

UNIT – IV

POLYMERS IN ELECTRONICS

4.1. INTRODUCTION

- Polymers are generally macromolecules formed by the repeated linking of large number of small molecules. They are used in various fields like electronic, electrical, automobile, defense and electrical goods.
For example vinyl chloride (monomer) can be used to synthesize polyvinyl chloride (polymer)
- Most polymers are electrically insulating and are often used as dielectric layers, insulators, and packaging materials for electronics devices.
- In electronics and polymer science, there are some outstanding polymers that can conduct electricity.
- Today, a wide range of electrical and electronic applications use thermoplastic and thermoset polymers, as well as their composites, to perform a variety of very distinct functions.
- The main advantages of polymers are that they are flexible, their structures are able to be modified, and their properties can be tuned. When applying a voltage to a semiconducting polymer, it emits light, providing excellent visibility as the basis for a new technology for flat-panel displays.

Polymers in Engineering and Technology

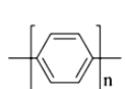
Polymer materials are applied in various fields of engineering and technology. Some of the important fields of applications are listed below.

- i) Radiation sensitive stencils to define devices and interconnect wiring on the chip and package (lithography)
- ii) Dielectric materials to use as insulators to prevent short between metal interconnections.
- iii) Encapsulation materials for correction and mechanical protection.
- iv) Conducting polymers for electronic applications.
- v) Non – linear optical materials to transmit or switch light for photonic application.

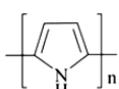
4.2. CONDUCTING POLYMERS

- In general polymers are insulators. Ex: Polypropylene, PVC etc.
- But some exceptional polymers conduct electricity in certain conditions.
- A polymer which can conduct electricity is termed as conducting polymer.
- The non-conducting nature of organic polymer is due to the absence of conjugation in the backbone or absence of conducting ingredients.
- First discovered conducting polymer is polyacetylene (1977).
- Nobel Prize in chemistry for the year 2000 for the pioneering work in the field of conducting polymers.

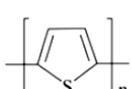
Examples:



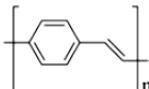
poly(p-phenylene)



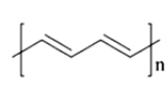
Polypyrrol



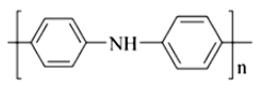
Polythiophene



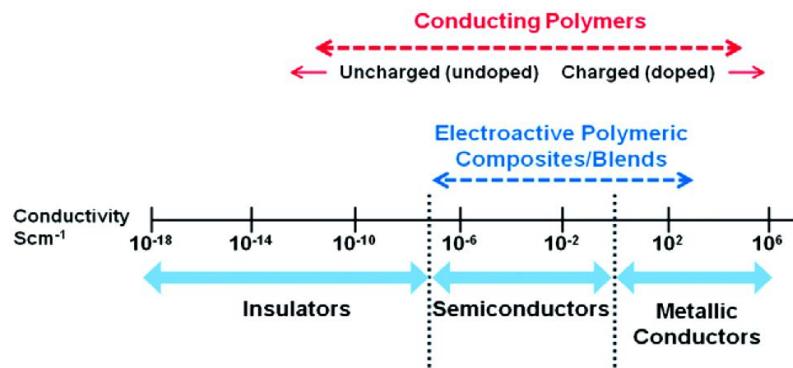
Poly(p-phenylene vinylene)



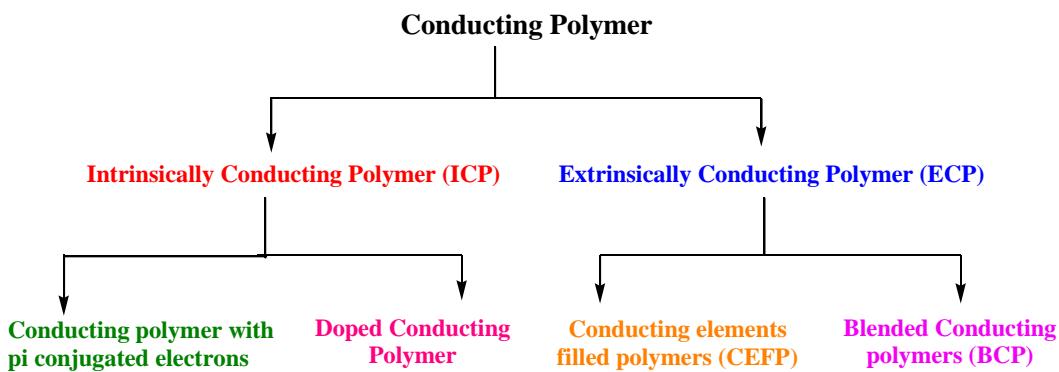
Polyacetylene



Polyaniline



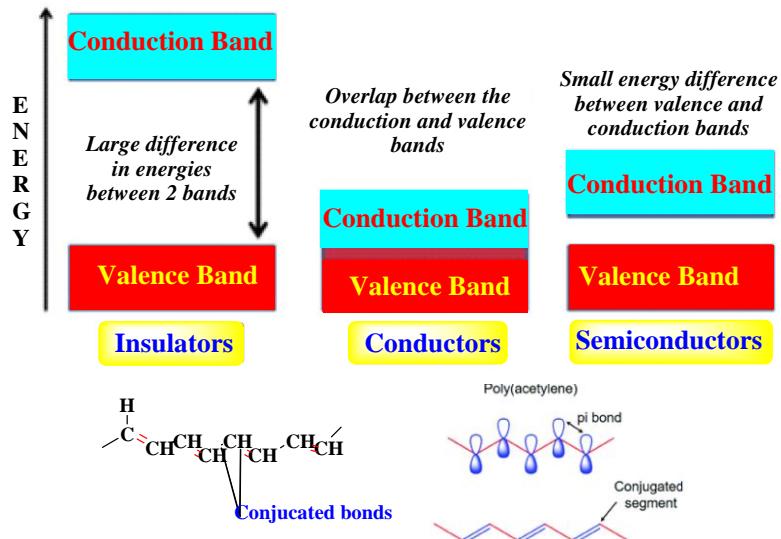
4.3. MECHANISM OF CONDUCTING POLYMERS



4.3.1. Intrinsically Conducting Polymer (ICP)

1. Conducting polymer with π -conjugated electrons

The orbitals of π electrons overlap resulting in the formation of valence band and conduction band.

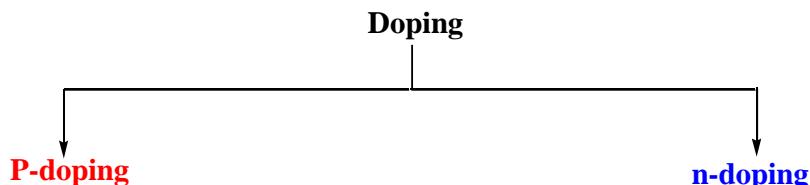


- Highest occupied band - Valence band (VB)
- Lowest unoccupied band - Conduction band (CB)

Electrical conductance occurs when electrons move from valence band to conduction band thermally or photolytically.

4.3.2. Doped Conducting Polymers

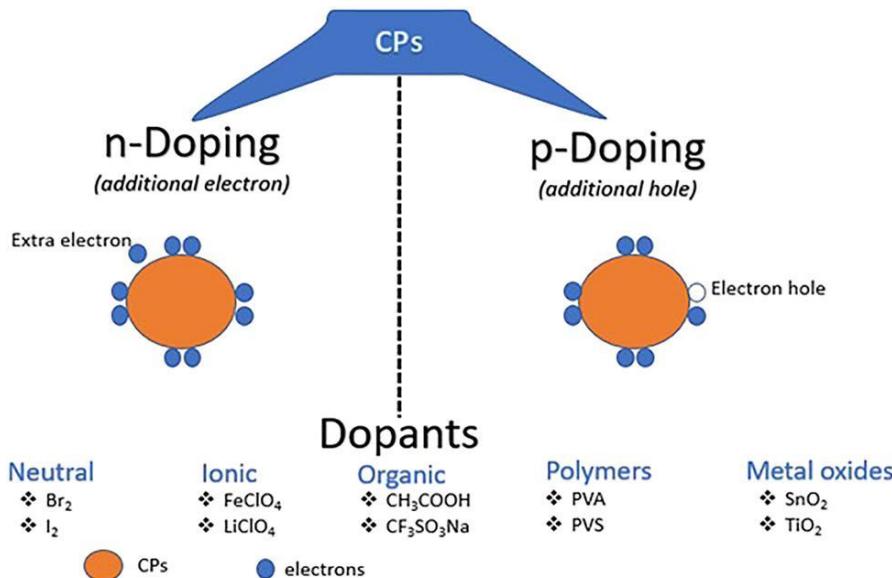
- Conductivity is due to +ve (or) -ve charge of polymer by the process of oxidation or reduction.



- (i) Oxidative process of +ve ions
- (ii) Some electrons from the pi-bond of conjugated double bonds are removed and holes are created.
- (iii) $P + \text{Acid} \longrightarrow P^+ \text{ Acid}$

Examples: Lewis acid, FeCl_3

- (i) -ve ions introduced into polymer
 - (ii) Reduction Process
 - (iii) $P + \text{Base} \longrightarrow P^- \text{ Base}$
- Examples: Lewis base

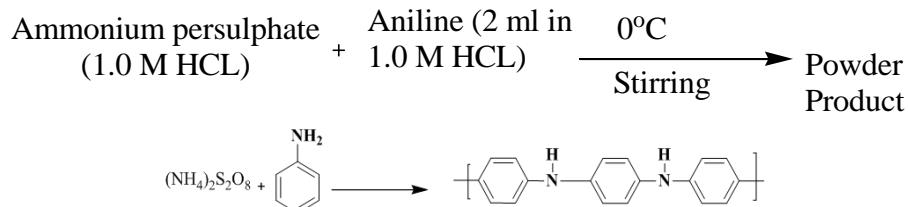


4.4. POLYANILINE (PANI)

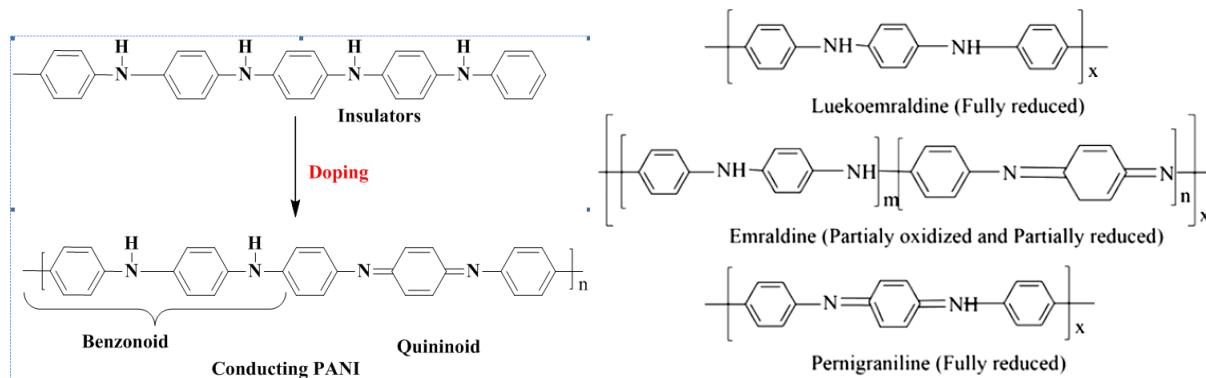
- Polyaniline is the most promising and most explored among conducting polymers.
- Polyaniline has high stability, high process ability, tunable conducting and optical properties.
- The conductivity of polyaniline is dependent upon the dopant concentration.
- Semi flexible rod polymer.
- Discovered in 1980 as a conducting polymer.
- It can be used as the precursor for the production of n-doped carbon materials through high temperature heat treatment.

Preparation of polyaniline

It can be prepared by the oxidative polymerization of aniline in presence of ammonium persulphate dissolved in 1M HCl.



Conducting mechanism of PANI

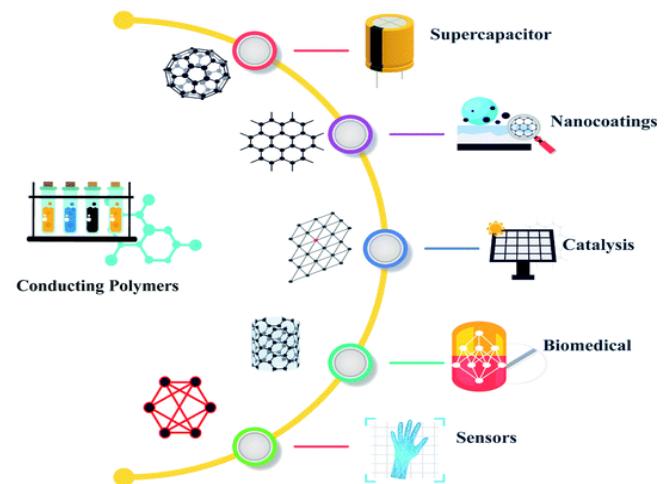


Advantages

- PANI is a very promising intrinsically conducting polymer because of its easy synthesis, low cost, tunable properties, high polymerization yield & environmental stability.
- PANI is also known as aniline black and it exists in various forms depending on its oxidation levels.

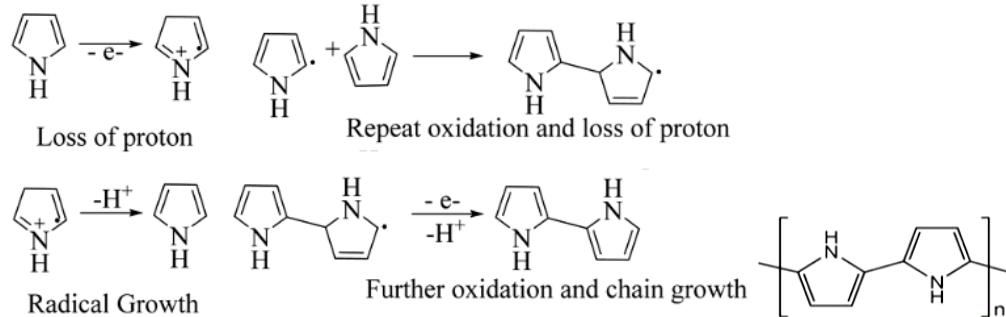
Applications of Polyaniline (PANI)

- Printed circuit board manufacturing
- Antistatic and ESD coating
- Microelectronics
- Photovoltaic cells
- Display devices
- Polymer light emitting diodes



4.5. POLYPYRROLE

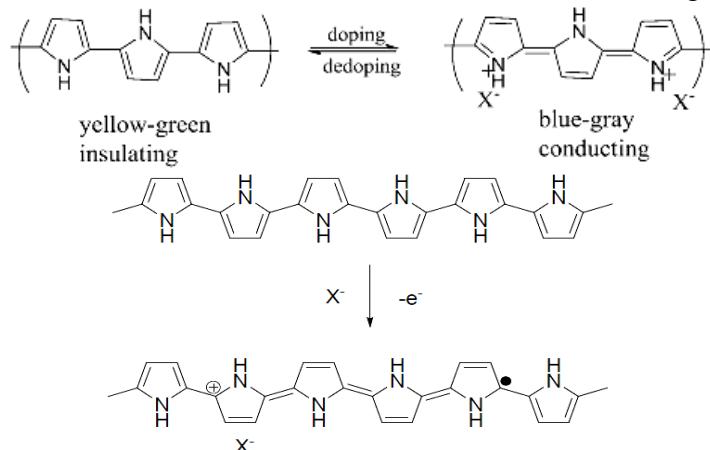
- First, a radical cation produced by the initial oxidation of pyrrole dimer makes an electrophilic attack on a neutral molecule.
 - The coupling of two radicals is favored over electrophilic attack on a neutral molecule.



- Probably, the growth of polypyrrole chains terminates when the ends of the growing chains becomes sterically blocked.
 - Conductive forms of polypyrrole are prepared by oxidation (“p-doping”) of the polymer.
 - $(C_4H_2NH)_n + x FeCl_3 \rightarrow (C_4H_2NH)_nCl_x + x FeCl_2$

Doping in polypyrrole

- Monomer is polymerized and charge carriers are generated via doping. As doping of the neutral polymer proceeds, the formation of structure and electronic defects will take place.
 - At low concentrations, the first predominant kind of defect will be polarons, which give rise to the formation of two localized states within the band gap.



Properties

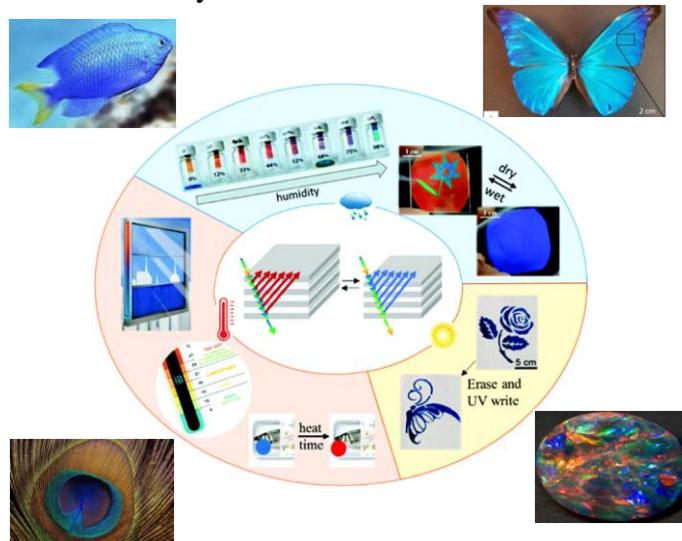
- Polypyrrole (PPy) is a widely researched π -electron conjugated conducting polymer.
 - Good electrical conductivity.
 - Good environmental stability in ambient conditions.
 - Excellent film-forming ability.
 - High permeability.

Applications

- It has been used to fabricate hybrid nanocomposites with inorganic components for biosensor and biomedical applications.
- Polypyrrole was used to coat silica and reverse phase silica to yield a material capable of anion exchange and exhibiting hydrophobic interactions.
- Used in the microwave fabrication of multiwalled carbon nanotubes.

4.6. PHOTONIC POLYMER

- Stimulus-responsive photonic polymer materials that change their reflection colour as function of environmental stimuli such as temperature, humidity and light, are attractive for various applications (e.g. sensors, smart windows and communication). Polymers provide low density, tunable and patternable materials.
- For example, the blue damselfish *Chrysiptera cyanea*, which changes from blue-green at daytime to violet at night in response to light and various beetles, which change their coloration in response to humidity.

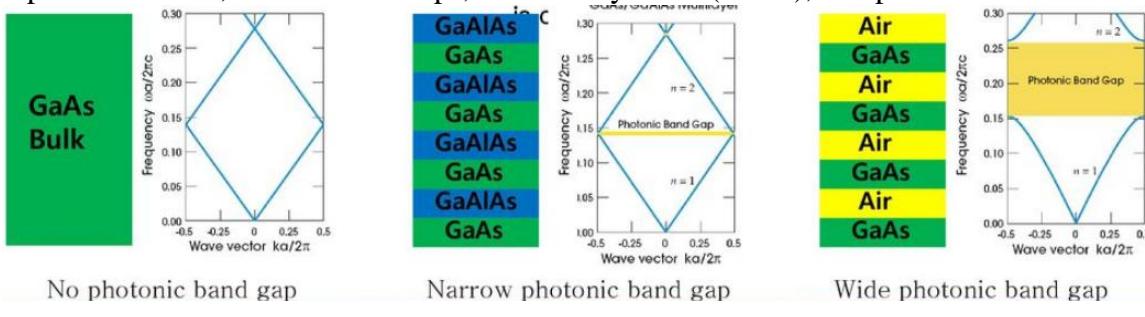


- These environmentally responsive systems found in nature have inspired scientists to fabricate artificial self-regulating, adaptive systems for sensors, energy saving, rewritable paper and security features.
- Environmentally triggered colour changes may arise from modulations of photonic structures. These structures, also called **photonic crystals** (PCs), consist of 1, 2 or 3 dimensional periodically nano-structured materials with different refractive indices.
- This periodic modulation of refractive index results in constructive interference of the light reflected at each boundary of refractive index change according to Bragg's law.
- As such, a photonic structure reflects light of a specific wavelength and may therefore give rise to the appearance of a structural colour.

4.6.1. PHOTONIC CRYSTALS (also known as photonic band-gap materials)

- Photonics is the physical science of light (photon) generation, detection, and manipulation through emission, transmission, modulation, signal processing, switching, amplification, and sensing.

- Photonic band-gap (PBGs) materials or photonic crystals (PhCs) are materials with a periodic dielectric profile, which can prevent light of certain frequencies or wavelengths from propagating in one, two or any number of polarisation directions within the materials.
- Photonic crystals are macroporous materials with interesting properties, especially optical properties.
- Periodic dielectric structures that have a band gap that forbids propagation of a certain frequency range of light.
- Photonic crystals are attractive optical materials for controlling and manipulating light flow.
- Photonic crystals are periodic optical nanostructures that affect the motion of photons in much the same way the ionic lattices affect electrons in solids.
- The atoms and molecules are replaced by macroscopic media with different dielectric constants.
- In some frequency range, the crystal has a complete photonic band gap; the photonic crystal prohibits the propagation of EM waves of any polarization travelling in any direction from any source.
- Photonics commonly uses semiconductor-based light sources, such as light-emitting diodes (LEDs), superluminescent diodes, and lasers. Other light sources include single photon sources, fluorescent lamps, cathode ray tubes (CRTs), and plasma screens.



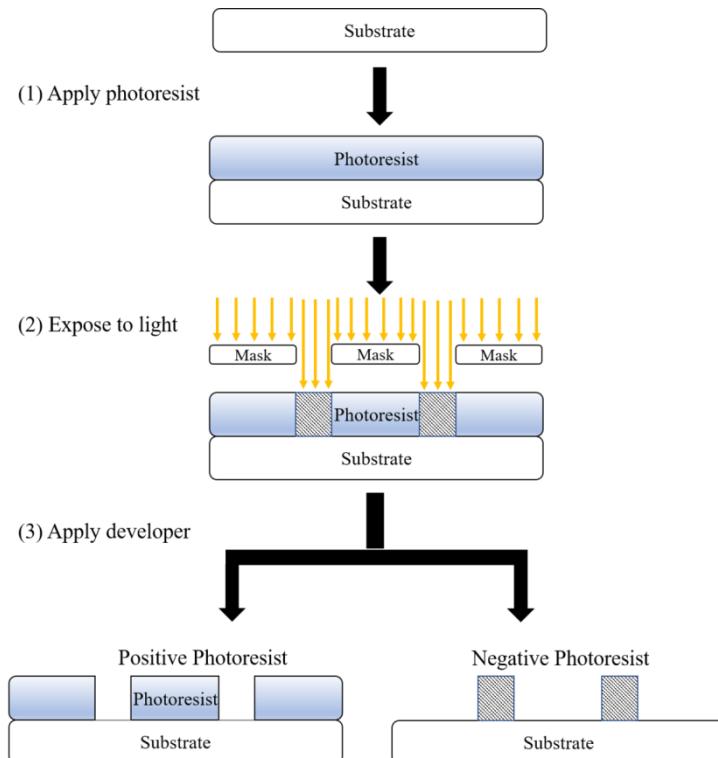
- **Photonic crystal with photonic band gap:** preventing light from propagating in certain directions with specified frequencies.
- Bandgap is due to a periodicity in the materials dielectric properties.

Photonic Crystal Applications

- Better lasers
- Medical diagnostics
- Lab on a chip
- Disease detection (Bioimaging)
- Optical insulators
- Thin-film optics
- Perfect dielectric mirrors
- Better LEDs & Polarizers
- Better optical filters
- Micron size optical benches
- Gas sensing to optical filters

4.7. PHOTORESIST

- Photoresist is an organic polymer which changes its chemical structure when exposed to ultraviolet light.
- It contains a light substance whose properties allow image transfer onto a printed circuit board.
- Photoresist is a light-sensitive material used in several processes, such as photolithography and photoengraving, to form a patterned coating on a surface. This process is crucial in the electronic industry.
- There are two types of photoresist: Positive and negative.



4.7.1. PHOTOLITHOGRAPHY

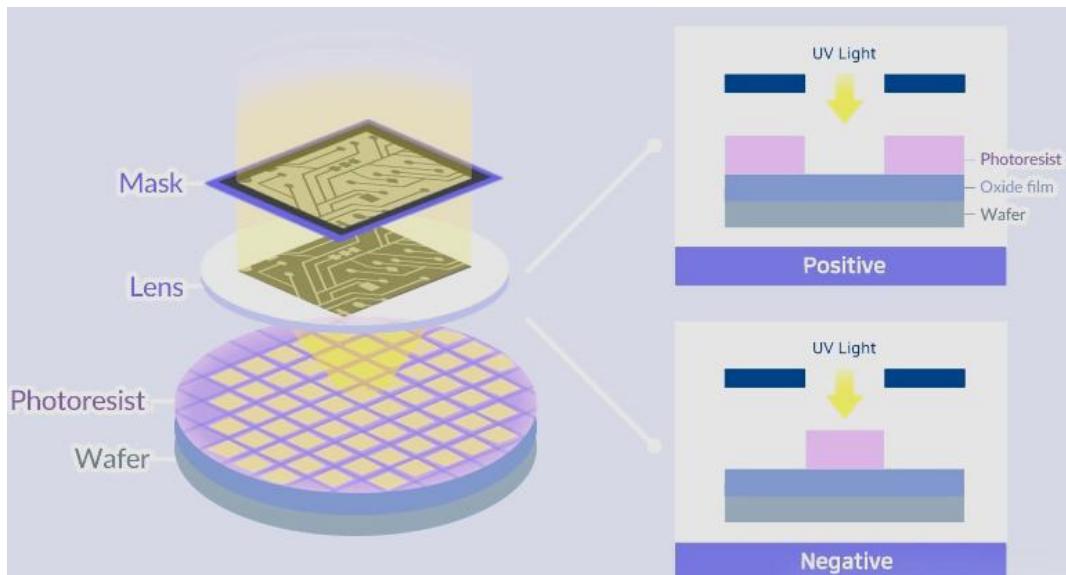
- Is a fabrication process in which a geometric pattern from a mask is transferred to a light sensitive chemical (photoresist) using electromagnetic radiation (UV, X-ray).
- Photolithography is a patterning process in which a photosensitive polymer is selectively exposed to light through a mask, leaving a latent image in the polymer that can then be selectively dissolved to provide patterned access to an underlying substrate.
- Photolithography is one of the most important and easiest methods of microfabrication, and is used to create detailed patterns in a material. In this method, a shape or pattern can be etched through selective exposure of a light sensitive polymer to ultraviolet light.

Photo lithography process (Photoresist in the semiconductor process)

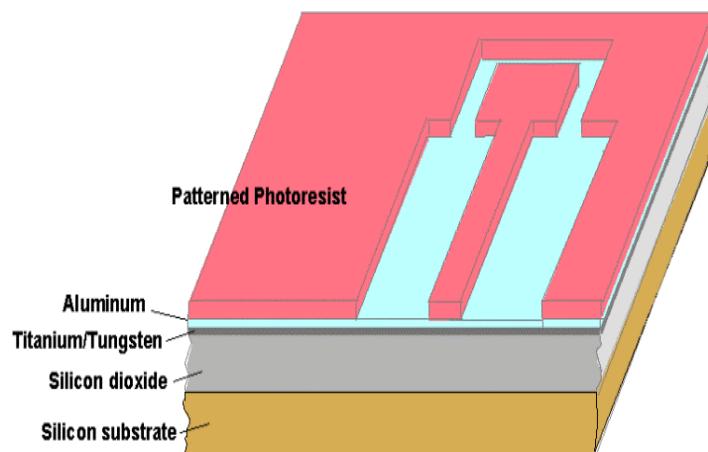
- In the **photolithography step**, a thin and uniform layer of photoresist is applied onto a wafer. This is like turning the wafer into a sheet of photographic paper. A mask, which is

a plate with transparencies or holes formed in the pattern of the desired semiconductor circuit, is placed above the photoresist with a light-gathering lens under it.

- Light is then emitted toward the wafer, transferring the circuit pattern on the mask to the wafer.
- The blueprint for the microcircuits can be drawn onto the wafer because of the photoresist.
- Once the circuit pattern has been transferred onto the wafer, the dissolved portion and the non-dissolved portion of the photoresist are removed selectively. This completes the photolithography process.
- The circuits on the wafer pass through an etching process to more clearly define them, and the semiconductor passes through a number of subsequent processes until completion.
- This makes photoresist irreplaceable in the semiconductor process. Clearly, materials play many important roles in the semiconductor industry.

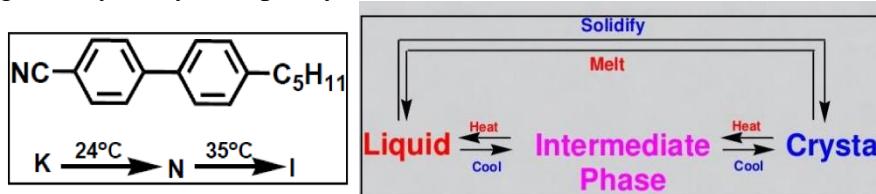


Photolithography on metal/oxide/silicon wafers



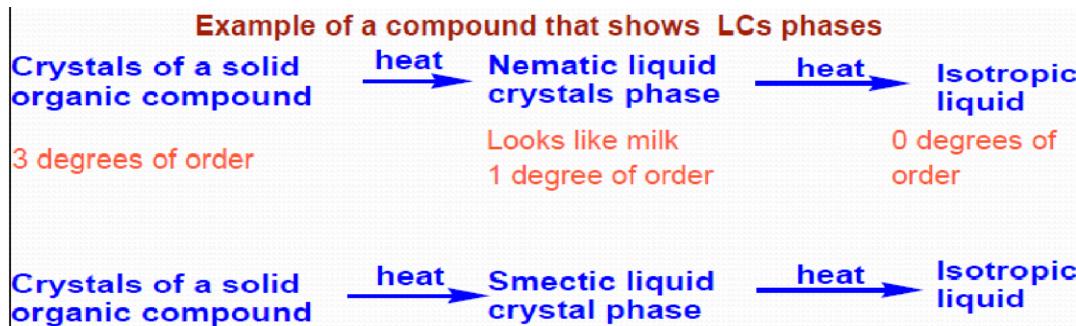
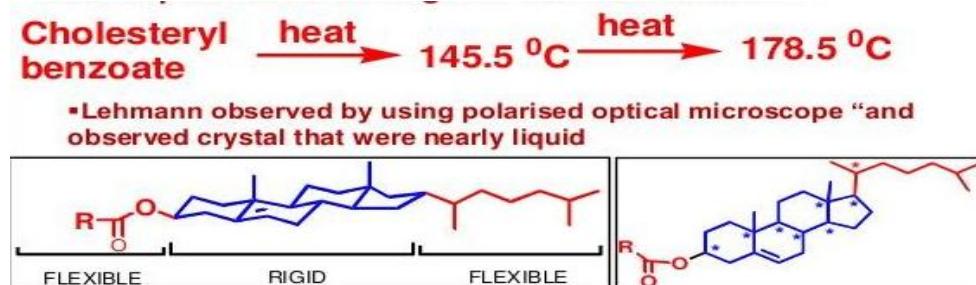
4.8. LIQUID CRYSTALS

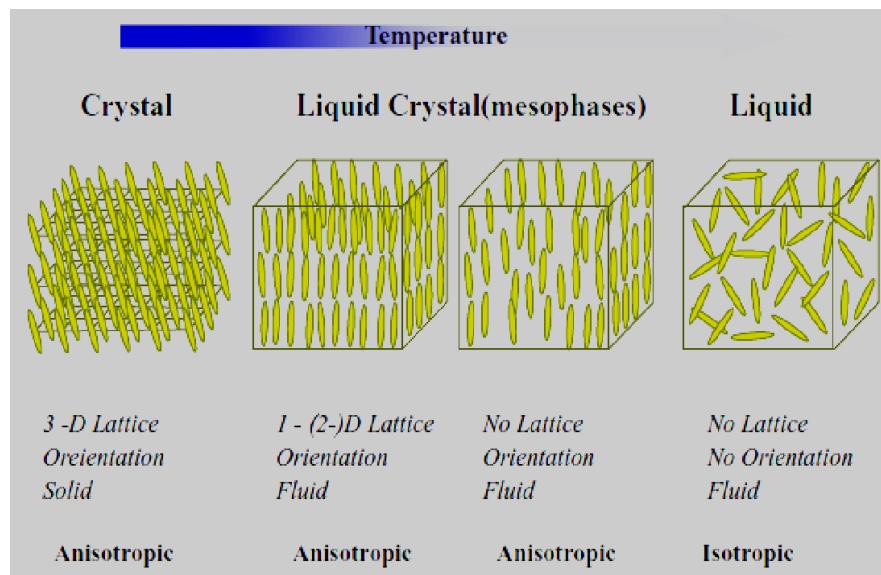
- An organic long-chain molecule possessing both solid like (anisotropic) molecular order and liquid like (isotropic) character is known as **Liquid crystal**.
- It is a phase between solid and liquid states (phases).
- Liquid crystals (LCs) are a state of matter which has properties between those of conventional liquids and those of solid crystals.
- For instance, a liquid crystal may flow like a liquid, but its molecules may be oriented in a crystal-like way.
- There are many different types of liquid-crystal phases, which can be distinguished by their different optical properties (such as textures).
- The contrasting areas in the textures correspond to domains where the liquid-crystal molecules are oriented in different directions.
- Within a domain, however, the molecules are well ordered.
- LC materials may not always be in a liquid-crystal state of matter (just as water may turn into ice or water vapor).
- Eg: 4-alkyl-4-cyanobiphenyl. This material is found in calculators or mobile phones.



Liquid crystal is discovered by Frederick Reinitzer in 1888.

- The cholesteryl benzoate had two distinct melting points.
- 145.5°C (293.9°F) it melts into cloudy liquid.
- At 178.5°C (353.3°F) it melts again and the cloudy liquid becomes clear.





The three degrees of orders in Liquid crystals are

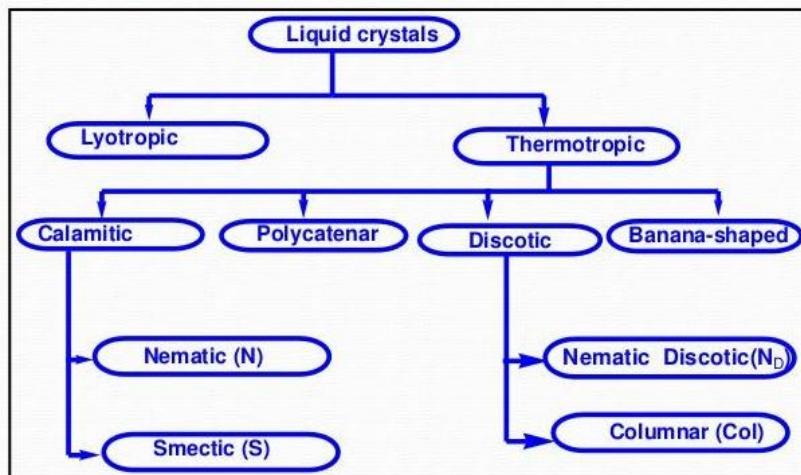
- Positional order
- Orientational order
- Bond orientation order

Director: it is the average direction of all molecules present in the liquid crystal.

Properties of liquid crystals:

- Liquid crystal can flow like a liquid, due to loss of positional order
- Liquid crystal is optically birefringent, due to its orientational order
- Transition from crystalline solids to liquid crystals caused by a change of temperature – gives rise to **THERMOTROPIC** liquid crystals.
- The change of concentration gives rise to **LYOTROPIC** liquid crystals.
- Substances that are most likely to form a liquid crystal phase at a certain temperature are molecules that are elongated and have some degree of rigidity.

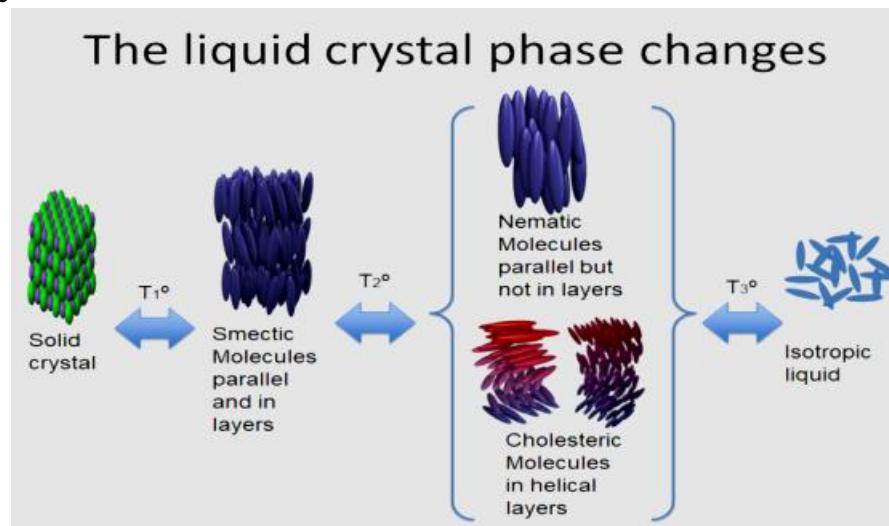
Types of liquid crystals:



4.8.1. THERMOTROPIC LIQUID CRYSTALS

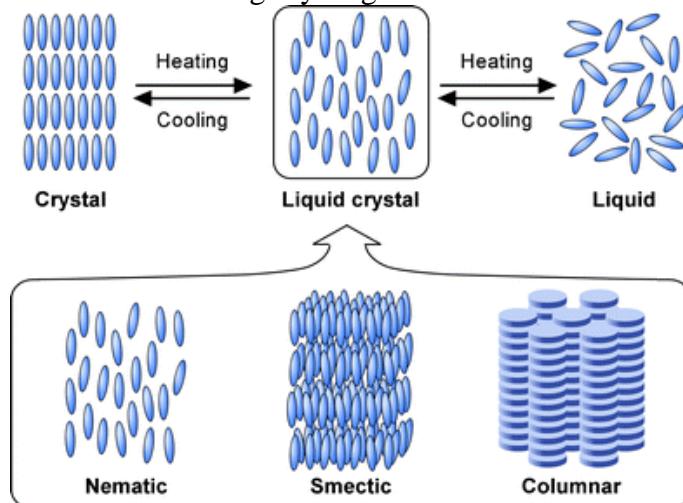
Types

- Nematic
- Sematic
- Cholesteric/Chiral
- Discotic



As temperature increases

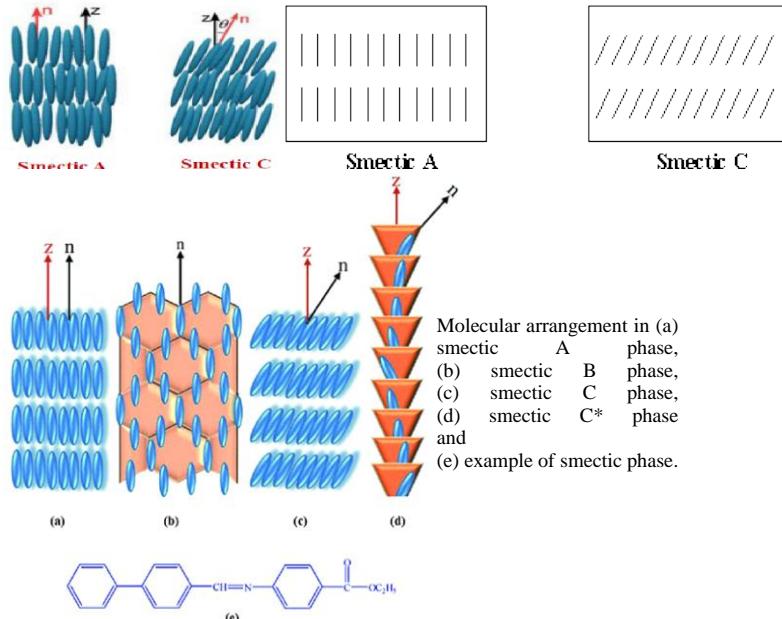
- The first liquid crystal phase is the smectic-A, where there is layer-like arrangement as well as translational and rotational motion of the molecules.
- A further increase in temperature leads to the nematic phase, where the molecules rapidly diffuse out of the initial lattice structure and form the layer-like arrangement as well.
- At the highest temperatures, the material becomes an isotropic liquid, where the motion of the molecules changes yet again.



1. Smectic:

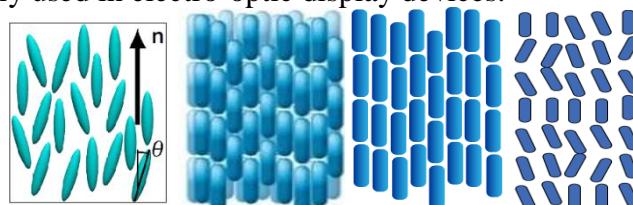
- **Smectic:** Latin word: Smecticus-meaning cleaning or having soap like properties.
- Smectic phase occurs at temperature below nematic or cholesteric.
- Molecules align themselves approximately parallel and are unidirectional.

- The smectics are thus positionally ordered along one direction.
- No correlation of the molecular position from one layer to the next.
- In the smectic A phase, the molecules are oriented along the director.
- While the smectic C phase they are tilted away from the director.
- Chiral smectic C liquid crystals are useful in LCDs.



2. Nematic phase:

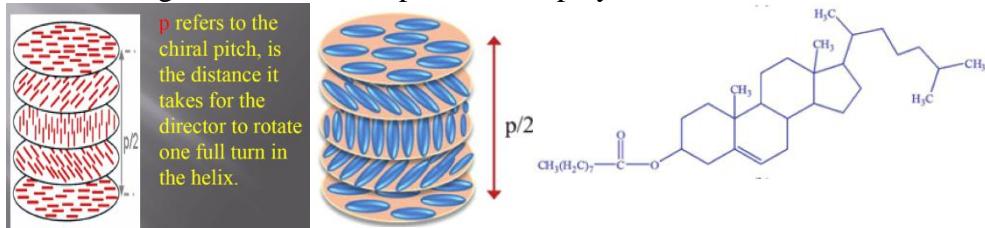
- **Nematic:** Greek word: **Nema**-meaning thread.
- Molecules maintain parallel or nearly parallel arrangement to each other along the director.
- All the molecules are not unidirectional.
- Molecules have orientational order but no longer range positional order.
- Structure of Nematic phase can be altered by using external electric and magnetic field.
- Thus possible to have microscopic order and macroscopic order.
- Most common Liquid crystal phase.
- They are widely used in electro-optic display devices.



3. Cholesteryl phase or chiral nematic phase:

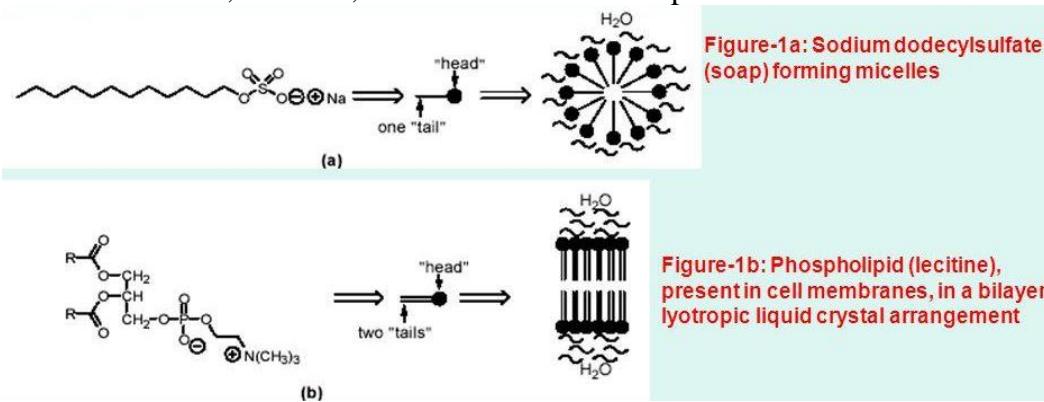
- This phase exhibits chirality.
- Only chiral molecules can give rise to this phase.
- There is orientational order and no positional order.
- The director is helical in nature.
- The structure depends on the pitch.
- **Pitch:** the distance over which the director makes one complete turn.

- **Pitch is affected by:** temperature, pressure, electric and magnetic field.
- The cholesteric liquid crystals have great potential uses as sensors, thermometer, fashion fabrics that change colour with temperature, display devices etc.,



4.8.2. LYOTROPIC LIQUID CRYSTAL

- Lyotropic liquid crystals result from the self-assembly process of amphiphilic molecules, such as lipids, into water, being organized in different mesophases.
- Lyotropic liquid crystal consists of a **hydrophilic region at one end** of the molecule and a **hydrophobic region at the other**. They exhibit mesophases when mixed with one or more solvent and the nature of the biphilicity produces membrane-like lamellar structures.
- A lyotropic liquid crystal is formed when, under certain circumstances of pressure, temperature and concentration, an amphiphilic molecule is melted in an appropriate solvent medium. The “lyotropic” liquid crystal mixture is controlled by varying the concentration of the solvent.
- These crystal phases include cubic-packed spherical micelles, hexagonal-packed cylindrical micelles, lamellae, and bicontinuous cubic phases.

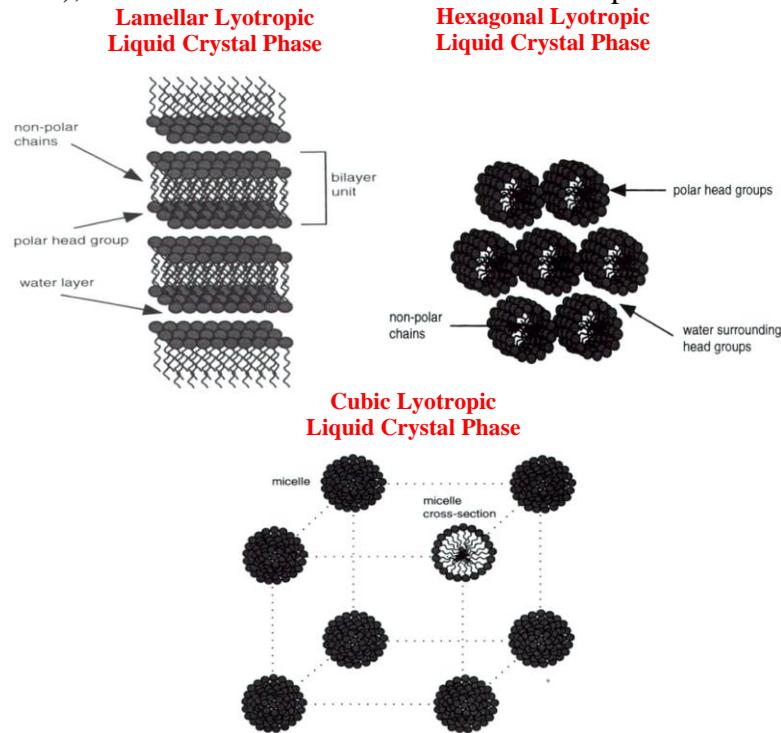


- Lyotropic phase shows liquid crystal properties only at certain concentrations.
- Extra solvent phase is required to provide fluidity to the system.
- Phase of liquid crystal changes with change in concentration and solvent.
- Soaps, detergents, surfactants are good examples of lyotropic liquid crystal.
- Lyotropic liquid crystals are extremely versatile drug delivery systems that can be used for delivering drugs across topical, oral, buccal, pulmonary, and intravenous routes.
- Examples: Molecules of soaps and various phospholipids like those present in cell membranes.

Structure of Lyotropic Liquid Crystals

- In general, the lyotropic liquid crystals phases of surfactant systems have been extensively investigated over the whole concentration range.

- Three different classes of lyotropic liquid crystal phase's structures are widely recognized. These are the
 - (a) Lamellar
 - (b) Hexagonal
 - (c) Cubic phases
- Their structures have been classified by X-ray diffraction techniques.
- *The lamellar lyotropic liquid crystals* phase consists of layered arrangements of amphiphilic molecules.
- *Hexagonal lyotropic liquid crystal* phases have a molecular aggregate ordering which corresponds to a hexagonal arrangement. There are two types, (i) the hexagonal phase (ii) reversed phase.
- *Cubic lyotropic liquid crystal* phases are not as the lamellar or hexagonal phases.
- Two types of cubic lyotropic liquid crystal phases have been established and each can be generated in the normal manner (water continuous) or in the reversed manner (non-polar chain continuous), which makes for a total of four different phases.



Comparison between Thermotropic and Lyotropic

THERMOTROPIC	LYOTROPIC
a) Absence of solvent	a) In solvent
b) Rigid organic molecules	b) Surfactants
c) Depends on temperature	c) Depends on temperature, concentration salt, alcohol
d) Structures: Smectic; Nematic; Cholesteric	d) Structures: Lameller; Hexagonal; Cubic

Applications of Liquid Crystals

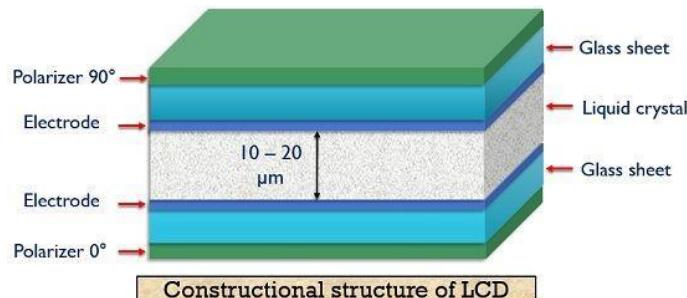
Liquid crystals can be found in the following devices

- Digital watches
- Pocket TVs
- Gas pumps
- Parking meters
- Tele communications
- Cell phones and pagers
- High speed computing
- Digital signs
- Personal digital assistants
- Electronic books
- Calculators
- Digital cameras and camcorder
- Thermometers

4.8.3. LIQUID CRYSTAL DISPLAY (LCD)

LCD is an acronym used for **Liquid Crystal Display**. It is basically a display technique in which liquid crystals are used in order to produce an image on the screen.

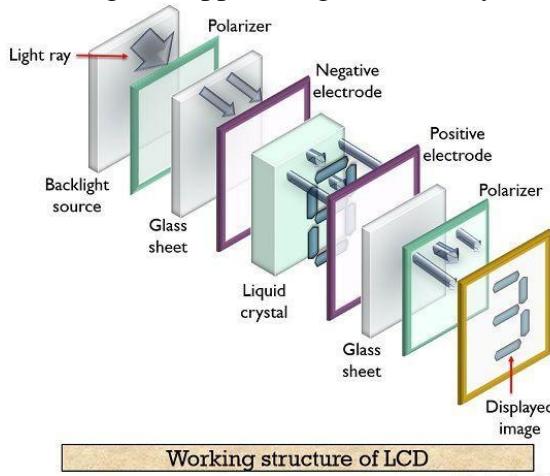
Construction of LCD



- The liquid crystal having a thickness of nearly about **10 to 20 micrometres** is placed between two glass sheets.
- On the inner surface of the two glass sheets, conductors are inserted. These conductors form electrodes.
- The two electrodes show positive and negative polarity to be applied.
- The external potential is provided to the display unit with the help of these two electrodes.
- These are basically formed by materials like indium oxide (IN_2O_3) and stannic oxide (SnO_3).
- Here, a fluorescent light source is used. The light emitted by this source is then fed to the polarizer here we have considered a vertical polarizer as the input polarizer. Also, a polarizer of opposite polarity as that of input is placed at another end of the display unit.
- At the opposite end of the electrode, a glass cover is placed at which the desired image is displayed.

Working of LCD

LCD is not an electroluminescent device. This means it does not have light-producing property instead of that it allows light to appear bright or dark by making use of a liquid crystal.



- When light from a backlight source is emitted and allowed to fall on the vertical polarizer. Then the unpolarized light by the source gets vertically polarized.
- Initially no external potential is provided between the two electrodes, the molecules of the liquid crystal remain twisted.
- This causes the vertically polarized light to get horizontally polarized due to the orientation of the molecules.
- The orientation of the two polarizers is 90° in accordance with each other. Thus the polarizer at the other end is a horizontal polarizer.
- When the horizontally polarized light from the output of the nematic crystal is fed to the horizontal polarizer then it passes the light thereby causing illumination of the pixel. Hence, generates a visible image on the screen.

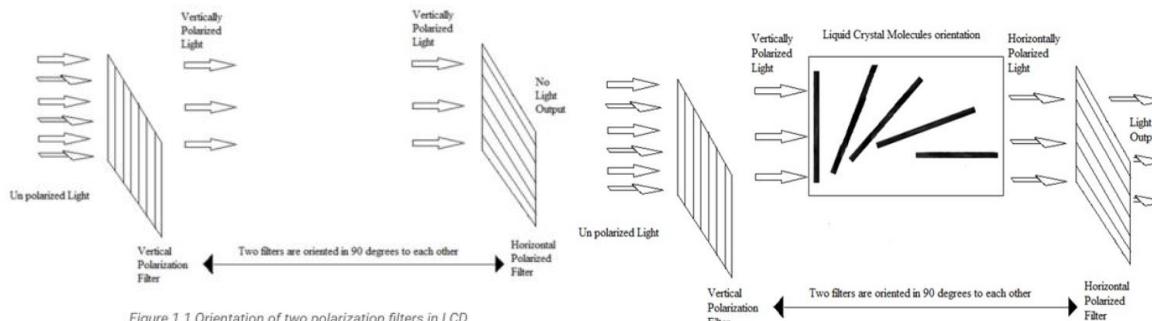


Figure 1.1 Orientation of two polarization filters in LCD

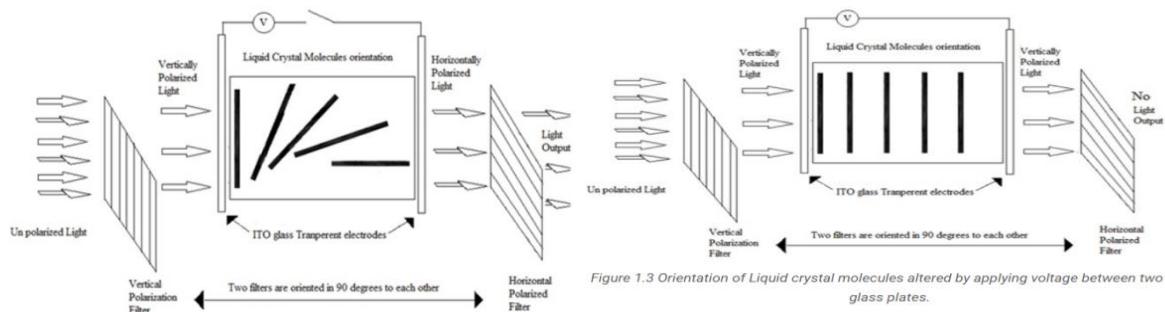


Figure 1.3 Orientation of Liquid crystal molecules altered by applying voltage between two ITO glass plates.

Characteristic	Twisted-Nematic Display
Voltage	3 V
Total current	6 μ A
Frequency	30 to 1,500 Hz
Operating temperature	-15 °C to +60 °C
Total capacitance	2 nF
Rise time	100 ms
Contrast ratio	50 : 1

Tabular representation of characteristics of LCD

Advantages of LCD

1. The heat generated during operation is less as compared to CRT and LED display.
2. The **power consumption** by an LCD is very less in comparison to other display devices.
3. LCDs can be suitably used with MOS integrated circuits.
4. The overall cost of the device is low.

Disadvantages of LCD

1. It needs an external source of light for displaying the image.
2. Its operating temperature range is limited that lies in between **0 to 60°C**.
3. LCD are **less reliable** display units.
4. The image visibility relies on light intensity.

Applications of LCD

- LCD finds its major applications in displaying the images in the screens of various electronic gadgets like television, calculator, computer monitor etc. These are also used in digital watches and mobile screens.
- These are also used in visualizing RF wave in transmission through waveguides and in medical applications like in liquid crystal thermometer etc.

Organic Light-Emitting Diode (OLED)

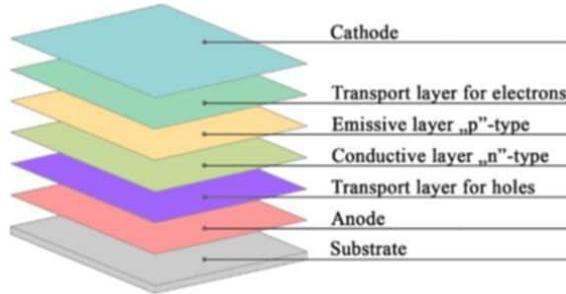
- It is a thin film display technology that contains OLED, an organic material which emits light when current is passed through it.
- OLED displays much better blacks & consume less power when displaying darker colors.
- An OLED in which an emissive electroluminescent layer as a film of organic compound is sandwiched between two conductors, which emits light.
- The OLED displays do not require backlighting.
- OLED displays also have a wide viewing angle up to 160 degrees.

Components in an OLED

1. An emissive layer
2. A conducting layer
3. A substrate

4. Anode and cathode terminals

- As the emissive layer and the conducting layer is made up of organic molecules (both being different), OLED is considered to be an organic semiconductor, and hence its name. The organic molecules have the property of conducting electricity and their conducting levels can be varied from that of an insulator to a conductor.
- The emissive layer used in an OLED is made up of organic plastic molecules, out of which the most commonly used is polyfluorene.
- The conducting layer is also an organic molecule, and the commonly used component is polyaniline.
- The substrate most commonly used may be plastic, foil or even glass.
- The anode component should be transparent. Usually indium tin oxide is used. This material is transparent to visible light. It also has a great work function which helps in injecting holes into the different layers.
- The cathode component depends on the type of OLED required. Even a transparent cathode can be used. Usually metals like calcium and aluminium are used because they have lesser work functions than anodes which helps in injecting electrons into the different layers.
- Organic emitters (organic material) – Perylene, Anthracene, Stilbene, Conjugated Polymers etc.,

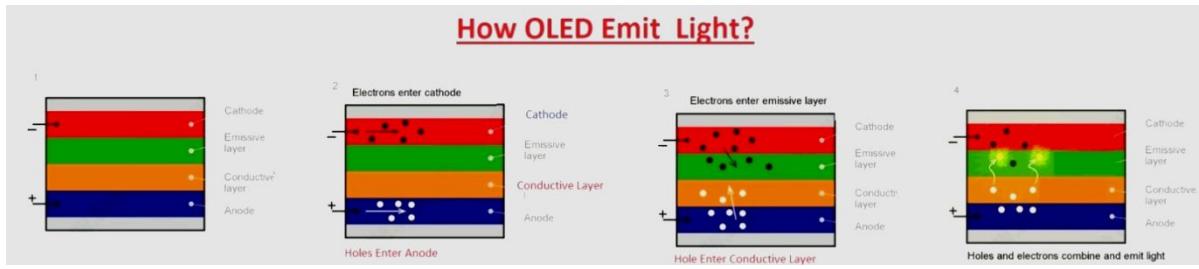


Working of OLED

The working of an organic light-emitting diode is alike to the general diode and light-emitting diode, but the difference is that instead of n-type and p-type semiconductors that comprise of the organic materials for production of electrons and holes.

How OLED Emit Light?

- For the emission of light, connect the negative terminal of a battery with the anode and positive terminal with the cathode.
- When current flows through the input supply electrons move towards the cathode and anode loses the electrons and makes the holes.
- Now the condition is like the n-type material at the cathode and like the P-type, the condition is the same at the anode.
- The holes move towards the emissive layer from the conductive layer and combine with the negative electrons and neutralize each other and energy with the light of photon is released.
- This process happens numerous times in one second and continuous light emitted through the Organic light.
- For the production of colored light place colored filter after a glass or bottom layer.



Advantages of OLED

- Less Price in Future
- Less weight and flexible plastic substrates
- High-Quality Picture
- Better response time
- Wider viewing angles
- Improved brightness
- Better power efficiency and thickness

Disadvantages of OLED

- Current cost are higher
- Limited lifespan
- Color balance issues
- Moisture sensitive
- UV sensitivity

Applications of OLED

- Mobile phones
- OLED Television set screen
- Digital cameras & Smart watches
- Advertising information & Indicators

Difference between LCD and OLED

S. No	OLED	LCD
1.	It uses organic materials like carbon to manufacture screens.	It screen made with the liquid crystal.
2.	It's every pixel that produces light radiations.	In this device background light such as lamp is used to provide light.
3.	To show different colors its pixels blink and then off independently.	While in LCD pixels are not on and off independently, they use light at the backend and pixels panels to block white light and make different colors.
4.	Its brightness is large	Its brightness is low.
5.	When the brightness of colors on the screen is less it consumes less power.	It uses large amount of energy.
6.	When the color is white it consumes high energy.	It uses a small amount of power.
7.	Usage of organic material decreases operating life.	Its working life is high.