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## Unit III

### Chemistry of Electronic Materials

#### Abstract

This unit focuses on various semiconducting materials used in microelectronic devices. It gives brief overview of inorganic and organic semiconductors and their applications in solid state electronic devices. This unit will also illustrate synthesis and important properties of GaAs, SiGe, InP, fullerenes, pentacene, and polyaniline. A glimpse on data storage and dielectric materials also given to help the students to understand the working of memory storage devices.

Sl No	Topic to be taught	Duration
1	Introduction to inorganic semiconductors, classification of semiconductors; extrinsic and intrinsic semiconductors, n- and p- type semiconductor	1 hour
2	Electronic grade semiconductor production, Czochralski method, working, Float zone method disadvantages	1 hour
3	GaAs, properties, drift velocity, optical property, semi-insulating property and its application,	1 hour
4	SiGe, thermoelectric property, band gap, synthesis and application of SiGe, InP, optoelectronic property, synthesis and application	1 hour
5	Introduction to organic semiconductor, origin of semiconducting property, classification, introduction to pentacene.	1 hour
6	Synthesis, fabrication of thin film, thermal evaporation technique, spin coating and application of pentacene	1 hour
7	Fullerene, synthesis of fullerene derivatives, and application. Conductive polymers, properties of conductive polymers	1 hour
8	Polyaniline, structure of PANI, synthesis of PANI, and application	1 hour
9	Data storage material, principle, dielectric material and application	1 hour

# Inorganic semiconducting materials

## Introduction

Devices in which a controlled flow of electrons can be obtained are the basic building blocks of all the electronic devices. Before the discovery of transistor in 1948, such devices were mostly vacuum tubes (also called valves) like the vacuum diodes. These vacuum tube devices are bulky, consume high power, operate generally at high voltages ( $\sim 100$  V) and have limited life and low reliability. The seed of the development of modern solid-state semiconductor electronics goes back to 1930's when it was realised that some solid-state semiconductors and their junctions offer the possibility of controlling the number and the direction of flow of charge carriers through them. Simple excitations like light, heat or small applied voltage can change the number of mobile charges in a semiconductor. Note that the supply and flow of charge carriers in the semiconductor devices are within the solid itself, while in the earlier vacuum tubes/valves, the mobile electrons were obtained from a heated cathode and they were made to flow in an evacuated space or vacuum. No external heating or large evacuated space is required by the semiconductor devices. They are small in size, consume low power, operate at low voltages and have long life and high reliability.

Inorganic semiconductor materials are commonly used in various fields, such as photovoltaics, photodetectors, light emitting diodes (LEDs), batteries, supercapacitors and photocatalysis. They have attracted significant attention in providing sustainable energy solutions (generation/storage).

Semiconductors can largely be classified as:

- (i) Elemental semiconductors: Si, Ge, and Se
- (ii) Compound semiconductors: Compound semiconductors are further classified as
  - Inorganic: CdS, GaAs, CdSe, InP, etc.
  - Organic: pentacene, fullerene, anthracene, doped phthalocyanines, etc. ·
  - Organic polymers: polypyrrole, polyaniline, polythiophene, etc.

Most of the currently available semiconductor devices are based on elemental semiconductors Si or Ge and compound inorganic semiconductors. However, after 1990, a few semiconductor devices using organic semiconductors and semiconducting polymers have been developed signalling the birth of a futuristic technology of polymer electronics and molecular-electronics.

## Classification of Inorganic Semiconductors

Inorganic semiconductors are broadly classified as;

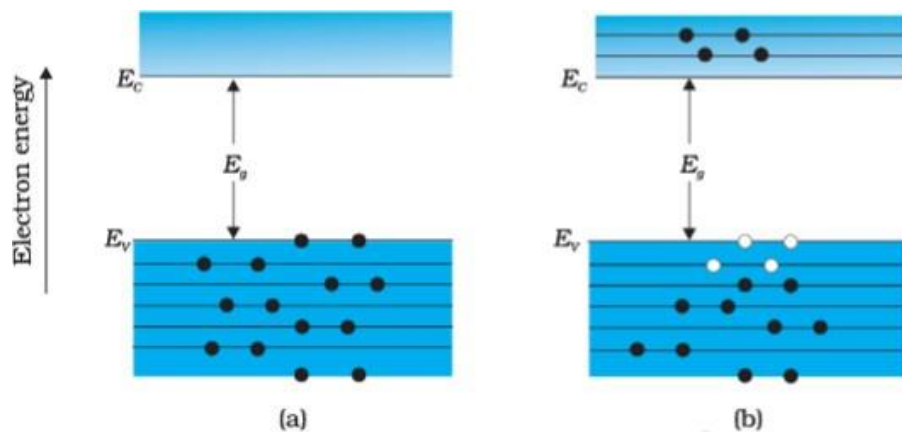
1. **Intrinsic semiconductor**
2. **Extrinsic semiconductors**

### 1. Intrinsic semiconductor

The term intrinsic simply means that there are no impurities in the crystal. We shall take the most common case of Si which has diamond- like structure. Each atom is surrounded by four nearest neighbours. Si and Ge have four valence electrons. In its crystalline structure, every Si or Ge atom tends to share one of its four valence electrons with each of its four nearest neighbour atoms, and also to take share of one electron from each such neighbor. These shared electron pairs are referred to as covalent bond.

In intrinsic semiconductors, the number of free electrons,  $n_e$  is equal to the number of holes,  $n_h$ . That is;  $n_e = n_h = n_i$  where  $n_i$  is called intrinsic carrier concentration.

An intrinsic semiconductor will behave like an insulator at  $T = 0\text{ K}$  as shown in Figure 3.1. It is the thermal energy at higher temperatures ( $T > 0\text{ K}$ ), which excites some electrons from the valence band to the conduction band. These thermally excited electrons at  $T > 0\text{ K}$ , partially occupy the conduction band. Here, some electrons are shown in the conduction band. These have come from the valence band leaving equal number of holes there.



**Figure 3.1** (a) An intrinsic semiconductor at  $T = 0\text{ K}$  behaves like insulator (b) At  $T > 0\text{ K}$ , four thermally generated electron-hole pairs. The filled circles (.) represents electrons and empty circles (o) represent holes.

### 2. Extrinsic Semiconductors

The conductivity of an intrinsic semiconductor depends on its temperature, but at room temperature its conductivity is very low. As such, no important electronic devices can be

developed using these semiconductors. Hence there is a necessity of improving their conductivity. This can be done by making use of impurities. When a small amount, say, a few parts per million (ppm), of a suitable impurity is added to the pure semiconductor, the conductivity of the semiconductor is increased manifold. Such materials are known as extrinsic semiconductors or impurity semiconductors. The deliberate addition of a desirable impurity is called doping and the impurity atoms are called dopants. Such a material is also called a doped semiconductor. The dopant has to be such that it does not distort the original pure semiconductor lattice.

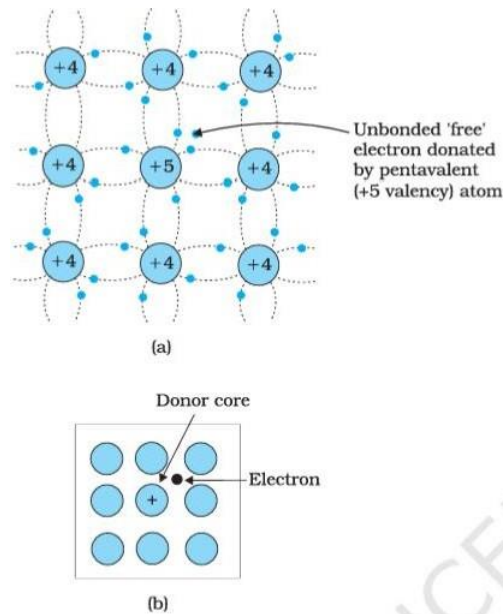
There are two types of dopants used in doping the tetravalent Si or Ge:

- (i) Pentavalent (valency 5); like Arsenic (As), Antimony (Sb), Phosphorous (P), etc.
- (ii) Trivalent (valency 3); like Indium (In), Boron (B), Aluminium (Al), etc.

Interestingly, the pentavalent and trivalent dopants in Si or Ge give two entirely different types of semiconductors as discussed below.

#### **i) n-type semiconductor**

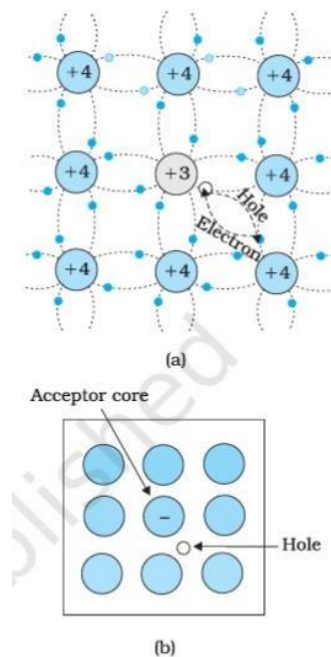
Suppose we dope Si or Ge with a pentavalent element as shown in Figure 3.2. When an atom of +5 valency element occupies the position of an atom in the crystal lattice of Si, four of its electrons bond with the four silicon neighbours while the fifth remains very weakly bound to its parent atom. This is because the four electrons participating in bonding are seen as part of the effective core of the atom by the fifth electron. As a result, the ionisation energy required to set this electron free is very small and even at room temperature it will be free to move in the lattice of the semiconductor. For example, the energy required is  $\sim 0.01$  eV for germanium, and 0.05 eV for silicon, to separate this electron from its atom. This is in contrast to the energy required to jump the forbidden band (about 0.72 eV for germanium and about 1.1 eV for silicon) at room temperature in the intrinsic semiconductor. Thus, the pentavalent dopant is donating one extra electron for conduction and hence is known as donor impurity. The number of electrons made available for conduction by dopant atoms depends strongly upon the doping level and is independent of any increase in ambient temperature. On the other hand, the number of free electrons (with an equal number of holes) generated by Si atoms, increases weakly with temperature. In a doped semiconductor the total number of conduction electrons  $n_e$  is due to the electrons contributed by donors and those generated intrinsically, while the total number of holes  $n_h$  is only due to the holes from the intrinsic source. In an extrinsic semiconductor doped with pentavalent impurity, electrons become the majority carriers and holes the minority carriers. These semiconductors are, therefore, known as n-type semiconductors. For n-type semiconductors, we have,  $n_e \gg n_h$



**Figure 3.2** (a) Pentavalent donor atom (As, Sb, P, etc.) doped for tetravalent Si or Ge giving ntype semiconductor, and (b) Schematic representation of n-type material which shows only the fixed cores of the substituent donors with one additional effective positive charge and its associated extra electron.

## ii) p-type semiconductor

This is obtained when Si or Ge is doped with a trivalent impurity like Al, B, In, etc. The dopant has one valence electron less than Si or Ge and, therefore, this atom can form covalent bonds with neighboring three Si atoms but does not have any electron to offer to the fourth Si atom. So the bond between the fourth neighbor and the trivalent atom has a vacancy or hole as shown in Figure 3.3. Since the neighbouring Si atom in the lattice wants an electron in place of a hole, an electron in the outer orbit of an atom in the neighborhood may jump to fill this vacancy, leaving a vacancy or hole at its own site. Thus the hole is available for conduction. Note that the trivalent foreign atom becomes effectively negatively charged when it shares fourth electron with neighboring Si atom. Therefore, the dopant atom of p-type material can be treated as core of one negative charge along with its associated hole. It is obvious that one acceptor atom gives one hole. These holes are in addition to the intrinsically generated holes while the source of conduction electrons is only intrinsic generation. Thus, for such a material, the holes are the majority carriers and electrons are minority carriers. Therefore, extrinsic semiconductors doped with trivalent impurity are called p-type semiconductors. For p-type semiconductors, the recombination process will reduce the number ( $n_i$ ) of intrinsically



**Figure 3.3** (a) Trivalent acceptor atom (In, Al, B etc.) doped in tetra-valent Si or Ge lattice giving p-type semiconductor. (b) Schematic representation of p-type material which shows only the fixed core of the substituent acceptor with one effective additional negative charge and its associated hole.

generated electrons to  $n_e$ . We have, for p-type semiconductors  $n_h \gg n_e$

### Production of Electronic Grade Silicon (EGS)

The synthesis and purification of bulk polycrystalline semiconductor material represents the first step towards the commercial fabrication of an electronic device. This polycrystalline material is then used as the raw material for the formation of single crystal material that is processed to semiconductor wafers.

The most frequently used and most important method of producing bulk single crystals of Si is by solidifying the material from its melt. This is commonly called as melt growth. Following are the two different crystal growth techniques used for production of EGS;

1. Czochralski method
2. Float zone method

#### 1. Czochralski method

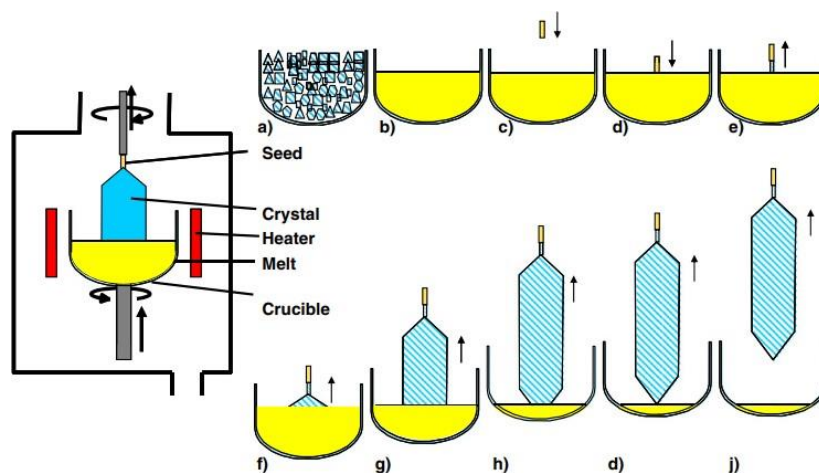
The Czochralski (Cz) method is a technique for growing single-crystal silicon ingots for use in manufacturing semiconductor devices. The finished crystals are called boules. The boules are later sliced into very thin, circular wafers and then diced into the little silicon chips from which large scale integrated circuits are made.

## Requirements

1. Furnace: It includes fused silica crucible ( $\text{SiO}_2$ ), a graphite susceptor, a rotation mechanism (clockwise), heating element and power supply.
2. A crystal pulling mechanism: It includes a seed holder and a rotation mechanism counter clockwise.
3. Ambient control: It is very important in growth system. There must not be any oxygen inside the system. The graphite susceptor and graphite heater will react with oxygen to form  $\text{CO}_2$ . It should not react with Si. Therefore, oxygen should be removed from the chamber and fill it with Argon. It includes gas source, a flow control & an exhaust system.
4. Control system: A puller has microprocessor based control system to control the process parameters such as temperatures, crystal diameter, pull rate & rotation speed.

## Working

At the beginning of the process, the feed material is put into a cylindrically shaped crucible and melted ( $1410^\circ\text{C}$ ) by resistance or radio-frequency heater. After the feed material is completely molten a seed crystal with a diameter of typically a few mm is dipped from shaft into the free melt surface and a small portion of the dipped seed is melted. The shaft rotates counter clockwise and the crucible rotates clockwise. Then, the seed is slowly withdrawn from the melt and the melt crystallizes at the interface by forming a new crystal portion. During the further growth process, the shape of the crystal, especially the diameter, is controlled by carefully adjusting the heating power, the pulling rate and the rotation rate of the crystal. The most important technical application of the Cz method is the growth of dislocation free silicon.



**Figure 3.4** Schematic of the principle of the Czochralski method (left) and illustration of the different steps(a-j) of the Cz process for growing a Si crystal. a) The polycrystalline feedstock is melted (b) in a crucible. (c,d) Seeding procedure: The seed crystal is dipped in to

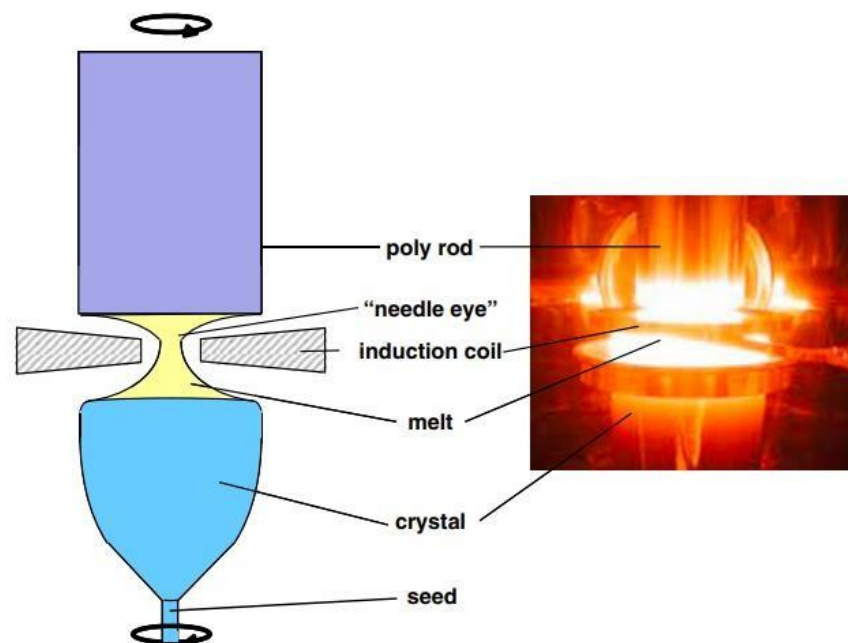
the melt, followed by Dash necking (e),shouldering (f),cylindrical growth(g),growth of end cone (h),lift off (i),cooling down and removing of the crystal (j).

crystals with diameters up to 300 mm and a weight up to 300 kg in industrial production.

### Float Zone (FZ) Method

Even though the Cz process is commonly used for commercial substrates, it has several disadvantages for high efficiency laboratory or niche market solar cells. Cz wafers contain a large amount of oxygen in the silicon wafer. Oxygen impurities reduce the minority carrier lifetime in the solar cell, thus reducing the voltage, current and efficiency. In addition, the oxygen and complexes of the oxygen with other elements may become active at higher temperatures, making the wafers sensitive to high temperature processing. To overcome these problems, Float Zone (FZ) wafers may be used.

The FZ technique is a crucible-free crystal growth method. In FZ growth, the molten zone is kept between two vertical solid rods by its own surface tension (Figure 3.5). The FZ process is started by dipping a seed crystal into one end of the molten zone. Then the molten zone is moved towards the feed rod and at the other zone end the crystal is growing. The main advantage of the FZ technique is the absence of a container which avoids any contamination by the crucible material. Furthermore, the generation of crystal defects caused by an interaction between the growing crystal and the container is avoided.



**Figure 3.5** Schematic principle (left) and photography (right) of the floating zone method for growing Si crystals.



### **Disadvantage of FZ**

The float zone method is very limited in the size of crystals that the system can grow. FZ wafers can only grow to 200 millimeters in diameter due to surface tension in the molten silicon. This limitation confines the resulting wafers into specific applications.

### **Gallium Arsenide (GaAs)**

GaAs has a wide usage area starting from microwave frequency integrated circuits to optical windows. Among III-V semiconductors, GaAs has remained attractive as a semiconductor material, widely being used in optoelectronic and microelectronic devices.

GaAs is an extremely poor conductor due to low intrinsic carrier density when present in an undoped or pure form. Hence it is mostly considered as semi-insulating. Adding the dopants of either the p- or the n-type impurity atoms alter this property. Many active devices have been able to be made on a single substrate due to this semi-insulating property, where each device's electrical isolation is provided by the GaAs.

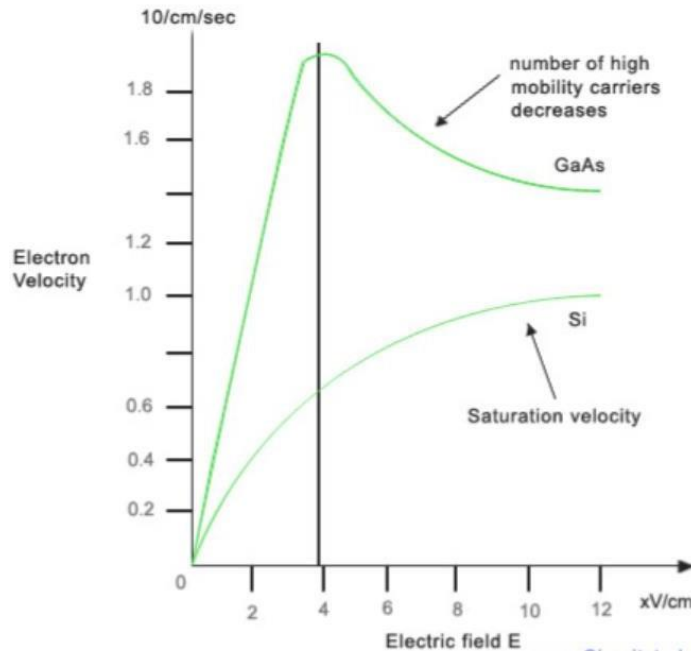
GaAs adopts fcc cubic symmetry, this crystal configuration is known as cubic sphalerite or zinc blende.

### **Properties of GaAs**

#### **Mobility and Drift Velocity**

GaAs has several advantages over silicon for operation in the microwave region primarily, higher mobility and saturated drift velocity and the capability to produce devices on a semi-insulating substrate.

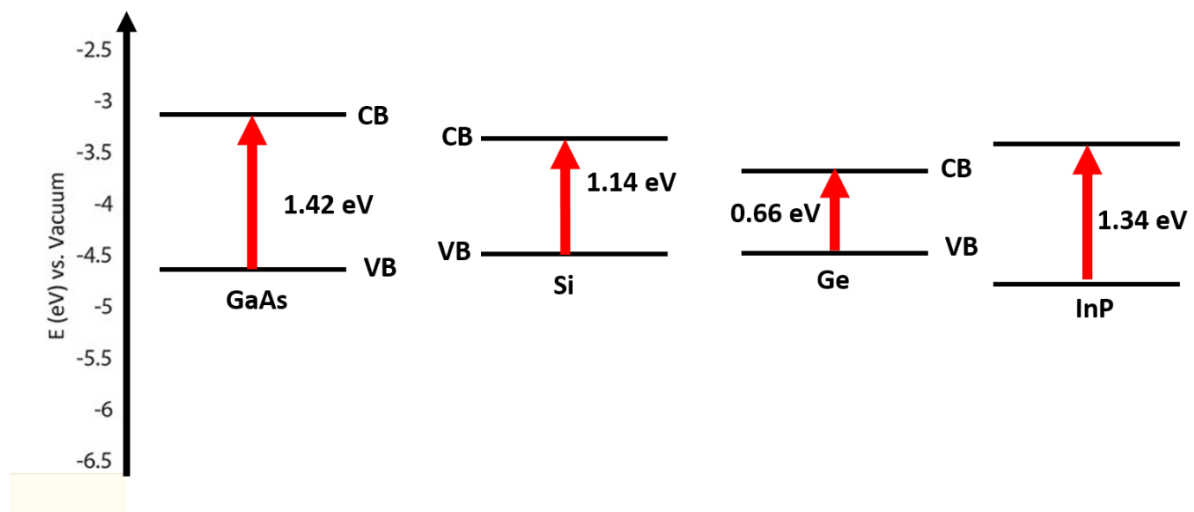
In a semiconductor, when a carrier (an electron) is subjected to an electric field, it will experience a force ( $F = -qE$ ) and will be accelerated along the field. During the time between collisions with other carrier ions and the semiconductor lattice, the carrier will achieve a velocity that is a function of the electric field strength. This velocity is defined as the drift velocity ( $v$ ). From the conservation of momentum, it can be shown that the drift velocity ( $v$ ) is proportional to the applied electric field (Figure 3.6). For convenience of comparison, characteristics for silicon are also illustrated. From the figure 3.6 it can readily be noted that in low electric field regions, silicon has a much lower mobility than gallium arsenide. This increases monotonically until the drift velocity saturates at a value of about  $1 \times 10^7$  cm/sec.



**Figure 3.6** Electron Velocity Field vs Electric Field.

### Optical properties

GaAs is a direct band gap semiconductor (1.42 eV), which means that the minimum of the conduction band is directly over the maximum of the valance band (Figure 3.7). Transitions between the valance band and the conduction band require only a change in energy, and no change in momentum, unlike indirect band-gap semiconductors such as silicon (Si). This property makes GaAs a very useful material for the manufacture of light emitting diodes and semiconductor lasers, since a photon is emitted when an electron changes energy levels from the conduction band to the valance band.



**Figure 3.7** Energy band diagram for GaAs, Si, Ge, InP.

## **Semi Insulating (SI) Property**

Semi-insulating semiconductor crystals have long been used for integrated circuit technology because high-resistivity substrates replace the function of the oxide in silicon devices to isolate discrete devices or layers within an integrated circuit. Common examples of semi-insulating semiconductors are chromium-doped GaAs (GaAs:Cr) and GaAs with native defects. These semi-insulating materials are formed by either intentional doping with transition metal impurities during growth from the melt, or by relying on the formation of native defects during crystal growth.

SI GaAs is mostly used as a substrate for the devices made by ion implantation method since it reduces parasitic capacitances.

The suitable properties of the SI substrates are;

1. High electrical resistivity
2. High carrier mobility
3. High thermal stability: No degradation of active layer properties by outdiffusion of impurities from substrate during thermal processing.
4. Lowest possible density of crystalline defects, such as dislocations, stacking faults, and precipitates.

GaAs bulk resistivity can range from  $10^{-6} \Omega \text{ cm}^{-1}$  to about  $10^{22} \Omega \text{ cm}^{-1}$ . This high resistivity is about six orders of magnitude greater than that of silicon and provides excellent isolation and substrate insulation. Undoped GaAs can be made semi-insulating by the addition of either oxygen or chromium to the melt during crystal growth.

## **Application of GaAs**

### **1. High-Frequency Technology Applications**

The electrons in GaAs wafers are accelerated at an increased speed, requiring lesser time to travel the transistor channel. GPS, PCS, WLAN, and mobile communications require working at high frequencies, which could not be accomplished by using silicon or germanium wafers.

In addition, GaAs offers a wider range of operating temperatures, allowing it to be used in smaller spaces with much less energy dissipated compared to other materials. This makes it an ideal choice for many applications such as radio frequency (RF) and microwave components, high-speed digital circuits, laser diodes, and more.

### **2. Transistors and Computers**

A GaAs wafer is widely used in transistors and computers. Although its physical and chemical properties complicate its application in the fabrication of transistors by

being a binary composite with lower thermal conductivity, its speed and performance make up for it. Electrons travel faster in GaAs than they do in silicon, allowing faster and better computing.

### **3. Defence and Aerospace**

GaAs has been used in military and aerospace applications, like radars, secure communications, and sensors. It allows circuits to perform at higher frequencies. GaAs is highly resistant to radiation which makes it suitable for space exploration.

In addition, the low cost and ease of fabrication make it a great choice for cost-effective, energy-efficient components. All of these benefits make GaAs an ideal material for electronic components and devices. With its superior properties, GaAs is a great choice for creating cost-effective and energy-efficient solutions with excellent performance. The lower noise figures of GaAs reduce the filtering requirements as well as provides compact circuit design in full duplex analog cell phones.

### **Silicon Germanium**

Silicon-germanium ( $\text{Si}_{1-x}\text{Ge}_x$ ) alloys have been researched since the late 1950s, but it is only in the past 30 years or so that these layers have been applied to new types of transistor technology.  $\text{Si}_{1-x}\text{Ge}_x$  was first applied in bipolar technologies, but more recently has been applied to metal-oxide-semiconductor (MOS) technologies.

Silicon and germanium are completely miscible over the full range of compositions and hence can be combined to form  $\text{Si}_{1-x}\text{Ge}_x$  alloys with the germanium content,  $x$ , ranging from 0 to 1 (0 -100%).  $\text{Si}_{1-x}\text{Ge}_x$  has a diamond-like lattice structure.

### **Thermoelectric property**

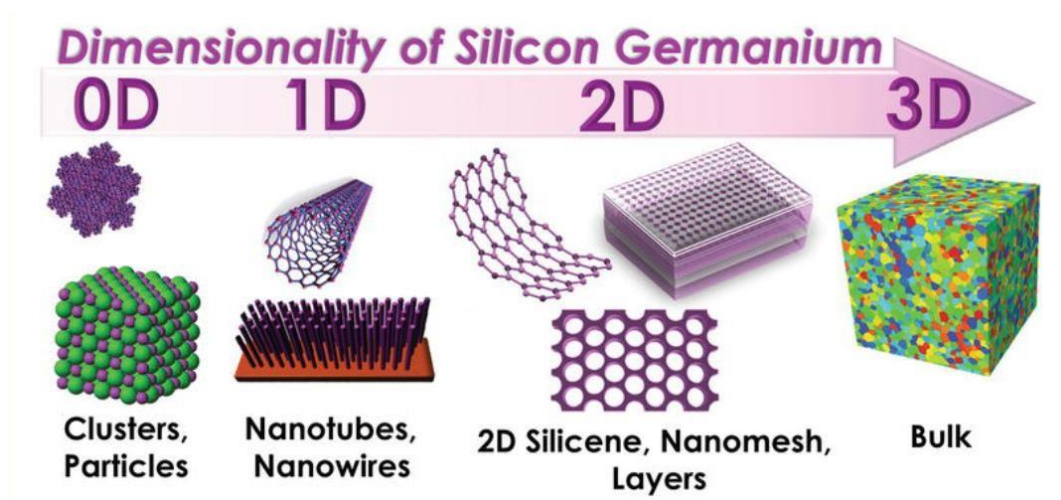
Although silicon is mainly associated with microchip devices and advances in computing, the SiGe alloy can be used as a thermoelectric material, which is, in the presence of a gradient of temperature, able to generate an electrical voltage and *vice versa*. Thermoelectric materials are those materials which transform heat into electricity. It depends primarily on thermoelectric material figure of merit, known as  $zT$ .

$$zT = \frac{S^2 \sigma}{\kappa} T$$

Where,  $zT$  – Figure of merit,  $S$  – Seebeck coefficient,  $T$  – temperature,  $\sigma$  – electrical conductivity,  $\kappa$  – thermal conductivity.

The voltage is produced by the Seebeck coefficient ( $S$ ). In addition, a low electrical resistivity  $\rho$  (or high electrical conductivity  $\sigma$ ) and low thermal conductivity  $\kappa$  is required for high efficiency.

SiGe devices can operate at temperatures up to about 1050°C without significant degradation. For high-temperature applications (above 600°C), SiGe alloys have a high thermoelectric efficiency and the carrier concentration in SiGe can be controlled by doping with phosphorous ( $n$ -type) or boron ( $p$ -type). SiGe used as thermoelectric conversion material has accumulated over 250 million devices working hours in space applications (running for over 40 years in Voyager missions) without failure. Different nanostructured SiGe are used to improve the efficiency of thermoelectric property (Figure 3. 8).



**Figure 3.8** One of the strategies that has been proven to be useful in improving thermoelectric performance is to reduce dimensionality. Here, different configurations that the silicon-germanium has been fabricated.

Silicon-germanium thin films can be easily  $p$ - or  $n$ -type doped at room temperature when the material is amorphous. Nevertheless, doping is particularly difficult when the material is crystalline, given that it is usually crystallized at high temperatures. Therefore, the main challenge with these  $\text{Si}_x\text{Ge}_{1-x}$  alloys, which are to be applied in large-scale practical applications, has not yet been overcome due to the difficulties in the growth of high-quality, highly crystalline, low-cost, and appropriately doped films.

### Band gap

SiGe is an indirect bandgap semiconductor and has narrower band gap than Silicon. The primary property of  $\text{Si}_{1-x}\text{Ge}_x$  i.e the band gap, controllable by varying the germanium content.

## **Application**

### **1. Space industry**

Si–Ge type alloys have aided as the desired material for thermoelectric conversion in thermoelectric generator (RTG) power systems for deep space planetary voyaging missions.

### **2. Automotive industry**

Si–Ge proved to have ideal rectifier performance by automobile industries and designers of varied systems working at elevated temperatures for better efficiency.

### **3. Electronics and telecommunication industry**

The Si–Ge heterojunction bipolar transistor (HBT), happens to be the foremost realistic bandgap-engineered gadget to be accomplished in the silicon material system.

### **4. Solar Industry**

Si–Ge possess both an elevated electron and hole mobility than Si, *i.e.*, with less energy loss and 4×faster carrier mobility in comparison to single crystal silicon; it can be utilized for enhanced processing power, reduced dimension, and power fetching for a unit of similar size.

### **5. Optical interconnects**

SiGe detectors offer high speeds (10 Gb/s and greater), high sensitivity, a broad detection spectrum, and the potential for optical interconnects in next generation ICs to overcome bottlenecks inherent in conventional microelectronic devices.

## **Indium Phosphide**

Group IIIA phosphide nanocrystalline semiconductors are of great interest among the important inorganic materials because of their large direct band gaps and fundamental physical properties. Their physical properties are exploited for various potential applications in high-speed digital circuits, microwave and optoelectronic devices. Compared to II–VI and I–VII semiconductors, the IIIA phosphides have a high degree of covalent bonding, a less ionic character.

## **Optoelectronic property**

InP is extensively used for photoluminescent applications. Photoluminescence (PL) is an optical phenomenon that semiconductors give light emissions by absorbing incident light whose energy is higher than the energy band gap of the semiconductor. Indium phosphide (InP)-based quantum dots (QDs) constitute one of the most promising compound types for display applications because;

1. Optical band gap can cover whole visible wavelengths by controlling the size.

2. Free from toxicity issues compared with Cd- and Pb-containing QD materials.

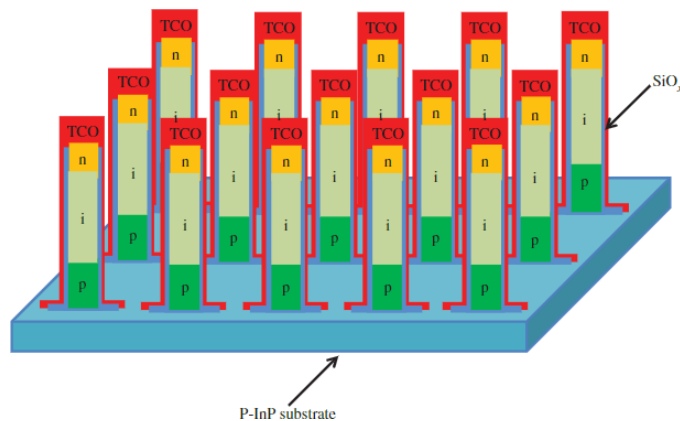
Optical band gap of InP is found to be 1.35 eV. InP emits light in the visible as well as Near infra-red (NIR) region. The band gap of InP is optimum for solar energy conversion.

Electronic property of the InP semiconductor can be easily engineered by the formation of heterojunction. Among different heterojunctions, InP/ZnS, InP/ZnSe, and InP/Graphene are most commonly used for light display, solar cell, photocatalytic and other optoelectronic applications.

## Applications of InP

### 1. InP nanowire-based solar cells

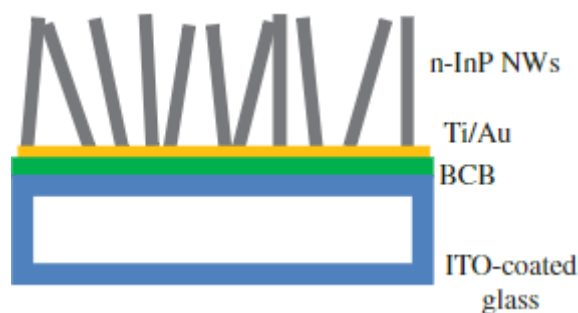
Photovoltaic device fabrication using core-shell p-n junction InP NWs array is used for solar cells. InP NW-based solar cells exhibited the record efficiency of 13.8% (Figure 3.9).



**Figure 3.9** Pictorial representation of InP NWs array solar cell.

### 2. Indium phosphide-polymer hybrid as photodiode

In order to increase the carrier collection efficiency and to eliminate the need for expensive substrate, InP NW-polymer photodiode grew on ITO substrate used in photodiodes (Figure 3.10).

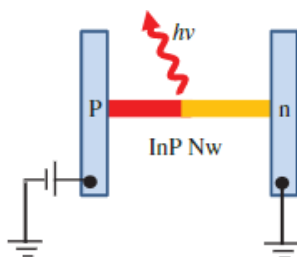


**Figure 3.10** Schematic of InP NW-polymer hybrid device.

### 3. Indium phosphide nanowires as light-emitting diodes

Schematic of InP NW LED is shown in figure 3.11. Individual InP NW devices, in

forward bias, exhibited highly polarized light emission from p-n junctions.



**Figure 3.11** Schematic illustration of InP NW LED.

#### **4. Field effect transistors**

ZnS-sensitized InP NWs were then used in the fabrication of FETs, which exhibited p-type transistor performance.

#### **5. Bioimaging**

CdSe QDs were extensively used for bioimaging due to optical/chemical thermal stability. However, due to the toxicity of Cd, InP found application in the bioimaging. Conjugated MAA capped InP QDs with folic acid in overexpressing tumour cells in human oral epidermoid carcinoma cells.

### **Organic semiconductors**

Organic semiconductors are a class of materials that combine the electronic advantages of semiconducting materials with the chemical and mechanical benefits of organic compounds such as plastics. Thus, the ability to absorb light, conduct electricity, and emit light is united with a material structure that can easily be modified by chemical synthesis, for example, to tailor electronic properties such as the desired emission wavelength, to render it soluble, or to allow for mechanically robust, lightweight, and flexible thin films.

The term organic semiconductors imply that the materials are mostly made up by carbon and hydrogen atoms, with a few heteroatoms such as sulfur, oxygen, and nitrogen and they show properties typically associated with a semiconductor material. The conductivity of organic semiconductors is extrinsic and results from the injection of charges at electrodes, from intentional or unintentional doping and from the dissociation of photogenerated electron-hole pairs that are bound by their mutual coulombic attraction.

#### **Origin of semiconducting property in organic molecules**

Organic semiconductor molecules have conjugated structures with alternating single and double bonds of carbon-carbon bonds. The molecules have  $\pi$ -orbitals delocalized and this orbital delocalization allows electrons to move within a molecule. In organic semiconductors, molecules are linked to each other by comparatively weak van der Waals interactions.



Therefore, electrons are largely localized to individual molecules except electrons in the  $\pi$  orbital, and the weak intermolecular interactions cause a narrow electronic bandwidth in molecular solids. As the interaction between  $\pi$  orbitals increases the degree of  $\pi$ - $\pi$  overlap increases. This condition is favourable for the formation of energy bands. The energy gap between highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbital (LUMO) creates energy gap as similar to the valence band and the conduction band in inorganic semiconductor.

Following are the three varieties of organic semiconductors:

### **1. Amorphous molecular films**

Organic molecules deposited as an amorphous film through evaporation or spin-coating. Thin amorphous films of molecules are employed for device applications such as LEDs, and molecularly doped polymer (MDP) films are used on a large technological scale in xerography.

### **2. Molecular crystals**

By definition, a crystal consists of a lattice and a basis. The molecules such as naphthalene or anthracene can form the basis of a crystal that is held together by van-der-Waals interactions. The charge mobilities that can be obtained in molecular crystals are high compared to those in noncrystalline organic materials. This renders them relevant for transistor applications.

Typical crystal-forming molecules are aromatic molecules such as the polyacenes, in particular naphthalene, anthracene, tetracene, and pentacene, as well as pyrene, perylene, and similar compounds.

### **3. Polymer films**

Polymers may be considered a chain of covalently coupled molecular repeat units. Usually, they are processed from solution, which allows for a range of deposition techniques including simple spin-coating, ink-jet deposition, or industrial reel-to-reel coating. They are also more suitable to blending than molecules since polymer blends are thermodynamically more stable and less susceptible to crystallization.

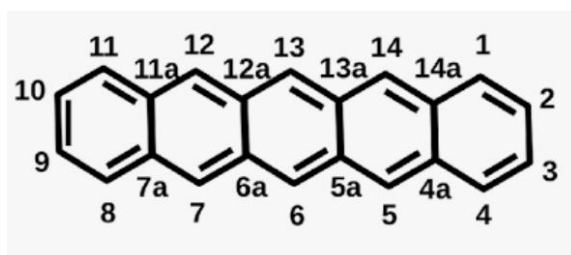
We shall discuss some of the examples of organic semiconductors;

#### **Pentacene**

Pentacene is known for its potential to build highly ordered organic thin films depending on

the substrate and the growth conditions making it one of the best candidates for organic thin film transistors (OTFTs).

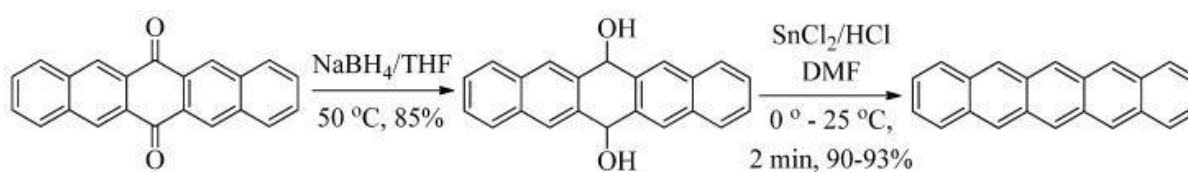
Pentacene is a type of acene molecule consisting of five linearly fused benzene rings (Figure 3.12). Pentacene forms bulk crystals (molecular crystal) with herringbone structure in which the face of one molecule is close to the edge of another. The delocalization of electrons occurs through the overlap between  $\pi$  orbitals along the molecular chains within a molecule. The bulk solid consists of a stack of these layers. Pentacene adopts triclinic lattice structure.



**Figure 3.12** Pentacene structure with carbon numbering.

### Synthesis

Solid  $\text{NaBH}_4$  was slowly added to a round bottom flask containing a suspension of pentacene-6,13-dione in THF at  $0^\circ\text{C}$ . After the addition of  $\text{NaBH}_4$  was complete, the reaction vessel was purged with  $\text{N}_2$  and water was added. The reaction mixture was heated to 50 to  $60^\circ\text{C}$  until homogeneous. After two hours of heating, THF was evaporated at reduced pressure, water was added, and the reaction mixture was filtered. The solids were washed with copious amounts of water. After drying, a white solid was recovered (85% yield) consisting of 6,13-dihydroxy-6,13-dihdropentacene (Scheme 3.1).



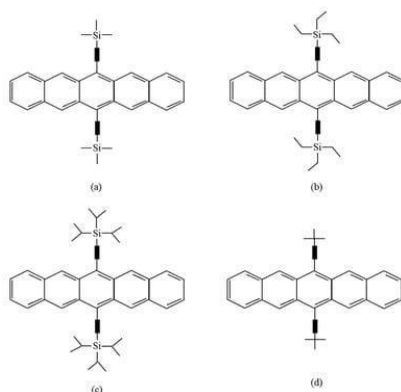
**Scheme 3.1** Synthesis of pentacene

Obtained 6,13-dihydro-6,13-dihydroxypentacene was stirred with  $\text{SnCl}_2$  (1:2 mole ratio) in acetone. The resulting crude pentacene was isolated by centrifuge, and washed with both methanol and THF. Purification by sublimation resulted in pure pentacene in 60% overall yield from 6,13-dihydro-6,13-dihydroxypentacene.

### Fabrication of thin film

Pentacene is sensitive to ambient air (moisture and oxygen) and has low solubility, making it unstable when used with common fabrication techniques. Thus, pentacene should only be deposited using evaporation techniques to fabricate thin films for electronic devices. It is

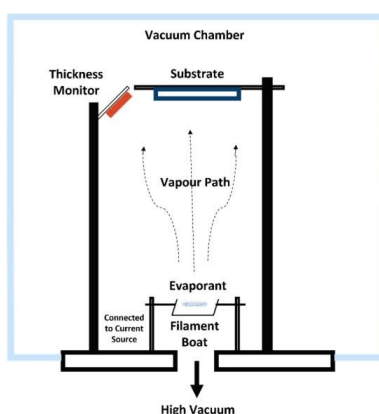
energy intensive process. To overcome this issue, substituents are introduced onto the aromatic core (Figure 3.13), which increases the stability and solubility of the pentacene. It can also improve the electrical properties due to the self-assembly of pentacene moieties, which causes them to be packed closely together.



**Figure 3.13** Structures of pentacene derivatives: (a) trimethylsilyl (TMS) pentacene; (b) triethylsilyl (TES) pentacene; (c) triisopropylsilyl (TIPS) pentacene (d) t-butyl pentacene.

### Thermal evaporation technique

Organic molecular beam deposition (OMBD), one of the thermal evaporation techniques is frequently used to produce high quality thin films of pentacene. It uses high to ultra-high vacuum ( $10^{-6}$ – $10^{-12}$  Torr) to evaporate the material (evaporant). The substrate is to be placed parallel to the sublimed molecules inside a vacuum chamber and a semiconductor layer is formed on the substrate. The advantage of this technique is the efficient control of the growth



**Figure 3.14** Thermal evaporation method.

conditions of the molecule film on the substrate. This means that the thin film produced on the substrate is in a well-ordered condition. The common thermal vacuum evaporation method is illustrated in Figure 3.14.

### Spin coating method

Spin coating is one of the most used methods in academic studies, as well as in industry, due to its capability for mass production at cheaper costs. It is also easier to perform as it only requires a few drops of solution (Figure 3.15).

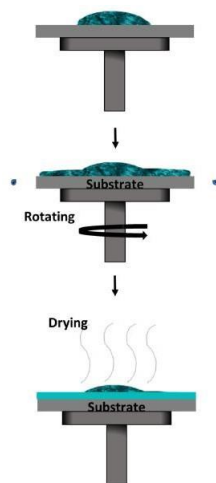
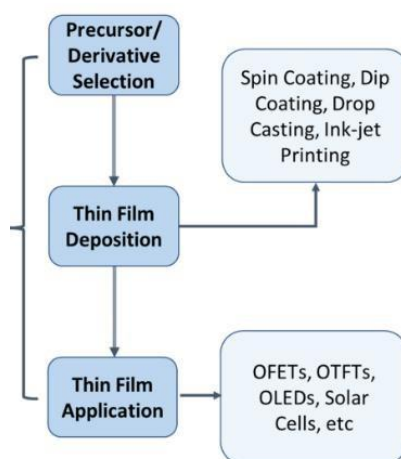


Figure 15. Spin coating method.

**Figure 3.15** Spin coating method.

The solution is dropped on top of a substrate that is held onto a chuck within the spin coater, as illustrated in Figure 3.15. The spinning process starts with a certain acceleration rate and remains at a constant speed for a period of time. Upon completion, the desired thin film will form via a combination of evaporation processes and liquid flow.



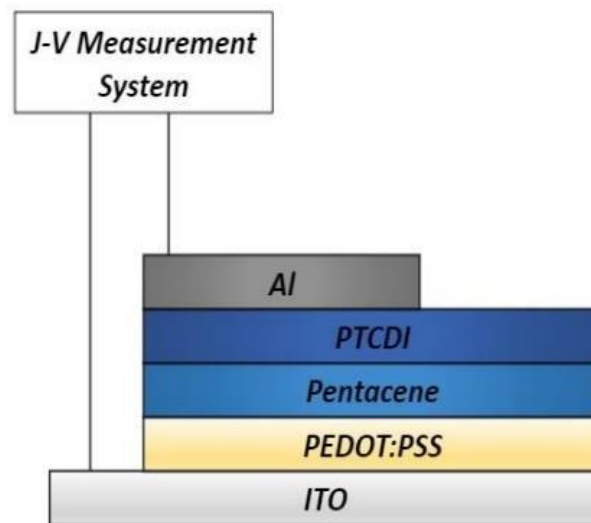
**Figure 3.16** Pentacene thin film deposition and applications.

## Application of Pentacene

### 1. Pentacene in Solarcell

Solar cell was fabricated with the use of pentacene as part of their active layer. The pentacene was stacked with perylene tetracarboxylic di-imide (PTCDI) to form a donor–acceptor solar cell. This was performed by depositing the pentacene layer beforehand onto a PEDOT–PSS layer via thermal evaporation at a pressure of  $3 \times 10^{-7}$  Torr with a deposition rate of  $1 \text{ \AA s}^{-1}$

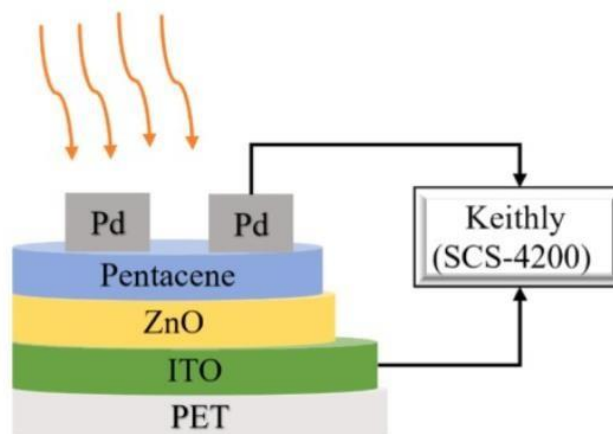
to obtain 50 nm of pentacene. PTCDI measuring 50 nm in thickness was later deposited on top of the pentacene. Figure 3.17 shows an illustration of the solar cell structure.



**Figure 3.17** Illustration of the solar cell's schematic structure.

## 2. Photodetector

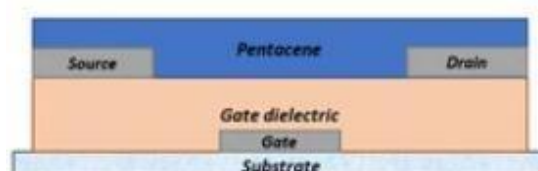
Flexible pentacene heterojunction are used for photodetector. Pd/Pentacene/ZnO/ITO is used as a flexible photodetector.



**Figure 3.18** Schematic diagram of Pd/Pentacene/ZnO/ITO photodetector device.

## 3. Organic thin film transistor

Pentacene is commonly employed in organic thin transistors and organic field effect

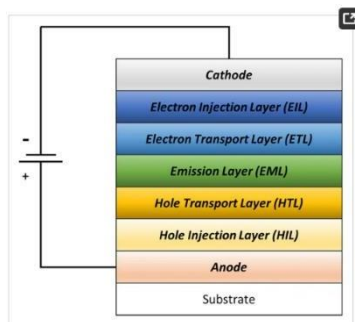


**Figure 3.19** Schematic illustration of Pentacene thin film transistor (TFT).

transistors because of its high mobility (Figure 3. 19).

#### 4. OLED

Pentacene with thickness of 4-8 nm found to show increased current efficiency of the device (OLED). Structure of the device is as follows;

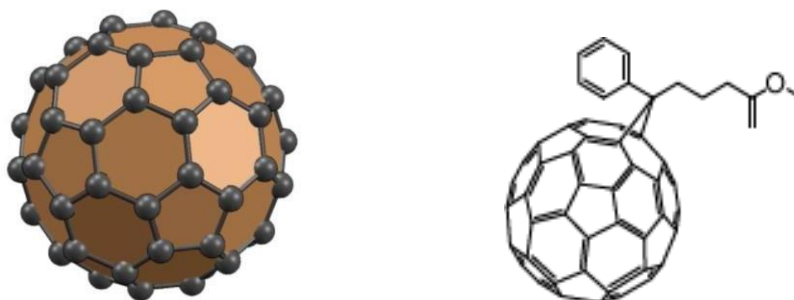


**Figure 3.20** Schematic of multilayers of an OLED structure.

#### Fullerenes

Fullerene is an allotrope of carbon. A fullerene is any series of hollow carbon molecules that form either a closed cage, as in a buckyball, or a cylinder, like a carbon nanotube. Fullerene molecules are named according to the number of carbon atoms in the structure. The most commonly created fullerene is the  $C_{60}$  molecule. It is also termed as Buckminsterfullerene. It has been named after an American architect Buckminster. The fullerene  $C_{60}$  is composed of 60 carbon atoms and has a diameter of  $7.09 \text{ \AA}$ .

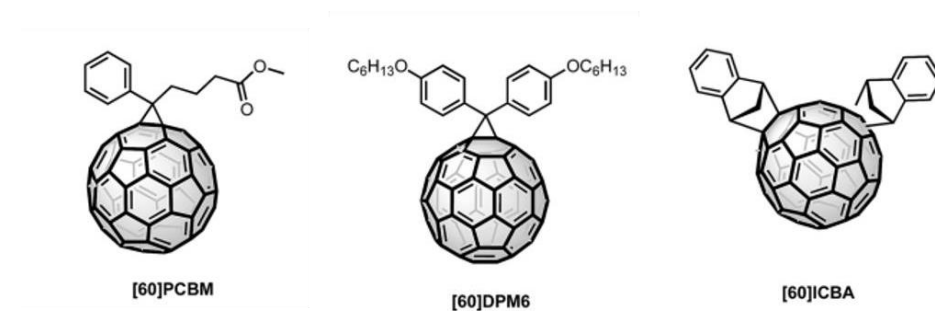
Fullerene is in the shape of a truncated icosahedron or the shape of a soccer ball. Each vertex contains one carbon atom and each carbon atom has a double bond with one other carbon atom and two single bonds with other atoms. In every fullerene, the hollow cage structure contains twelve pentagons. We can, to a first approximation, think of the  $C_{60}$  molecule as a "rolled-up" graphene sheet (a single layer of crystalline graphite).



**Figure 3.21** depicts the structure of fullerene and fullerene derivative PCBM.

Fullerenes have unique properties that make them good candidates as electron acceptors in the construction of photo induced charge transfer systems. Due to their low energy and triply degenerate LUMO orbital, they can accept electrons easily. Another important property is that their reorganization energy upon reduction is very low because of their rigid spherical

geometry and electron delocalization through the whole molecule. According to Marcus' theory of electron transfers the low reorganization energy favours charge separation while slowing down the charge recombination, thus leading to long lived charge separated states. Therefore, many fullerene and fullerene derivatives have been studied as electron acceptor materials as has the coupling through covalent bonding of the electron donor moieties and the fullerene to produce molecular dyads. C<sub>60</sub>-derivatives have been largely employed as n-type organic semiconductors due to their excellent electron accepting capability. Examples of Fullerene derivatives are illustrated in the figure below.



**Figure 3.22** Structure of fullerene derivatives.

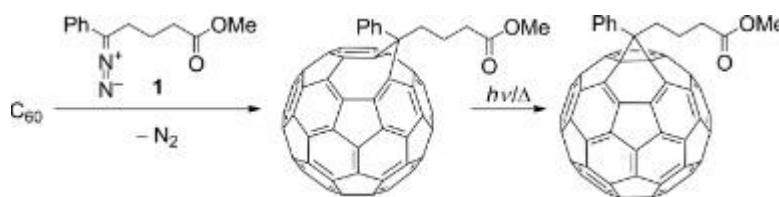
Fullerenes in their pure form have relatively low solubility in most widely used solvents. However, by using proper functionalization, it is possible to dissolve fullerene

### Synthesis of PCBM

The general method for the synthesis of PCBM comprises two steps:

- (i) [2+1] cycloaddition to prepare fulleroid from C<sub>60</sub> and diazoalkane.
- (ii) Isomerization of leading to PCBM (Scheme 3.2).

The second step can be performed by thermal isomerization or photoisomerization (Scheme 2)

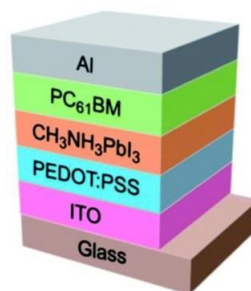


**Scheme 3.2** Synthesis of PCBM.

### Application of Fullerene derivatives

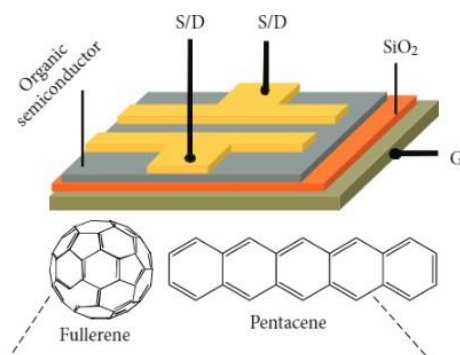
#### 1. Solar cell

Fullerenes are known to be efficient electron acceptors, which makes them promising candidates for the construction of a solar panel when combined with P3HT as the donor of electrons.



**Figure 3.23** Perovskite fullerene based solar cell.

## 2. Organic thin film transistor (OTFT)



**Figure 3.24** Illustration of OTFT layout, fullerene, and pentacene semiconductors.

## 3. Batteries/Supercapacitors

$C_{60}$  and their derivatives are used for lithium batteries as they showed the electrochemical intercalation of lithium into solid  $C_{60}$ , which corresponds to the  $C_{60}Li_{12}$  form. It can be effectively used for anode materials in lithium-ion batteries.


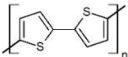
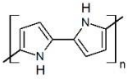

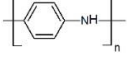
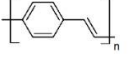
4. Excellent conductivity properties, charge transport, and charge separation make fullerene an ideal material for sensors. It has been used in various sensors, such as strain and gas sensors, photoelectrochemical sensors, and electrochemical and optical sensors.
5. **Biomedical application** Due to its excellent electrochemical sensitivity,  $C_{60}$  can be used for the detection of numerous biomolecules, in particular, dopamine, glucose, and uric acid.
6. Studies have shown that when an alkali metal is embedded within the voids of fullerene  $C_{60}$ , the new composite formed becomes a super conductor (Wang et al., 2015). Accordingly, it has been reported that  $K_3C_{60}$  composite possess high super conducting critical temperature with almost a perfect 3-D superconductivity, current density, ductility and high stability.

## Conductive polymers



Traditionally polymers were seen as good electrical insulators and most of their applications had relied on their insulating properties. However, until three decades ago researchers showed that certain class of polymers exhibits semiconducting properties. They are referred as organic conductive polymers. A conducting polymer is an organic based polymer that can act as a semiconductor or a conductor. They are also known as intrinsically conducting polymers (ICPs) and they have alternating single and double bonds along the polymer backbone (conjugated bonds) or that are composed of aromatic rings such as Phenylene, naphthalene, anthracene, pyrrole, and thiophene which are connected through carbon-carbon single bonds. The first polymer with significant conductivity synthesized was polyacetylene (polyethyne). Its electrical conductivity was discovered by Hideki Shirakawa, Alan Heeger, and Alan MacDiarmid who received the Nobel Prize in Chemistry in 2000 for this discovery.

Examples of conductive polymer; Polyacetylene, Polyaniline, Poly-p-phenylene sulphide, and Polypyrrole

ELECTRICAL CONDUCTIVITY OF SOME CONDUCTIVE POLYMERS		
Compound	Repeating Unit	Conductivity (S cm <sup>-1</sup> )
trans-Polyacetylene		10 <sup>3</sup> - 10 <sup>5</sup>
Polythiophene		10 <sup>3</sup>
Polypyrrole		10 <sup>2</sup> - 7.5 · 10 <sup>3</sup>
Poly(p-phenylene)		10 <sup>2</sup> - 10 <sup>3</sup>
Polyaniline		2 · 10 <sup>2</sup>
Poly(p-phenylene vinylene)		2 · 10 <sup>4</sup>

## Properties of Conducting Polymers

1. Conductivity polymers have high melting and softening points because the mobility of the repeat units is highly restricted due to the presence of a fully aromatic ring structure and the absence of free rotating groups.
2. Conductivity polymers show excellent chemical, thermal and oxidative stability due to low hydrogen content and aromatic structure.
3. They can be processed into a highly ordered crystalline thin film that is electrically conducting upon doping.

Conductive organic polymers often have extended delocalized bonds (often composed of aromatic units). At least locally, these create a band structure similar to silicon. When charge carriers (from the addition or removal of electrons) are introduced into the conduction

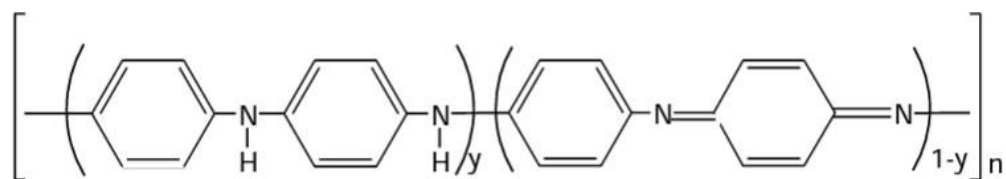
or valence bands the electrical conductivity increases dramatically. Delocalization can be accomplished by forming a conjugated backbone of continuous overlapping orbitals. For example, alternating single and double carbon-carbon bonds can form a continuous path of overlapping p orbitals. However, non-doped polymers have a rather low conductivity. Only when an electron is removed from the valence band by oxidation (p-doping) or is added to the conducting band by reduction (n-doping) does the polymer become highly conductive.

## Polyaniline

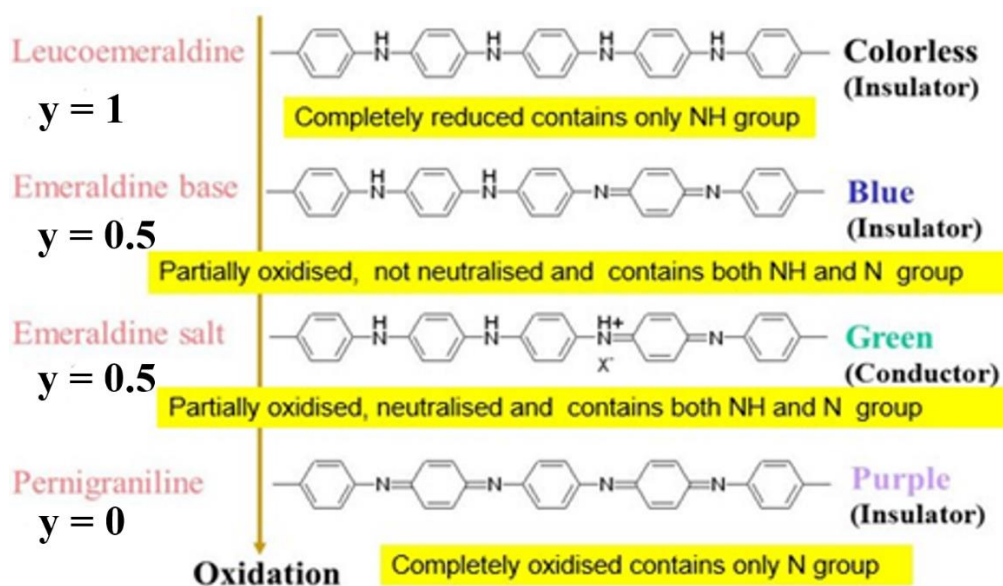
Polyaniline (PANI) was initially discovered in 1834 by Runge, and it was referred to as aniline black. PANI is known as a mixed oxidation state polymer composed of reduced benzoid units and oxidized quinoid units. Furthermore, it was discovered that PANI had characteristics of switching between a conductor and an insulator under certain experimental conditions. Since then, the material has become a subject of great interest in research.

### Structure of PANI

Structure of Polyaniline as a mixed oxidation state polymer consisting of benzoid and oxidized quinoid units, PANI's average oxidation state is denoted as  $1-y$  whereby the value of  $y$  determines the existence of each of the three distinct PANI oxidation states as shown in Figure 3.25. Thus PANI exists as fully reduced leucoemeraldine (LE) where  $1-y = 0$ , half oxidized emeraldine base (EB) where  $1-y = 0.5$  and fully oxidized pernigraniline (PE) where  $1-y = 1$ . The EB is regarded as the most useful form of polyaniline due to its high stability at room temperature, it is composed of two benzoid units and one quinoid unit that alternate and it is known to be a semiconductor

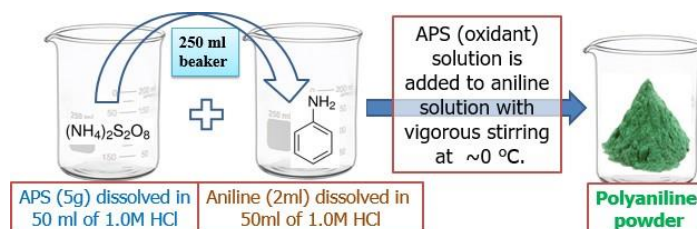


**Figure 3.25** Different oxidation states of polyaniline ( $y = 1$ : leucoemeraldine,  $y = 0.5$ : emeraldine and  $y = 0$ : pernigraniline).

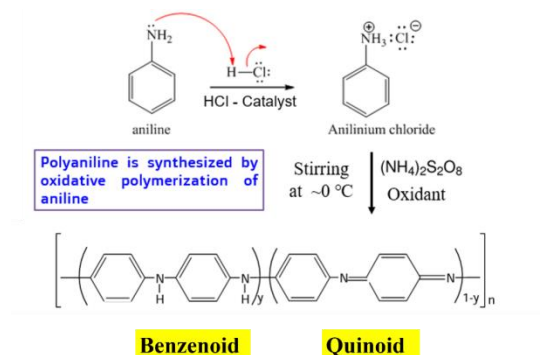


### Preparation of Polyaniline

1. After the polymerization reaction, the resultant mixture is filtered and washed successively using 1.0 M HCl followed by double distilled water, several times until the washings become colorless.
2. Finally, the residue was washed with acetone and dried at 60 °C.



**Figure 3.26** Reaction of polyaniline synthesis



**Scheme 3.3** Polyaniline (PANI) polymerization reaction.

The reaction mechanism of conversion of aniline to conducting polyaniline is as shown below.

### **Application**

#### **1. Solar cell**

PANI is utilized in DSSC because of its easy synthesis, low price, and good conductivity.

#### **2. Electrochromic Glasses**

The smart or electrochromic glass will change colour if an electric current pass through it. The degree of turbidity of the glass will be determined by the grade of voltage transfer over an electrochromic glass. PANI, which is capable of reflecting blue is used in electrochromic glasses. The darkness of a car window can be adjusted by an electric current or by using current over a wide range of potentials.

#### **3. Electroluminescence Machines**

#### **4. Sensors**

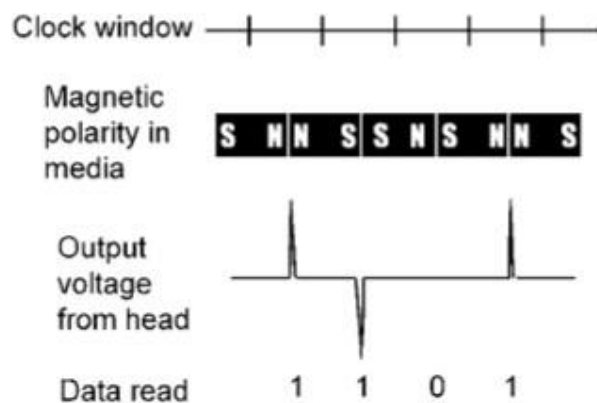
## Magnetic materials

### Data storage materials

Any data storage system/device needs to satisfy certain basic criteria. The first basic requirement is a storage medium. On this storage medium, the data will be written. The other requirements are that there should be ways to write, read, and interpret the data. In magnetic recording, a disk that comprises several magnetic layers serves as the recording medium. Whether the medium is tape or disk, magnetic recording relies on two basic principles. First, magnets have north and south poles out of which its magnetic field emanates and can be sensed by a magnetic-field sensor. The sensing of a magnetic field by a magnetic-field sensor provides a way of reading information. Second, the polarity of the magnets can be changed by applying external magnetic fields, which is usually achieved using an electromagnet. This provides a way of writing information.

### Principle

When two identical poles are next to each other (S–S or N–N), a strong magnetic field will emerge from the recording medium, but no field will emerge when opposite poles (S–N) are next to each other. Therefore, when a magnetic-field sensor (a giant magnetoresistive [GMR]



**Figure 3.27** Illustration of the recorded pulses from magnetic transitions and the recording principle.

sensor, for example) moves across this surface, a voltage will be produced only when the GMR sensor goes over the transitions (regions where like poles meet). This voltage pulse can be synchronized with a clock pulse. If during the clock window the GMR sensor produces a voltage, the voltage is represented as “1.” If no voltage is produced during the clock window, the absence of voltage is represented by “0.” This is a simple illustration of how 1s and 0s are stored in hard disk media (Figure 3. 27).

Elements such as iron, nickel and cobalt, and their chemical compounds, are commonly utilized in magnetic nanoparticles for data storage purposes. High recording density has been

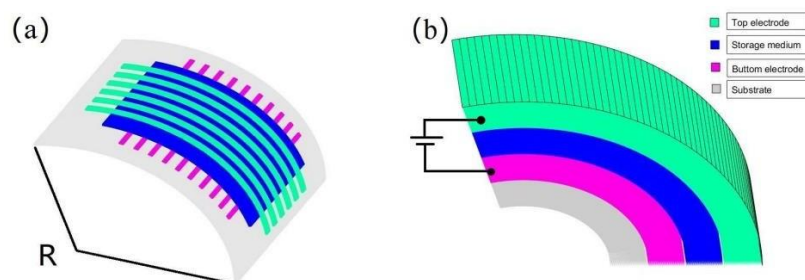
demonstrated for cobalt alloy Co-Pd nanoparticles. Furthermore, Pt-Fe nanoparticles enable magnetic data storage in bits with sizes down to 4nm; hence, a high capacity can be achieved in a single data storage device. Recently, a single-atom magnetic memory based on Ho atoms on MgO has been demonstrated<sup>98</sup>, in which the information was retained for a few hours. The most popular magnetic material has been ferrimagnetic  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. Thin magnetic films consisting of Co-Ni-Pt or Co-Cr-Ta are frequently used in hard-disk devices. They are laid down on an aluminium substrate and are covered by a 40 nm thick carbon layer for lubrication and corrosion resistance.

### Dielectric material for storage devices

Dielectric materials are the poor conductor of electricity but it gets polarized under applied voltage. Dielectric materials are mostly used for memory storage devices such as volatile and non-volatile memory devices. DRAM (Dynamic Random Access Memory) and RRAM (Resistive Random Access Memory), utilize dielectric materials as memory storage media. RRAM is a new non-volatile information storage technology which has the characteristics of high speed, durability, stability, low power consumption, non-volatile and a wide selection of materials, and it is regarded as one of the important candidates for future flexible memory devices.

### Working principle

RRAM is a simple “electrode/dielectric/electrode” sandwich structure, where the dielectric is the carrier for resistance transformation, so it is also called storage medium. Flexible RRAM uses a passive cross-array structure (a cross-array structure is considered to have the highest theoretical integration) and achieves high-density integration to improve storage density. The storage medium uses the high-resistance state (HRS) and low-resistance state (LRS) to represent the 0 and 1 of binary code, respectively.



**Figure 3.28** (a) Schematic of a flexible crossbar resistive switching memory array bent with radius R; (b) Schematic memory cell structure with measurement configuration.

## **Dielectric Materials System for Memory devices**

### **1. Inorganic materials**

Binary metal oxides such as  $\text{TiO}_2$ ,  $\text{NiO}_x$ ,  $\text{ZnO}_x$ ,  $\text{AlO}_x$ ,  $\text{WO}_x$ ,  $\text{HfO}_x$ ,  $\text{MoO}_x$  and flexible multimetal oxides such as  $\text{HfTiO}_4$ ,  $\text{ZnSnO}_x$  are used RRAM and DRAM devices. Amorphous Si, BN, and  $\text{Si}_3\text{N}_4$  are commonly used as flexible dielectric materials for memory devices.

### **2. Organic materials**

Organic materials with excellent mechanical properties are increasingly being used as resistance dielectric layers.

Lignin, polyparaxylene, polyimide (PI), polyethylene glycol dimethacrylate (pEGDMA), poly (1,3,5-trimethyl-1,3,5-trivinyl cyclotrisiloxane) (pV3D3), starch, nitrocellulose (NC), conjugated polyrotaxane.

Compared with flexible inorganic materials, flexible organic materials show a little weakness in electrical properties, but better flexibility.

### **3. Organic-Inorganic composite materials**

Considering the excellent flexibility of organic materials and the electrical reliability of inorganic materials, using organic-inorganic composite materials found to be a good choice.

Examples; poly (4-vinylphenol): graphene oxide (PVP:GO) and ultrathin  $\text{HfO}_x$  composite,

HKUST-1 ( $\text{Cu}_3(\text{BTC})_2$ , BTC = benzo-1,3,5-tricarboxy acid), a composite material based on a metal-organic framework.

## **Application**

1. Resistive switching memory
2. Thin film transistors
3. Film capacitor
4. Dielectric elastomer actuators
5. Capacitive sensors

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