

INTRODUCTION TO MOLECULAR ELECTRONICS Introduction: Charge transport carriers: Soliton - Polaron and bipolaron. Conducting polymers: Polyacetylene - Polyaniline. Applications of conducting polymers. Polymer Structures for LEDs: Polyphenylenes - Polythiophene. Organic Photovoltaics- Construction, Principle and working of OPV, Molecular devices based on conducting polymers.

Introduction

Molecular electronics, also called as molelectronics, involves the use of single or small group of molecules in device-based structures which forms the fundamental unit for electronics such as wires, switches and memory. It is an interdisciplinary study which comprises physics, chemistry, biology, electronics and information technology. Molecular electronics has evolved as a platform technology where almost all electronic devices are generated or fabricated. It is regarded as an alternative to semiconductor silicon based electronic technology. In silicon semiconductor, even the advanced silicon chip can store million bytes of information in less than 1cm^2 area. Even the Pentium 4 chip contains 42 million bytes in less than 1cm^2 area. The silicon chip suffers from a major limitation in storing the density of information. If the size of the chip is reduced, there may be an increase in capacity but other limitation like over-heating and increase Signal/Noise ratio affects its performance. In order to overcome the present scenario, organic materials like proteins, pigments, polymers are used to replace the semiconductor devices since a single mole of an organic molecule contains 6×10^{23} molecules. In a molecular circuit, every single molecule is connected to a power supply an extremely large number of switches are available in a small mass so that molecular electronics can be a powerful tool in future electronics.

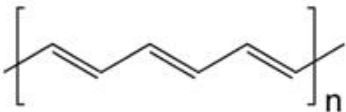
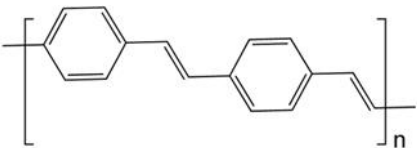
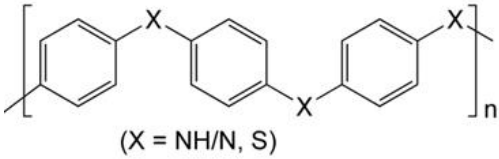
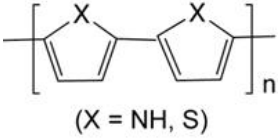
Among different organic materials, conducting polymers are attractive for fabricating molecular devices due to their unique properties and versatility. These polymers possess delocalized π -electronic structure and undergo geometrical modification during electronic excitation. These polymers can be tuned from insulating to semiconducting regime by chemical modification. Besides, these polymers offer other advantages of light weight, flexibility, high chemical inertness, electrical insulation property and ease of processing. Owing to their unique electrical, electronic and optical properties, several technological and commercial devices such as optical, memory, electronic, biosensing and display units have been developed.

Conducting Polymers

Conductive polymers are polyconjugated organic polymers that conduct electricity because of their conjugated π -bonds. Such compounds can have either metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not thermoplastics, *i.e.*, they are not thermoformable. But, like insulating polymers, they are organic materials. They can offer high

electrical conductivity but do not show similar mechanical properties to other commercially available polymers. The electrical properties can be fine-tuned using the methods of organic synthesis and by advanced dispersion techniques.

Some examples of conducting polymers are:

Conducting Polymer	Structure	Conductivity (S/cm)
Polyacetylene		$10^3 - 1.7 \times 10^5$
Polyphenylene vinylene		$3 - 5 \times 10^3$
Polyaniline (X = NH/N) Polyphenylene sulfide (X = S)		30 - 200
Polypyrrole (X = NH) , Polythiophene (X = S)		$10^2 - 7.5 \times 10^3$

In pure form (undoped or pristine state), conducting polymers have low electrical conductivity and behaves like an insulator or as a semiconductor. These polymers can be converted to polymer salts having electrical conductivities comparable to that of metals by treating with suitable oxidizing or reducing agents. These types of doped polymers having high electrical conductivities are called synthetic metals.

The electrical conductivities of undoped conjugated polymers have the range in the order of 10^{-10} S/cm from those of the typical insulators and in the range of 10^{-5} S/cm from those of the semiconductors.

Molecular Basis of Electrical Conductivity

In traditional polymers such as polyethylenes, the covalent bonds are formed as a result of sp^3 hybridization. Such sigma bonds have low mobility and do not contribute to the electrical conductivity of the material. But, in conjugated polymers, the covalent bonds are formed as a result of sp^2 hybridization. One valence electron on each center resides in a p_z orbital, which is

orthogonal to the other three sigma-bonds. All the p_z orbitals combine with each other to a set of delocalized orbitals. Hence the electrons are delocalized over the entire molecule rather than residing at one particular carbon atom. The electrons in these delocalized orbitals have high mobility when the polymer is doped by oxidizing or reducing agents, which donate or removes some of the delocalized electrons respectively.

In practice, most organic conductors are doped oxidatively to give p-type materials. The redox doping of organic conductors is analogous to the doping of silicon semiconductors, whereby a small fraction of silicon atoms are replaced by electron-rich, e.g., phosphorus, or electron-poor, e.g., boron, atoms to create n-type and p-type semiconductors, respectively.

Although typically "doping" of conductive polymers involves oxidizing or reducing the material, conductive organic polymers associated with a protic solvent may also be "self-doped."

Undoped conjugated polymers are semiconductors or insulators. In such compounds, the energy gap can be greater than 2 eV, which is too high for thermally activated conduction. Therefore, undoped conjugated polymers, such as polythiophenes, polyacetylenes have a low electrical conductivity of around 10^{-10} to 10^{-8} S/cm. Even at a very low level of doping ($< 1\%$), electrical conductivity increases several orders of magnitude up to values of around 0.1 S/cm. Subsequent doping of the conducting polymers will result in a saturation of the conductivity at values around 0.1–10 kS/cm for different polymers. Highest values reported now are for the conductivity of stretch oriented polyacetylene with confirmed values of about 80 kS/cm. Although the pi-electrons in polyacetylene are delocalized along the chain, pristine polyacetylene is not a metal.

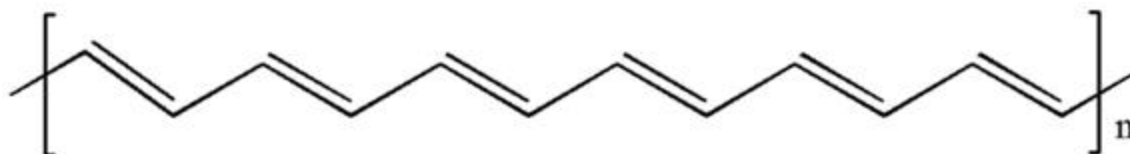
Polyacetylene

It is the first conducting polymer to be synthesized. Poly(acetylene) is the simplest conjugated polymer. In its linear form it precipitates as a black, air sensitive, infusible and intractable powder out of solution and cannot be processed.

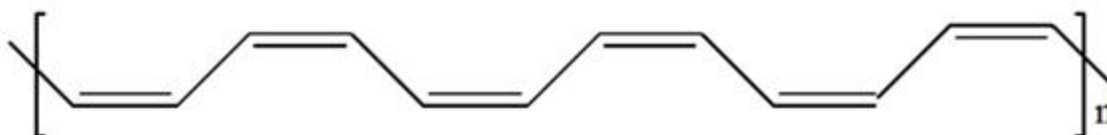
In 1977, Alan J. Heeger, Alan MacDiarmid and Hideki Shirakawa reported similar high conductivity in oxidized iodine-doped polyacetylene. For this research, they were awarded the 2000 Nobel Prize in Chemistry for the discovery and development of conducting polymers. Polyacetylene itself did not find practical applications, but drew the attention of scientists and encouraged the rapid growth of the field.

Polyacetylenes exists in isomeric forms: cis-polyacetylene and trans-polyacetylene.

In cis-configuration, the hydrogen atoms are on the same side of the carbon-carbon double bonds.



Trans polyacetylene

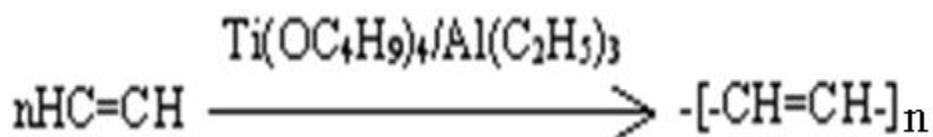


Cis polyacetylene

In trans-configuration, the hydrogen atoms are on the opposite sides of the carbon-carbon double bonds.

Synthesis

The scientist, Shirakawa, prepared poly(acetylene) by passing acetylene gas over the Zeigler-Natta catalyst. Zeigler-Natta catalyst is the coordination complex of tetra butoxy titanium, $[\text{Ti}(\text{OBu})_4]$, an organo metallic compound and triethyl aluminium, $[\text{Et}_3\text{Al}]$.



The reaction forms copper coloured cis-poly(acetylene), having conductivity in the range 10^{-8} - 10^{-7} S/cm, at low temperature (-78°C). At higher temperatures (150°C), more stable silver coloured trans-poly(acetylene), having conductivity in the range 10^{-3} - 10^{-2} S/cm is formed. Cis-poly(acetylene) can be converted to trans-poly(acetylene) by heating it at 150°C for few minutes.

Polyaniline

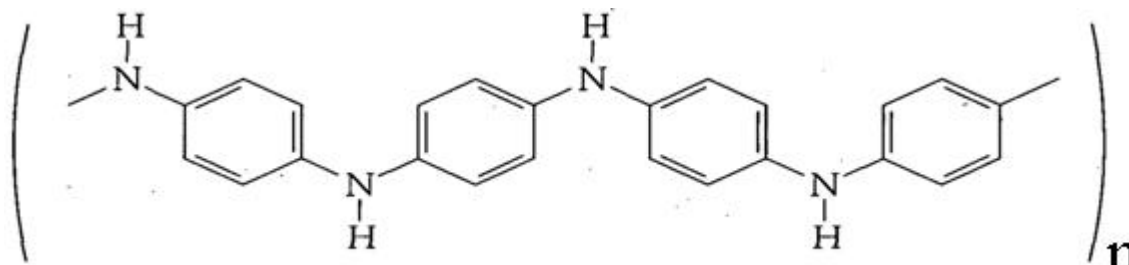
Polyaniline was first described in the mid-19th century by Henry Letheby, who investigated the electrochemical and chemical oxidation products of aniline in acidic media. He noted that the reduced form was colourless but the oxidized forms were deep blue.

Polyaniline consists of alternate benzenoid amine (reduced form) and quinoid imine (oxidized form) structure.

Oxidation States of Polyaniline

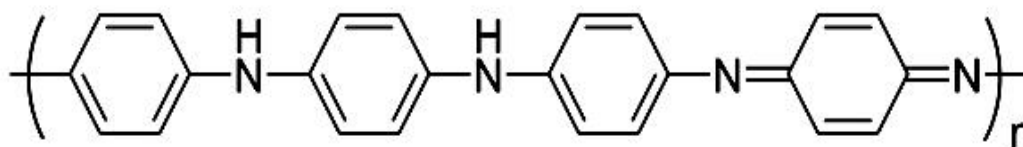
From the generalized formula of polyaniline, it is possible to have three different oxidation states.

1. When $x=1$, completely reduced form of the polymer consisting of only benzenoid amine structure is obtained. This type of polyaniline is called "Leucoemeraldine". This form undergoes easy oxidation when exposed to air. Therefore it is less stable.

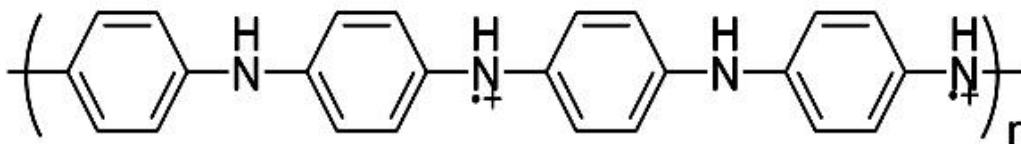
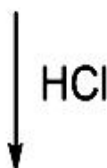


Leucoemeraldine

2. When $x=0.5$, the polymer consisting of partially oxidized quinoid imine structure and partially reduced benzenoid amine structure called "emeraldine" is obtained.



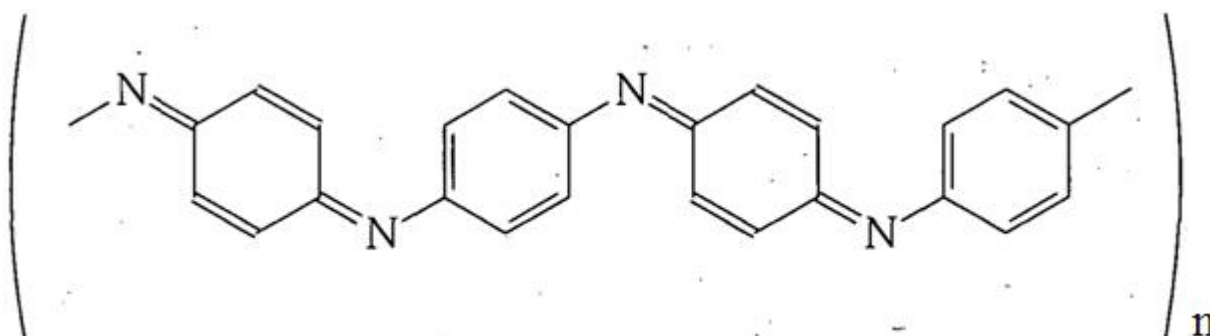
Polyaniline (Emeraldine Base)



Polyaniline (Emeraldine Salt)

The emeraldine base form is the most stable form.

3. When $x=0$, completely oxidized state of the polymer consisting of quinoid imine structure called "pernigraniline" is obtained. This form undergoes degradation easily.

**Pernigraniline****Electrical Conductivity in Conjugated Conducting Polymers**

The electrical conducting in conducting polymers is different from inorganic semiconductors in two aspects:

1. Polymers are macromolecular in nature and lack long range of orderliness.
2. Doping in a polymer is a charge-transfer process.

Doping

Doping involves a partial redox or non-redox reaction (acid reaction) occurring at the polymeric chain. It is carried out by exposing the polymeric film or powder to dopants. Dopants are chemical species or agents which are used in doping process. Redox doping is of two types

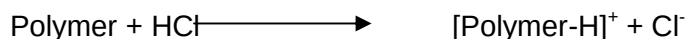
1. p-Doping (oxidation Doping): It is an oxidation reaction where an electron is removed from the valence band leaving the polymer with a positive charge.



2. n-Doping (Reduction doping): It is reduction reaction where an electron is added to the conduction band leaving the polymer with a negative charge.



Non-Redox doping (Protonic acid): It is an acidic reaction where a proton is added to the polymeric chain leaving the polymer with a positive charge.



These doping reactions occur in conjugated polymers with π electrons, since the electrons can be easily added or removed from the polymeric chain to form polyions which exhibit high electrical conductivity.

Nature of Charge Carriers in Conducting Polymers:

The interaction of a polymer unit cell with all its neighbours in a polymeric chain leads to the formation of electronic band as explained in section 1.3. The highest occupied electronic levels or molecular orbitals constitute the valence band (VB) and the lowest unoccupied levels represent the conduction band (CB). The difference in energy between the VB and CB is known as band gap energy which determines the intrinsic electrical property of polymers. On doping, the electrical conductivity of the polymer is increased due to the formation of self-localized

excitations such as solitons, polaron and bipolaron (quasi-particles). These particles arise from strong interaction between the charge on the polymeric chain (electron or hole) acquired as a result of doping and the molecular structure. Thus, the charge carrying species in doped conjugated polymers are not free electrons or holes but quasi-particles which move relatively free through the polymeric chain.

The nature of charge carriers and the mechanism of doping in trans-polyacetylene (PA) is explained as follows;

The trans-PA exists in two alternate structures (A and B) with same ground state energies known as degenerate state. When these two degenerate states dimerize, a structural defect (kink) occurs in the chain with a change in bond alternation. A single unpaired electron exists where the structural defect occurs and it produces an energy level at the centre of the band gap, known as neutral soliton. The neutral soliton carries a single electron which possesses $1/2$ spin and exhibits paramagnetic behaviour. It can move along the chain without any distortion. In a pure (undoped) trans PA, there are only neutral solitons which are on an average of 1 in every 3000 CH units.

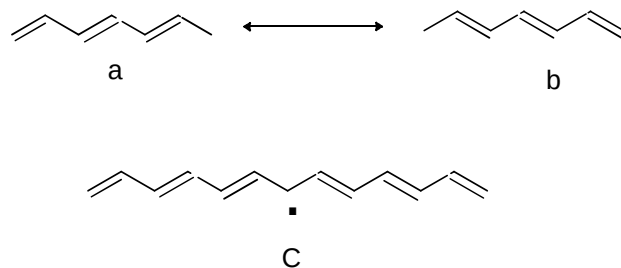


Fig 1.1 a) and b) Degenerate States of trans-PA

c) PA chain with a defect (neutral soliton)

When trans-PA is doped a number of neutral solitons is used (at very low doping level) to form charged solitons. In some cases, a charge transfer can occur directly between a doping agent and VB or CB to produce an ion radical in the chain (i.e. a defect pair). The mechanism of p and n-doping in trans-PA is as follows:

During doping, an electron is added (or removed) to the bottom of the conduction band (or from the top of the valence band) of trans-PA, the conduction (valence) band is partially filled and a radical anion (or cation), polaron is formed. The formation of polaron causes the injection of states from the bottom of the CB and top of the VB into the band gap. The polaron carries both charge and spin exhibiting paramagnetic behaviour. The addition (or removal) of a second electron to the chain will result in a negative (positive) polaron and bipolaron (spinless). The bipolaron further lowers their energy by dissociating into two spinless charged solitons (positive charge in p-doping and negative charge in n-doping) which occupies at one-half of the band gap energy. The number of polaron, bipolaron and soliton formed increases with the doping level. At high doping, polaron, bipolaron and soliton near to the individual dopant ions could overlap leading to new bands between (or even overlapping) the VB and CB through which electrons can flow. Doping of trans-PA by I_2/CCl_4 introduces positive charges which are delocalized over 12-15 CH units to give positive solitons thereby the conductivity increases from 10^{-5} to 10^2 S/cm (or by the order of 10^7).

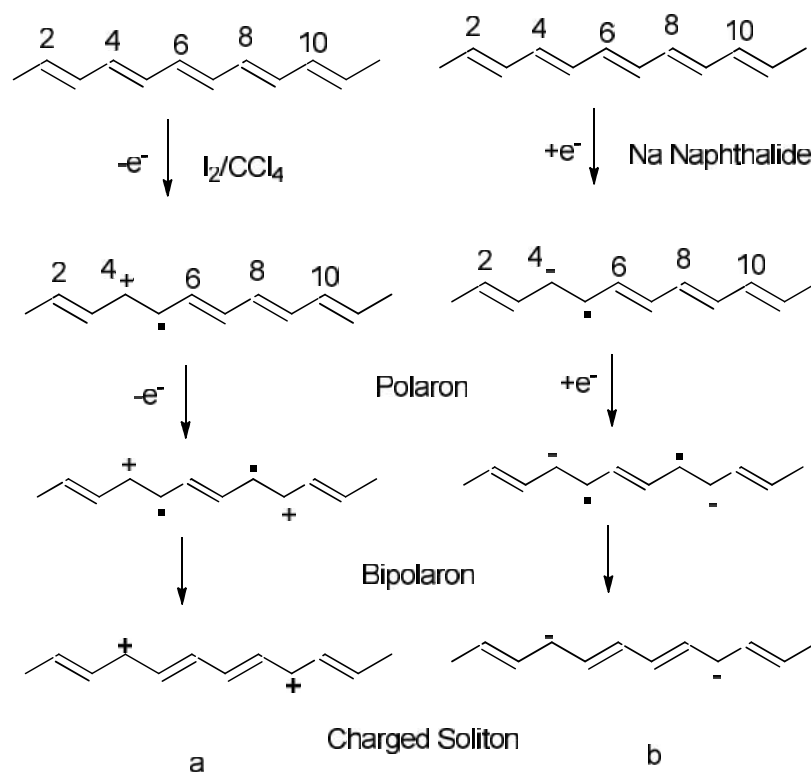


Fig 1.2 a) p-doping b)n-doping in trans-PA

In general, trans-PA forms soliton energy level which can accommodate either 0, 1 or 2 electrons with unusual spin and charge property. When the electrons are removed (i.e) Zero, a positive soliton of zero spin results. When two electrons are accommodated, a negative soliton of zero spin is observed. Both these charged solitons are non-magnetic. A neutral soliton carries a single electron and exhibits paramagnetic behaviour.

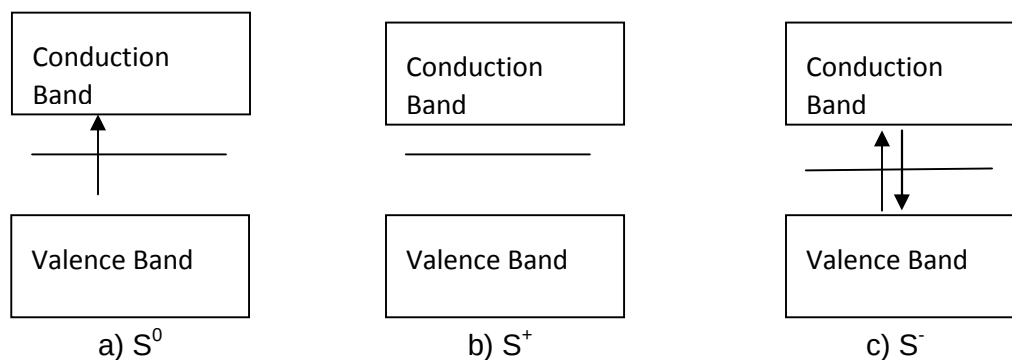


Fig 1.3 Charge and spin separation in a) Neutral Soliton (S^0), b) Positive Soliton (S^+) c) Negative Soliton (S^-)

Mechanism of doping polyaniline

The emeraldine base of polyaniline consists of equal proportion of amino ($-NH-$) and imine ($=N-$) sites. On doping with acids like HCl, dl-camphor sulphonic acid the imino nitrogen are protonated to form bication salt, bipolaron. It is highly unstable due to the presence of $C=N$

bonds of quinoid imine which dissociates to form polaron. The positive charges on the polaron are delocalized over the entire polymeric chain which are stabilized by resonance. The resulting emeraldine salt has a conductivity of 300 S/cm, increased by the order of 10^{11} magnitude.

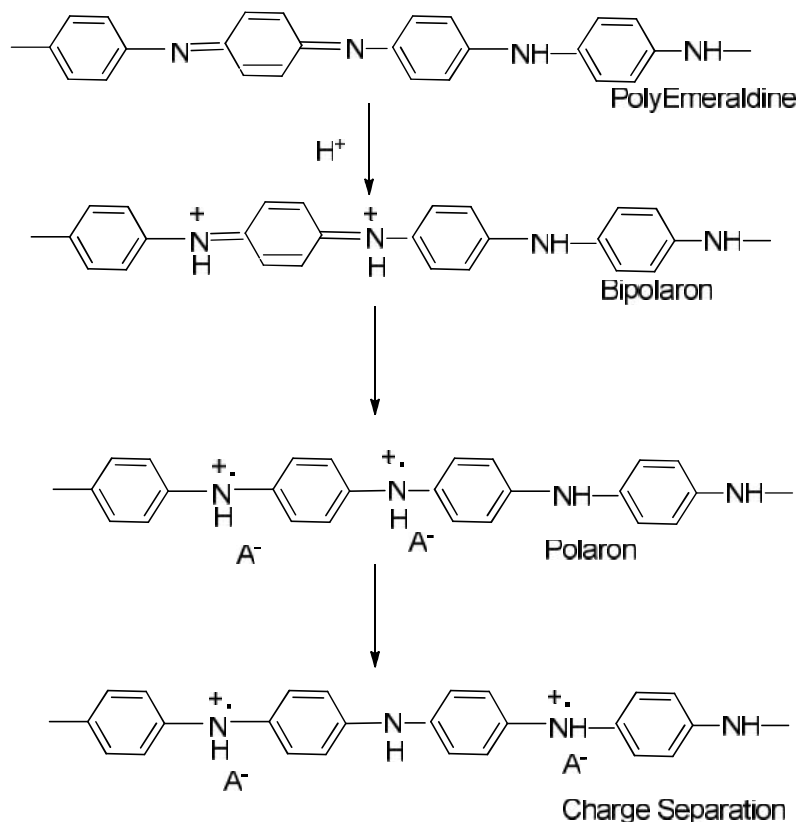


Fig 1.4 Protonic acid doping in Polyaniline.

Factors Influencing the Conductivity of Polymers

The conductivity of organic polymers is influenced by the following factors:

- 1) **Conjugation length:** The conductivity of a polymer increases with the increase in the length of the polymer chain and increase in the number of conjugation
- 2) **Doping level:** The conductivity of a polymer increases with the increase in doping level till the saturation point is reached
- 3) **Temperature:** Conductivity of a polymer increases with increase in temperature. Sometimes, the conductivity becomes constant at a particular temperature
- 4) **Frequency of current:** Conductivity of a polymer depends on the frequency of current as doping is the transport mechanism in these materials

Applications of Conducting Polymers

Due to their poor processability, conductive polymers have few large-scale applications.

- Conducting polymers are used in rechargeable batteries
- Conducting polymers are used in making analytical sensors like oxygen, glucose sensors etc.
- They are used in medicinal field for controlled release of drugs.
- They are used for making electronic displays and optical fibers.
- They are used in LEDs, storage devices, computers etc.
- They are used in circuit boards.
- Conducting polymers are also used in fuel cells as electrocatalytic materials.
- They have promise in antistatic materials and they have been incorporated into commercial displays and batteries, but there have had limitations due to the manufacturing costs, material inconsistencies, toxicity, poor solubility in solvents, and inability to directly melt process.
- Literature suggests they are also promising in organic solar cells, printing electronic circuits, organic light-emitting diodes, actuators, electrochromism, supercapacitors, chemical sensors and biosensors, flexible transparent displays, electromagnetic shielding and possibly replacement for the popular transparent conductor indium tin oxide.
- It is used for microwave-absorbent coatings, particularly radar-absorptive coatings on stealth aircraft.

Applications of conducting polymers are grouped into two types based on their conductivity and electroactivity. The first group utilizes their conductivity as its main property because of their light weight, biological compatibility for ease of manufacturing or cost. The second group utilizes their electroactivity. The extended π -systems of the conjugated polymers are highly susceptible to chemical or electrochemical oxidation or reduction. These alter the electrical and optical properties of the polymer, and by controlling this oxidation and reduction, it is possible to precisely control these properties. It is even possible to switch from a conducting state to an insulating state. The two groups of applications are given below:

Group 1	Group 2
Electrostatic materials	Molecular electronics
Conducting adhesives	Electrical displays
Electromagnetic shielding	Chemical, biochemical and thermal sensors
Printed circuit boards	Rechargeable batteries and solid electrolytes
Artificial nerves	Drug release systems
Antistatic clothing	Optical computers
Piezoceramics	Ion exchange membranes
Active electronics (diodes, transistors)	Electromechanical actuators
Aircraft structures	'Smart' structures switches

Conducting polymers are rapidly gaining attraction in new applications with increasingly processable materials with better electrical and physical properties and lower costs. The new nanostructured forms of conducting polymers particularly, augment this field with their higher surface area and better dispersability. With the availability of stable and reproducible dispersions, PEDOT (poly(3,4-ethylenedioxythiophene)) and polyaniline have gained some large scale applications. While PEDOT is mainly used in antistatic applications and as a transparent conductive layer in the form of PEDOT:PSS dispersions (PSS=polystyrene sulfonic acid), polyaniline is widely used for printed circuit board manufacturing – in the final finish, for protecting copper from corrosion and preventing its solderability.

Conducting Polymers - Device Applications

(A) **Polyaniline and substituted polyaniline** are used as : (1) Electrochromic display (2) Photolithography (3) Rechargeable battery (4) Electrochemical capacitors (5) Corrosion inhibitors (6) Sensors

(B) **Polypyrrole and substituted polypyrrole** has applications in : (1) Electrochromic display (2) Light weight battery (3) Sensors (4) Solar energy cells

(C) **Polythiophene and substituted Polythiophene** are used in : (1) Electroluminescence (2) Electrochemical capacitors (3) Cathode materials for battery (4) Microlithography (5) Corrosion inhibitors

(D) **Poly-p-phenylene (PPP) p-phenylene vinylene (PPV)** find application in (1) Electroluminescence (2) Photoconductors (3) Solar energy cells (4) Laser materials

Barriers to Applications

Most conductive polymers require oxidative doping in which the properties of the resulting state are crucial. Such materials are salt-like (polymer salt), which diminishes their solubility in organic solvents and water and hence their processability. Also, the charged organic backbone is often unstable towards atmospheric moisture. The poor processability for many polymers requires the introduction of solubilizing or substituents, which can further complicate the synthesis. Experimental and theoretical thermodynamical evidence suggests that conductive polymers may even be completely and principally insoluble so that they can only be processed by dispersion.

Polymer structure for LEDs

Conjugated polymers possess strongly anisotropic electrical and optical properties since the π -electron delocalisation occurs along the chain direction. An ideal conjugated polymer chain possesses a one-dimensional structure which leads to the electronic structure of a monodimensional semiconductor with an energy gap in the 1.5 – 3.5 eV range. According to Su, Schrieffer and Heeger theory, electron–electron interactions are neglected and describe the properties of the polymeric semiconductors by introducing a strong electron-phonon interaction. Based on this theory, for non degenerate ground state polymers, injection of charges leads to the formation of singly charged polarons or doubly charged bipolarons. Neutral species (exciton-polarons) can be generated by photoexcitation via e-h separation or by the fusion of two polarons with opposite charges, obtained via charge injection from the electrodes, and are

responsible for photoluminescence and electroluminescence respectively. Both the charged and the neutral excitations are stabilized through a local modification of the bond alternation. This produces two localized electronic states within the forbidden energy gap. The energy position of these levels, which are symmetrically displaced from the midgap, depends on the spatial extent of the defect. The more extended the defect, the closer the levels to the midgap. The optical transitions occurring between these levels and the conduction and the valence bands account for the sub-gap optical absorption bands observed by chemical doping, by photoinduced absorption, and by charge injection.

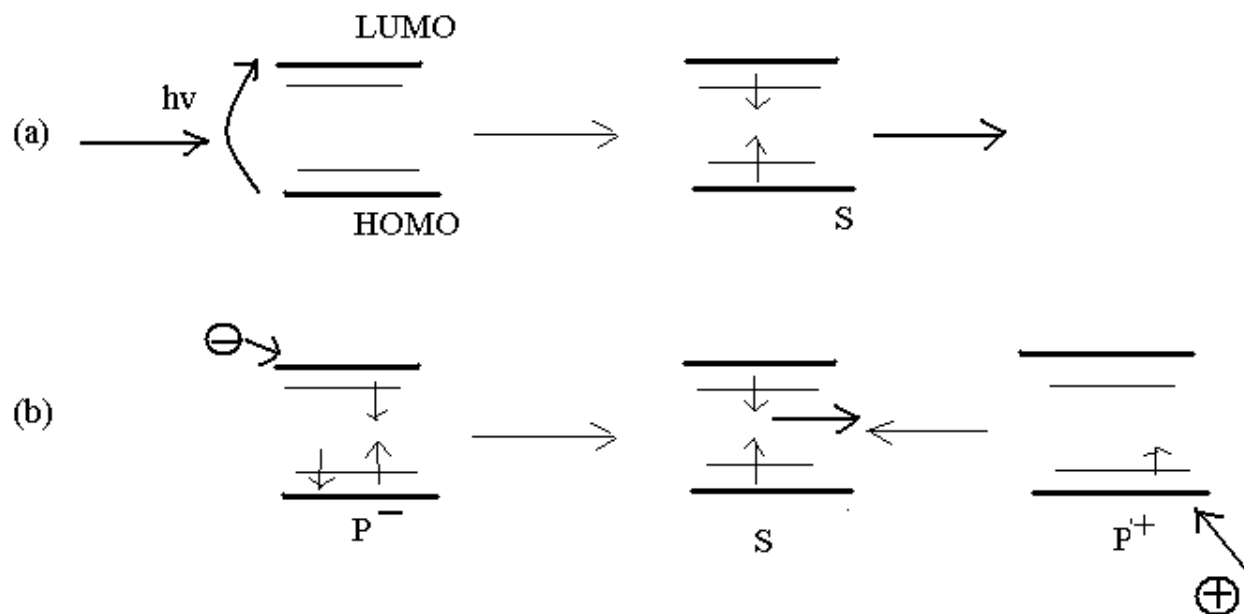


Fig 1.5 Scheme of the generation and radiative recombination of the singlet exciton S by photoexcitation (a), and by charge injection (b) mechanisms

The tailoring of polymeric structures plays a significant role in the development of LEDs. The structural control can be extended to several physicochemical parameters:

- 1) The band gap of a conjugated polymer is responsible for the photoluminescence and electroluminescence peak positions
- 2) The electron affinity and ionization potential of the polymer strongly affect the charge injections from the electrodes into the polymers which is related to the photoluminescence and electroluminescence efficiency
- 3) The solid state packing of the macromolecules influences the stability and the emission efficiencies
- 4) The surface polarity of the polymer is responsible for the adhesion between the active polymer and the electrodes which is an important factor in charge injection
- 5) Resistance to oxidation and temperature of the active polymeric layer are fundamental to the lifetime of the device.

Electroluminescence

Electroluminescence is light emission stimulated by electric current. In organic compounds, electroluminescence has been known since the early 1950s, when Bernanose and coworkers

first produced electroluminescence in crystalline thin films of acridine orange and quinacrine. In 1960, researchers at Dow Chemical developed AC-driven electroluminescent cells using doping. In some cases, similar light emission is observed when a voltage is applied to a thin layer of a conductive organic polymer film. While electroluminescence was originally mostly of academic interest, the increased conductivity of modern conductive polymers means enough power can be put through the device at low voltages to generate practical amounts of light. This property has led to the development of flat panel displays using organic LEDs, solar panels, and optical amplifiers.

Electroluminescent materials for various colours

Colour of the emission light	Luminescent material
Red	Cyano-derivative of PPV, POPT
Yellow	Poly(2,5-bis(cholestanoxo)-1,4 phenylene vinylene and poly(3-cyclohexane thiophene) (PCHT)
Orange	MEH-PPV
Green	Poly(p-phenylene vinylene) (PPV)
Blue	Poly(3,4 ethylene-dioxy thiophene) (PEDOT), Poly(3-methyl-4,cyclo-hexane thiophene) (PCHMT)

Another favourable aspect of the polymer LED (PLED) is that it is possible to cover the spectral range from blue to near infrared, even within a single family of conductive polymers such as polythiophene. The recent demonstration of voltage-controlled electroluminescence colours from polymer blends in LEDs as well as the possibility of obtaining polarised light from oriented polymers in LED devices extends the possibilities of fabricating 'exotic' polymer devices. Polymer LEDs are constructed by sandwiching a layer of conjugated polymer between a pair of electrodes.

Preparation of LED

LEDs are devices that transform electrical signals into optical signals. The typical structure of a single-layer polymeric LED is shown the figure below. A glass substrate coated by indium-tin-oxide (ITO) is used as a transparent (positive) electrode. A polymer layer is deposited onto the substrate by a spin coating technique. On the polymer is deposited a metallic layer by vacuum evaporation which forms the negative electrode. By applying a bias voltage at the electrodes, light emission is obtained through the transparent electrode.

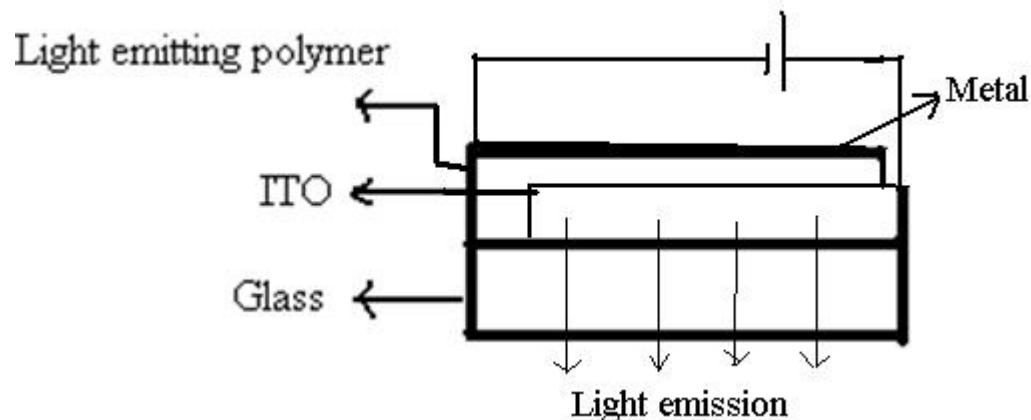


Fig 1.6 Scheme of a single layer LED

One of the advantages with polymer LEDs is the possibility to choose size and geometry freely. So far, this has mainly been exploited in making large (several square centimeters) LEDs. Granstrom and Inganas have shown that it is possible to go in the other direction and make the light source very much small if the micrometer and nanometer sized polymeric LEDs are fabricated. In gold coated glass, PEDOT is deposited as a hole injecting electrode and PTOPT is deposited on PEDOT as an electroluminescent polymer. Two different conjugated polymers have been used in making these small LEDs. The first one poly(3,4-ethylene dioxy thiophene) (PEDOT) was used as the hole injecting contact; the other poly(3-(4-octyl phenyl) 2,20 - bithiophene) (PTOPT) was used as the electroluminescent layer. Electroluminescence from substituted polythiophene polymer covers the full visible spectrum, from the blue into the near infra-red. The substituted polythiophenes have all been designed to give varying degrees of main chain planarity. In this way, the conjugation length and band gap are controlled in a systematic manner. The extended family of substituents include alkyl± alkyl, cyclo-alkyl and alkyl±phenylene group. These four different polythiophene derivatives with band gaps varying by 2.0 eV display electroluminescence from blue into the infrared. It is possible to achieve a colour spectrum in the whole visible region simply by substituting an appropriate functional group in a luminescent polymer. For example, moieties like pyrazoloquinoline (PAQ) and bispyrazolopyridone (PAPI) derivatives have been incorporated in luminescent polymeric system to get full visible spectrum.

Advantages of PLED

1. Light weight and flexible, hence can be made to form thin films
2. High resolution giving high quality imaging
3. Energy efficient
4. Consumes less power
5. High levels of brightness and intensity
6. High reliability
7. Low voltage and current requirements

Applications of PLED

1. Used in small screen devices such as cell phones, digital cameras.
2. LED displays such as Laptops, computers, TVs, smart phones.
3. In fiber optic data transmission
4. In remote controls
5. Indicator lights.

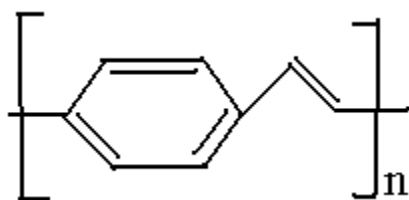
Disadvantages of PLED

1. They have color imbalance due to the lifetime of the organic materials. Red and green films have longer life time while blue has shorter.
2. Expensive
3. Poor water resistance

Poly(*p*-phenylene vinylene or polyphenylene vinylene) - PPV

It is a conducting polymer of the rigid-rod polymer family. PPV is the only polymer of this type that has been processed into a highly ordered crystalline thin film. PPV and its derivatives are electrically conducting upon doping. Although insoluble in water, its precursors can be manipulated in aqueous solution. The small optical band gap and its bright yellow fluorescence make PPV a candidate in applications such as light-emitting diodes (LED) and photovoltaic devices. Moreover, PPV can be doped to form electrically conductive materials. Its physical and electronic properties can be altered by the inclusion of functional side groups. PPV was one of the first polymers studied, for its good photoluminescence (PL) and electroluminescence (EL) efficiencies. Several synthetic routes have been reported for the preparation of this polymer. Its insolubility is a great problem in the preparation of high molecular weight materials.

The structure and EL spectrum of an LED prepared with PPV is shown below:

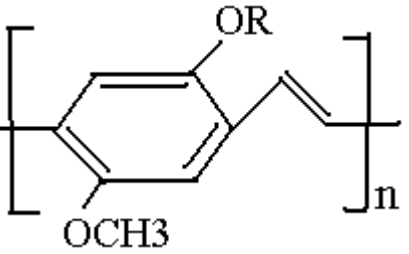
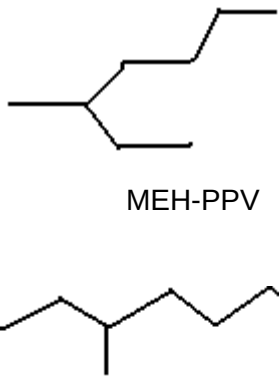
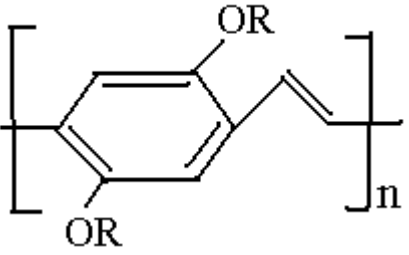
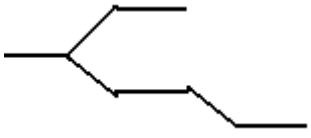
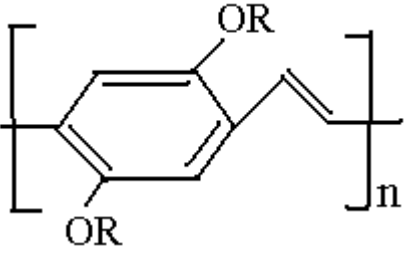


Structure of PPV

Figure1.7: Electroluminescence spectrum of PPV

The figure shows an emission centered at 525 nm corresponding to yellow-green light. The first EL from PPV stimulated the work of chemists to develop new alternative routes to improve the preparation of this polymer. The idea of having a polymer soluble in organic solvent in its conjugated form led to the introduction of solubilizing groups in the PPV backbone which also has the effect of modulating the gap, resulting in a change in color emission. As most of the semiconducting polymers are easily p-doped and not n-doped, the increase of the electron affinity through the introduction of suitable electron withdrawing substituents has been found to

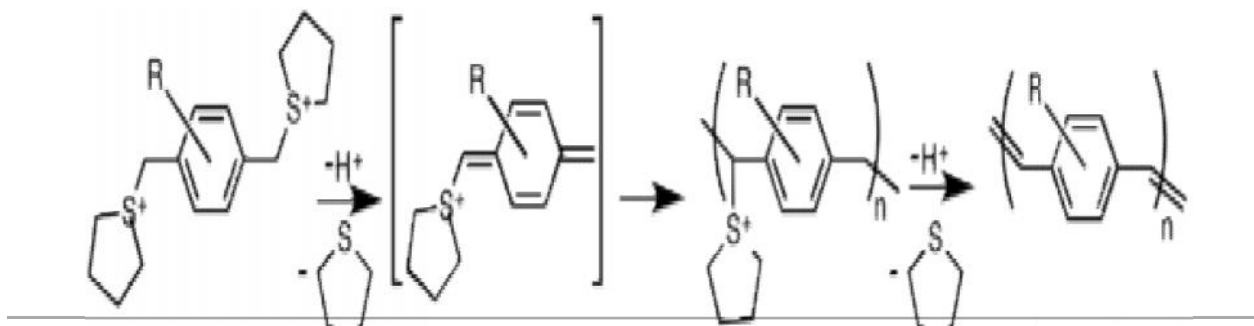
be very promising. Some of the most studied structures that were developed are given in the following table.

PPV derivatives used in LEDs	Substituent Groups (R)	EL wavelength/ Cathode
	 MEH-PPV	EL= 620 nm/Ca
		EL = 560 nm
	$R = \begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ $R' = \text{H}$	EL = 540 nm/Al

Highly ordered structures, packed in three dimensions, have the tendency to decrease the PL and consequently the EL efficiency. The PL efficiencies are found to be high in solution and generally decrease in the solid state.

Preparation

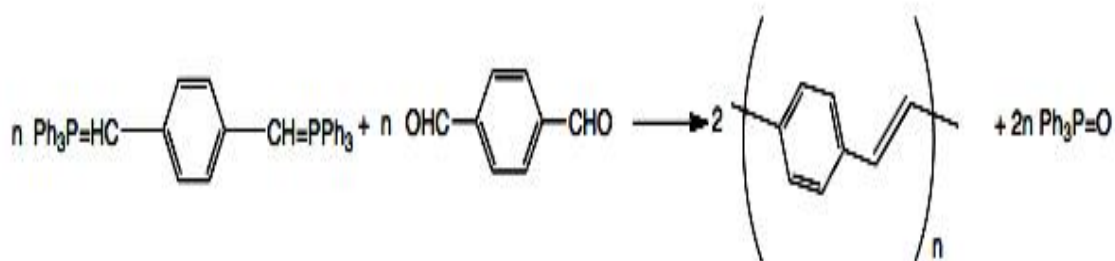
PPVs can be synthesized by a variety of methods, the details of which determine purity and molecular weight. The most popular methods proceed via p-xylene intermediates after a base induced elimination from α, α' -disubstituted para-xylenes.



Although xylene-based routes dominate the synthetic methodology, many other routes have been evaluated.

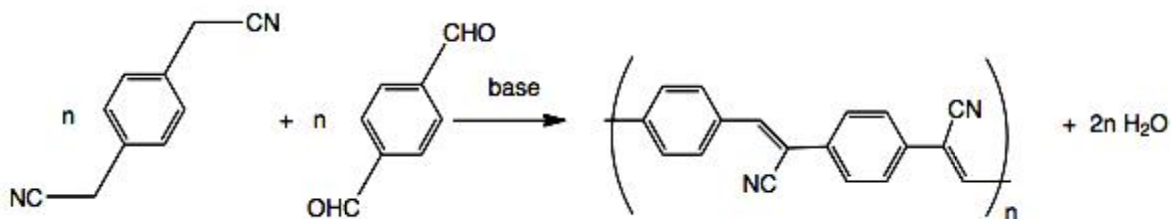
Step growth routes

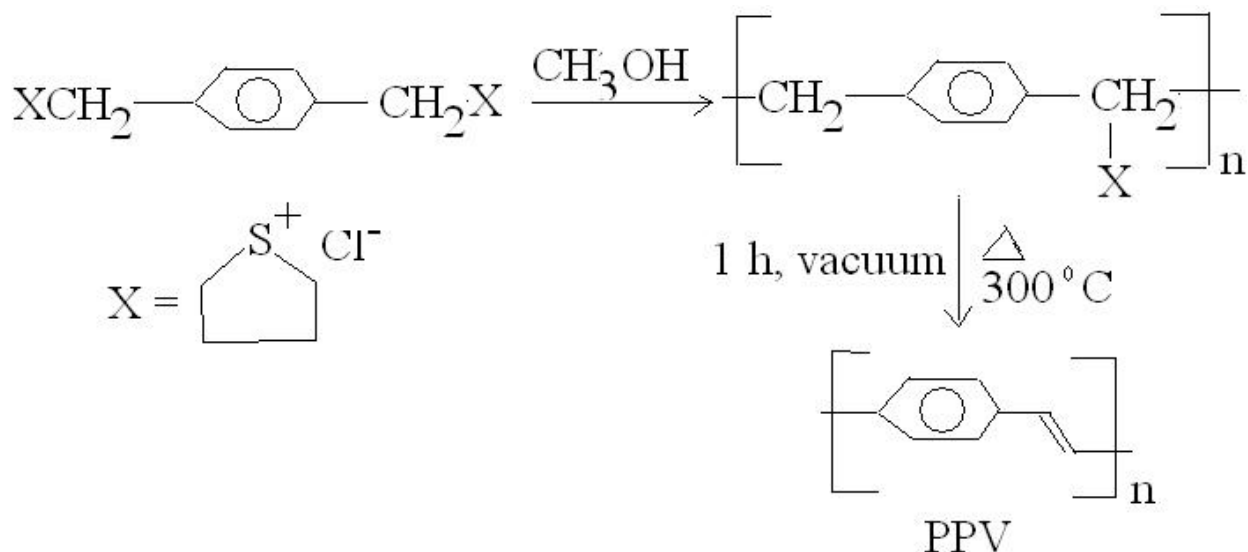
PPV can be synthesized by Wittig-type couplings between the bis(ylide) derived from an aromatic bisphosphonium salt and dialdehyde, especially 1,4-benzenedialdehyde as follows:



Step growth coupling reactions, such as this Wittig condensation, usually yield low molecular weight oligomer with 5-10 repeat units. Incorporation of various side groups (alkyl, alkoxy, or phenyl) increases the solubility of the polymer and gives higher molecular weights. An advantage of the step-polymerization approach is that ortho-, meta-, and para-xylylene linkages can be incorporated in the main chain. Copolymers of defined stereoregularity can also be easily made in this way.

PPV derivatives can be also produced via the Knoevenagel condensation between a benzylic nitrile and an aromatic dialdehyde. Since this method produces many side reactions, such as hydrolysis of nitrile group, careful optimization of the reaction conditions is required.



Synthesis of PPV by Wessling method

The other methods of synthesis of conducting polymers are Heck coupling routes and ring-opening routes.

PPV is a diamagnetic material and has a very low intrinsic electrical conductivity, on the order of 10^{-13} S/cm. The electrical conductivity increases upon doping with iodine, ferric chloride, alkali metals, or acids. However, the stability of these doped materials is relatively low. In general, unaligned, unsubstituted PPV presents only moderate conductivity with doping, ranging from $<<10^{-3}$ S/cm (I_2 doped) to 100 S/cm (H_2SO_4 -doped). Alkoxy-substituted PPVs are generally easier to oxidize than the parent PPV and hence have much higher conductivities. Longer side chains lower the conductivity and hinder interchain hopping of charge carriers.

PPV has very low intrinsic electrical conductivity, on the order of 10^{-13} S/cm. The electrical conductivity increases upon doping with iodine, ferric chloride, alkali metals, or acids. However, the stability of these doped materials is relatively low. In general, unaligned, unsubstituted PPV presents only moderate conductivity with doping, ranging from $<<10^{-3}$ S/cm (I_2 doped) to 100 S/cm (H_2SO_4 -doped). Alkoxy-substituted PPVs are generally easier to oxidize than the parent PPV and hence have much higher conductivities. Longer side chains lower the conductivity and hinder interchain hopping of charge carriers.

Applications

Due to its stability, processability, and electrical and optical properties, PPV has been considered for a wide variety of applications. In 1989 the first polymer-based light emitting diode (LED) was discovered using PPV as the emissive layer. Polymers are speculated to have advantages over molecular materials in LEDs, such as ease of processing, reduced tendency for crystallization, and greater thermal and mechanical stability. Ever since the first breakthrough in 1989, a large number of PPV derivatives have been synthesized and used for LED applications. Although solid-state lasing has yet to be demonstrated in an organic LED, poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) has been proven to be a promising laser dye due to its high fluorescence efficiency in solution.

Polyphenylene vinylene is capable of electroluminescence, leading to applications in polymer-based organic light emitting diodes. PPV was used as the emissive layer in the first polymer light-emitting diodes. Devices based on PPV emit yellow-green light, and derivatives of PPV obtained by substitution are often used when light of a different color is required. In the presence of even a small amount of oxygen, singlet oxygen is formed during operation, by energy transfer from the excited polymer molecules to oxygen molecules. These oxygen radicals then attack the structure of the polymer, leading to its degradation. Special precautions therefore have to be kept during manufacturing of PPV in order to prevent oxygen contamination.

PPV is also used as an electron-donating material in organic solar cells. Although PPV-based devices suffer from poor absorption and photodegradation, PPV and PPV derivatives (especially MEH-PPV and MDMO-PPV) find frequent application in research cells.

Polythiophene

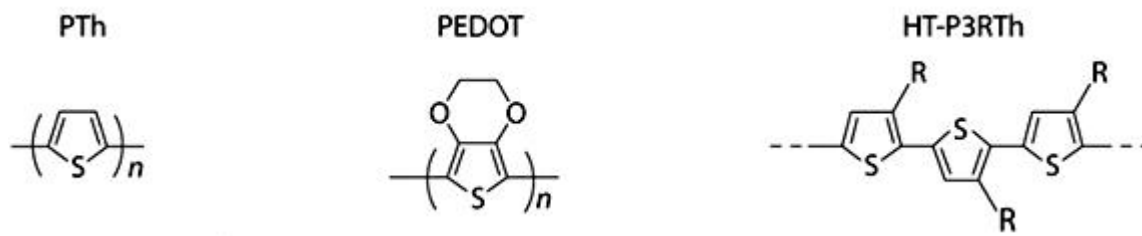
Polythiophene has been widely used as environmentally and thermally stable conjugated polymer materials, such as chemical and optical sensors, light-emitting diodes and displays, photovoltaic devices, molecular devices, DNA detection, polymer electronic interconnects, solar cells and transistors, since 1980.

Three approaches to polymerization of thiophene have been reported in the literature: (1) electropolymerization, (2) metal-catalyzed coupling reactions, and (3) chemical oxidative polymerization. Waltman et al. prepared high conductivity polythiophene films by electropolymerization in the year 1983, but it is rarely used in the preparation of electroluminescent materials. Since then various different methods of synthesis of polythiophene have been developed. Recently, Kim and his co-workers prepared polythiophene in aqueous dispersion via Fe^{3+} -catalyzed oxidative polymerization and tested its photoluminescence properties.

The stable morphologies, such as spherical particles, nanofibers, sphere-fiber-transition, and submicro/nanoribbons, have been obtained by controlling the ratio of the oxidant to reductant.

Polythiophene and its derivatives in particular have been the subject of many recent studies. p-Doped poly(3,4-ethylenedioxythiophene) (PEDOT) is used industrially in capacitor electrodes and as an antistatic material amongst a range of device applications, and polythiophenes with side chains bearing sulfo groups are used as antistatic materials in electron-beam lithography.

Structures of the simple and substituted polythiophenes are shown below:



Polythiophene (PTh): Polythiophenes are insoluble, so, alkyl groups are introduced to increase its solubility. The emission intensity increases with increasing side chain length and emission

wavelength is blue shifted with alkyl substitution in both 3 and 4 positions. Electroluminescence value for simple polythiophene is 660 corresponding to red color.

Poly(3-alkyl thiophene) (PAT) : It gives electroemission in the yellow or orange region. When $R = H_{17}C_8-C_6H_4-C_8H_{17}$ the electroluminescence value is 640, corresponding to reddish orange color.

Poly(3,4 – ethylene dioxythiophene) (PEDOT) : It is a conducting polymer based on EDOT monomers. It is optically transparent and has high stability. It has poor solubility. It has electroluminescence value corresponding to the blue region.

Synthesis of Polythiophene

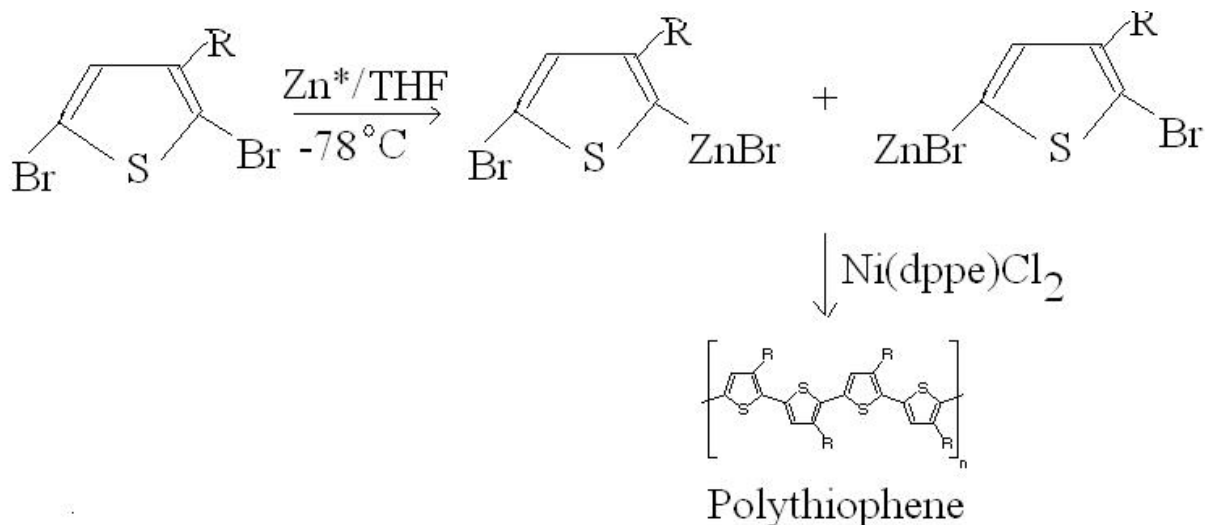
Polythiophenes can be synthesized electrochemically, by applying a potential across a solution of the monomer, or chemically, using oxidants or cross-coupling catalysts. All methods have their own advantages and disadvantages.

In an electrochemical polymerization, a solution containing thiophene and an electrolyte produces a conductive polythiophene film on the anode. Electrochemical polymerization is convenient, since the polymer does not need to be isolated and purified, but it can produce polymers with undesirable alpha-beta linkages and varying degrees of regioregularity.

Chemical synthesis has two advantages compared with electrochemical synthesis of polythiophenes: a greater selection of monomers, and, by using proper catalysts, has the ability to produce perfectly regioregular substituted polythiophenes. While polythiophenes may have been chemically synthesized by accident, the first planned chemical syntheses using metal-catalyzed polymerization of 2,5-dibromothiophene were reported by two groups independently in 1980. Yamamoto *et al.* used magnesium in tetrahydrofuran (THF) and nickel(bipyridine) dichloride, analogous to the Kumada coupling of Grignard reagents to aryl halides. Lin and Dudek also used magnesium in THF, but with a series of acetylacetonate catalysts ($Pd(acac)_2$, $Ni(acac)_2$, $Co(acac)_2$, and $Fe(acac)_3$).

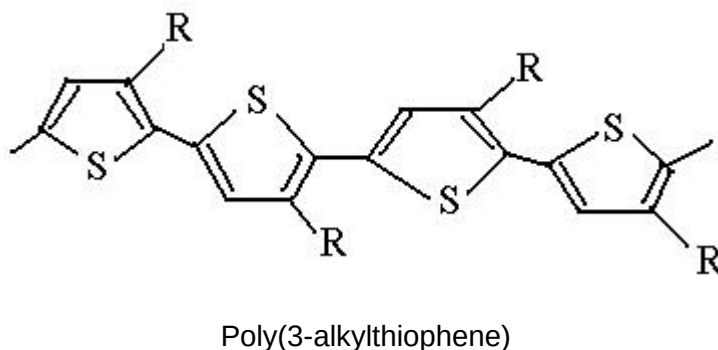
Later developments produced higher molecular weight polythiophenes than those initial efforts, and can be grouped into two categories based on their structure. Regioregular polythiophenes can be synthesized by catalytic cross-coupling reactions of bromothiophenes, while polymers with varying degrees of regioregularity can be simply synthesized by oxidative polymerization.

One of the simple methods of synthesis of regioregular polythiophenes described by Rieke *et al.* developed in the year 1993 is given below:



In this method, 2,5-dibromo-3-alkylthiophene is treated with highly reactive "Rieke zinc" to form a mixture of organometallic isomers. Addition of a catalytic amount of $\text{Pd(PPh}_3)_4$ produces a regiorandom polymer, but treatment with Ni(dppe)Cl_2 yields regioregular PAT in quantitative yield.

Recently, PTh with long side chains (e.g. alkyl (R) side chains) and regio-regular structures along the PTh main chain have been attracting strong interest. For example, the synthesis of head-to-tail (HT) poly(3-alkylthiophene-2,5-diyl) (P3RTh) initiated active studies of the molecular assembly of the π -conjugated polymers. Poly(3-alkylthiophenes) (PATs) in a head-to-tail configuration are almost planar; the so called trans conformation minimises the steric hindrance between the adjacent monomeric units. Structure of a trans conformation of a regioregular poly(3-alkylthiophene) is shown below.



By copolymerising 3,4-disubstituted thiophene and 3-alkylthiophene in different ratios, it is possible to obtain copolymers with different absorptions from 320-450 nm. A series of polymeric structures have been used to prepare LEDs covering all the visible range. By blending the different copolymers in a matrix such as PMMA, the colour emission could be varied by a proper applied voltage from orange to blue. Tuning of the EL was also obtained by preparing copolymers of 3-alkylthiophene and unsubstituted thiophenes in different molar ratios.

Various other types of thiophene (Th)-based polymers consisting of regularly repeating units also show a tendency to self-assemble. For example, Th(R)–Ar–Th(R) polythiophenes and head-to-head (HH) poly(thiophene-2,5-diyl) (HH-P3(C=C–R)Th) with –C=C–R side chains form self-assembled structures in colloidal solutions and in the solid phase.

It has been reported that π -conjugated polymers with Th(R)–Ar–Th(R) repeating units (Ar, aromatic or heteroaromatic unit) produce π -stacked molecular assemblies. McCulloch and co-workers synthesized such polythiophenes with fused Th units as the central –Ar– unit, and the resulting polymer showed a large hole mobility of about $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, comparable to that of amorphous silicon. Th(R)–Ar–Th(R) polymers often form π -stacked molecular assemblies, and their applicability to polymer transistors and solar cells has been actively tested.

Through these studies, it is now recognized that self-assembled π -conjugated polymers show superior electronic and optical functionalities. π -Conjugated polymers usually respond very rapidly to light through a change in the refractive index on time scales of about 10^{-12} s . Consequently, π -conjugated polymers with large χ are considered to be important materials for future high-speed photo-communication systems.

Various π -conjugated aromatic and heterocyclic polymers have been prepared by oxidative polymerization of the corresponding monomer (e.g. pyrrole and 3,4-ethylenedioxythiophene) or by organometallic polycondensation using dihalo-aromatics and dihalo-heterocycles (e.g. *p*-dibromobenzene, 2,5-dibromothiophene, 2,5-dibromopyridine) as the monomer.

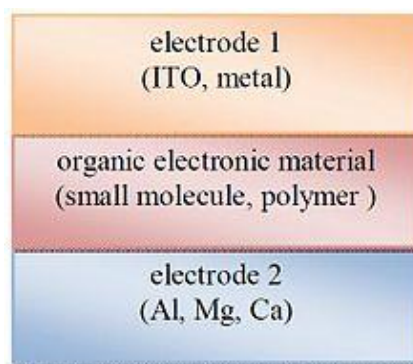
Organic Photovoltaics

The process by which light is converted into electricity using conducting polymers is the basis of photovoltaics. Organic photovoltaics (OPVs) offers low cost solution processing, flexible substrates and high speed processing. The major disadvantage of OPVs is the low power conversion efficiency.

Structure of OPVs

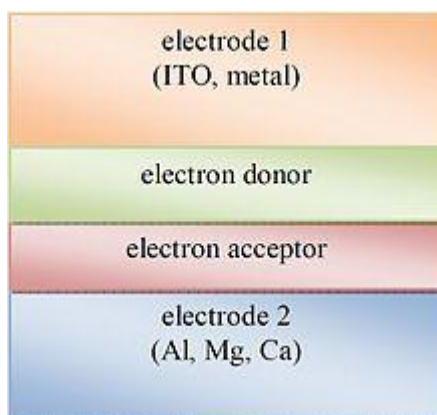
All organic photovoltaics cells have a planar layered structure where the organic active layer is sandwiched between two different electrodes, one of them is transparent conductive Indium tin oxide (ITO) and the other electrode is aluminium. The polymer solar cells have different architectures.

1. Single layer cell: An organic polymer is sandwiched between two electrodes. The photoactive region is very thin and the positive and negative photoexcited charges travel through the same material where recombination losses are high.



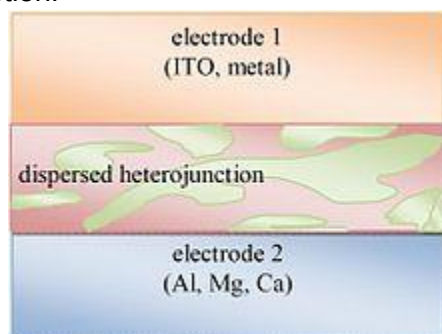
Single layer organic photovoltaic cell

2. Bi-layer cell: The sandwiched organic polymer consists of two constituents, electron donor and electron acceptor layer at ITO and Al electrodes respectively. The donor constituents are conjugated polymers of PPV, polythiophene and their derivatives with low band gap energy. The electron acceptor materials are C60 and conjugated polymer with cyano group having strong electron affinity. The lowest occupied molecular orbital (LUMO) level of donor material should be 0.3 -0.4 eV higher than that of acceptor.



A multilayer organic photovoltaic cell

3. Bulk heterojunction: The organic polymer consists of a nanoscale blend of donor and acceptor materials. The size of the blend is of nms allowing excitons to dissociate at the interface. It requires a percolating network that allows charge separation to occur. It has an advantage over other structures as they can be made thick enough for effective photon absorption.



A dispersed junction photovoltaic cell

Principle and Working of OPVs

The process of conversion of light into electricity by organic polymers takes place in following steps:

1. Exciton generation
2. Exciton diffusion
3. Exciton dissociation
4. Charge transport.

Exciton Generation: Absorption of photon from the solar spectrum by organic conducting polymers with bandgap energy 1.1- 2.0 eV produces electrostatically coupled electron-hole pairs called excitons.

Exciton diffusion: The photogenerated excitons are characterized by small life time of few picoseconds which limits the mobility of excitons to 5-10 nm called exciton diffusion length. As the excitons are dissociated within this range, exciton diffusion length plays a crucial role in the performance of the OPVs.

Exciton dissociation: It refers to splitting of electrostatically bounded electron-hole pair into free charges. The dissociation of excitons occurs at the donor-acceptor interfaces or junctions. The donor and acceptor materials are designed such that there exists a difference in LUMO levels of the donor and acceptor materials. For efficient dissociation, the difference in energy level of LUMO of donor and acceptor should be higher than that of exciton binding energy.

$$\Delta(\text{LUMO}_D - \text{LUMO}_A) > \text{exciton binding energy.}$$

Charge transport: The charges produced travel through specific electrode materials which are connected to external circuit. The donor material serves to transport holes while the electrons travel within the acceptor material.

Molecular Devices Based on Conducting Polymers**Diode**

Diodes are basic components of electronic devices. Conducting polymers play a vital role in fabricating flexible, low-cost diodes by combining either with a semiconductor (n or p-doped semiconductor) to form a hetero junction or with a metal to form Schottky junction. Most of the conducting polymers forms a Schottky junction diode rather than a hetero junction due to their inherent difficulty in forming a conducting polymeric film onto the semiconductor. The Schottky junction diode is also referred as 'majority carrier device'. A schematic diagram of Schottky diode is shown in the Fig in which the conducting polymeric film is coated onto the SnO_2 or SnO_2 coated substrate. The polymeric film is in contact with metals like Cu, Al, Ag, Au or In. On applying temperature or light rays, the electrons are injected from the metal electrode into the conduction band of the polymer (p-doped) to form free moving electronic carriers along the polymeric chain. The diode ceases its conduction faster than p-n junction due to low or no recombination of n and p- type of charge carriers. The conducting polymers used in Schottky diode are polypyrrole, polyaniline and poly(3)-alkyl thiophene which finds their application in photovoltaic cell. Poly alkyl based thiophenes are used as sensors for analyzing nitric oxide, ammonia in ambient air due to their high selectivity, low cost and can be operated at room conditions.

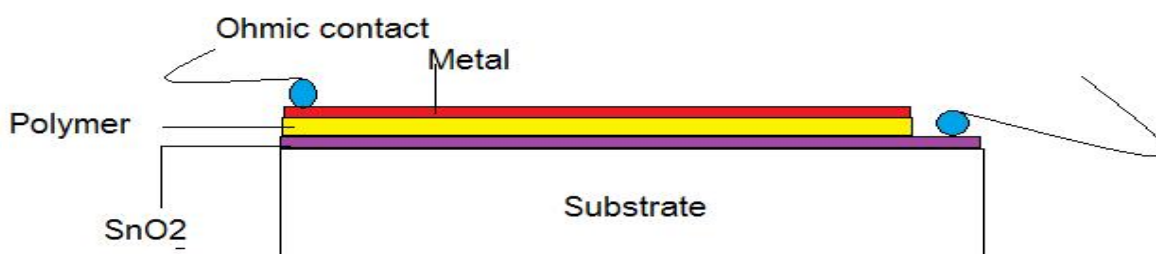


Fig 1.8 Schematic representation of conducting polymer based Schottky diode

Field-Effect Transistor

FET is the basic building block for solid-state electronics. The FET consists of 3 components viz. source, Drain and Gate. The source and the drain operate as a conducting channel between the two ohmic contacts while the Gate controls the charge induced onto the channel. The direction and movement of carriers in the channel (electrons or holes or both) is from the source to drain. The three components are inter-related with the Gate controls the carrier movement. It acts as a molecular switch or as an amplifier where the current is controlled across the two electrodes, source and drain in response to the voltage at the third electrode, gate. There are three types of FET,

- a. Metal-Insulator semiconductor Field Effect Transistor (MISFET):** The source and the drain are connected by a semiconductor and the Gate is separated from the channel by a layer of insulator.
- b. Metal-semiconductor Field Effect Transistor (MESFET):** The source and the drain are connected by n-region of semiconductor.
- c. Thin-Film transistor (TFT):** The source and the drain are deposited onto the conducting channel with a thin film of insulator is placed between the semiconductor and the Gate.

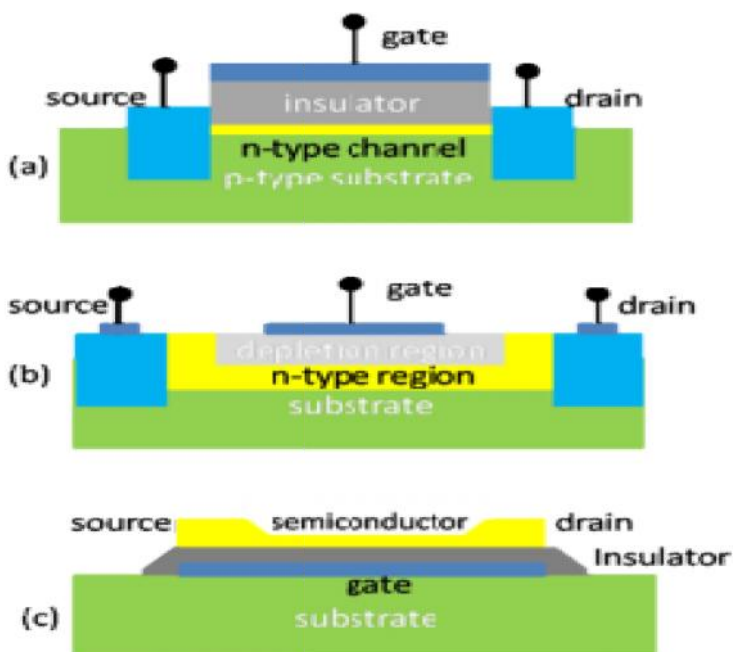


Fig 1.9 Schematic representation of three types of FET a) MISFET b) MESFET c) TFT

Conducting polymers offers a promising candidate for fabricating TFT over conventional semiconductor due to their low cost and ease of processing.

Construction of Polymer field-effect Transistor (PFET)

A PFET is constructed by applying a layer of Al onto the SiO₂ wafer to form contact pads. The source, drain and the gate electrode are made of poly ethylenedioxythiophene, PEDOT. A PEDOT is coated onto the Al to form Gate electrode. An insulating polymer (polyvinyl pyrrolidone) acts as dielectric is dispersed onto the Gate. An conducting polymer (Polypyrrole or poly alkylthiophene) is dispersed onto the Gate which forms the active layer. On top of the conducting polymer, the source and drain electrodes are deposited and extended to Al contact pads. When a positive charge is applied, electrons are accumulated at the interface to form a conducting channel at the interface. The performance of PFET is slow and have limited life time with field mobilities in the range of $0.5\text{--}1 \times 10^{-4} \text{cm}^2 \text{V}^{-1} \text{s}^{-1}$. These polymers can be fabricated into flexible flat panel devices which opens a new era of low cost plastic electronics.

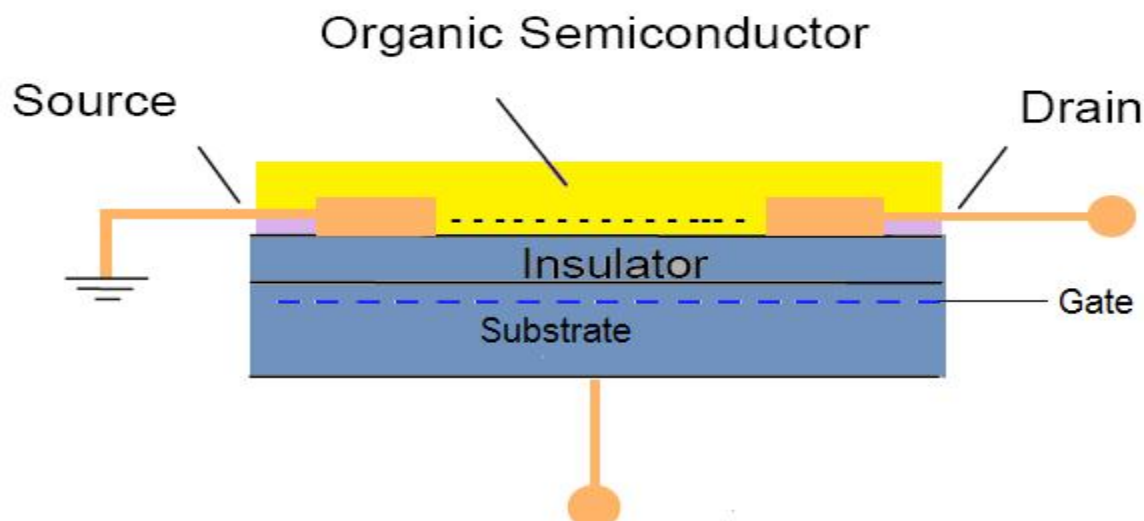


Fig 1.10 Schematic representation of PFET

PFET is applied to analyse specific ions mostly metals as in ion-selective FET. It is prepared by electrochemically depositing polycarbazole films onto Pt electrode which is specific to copper ions. The device response is measured by monitoring the drain current and it is linear from $2.5 \times 10^{-6} \text{M}$ to 10^{-4}M of copper ions. The drain current increases with increase in copper ions due to accumulation of copper ions onto the polymer matrix.

Biosensors

A biosensor is an analytical device incorporating either a biological or biological sensing element which is integrated or intimately connected with a physicochemical transducer. The transducer can be either an electrical, optical, thermal or piezoelectric device. A biosensor is a combination of an electrochemical device and an immobilized biomolecule to measure the concentration of the analyte. A number of biomolecules such as enzymes, antibodies, organelles, cells and receptors are used as sensing probes for the fabrication of biosensor. Organic conducting polymers provide a convenient tool for immobilizing enzymes at the electrode surface and its interaction with metallic or carbon electrode surface. These conducting polymers provide a suitable matrix for biomolecules in order to enhance stability, speed and sensitivity. Enzyme-immobilization technique plays a vital role to develop a stable and long

lasting sensor. Enzymes are immobilized on to the transducer either by adsorption, covalent attachment by cross-linking and entrapment. In adsorption method, the hydrophobic or hydrophilic nature of the polymer is used to develop the enzyme electrode while in covalent attachment, the functional groups in biomolecules ($-\text{NH}_2$, $-\text{COOH}$, $-\text{SH}$) are used for binding with the conducting polymer. In the recent years, most of the enzyme electrode constructed is based on enzyme entrapment in which the polymer forms a porous, homogeneous morphology with an ideal size to entrap the enzyme molecule.

Applications

1) In case of glucose biosensor, the glucose oxidase (GOX) enzyme is entrapped on to polypyrrole or polyaniline which is electrochemically deposited on a Pt electrode. The glucose concentration is determined either by the decrease in oxygen consumption or by generation of hydrogen peroxide.

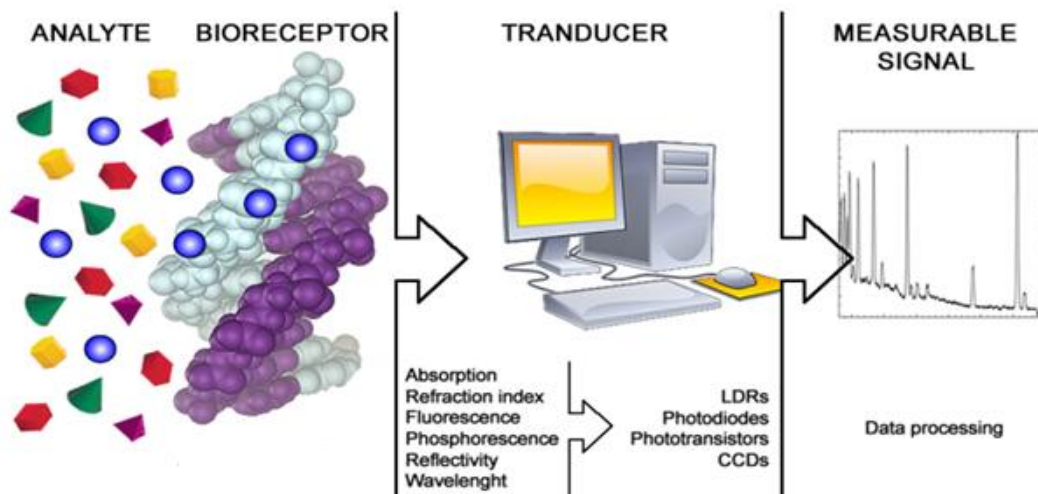


Fig 1.11 Schematic representation of a biosensor.

2) Amperometric acetylcholine esterase (AChE) biosensors are employed to analyse organophosphate pesticide. The acetylcholine esterase is immobilised on to polypyrrole and polyaniline copolymer doped in multiwalled carbon nanotubes. The copolymer provides an ideal size and biocompatible environment for enzyme molecules and it is used to analyse organophosphates.

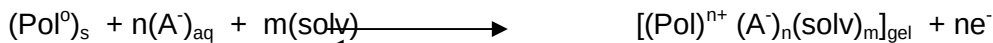
Actuators

Actuators are devices which convert electrical energy to mechanical energy by undergoing volume changes during oxidation and reduction. Actuators are bilayer device consisting of a passive substrate on which the active conjugated polymer like polypyrrole, polyaniline and polythiophene is deposited by electrochemical method. During oxidation and reduction reactions, there is a change in volume in the active layer which forces the device to bend. The bilayers are few cm long and few mms wide. The volume change in conducting polymer is dominated by movement of ions in and out of the polymer takes place by oxidation and reduction reactions.

Oxidation reaction :

During p-doping, the electrons are extracted from the polymeric chain to form positive charges or holes which are compensated by ions from the electrolytic medium. The transformation from a neutral polymer to an oxidised material can occur through two different ways:

1. Anion Exchange: During oxidation, the polymeric chains generate free volume and anions penetrate from the solution to balance the positive charges along the chain. The high concentration of charges inside the oxidised material induces the entrance of solvent from the solution required to maintain the osmotic pressure. The volume of the material increases during oxidation and decreases in the reverse reaction.



where subscript s,aq represents the solid and aqueous solution. The volume change and transition is promoted by the reaction from a packed solid state to a gel state.

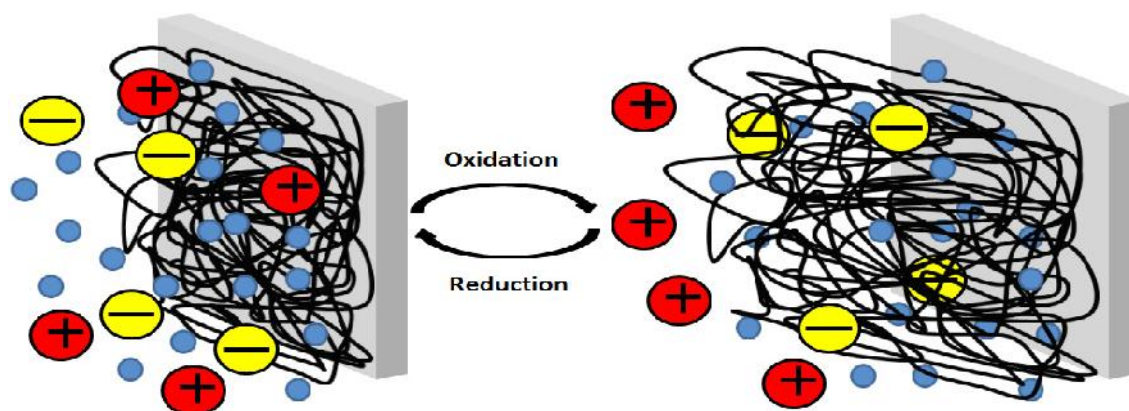


Fig 1.12 Complex polymer structure, showing volume changes (swelling/shrinking) produced during p-doping of polypyrrole film. Anions go inside the film during oxidation and are released during neutralization. Blue circles represent solvent molecules.

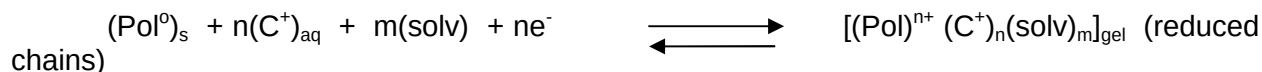
2. Cation Exchange: When the polymeric chain is oxidized in the presence of big macro anion, the anion gets trapped inside the polymeric matrix with the cations expelled. The material shrinks during oxidation and swells during reduction.



where MA represents the macroanion (organic, polymer or inorganic) trapped inside the conducting polymer and C^+ represents the cation.

n-Doping:

Conducting polymers such as PEDOT, polythiophene, polyfluorenes possessing high electron affinity are able to store negative charges on the polymeric chain during reduction. The cations, solvents enter the polymeric material which enables them to swell during reduction and shrinks during oxidation.



Applications

1. **Micropump:** Micropumps are capable of transporting fluids at a microflow rate with high precision. These pumps are used in microfluidic systems and in biosensors. The energy consumption rate of these polymeric micropumps is lower than conventional micropumps.
2. **Steerable Microcatheters:** Two conducting films around a positive catheter and a ionic electrolyte are used to control the movement of catheter tip which bends at an angle of 20° and are used to produce high resolution 3D imaging.

Test your understanding

1. Describe the synthesis of polyacetylene and explain its isomeric forms.
2. Describe electronic conduction in conjugated conducting polymers.
3. Explain in detail the mechanism of p-doping in trans-PA.
4. Explain in detail the mechanism of n-doping in trans-PA.
5. Describe the mechanism of protonic acid doping in polyaniline.
6. Explain the principle, construction and working of PLED.
7. Give the structural relationships of different PPV and polythiophene with their electroluminescence values.
- 8 Explain the construction and working of organic photovoltaics.
9. Explain in detail the application of conducting polymers in molecular devices.
10. Write short note on polyaniline.

Introduction, absorption of radiation, Beer-Lambert's law – Definition, Problems - UV-Visible Spectrophotometer: Instrumentation and application, IR Spectrophotometer: Instrumentation and application, Thermal methods of analysis- TGA, DTA, DSC, Sensors: Oxygen and Glucose sensor, Cyclic Voltammetry for redox system.

INTRODUCTION

Analytical instrumentation plays an important role in the production and evaluation of new products and in the protection of consumers and environment. It is used in checking the quality of raw materials such as substances used in integrated circuit chips, detection and estimation of impurities to assure safe foods, drugs, water and air, process optimization and control, quality check of finished products and research and development. Most of the modern instruments are microprocessor/computer controlled with user friendly software for collection of data, analysis and presentation.

This chapter deals with the different types of analytical instrumental methods that find use in a variety of industries. These include molecular spectroscopic methods, thermal methods of analysis, X-ray diffraction, scanning electron microscope and sensors.

SPECTROSCOPY

It is the study of interaction of electromagnetic radiation with matter consisting of atoms and molecules. When a substance is irradiated with electromagnetic radiation, the energy of the incident photons may be transferred to atoms and molecules raising their energy from ground state level to excited state. This process is known as absorption and the resultant spectrum is known as absorption spectrum. The process of absorption can occur only when the energy difference between the two levels E is exactly matched by the energy of the incident photons as given by the equation

$$E = h\nu = hc/\lambda$$

where h is Planck's constant (6.63×10^{-34} Js), ν is the frequency of incident radiation, c is the velocity of light and λ is the wavelength of the incident radiation. The excited state atoms and molecules then relax to the ground state by spontaneous emission of radiation. The frequency of the radiation emitted depends on E .

The energy changes that occur in atoms and molecules during interaction with different regions of electromagnetic radiation are given below.

Radiation absorbed	Energy of the radiation (J/mole)	Effect on the atoms/molecules	Applications
<i>γ-radiation</i>	$> 10^9$	<i>Change in nuclear Configuration</i>	<i>Used for cancer radiotherapy.</i>
X- radiation	$10^7 - 10^9$	Change in core electron Distribution	Chemical crystallography, qualitative and quantitative analysis.
Ultraviolet And Visible radiation	$10^5 - 10^7$	Change in valence shell electron distribution.	In qualitative and quantitative analysis.
Infra- red rays	$10^3 - 10^5$	Change in the vibrational and rotational energy Levels	Detection of functional groups in compounds, calculation of force constant, bond length, etc., and in quantitative analysis
Microwave radiation	$10 - 10^3$	Change in rotational energy levels	Calculation of force constant, bond length , bond angle, etc.
Radio frequency	$10^{-3} - 10$	Changes in nuclear and electron spin in the presence of external magnetic field.	Detection of proton environment and paramagnetic ions.

UV-Visible spectroscopy

The UV –Visible spectroscopy is also known as electronic absorption spectroscopy as molecules absorb radiation resulting in transitions between electronic energy levels. Absorption of radiation in the UV (wavelength range 190-400nm) and visible (wavelength 400–800nm) regions result in transitions between electronic energy levels. The principle of electronic transitions and the instruments required to record electronic transitions are common for both the regions. The electronic transition occurs based on *Franck Condon* principle which states that electronic transition takes place so rapidly that a vibrating molecule does not change its inter-nuclear distance appreciably during the transition.

Polyatomic organic molecules, according to molecular orbital theory, have valence shell electronic energy structure as shown in **Fig 1**.

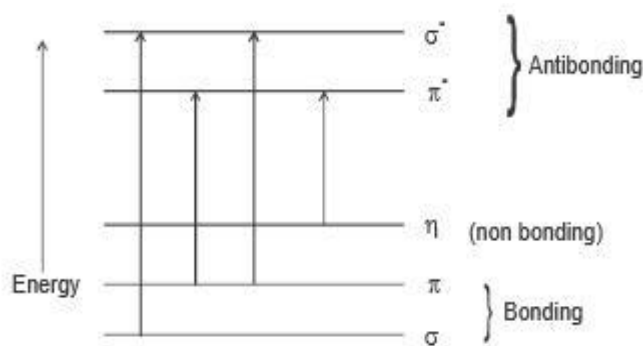


Fig.1 Valence shell electronic structure of polyatomic molecules and possible electronic transitions

In most of the organic molecules, the bonding and non-bonding molecular orbitals are filled, and the anti-bonding orbitals are vacant. The various electronic transitions that can take place include

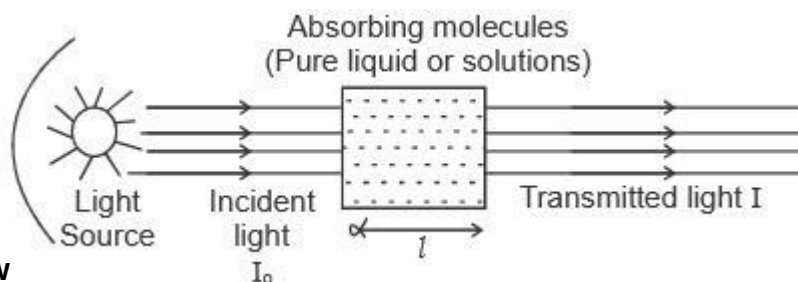
(i) $\sigma \rightarrow \sigma^*$ (ii) $n \rightarrow \sigma^*$ (iii) $\pi \rightarrow \pi^*$ and (iv) $n \rightarrow \pi^*$. The relative energy changes involved in these transitions are in the increasing order $n \rightarrow \pi^* < \pi \rightarrow \pi^* \sim n \rightarrow \sigma^* \ll \sigma \rightarrow \sigma^*$.

$n \rightarrow \pi^*$, $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions account for the absorption in 200 – 800 nm region of the electromagnetic spectrum. On the other hand, $\sigma \rightarrow \sigma^*$ transition occurs in vacuum UV region below 200 nm.

Laws of Absorption

The fraction of the photons absorbed by the molecule at a given frequency depends on

1. The nature of the absorbing molecules.
2. The concentration of the molecules (C). The higher the molar concentration, the higher is the absorption of photons.
3. The length of the path of the radiation through the substance or the thickness of the absorbing medium. Larger the path length (in cm), larger is the number of molecules exposed and greater is the probability of photons being absorbed.



Lambert's law

When a monochromatic beam of radiation passes through an absorbing medium, the intensity of the transmitted radiation decreases exponentially with the thickness of the absorbing medium. The law is expressed as

$$I_t = I_0 10^{-kx} \quad (1)$$

I_t and I_0 are the intensities of the transmitted and incident beams of radiations, x is the thickness of the absorbing medium and k is a constant.

Beer's law

When a monochromatic beam of radiation passes through an absorbing medium, the intensity of the transmitted radiation decreases exponentially with the concentration of the absorbing substance. The law is expressed as

$$I_t = I_0 10^{-k'C} \quad (2)$$

where C is the molar concentration of the absorbing substance and k' is another constant.

Beer-Lambert's law

When a beam of monochromatic radiation is passed through a transparent

absorbing medium, the decrease in the intensity of radiation is directly proportional to the concentration of the absorbing substance and the thickness of the absorbing medium.

$$-dI = kCdx$$

where I is the intensity of radiation, C is the molar concentration of the absorbing species, x is the thickness of the absorbing medium and k is the proportionality constant. If I_0 is the intensity of incident radiation and I is the intensity of transmitted radiation, after passing through a path length (thickness) of l cm in the solution, and upon integrating the above equation, between the limits $I = I_0$ when $x = 0$ and $I = I$ at $x = l$,

$$-\ln I / I_0 = kCl$$

$$-2.303 \log I / I_0 = kCl$$

$$-\log I / I_0 = kcl/2.303$$

$$-\log I / I_0 = \epsilon Cl \text{ (where } \epsilon = k/2.303)$$

$$\log I_0 / I = \epsilon Cl$$

ϵ is the molar absorptivity or molar extinction coefficient, and $\log I_0 / I = A$ which is known as the **absorbance** of the material.

$$A = \epsilon Cl \quad (3)$$

Thus absorbance **A**, also known as **optical density**, is directly proportional to (i) the concentration **C** of the absorbing species and (ii) the path length **l** and has no units. Eq. (3) is the mathematical expression for Lambert's Beer law.

ϵ is defined as the absorbance of the solution of unit molar concentration (1M) placed in a cell of path length one cm. If **C** is expressed in mol dm^{-3} , then the unit for ϵ is $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$.

Limitations of Beer –Lambert's law

Beer-Lambert's law is strictly valid only in dilute solutions. For dilute solutions, a

linear relationship is exhibited by a plot of absorbance (A) as a function of concentration of the absorbing substance (C), as shown in **Fig 2**.

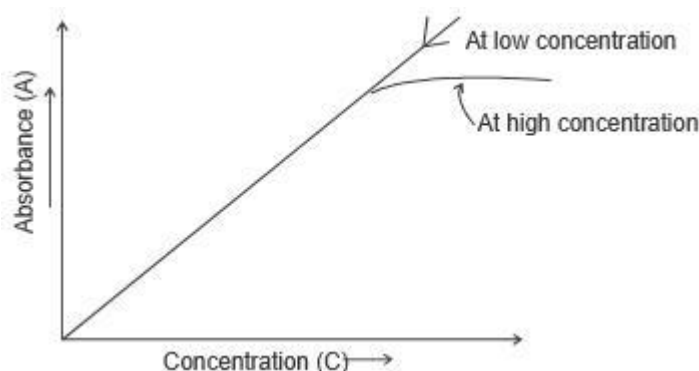


Fig 2 Plot of Absorbance versus Concentration

- (i) Real deviations occur at higher concentration of the absorbing species. At higher concentrations ($>10^{-3}\text{M}$), there is a change in the refractive index of the solution.
- (ii) Chemical deviations occur when there is more than one absorbing species present in the solution. When the absorbing molecules associate or dissociate in the solution, there is a change in the number of absorbing species.
- (iii) Instrumental deviation occurs due to changes in absorptivity of the species as a function of instrumental bandwidth.

Transmittance T

Transmittance is defined as the “fraction of the incident light that is transmitted by a given species”.

$$T = I / I_0$$

where I is the intensity of transmitted light and I_0 is the intensity of incident light.

$$\text{Absorbance } A = \epsilon C l$$

$$\log I/I_0 = \epsilon C l$$

$$A = -\log T$$

$$A = \log 1/T = \epsilon C l$$

Transmittance T is expressed as % T.

Instrumentation of UV-Visible spectrophotometer

The instrument used to record the spectra of molecules is called a spectrometer. The sophisticated double beam recording UV-Visible spectrophotometer covers the entire wavelength range of 190 - 800 nm. The basic components are

1. Source of radiation
2. Monochromator
3. Sample cell
4. Detector
5. Display/ Recorder

The block diagram of ultraviolet and visible spectrophotometer is shown in **Fig 3**.

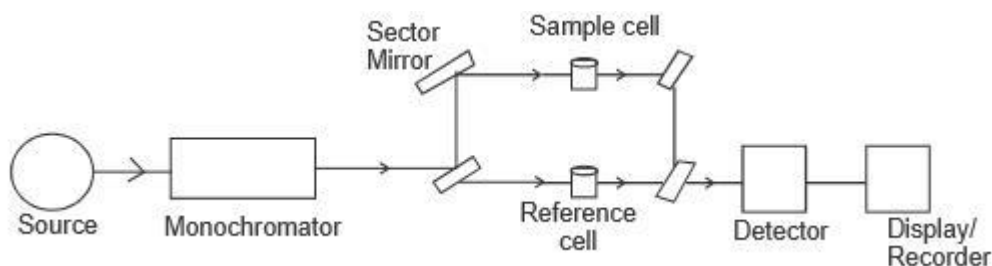


Fig 3. Block diagram of UV-Visible spectrophotometer

1. **Radiation source:** Hydrogen discharge lamp or deuterium lamp is used as UV radiation source. For visible light, tungsten filament lamp is used.
2. **Monochromator:** It disperses the polychromatic radiation from the source to a narrow range of wavelength. For UV and visible light, quartz prism or a grating is used. Two types of prisms, namely 60° Cornu quartz prism and 30° Littro prisms are employed. For visible light, a glass prism can be used.
3. **Sample holder (cells or cuvettes):** Sample containers should be transparent to UV and visible radiation. Cuvettes made of quartz are used for both UV and Visible region, whereas for visible light, glass cuvettes are used. Standard path length of these cuvettes is usually 1 cm.
4. **Sector mirror:** The monochromatic beam of radiation is split into two parallel beams by the sector mirrors which pass through the sample and reference cells and reach the detector.
5. **Solvents for UV region:** Electronic absorption spectra are usually recorded for solutions. Solvent used should absorb in the same region as the solute. Solvents used in the UV and visible region are water, methyl alcohol, ethyl alcohol, chloroform, hexane, etc. 95% ethyl alcohol is the most widely used solvent in UV region since it is a polar solvent, cheaper and transparent up to 210 nm.
6. **Detectors:** Photovoltaic cells or photo emissive cells or the more sensitive photomultiplier tubes are used to convert the incident photons into electric

current.

- 7. Display/Recorder:** The wavelength drive of the recorder and display unit are synchronized so that the detector signal converted into the transmittance or absorbance units is recorded as a function of wavelength of the incident beam of radiation.

In UV-visible spectrometer, a beam of light is split into two equal halves. One half of the beam (sample beam) is directed towards the sample cell containing the solution of the compound being analyzed and the other half (reference beam) through the reference cell that contains only the solvent. The instrument is so designed that it can compare the intensities of both the beams at each wavelength of the region 190-800 nm. If the compound absorbs light at a particular wavelength, the intensity of the sample beam, I will be less than the intensity of the reference beam I_0 . An output graph, which is a plot of the wavelength (λ) versus the absorbance (A) at each wavelength obtained, is known as absorption spectrum.

Characteristics of UV and Visible spectra

1. $\lambda_{\max}$ value is the wavelength at which absorption maximum occurs and is different for different molecules.
2. ϵ value (molar absorptivity) for a given concentration of the compound is related to the height of the absorption band.

The $\lambda_{\max}$ and ϵ value depend upon the concentration and structure of the molecule and therefore used in characterization and in quantitative estimation of a compound. Unsaturated groups having n or electrons are essentially responsible for absorption and these fragments are known as chromophores. Simple chromophores such as $C=C$, $C\equiv C$, $C\equiv N$, $N=N$, $C=O$ undergo $n-\pi^*$ transitions in the short wavelength regions of UV light. Saturated groups containing hetero atoms which modify the absorption of the chromophores are called auxochromes - e.g. $-OH$, $-Cl$, $-OR$, NR_2 , etc. UV visible spectrum of benzene in ethanol is shown below.

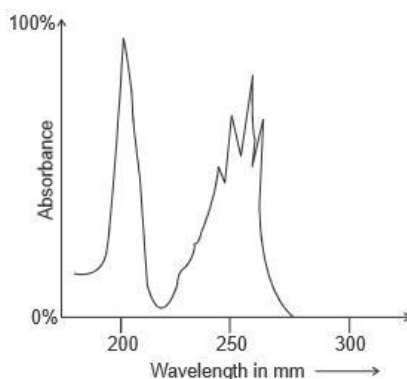


Fig. 4. Electronic absorption spectrum of a solution of benzene in hexane ($\lambda_{\max} = 225$ nm)

Applications of UV-Visible Spectrophotometry

1. Qualitative Analysis

(a) UV-Visible spectra aids in the identification of unknown organic samples.

Observation	Possible conclusion
Absorption below 200 nm	Molecules contain only σ bonds or lone pairs or isolated double bonds. E.g. $\text{CH}_2=\text{CH}_2$ ($\lambda_{\text{max}}=180\text{nm}$) Presence of conjugated double bonds is indicated by an increase in λ_{max} E.g. butadiene ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$) absorbs at 210 nm. Long chain conjugated molecules such as polyenes, carotenes, etc absorb in the visible region with very high ϵ value.
Strong absorption between 200 and 250 nm ($\epsilon=1000$)	Presence of aromatic ring. E.g. benzene ($\lambda_{\text{max}} = 250 \text{ nm}$)
Weak absorption near 300 nm	Carbonyl compound (containing $\text{C}=\text{O}$)

(b) Purity check: ϵ value is used in the identification of the substance. The magnitude of ϵ value depends on the chemical nature of the absorbing substance and the wavelength of incident light(λ).The purity of the sample can be checked by comparing the ϵ values of the test sample with the standard sample. Deviations show the presence of impurity or adulteration in the test sample.

2. Quantitative analysis - Many organic compounds and inorganic complexes may be determined by direct absorbance measurement values using the Lambert's Beer law.

$$A = \epsilon C l$$

A plot of Absorbance (A) vs. C the concentration gives a linear plot.

3. Determination of dissociation constants of weak acids and bases from the change in absorption spectra with pH.

4. Study of kinetics of chemical reactions.

5. Study of electronic structure of molecules such as vitamins, detecting steric hindrance, etc.

IR SPECTROSCOPY

Definition

It is the spectroscopy which deals with the infrared region (700nm to 1000 μ m) of the electromagnetic spectrum with a longer wave length and lower frequency than visible light.

Principle

An IR spectrum is produced by the absorption of energy by a molecule in the infrared region and the transitions occur between vibrational levels. Hence IR spectroscopy is also known as vibrational spectroscopy. It is divided into three regions.

- (i) Near IR – 12500 to 4000 cm^{-1}
- (ii) Middle IR – 4000 to 670 cm^{-1}
- (iii) Far IR – 670 to 50 cm^{-1}

The most useful IR region lies between 4000 to 670 cm^{-1}

Theory of IR absorption

IR radiation does not have sufficient energy to induce electronic transitions like UV-Visible spectroscopy. It causes only vibrational and rotational changes. For a molecule to absorb IR radiation, two conditons must be satisfied.

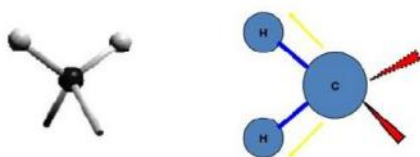
- (i) There must be change in the net dipole moment of the molecule during the vibration.
- (ii) The energy of the IR radiation must match the energy difference between two vibrational levels.

The bonds of a molecule experience various types of vibrations. The atoms are not stationary and fluctuate continuously. Vibrational motions are defined by stretching and bending modes. There are two types of vibrations.

- (i) Stretching Vibration – Symmetric and Asymmetric
- (ii) Bending Vibration – (a) Inplane bending – Rocking, Scissoring,
(b) Outplane bending – Wagging and Twisting.

a) Symmetrical stretching:

2 bonds increase or decrease in length simultaneously.



b) Asymmetrical stretching

in this, one bond length is increased and other is decreased.



a) In plane bending

i. Scissoring:

- This is an in plane bending
- 2 atoms approach each other
- Bond angles are decrease



ii. Rocking:

- Movement of atoms take place in the same direction.



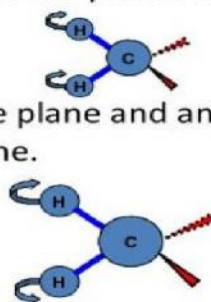
b) Out plane bending

i. Wagging:

- 2 atoms move to one side of the plane. They move up and down the plane.

ii. Twisting:

- One atom moves above the plane and another atom moves below the plane.



Instrumentation

The basic components of an infrared spectrophotometer are as follows.

- (i) Source – The most common sources used are the Nernst glower and the globar. The

Nernst glower is a tube made up of zirconium, yttrium and thorium. The globar is a cylindrical rod made up of SiC. Both need to be heated to 1000°C to 1800°C to emit IR radiation.

- (ii) Sample cells and Sampling techniques – The sample cells are made up of NaCl and it is transparent to IR light. Gaseous samples are taken in a 10 cm long cell. Liquid samples are placed between two discs of NaCl. Solid samples are made into a mull by grinding with Nujol (mineral oil) or a pellet by grinding with KBr pellets.

- (iii) Solvents – The solvent should be transparent to IR light and must dissolve the sample completely. Eg., CCl_4 , CS_2 , etc.

- (iv) Monochromator – The monochromator separates polychromatic radiation into individual wavelengths. Eg., NaCl, LiF, CaF_2 , etc.

- (v) Detectors – They convert the light signal into electrical signal. Photovoltaic cells, photoconductive cells, bolometers, thermocouples, etc are used as detectors.

- (vi) Amplifier / Recorder – The electrical signal is amplified and converted to percentage transmittance as a function of wavenumber and recorded.

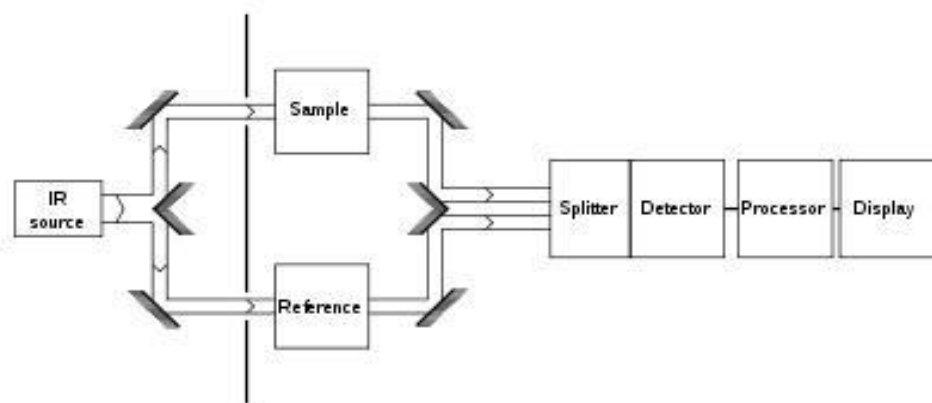


Fig 5 Block diagram of IR spectrophotometer

Application

i. Identification of functional group and structure elucidation

Entire IR region is divided into group frequency region and fingerprint region. Range of group frequency is $4000\text{--}1500\text{ cm}^{-1}$ while that of finger print region is $1500\text{--}400\text{ cm}^{-1}$.

In group frequency region, the peaks corresponding to different functional groups can be observed. According to corresponding peaks, functional group can be determined.

Each atom of the molecule is connected by bond and each bond requires different IR region so characteristic peaks are observed. This region of IR spectrum is called as finger print region of the molecule. It can be determined by characteristic peaks.

(ii) Identification of substances

IR spectroscopy is used to establish whether a given sample of an organic substance is identical with another or not. This is because large number of absorption bands is observed in the IR spectra of organic molecules and the probability that any two compounds will produce identical spectra is almost zero. So if two compounds have identical IR spectra then both of them must be samples of the same substances.

IR spectra of two enantiomeric compound are identical. So IR spectroscopy fails to distinguish between enantiomers.

For example, an IR spectrum of benzaldehyde is observed as follows.

C-H stretching of aromatic ring	3080 cm^{-1}
C-H stretching of aldehyde	2860 cm^{-1} and 2775 cm^{-1}
C=O stretching of an aromatic aldehyde	1700 cm^{-1}
C=C stretching of an aromatic ring	1595 cm^{-1}
C-H bending	745 cm^{-1} and 685 cm^{-1}

(iii) Studying the progress of the reaction

Progress of chemical reaction can be determined by examining the small portion of the reaction mixture withdrawn from time to time. The rate of disappearance of a characteristic absorption band of the reactant group and/or the rate of appearance of the characteristic absorption band of the product group due to formation of product is

observed.

(iv) Detection of impurities

IR spectrum of the test sample to be determined is compared with the standard compound. If any additional peaks are observed in the IR spectrum, then it is due to impurities present in the compound.

(v) Quantitative analysis

The quantity of the substance can be determined either in pure form or as a mixture of two or more compounds. In this, characteristic peak corresponding to the drug substance is chosen and $\log I_0/I_t$ of peaks for standard and test sample is compared. This is called base line technique to determine the quantity of the substance.

Limitation

- i. Molecular weight cannot be predicted.
- ii. It is frequently non- adherence to Beers law of complexity spectra.
- iii. IR spectroscopy does not provide information of
- iv. Relative position of different functional group on a molecule.

THERMAL ANALYSIS

Thermal analysis includes a group of techniques which monitors the change in physical properties such as weight, temperature or enthalpy of a sample material as a function of temperature. The sample is subjected to a programmed heating from an initial lower temperature to a final higher temperature at a specified heating rate during the analysis. The most commonly used techniques include thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Thermal analysis has been used to determine the physical and chemical properties of polymers, electronic circuit boards, geological materials, etc. Thermal events that may occur in the sample as it is undergoing a change in temperature include phase transitions, melting, sublimation/volatilization, decomposition, glass transition in polymers, oxidation/reduction, etc. The summary of thermal analysis techniques is given below.

Technique	Quantity measured	Typical applications
Thermogravimetric analysis (TGA)	Change in weight of the sample is recorded as a function of temperature.	Thermal stability of a substance and compositional analysis of alloys and mixtures and corrosion studies.
Differential thermal analysis (DTA)	Temperature difference between a sample substance and the reference material is measured as a function of temperature when subjected to a controlled temperature programme.	Generation of phase diagrams and study of phase transitions of a solid sample, thermal stability and characterization of polymers
Differential scanning calorimetry (DSC)	Difference in energy inputs into a sample substance and a reference material is measured as a function of temperature when subjected to a controlled temperature programme.	Reaction kinetics, purity analysis of drugs

The thermal analysis instrumentation consists of four components

- (i) The furnace which is controlled by the computer and a temperature sensor and has a controlled atmosphere such as air or inert gases (N_2 , He, Ar).
- (ii) The sample and its container
- (iii) The sensors for measuring temperature and sample properties
- (iv) The computer, data collection and processing equipment and a display device for the results

THERMOGRAVIMETRY (TG)

Definition: Thermogravimetry is a technique in which a change in weight of the sample is recorded as a function of temperature.

Principle: The weight of the sample is continuously monitored as a function of temperature when the sample is heated at a controlled heating rate of $10\text{--}20^\circ\text{C}/\text{minute}$. When the temperature is increased from ambient to 1200°C , the sample may undergo dehydration, decomposition or volatilization which results in direct weight loss. The online plot of sample weight versus temperature is called a TG thermogram.

Instrumentation: The major component of TG is the thermobalance or thermogravimetric analyzer for measuring the mass. It includes a thermobalance and a microprocessor controlled tubular furnace. **Fig 6** shows the instrumentation of TG.

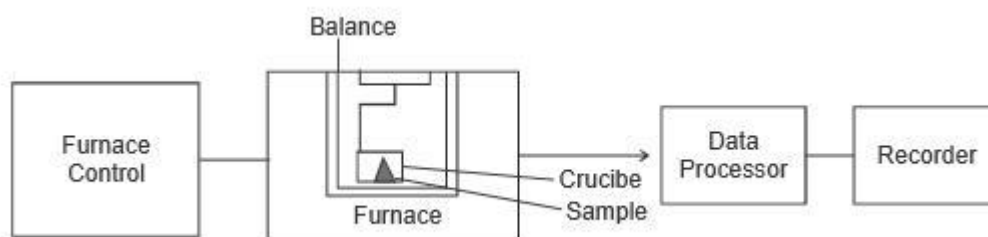


Fig 6 Block diagram of TG apparatus

1. **Sample:** A solid sample of 5-50 mg is placed in a platinum crucible (sample container) and connected to a sensitive microbalance. The sensitive microbalance can detect a weight change of $1\mu\text{g}$ of the sample.
2. **Thermobalance:** The balance is placed inside the tubular furnace. A thermocouple,

located immediately below the crucible, monitors the furnace temperature. The temperature of the furnace is accurately controlled and programmed for any change by the microprocessor.

3. The **null point** balance is used in TG. When there is a **change in the weight** of the sample, the balance beam will deviate from its usual position. A sensor detects the deviation and initiates a force that will restore the balance to the null position. The restoring force is proportional to the change in weight. The atmosphere inside the furnace can be controlled by using inert gases such as nitrogen, helium or argon or reactive gases such as oxygen, hydrogen, etc.
4. **Data processor and recorder:** The balance assembly measures the initial weight of the sample and continuously monitors changes in sample weight as heat is applied to the sample inside the furnace. The furnace data and balance data are collected during the experiment and sent to the computer for manipulation. The computer records the TG curve.

The thermogram obtained for calcium oxalate monohydrate is shown in **Fig 7** and the various thermal reactions that occur when calcium oxalate monohydrate is heated from 30°C to about 1000 °C is summarized in Table 2.1. The horizontal portions or plateaus indicate regions where there is no weight loss and the curved portion or downward steps indicate regions of weight loss.

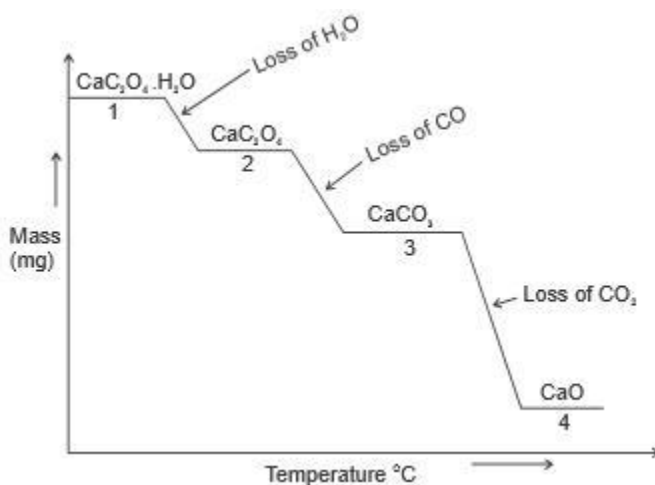


Fig 7 TG curve for decomposition of $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$

Table 2.1 Summary of thermal reactions in the decomposition of calcium oxalate monohydrate

Temperature range in °C	Thermal reaction	Change in mass
30 - 130	1 st plateau region. $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ is thermally stable	No change in mass
130 - 190	1 st downward step. $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O} \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O}$	Loss of water of crystallization and there is decrease in mass
190 - 400	2 nd plateau region. Anhydrous CaC_2O_4 is thermally stable	No change in mass
400 - 470	2 nd downward step. $\text{CaC}_2\text{O}_4 \rightarrow \text{CaCO}_3 + \text{CO}$	Decrease in mass due to loss of CO.
470 - 700	3 rd plateau CaCO_3 is thermally stable.	No change in mass
700 - 840	3 rd downward step $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$	Decrease in mass due to loss of CO_2
840 - 1000	4 th plateau CaO is thermally stable	No change in mass. The residue obtained is CaO.

The thermogram obtained for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is shown in the **Fig 8** and thermal events are summarized in the Table 2.2.

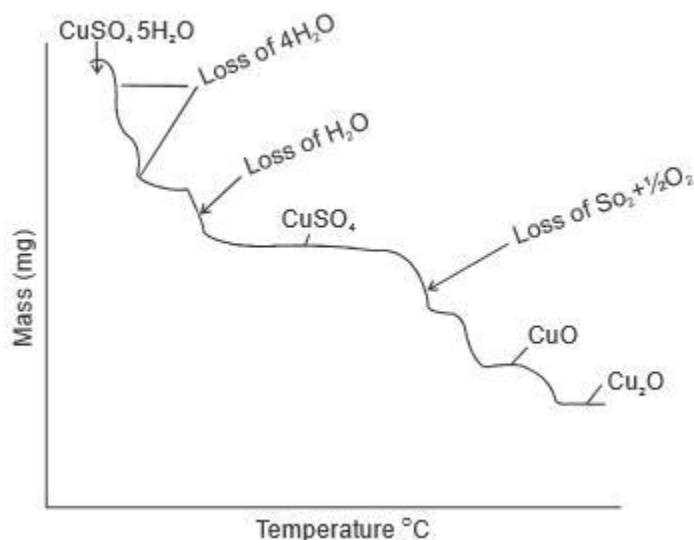


Fig. 8 TG curve for $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Table .2 Summary of thermal reactions in the decomposition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Temperature range in °C	Thermal reaction		Change in mass
30 - 90	1 st plateau region. CuSO ₄ .5H ₂ O is thermally stable		No change in mass
90 - 150	1 st downward step.		Loss of water of crystallization and there is decrease in mass
	CuSO ₄ .5H ₂ O	CuSO ₄ . H ₂ O+3 H ₂ O	
	→		
150 - 200	2 nd plateau region. CuSO ₄ . H ₂ O is thermally stable		No change in mass
200 - 275	2 nd downward step. CuSO ₄ . H ₂ O → CuSO ₄ + H ₂ O		Decrease in mass due to

		loss of H ₂ O
275 - 700	3 rd plateau anhydrous CuSO ₄ is thermally stable.	No change in mass
700 - 900	3 rd downward step. CuSO ₄ → CuO+SO ₂ +1/2O ₂	Decrease in mass due to decomposition
900 - 1000	4 th plateau CuO is thermally stable	No change in mass.
1000 - 1100	4 th downward step 2CuO → Cu ₂ O+1/2O ₂ .	Reduction of CuO to Cu ₂ O and there is decrease in mass.

Applications of TGA

1. In the analysis of thermal decomposition of inorganic salts and complexes which are used as catalysts, semiconductors and fine chemicals.
2. The decomposition temperature of commodity plastics and rubber are investigated by TGA. Each kind of polymer has a characteristic thermogram and can be used for identification purposes. **Fig 9** shows the thermogram of some common polymers. The thermal stability of polymers decreases in the order PTFE < LDPE < PMMA < PVC. PVC shows two-stage decomposition.

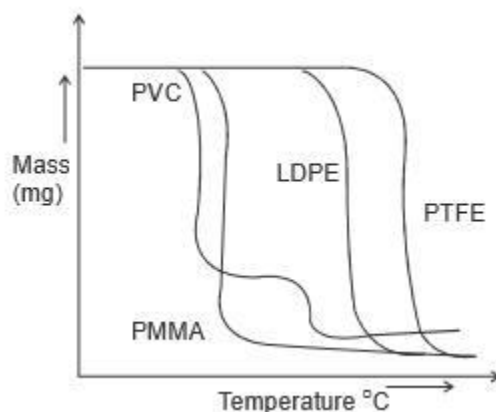


Fig. 9 TG curve for the determination of thermal stability of polymers.

3. TGA of pharmaceuticals, coal and minerals is useful in the study of complex thermal reactions.
4. In the determination of composition of alloys and mixtures. E.g. determination of a mixture of calcium and strontium as their carbonates. Both undergo decomposition with evolution of CO_2 . But the decomposition of CaCO_3 occurs in the temperature range $650\text{--}850^\circ\text{C}$ whereas SrCO_3 decomposes in the higher range $950\text{--}1150^\circ\text{C}$.
5. In qualitative analysis of compounds.
6. In studying the oxidation of alloys.

DIFFERENTIAL THERMAL ANALYSIS (DTA)

Definition: Differential thermal analysis is a technique in which the temperature difference (ΔT) between the sample and an inert reference material is measured as a function of sample temperature when both are heated uniformly.

Principle: When the sample undergoes any transition like melting, dehydration, decomposition etc., there is liberation or absorption of energy by the sample with the corresponding deviation of its temperature from that of the reference. When the sample does not undergo any physical or chemical change, both the sample and the inert reference material are at the same temperature and ΔT is zero. If any endothermic or exothermic reaction occurs in the sample, the temperature of the sample decreases or increases and causes a difference in temperature (ΔT) between the sample and reference. A plot of ΔT vs. T gives the DTA thermogram.

Instrumentation: The instrument consists of a microprocessor controlled furnace, data processor and recorder and a facility to control the atmosphere. A block diagram of the DTA instrument is shown in **Fig 10**.

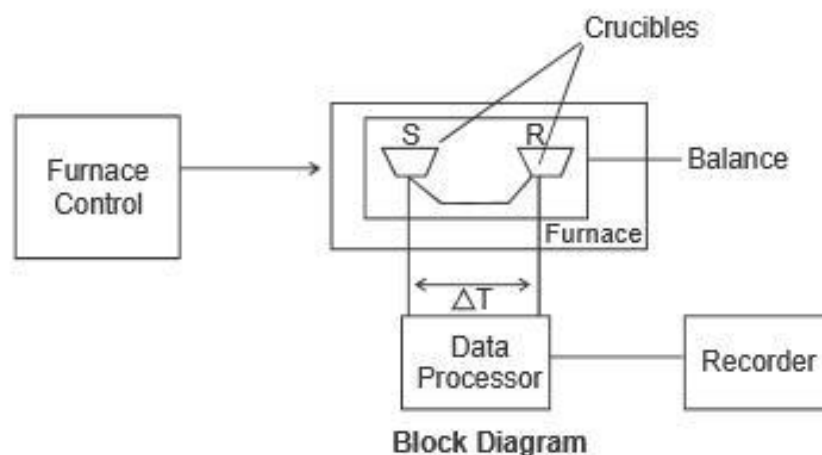


Fig. 10 Block diagram of the DTA instrument

- 1. Sample holder assembly:** The solid sample and the reference material (usually an inert substance) like alumina of 10 mg is placed in a platinum crucible (sample container) and connected to a sensitive microbalance. The temperature of the sample and reference is measured by an individual thermocouple.
- 2. Microprocessor controlled furnace:** The whole sample holder assembly is placed inside the furnace. The sample and the reference are heated at the same heating rate from ambient to 1500°C. A temperature programmer or furnace control maintains a constant heating rate of 1°C/min -100°C/min.
- 3. Facility to control atmosphere:** Sample and reference chamber are designed to permit the circulation of inert gases such as nitrogen or reactive gases such as oxygen or air.
- 4. Data processor and recorder:** The difference in temperature (ΔT) between the sample and the reference (S and R) thermocouples is continuously measured. After amplification, the difference in signal is recorded on the y-axis. The temperature of the furnace is measured by an independent thermocouple and recorded on the x axis. The balance and furnace data collected is sent to the PC for manipulation and a DTA plot of (ΔT) vs. T is obtained.

An idealized DTA curve is shown in **Fig 11**. Peak 1 is an exothermic peak and peak 2 is an endothermic peak. Endothermic peaks signify changes in crystallinity or dehydration reactions while exothermic curves results due to chemical reactions such as oxidation.

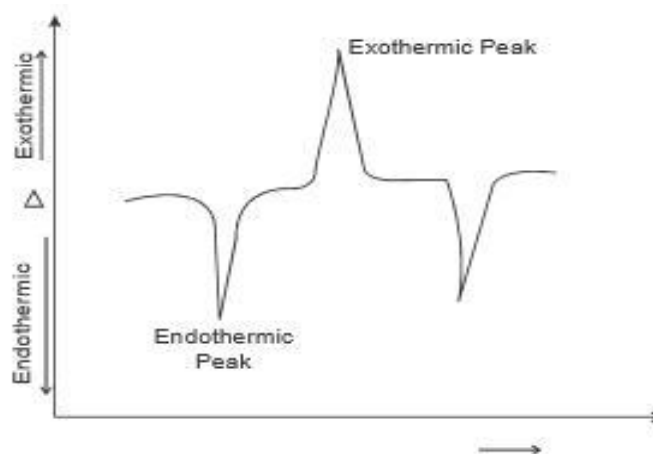


Fig. 11 Idealized DTA curve.

Applications of DTA

1. **Qualitative analysis of materials:** DTA measurements provide a rapid method for the finger

printing of minerals, clays and polymeric materials. E.g. **Fig 12** shows the DTA thermogram of calcium oxalate monohydrate in flowing air (O_2) obtained by increasing the temperature at a rate of $8^\circ C/min$. It contains two endothermic peaks and one exothermic peak. The decomposition and oxidation reactions are shown below.

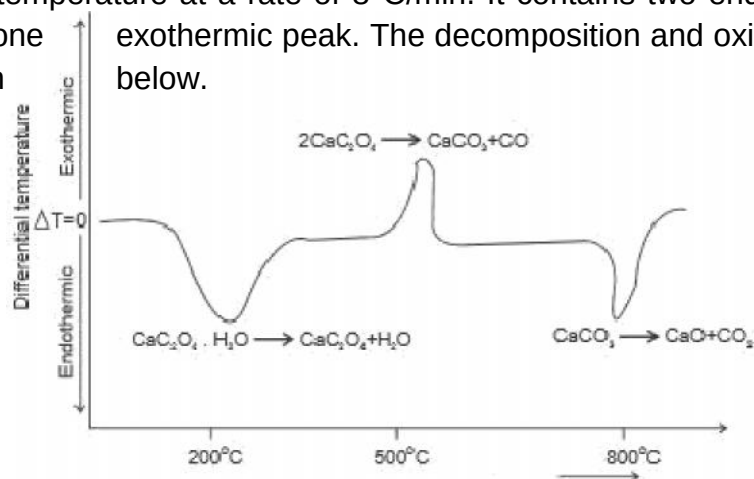


Fig 12 DTA curve of calcium oxalate monohydrate in O_2 atmosphere

2. DTA provides information regarding processes like fusion, dehydration, oxidation,

reduction, adsorption and solid state reactions and in generation of phase diagram and the study of phase transitions.

3. It provides an accurate way of determining the melting and boiling points for organic compounds.
4. It has been widely used to study and characterization of polymers and qualitative analysis of polymer mixture. **Fig 13** is the DTA curve which illustrates the various types of transitions that occurs during heating of a polymer.

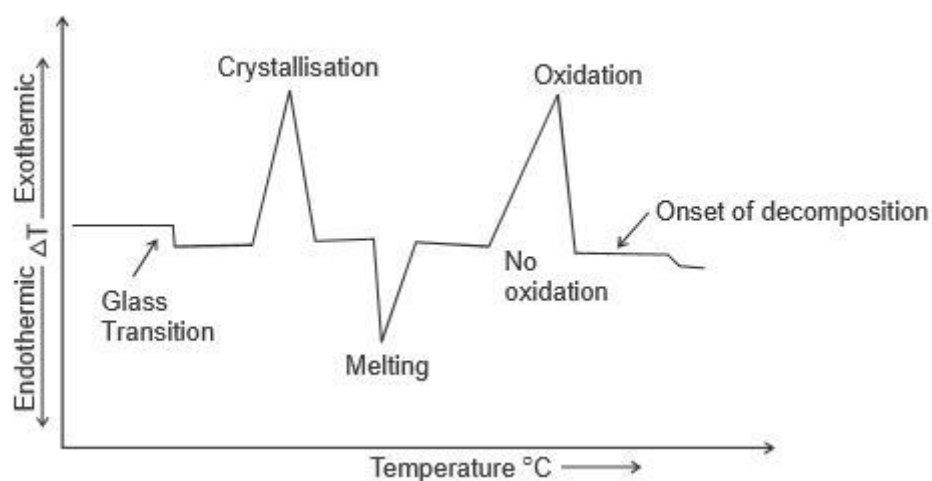


Fig 13 DTA thermogram of polymer

DIFFERENTIAL SCANNING CALORIMETRY (DSC)

Definition: DSC is a thermal method in which the difference in heat flow into the sample and the reference material is measured as a function of linear increase or decrease of the sample temperature.

Principle: DSC measures the difference in heating power (heat flow) required to keep the temperature of a sample and a reference material the same. The sample and the reference are heated by separate electrical heaters exactly at the same rate. Whenever the sample undergoes an endothermic or exothermic reaction, there is a change in sample temperature with respect to the reference temperature. The power to the sample heater is modified so that the difference in temperature between the sample and the reference, $\Delta T = 0$. The difference in power supplied to the sample and the

reference represents the energy change or enthalpy change (ΔH) in the sample.

Instrumentation: DSC instrumentation is the same as DTA. DSC is a calorimetric method in which the difference in heat energy (ΔH) is recorded as a function of sample temperature. The block diagram of DSC instrument is shown in **Fig 14**.

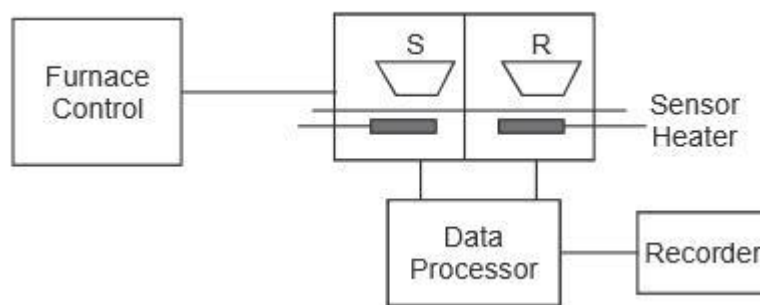


Fig 14 Block diagram of DSC instrument

The main components are a microprocessor controlled furnace provided with individual heater and thermocouples for measuring the temperature of sample and reference, data processor and recorder, and a facility for atmosphere control.

- 1. Sample holder assembly:** The solid sample and the reference material (usually an inert substance) like alumina of 10 mg is placed in a separate platinum crucible (sample container) and connected to a sensitive microbalance. The sample and the reference are heated separately and the temperature of the sample and reference is measured by individual thermocouple. The thermocouples measure the difference in heat flow.
- 2. Microprocessor controlled furnace:** The whole sample holder assembly is placed inside the furnace. The sample and the reference are heated at the same heating rate from ambient to 700°C. A temperature programmer or furnace control maintains a constant heating rate of 1°C/min -100°C/min.
- 3. Facility to control atmosphere:** Sample and reference chamber are designed to permit the circulation of inert gases such as nitrogen or reactive gases such as oxygen or air.

4. **Data processor and recorder:** The difference in heat flow (ΔH) between the sample and the reference (S and R) thermocouples is continuously measured. After amplification, the difference in signal is recorded on the y-axis. The temperature of the furnace is measured by an independent thermocouple and recorded on the x axis. The balance and furnace data collected is sent to the PC for manipulation and the DSC thermogram which is a plot of ΔH vs. T is obtained. A typical DSC thermogram for the decomposition of calcium oxalate monohydrate is shown in **Fig 15**.

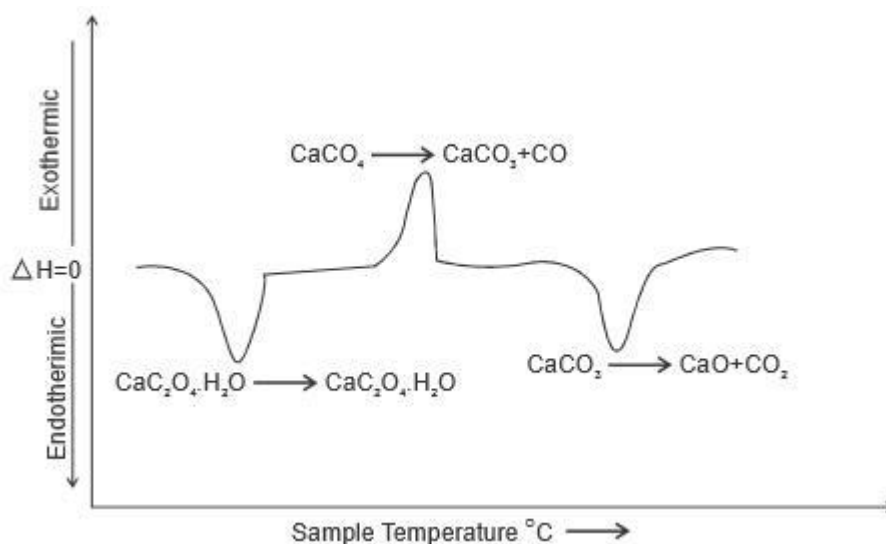


Fig 15 DSC thermogram for the decomposition of calcium oxalate monohydrate

Applications of DSC

1. DSC is highly useful in the study of phase transitions and temperature induced changes that occur at very low temperatures in the case of polymers, biological samples, pharmaceutical samples, etc.
2. It finds widespread application in calculating the enthalpy of transitions such as enthalpy of melting, enthalpy of crystallization, enthalpy of fusion, etc. of polymeric materials.
3. DSC also provides accurate method of determining melting, boiling and decomposition points for organic compounds.
4. It is used for the determination of purity of drug samples.

SENSORS

Devices used to detect changes in physical and chemical quantities are called sensors.

OXYGEN SENSORS

An oxygen sensor or lambda sensor is an electronic device that measures the proportion of oxygen (O₂) in the gas or liquid being analysed.

CLARKE ELECTROCHEMICAL OXYGEN SENSOR

An electrochemical oxygen analyzer is based on electrochemical reduction of O₂ at a negatively polarized electrode. This electrode is known as "Clark Type" after their inventor, Dr. Leland Clark. The Clark electrode consists of a silver anode and a platinum cathode in contact with 0.01M KCl electrolyte solution (**Fig. 16**). It is covered at the tip by a semi-permeable membrane usually polypropylene membrane or Teflon membrane which is permeable to gases but impermeable to the electrolyte. The sensor is placed in contact with the sample solution containing dissolved oxygen. O₂ diffuses through the membrane and comes into contact with the cathode. The silver/ silver chloride (Ag/AgCl) anode provides electrons for the cathode reaction. Silver at the anode undergoes oxidation. A potential difference of 1.5V is applied between the two electrodes, the cathode being sufficiently polarized (-0.6V) to reduce all of the oxygen. The current in the circuit is proportional to the quantity of gas migrating across the membrane and measures the oxygen concentration in the solution.

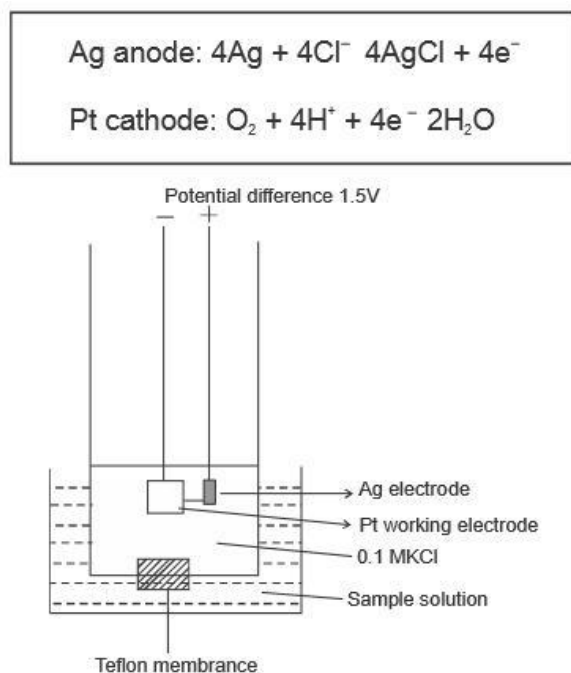


Fig. 16 Clarke electrochemical O₂sensor.

Limitations:

It is susceptible to damage in the presence of acidic gases such as HCl, H₂S, SO₂ etc.,

PARAMAGNETIC OXYGEN SENSOR

Oxygen, nitric oxide and nitrogen dioxide are unique among the ordinary gases in that they are paramagnetic; that is they are attracted into a magnetic field. Oxygen is several times more paramagnetic than nitric oxide or nitrogen dioxide. This property of oxygen is taken advantage in gaseous oxygen analyzers.

In the cell, two glass spheres filled with nitrogen gas are suspended with strong metal (**Fig. 17**). At first, the spheres are kept in balance in a homogeneous magnetic field. When oxygen molecules having a large magnetic susceptibility flow there, the molecules are pulled toward the stronger magnetic field zone and the spheres are moved away from the zone. The resulting deviation of the spheres is detected with the light source, reflecting mirror and light receiving element, and a current is supplied through the feedback loop to control so that the spheres can return to the initial balanced state. The current flowing through the feedback loop is proportional to oxygen concentration. Thus, oxygen concentration is converted into an electric signal.

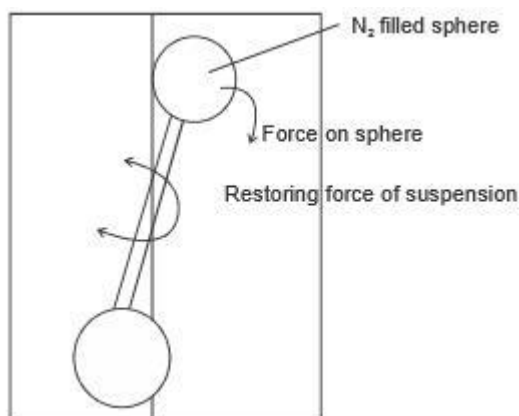


Fig. 17 Paramagnetic oxygen sensor

ZIRCONIA OXYGEN SENSORS

Solid state potentiometric oxygen sensors typically use an oxygen ion conducting material as electrolyte. Yttria stabilized zirconia (YSZ) has been the material of choice due to its ionic nature and better stability in harsh environments. A doping level of 6–12 mol% of yttria stabilizes zirconia in the cubic phase, a more favourable phase for ionic conduction at high temperatures. High temperature electrochemical sensor consists of a cell made up of YSZ which acts as a solid electrolyte.

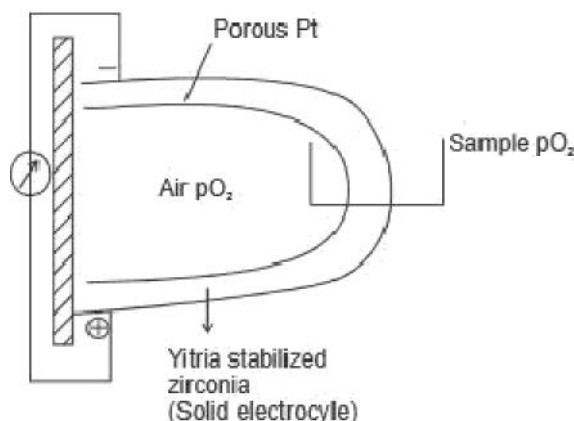


Fig. 18 Zirconia or high temperature oxygen sensor

Fig. 18 shows a schematic diagram of a thimble type YSZ based oxygen sensor. It consists of a ceramic tube made up of YSZ coated with ultra thin layer of porous platinum on the inner and outer surfaces to act as anode and cathode electrodes. At high temperature (above 450°C), openings in the crystal lattice permits the movement of oxygen ions(O^{2-}). As long as partial pressures are equal on both the sides, the movement of ions into the lattice is random and no net flow within the lattice. When a sample gas containing O_2 is introduced on one side, oxygen ions migrates through the crystal lattice to form a concentration gradient from the higher O_2 partial pressure to the lower pressure inside (reference air). The concentration gradient which determines the amount of O_2 in the sample gas is determined by Nernst equation expression. At a high temperature, the potential difference across the cell is given by Nernst equation.

$$E = \frac{RT}{4F} \log_e \frac{P_1}{P_2}$$

Where,

E is the potential difference (volts)

R is the gas constant($8.314 \text{ J mol}^{-1}\text{K}^{-1}$)

T is the absolute temperature (K)

F is the Faraday constant (96500C)

P_1 & P_2 are the partial pressures of the oxygen on either side of the zirconia tube.

Thus if oxygen partial pressure at one side is known and the temperature of the sensor is controlled, the potential difference measured enables us to determine the unknown partial pressure of oxygen in the test sample.

Applications of oxygen sensors

1. To measure the exhaust gas concentration of oxygen for IC engines in automobiles and other vehicles.
2. To measure the partial pressure of oxygen in the breathing gas used by the deep sea divers.
3. Used in anesthesia monitors, respirators and oxygen concentrators.

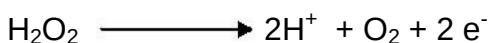
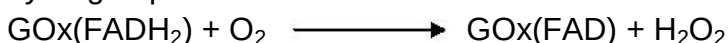
GLUCOSE SENSORS

Sensitive and selective glucose sensors are not only relevant for use in blood sugar monitoring, but also in the food industry, bio-processing and in the development of renewable, sustainable fuel cells. The first amperometric enzyme glucose sensor was developed in 1973 in which the anodic production of hydrogen peroxide was analysed.

The enzyme glucose 1-oxidase (GOx) is the main catalytic component used in enzymatic biosensors. It is the 'ideal enzyme' for glucose oxidation, owing to a relatively high selectivity, sensitivity and stability, compared to other enzymatic materials. The key component of the large protein molecule is the redox centre, flavin adenine dinucleotide (FAD). The flavin group is reduced on interaction with glucose, thus producing the redox product of glucolactone, in the first step.



The cofactor is regenerated by reacting with oxygen, leading to the formation of hydrogen peroxide.



Glucose concentration is determined by direct measurement of the hydrogen peroxide produced. Hydrogen peroxide is oxidised at a catalytic platinum (Pt) anode. The electrode easily recognises the number of electron transfers and this electron flow is proportional to the number of blood glucose present in the blood. Sensing of hydrogen peroxide at the anodic potential of 0.6V vs. SCE (Saturated calomel electrode), gave a current directly proportional to the glucose concentration. This method offers a more simple, precise and selective approach to blood glucose testing. The oxygen is regenerated in the oxidation of the peroxide, thus replenishing

the oxygen electron mediator.

CYCLIC VOLTAMMETRY

Definition

Cyclic voltammetry (CV) is an electrochemical method which measures the current that develops in an electrochemical cell under conditions where voltage is in excess of that predicted by the Nernst equation. CV is performed by cycling the potential of a working electrode, and measuring the resulting current.

Explanation

In cyclic voltammetry, experiment the working electrode potential is ramped linearly versus time. Unlike in linear sweep voltammetry, after the set potential is reached in a CV experiment, the working electrode's potential is ramped in the opposite direction to return to the initial potential. These cycles of ramps in potential may be repeated as many times as desired. The current at the working electrode is plotted versus the applied voltage (i.e., the working electrode's potential) to give the cyclic voltammogram trace. Cyclic voltammetry is generally used to study the electrochemical properties of an analyte in solution.

In cyclic voltammetry, the electrode potential ramps linearly versus time in cyclical phases(**Fig 19**) . The rate of voltage change over time during each of these phases is known as the experiment's scan rate (V/s). The potential is applied between the working electrode and the reference electrode while the current is measured between the working electrode and the counter electrode. These data are plotted as current (i) vs. applied potential (E , often referred to as just 'potential'). In Figure 2, during the initial forward scan (from t_0 to t_1) an increasingly reducing potential is applied; thus the cathodic current will, at least initially, increase over this time period assuming that there are reducible analytes in the system. At some point after the reduction potential of the analyte is reached, the cathodic current will decrease as the concentration of reducible analyte is depleted. If the redox couple is reversible then during the reverse scan (from t_1 to t_2) the reduced analyte will start to be re-oxidized, giving rise to a current of reverse polarity (anodic current) to before. The more reversible the redox couple is, the more similar the oxidation peak will be in shape to the reduction peak. Hence, CV data can provide information about redox potentials and electrochemical reaction rates.

For instance, if the electron transfer at the working electrode surface is fast and

the current is limited by the diffusion of analyte species to the electrode surface, then the peak current will be proportional to the square root of the scan rate. This relationship is described by the Cottrell equation. In this situation, the CV experiment only samples a small portion of the solution, i.e., the diffusion layer at the electrode surface.

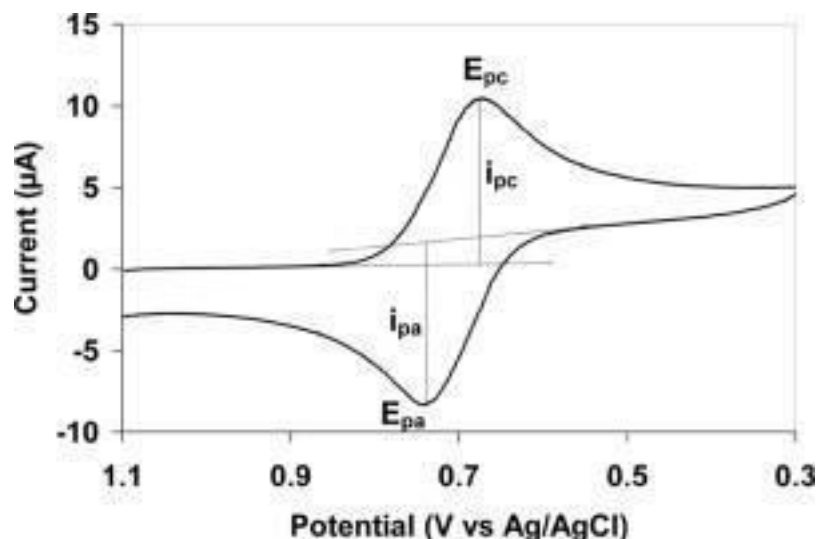


Fig. 19 Cyclic Voltammetry

Typical cyclic voltammogram where i_{pc} and i_{pa} show the peak cathodic and anodic current respectively for a reversible reaction.

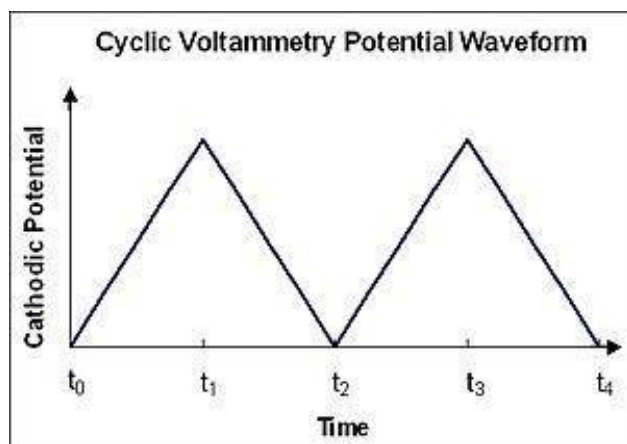


Fig.20 Cyclic voltammetry waveform

In cyclic voltammetry, the electrode potential ramps linearly versus time .

Advantages

1. A technique usually used to acquire qualitative information about electrochemical reactions
2. Offers a rapid location of redox potentials of the electroactive species
3. Can be used to get valuable kinetic information of electrode reaction
4. Electrode reaction usually involve e-transfer reaction which is influenced by electrode potential
5. Mass transfer (diffusion) in some cases can control over-all electrode reaction
6. It is a technique to control electrode's potential and measure resultant current.

Disadvantages

1. The effects of slow heterogeneous electron transfer and chemical reactions cannot be separated. If both of these effects are present, then the rate constants for these processes can only be calculated using simulation methods.
2. There is a background charging current throughout the experiment of magnitude nC_{dl} (where C_{dl} is the capacitance of the interface at the working electrode). This restricts the detection limit to about 10^{-5} M. In addition, the ratio of the peak faradaic current to the charging current decreases with increasing n (since i_p is proportional to $n^{1/2}$), and this places an upper limit on the value of n that can be used.

Application

1. Cyclic Voltammetry can be used to study qualitative information about electrochemical processes under various conditions, such as the presence of intermediates in oxidation-reduction reactions, the reversibility of a reaction.
2. CV can also be used to determine the electron stoichiometry of a system, the diffusion coefficient of an analyte, and the formal reduction potential, which can be used as an identification tool.
3. In addition, because concentration is proportional to current in a reversible,

Nernstian system, concentration of an unknown solution can be determined by generating a calibration curve of current vs. concentration.

Test your understanding

1. Explain the laws of absorption. Derive the mathematical expression of Beer-Lambert's law. Give its limitations.
2. Explain the instrumentation of UV-Visible spectrophotometer with a neat block diagram.
3. Explain the instrumentation of IR spectrophotometer with a neat block diagram.
4. Explain the principle, instrumentation and applications of thermogravimetry.
5. Explain the principle, instrumentation and applications of Differential thermal analysis.
6. Explain the principle, instrumentation and applications of differential scanning calorimeter.
7. What are sensors? Explain the different types of oxygen sensors.
8. What are biosensors? Explain glucose sensor.
9. Explain the working principle of cyclic voltammetry with a neat diagram.

Problems

1. A solution of tryptophan has an absorbance at 280 nm of 0.54 in a 0.5 cm length cuvette. Given the absorbance coefficient of tryptophan is 6.4×10^3 L/Mol/Cm. What is the concentration of solution.

Ans : $A = \epsilon cl$

$$c = A / \epsilon l$$

$$c = 0.54 / 6.4 \times 10^3 \times 0.5 = 1.68 \times 10^{-4} \text{M}.$$

2. A solution of thickness 2 cm transmits 40% incident light. Calculate the concentration of the solution, given that $\epsilon = 6000$ dm³/mol/cm, $A = 0.398$.

Ans : $A = \epsilon cl$

$$c = A / \epsilon l$$

$$c = 0.398 / 6000 \times 2 = 3.316 \times 10^{-5} \text{M.}$$

3. Calculate the molar absorptivity of a 0.5×10^{-3} M solution, which has an absorbance of 0.17, when the path length is 1.3 cm.

Ans: $A = \epsilon cl$

$$\epsilon = A / cl$$

$$\epsilon = 0.17 / 0.5 \times 10^{-3} \times 1.3 = 261.53 \text{ dm}^3/\text{mol/cm.}$$

Introduction: Lithography. Thin-Film deposition: Chemical Vapour Deposition – Physical Vapour Deposition, Pulsed Laser and Atomic Layer Deposition. Epitaxy: Vapour Phase Epitaxy- Liquid Phase Epitaxy – Molecular Beam Epitaxy. Evaporation: Thermal Evaporation and e-beam evaporation. Sputtering Techniques: Direct Current (DC) Sputtering and Radio Frequency (RF) sputtering. Preparation of Si/Ge semiconductors –Czochralski crystal growth technique: Doping of semiconductors by ion implantation.

Lithography

For decades, micro- and nanolithography technology has been contributed to the manufacturing of integrated circuits (ICs), microelectromechanical system (MEMS) devices and microchips. In Greek lithos, meaning "stone" and Graphy means "writing".

Lithography Definition:

It is the process of printing from a plane surface on which image to be printed is ink-receptive and the blank area ink-repellent.

(Or)

It is the process of producing patterns on semiconductors crystals for use as integrated circuits.

Lithography techniques are divided into two types by the use of masks or templates:

- (1) Masked lithography: Masked lithography makes use of masks or molds to transfer patterns over a large area simultaneously.

Ex: Photolithography, Soft lithography and nano-imprint lithography.

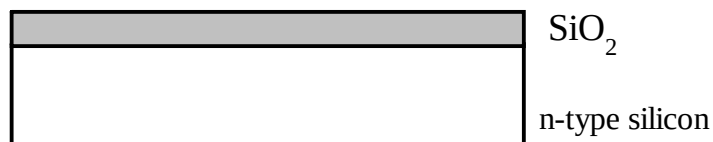
- (2) Maskless lithography: Which fabricates arbitrary patterns by a serial writing by without using masks.

Ex: Electron beam lithography, focused ion beam lithography and scanning probe lithography

PHOTOLITHOGRAPHY:

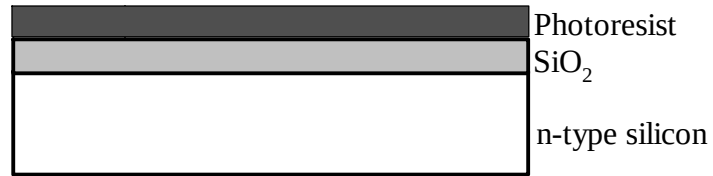
It is an optical technique for transferring patterns from a glass photomask onto a semiconductor substrate.

1. Surface Preparation: Clean and dry wafer surface was needed for Photolithographic process. The grease, oil or wax stains will be removed by ultrasonic bath. The spin dry (wafer) by N₂ blow results the clean surface.

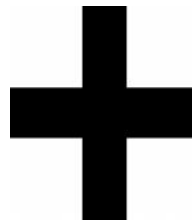


2. Photoresist - Apply:

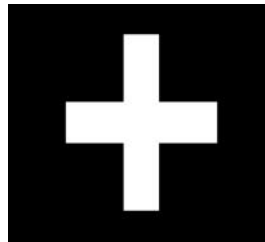
Photoresist is a light-sensitive liquid (hydrocarbon) compound. A thin layer of photoresist was applied on the prepared surface.



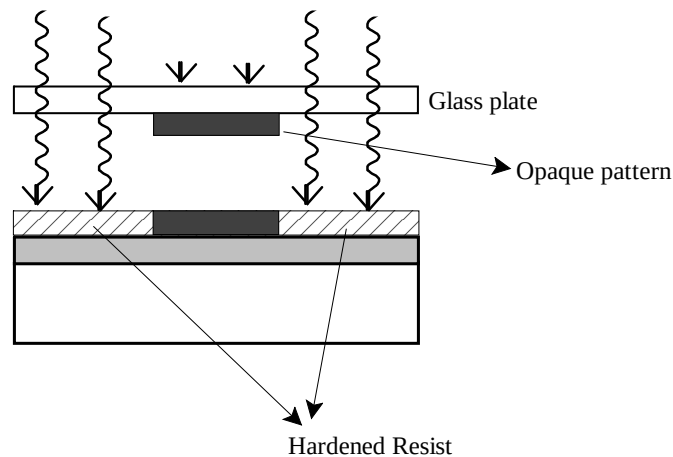
- a) Positive Photoresist: On exposure to UV light breaks the chemical bonds in the material, so that the exposed region dissolves in developer, unexposed region remains. Pattern on resist same as pattern on mask. Positive resist more common, have better resolution, cheaper.



- b) Negative Tone: On exposure to UV light strengthens the chemical bonds in the material, so that the exposed region stays but the unexposed region dissolves in developer.

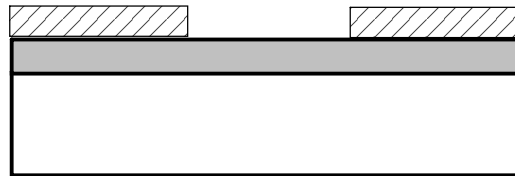
3. Softbake: Partial evaporation of photoresist solvents leads to the strong adhesion between SiO₂ and Photoresist.

4. Exposure: Precise alignment of mask on glass plate to wafer and exposure to U.V. light.



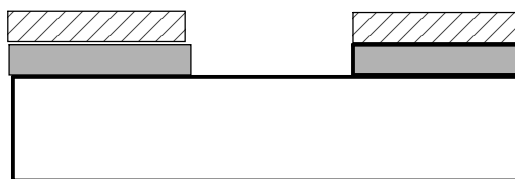
5. Development:

Wafer is rinsed in developing solution, to remove unexposed areas of photo resist. This results in bare and photo resist coated areas of oxide.



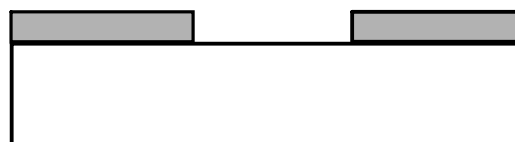
6. Etching:

Etching is traditional process of using strong acid to remove or cut into the unprotected parts of substrate surface to create a design. In present case, the wafer is placed in an etchant (eg HF or NH_4F), this attacks oxide and not on the photo resist.



7. Photo resist removal:

Positive photoresists could be removed by acetone, trichloroethylene, phenol-based strippers. Negative photoresists could be removed by Methyl ethyl ketone, Methyl isobutyl ketone. In the present case photo resist is stripped off with a Strong acid (H_2SO_4), this attacks only the photo resist, not on Si or SiO_2 .



Applications:

1. Commercial microelectromechanical system (MEMS) devices and photolithographic stamps
2. Electronic gadgets to health care and medical devices: Microneedles for transdermal drug delivery, artificial retina microchip, and microfluidic devices
3. MEMS accelerometers employed in automobiles and consumer electronic devices :
MEMS accelerometers are employed for crash-airbag deployment in automobiles and for motion detection in consumer electronic devices such as game controllers (e.g., Nintendo Wii), iPhone and other smartphones.
4. Digital micromirror devices (DMD) for display applications in projectors and televisions
5. MEMS pressure sensors for detecting pressures in car tires and blood vessels.

THIN FILM DEPOSITION:

Deposition: Transfer atoms from a target to a vapor (or plasma) to a substrate.

Thin film: A thin film is a layer of material ranging from fractions of a nanometer to several micrometers in thickness.

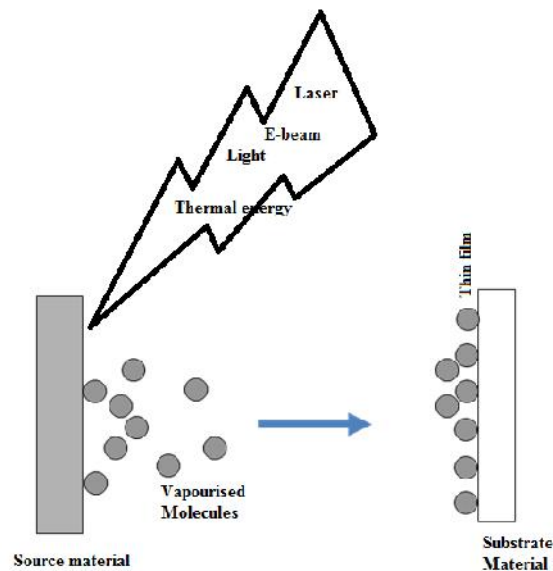
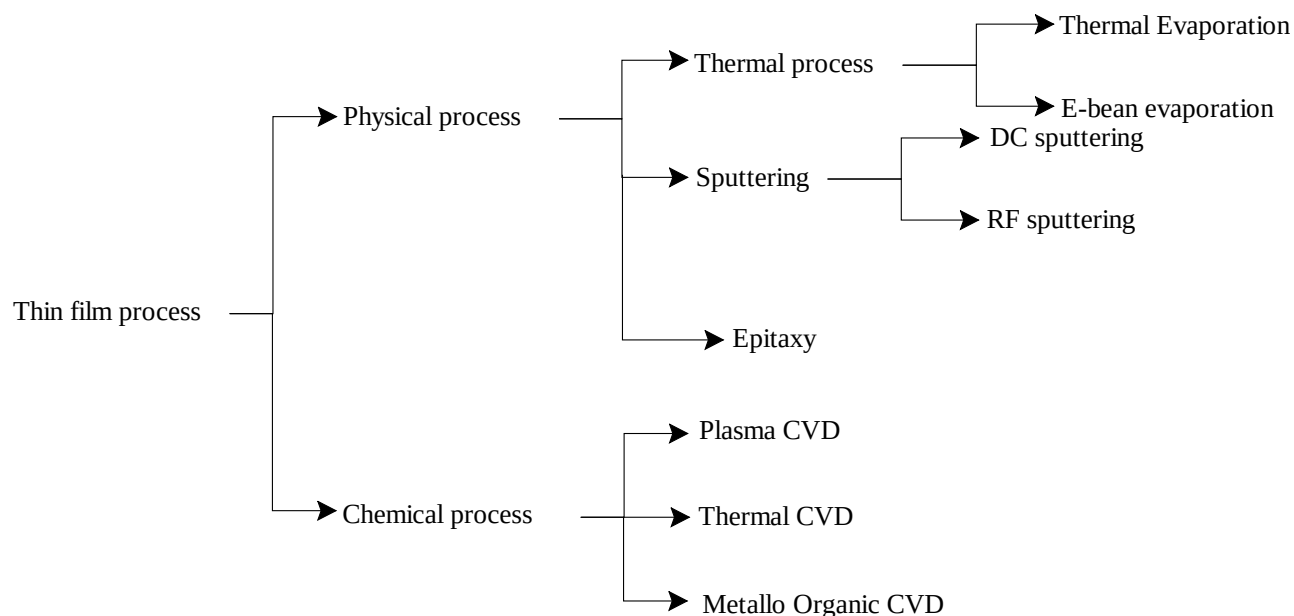


Fig.1 Schematic representation of Thin film deposition

CLASSIFICATION OF THIN FILM DEPOSITION PROCESS:



CHEMICAL VAPOUR DEPOSITION

Chemical vapour deposition (CVD) method involves a transport of reactant gases towards the substrate kept at some temperature, where reactants crack into different products, which diffuse on the surface and undergo certain chemical reactions at appropriate site, nucleate and grow to form desired films, coatings, wires and tubes.

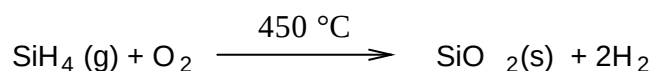
Precursors

The common precursors used in CVD reactions are

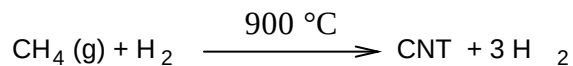
- i) Metalhydrides – SiH_4 , GeH_4
- ii) Metalhalides- TiCl_4 , TaCl_5 , WF_6
- iii) Metal organics- AlMe_3 , AlBu_3 , $\text{Fe}(\text{CO})_5$, $\text{Ni}(\text{CO})_4$

Types of CVD Reactions:

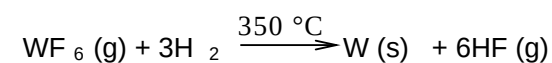
- (i) Thermal Decomposition (Pyrolysis)



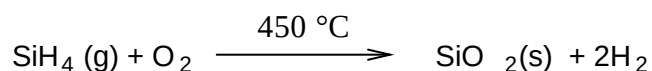
- (ii) CNT synthesis Thermal CVD: Fe, Co and Ni impregnated zeolite or SiO_2 was used as substrate to grow the CNT.



- (iii) Reduction:



- (iv) Oxidation:



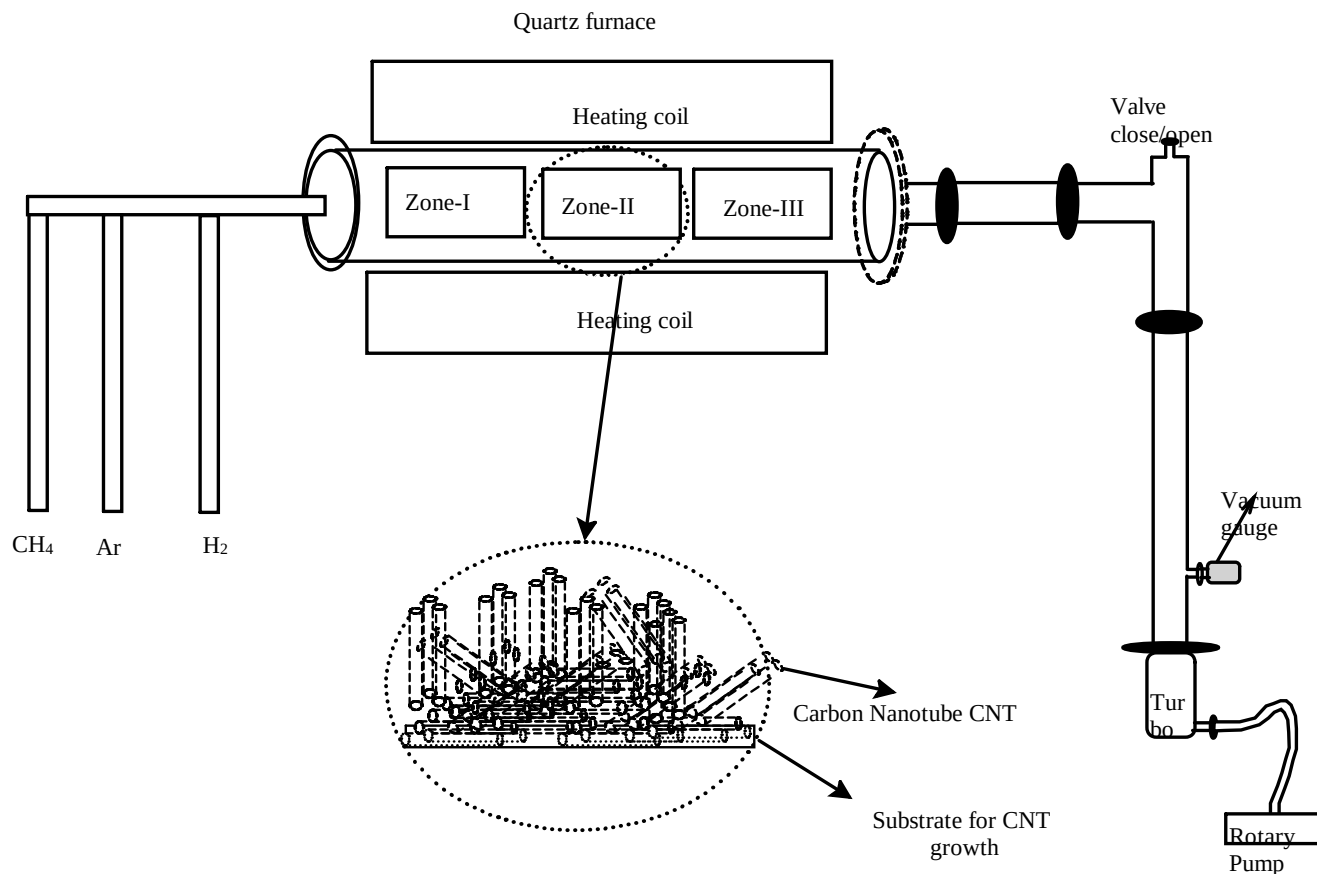


Fig.2 Schematic diagram of Thermal CVD designed for CNT Synthesis

TYPES OF CVD

In CVD, the temperature of 300-1200°C is usually used. The heat input can be in the form of thermal, light, plasma and so on. This give rise to number of CVD techniques.

S.No.	Name of the CVD	Source of thermal energy
1	Thermal activated CVD	IR radiation, RF heating
2	Photo assisted CVD	Arc Lamps, CO ₂ laser, Nd:YAG laser, Argon ion laser
3	Plasma assisted CVD	RF diode, Microwave
4	Metallo-organic CVD	It uses organometallic as precursors

MECHANISM

Whatever may be the type of CVD, the system follows a five step mechanism.

- (i) Transport of precursors into reactors
- (ii) Absorption and diffusion of precursors on the surbstrate
- (iii) Chemical reaction or decomposition at the substrate
- (iv) Thin film Deposition

- (v) Removal of unreacted precursors and by-products

ADVANTAGES

- (i) Versatile- CVD can deposit any element or compound
- (ii) High purity of 99.99%-99.999% can be obtained.
- (iii) CVD produces a high dense films
- (iv) Economical in production since many products can be coated at time

APPLICATIONS

- (i) CVD can be used for the synthesis of nanotubes and nanowires
- (ii) CVD can be used for hard coatings and metal films which are used in microelectronics
- (iii) CVD can also be used for preparing semiconducting devices, dielectrics, energy conversion devices etc.

ATOMIC LAYER DEPOSITION

ALD is a method of applying thin films to various substrates with atomic scale precision. In ALD method the precursor gases or vapors are alternately pulsed on to the substrate surface. They will chemisorb or surface reaction takes place at the surface. The Surface reactions on ALD are complementary and self-limiting.

Precursor Gas requirements for ALD:

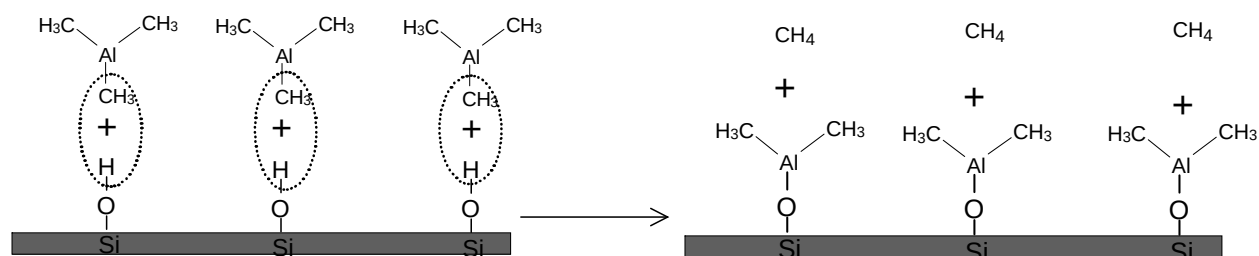
1. Must be volatile and thermally stable
2. Preferably liquids and gases
3. Should Chemisorb onto the surface or rapidly react with surface and react aggressively with each other
4. Short saturation time, good deposition rate, no gas phase reactions
5. Should not self-decompose and should not etch, dissolve into film or substrate

Mechanism:

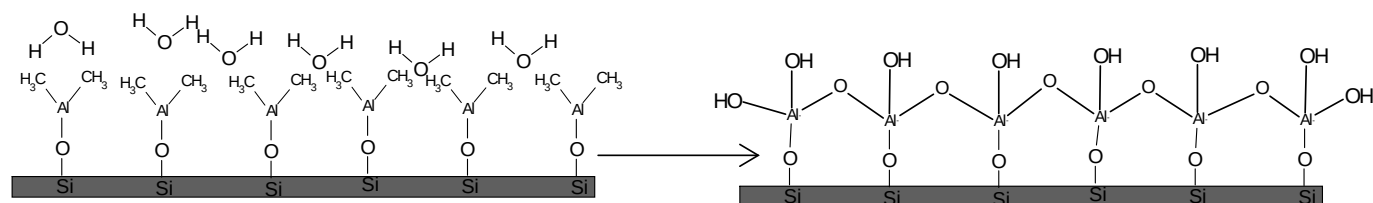
Step-I: In air H_2O vapor is adsorbed on most surfaces, forming a hydroxyl group.



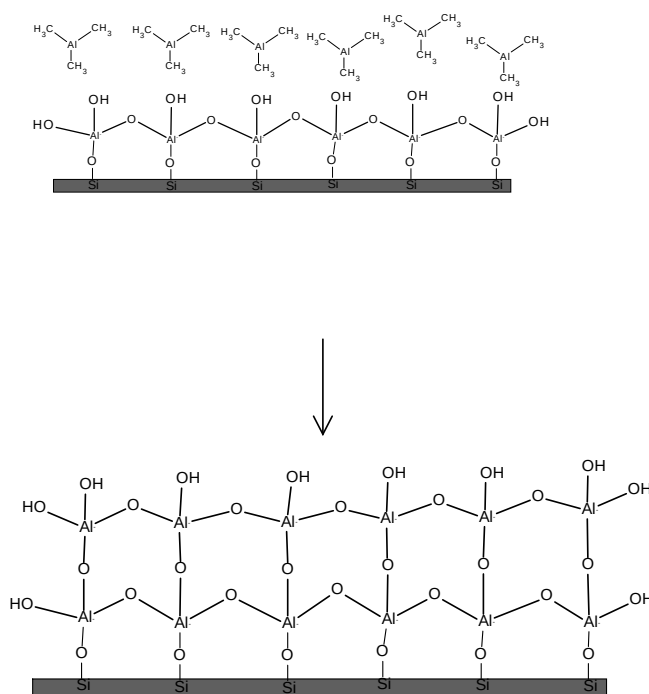
Step-II: Release of sequential precursor gases (TMA-Trimethyl aluminium) pulses to deposit a monolayer of gas on the Si surface until the surface is passivated and producing methane as the reaction product.



Step-III: The second precursor of H_2O vapour is introduced into the chamber. The H_2O reacts with the dangling methyl groups on the new surface forming Aluminum-oxygen (Al-O) bridges and hydroxyl surface groups,



Step-IV: Again TMA and water vapour was purged simultaneously results one more monolayer was formed.



Recently, it turned out that ALD method also produces outstanding dielectric layers and attracted semiconductor industries for making High-K dielectric materials.

ALD Applications:

1. High-k gate oxides
2. Storage capacitor dielectrics
3. Pinhole-free passivation layers for OLEDs and polymers
4. Passivation of crystal silicon solar cells
5. High aspect ratio diffusion barriers for Cu interconnects
6. Adhesion layers
7. Organic semiconductors
8. Highly conformal coatings for microfluidic and MEMS applications
9. Other nanotechnology and nano-electronic applications
10. Coating of nanoporous structures
11. Fuel cells, e.g. single metal coating for catalyst layers
12. Bio MEMS

THE DIFFERENCES BETWEEN CVD AND ALD:

	CVD	ALD
Growth mode	Continuous	Step wise – layer by layer
Growth rate	Variable	Growth per step is accurately defined
Thickness control	Rate x Time	Dialed in with a selected number of steps
Growth initiation	Nucleation, grain growth	Continuous film
Precursor	Less reactive and must decompose at temperature	Highly reactive and can decompose at temperature

PHYSICAL VAPOR DEPOSITION

Physical Vapor Deposition (PVD) is a collective set of processes used to deposit thin layers of material, typically in the range of few nanometers to several micrometers. PVD processes are environmentally friendly vacuum deposition techniques consisting of three fundamental steps.

- 1) Vaporization of the material from a solid source assisted by high temperature vacuum or gaseous plasma.
- 2) Transportation of the vapor in vacuum or partial vacuum to the substrate surface.
- 3) Condensation onto the substrate to generate thin films.

EVAPORATION

The source material used in this process are generally refractory metals such as W, Ta, Mo etc. In evaporation technique, both substrate and source materials (to be deposited) are placed inside the vacuum chamber (10^{-6} to 10^{-7} torr). The vacuum is required to allow the molecules to evaporate and to move freely in the chamber.

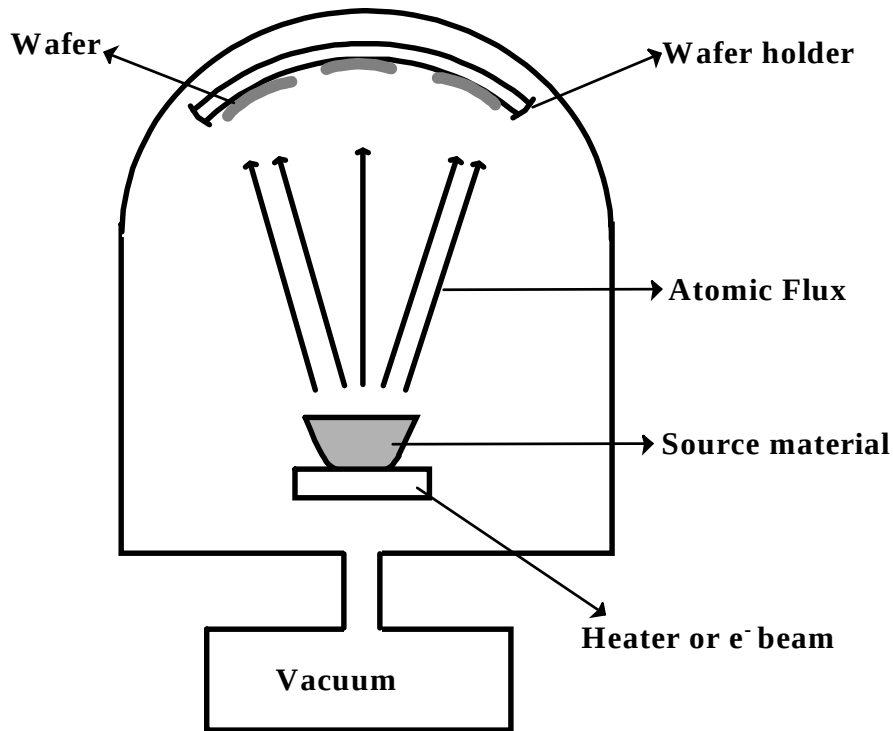


Fig.3 Schematic diagram of evaporation equipment

Thermal Evaporation:

The thermal evaporation process comprises evaporating source materials in a vacuum chamber below 1×10^{-6} torr (1.3×10^{-4} Pa) and condensing the evaporated particles on a substrate. The thermal evaporation process is conventionally called vacuum deposition. Two types of thermal evaporation processes are available.

Resistive heating:

In thermal evaporation the materials to be evaporated is put on conductive (graphite or tungsten) crucibles which are intensely heated by filament. It is most commonly used for the deposition of thin films. The source materials are evaporated by a resistively heated filament or boat, generally made of refractory metals such as W, Mo or Ta, with or without ceramic coatings.

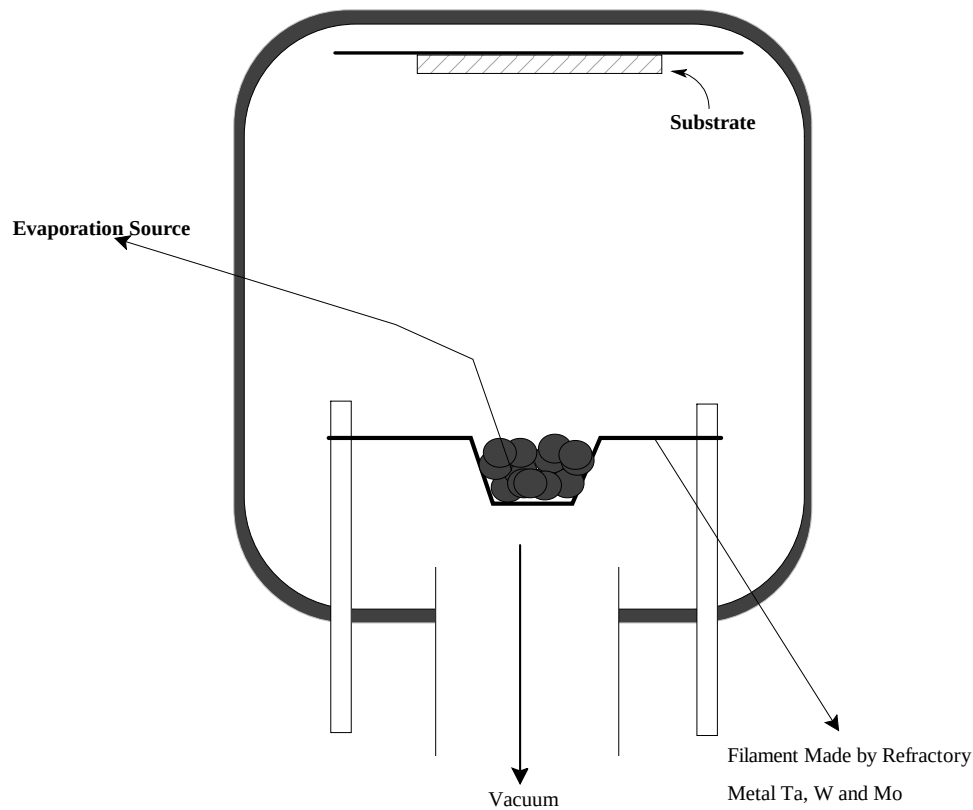


Fig.4 Resistive heating

Limitations:

Contamination Problem with Thermal Evaporation Container material also evaporates, which contaminates the deposited film.

E-beam evaporation:

Al electron gun (e-gun) is used to produce electron beam of 10 keV. This beam is directed at the source material in order to develop sufficient vapour so as to produce deposits on wafer or substrates. In the e-beam evaporation the necessary vapours for the production of the

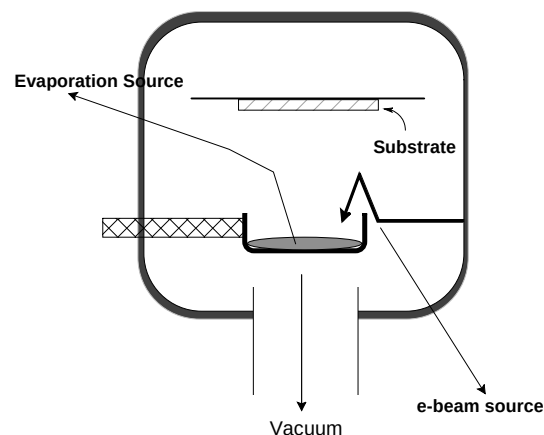


Fig.5 E-beam evaporation

coating are obtained by focussing an energetic electron beam on the crucible containing the material, and heating it until reaching its evaporation. Crucibles of quartz, graphite, alumina, beryllia, boron-nitride or zirconia are used with indirect heating. The refractory metals are evaporated by electron-beam deposition since simple resistive heating cannot evaporate high melting point materials.

The thin film thickness will be depending on mass, density of the source ions and the distance between source and target

$$f = \frac{m}{4 d \otimes h^2}$$

f = film thickness

m = mass of the source ions

d = density of the source ions

h = The distance between source and target

SPUTTERING:

When a solid surface is bombarded with energetic particles such as accelerated ions, surface atoms of the solid are scattered backward due to collisions between the surface atoms and the energetic particles. This phenomenon is called sputtering. The source materials used in this process are generally an alloy, ceramic or a compound. In sputtering technique, a high energy atom in ionized form (usually Ar^+) is used to hit the surface atoms of the targeted source (Cathode) material. Then the knocked out atoms in vapour form are deposited on the surface of the (Anode) substrates to produce an uniform coating.

DC sputtering:

This composed of a pair of planar electrodes. One of the electrodes is a cold cathode and the other is the anode. The front surface of the cathode is covered with target materials to be

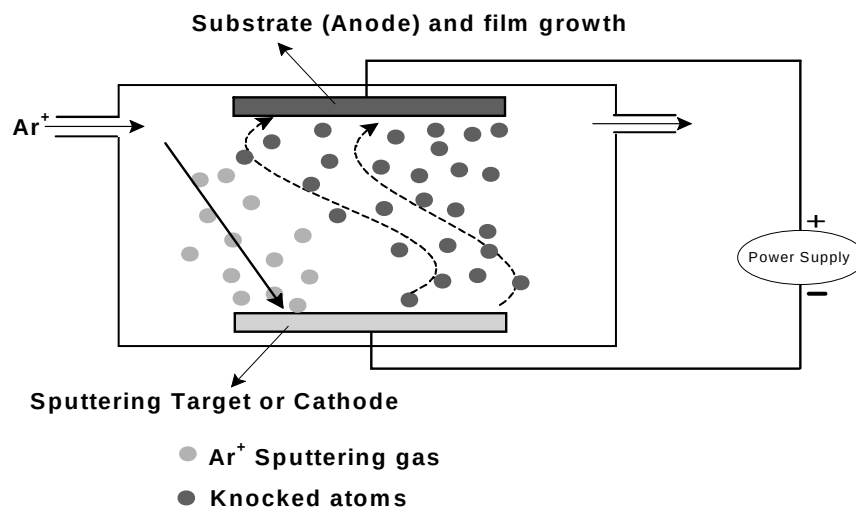


Fig.6 Schematic diagram for DC sputtering

deposited. The substrates are placed on the anode. The sputtering chamber is filled with sputtering gas, typically argon gas at 5 Pa (4×10^{-2} torr). The glow discharge is maintained under the application of DC voltage between the electrodes. The Ar^+ ions generated in the

glow discharge are accelerated at the cathode fall (Sheath) and sputter the target, resulting in the deposition of the thin films on the substrates. In the DC sputtering system, the target is composed of metal since the glow discharge (current flow) is maintained between the metallic electrodes.

RF Sputtering:

An rf diode and a dc diode are visually the same thing. The only real difference is that, for diodes, the power supply is operated at high frequency. The most common frequency is 13.56 MHz, although experiments have run the gamut from 60 Hz to 80 MHz or more. Most manufacturing systems use 13.56 MHz. The rf diode operates in a slightly different way than the dc diode: for a small part of the rf cycle, the cathode and anode are electrically reversed and shielded by guard rings. This eliminates charge buildup on an insulating surface by providing an equal number of ions, then electrons, then ions, and so on. This allows insulators to be sputtered or metals to be sputtered in reactive environments. By simple substitution of an insulator for the metal target in the dc sputtering discharge system, the sputtering discharge cannot be sustained because of the immediate buildup of a surface charge of positive ions on the front side of the insulator.

The sputtering procedure is commenced by evacuating the chamber to pressures lower than 10^{-6} Torr. Ar, being a noble gas which does not react with either the target or substrate, is then introduced into the chamber at a specified pressure. This is followed by allowing O_2 into the chamber at a set rate. The r.f. supply is then switched on and stabilised to the required power and induced d.c. bias levels; this bias is an indication of the sheath potential and is a good sign of the ion bombardment energy. During this time the substrate is shielded by the top shutter. Once pre-conditioning is complete, the top shutter is opened marking the beginning of the deposition process.

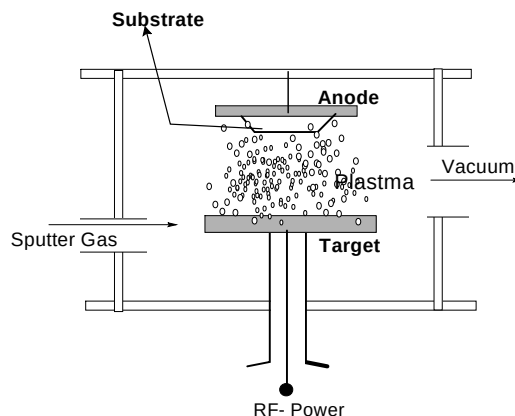


Fig.7 Schematic diagram for RF sputtering

The difference between RF and DC sputtering process

DC sputtering	RF sputtering
DC power is used	AC power is used
Applicable for Metals or Conductors	Applicable for both Conductor and Insulators
It is Cheap	It is expensive

The difference between Evaporation and Sputtering processes

Evaporation	Sputtering
Low energy atoms	Higher energy atoms
High vacuum path Few collisions Line of sight deposition Little gas in film	Low vacuum, plasma path Many collisions Less line of sight deposition Gas in film
Larger grain size	Smaller grain size
Fewer grain orientation	Many grain orientations
Poorer adhesion	Better adhesion

PULSED LASER DEPOSITION:

Pulsed Laser Deposition (PLD) is a thin film deposition technique that is used to deposit materials on substrates. A base system consists of a target, substrate carrier which is mounted in a vacuum chamber. An excimer laser is used to energize the surface of a target to produce a deposition plume. The plume is typically directed towards the substrate where a thin-film is deposited. Since each shot of the laser is directly related to the amount of material ablated, the deposition rate can be calibrated and controlled very precisely.

Advantages:

- [1] Flexible and easy to implement
- [2] Growth in any environment
- [3] Exact transfer of complicated materials (YBCO)
- [4] Variable growth rate
- [5] Epitaxy at low temperature
- [6] Resonant interactions possible (i.e., plasmons in metals, absorption peaks in dielectrics and semiconductors)
- [7] Atoms arrive in bunches, allowing for much more controlled deposition
- [8] Greater control of growth (e.g., by varying laser parameters)

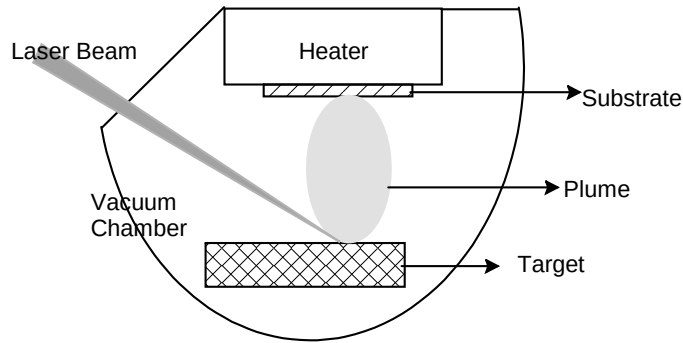


Fig.8 Schematic diagram of Pulsed Laser Deposition

Disadvantages:

- [1] Uneven coverage
- [2] High defect or particulate concentration
- [3] Not well suited for large-scale film growth
- [4] Mechanisms and dependence on parameters not well understood

EPITAXY:

The word Epitaxy is derived from the Greek “epi” – upon and “taxis” – to arrange. Epitaxy means the regularly oriented growth of a crystal substance upon another.

Types of Epitaxy

Based on Substrate and Thin Film

- 1] Homo epitaxy
The film and the substrate are the same material. Ex: Si on Si growth.
- 2] Heteroepitaxy
Film and substrate are different materials. Ex: AlAs, GaAs on Si.

Requirements of Epitaxial growth:

- [1] Clean substrate surface needed
- [2] Defects of substrate surface results defects in epitaxial layer
- [3] Hydrogen passivation of surface with water/HF
- [4] High temperature is required heated substrate

Advantages of Epitaxial growth:

- [1] High purity
- [2] Low defect density
- [3] Abrupt interfaces
- [4] Controlled doping profiles
- [5] High repeatability and uniformity
- [6] Safe, efficient operation

Vapour Phase Epitaxy:

During vapour phase epitaxy, epitaxial layers are grown on silicon substrates by the controlled deposition of Si atoms from a chemical vapour containing Si. Silicon tetrachloride

(SiCl_4), Dichlorosilane (SiH_2Cl_2), Trichlorosilane (SiHCl_3) and silane (SiH_4) are the sources used for vapour phase epitaxial growth. The silicon wafer on which epitaxial growth has to take place is kept on a graphite susceptor placed inside a quartz reaction chamber and hydrogen gas is passed through the quartz tube. The entire system is RF heated to a temperature above 1100°C .



The above reaction which occurs on the silicon surface is surface catalysed and the Si atoms released can be deposited as an epitaxial layer. As the reaction is reversible the reaction can be driven to the left by adjusting the process parameters and provides etching of the silicon rather than deposition. This etching can be used for preparing an atomically clean surface on which epitaxy occurs. To grow epitaxial layer of silicon with desired doping, the dopant is introduced along with SiCl_4 . Gaseous diborane (B_2H_6) is used as a P-type dopant and arsine (AsH_3) is used as the N-type dopant.

Advantages:

- 1) It can be Performed at low temperature
- 2) High purity epitaxial growth can be achieved.

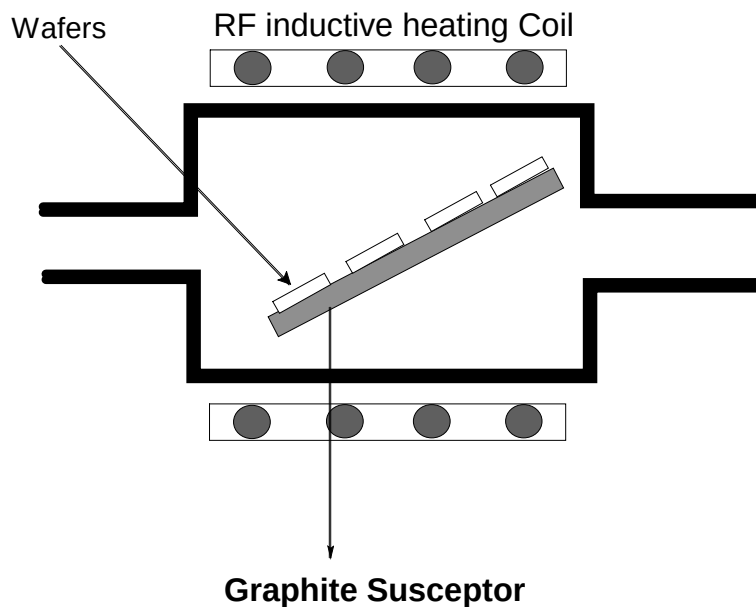


Fig.9 Schematic representation of Vapour Phase Epitaxy

Liquid Phase Epitaxy:

Liquid phase epitaxy is a method of grow semiconductor crystal layers from the melt on solid substrates. This happens at temperatures well below the melting point of the deposited semiconductor. The semiconductor is dissolved in the melt of another material. At conditions that close to the equilibrium between dissolution and deposition of the semiconductor crystal on the substrate is slowly and uniform. The equilibrium conditions depend very much on the

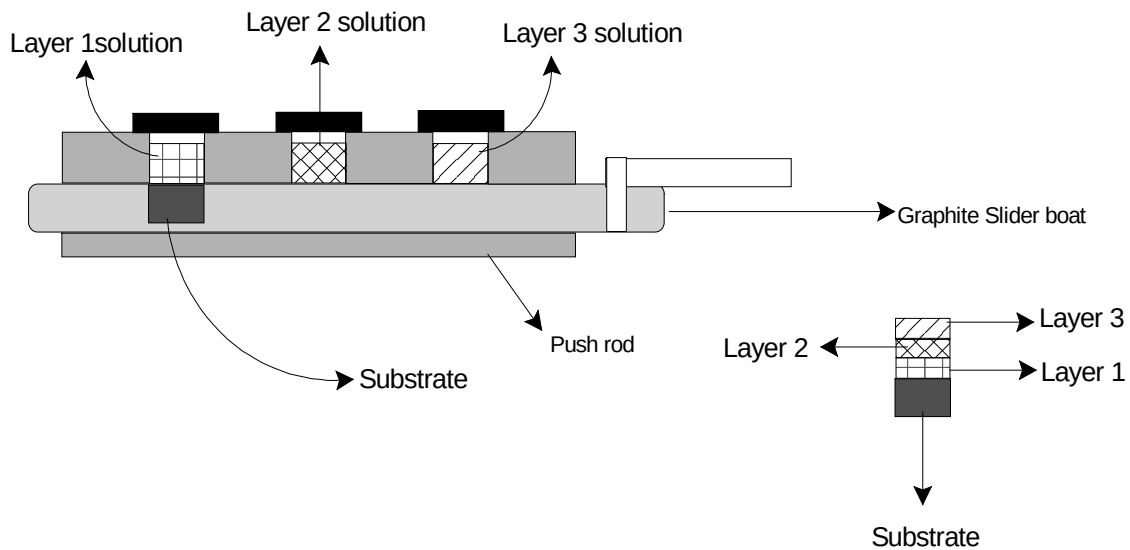


Fig.10 Schematic representation of Liquid phase epitaxy

temperature and on the concentration of the dissolved semiconductor in the melt. The growth of the layer from the liquid phase can be controlled by a forced cooling of the melt. Impurity introduction can be strongly reduced. Doping can be achieved by the addition of dopants.

A typical example for the liquid phase epitaxy method is the growth of ternary and quaternary III-V compounds on Galliumarsenide GaAs substrates. As a solvent quite often Gallium is used in this case. Another frequently used substrate is Indiumphosphide InP. However also other substrates like glass or ceramic can be applied for special applications. To facilitate nucleation, and to avoid tension in the grown layer the thermal expansion coefficient of substrate and grown layer should be similar.

The basic requirement is to bring the substrate and growth solution into contact while the epitaxial layer grows, and then to separate them cleanly at the end of the growth cycle. The method is mainly used for the growth of compound semiconductors. Very thin, uniform and high quality layers can be produced.

Advantages

- Less expensive and higher deposition rates wrt MBE
- Low defect concentration
- Excellent control of stoichiometry

Disadvantages

- Solubility considerations greatly restrict the number of materials for which this method is applicable
- Morphology (crystal orientation) control is difficult
- Surface quality often poor

Molecular Beam Epitaxy:

Molecular Beam Epitaxy (MBE) is an advanced ultra-high-vacuum facility (basic pressure 10^{-13} bar) to make compound semiconductor materials with great precision (< 0.01 nanometer). Because of the very low pressure, the mean free path is very long (can be hundreds of meters). Thus, the evaporated material travels in a straight line (a molecular beam) toward a hot substrate resulting in highly efficient raw materials. The epitaxial layers are deposited on the heated substrate from molecular beams impinging upon its surface. These beams are thermally generated in effusion cells containing the constituent elements such as Ga, As etc.. All the effusion cells are located in an ultra high vacuum chamber. Each cell is provided with a shutter to control the composition or doping of the film. The duration in which each shutter opens and the temperature of the oven determines the flux of each element towards the substrate. The temperature of the cell is also accurately controlled to maintain the required intensity of the beams. Fig.11 Schematic representation of MBE growth

There are several variables within MBE to improve the quality of growth, these are:

- a) Flux rate: The number of atoms arriving at the substrate surface is known as Flux rate.
- b) Substrate temperature (affects diffusive properties of impinging atoms)
- c) Source temperature (speed of atomic arrival and flux rate)

Applications:

These materials are layered one on top of the other to form semiconductor devices such as transistors and lasers, which are devices being used in such applications as fiber-optics, cellular phones, satellites, radar systems, solar cells, and display devices.

Disadvantages:

- a) It is highly expensive and complicated system
- b) The thickness rises then strain energy is too high and defects are generated.
- c) Higher temperatures result in more mobile surface atoms and the disadvantage is that interfaces become smoothed due to diffusion of atoms.
- d) Lower temperatures generate more abrupt interfaces and introduces more point defects into the layer.

The Czochralski technique for Si crystal growth

A crystal growth technique proposed by Jan Czochralski, the so-called Czochralski method, has been widely applied for growing various types of single crystals such as silicon (Si), germanium (Ge) and oxide materials in industry. In fact, if this growth method had not been discovered, the current development of Si technology using large-scale dislocation-free crystals would not be possible.

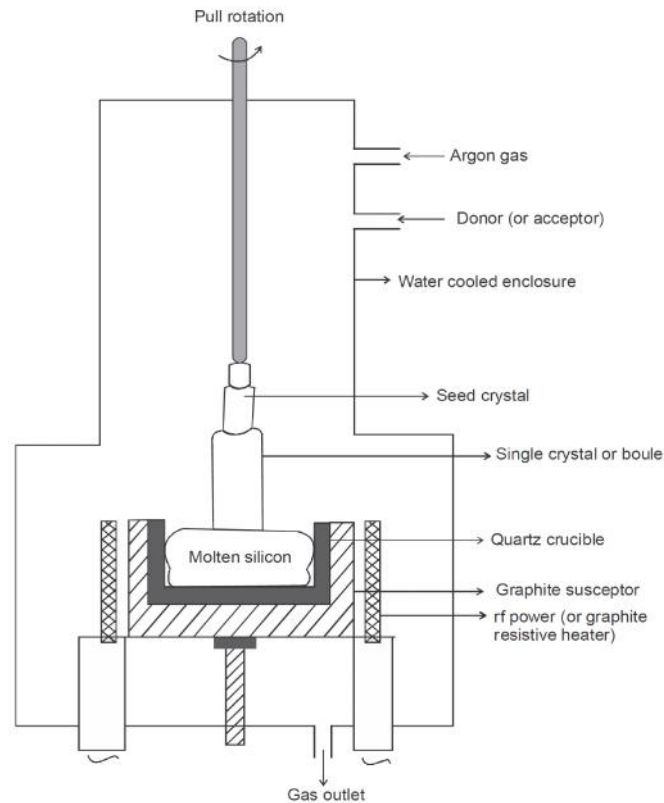


Fig.12 Schematic representation of Czochralski technique for Si crystal growth

In this method solid polycrystalline semiconducting material silicon is taken in a fused quartz crucible (wall contains Pt/Ir/Graphite) placed in an evacuated chamber. The furnace chamber is filled with an inert argon gas and heated to around 1500°C just above the melting point of silicon which is 1412°C . When the silicon is fully melted, a small seed crystal mounted on the end of a rotating shaft is slowly lowered until it just dips below the surface of the molten silicon. The shaft rotates counterclockwise and the crucible rotates clockwise. The rotating rod is then drawn upwards very slowly, allowing a roughly cylindrical boule to be formed. The melt in contact with the seed crystal starts solidifying and produce the orientation identical to that of the seed crystal. After this the pull rate is fixed at about 1.5 to 5 cm/min and the rotation speed is maintained at 100rpm. The boule can be from one to two metres, depending on the amount of silicon in the crucible. Finally large single crystals of about 15cm diameter and 10 cm length is grown which is tested for its conductivity and is cut into wafers.

DOPING OF SEMICONDUCTOR BY ION IMPLANTATIONS

In the ion implantation method, charged dopants (ions) are accelerated in an electric field and irradiated onto the wafers. The penetration depth can be set very precisely by reducing or increasing the voltage needed to accelerate the ions. Since the process takes place at room temperature, previously added dopants cannot diffuse out. Regions that should not be doped, can be covered with a masking photoresist layer. This technique is now commonly employed for implanting As, P and B to a depth of 0.5, 1 and μm at 1000KV in silicon.

Process

An ion implanter consists of the following components:

- 1) Ion source: The dopants in the gaseous state (e.g. boron trifluoride BF_3) are ionized.
- 2) Accelerator: The ions are accelerated with approximately 30 keV out of the ion source.
- 3) Mass separator: The charged particles are deflected by a magnetic field by 90° . Too light/heavy particles are deflected more/less than the desired ions and trapped with screens behind the separator.
- 4) Lenses: Lenses are distributed inside the entire system to focus the ion beam.
- 5) Deflectors: The ions are deflected with electrical fields to irradiate the desired location.
- 6) Wafer station: The wafers are placed on a large rotating wheels and held into the ion beam

Method

The ion source has a heated filament which breaks the dopant gas such as BF_3 or AsH_3 into charged ions (B^+ or As^+). The ions then pass through a mass separator to eliminate unwanted ionic species. The selected ions then enter the accelerator and gets accelerated to high energies by an electric field, deflected and gets implanted into the semiconductor substrate. The average depth of implantation can be controlled by adjusting the acceleration energy. The dopant dose concentration can be controlled by monitoring the ion current during implantation. Typical ion energies used are between 30-300KeV and typical ion doses vary from 10^{11} to 10^{16} ions/cm. The dose is usually expressed as the number of ions implanted into 1cm^2 area of the semiconductor surface.

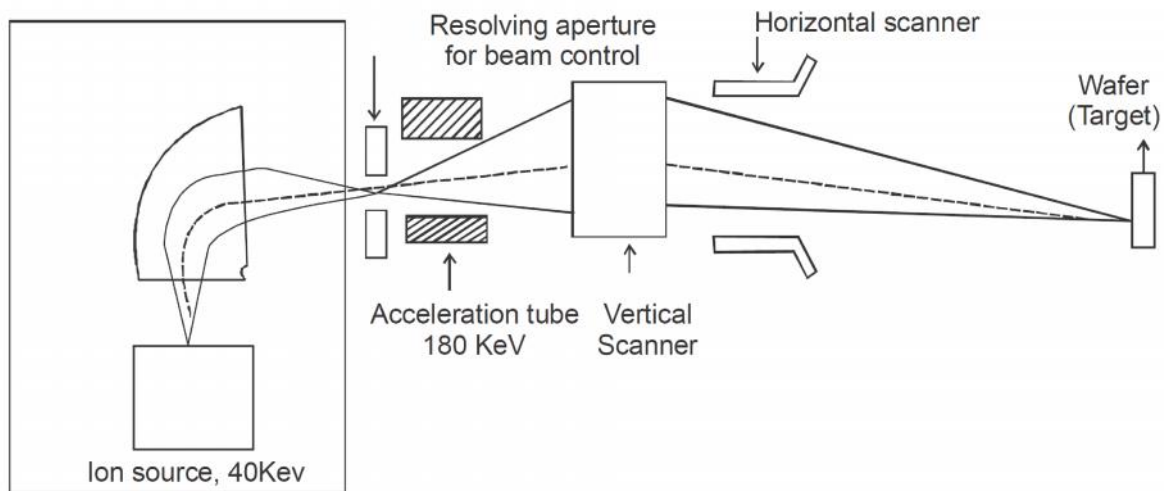


Fig.13 Schematic representation for Ion implantation

Advantages:

- a. The reproducibility of ion implantation is very high.
- b. Nearly every element can be implanted with highest purity.
- c. Independent control of impurity depth and dose
- d. Complex profiles can be achieved by multi-energy implants.

Disadvantages:

- a) Very deep and very shallow profiles are difficult
- b) Semiconductor lattice can be damaged due to ion collisions during ion implantation.
- c) Hence a subsequent annealing treatment is needed to remove these damages. Not all the damage can be corrected by annealing.
- d) Three-dimensional structures cannot be doped by ion implantation
- e) Often uses extremely toxic gas sources such as arsine (AsH_3) and phosphine (PH_3).
- f) Ion implanters are very expensive, the costs per wafer is relatively high.

Test your understanding

- 1] Explain the sequential steps involved in Photolithography.
- 2] Explain the mechanism of Atomic Layer Deposition
- 3] What is CVD. Explain the mechanism involved in Thermal CVD.
- 4] Write an essay on Czochralski technique for Si crystal growth with neat diagram
- 5] Write a short notes on Sputtering and Evaporation.
- 6] Write an essay on various Epitaxy methods.
- 7] Write an short note on Ion implantation method.

Electrical Insulating Materials: Introduction – Requirements – Characteristics of dielectrics – Classification based on operating temperature and classification based on substances and materials. Gaseous electrical insulating materials – Air and SF₆. Liquid electrical insulating materials – Askarels – Transformer oil – Factors affecting properties of Transformer oil – Transformer oil tests. Solid electrical insulating materials – Epoxy resin, ceramic products: white wares and glass. Electrical resistivity: Classification of electrical resistivity materials – Factors influencing electrical resistivity of materials - Composition, properties and applications of high resistivity materials: Manganin - Constantan - Molybdenum silicide - Nichrome.

ELECTRICAL INSULATING MATERIALS (DIELECTRICS)

INTRODUCTION

A dielectric material is a substance that is a poor conductor of electricity, but an efficient supporter of electrostatic field. If the flow of current between opposite electric charge poles is kept to a minimum while the electrostatic lines of flux are not impeded or interrupted, an electrostatic field can store energy. This property is useful in capacitors, especially at radio frequencies. Dielectric materials are also used in the construction of radio-frequency transmission lines.

When the main function is that of insulations, the materials are called insulators; when the main function is that of charge storage, they are called dielectrics.

Materials which offer a very large resistance to flow of current are called electrical insulating material.

REQUIREMENTS OF A GOOD ELECTRICAL INSULATOR

1. A good electrical insulator should be a bad conductor of electricity having high specific resistance.
2. A good electrical insulator should possess low dielectric constant.
3. It should have high dielectric strength and low dielectric loss.
4. It should be chemically inert.
5. It should have least thermal expansion and contraction.

CHARACTERISTICS OF DIELECTRICS

A. Resistivity

Resistivity is the electrical resistance of a conductor of unit cross-sectional area and unit length. A characteristic property of each material, resistivity is useful in

comparing various materials on the basis of their ability to conduct electric currents. High resistivity designates poor conductors. Good insulators, or dielectrics, have high resistivities and low conductivities. Electrical resistivity is represented by the Greek letter ρ (rho).

B. Dielectric Polarization

Dielectrics are non-conducting substances. They do not have charge carriers or free electrons. If an external field is applied, charges are induced on the surface which in turn produces a field and opposes the external field. The opposing field does not exactly cancel the external field but only reduces it.

To understand this concept, one has to look into the charge distribution of a dielectric in its molecular level. The molecules of a dielectric are classified as polar or non-polar.

The “Polar molecules” is one in which the centre of gravity of protons (positive charges) and electrons (negative charges) do not coincide. They have an asymmetrical distribution of charge and have permanent dipole moments in the range of 10^{-30} cm. Examples: H_2O , CO_2 , NO_2 etc. In the absence of an external electric field, the electric dipole moment of molecules is in random direction and cancels with each other and the average electric dipole moment per unit volume of a dielectric is zero. In the presence of an external electric field, the molecules align in the direction of the electric field, and are complete when working at a low temperature and stronger electric field.

The “Non-polar” is that molecule in which the centre of gravity of protons (positive charges) and electrons (negative charges) coincide. In normal state, they have no dipole moment. Example: O_2 , N_2 , H_2 etc. When an external electric field is applied, the protons as a whole are pulled in the direction of the electric field, while electrons are pulled in the opposite direction. The separation of charges continues till the external electric fields are balanced by the internal forces. This creates two new centre of charge, the molecule is said to be polarized and is known as induced electric dipole. The dipole moment so acquired is known as induced electric dipole moment. The induced dipole moment is proportional to the applied field and is almost independent of the temperature. The direction of induced dipole moment is parallel to the direction of electric field.

Polarization is the alignment of the dipole moments of the permanent or induced dipoles in the direction of the applied electric field.

C. Dielectric constant

Dielectric constant is a property of an electrical insulating material (a dielectric) which is the ratio of the capacitance of a capacitor filled with the given material to

the capacitance of an identical capacitor in a vacuum without the dielectric material. If C is the value of the capacitance of a capacitor filled with a given dielectric and C_0 is the capacitance of an identical capacitor in a vacuum, then the dielectric constant, symbolized by the Greek letter kappa, κ , is simply expressed as

$$\kappa = C/C_0.$$

Dielectric constant gives the capacity of a material to store electric charge in the presence of an applied electric field. A good electrical insulator should have a low dielectric constant.

D. Dielectric strength

Dielectric strength is a measure of the electrical strength of a material as an insulator. Dielectric strength is the maximum electric field strength that it can withstand intrinsically without breaking down, i.e., without experiencing failure of its insulating properties. Dielectric strength is defined as the maximum voltage required to produce a dielectric breakdown through the material and is expressed as Volts per unit thickness. The higher the dielectric strength of a material the better its quality as an insulator.

Factors affecting dielectric strength

- It increases with the increase in thickness of the material.
- It decreases with the increase in operating temperature.
- It decreases with the increase in frequency.
- It decreases with the increase in humidity.

E. Dielectric losses

Dielectric loss is the amount of electrical energy that is lost in heating of dielectric material in a varying electric field. These are caused by internal dipole friction called absorption of electrical energy and by leakage of current through the medium. A good insulating material should have minimum dielectric loss.

H. Thermal ageing

When electrical insulators are continuously worked at elevated temperatures, they become weak particularly in contact with oxygen or air of the surroundings. A good insulator should have least thermal ageing.

I. Thermal expansion and contraction

An ideal insulating material should have minimum thermal expansion and contraction as they lead to gaps in the insulator.

G. Porosity

Porosity of a dielectric material affects the properties because porosity increases the moisture holding capacity.

CLASSIFICATION BASED ON SUBSTANCES AND MATERIALS

They are classified into solids, liquid and gaseous insulating materials depending on their physical state.

Gaseous insulating materials

They are further classified into

1. Simple gases: Air, Nitrogen, Hydrogen
2. Oxide gases: CO₂, SO₂
3. Hydrocarbon gases: Methane, Ethane, Propane
4. Electronegative gases: Freon, Sulphur hexafluoride (SF₆)

Liquid insulating materials

They are further classified into

1. Mineral insulating oils: Transformer oil, Capacitor oil, Cable oil
2. Synthetic insulating oil: Askarels, Pyranols
3. Miscellaneous insulating oils: Vegetable oils, Silicone oil, Fluorinated liquids

Solid insulating materials

They are further classified into

1. Fibrous insulating materials: Paper, Wood, Cotton, Silk
2. Plastic insulating materials: Epoxy resin, Polyester resin, Cellulose derivatives, Silicon resin
3. Rubber insulating materials: Natural and Synthetic rubbers
4. Mineral insulating materials: Mica, Marble, Slate
5. Rigid insulating materials: Glass, Ceramics

CLASSIFICATION OF ELECTRICAL INSULATORS BASED ON OPERATING TEMPERATURE

S.NO	CLASS	MAXIMUM WORKING TEMP	EXAMPLES OF INSULATING MATERIALS
1	Y	90°C	Cotton, silk, paper, wood unsuitable for electrical machines and apparatus as they deteriorate rapidly
2	A	105°C	Class Y materials impregnated with oils, natural resin, cellulose ester etc
3	E	120°C	Materials operate at 15°C higher than class A
4	B	130°C	Mica, glass, Asbestos with suitable bonding materials
5	F	155°C	Materials operate at 155°C of class B with bonding materials of higher thermal stability
6	H	180°C	Class B materials + Silicon resin
7	C	>180°C	Class B materials + Inorganic binder

GASEOUS INSULATING MATERIALS

A **dielectric gas** or **insulating gas** is a dielectric material in gaseous state. Its main purpose is to prevent or rapidly quench electric discharges. Dielectric gases are used as electrical insulators in high voltage applications, eg. Transformers, circuit breakers, switch gear etc.

A good dielectric gas should possess

1. High dielectric strength
2. High thermal stability
3. Chemical inertness against the construction materials
4. Non-flammability and low toxicity
5. low boiling point
6. Good heat transfer properties and low cost.

Air

Air is low cost and freely available and hence it is the most important insulating material as compared with all other dielectric gases. Air is a good insulator, both of heat and electricity.

Properties:

1. It is a good insulator of electricity as it does not contain any delocalised electrons, which carry electrical charge.
2. The dielectric strength of air is small.
3. Pressure has considerable effect on the dielectric strength of air. With the increase of pressure, dielectric strength of air increases.
4. Oxygen of air causes oxidation which reduces the life of electrical equipment.
5. Leakage of current is much less than through solid or liquid insulating materials under the same operating conditions.

Applications:

1. The air provides insulation between the overhead transmission lines.
2. Air is generally used as insulating material when voltages are not very high.
3. It is used as insulating material in air condensers and various electrical machines.

Sulphur hexafluoride

SF₆ or **sulfur hexafluoride** gas molecules are combined by one sulfur and six fluorine atoms. In the year of 1937, General Electrical Company first realized that SF₆ gas i.e. sulfur hexafluoride gas can be used as insulating material.

Preparation:

SF₆ or sulfur hexafluoride gas commercially is manufactured by reaction of fluorine (obtained by electrolysis) with sulfur. During process of producing of this gas, other by products like SF₄, SF₂, S₂F₂, S₂F₁₀ are also produced in small percentages.



Properties:

1. Sulphur hexafluoride (SF₆) is nonflammable and nontoxic gas
2. It is an electron-attracting gas with a breakdown voltage at atmospheric pressure more than twice that of air.
3. It possesses cooling characteristics far better than air and nitrogen.
4. It is chemically stable and does not decompose even when heated up to 800°C.

5. The SF_6 gas is one of the heaviest gases. Density of this gas at 20°C at one atmospheric pressure, is about 6.139 kg/m^3 which is about 5 times higher than air at same conditions.
6. Density is around 3.7 times more than that of air and it has also tremendous cooling effect in electrical equipment.
7. The thermal conductivity of this gas is lower than air. SF_6 gas is highly electronegative.
8. Sulphur hexafluoride has very excellent dielectric property. Dielectric strength of sulfur hexafluoride gas is about 2.5 times more than that of air.

Applications:

1. It is used in electrical devices like capacitors, cables etc.
2. SF_6 is used in several non-electric and electronic applications.
3. In magnesium casting, a protective atmosphere of SF_6 based gas mixture prevents the formation of undesirable byproducts.
4. SF_6 is also used in the semi-conductor industry, as etching gases for plasma etching or as cleaning gases to clean the chambers after the etching process.
5. Several minor applications are regarding leak detection, tracer gas studies, loud speakers and lasers.

LIQUID INSULATING MATERIALS

A **liquid dielectric** is a dielectric material in liquid state. Its main purpose is to prevent or rapidly quench electric discharges. Dielectric liquids are used as electrical insulators in high voltage applications, eg. Transformers, capacitors, high voltage cables and switch gear etc.

The liquid insulating materials should have following characteristics.

1. Arc quenching characteristics should be good.
2. It should be non-flammable.
3. It should have high electric strength, impulse strength and volume resistivity.
4. It should possess high specific heat and thermal conductivity.
5. It should have good chemical stability and gas absorbing properties.
6. It must have low viscosity, low density, low volatility and high flash point.

Functions of insulating liquids

1. The function of insulating liquids is to provide electrical insulation and heat transfer.
2. As an insulator the liquid displaces air in the system and provides a medium of high dielectric strength.

3. If air is completely displaced the corona threshold voltage and breakdown voltage for the system are greatly increased.
4. It also serves as coolant.

Transformer oil

Transformer oil is a mineral oil and it should be perfectly free from moisture.

Preparation: It is prepared by hydrocarbon oil distillate from any available crude naphthenic petroleum oil of low sulphur content (below 0.7 wt %), viscosity is 100° F, flash point is between 200 and 300° F in the presence of hydrogen under specified conditions.

Properties:

1. It is non-flammable, non-sludging and has high permittivity.
2. It has oxidation resistance.
3. Rate of heat transfer is reduced in presence of sludge.
4. It possesses the property of low moisture formation and low acid production.
5. The electrical properties and resistance to thermal expansion of mineral oils are influenced by the presence of non-hydrocarbon compounds like oxygen, nitrogen, sulphur etc.
6. They are stable at high temperature.
7. Presence of water reduces insulating properties.

Applications: They are used in transformer for two purposes

1. It transfers heat by convention from windings and core to the cooling surfaces.
2. It maintains the insulation of the windings.

Advantages of Transformer oil

Transformer oil offers the following advantages

1. High dielectric strength.
2. Low viscosity.
3. Freedom from inorganic acids, alkali and corrosive sulphur.
4. Good resistance to emulsification.
5. Freedom from sludging under normal operation.
6. Rapid settling of products.
7. Low pour point.
8. High flash point.

Factors affecting the properties of Transformer oil:

Transformer oil has few enemies and the manufacturers and users make an effort to protect it from these factors.

1. **Oxidation:** It is the most common cause of oil deterioration. The oil storage tanks are well sealed from the atmosphere. Careful drying and vacuum processing is conducted to remove air and moisture before sealing of tank and after which it is filled with dry air or nitrogen to minimize the exposure to oxygen.
2. **Contamination:** Moisture is the chief among the potential oil contaminants. Its presence provides a source of reactive products with the oil in the presence of heat. It also lowers the dielectric property of the oil. The same precaution procedures similar to the prevent oxidation is followed to protect oil from moisture.
3. **Excessive temperature:** Exposure to excessive heat causes decomposition of the oil and it increases the rate of oil oxidation. The best way to protect against excessive heat is to avoid overload of the transformer.
4. **Corona discharges:** Sparking and overheating can also breakdown the oil producing gases and water which can lead to the formation of acids and sludge.

Transformer oil tests

The various tests which are carried out on transformer oil are given below:

1. Moisture test:

A test oil sample is cooled in a closed vessel upto 25°C. This oil is taken in a dry test tube and heated rapidly with help of an electric heater till the oil begins to boil. During this process oil should not produce cracking.

2. Acidity test:

The procedure of this test is given below:

- a. Add 1 ml of phenolphthalein solution to 50 ml of alcohol.
- b. The mixture is heated to 40 – 50 °C and neutralize with a solution of KOH.
- c. Weigh 10 g of oil in 250 ml conical flask.
- d. Add the neutralized alcohol to the oil sample.
- e. Heat the sample to boiling point and boil for 5 minutes.
- f. Add again 1 ml of phenolphthalein, cool to 40 – 50 °C and titrate quickly against KOH solution.

Then acidity of KOH in milligrams required to neutralize the acidity of 1 g of sample is $56 - 1 (NV/W)$

Where N = Normality of KOH solution

V = Volume of KOH solution in litre

W = Weight of sample in grams

3. Sludge resistance test:

In sludge accumulation test the rate at which the sludge is formed at 120°C under definite conditions of oxidation is determined. Normally the test is completed within 35 to 40 days but addition of copper which acts as catalyst reduces the test duration to 14 days.

4. Contamination and Purification of Transformer oil:

Impurities such as water, resins, fibre and carbon particles may be present in transformer oil due to imperfect purification. These impurities may also enter into transformer oil during transportation, while in service and during storage. Such impurities when present in oil decrease the breakdown voltage of the oil. Water in the oil is usually present as tiny bubbles suspended in the oil.

Purification:

The oil is purified in the following ways.

1. The oil is boiled in vacuum to evaporate the water.
2. The impurities are heavier than oil thus they can be removed by quickly rotating the oil in the centrifuge. The impurities are pressed against the sides of the vessel by centrifugal force.
3. The solid impurities are removed by filtering through a special filter card board under pressure.
4. Adsorbents are added whose particles readily adsorb the products of ageing and moisture on its surface. The heated oil is thoroughly mixed with the crushed adsorbent and then filtered or can be passed through a thick layer of the adsorbent. Silica gel, alumina, Clays etc are used as adsorbents to purify transformer oil.

Askarels

Askarels are synthetic insulating liquids which are non – inflammable and under the influence of dielectric arc does not decompose to form inflammable gases. Example for an askarel is polychlorinated biphenyl which is an organic chlorine compound of formula $C_{12}H_{10-x}Cl_x$

Chlorinated hydrocarbons are the most widely used askarels.

Properties:

1. They possess excellent arc resistant, high dielectric strength, dielectric constant of the order of 4 to 6, tolerable dielectric loss at normal temperature and power frequencies
2. They possess adequate thermal, chemical and electrical stability.

Applications:

1. They are used as transformer fluids.
2. They are widely used as dielectric and coolant fluids in transformers, capacitors, and electric motors.

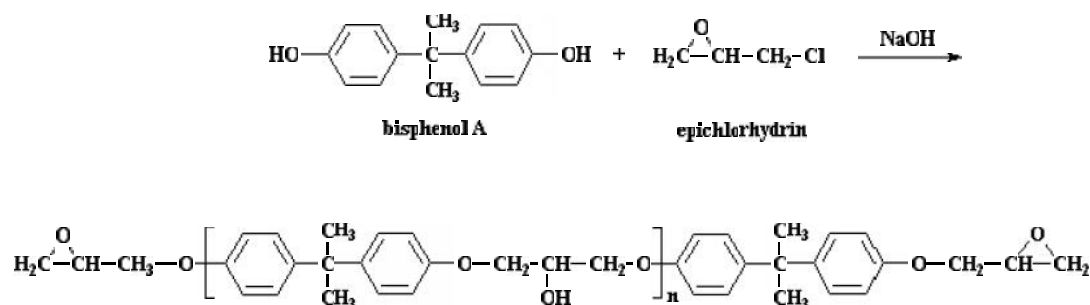
SOLID INSULATING MATERIALS

Most of the non-metals and compounds like mica, polymers, silk, paper, asbestos etc fall under this category. These are capable of retaining their insulating properties up to a fixed temperature called limiting temperature.

Epoxy resin

Preparation: Epoxy resin is prepared by the alkaline condensation of epichlorohydrin and polyhydric compounds. These are hardened by using hardeners like organic acids.

A particularly versatile group of epoxy resins are manufactured from epichlorohydrin and a dihydric phenol such as 2,2-bis(4-hydroxyphenyl)propane, often called p,p'-bisphenol A or simply bisphenol A.

**Properties:**

1. They have good electrical and mechanical strength, excellent stability and used as good adhesive metals.
2. They are extensively used for the casting of insulators, bushing, etc for high voltages
3. They have less shrinkage and excellent dimensional stability after casting.
4. They possess good adhesion to metals.
5. They possess high chemical resistance.
6. They have high stability.
7. They have good resistance to shock and vibration.

Applications:

1. The compounds of epoxy resin are used in the manufacture of high quality insulating material for high voltage electrical machines.
2. It is used for laminated insulating boards and insulated varnishes.
3. They can easily be casted into any desired shape at temperature below 150°C.
4. They are used as bushing to reduce vibrations.

Ceramic products**1. Glass****Preparation:**

It is a thermoplastic organic material obtained by fusion of different oxides. After cooling, glass remains in amorphous state. It is annealed tough glass. The raw materials used are sand (SiO_2), boric acid (H_2Bo_3), soda (Na_2Co_3), potash (K_2Co_3), chalk (CaCo_3), magnesite (MgCo_3), dolomite (CaCo_3 , MgCo_3), Red lead (Pb_3O_4), kaoline and feldspar.

Properties:

1. Glasses are normally transparent, brittle and hard.
2. Glasses are resistant to chemicals.
3. They are fragile, dense and heavy.
4. They have low dielectric loss and high dielectric strength.
5. They possess low coefficient of thermal expansion.
6. They have high tensile strength.

Applications:

1. It is used in transmission lines, line insulators, fuse bodies etc.
2. It is also used as support insulators.
3. It is used in lightening rods and cables.

2. White wares

The composition of the whirewares is 35 wt.% kaolin, 28 wt.% quartz, and 37 wt.% feldspar.

Preparation: The raw material is wet milled and homogenised to obtain the typical size distribution and it was dried. The dried raw mixture of china clay, feldspar and flint (SiO_2) is heated to 1450 – 1500°C. After heating, the samples were naturally cooled to room temperature. Finally, the fired samples were subjected to physical analysis.

Whiteware products are categorized into three main classes according to their degree of vitrification (and resulting porosity) as porous, semivitreous, and vitreous. All vitreous whitewares are often referred to as porcelains.

Properties:

1. It is strong and possess impact-resistant.
2. It is chemically inert in corrosive environments

3. They are excellent insulators against electricity.
4. It is non-combustible and absolutely heat resistant up to 1000 °C.

Applications:

1. It is used in chemical ware, dental implants, electric insulators, including spark-plug insulators in automobile engines.
2. Porcelain is an excellent insulation material for electrical engineering (high and low voltage).
3. It is a dielectric used even under the influence of humidity.
4. Ceramics made from alumina and porcelain is widely used in insulators that protect electrical equipment outdoors.
5. These are used as High-temperature superconductors in high-speed and super-fast computers.

ELECTRICAL RESISTIVITY

One of the significant characteristics of the materials is their ability to permit or resist the flow of electricity. Metals with high electrical resistance are used as heating elements and metals with low electrical resistance are used for long distance transmission lines.

Materials to be used in electrical equipments can be selected on the basis of their electrical properties such as,

1. Resistivity
2. Conductivity
3. Temperature coefficient of resistance
4. Dielectric strength
5. Thermoelectricity etc.

Resistivity is an electrical property of the material which impedes or resists the flow of electricity through it. It is defined as the resistance offered by a unit cube of a material and is given by

$$R = \rho (L/A)$$

P is Resistivity, ohm m

R is the resistance of a conductor (ohms)

A is the area of the conductor (m²)

L is the length of the conductor (m)

FACTORS AFFECTING ELECTRICAL RESISTIVITY

The electrical resistivity is affected by the following factors.

1. Effect of temperature

The electrical resistivity of a conductor increases with increase in temperature. This is because increase in temperature increases thermal agitation of metallic ions and they vibrate about their mean position. This restricts the flow of electrons thereby increasing the resistivity of the material. Higher temperature results in higher resistance. Higher the temperature, faster will be the oscillations of the ions in the conductor and the moving electrons will have to undergo more number of collisions per unit length of the wire, which results in lesser current and higher resistance.

The effect of temperature on electrical resistivity is mathematically expressed as

$$\rho_t = \rho_{20} [1 + \alpha_0 (t - 20)]$$

where ρ_t = Resistivity at temperature $t^\circ\text{C}$

ρ_{20} = Resistivity at 20°C

α_0 = Coefficient of temperature resistance

The coefficient of temperature resistance of a material is defined as the change in resistance of one ohm at 0°C per degree rise of temperature.

2. Effect of mechanical cold work

Resistivity of the metal can be increased by mechanical pressing or rolling or drawing (cold work) as it changes the crystal structure and cause grain boundaries, localized strain etc which interferes with the movement of electrons. However subsequent annealing decreases the resistivity. Eg. Hand drawn copper wire has higher resistivity than annealed copper.

3. Effect of alloying elements

Alloying elements increase the resistivity of the materials due to the presence of solute atoms in solid solutions. The solute atoms interfere with the flow of electrons. In Cu-Ni alloy, the copper atoms do not impede the motion of free electrons but solute nickel atoms impede their motion.

4. Effect of impurities

A small amount of impurities can increase the resistivity. Eg. Presence of 0.05% of phosphorous reduces the conductivity of copper by 40%.

CLASSIFICATION OF ELECTRICAL RESISTIVITY MATERIALS

Electrical resistivity materials are of two types.

1. Low resistivity materials
2. High resistivity materials

1) LOW RESISTIVITY MATERIALS

1. They have low value of resistivity.
2. They have low coefficient of temperature resistance values. (i.e. the change of resistance with change in temperature is low) This property will avoid variation in voltage drop and power loss with the changes in temperature and is essentially used in transmission lines.
3. They have good ductility and high mechanical strength, high melting point etc.
4. They are used for transmitting power from a generating station to other places.
5. They are used in house wiring, windings of transformer, motors and in generators.
6. Eg. copper and aluminium

2) HIGH RESISTIVITY MATERIALS

1. They have high value of resistivity
2. They have low coefficient of temperature resistance
3. They have high melting point
4. There is no tendency of oxidation
5. Has high mechanical strength
6. They are ductile
7. They are used in heating devices, electric motor starters, filaments of incandescent lamps, loading resistances, rheostats and resistances for precise measuring instruments.
8. Eg. Nichrome, Molybdenum silicide, tungsten, constantan, german silver, manganin.

IMPORTANT HIGH RESISTIVITY MATERIALS

Manganin

Manganin is the trademarked name for an alloy that consists of three metallic elements – Copper, Nickel and Manganese.

Composition:

This metal alloy consists of the following metals in the following proportions: Copper (Cu): 84%, Manganese (Mn): 12% and Nickel (Ni): 4%.

The chemical formula of this substance is CuMnNi. It consists of the formulas of all the constituent metals, namely CU for Copper, Mn for Manganese and Ni for Nickel.

Properties:

1. It has the formula weight (sum of the molecular masses of the atoms in the formula) of 177.18 g/mole.
2. Its temperature coefficient of resistance is larger at higher temperature.
3. They are easily drawn into wires.
4. The resistivity of this resistance alloy is 44×10^{-5} ohm.m and it is electrically conductive.
5. It has a melting point of 960 °C. The tensile strength of this substance ranges between 300-600 MPa.
6. The density of this alloy is 8.4 g/cm³. It has a specific gravity of 8.5.
7. Its electrical resistance is found to be constant over a range of temperatures.
8. The permissible working temperature = 60 -70°C.

Applications:

1. The wire and foil of this material are mainly used to manufacture various resistors – mainly ammeter shunts. Shunt refers to a device that controls the passage of electric current in different points of a circuit.
2. It is used in resistance boxes.

Constantan**Composition:**

It is also known as Eureka, Advance and Ferry. It is usually consisting of 55% **copper** and 45% **nickel**.

Constantan is a Nickel-Copper based alloy wire that has a high resistivity and is mainly used for thermocouples and electrical resistance heating.

Properties:

1. It has high specific heat resistance and negligible temperature coefficient.
2. Easily ductile and resistant to atmospheric corrosion.
3. Melting point – 1225 to 1300°C. Specific Gravity – 8.9 g/cc.
4. Electrical resistivity is 49×10^{-5} ohm. m at room temperature. Density is 8.89 g/cm³.
5. Constantan has a good fatigue life and a very high elongation capacity also.
6. Constantan has the highest resistivity among all the other alloys, which makes it insensitive to the level of strain and temperature.
7. Its permissible working temperature = 500°C

Applications:

1. It is used for the formation of thermocouple, along with the wires of other metals such as copper, iron and chromel.
2. It is especially used in resistance elements since its resistance does not change much with the change in its temperature.
3. Constantan is an ideal alloy for the electric motor starter resistances and for heavy duty industrial rheostats.
4. Constantan is one of the most widely used alloys in wire wound precision resistors, volume control devices and temperature stable potentiometers.

Molybdenum silicide

Composition: Molybdenum silicide (MoSi_2) is an intermetallic compound of molybdenum and silicon.

Properties:

1. It has an electrical resistivity of 3.5×10^{-5} ohm m
2. It has moderate density, with a melting point of 2230°C , and is electrically conductive.
3. At high temperatures it forms a passive layer of silicon dioxide, protecting it from further oxidation.
4. It possess oxidative resistance and elasticity.
5. While MoSi_2 has excellent resistance to oxidation and high Young's modulus at temperatures above 1000°C , it is brittle at lower temperatures. Also, at above 1200°C it loses creep resistance. These properties limits its use as a structural material, but may be offset by using it together with another material as a composite material. While the elements are brittle, they can operate at high power, and their electrical resistivity does not increase with operation time.

Applications:

1. They are used in glass industry, ceramic sintering, furnaces,
2. It finds applications in gas turbine engines, microelectronics etc.
3. It is frequently used as a shunt over polysilicon.
4. It is primarily used in heating elements till 1800°C .

Nichrome:Composition: Nichrome is Nickel – Chromium based alloy consisting of 80% nickel, 20% chromium.

Properties:

1. It is silvery-grey in color, corrosion-resistant, and has a high melting point of about 1400°C.
2. It has high electrical resistivity of 108×10^{-5} ohm m
3. It can be easily drawn into thin wires.
4. It has resistance to oxidation at high temperatures.
5. It has good mechanical strength.
6. Its permissible working temperature = 1100°C

Applications:

1. It is widely used in electric heating elements, such as in hair dryers, electric iron, room heaters, electric furnaces, electric ovens, soldering iron, toasters, and even electronic cigarettes.
2. A heating element converts electricity into heat through the process of Joule heating. Electric current through the element encounters resistance, resulting in heating of the element.
3. Most heating elements use Nichrome since it is an ideal material due to its relatively high resistance and its tendency to form an adherent layer of chromium oxide when it is heated for the first time. Material beneath this layer will not oxidize, preventing the wire from breaking or burning out.

Test your understanding

1. Explain the characteristics of dielectrics.
2. Give an account on the classification of electrical insulating materials based on substances and operating temperature.
3. Explain the factors affecting electrical resistivity.
4. Discuss the composition, properties and applications of high resistivity materials with examples.
5. Briefly explain the factors affecting the properties of transformer oils.
6. Discuss the various tests for the quality of transformer oil.
7. Write short notes on gaseous insulating materials with two examples.
8. Explain the preparation, properties and applications of epoxy resins and ceramics products.
9. Give the classification of electrical resistivity materials.
10. Write a note on liquid insulating materials with two examples.

Introduction: Computer representation of chemical compounds: Line notations - Wiswesser line notation - ROSDALnotation - SMILES coding - Advantages and disadvantages of different types of notations. Standard structure exchange formats: Structure of Mol files and SD files. Chemical structure drawing softwares. Molecule editors: CACTVS molecule editor - Chemdraw - ChemSketch - Chemwindow. Searching chemical structure: Similarity search

Cheminformatics – terminology

Cheminformatics also referred as Chemoinformatics, cheminformatics, chemical informatics, molecular informatics and even chemo-bioinformatics. The term chemoinformatics was probably first introduced in the literature in 1998 by Frank Brown.

Chemoinformatics is the mixing of the information resources to transform data into information and information into knowledge for the intended purpose of making better decisions faster in the areas of chemical, Pharama industries, Agrochemical discover and research organizations.

Chemical informatics is the application of information technology to help chemists investigate new problems and organize, analyze, and understand scientific data in the development of novel compounds, materials, and processes.

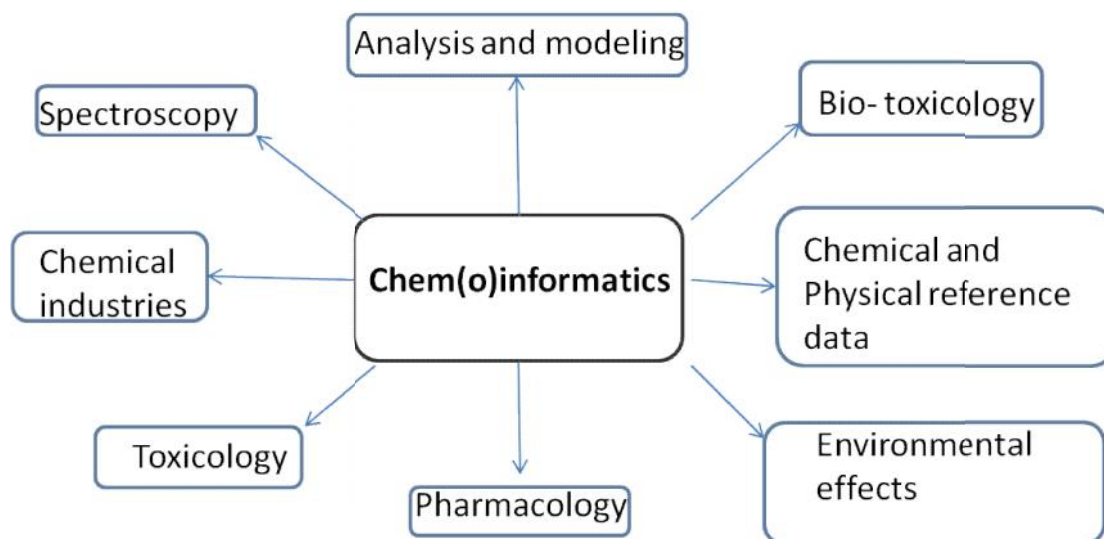
Importance of Cheminformatics:

- 1) Advances in theoretical and computational chemistry now allow chemists to model chemical compounds “in silico” with ever-increasing accuracy.
- 2) Molecular properties now becoming accessible through computation include molecular shape, electronic structure, physical properties, chemical reactivity, protein folding, structures of materials and surfaces, catalytic activity, and biochemical activities
- 3) Information Acquisition: Methods for generating and collecting data empirically (experimentation) or from theory (molecular simulation)
- 4) Information Use: Data Analysis, correlation, and application to problems in the chemical and biochemical sciences

Representation of chemical compounds

One of the major tasks in chemoinformatics is to represents chemical structures and transfers the various types of representation into application programs. A first basic step to "teaching" computer chemistry is to transform the molecular structure into language amenable to computer representation and manipulation. Basically computers can only handle bits of 0 and 1. Thus coding is the basis for transferring data. In chemistry the

chemical structures have to be represented in machine -readable form by scientific, artificial languages.



Chemical structures are usually stored in a computer as molecular graphs. Graph theory is a well-established area of mathematics that has found application not just in chemistry but in many other areas, such as computer science. A graph is an abstract structure that contains nodes connected by edges. The nodes and edges may have properties associated with them. For example, the atomic number or atom type may be associated with each node and the bond order with each edge. These atom and bond properties are important when performing operations with or upon the molecular graph. A graph represents the topology of a molecule only, that is, the way the nodes (or atoms) are connected.

The 2D graphical representation of chemical structures in structure diagrams can be considered to be the universal "natural language" of chemists. The computational representation of the molecular structures and the creation of structural databases usually follows the natural language. The procedures used to accomplish common tasks such as substructure searching are considered, including the use of graph theoretic methods, bit string screens and the use of canonical structure representations. The focus is on "2D representations" that are concerned with the chemical bonding between atoms rather than their 3D structures of the molecules.

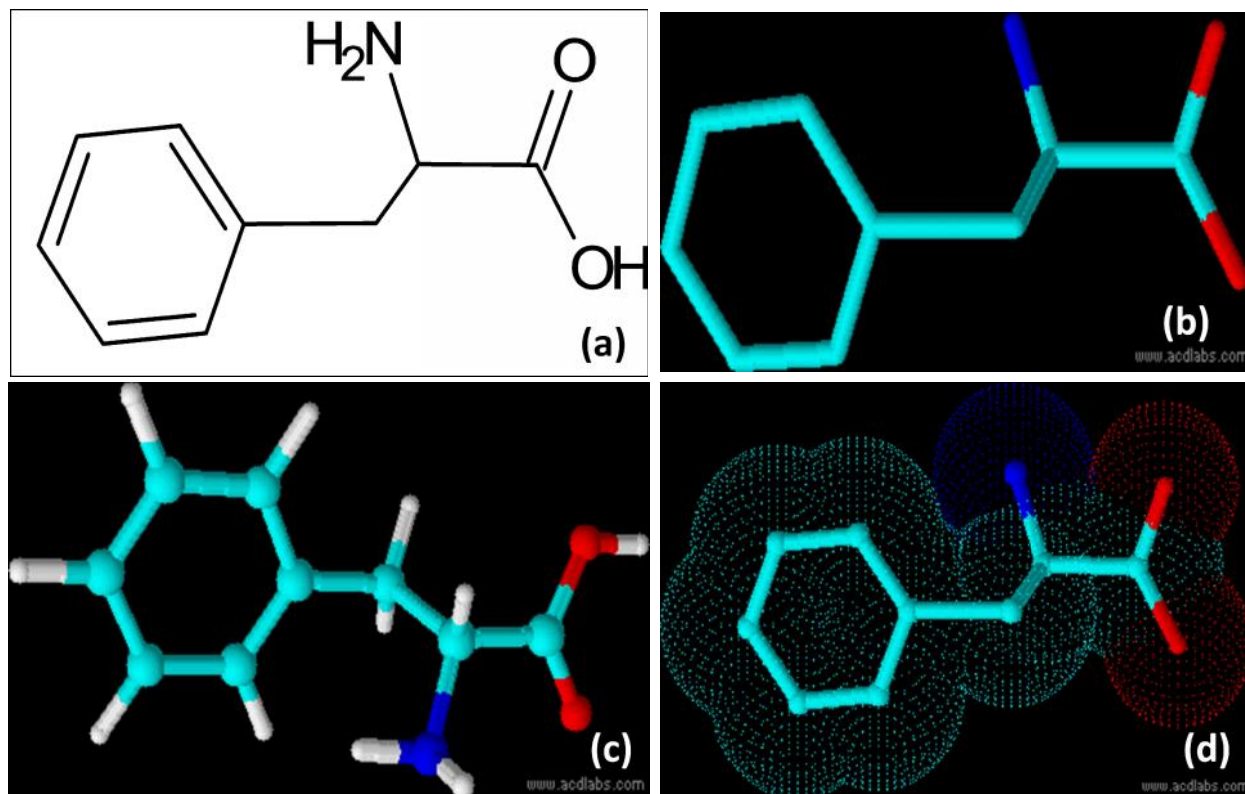


Figure 2: Representations of a Phenylalanine (a) 2-Dimensional structure (b) Stick model (c) Ball and Stick model (d) Space filled model

Notations and coding

An alternative way to represent and communicate a molecular graph is through the use of a linear notation. The line notations could enter the code of large molecules faster than with a structure-edition program.

Types of linear notations

- 1) Line notations
- 2) Wiswesser Line Notation(WLN)
- 3) Representation of Organic Structures Description Arranged Linearly (ROSDAL) notation
- 4) Simplified Molecular Input Line Entry Specification (SMILES) notation

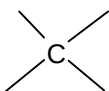
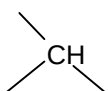
Line notations

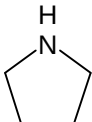
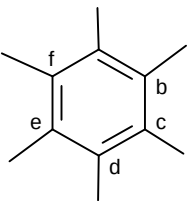
Line notations represent the structure of chemical compounds as a linear sequence of letters and numbers. The IUPAC nomenclature represents such kind of the line notations. However, the IUPAC nomenclature makes an alternative way to represent and communicate a molecular graph is through the use of a linear notation. A linear notation uses alphanumeric characters to encode the molecular structure. Linear notations are more compact than connection tables and so they can be particularly useful for storing and transmitting large numbers of molecules.

Wiswesser Line Notation (WLN)

The Wiswesser line notation was introduced in 1946, in order to organize and to systematically describe the cornucopia of compounds in more concise manner. A line notation represents a chemical structure by the computer. In many cases the WLN uses the standard symbols from the chemical elements. Additionally, functional groups rings systems, positions of rings substituents, and positions of condensed rings are assigned to individual letters or combinations of symbols.

Table.1: WLN coding of some important structural units

Class	Structural Unit	WLN coding
Hydrogen	H	H
Alkanes	C_nH_{2n+2}	n
Alkenes and Alkynes	$H_2C=CH_2$	U
	$HC\equiv CH$	UU
Branched Chains		X
		Y
Heterocycles and cyclic		L.n.J for carbocyclics L= beginning of the

Rules	compounds	 cyclopentane L.5.J	carbocyclic ring n= no. of atoms of the ring system J= Termination of the system
		 pyrrolidine T.5.J	T.n.J for Heterocyclics T= beginning of the heterocyclic ring n= no. of atoms of the ring system J= Termination of the system
	Aromatic ring Substituted derivatives		R R,B, C, D, E,F
	Alkyl halides	-X (X=F, Cl, Br, I)	F, G, E, I
	Alcohols, Ethers	OH; -O-	Q; O
	Ketones; aldehydes	-CO-; -CO-H	V; VH
	Carboxylic acids and Esters	-COOH; -CO-OR	VQ; VO

for WLN

Notation:

WLN uses a very simple system of canonicalization based on alphanumeric order.

- 1) Capital Letter: A-Z are used for elements, atom groups, branches and ring positions
- 2) Numbers: 0-9 indicate the length of an alkyl chain or the ring number
- 3) Special characters: "&", "/", "-", and " " (blank) indicate rings and substitution positions.
- 4) Priority increases in the direction:
 - a. Symbols;
 - b. Numbers in numerical order; and
 - c. Letters in alphabetical order (with the exception of R which has lower priority than symbols).Coding generally begins at the substituent assigned the highest priority.

Examples WLN Notation

WLN for CH₄ (Methane) : 1H

WLN for CH₃-CH₃ (Ethane): 2H

WLN for CH₃-CH₂-CH₃ (Propane) :3H

WLN for C₇HCl₅O₂ (Pentachlorobenzoate) : QVR BG CG DG EG FG

Acetone:

The two "1"s stand for saturated one-carbon chains, i.e. methyl groups. The "V" stands for a carbon doubly-bonded to oxygen.

Diethyl Ether:

Given nothing more than the above example, the encoding of diethyl ether should be completely clear:"O" simply stands for a divalent oxygen atom.

Acetophenone:

The benzene ring is one of the most ubiquitous functional groups in organic chemistry. Wiswesser knew this and wanted to make it easy to encode aromatic compounds. His solution is simplicity itself. Consider acetophenone: The "R" stands for a benzene ring. WLN canonicalization gives it the lowest priority and this is why it appears last.

4-chloroacetophenone:

The "G" symbol stands for chlorine. The " DV1" stands for the 4-acyl substituent. Here, the "D" denotes the 4-position. The 3- position would result in " CV1", and the 2- position would give " BV1". The space character means that the character following it should be interpreted as ring locant.

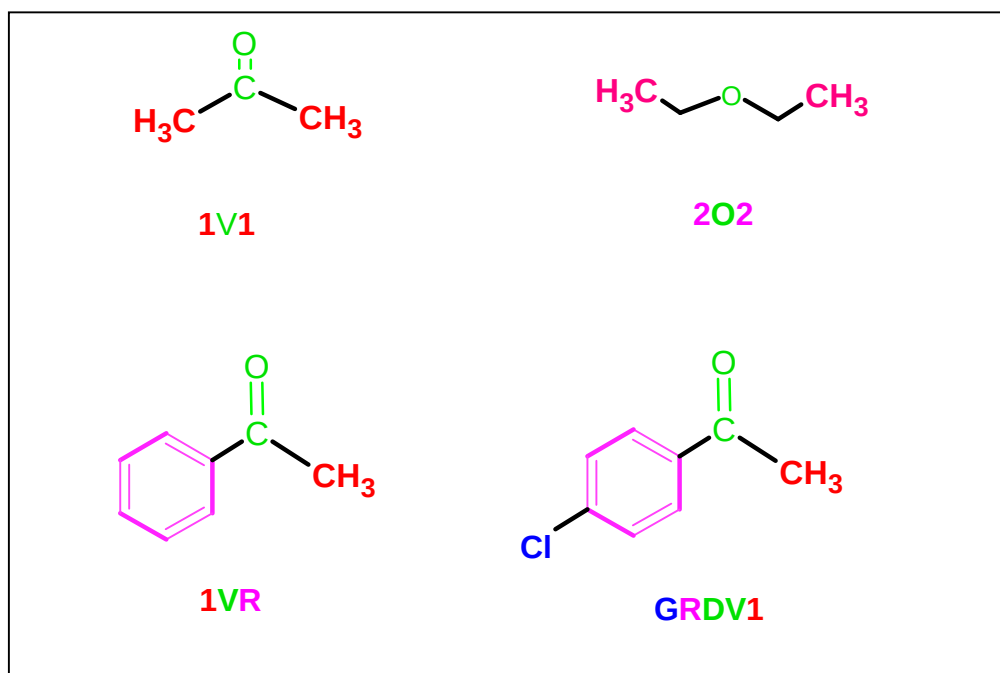
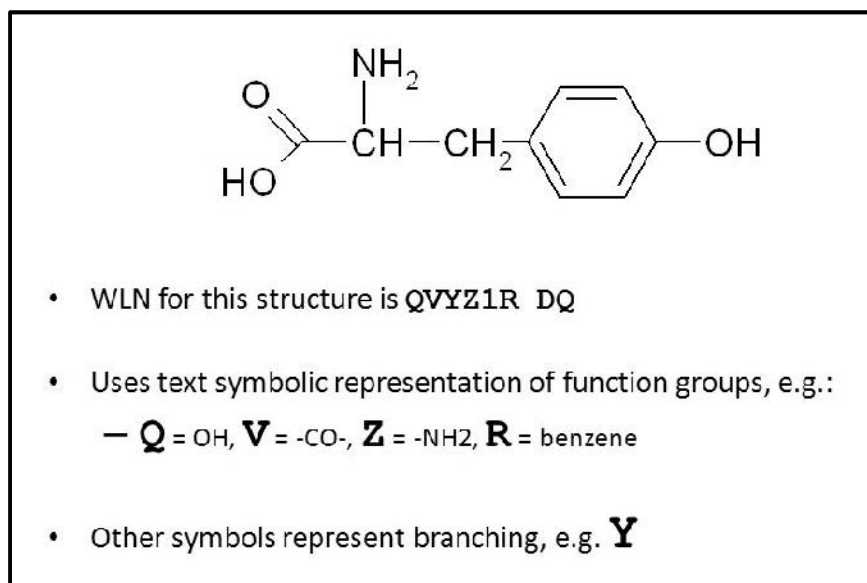


Fig. WLN Notation of Acetone, Diethylether, Acetophenone, Chloroacetophenone

Phenyl alanine



Advantages:

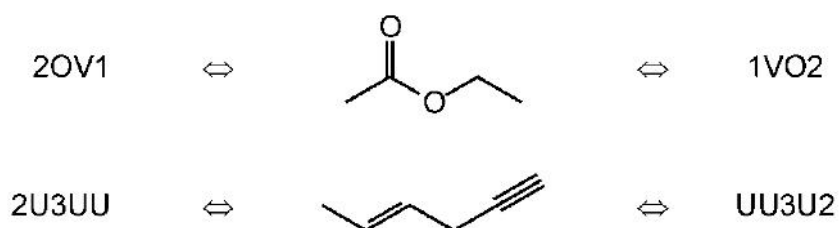
- WLN is remarkably compact, especially when compared to SMILES and InChI.
 WLN for 4-chloroacetophenone : **GRDV1**
 InChI for 4-chloroacetophenone: **InChI=1/C8H7ClO/c1-6(10)7-2-4-8(9)5-3-7/h2-5H,1H3**

- 2) The functional group recognition is easy for humans, it's orders of magnitude easier for Machines.
- 3) WLN is concise linear code
- 4) Unambiguous, Simple substructure search
- 5) Includes stereochemistry and it is unique if rules are followed.

Disdvantages:

- 1) Encoding WLN rules into a computer programme is difficult, and the rules for the canonicalization were computationally intractable.

Example:



- 2) Large number of complex rules and coding prone to errors
- 3) difficult to translate into a connection table and No support for coding reaction
- 4) Only those substructures contained in the coding can be retrieved in a substructure search

Applications

The WLN was applied to indexing the chemical structure index (CSI) at the institute for scientific information (ISI) and the index chemicus registry systems (ICRS) as well as the crossbow systems of imperial chemical industries (ICI). With the introduction of commotion tables in the chemical abstracts service (CAS) in 1965 and the advent of molecular editors in the 1970S, which directly produced connection tables, the WLN lost its importance.

ROSDAL

ROSDAL (Representation of organic structure description arranged linearly) syntax was developed by S. Welford, J.Barnard and M.F.Lynch n 1985 for the beilsten institute. This line notation was intended to transmit structure information between the user and the beilsten was DIALOG system (Beilsten-Online) during database retrieval queries

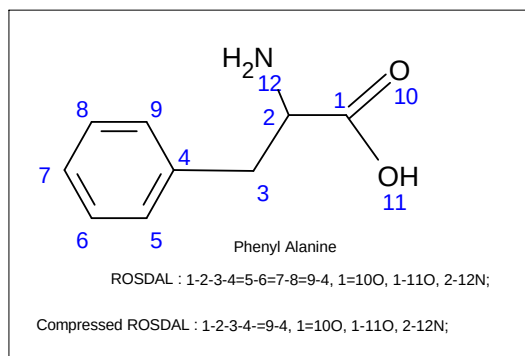
and structure displays. This exchange of structure information by the ROSDAL ASCII character string is very fast.

ROSDAL syntax is characterized by

- a) A simple coding of a chemical structure using alphanumeric symbols which can easily be learned by a chemist.
- b) In the Linear structure representation, each atom of the structure is arbitrarily assigned a unique number, except for the hydrogen atoms.
- c) Carbon atoms are shown in the notation only by digits.
- d) The other types of atoms carry, in addition their atomic symbols.
- e) In order to describe the bonds between atoms, bond symbols are inserted between the atoms numbers.
- f) Branches are marked and separated from the other parts of the code by commas. The ROSDAL linear notation is unambiguous but not unique.

The sequence for setting up a ROSDAL notation is

- 1) The structure diagram is drawn and the atoms are arbitrarily numbered (each atom is assigned a unique number).
- 2) Atomic symbols are usually written directly behind the index of an atom.
- 3) Usually only the indices of the carbon atoms are written, not the symbols: hydrogen atoms can have, but do not need, an atom number.
- 4) Bond types are described as follows:
 - a. "-" for a single bond
 - b. "=" for a double bond
 - c. "#" for triple bond
 - d. "?" for any connection
- 5) Simplifications are allowed, such as writing alternating bonds as "-=".
- 6) Commas separate branches and substituents.
 - e. Examples:

Phenylalanine:**ROSDAL Advantages and disadvantages****Advantages:**

- 1) Simple code, easy to learn
- 2) Fast data exchange format
- 3) Includes stereochemistry

Disadvantages

- 1) No support for coding reactions
- 2) Not Unique

SMILES Coding

In 1986 David Weininger the SMILES notation at the US Environmental Research Laboratory USEPA, Duluth, MN, for chemical data processing. The Chemical structure information is highly compressed and simplified in the notation. The flexible, easy to learn language describes chemical structure as a line notation. The SMILES language has found widespread distribution as a universal chemical nomenclature.

SMILES Definition: The simplified molecular-input line-entry system (SMILES) is a specification in form of a line notation for describing the structure of chemical species using short ASCII strings.

The basic SMILES rules are:

1) Atoms represented by their symbols.

Atoms are represented by their atomic symbols: this is the only required use of letters in SMILES. Each non-hydrogen atom is specified independently by its atomic symbol enclosed in square brackets, [].

[H ⁺]	proton
[Fe ⁺²]	iron (II) cation
[OH ⁻]	hydroxyl anion
[Fe ⁺⁺]	iron (II) cation
[OH ₃ ⁺]	hydronium cation
[NH ₄ ⁺]	ammonium cation

Atoms in aromatic rings are specified by lower case letters, e.g., aliphatic carbon is represented by the capital letter C, aromatic carbon by lower case c. Since attached hydrogens are implied in the absence of brackets, the following atomic symbols are valid SMILES notations.

2) Hydrogen atoms automatically structure free valences and are omitted (Simple hydrogen connection)

The second letter of two-character symbols must be entered in lower case. Elements in the "organic subset" B, C, N, O, P, S, F, Cl, Br, and I may be written without brackets if the number of attached hydrogens conforms to the lowest normal valence consistent with explicit bonds. "Lowest normal valences" are B (3), C (4), N (3,5), O (2), P (3,5), S (2,4,6), and 1 for the halogens.

C	Methane	CH ₄
P	Phosphine	PH ₃
N	Ammonia	NH ₃
S	Hydrogen Sulfide	H ₂ S
O	Water	H ₂ O
Cl	Hydrochloric acid	HCl

3) Neighboring atoms stand next to each other.

4) Double and triple bonds are characterized by "=" and "#" respectively.

CC	ethane	(CH ₃ CH ₃)
C=O	formaldehyde	(CH ₂ O)
C=C	ethene	(CH ₂ =CH ₂)
O=C=O	carbon dioxide	(CO ₂)
COC	dimethyl ether	(CH ₃ OCH ₃)
C#N	hydrogen cyanide	(HCN)
CCO	ethanol	(CH ₃ CH ₂ OH)
[H][H]	molecular hydrogen	(H ₂)

5) Branches are represented by parentheses.

6) Rings are described by allocating digits to the two "connecting: rings atoms"

Example:

C1CCCCC1 Cyclohexane (C_6H_{12})

c1ccccc1 Benzene (C_6H_6)

SMILES Representation of Organic Compounds

C Methane (CH_4)

CC Ethane (CH_3CH_3)

C=C Ethene (CH_2CH_2)

C#C Ethyne ($CHCH$)

COC Dimethyl ether (CH_3OCH_3)

CCO Ethanol (CH_3CH_2OH)

CC=O Acetaldehyde ($CH_3-CH=O$)

C#N Hydrogen Cyanide (HCN)

[C-]#N Cyanide anion

Branches are specified by enclosures in parentheses and can be nested or stacked, as shown in these examples.

CC(C)CO Isobutyl alcohol ($CH_3-CH(CH_3)-CH_2-OH$)

CC(CCC(=O)N)CN 5-amino-4-methylpentanamide

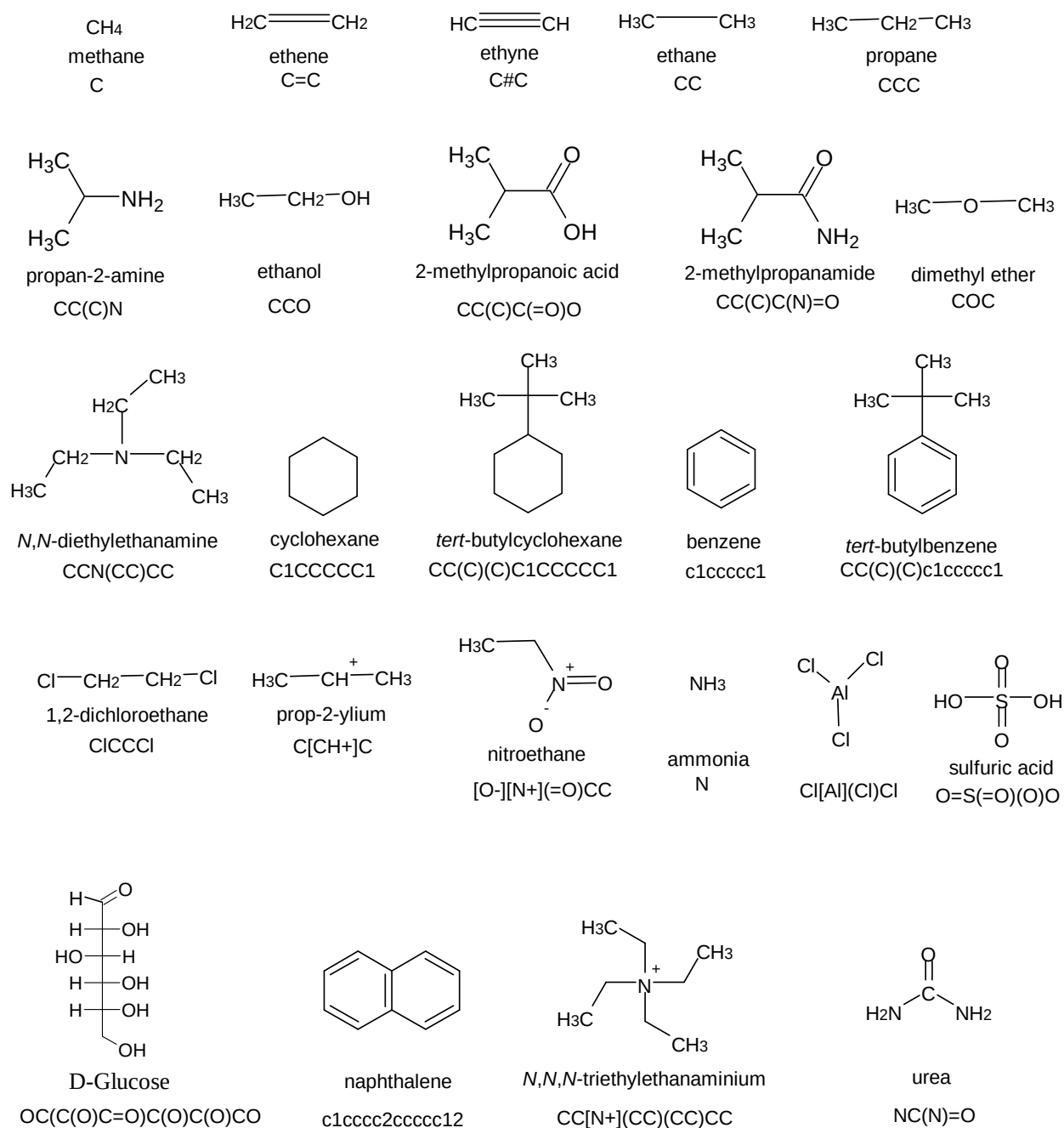
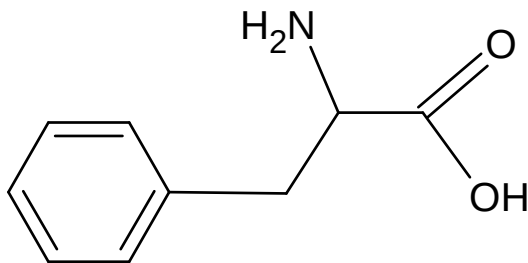


Fig. SMILES representation of inorganic and organic molecules

Example:



SMILES: NC(Cc1ccccc1)C(=O)O

SMILES Advantages and Disadvantages

Advantages:

- 1) Simplest linear code and easy to learn
- 2) Fast data exchange format
- 3) Supports Markush, stereochemistry and reaction coding
- 4) Unambiguous

Disadvantages:

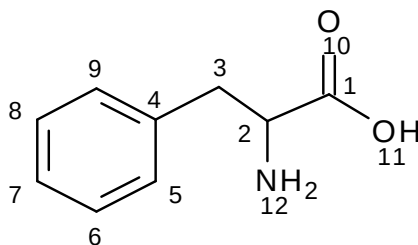
- 1). Not unique (except Unique SMILES)
- 2). Some problems with aromaticity perception

Application

The compact textual coding requires no graphical input and additionally permits a fast transmission. These are important advantages of using SMILES in chemical applications via the internet and in online services. SMILES are also for the input of structure in the daylight toolkit.

Limitations:

- a) SMILES is proprietary and it is not an open project. This has led different chemical software developers to use different SMILES generation algorithms, resulting in different SMILES versions for the same compound.
- b) SMILES strings obtained from different databases or research groups are not interchangeable unless they used the same software to generate the SMILES strings.
- c) With an aim to address this interchangeability issue of SMILES, an open-source project has launched to develop an open, standard version of the SMILES language called OpenSMILES.²⁸

WLN, SMILES, ROSDAL Notation of Phenyl alanine

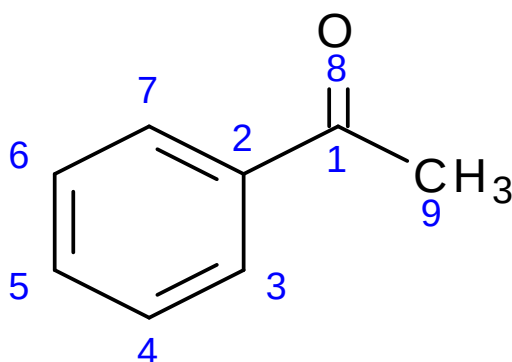
IUPAC: 2-amino-3-phenylpropanoic acid

Systematic Name: Phenyl alanine

WLN: VQYZ1R

SMILES: NC(Cc1ccccc1)C(=O)O

ROSDAL: 1-2-3-4-5=6-7=8-9=4, 1=10O,1-11O, 2-12N,

WLN, SMILES, ROSDAL Notation of Acetophenone

Common Name: Acetophenone

IUPAC Name: 1-phenylethanone

WLN : 1VR

SMILES : CC(=O)c1ccccc1

ROSDAL: 1-2-3=4-5=6-7=2, 1=8O,1-9C

Structure exchange formats

The chemistry of the numerous software programs is available to handle structure information on molecules. The scope of the programs leads from drawing structure diagrams to expert systems that process the data and produce new information. All of these systems have one task in common: to save data in file. Many organizations and software's suppliers have developed their own connection table format and quite a few have made provisions for the import or export of other files format. The processing of data from data to information and finally to knowledge, usually asks for the interaction and cooperation of several different softwares systems and databases. In this process, the exchange of chemical structure information plays a pivotal role : the internal file formats of one software systems has to be understood by another, i.e converted into its internal file format. This exchange process is usually handled through an external ASCII, file format.

Format type	Codename of the format
Document formats	mrv, Marvin Documents (MRV) cdx, cdxml, ISIS/Draw sketch file (SKC) skc, ChemDraw sketch file (CDX, CDXML)
Molecule file formats	mol, rgf, sdf, rdf, csmol, csrgf, cssdf, csrdf, cml, smiles, cxsmiles, abbrevgroup, peptide, _ sybyl, mol2, pdb, xyz, inchi, name
Graphics formats	jpeg, msbmp, png, pov, svg, emf, tiff, eps
Compression and Encoding	gzip, base64

There are many file formats for storing information about molecular structures. Only some of them have widely accepted by the cheminformatics community and are used as standard format for the exchange of information of chemical structures and reactions.

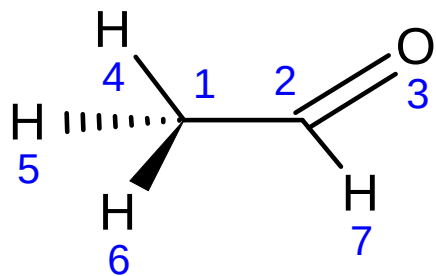
The Molfile and SDfile formats were developed by Molecular Design Limited (MDL website). These formats became popular for the storage and exchange of information on molecular structures and properties.

Molfile: It describes a single molecular structure which can contain disjointed fragments. The default filename extension for Molfiles is ".mol".

In order to understand the Molfile format let us look at a sample files and recognize its fundamental structure. For simplicity, some less important details will be omitted in the discussion.

Table: The most important file formats for exchange of chemical structure information

<i>File format</i>	<i>Suffix</i>	<i>Comments</i>	<i>Support</i>
MDL Molfile	*.mol	Molfile; the most widely used connection table format	www.mdli.com
SDfile	*.sdf	Structure-Data file; extension of the MDL Molfile containing one or more compounds	www.mdli.com
RDfile	*.rdf	Reaction-Data file; extension of the MDL Molfile containing one or more sets of reactions	www.mdli.com
SMILES	*.smi	SMILES; the most widely used linear code and file format	www.daylight.com
PDB file	*.pdb	Protein Data Bank file; format for 3D structure information on proteins and polynucleotides	www.rcsb.org
CIF	*.cif	Crystallographic Information File format; for 3D structure information on organic molecules	www.iucr.org/iucr-top/cif/
JCAMP	*.jdx, *.dx, *.cs	Joint Committee on Atomic and Molecular Physical Data; structure and spectroscopic format	www.jcamp.org/
CML	*.cml	Chemical Markup Language; extension of XML with specialization in chemistry	www.xml-cml.org

Molfile Example: Ethanal or Acetaldehyde**Ethanal or Acetaldehyde**

The header consists of up to 3 lines:

Line:1 Comment or molecule name line;

Line:2 A line detailing the type of application which generated the table, the date and time of its creation.

04131617572D

04thMonth/13th date/16 th year/1757 Time of created/2D structure

Line:3 Comment or description line that even if empty must be present.

Line:4 These lines are followed by the counts line which gives the number of atoms and bonds (plus several additional flags) in the molecule.

Line: 5 to 11

The atom block , containing the x, y, and z co-ordinates of the atom and the element symbol for the atom. As this study used only topological (rather than topographical) structural information the positional coordinates were not used.

Line: 12 to 17

Finally, for the bond block , the first two numbers of each line indicates the numbers of the respective atoms from the atom list, and the third number indicates the bond type between these two atoms. (A value of 1 indicates a single bond connection, 2 a double bond and 3 a triple bond.)

Line: 18 to 24

Line: 25 END

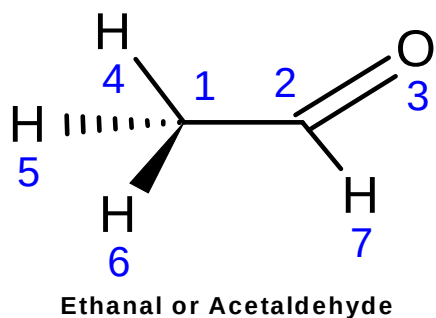
1. Blank Line or Molecule Name	}	Header block (Line:1 to 3)
2. ACD/Labs04131617572D [Creator Name]		
3. Blank Line		
4. 7 6 0 0 0 0 0 0 0 0 0 8 V2000	}	Counts Line (Line: 4)
5. -0.8077 -0.0155 0.1782 C 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		
6. 0.6883 -0.0351 -0.0110 C 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	}	Atom Block (Line:5 to 11)
7. 1.2933 1.0026 -0.1570 O 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		
8. -1.1027 0.8443 0.8174 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		
9. -1.2933 0.0808 -0.8174 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		
10. -1.1471 -0.9553 0.6649 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		
11. 1.2343 -1.0026 -0.0232 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0		
12. 1 2 1 0 0 0 0	}	Bond block (Line:12 to 17)
13. 1 4 1 0 0 0 0		
14. 1 5 1 0 0 0 0		
15. 1 6 1 0 0 0 0		
16. 2 3 2 0 0 0 0		
17. 2 7 1 0 0 0 0		
18. M ZC 1 1	}	Stereochemistry (Line:18 to 24)
19. M ZC 2 2		
20. M ZC 3 3		
21. M ZC 4 4		
22. M ZC 5 5		
23. M ZC 6 6		
24. M ZC 7 7		
25. M END		

Fig. Schematic Representation of Molfile for Acetaldehyde molecule or Ethanal molecule

SDfile Format:

SDfile contains the structural information and non structural information. This makes it is useful for exchange of data between databases and between two computational softwares. Within an SDfile, each molecule is represented by its Molfile with additional data items describing its non-structural properties molecular weight, heat of formation, molecular descriptors, biological activity, CAS number etc.)

In order to understand the SDfile format let us look at a Acetaldehyde or Ethanal molecule.



The header consists of up to 3 lines:

Line:1 Comment or molecule name line;

Line:2 A line detailing the type of application which generated the table, the date and time of its creation.

07011509283D

07th Month/1st date/15th year/09.28 time/ 3D file

Line:3 Comment on copy right

Line:4 These lines are followed by the counts line which gives the number of atoms and bonds (plus several additional flags) in the molecule.

Line: 5 to 11

The atom block , containing the x, y, and z co-ordinates of the atom and the element symbol for the atom. As this study used only topological (rather than topographical) structural information the positional coordinates were not used.

Line: 12 to 17

Finally, for the bond block, the first two numbers of each line indicates the numbers of the respective atoms from the atom list, and the third number indicates the bond type between these two atoms. (A value of 1 indicates a single bond connection, 2 a double bond and 3 a triple bond.)

Line: 18 End for structural data.

Line 19 to 20: Header block for non structural data

Line 21 to 47: Nonstructural data like, date of creation, CAS number, Method of generation, Dipole moment, Electronic Energy, Rotational constants, Software used for generation and Contributor name.

Line: 48: Delimiter.

Line No:

```

1. Acetaldehyde or Ethanal
2. NIST 07011509283D 1 1.00000 -153.83012
3. Copyright by the U.S. Sec. Commerce on behalf of U.S.A. All rights reserved.
4. 7 6 0 0 0 0 0 0 0 0999 V2000
5. 0.5984 0.8354 0.7035 C 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
6. 2.0205 1.1102 1.1250 C 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
7. 2.5939 2.1646 0.9686 O 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
8. 0.0019 0.5440 1.5781 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
9. 0.1623 1.7187 0.2315 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
10. 0.5736 -0.0140 0.0082 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
11. 2.5387 0.2513 1.6103 H 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
12. 1 2 1 0 0 0 0
13. 1 4 1 0 0 0 0
14. 1 5 1 0 0 0 0
15. 1 6 1 0 0 0 0
16. 2 3 2 0 0 0 0
17. 2 7 1 0 0 0 0
18. M END
19. > <COPYRIGHT>
20. Collection (C) 2016 copyright by the U.S. Secretary of Commerce on behalf of the United States of America. All rights reserved.
21.
22. > <DATE>
23. 2015-07-01
24.
25. > <CAS.NUMBER>
26. 75-07-0
27.
28. > <METHOD>
29. B3LYP/6-31G*
30.
31. > <DIPOLE.MOMENT>
32. 2.6401 debye
33.
34. > <ELECTRONIC.ENERGY>
35. -153.830121544 hartree
36.
37. > <ROTATIONAL.CONSTANTS>
38. 56.86315 GHz
39. 10.07531 GHz
40. 9.03745 GHz
41.
42. > <SOFTWARE>
43. Gaussian 09, Revision D.01
44.
45. > <CONTRIBUTOR>
46. Avi Newman
47.
48. $$$

```

Line 1 to 3: Header block

Line 4: Counts line

Line 5 to 11: Atom block

Line 12 to 17: Bond block

Line 18: End

Line 21 to 48: Non structural data

Fig. Schematic Representation of SDfile for Acetaldehyde molecule or Ethanal molecule

Chemical structure drawing soft wares

Chemical structure drawing soft wares aids in teaching key chemistry concepts to high school, undergraduate, and graduate chemistry students and researchers at higher education. In addition, students benefit from exposure in the learning environment to the same tools they will encounter in the workforce

Types of the Structure drawing tools:

a) ChemDraw:

Molecule editor developed by the cheminformatics company CambridgeSoft. For Windows and Mac.

b) ACD/ChemSketch:

Molecule editor developed by ACD/Labs. Also available as freeware, with tools for 2D structure cleaning, 3D optimization and viewing, InChI generation and conversion, drawing of polymers, organometallics, and Markush structures. For Windows only.

c) ChemWindow:

It is the software chemists choose for chemical structure drawing and publishing worldwide. Now with integrated solutions to modify, store, search, and retrieve chemical structures and properties, ChemWindow offers scientists even more solutions.

- i. 2D Chemical Structure Drawing
- ii. 3D Molecular Rendering
- iii. Chemistry Database Building (structures, chemical property information, etc.)
- iv. Scientific Publishing / Reporting Tools

d) CACTV/JME Molecular Editor:

The CACTVS molecule editor is a graphical mouse-oriented X11 Unix-based tool for the input of molecular structures. It can be used both in stand-alone mode, optionally with Drag&Drop to and from other stand-alone programs from the CACTVS tool series.

Java applet which allows to draw / edit molecules and reactions (including generation of substructure queries) and to depict molecules directly within an HTML page. Editor can generate Daylight SMILES or MDL Molfile of created structures.

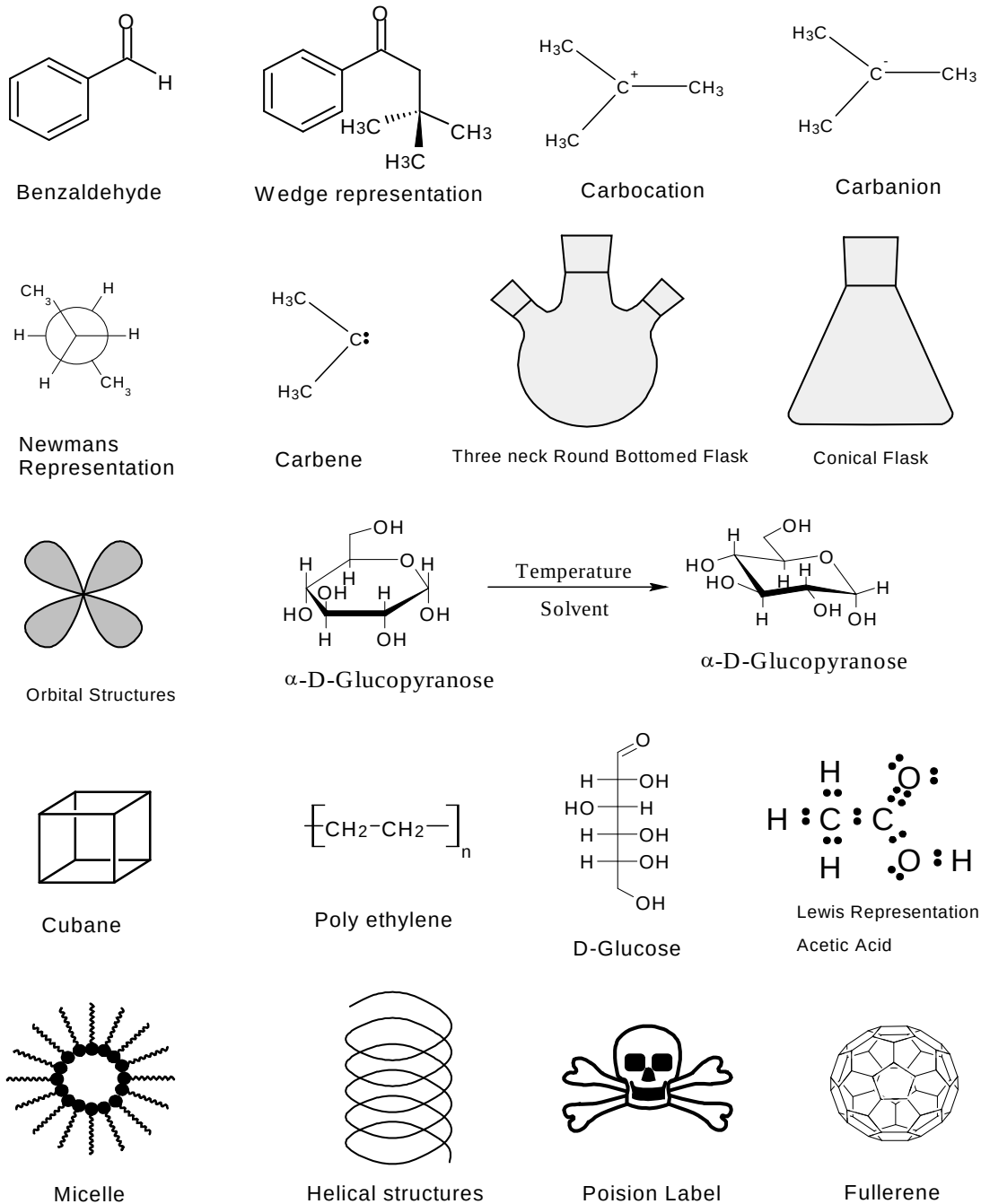
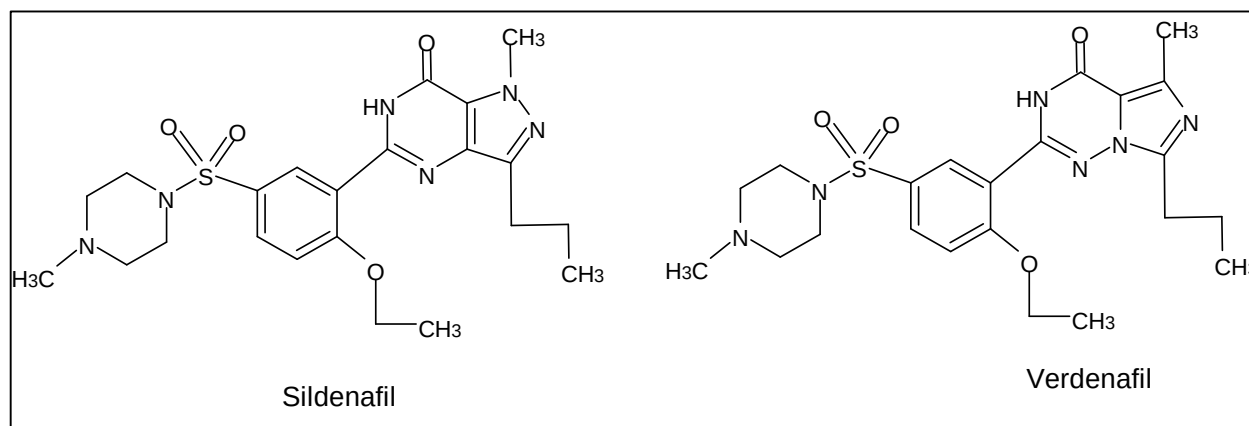


Fig. Schematic representation of possible representation of chemical structures by using the molecular editor softwares (Chemsketch, Chemdraw, ChemWindo Softwares)

Similarity Search:

Similarity search finds molecules with a high percentage of features that are common to the target molecule. Unlike a substructure search, the molecules found may not actually match the target.

For example, suppose you are looking for compounds related to Sildenafil. A substructure search would miss the closely-related drug Vardenafil because one nitrogen is moved.



By contrast, a similarity search will find Sildenafil as well as Vardenafil and its relatives. Although the core ring systems of the two drugs have significant differences, their similarity index is moderately high (0.7) because most of the structural features are shared.

Similarity Metrics

1. 2D topology:

This is the most widely used similarity metric. That is, they use the "2D connectivity" of the molecule's atoms and bonds to create a fingerprint, and search using the Tanimoto coefficient.

2. 3D configuration:

One of the most important uses of similarity is in the discovery of new drugs, and a molecule's shape is critical to its medicinal value (see QSAR).

3D similarity searches are uncommon for two reasons: they're difficult and slow. The difficulty comes from the complexity of molecular interactions: a molecule is not a fixed

shape, but rather a dynamic object that changes according to its environment. And the slowness comes from the difficulty: to get better results, scientists employ very complex algorithms.

3. Physical Properties:

The above 2D and 3D similarity are based on the molecule's structure. Another technique compares the properties, either computed or measured or both, and declares that molecules with many properties in common are of interest. It is the idea of QSAR taken to the database.

4. Clustering:

"Clustering" is the process of differentiating a set of things into groups based on common features. Molecules can be clustered using a variety of techniques, such as common 2D and/or 3D features