# **CHAPTER 1**

# **The Crystal Structure of Solids**

2009/2010

Department of Microelectronics & Computer Engineering



# **Semiconductor Materials**

| Group<br>III | Group<br>IV | Group<br>V |
|--------------|-------------|------------|
| В            |             |            |
| Al           | С           | Р          |
| Ga           | Si          | As         |
| In           | Ge          | Sb         |

A portion of the periodic table

 possible elements for making semiconductor materials

•Si most well known semiconductor. C and Ge can also be semiconductors.

• Other possibilities combinations of III and V group. Eg. GaAs



Department of Microelectronics & Computer Engineering



# Elemental and Compound Semiconductors

| Elemental Semiconductors |           |  |
|--------------------------|-----------|--|
| Si                       | Silicon   |  |
| Ge                       | Germanium |  |

| Compound Semiconductors |                     |  |
|-------------------------|---------------------|--|
| AIP                     | Aluminium Phosphide |  |
| AlAs                    | Aluminium Arsenide  |  |
| GaP                     | Gallium Phosphide   |  |
| GaAs                    | Gallium Arsenide    |  |
| InP                     | Indium Phosphide    |  |

*Binary Semiconductor ( 2 elements):* Si<sub>1-x</sub>Ge<sub>x,</sub>SiC

*Ternary Semiconductor (3 elements): Al<sub>x</sub>Ga<sub>1-x</sub>P* 

Quaternary Semiconductor (4 elements) : AlGaAsP

•Single element  $\rightarrow$  elemental semiconductor

•More than one element  $\rightarrow$  compound semiconductor

Properties of comp semi can be controlled by changing the concn of the elements

#### 2009/2010





GaN and ZnO are recently discovered semiconductor materials which are promising materials for laser diodes (blue light).

These laser diodes are used in blue-ray DVD recorders. Blue light having smaller wavelength helps in lowering the resolution and increasing the packing density of bits.

## A light emitting diode

2009/2010

4



# Types of Solids



Three general types of solids : (a) amorphous, (b) polycrystalline and (c) crystalline



# Amorphous Si

Advantages

- Low temperature deposition (~ 250°C)
- Large Area deposition possible at low cost

Disadvantages

- Low conductivity
- Cannot be used for High speed circuits



#### 2009/2010



# **Uses of amorphous-Si**

# Solar cells

# Thin Film Transistors for LCDs



2009/2010



# polycrystalline-Si

# Gate for MOSFETs

Semiconductor layer for TFTs (recent development)



Polycrystalline silicon has higher conductivity as compared to amorphous silicon.

2009/2010

Department of Microelectronics & Computer Engineering



# Crystal



In a very broad sense crystal means something that repeats

So even a wall paper with a repeating pattern is a crystal !!

2009/2010

Department of Microelectronics & Computer Engineering



# Lattice and unit cell

Lattice : A regular periodic arrangement of points in space as in the arrangement of atoms or molecules in a crystal.

Each point in the lattice is a lattice point. It can be an atom, a group of atoms, an ion or a molecule.

Unit cell : A small volume of a crystal that can be used to reproduce the entire crystal Lattice point



Two dimensional representation of a single crystal lattice



2009/2010

Department of Microelectronics & Computer Engineering



The relationship between the cell and the lattice is characterized by three vectors  $\vec{a}$ ,  $\vec{b}$  and  $\vec{c}$ . These vectors need not to be perpendicular to each other and need not to be of the same length. Every equivalent lattice point in the crystal can be found using the equation –





#### **Basic Crystal Structures**

The easiest 3-D lattice to work with is the simple cubic lattice (SCC) which has lattice points on all the corners of a cube. The Cubic (Isometric) crystal system is characterized by its total symmetry. It has three crystallographic axes that are all perpendicular to each other and equal in length. The cubic system has one lattice point on each of the cube's four corners.





# **Lattice constant**

2009/2010

Department of Microelectronics & Computer Engineering



#### Other crystal structures



Crystal structures which are combinations of these are also possible.

#### 2009/2010







FCC lattice structure has high packing density

See Video and Quiz question on packing density.

Al, Cu, Ni, Pd, Ag, Ce, Pt, Au, Pb...







Also Na, K, V, Cr, Fe, Rb, Nb, Mo, Cs, Ba, Eu, Ta etc. have BCC lattice structure.

SCC

SCC is the most spacious crystal structure with least packing density. So nature does not prefer it !! Almost no naturally occurring crystal has SCC structure.







# Atomium in Brussels has BCC structure !!

#### 2009/2010

Department of Microelectronics & Computer Engineering



## **Hexagonal structure**



The Hexagonal crystal system has four crystallographic axes consisting of three equal horizontal or equatorial (a, b, and d) axes at 120°, and one vertical (c) axis that is perpendicular to the other three. Hexagonal structure is characterized by close packing density.









# Diamond structure

2009/2010

18



#### The Diamond Structure





The tetrahedral structure of closest neighbors in the diamond lattice

The tetrahedral structure is basically a body-centered cubic with four of the corner atoms missing. Every atom in the tetrahedral structure has four nearest neighbors with equal distance. This is the basic building block of the diamond lattice.

2009/2010

Department of Microelectronics & Computer Engineering





Bottom half (a) and top half (b) portions of diamond lattice.

2009/2010

Department of Microelectronics & Computer Engineering



## The Diamond Structure



The diamond structure can also be interpreted as two Interpenetrating FCCs.

See video in course material.

#### 2009/2010

Department of Microelectronics & Computer Engineering



## Zincblend structure in GaAs



Zincblend structure is similar to diamond structure, but atoms in penetrating FCC are different.



#### Crystal plane and Miller Indices

Surface or plane through the crystal can be described by the intercepts of the plane along the a, b and c axes used for the lattice. Reciprocal of these intercepts are called the miller indices.



# **Miller indices**



The plane (a) is parallel to the b and c axes so the intercepts are given as 1, infinite and infinite. Taking reciprocal, we obtain Miller indices as (1,0,0), so the plane is referred to as (100) plane. Any plane parallel to this is equivalent and is referred to as the (100) plane.



For an example on how to find the Miller indices of a plane, refer to example 1.2 in the reference book.

For an example on how to find the surface density of atoms on a particular crystal plane, refer to example 1.3 in the reference book.

2009/2010

Department of Microelectronics & Computer Engineering



## **Atomic Bonding**



2009/2010

Department of Microelectronics & Computer Engineering



## Covalent bonding

$$\widehat{\mathbb{H}}$$
 - -  $\widehat{\mathbb{H}}$   $\widehat{\mathbb{H}}$  =  $\widehat{\mathbb{H}}$   
(a) (b)

Representation of (a) hydrogen valence electrons and (b) covalent bonding in hydrogen molecule



Representation of (a) silicon valence electrons and (b) covalent bonding in the silicon crystal

![](_page_27_Picture_5.jpeg)

|    |    | К               | L                               | Μ  | Ν                               |
|----|----|-----------------|---------------------------------|--|---------------------------------|
| 6  | С  | 1s <sup>2</sup> | 2s <sup>2</sup> 2p <sup>2</sup> |  |                                 |
| 14 | Si | 1s <sup>2</sup> | 2s <sup>2</sup> 2p <sup>6</sup> | 3s <sup>2</sup> 3p <sup>2</sup>                  |                                 |
| 32 | Ge | 1s <sup>2</sup> | 2s <sup>2</sup> 2p <sup>6</sup> | 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> | 4s <sup>2</sup> 4p <sup>2</sup> |

Atomic structure for C, Si and Ge

![](_page_28_Picture_2.jpeg)

Silicon has only 2 unpaired electrons. Then why does Si form 4 covalent bonds?

2009/2010

![](_page_28_Picture_6.jpeg)

![](_page_29_Figure_0.jpeg)

Promotion of one electron from s-orbital to p-orbital to form four orbitals of equal energy is hybridisation. This happens so that all available energy states in the outermost shell are occupied. Else it will lead to instability.

With electrons in two different kinds of orbitals, we cannot get four identical covalent bonds. Hybridisation results in four similar electronis and hence ideantical bonds.

![](_page_29_Picture_3.jpeg)

![](_page_30_Figure_0.jpeg)

#### 2009/2010

![](_page_30_Picture_4.jpeg)

# Valence electron cloud

Orbitals in n=3 shell after hybridisation

The silicon atom in its crystalline surroundings has a similarly shaped electron cloud

![](_page_31_Picture_3.jpeg)

2009/2010

Department of Microelectronics & Computer Engineering

![](_page_31_Picture_6.jpeg)

![](_page_32_Figure_0.jpeg)

Similar hybridisation phenomenon happens in carbon. Above figure is after bonding with Hydrogen in  $CH_4$ .

![](_page_32_Picture_2.jpeg)

# Metallic bonding

![](_page_33_Figure_1.jpeg)

delocalised electrons

Sodium has the electronic structure 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>1</sup>. When sodium atoms come together, the electron in the 3s atomic orbital of one sodium atom shares space with the corresponding electron on a neighbouring atom to form a molecular orbital - in much the same sort of way that a covalent bond is formed.

The difference, however, is that each sodium atom is being touched by eight other sodium atoms (BCC structure) and the sharing occurs between the central atom and the 3s orbitals on all of the eight other atoms. And each of these eight is in turn being touched by eight other sodium atoms and so on. So electrons are shared over a large distance and this makes flow of electrons easy.

This same reason also makes metals malleable !!

![](_page_33_Picture_6.jpeg)

# Van der Waals bond

Effective center of the positive charge is not the same as the negative one, e.g., HF molecule.

The electric dipole interacts with the other dipole.

Inert Gas Elements – He, Ne, Ar, Kr, Xe

![](_page_34_Picture_4.jpeg)

![](_page_34_Picture_5.jpeg)

![](_page_34_Picture_8.jpeg)

# **Hydrogen bonding**

![](_page_35_Figure_1.jpeg)

#### Van der Waal's bonds in water

![](_page_35_Picture_3.jpeg)

Department of Microelectronics & Computer Engineering

![](_page_35_Picture_5.jpeg)

![](_page_36_Picture_0.jpeg)

Diamond is one of the hardest material in nature because covalent bonding is very strong. In graphite, bonding between 2 graphene layers is weak Van der Waals bonding. This makes graphite very soft and graphene layers can be easily separated.

Recently a single layer of graphene has been found to be a promising semiconductor material.

![](_page_36_Picture_3.jpeg)

#### Carbon nanotube (1D crystal)

![](_page_37_Figure_1.jpeg)

Carbon nano-tubes are formed by rolling a single layer of graphene. These are used to make quantum devices !!

2009/2010

Department of Microelectronics & Computer Engineering

![](_page_37_Picture_5.jpeg)

# **Ionic Bond**

![](_page_38_Figure_1.jpeg)

• Bond between two oppositely charged ions.

2009/2010

![](_page_38_Picture_6.jpeg)

# **Imperfections in solids**

Lattice imperfection is any deviation from perfect periodic arrangement of lattice points. Point defects can be in the form of vacancy (missing atom), substitutional impurity (atom replaced by another atom) or interstitial impurity (additional impurity not at lattice point)

![](_page_39_Figure_2.jpeg)

Department of Microelectronics & Computer Engineering

![](_page_39_Picture_5.jpeg)

# **Line Defects**

![](_page_40_Picture_1.jpeg)

Edge dislocation is a type of line defect.

#### 2009/2010

Department of Microelectronics & Computer Engineering

![](_page_40_Picture_5.jpeg)

# **Plane & Volume Defects**

![](_page_41_Picture_1.jpeg)

![](_page_41_Picture_2.jpeg)

# Precipitates are a type of volume defect

Grain boundaries are type of plane defect

2009/2010

41

![](_page_41_Picture_7.jpeg)

## Crystalline defects in semiconductors.

| Defect Type | Examples                                    |
|-------------|---|
| Point       | Vacancies, interstitials, impurity atoms    |
| Line        | Dislocations                                |
| Plane       | Stacking faults, twins and grain boundaries |
| Volume      | Precipitates and voids                      |

Department of Microelectronics & Computer Engineering

![](_page_42_Picture_4.jpeg)

# **Growth of Semiconductor Materials**

- Growth from Melt
- Epitaxial growth

2009/2010

43

![](_page_43_Picture_6.jpeg)

# Czochralski method

![](_page_44_Figure_1.jpeg)

![](_page_44_Picture_2.jpeg)

**Growth from melt** 

Silicon ingot from czochralski process

# Larger diameter , impurity from crucible

#### 2009/2010

Department of Microelectronics & Computer Engineering

![](_page_44_Picture_7.jpeg)

# **µ-Czochralski (Grain-Filter) Process with Excimer-Laser**

![](_page_45_Figure_1.jpeg)

![](_page_45_Picture_2.jpeg)

#### Remnant solid at the Grains formed after bottom crystallisation. acts as a seed

Initially holes which act as seeds are formed by photolithography. Then excimer laser is used to melt silicon. Square shaped grains are formed at the seed locations.

![](_page_45_Picture_5.jpeg)

# **Epitaxial growth**

Single-crystalline layer growth on a single-crystalline substrate with the same crystal structure

Homo-epitaxy Hetero-epitaxy Si on Si Si on SiGe, AlGaAs on GaAs

by means of

Chemical vapor deposition (CVD) Liquid Phase Epitaxy (LPE) Molecular Beam Epitaxy (MBE)

2009/2010

Department of Microelectronics & Computer Engineering

![](_page_46_Picture_7.jpeg)

# **Chemical Vapour Deposition (CVD)**

Used mainly for silicon but also for SiGe, GaN

![](_page_47_Figure_2.jpeg)

## Good for production, safety consideration

Department of Microelectronics & Computer Engineering

![](_page_47_Picture_6.jpeg)

# Liquid Phase Epitaxy (LPE)

![](_page_48_Figure_1.jpeg)

## Used for GaAs, InP, HgCdTe

# High quality compound semiconductors, difficult to monitor

2009/2010

Department of Microelectronics & Computer Engineering

![](_page_48_Picture_6.jpeg)

![](_page_49_Figure_0.jpeg)

Precise growth monitor, high quality (compound) semiconductor layers, slow growth rate

2009/2010

49

![](_page_49_Picture_5.jpeg)

# Floating zone method (for purifying silicon ingot)

![](_page_50_Figure_1.jpeg)

Floating zone method relies on the segregation co-efficient. For this process to be used for purification this coefficient should be less than 1.

2009/2010

Department of Microelectronics & Computer Engineering

![](_page_50_Picture_5.jpeg)

# Segregation coefficient (k<sub>0</sub>)

# Impurity concentration ratio between the solid and liquid

$$k_0 = \frac{C_{Solid}}{C_{Liquid}}$$

2009/2010

Department of Microelectronics & Computer Engineering

![](_page_51_Picture_6.jpeg)

|    | Ko     | D (x 10 <sup>-4</sup> cm <sup>2</sup> /s) |
|----|--------|---|
| В  | 0.8    | 2.4                                       |
| Al | 0.002  | 7.0                                       |
| Ga | 0.008  | 4.8                                       |
| In | 0.0004 | 6.9                                       |
| С  | 0.07   | 2   |
| Ρ  | 0.35   | 2.3                                       |
| As | 0.3    | 3.3                                       |
| Sb | 0.023  | 1.5                                       |
| 0  | 1.40   | 3.3                                       |

Oxygen cannot be removed by floating zone method because its segregation coefficient is more than 1. The diffusion co-efficient (D) determines the speed of purification.

2009/2010

Department of Microelectronics & Computer Engineering

![](_page_52_Picture_4.jpeg)

# Si wafer fabrication

SiO2

Metallic Si

![](_page_53_Picture_3.jpeg)

![](_page_53_Picture_4.jpeg)

 $SiC + SiO2 \rightarrow Si + SiO + CO$ 

Pure poly-Si 99.9999999999%

Pure trichlorosilane

 $Si + 3SiCl4 + 2H2 \rightarrow 4SiHCl3$ 

![](_page_53_Figure_7.jpeg)

## Single-crystalline Si

![](_page_53_Picture_9.jpeg)

![](_page_53_Picture_10.jpeg)

2009/2010

53

![](_page_53_Picture_14.jpeg)