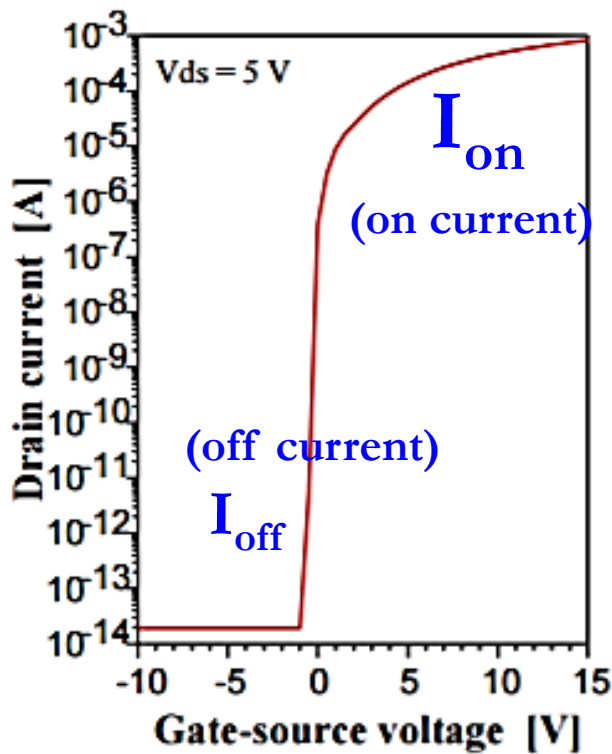
**LTPS : Low Temperature Poly-Si**



# ON/OFF Switching of Transistors

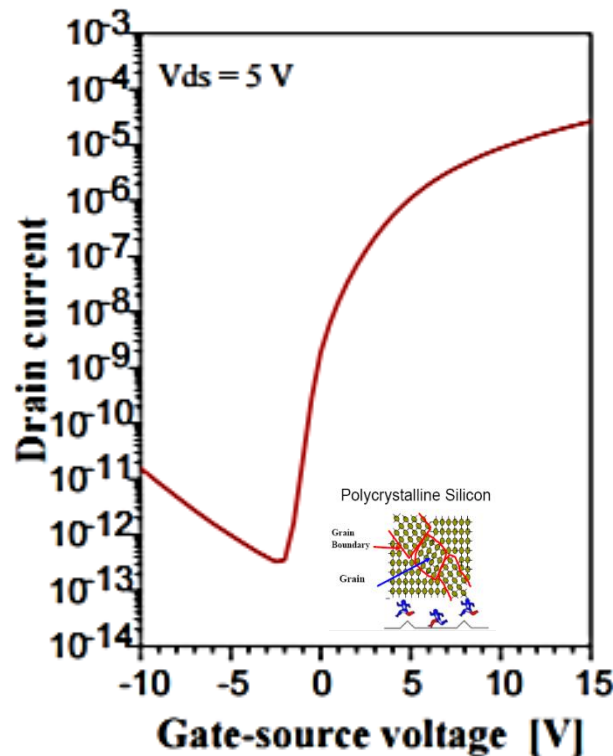
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## Crystalline Si



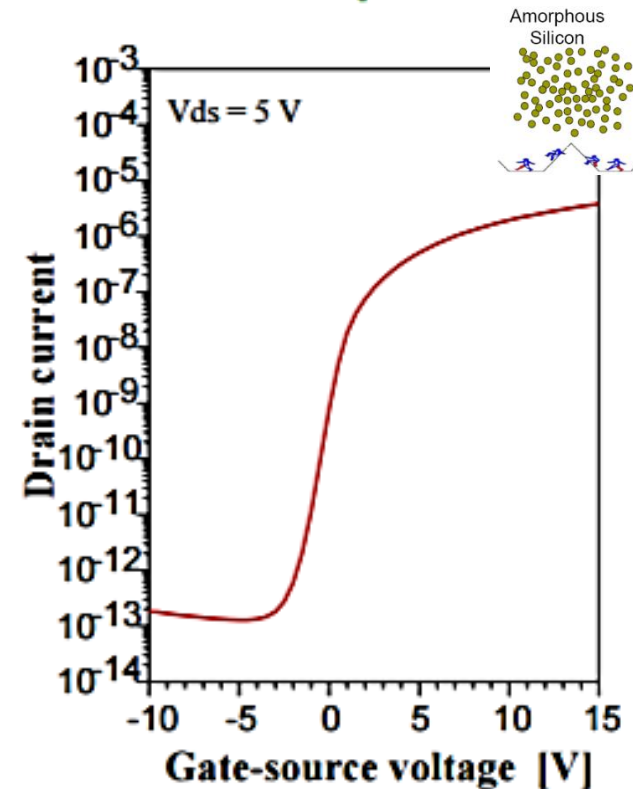
High  $I_{on}$   
Low  $I_{off}$

## Poly-Si



High  $I_{on}$   
High  $I_{off}$

## Amorphous Si

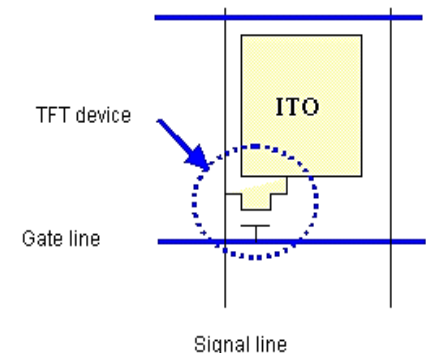


Low  $I_{on}$   
Low  $I_{off}$

# Hydrogenated Amorphous Silicon

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- $\alpha$ -Si:H solar cell are based on a  $\alpha$ -Si being deposited with H to form  $\alpha$ -Si:H, in which the hydrogen concentration is typically 10 at.% (atomic %).
- The advantage of  $\alpha$ -Si:H is that it can be grown on large area, like applications as photovoltaic cell (solar cell) and flat panel displays (FPD).



# Si Crystallinity

**Table 1.5** Crystalline and amorphous silicon

	Crystalline Si (c-Si)	Amorphous Si (a-Si)	Hydrogenated a-Si (a-Si:H)
Structure	Diamond cubic.	Short-range order only. On average, each Si covalently bonds with four Si atoms. Has microvoids and dangling bonds.	Short-range order only. Structure typically contains 10% H. Hydrogen atoms passivate dangling bonds and relieve strain from bonds.
Typical preparation	Czochralski technique.	Electron beam evaporation of Si.	Chemical vapor deposition of silane gas by RF plasma.
Density (g cm <sup>-3</sup> )	2.33	About 3–10% less dense.	About 1–3% less dense.
Electronic applications	Discrete and integrated electronic devices.	None	Large-area electronic devices such as solar cells, flat panel displays, and some photoconductor drums used in photocopying.

# Outline

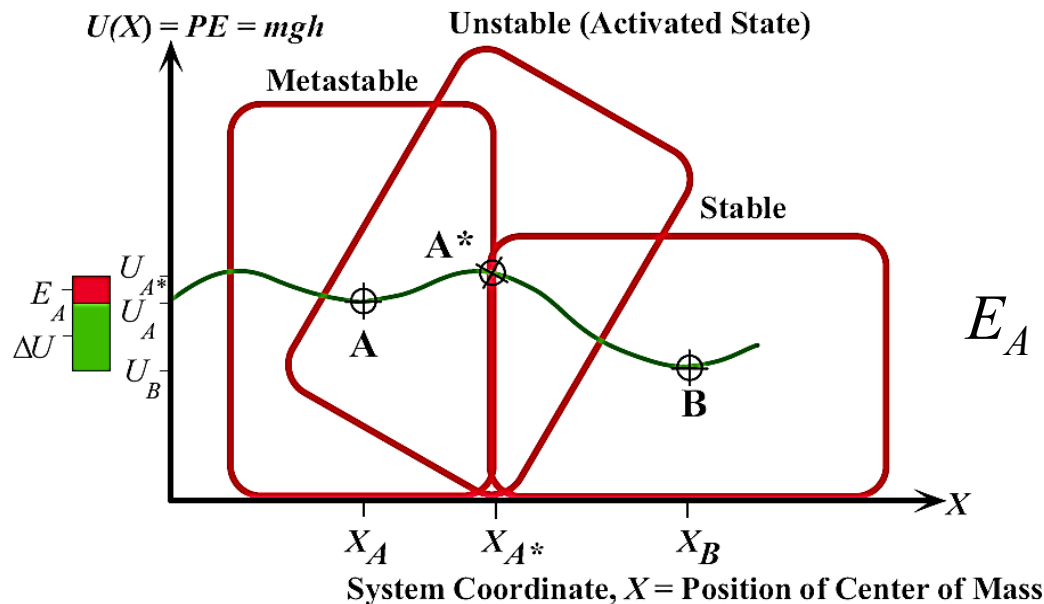
- Si Crystallinity
- **Thermally Activated Processes**
- Crystal Defects
- Crystal Surface and Its Properties

# Thermally Activated Processes

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- Tilting a filing cabinet from state  $A$  to its edge in state  $A^*$  requires an energy  $E_A$ . After reaching  $A^*$ , the cabinet spontaneously drops to the stable position  $B$ .  $PE$  of state  $B$  is lower than  $A$  and therefore state  $B$  is more stable than  $A$ .
- Example: thermal excitation of electron, diffusion

□



# Thermally Activated Processes

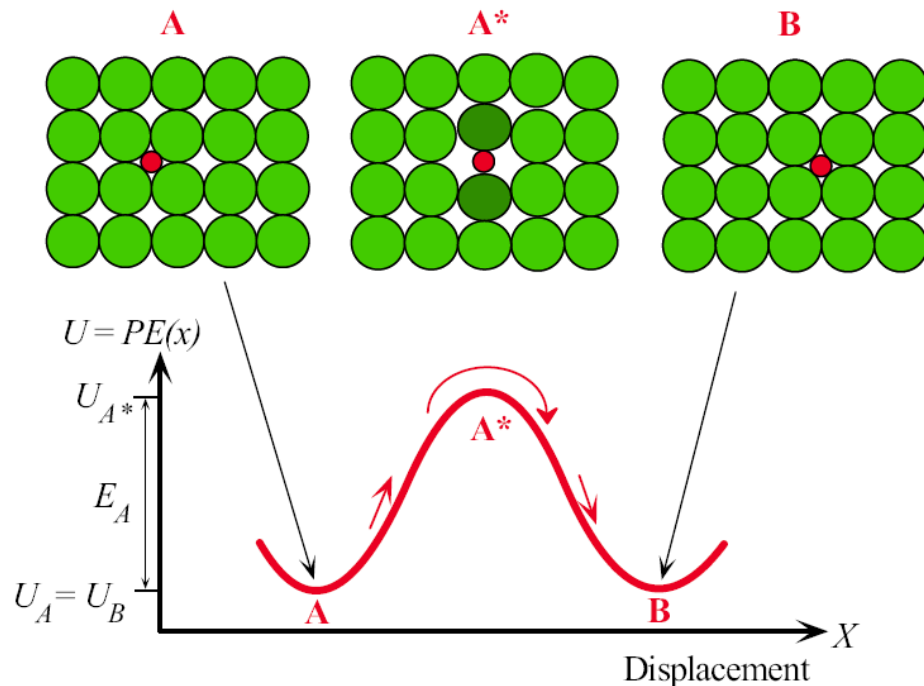
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- **Diffusion** of an **interstitial impurity** atom in a crystal from one void to a neighboring void. The impurity atom at position A must possess an **energy**  $E_A$  to push the host atoms away and move into the neighboring void at B.

$A^*$ : activated state

$E_A$ : activation energy

$$E_A = U_{A^*} - U_A$$



# Thermally Activated Processes

- **Diffusion:** Thermally Activated Processes
  - ✓ Temperature plays a significant role in diffusion
  - ✓ Driving force for diffusion is chemical potential difference (concentration).
- **Diffusion:**
- **Diffusion Coefficient** is proportional to **jump frequency** (jumps per second)
- **Jump frequency** is proportional to the **probability** that an impurity atom has  $E > E_A$

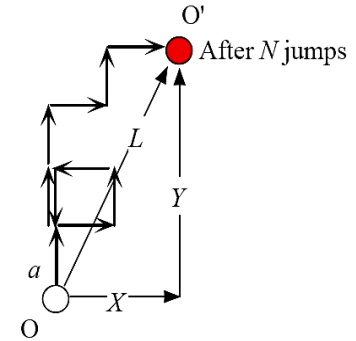
# Diffusion Coefficient

## Mean Square Displacement

$$L^2 = a^2 \mathcal{G}t = 2Dt$$

$L$  : root mean square (rms) displacement

$L$  = “distance” diffused after time  $t$ ,  $a$  = closest void to void separation (jump distance),  $\mathcal{G}$  = frequency of jumps,  $t$  = time,  $D$  = diffusion coefficient



## Diffusion coefficient is thermally activated

$$D = \frac{1}{2} a^2 \mathcal{G} = \frac{1}{2} a^2 v_0 A \exp\left(-\frac{E_A}{kT}\right) = D_o \exp\left(-\frac{E_A}{kT}\right)$$

Diffusion Coefficient is proportional to jump frequency (jumps per second)



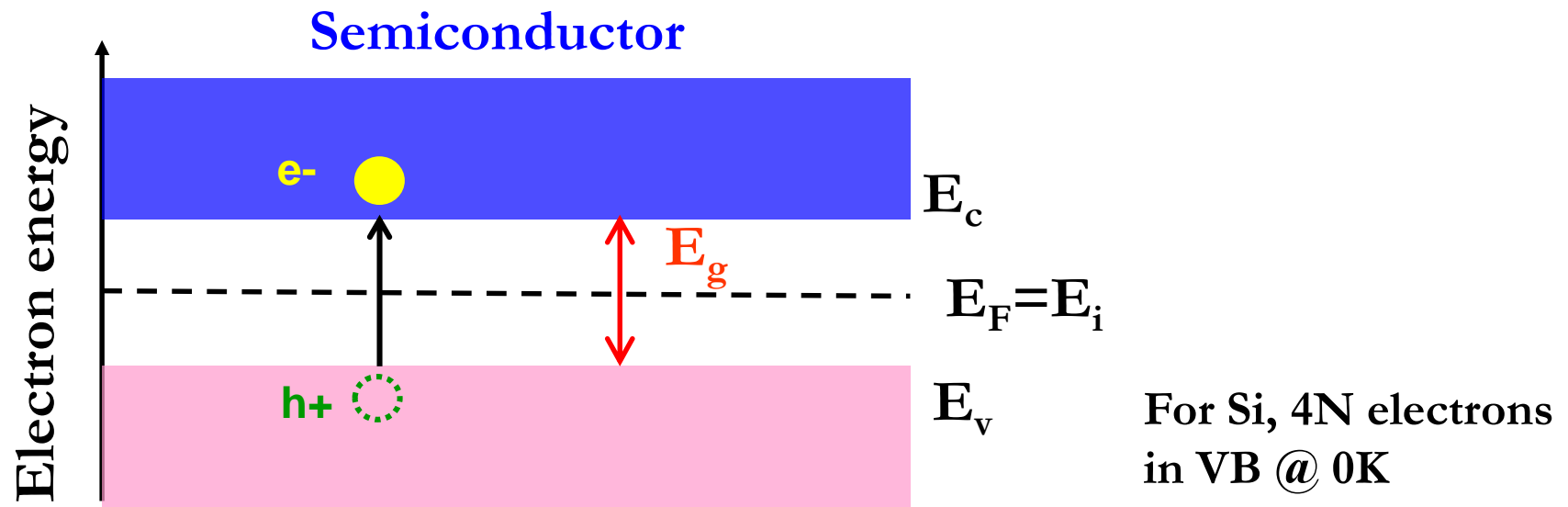
# Thermal Excitation

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- **Intrinsic carrier concentration**,  $n_i$  is the number of electrons in the conduction band.

$$n = n_o \exp\left(-\frac{E_g}{2kT}\right)$$

Intrinsic semiconductor



# Arrhenius Behavior

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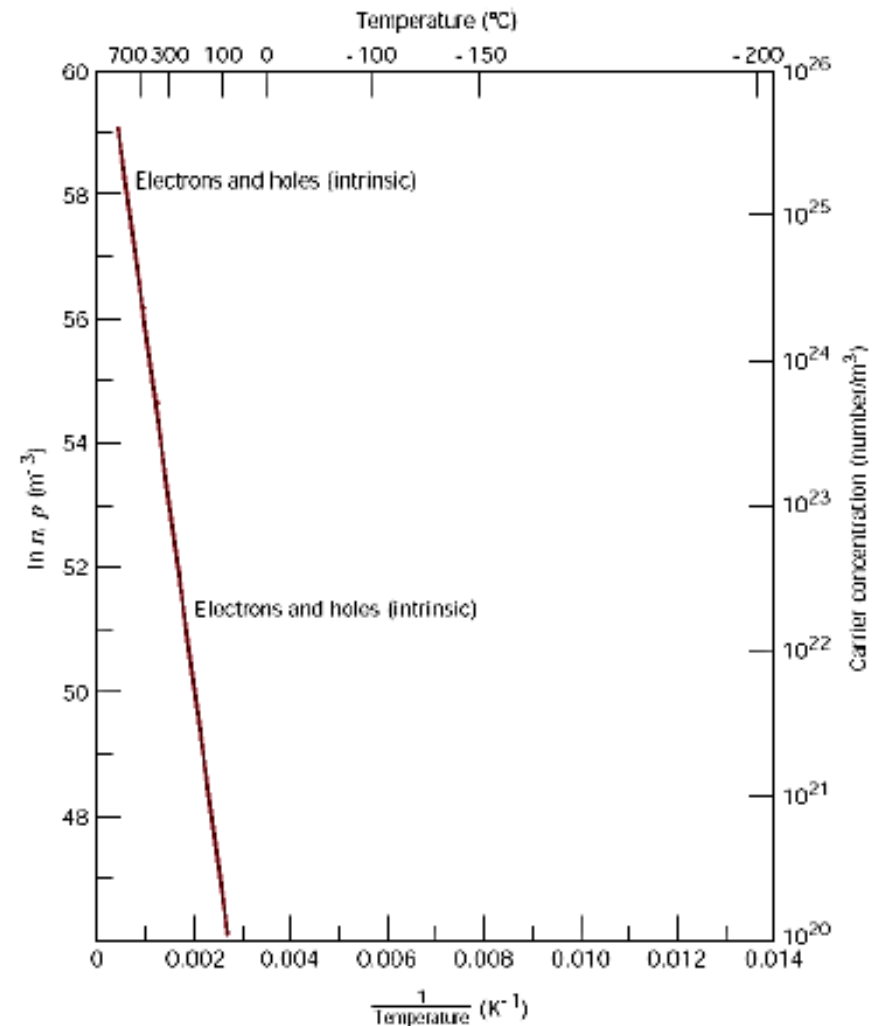
Carrier concentration in semiconductors:

$$n = n_o \exp\left(\frac{-(E_g / 2)}{kT}\right)$$

$$\ln(n) = \ln(n_o) - \frac{E_g}{2kT}$$

$$\log(n) = \log(n_o) - \frac{E_g}{2.3(2k)} \left(\frac{1}{T}\right)$$

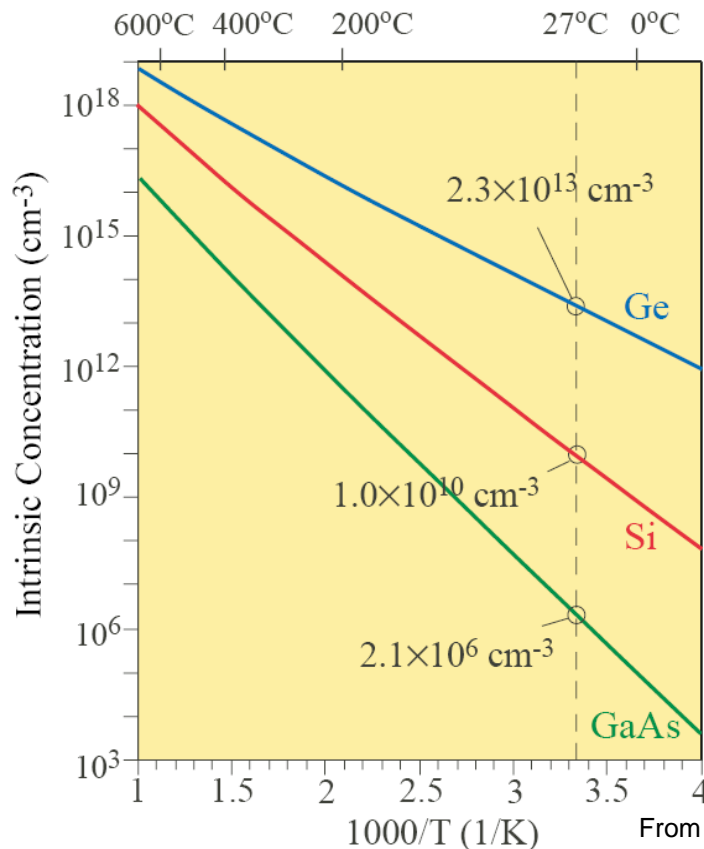
$$y = b + m x$$



# Arrhenius Behavior

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- Intrinsic carrier concentration as a function of  $1/T$  (Arrhenius plot).



$$n = n_o \exp\left(-\frac{E_g}{2kT}\right)$$

Intrinsic semiconductor

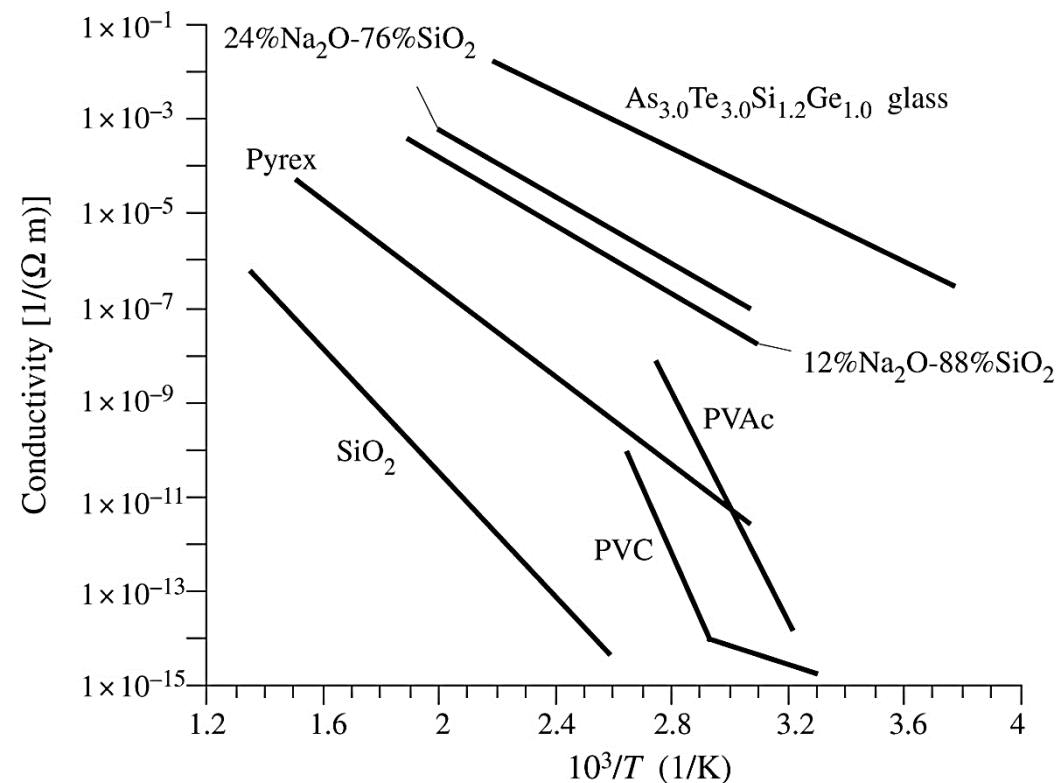
# Arrhenius Behavior

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- Conductivity of insulator is thermally activated, so it also follows an exponential or Arrhenius-type temperature dependence.

$$\sigma = \sigma_0 e^{\left(-\frac{E_\sigma}{KT}\right)}$$

- Useful in predicting the conductivity at various temperature & evaluate the thermal stability of insulators.



# Example 1.

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## EXAMPLE 1.12

**DIFFUSION OF DOPANTS IN SILICON** The diffusion coefficient of P atoms in the Si crystal follows Equation 1.34 with  $D_o = 10.5 \text{ cm}^2 \text{ s}^{-1}$  and  $E_A = 3.69 \text{ eV}$ . What is the diffusion coefficient at a temperature of  $1100^\circ \text{C}$  at which dopants such as P are diffused into Si to fabricate various devices? What is the rms distance diffused by P atoms in 5 minutes? Estimate, as an order of magnitude, how many jumps the P atom makes in 1 second if you take the jump distance to be roughly the mean interatomic separation,  $\sim 0.27 \text{ nm}$ .

### SOLUTION

From Equation 1.34,

$$\begin{aligned} D &= D_o \exp\left(-\frac{E_A}{kT}\right) = (10.5 \text{ cm}^2 \text{ s}^{-1}) \exp\left[-\frac{(3.69 \text{ eV})(1.602 \times 10^{-19} \text{ J eV}^{-1})}{(1.381 \times 10^{-23} \text{ J K}^{-1})(1100 + 273 \text{ K})}\right] \\ &= 3.0 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1} \end{aligned}$$

The rms distance  $L$  diffused in a time  $t = 5 \text{ min} = 5 \times 60 \text{ seconds}$  is

$$L = \sqrt{2Dt} = [2(3.0 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1})(5 \times 60 \text{ s})]^{1/2} = 1.3 \times 10^{-5} \text{ cm} \quad \text{or} \quad 13 \mu\text{m}$$

Equation 1.33 was derived for a two-dimensional crystal as in Figure 1.30, and for an impurity diffusion. Nonetheless, we can still use it to estimate how many jumps a P atom makes in 1 second. From Equation 1.33,  $\vartheta \approx 2D/a^2 \approx 2(3.0 \times 10^{-17} \text{ m}^2 \text{ s}^{-1})/(0.27 \times 10^{-9} \text{ m})^2 = 823$  jumps per second. It takes roughly 1 ms to make one jump. It is left as an exercise to show that at room temperature it will take a P atom  $10^{46}$  years to make a jump! (Scientists and engineers know how to use thermally activated processes.)

# Example 2.

- The diffusion coefficient of boron (B) atoms in a single crystal of Si has been measured to be  $1.5 \times 10^{-18} \text{ m}^2 \text{ s}^{-1}$  at  $1000^\circ\text{C}$  and  $1.1 \times 10^{-16} \text{ m}^2 \text{ s}^{-1}$  at  $1200^\circ\text{C}$ .
  - a. What is the activation energy for the diffusion of B, in eV/atom?
  - b. What is the preexponential constant  $D_o$ ?
  - c. What is the rms distance (in micrometers) diffused in 1 hour by the B atom in the Si crystal at  $1200^\circ\text{C}$  and  $1000^\circ\text{C}$ ?
  - d. The diffusion coefficient of B in polycrystalline Si has an activation energy of 2.4-2.5 eV/atom and  $D_o = (1.5-6) \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ . What constitutes the diffusion difference between the single crystal sample and the polycrystalline sample?

## Solution

Given diffusion coefficients at two temperatures:

$$T_1 = 1200\text{ }^\circ\text{C} + 273 = 1473\text{ K} \quad D_1 = 1.1 \times 10^{-16}\text{ m}^2/\text{s}$$

$$T_2 = 1000\text{ }^\circ\text{C} + 273 = 1273\text{ K} \quad D_2 = 1.5 \times 10^{-18}\text{ m}^2/\text{s}$$

a. The diffusion coefficients  $D_1$  and  $D_2$  at  $T_1$  and  $T_2$  respectively are given by:

$$D_1 = D_o \exp\left(-\frac{qE_A}{kT_1}\right) \quad D_2 = D_o \exp\left(-\frac{qE_A}{kT_2}\right)$$

where  $E_A$  is the activation energy in eV/atom and  $q = 1.6 \times 10^{-19}\text{ J/eV}$  (conversion factor from eV to J).  
Since,

$$\frac{\exp(-x)}{\exp(-y)} = \exp(y-x)$$

we can take the ratio of the diffusion coefficients to express them in terms of  $E_A$  (eV):

$$\frac{D_1}{D_2} = \frac{D_o \exp\left(-\frac{qE_A}{kT_1}\right)}{D_o \exp\left(-\frac{qE_A}{kT_2}\right)} = \exp\left(\frac{qE_A}{kT_2} - \frac{qE_A}{kT_1}\right) = \exp\left(\frac{q[T_1 - T_2]E_A}{kT_1T_2}\right)$$

$$E_A = \frac{kT_1T_2 \ln\left(\frac{D_1}{D_2}\right)}{q(T_1 - T_2)} \quad (\text{in eV})$$

$$E_A = \frac{(1.381 \times 10^{-23}\text{ J K}^{-1})(1473\text{ K})(1273\text{ K}) \ln\left(\frac{1.1 \times 10^{-16}\text{ m}^2/\text{s}}{1.5 \times 10^{-18}\text{ m}^2/\text{s}}\right)}{(1.602 \times 10^{-19}\text{ J/eV})(1473\text{ K} - 1273\text{ K})}$$

$$E_A = 3.47\text{ eV/atom}$$

b. To find  $D_o$ , use one of the equations for the diffusion coefficients:

$$D_1 = D_o \exp\left(-\frac{qE_A}{kT_1}\right)$$

$$\therefore D_o = \frac{D_1}{\exp\left(-\frac{qE_A}{kT_1}\right)} = \frac{(1.1 \times 10^{-16} \text{ m}^2/\text{s})}{\exp\left[-\frac{(1.602 \times 10^{-19} \text{ J/eV})(3.47 \text{ eV})}{(1.381 \times 10^{-23} \text{ J K}^{-1})(1473 \text{ K})}\right]}$$

$$\therefore D_o = 8.12 \times 10^{-5} \text{ m}^2/\text{s}$$

c. Given: time ( $t$ ) = (1 hr)  $\times$  (3600 s/hr) = 3600 s

At 1000 °C, rms diffusion distance ( $L_{1000 \text{ °C}}$ ) in time  $t$  is given by:

$$L_{1000 \text{ °C}} = \sqrt{2D_2t} = \sqrt{2(1.5 \times 10^{-18} \text{ m}^2/\text{s})(3600 \text{ s})}$$

$$\therefore L_{1000 \text{ °C}} = 1.04 \times 10^{-7} \text{ m or } 0.104 \text{ }\mu\text{m}$$

At 1200 °C:

$$L_{1200 \text{ °C}} = \sqrt{2D_1t} = \sqrt{2(1.1 \times 10^{-16} \text{ m}^2/\text{s})(3600 \text{ s})}$$

$$\therefore L_{1200 \text{ °C}} = 8.90 \times 10^{-7} \text{ m or } 0.89 \text{ }\mu\text{m (almost 10 times longer than at 1000 °C)}$$

d. Diffusion in polycrystalline Si would involve diffusion along grain boundaries, which is easier than diffusion in the bulk. The activation energy is smaller because it is easier for an atom to break bonds and jump to a neighboring site; there are vacancies or voids, broken bonds, and strained bonds in a grain boundary.



# Outline

- Si Crystallinity
- Thermally Activated Processes
- **Crystal Defects**
- **Crystal Surface and Its Properties**

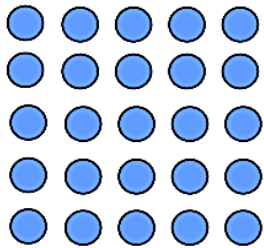
# Crystal Defects

- 4 types of crystal defects
  - ✓ Point defects
  - ✓ Line defects (extend in one direction)
  - ✓ Area defects (2-D)
  - ✓ Volume defects (3-D)
- Each type affects different areas of the fabrication process
  - ✓ Point defects affect doping and diffusion
  - ✓ Preventing line defects is important for any thermal processing
    - especially rapid thermal processing
  - ✓ Volume defects can be important in yield engineering

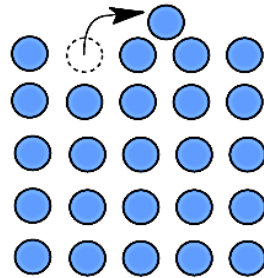
# Vacancy Formation

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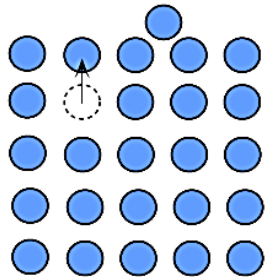
- Generation of a vacancy by the diffusion of atom to the surface and the subsequent diffusion of the vacancy into the bulk.



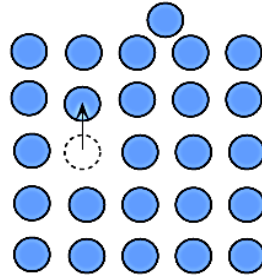
(a) Perfect crystal without vacancies



(b) An energetic atom at the surface breaks bonds and jumps on to a new adjoining position on the surface. This leaves behind a vacancy.



(c) An atom in the bulk diffuses to fill the vacancy thereby displacing the vacancy towards the bulk.



(d) Atomic diffusions cause the vacancy to diffuse into the bulk.

## Equilibrium Concentration of Vacancy

$$n_v = N \exp\left(-\frac{E_v}{kT}\right)$$

$n_v$  = vacancy concentration

$N$  = atoms concentration

$E_v$  = vacancy formation energy

$k$  = Boltzmann constant

$T$  = temperature (K)



**VACANCY CONCENTRATION IN A METAL** The energy of formation of a vacancy in the aluminum crystal is about 0.70 eV. Calculate the fractional concentration of vacancies in Al at room temperature, 300 K, and very close to its melting temperature 660 °C. What is the vacancy concentration at 660 °C given that the atomic concentration in Al is about  $6.0 \times 10^{22} \text{ cm}^{-3}$ ?

### SOLUTION

Using Equation 1.35, the fractional concentration of vacancies are as follows:

At 300 °C,

$$\begin{aligned}\frac{n_v}{N} &= \exp\left(-\frac{E_v}{kT}\right) = \exp\left[-\frac{(0.70 \text{ eV})(1.6 \times 10^{-19} \text{ J eV}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(300 \text{ K})}\right] \\ &= 1.7 \times 10^{-12}\end{aligned}$$

At 660 °C or 933 K,

$$\begin{aligned}\frac{n_v}{N} &= \exp\left(-\frac{E_v}{kT}\right) = \exp\left[-\frac{(0.70 \text{ eV})(1.6 \times 10^{-19} \text{ J eV}^{-1})}{(1.38 \times 10^{-23} \text{ J K}^{-1})(933 \text{ K})}\right] \\ &= 1.7 \times 10^{-4}\end{aligned}$$

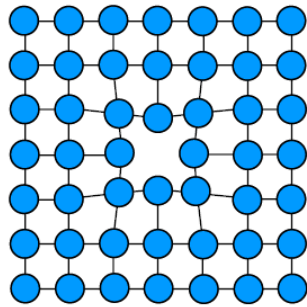
That is, almost 1 in 6000 atomic sites is a vacancy. The atomic concentration  $N$  in Al is about  $6.0 \times 10^{22} \text{ cm}^{-3}$ , which means that the vacancy concentration  $n_v$  at 660 °C is

$$n_v = (6.0 \times 10^{22} \text{ cm}^{-3})(1.7 \times 10^{-4}) = 1.0 \times 10^{19} \text{ cm}^{-3}$$

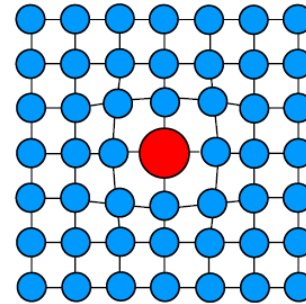
The mean vacancy separation (on the order of  $n_v^{-1/3}$ ) at 660 °C is therefore roughly 5 nm. The mean atomic separation in Al is  $\sim 0.3 \text{ nm}$  ( $\sim N^{-1/3}$ ), so the mean separation between vacancies is only about 20 atomic separations! (A more accurate version of Equation 1.35, with an entropy term, shows that the vacancy concentration is even higher than the estimate in this example.) The increase in the linear thermal expansion coefficient of a metal with temperature near its melting temperature, as shown for Mo in Figure 1.20, has been attributed to the generation of vacancies in the crystal.

# Point Defect Distortion

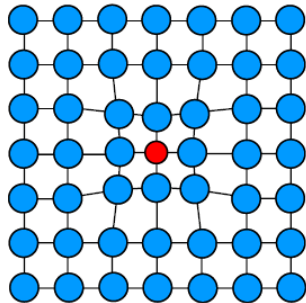
- **Point defects** in the crystal structure. The regions around the point defect become **distorted**; the lattice becomes **strained**.



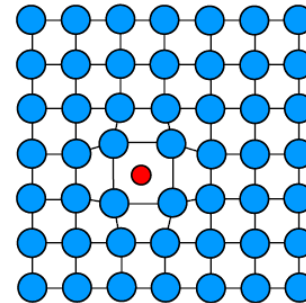
(a) A vacancy in the crystal.



(b) A substitutional impurity in the crystal. The impurity atom is larger than the host atom.

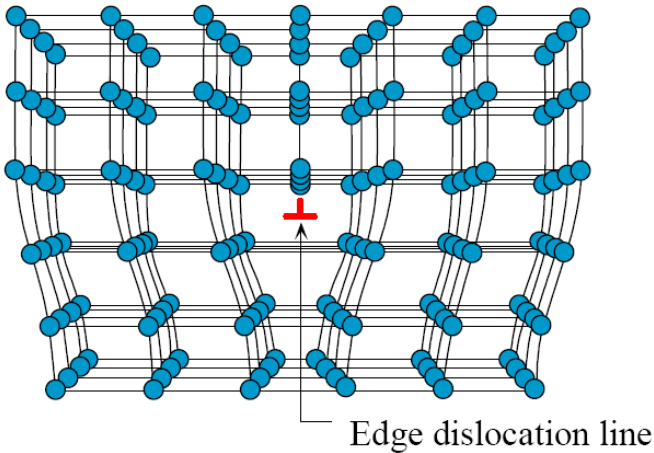


(c) A substitutional impurity in the crystal. The impurity atom is smaller than the host atom.

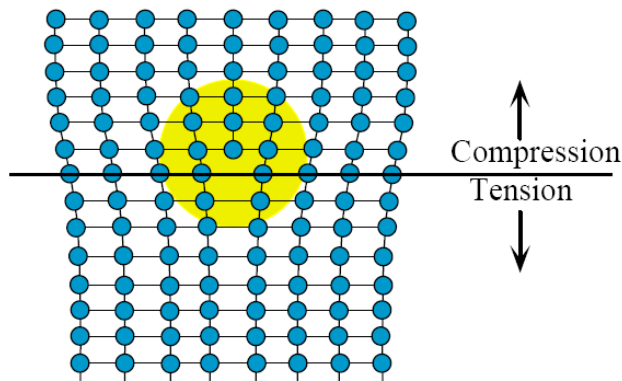


(d) An interstitial impurity in the crystal. It occupies an empty space between host atoms.

# Line Defect

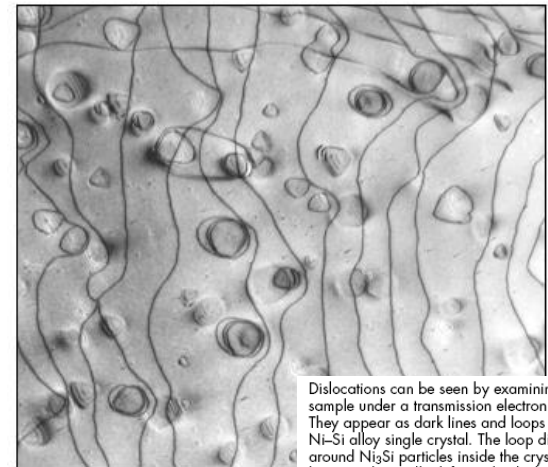


(a) Dislocation is a line defect. The dislocation shown runs into the paper.



(b) Around the dislocation there is a strain field as the atomic bonds have been compressed above and stretched below the dislocation line

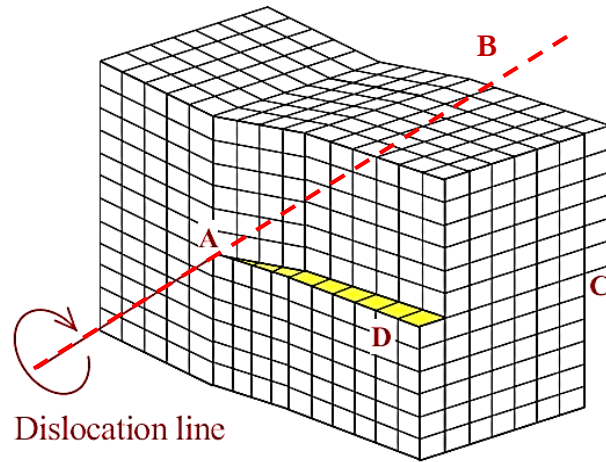
Dislocation in a crystal is a line defect which is accompanied by lattice distortion and hence a lattice strain around it.



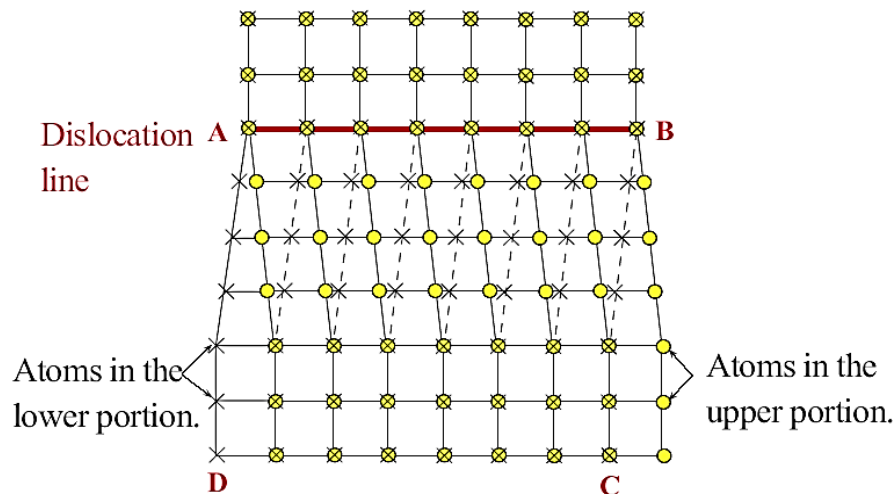
Dislocations can be seen by examining a thin slice of the sample under a transmission electron microscope (TEM). They appear as dark lines and loops as shown here in a Ni-Si alloy single crystal. The loop dislocations are around Ni<sub>3</sub>Si particles inside the crystal. The sample had been mechanically deformed, which generates dislocations.

SOURCE: Courtesy of Professor John Humphreys, UMIST, England. (J. Humphreys and V. Ramaswamy in *High Voltage Electron Microscopy*, ed. P. R. Swann. C. J. Humphreys and M. J. Goringe, New York: Academic Press, 1974, p. 26.)

# Screw Dislocation



(a) A screw dislocation in a crystal.



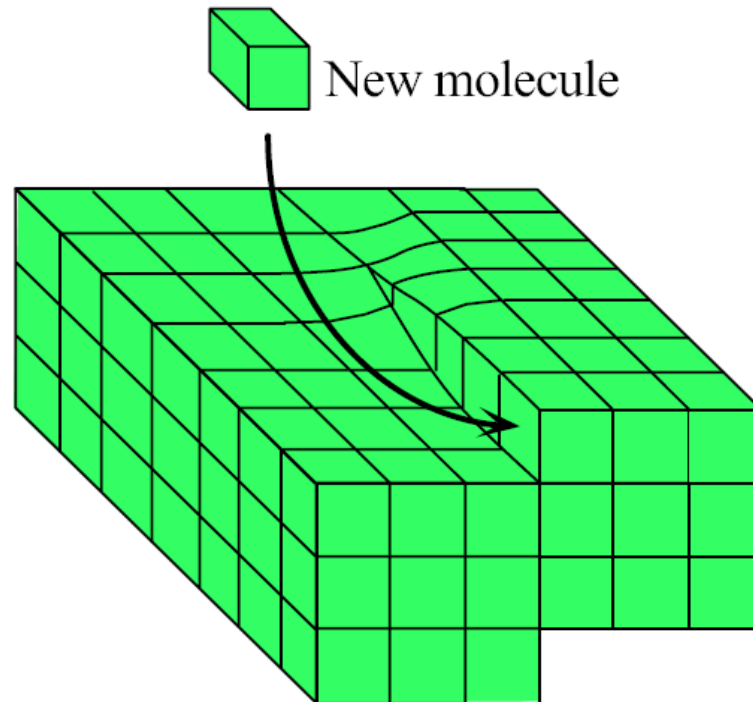
(b) The screw dislocation in (a) as viewed from above.

A **screw dislocation** involves **shearing** one portion of a perfect crystal with respect to another portion on one side of a line (AB)

# Screw Dislocation

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- Screw dislocation aids crystal growth because the newly arriving atom can **attach to two or three atoms** instead of one atom and thereby form **more bonds**.

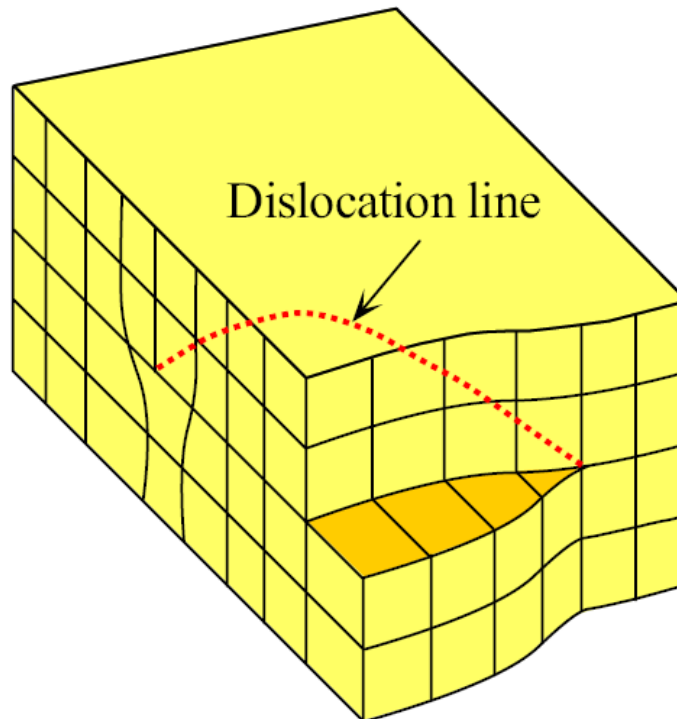




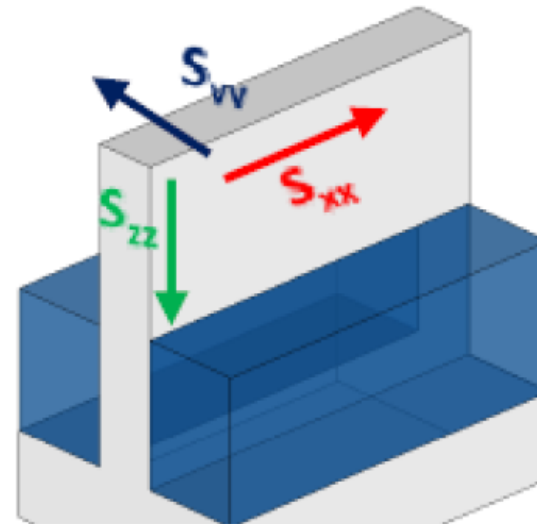
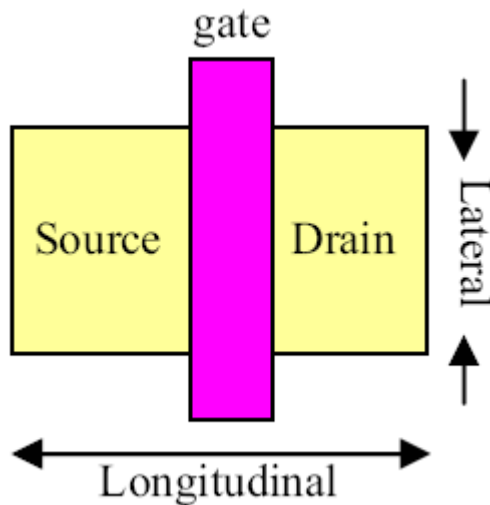
# Mixed Dislocation

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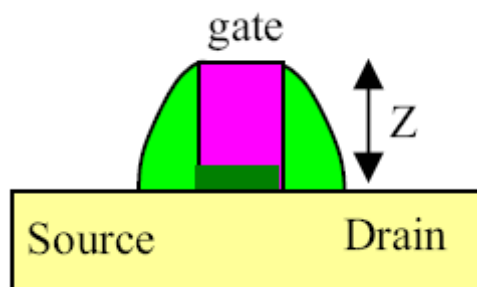
- The exact structure of dislocations in real crystals is usually more complicated than edge and screw dislocations. Most dislocations have **mixed edge/screw** character.



# Stress Components



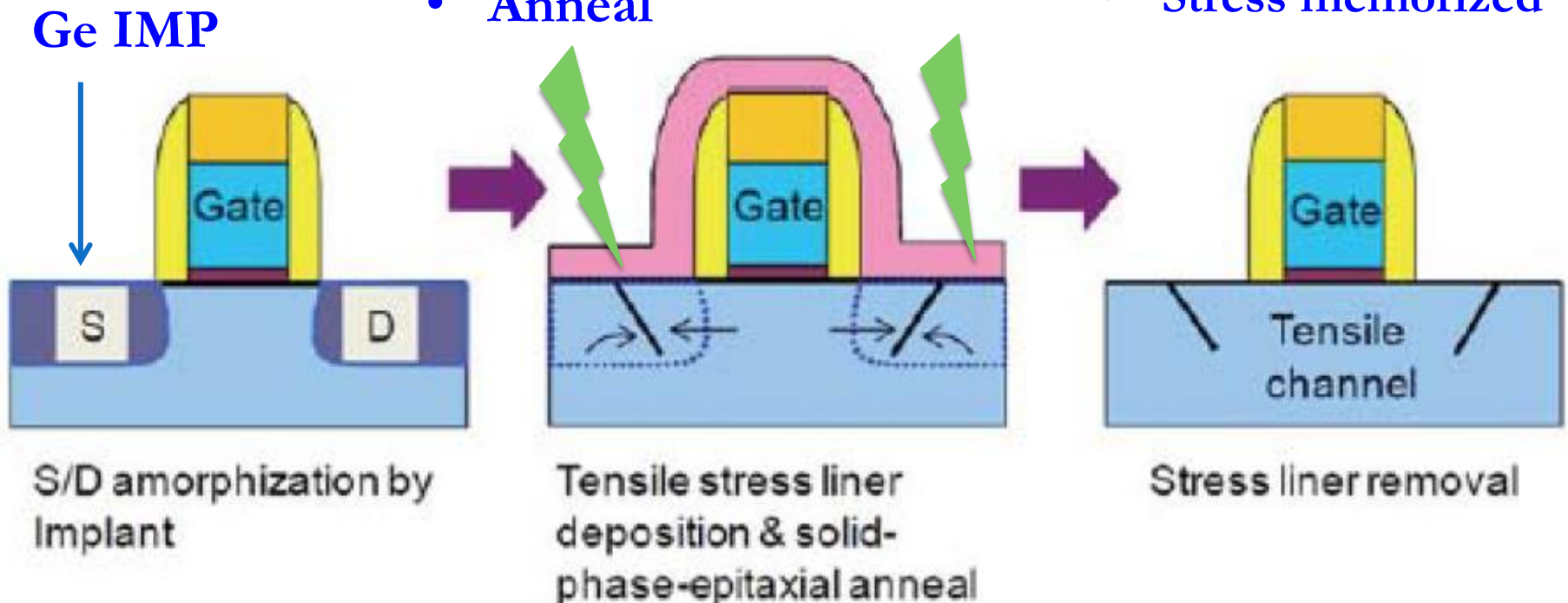
T = Tensile (+ve); C = Compressive (-ve)



Stress (1 Gpa)	NMOS	PMOS
$S_{xx}$ Longitudinal	T (65%)	C (63%)
$S_{yy}$ Transverse	T (19%)	T (22%)
$S_{zz}$ Vertical	C (60%)	T (26.5%)

□ Resulting longitudinal tensile (major)+ Vertical Compressive stress → Good for **NMOS** mobility

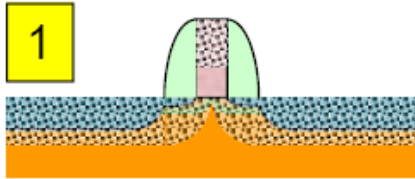
- Deposition Tensile film
- Remove Tensile film
- Anneal
- Stress memorized



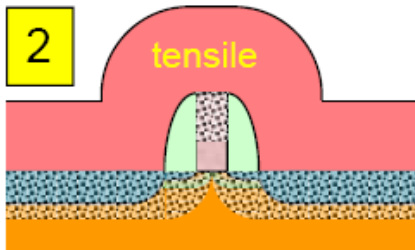
# Stress Memorization Technique (SMT)

## NMOS ☺

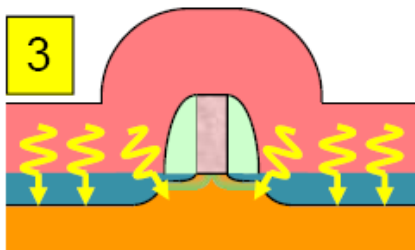
36



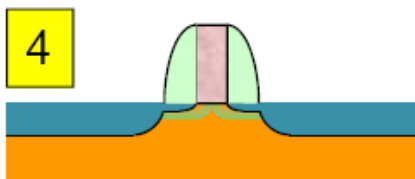
Amorphize poly & diffusion with silicon implant



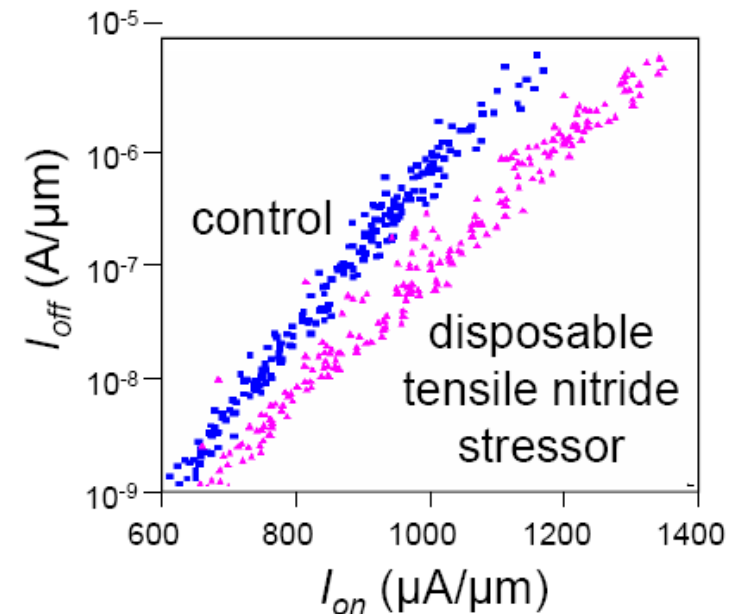
Deposit tensile nitride



Anneal to *make nitride more tensile* and transfer nitride tension to crystallizing amorphous channel



Remove nitride stressor (tension now frozen in diffusion)

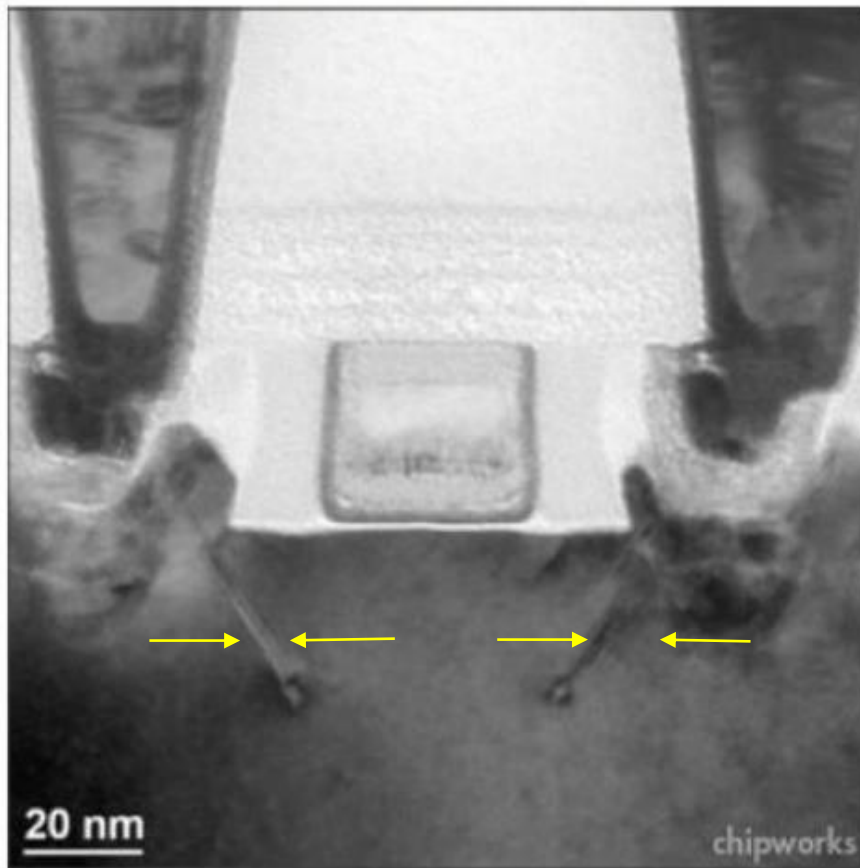


V. Chan et al., "Strain for CMOS performance improvement," in Proc. IEEE Custom Integrated Circuits Conf., pp. 667–674, Sep. 2005.

# {111} Stacking Fault (Planar defect)

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Intel 32nm NMOSFET



- During SPER with restricted boundary, amorphized Si S/D gets dislocations with {111} stacking faults
- Each stacking fault is a missing {111} plane (i.e. vacancies)
- The missing {111} plane creates tensile stress in the direction perpendicular to the plane

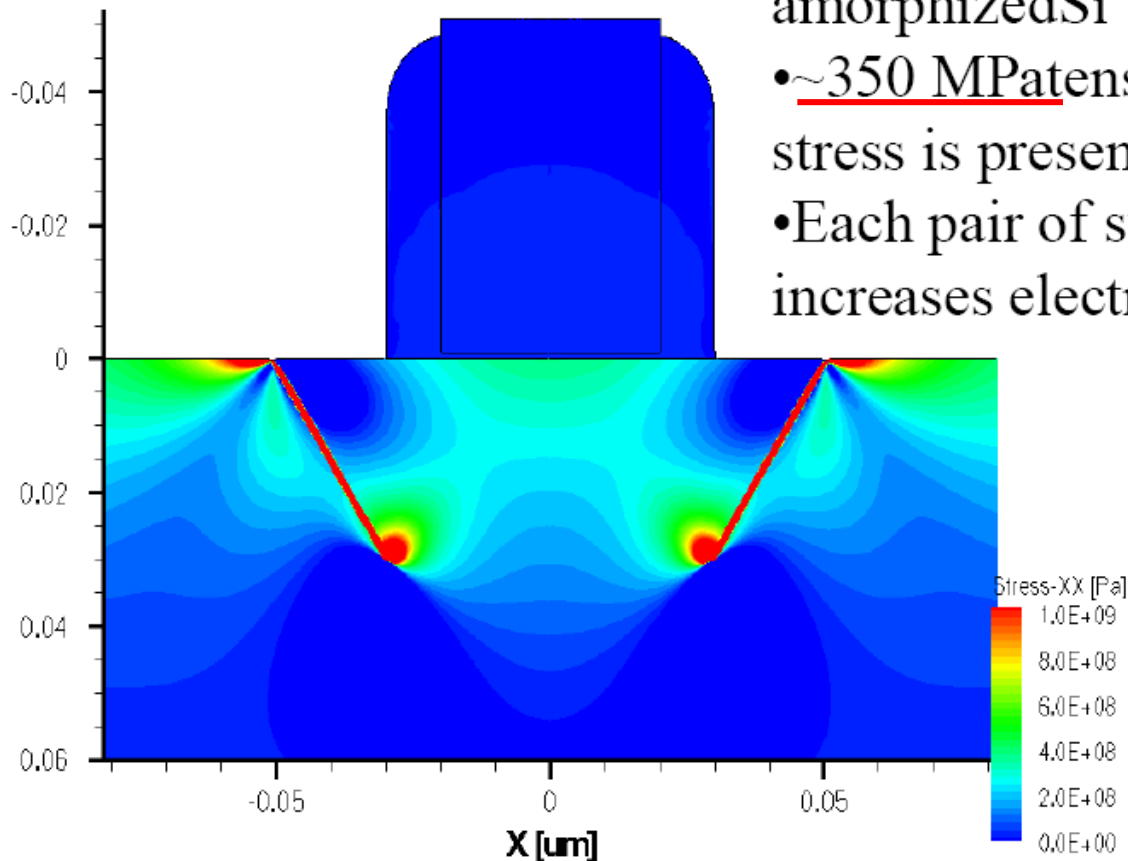
Solid phase epitaxial regrowth (SPER)

# Simulation Results

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Missing (i.e. vacancy)  $\{111\}$  plane  
due to SMT for a 30nm deep  
amorphizedSi

- ~350 MPa tensile longitudinal stress is present in the channel
- Each pair of stacking faults increases electron mobility by 5%

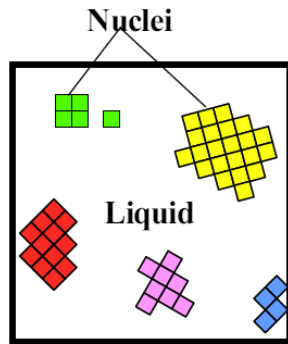


Victor Moroz at Berkeley Seminar

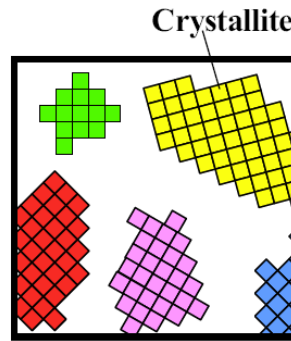
# Planar Defect

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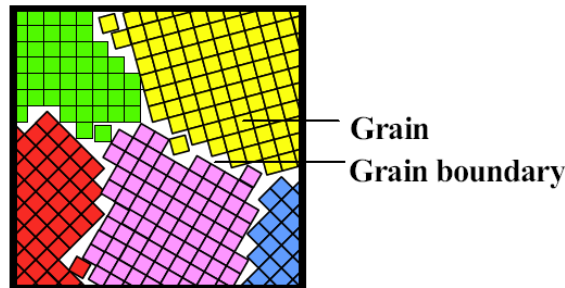
- Solidification of a polycrystalline solid from the melt. For simplicity cubes represent atoms.



(a)



(b)



(c)

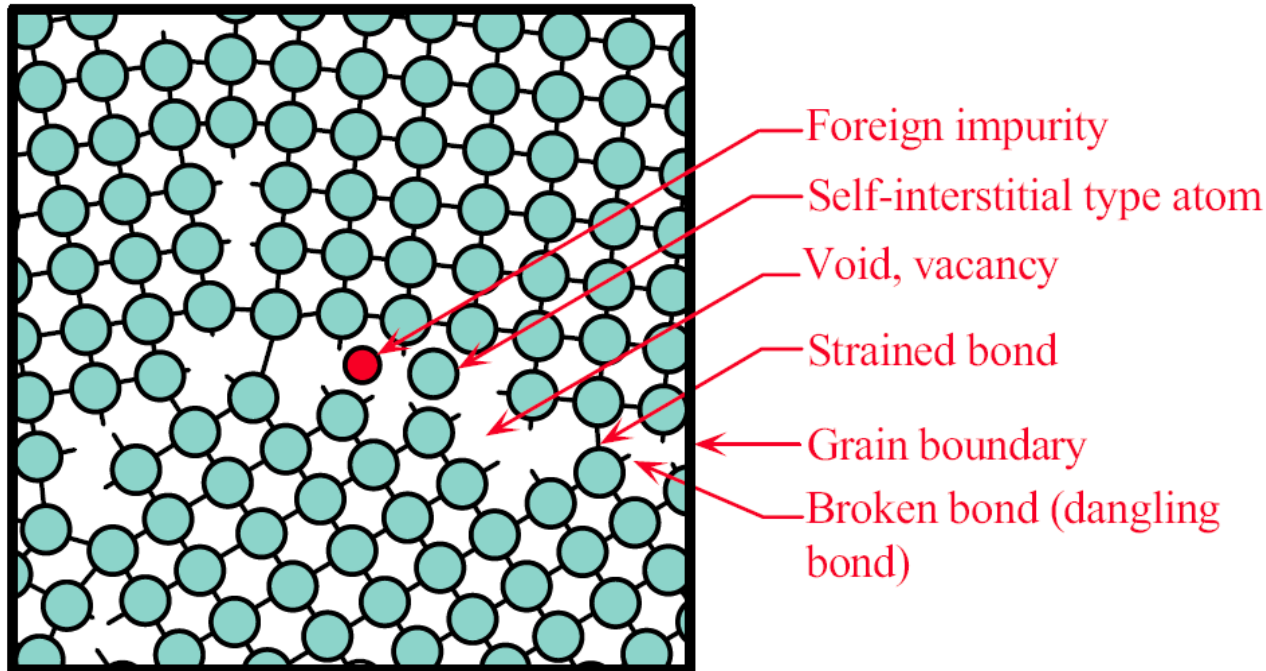
(a) Nucleation.

(b) Growth.

(c) The solidified polycrystalline solid.



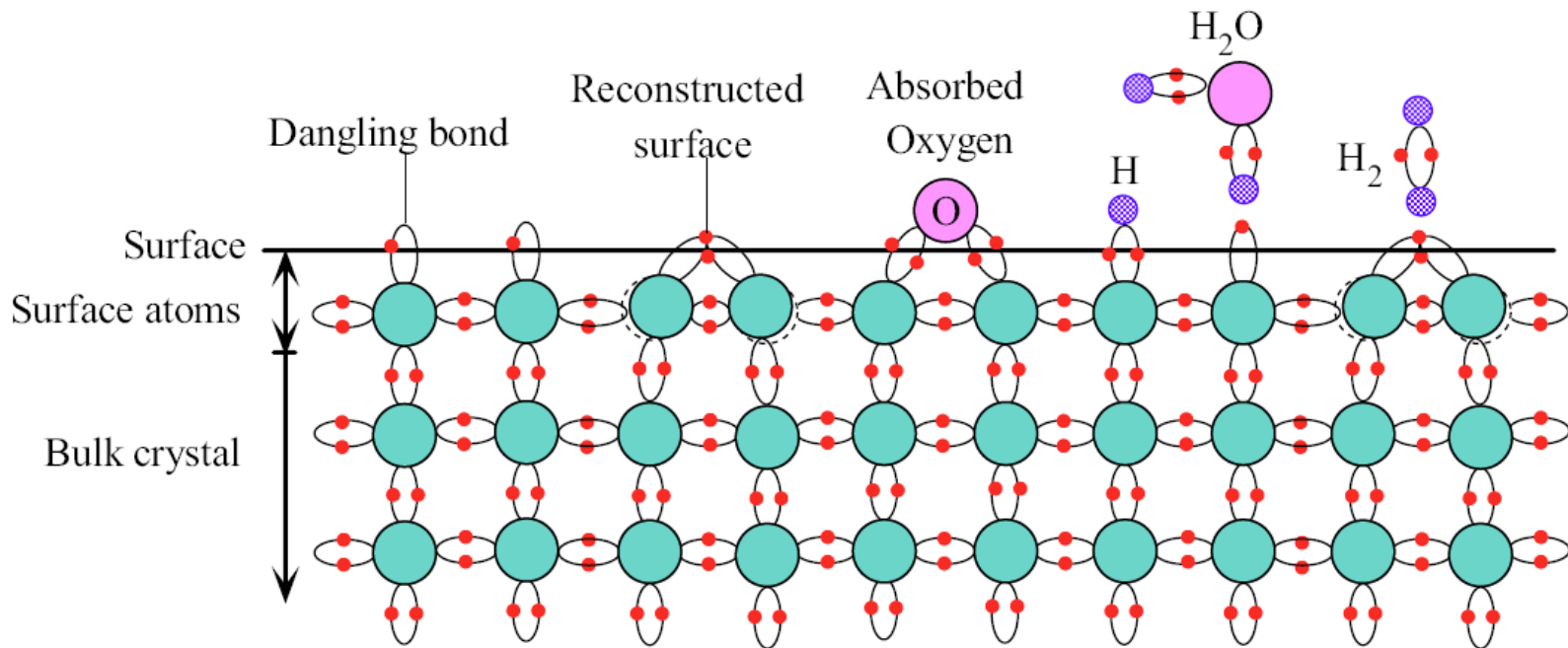
# Grain Boundary (GB)



The grain boundaries have **broken bonds**, **voids**, **vacancies**, **strained bonds** and “**interstitial**” type atoms. The structure of the grain boundary is disordered and the atoms in the grain boundaries have **higher energies** than those within the grains.



# Si Surface

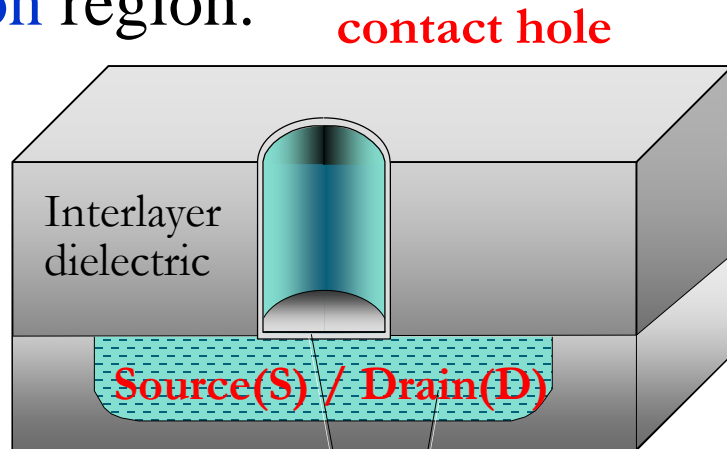


At the surface of a hypothetical 2D crystal, the atoms cannot fulfill their bonding requirements and therefore have broken, or **dangling bonds**. Some of the surface atoms bond with each other; the surface becomes **reconstructed**. The surface can have **physisorbed** and **chemisorbed** atoms.

# Native Oxide

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- Si exposed to air or DI water has a **native oxide** on its surface. Native oxide is approximately **1~2 nm** thick at room temperature.
- Native oxide lines the bottom of the **contact hole**, creating poor electrical contact between **tungsten** and the **doped silicon** region.



Native oxide grows inside the contact hole prior to tungsten deposition.

