UNIT – 4

MATERIALS FOR MEMORY AND DISPLAY SYSTEMS

Memory devices:

Conventional memory devices are implemented on semiconductor-based integrated circuits, such as transistors and capacitors. With the advancement of technology, there is an increase in the demand for high performance digital gadgets. To improve the performance of gadget, capacity of data storage device needs to be improved. In order to achieve greater density of data storage and faster access to information, more components are deliberately packed onto a single chip. The size of transistors has decreased from 130 nm in the year 2000 to 32 nm at present. Silicon- based semiconductor devices become less stable below 22 nm reducing their reliability to store and read individual bits of information. Reduction in size of transistor below certain level increases power consumption and results in unwanted heat generation. **A Semiconductor device having the primary function of electronically storing information is called as a memory device.**

BASIC CONCEPTS OF ELECTRONIC MEMORY

An electronic memory device is a form of semiconductor storage which is fast in response and compact in size, and can be read and written when coupled with a central processing unit (CPU, a processor).

For a material to show memory effect, the main essential requirements are:

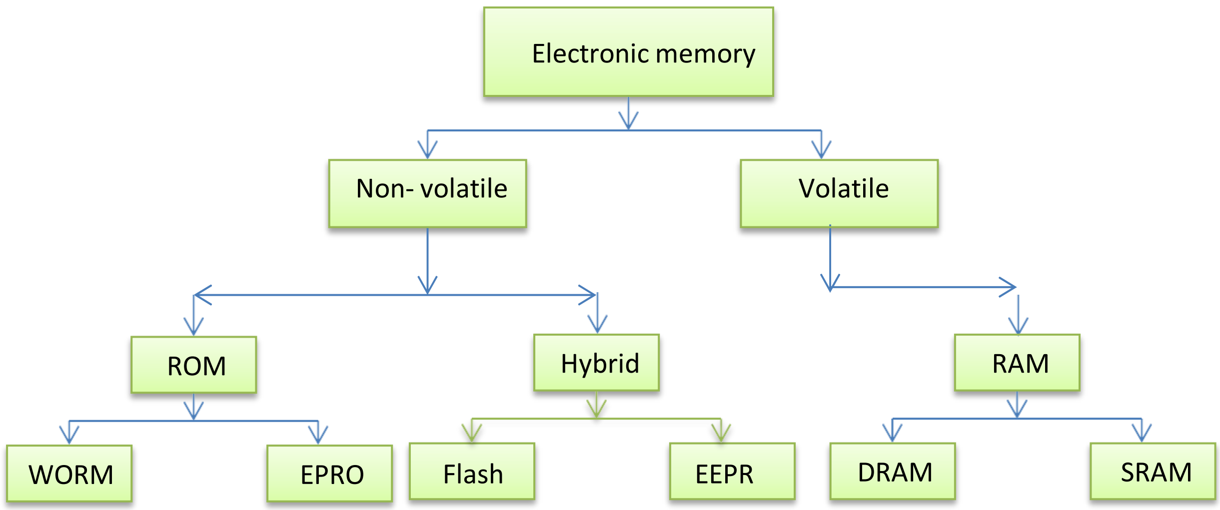
1) The individual memory cells, must possess at least two stable states, which are coded as “0” and “1”.
2) These states must be stable for a period appropriate for the data storage.
3) They can be switched between two states by an external stimulus. This is called as the writing process.
4) The states can be distinguished by applying a further external signal. This calledas the reading process.

New organic/polymeric materials exhibit two electrical stable states known as electrical bistability. They shift from one state (ON state) to other state (OFF state) when an external electric field is applied. In these devices, information is stored and retrieved by encoding these two states. Therefore, these chemical materials store information in the form of change in their properties under applied electric field.

CLASSIFICATION OF ELECTRONIC MEMORIES

A computer system contains several kinds of storage. Each type of storage is used for adifferent purpose.

The classification of Electronic memories is given below:



According to the storage type of the device, electronic memory can be divided into two primary categories:

1. **Volatile memory:** Volatile memory eventually loses the stored information unless it is provided with a constant power supply or refreshed periodically with a pulse. The most widely used form of primary storage today is volatile memory.

   Random access memory (RAM): It is a volatile memory. RAM requires the stored information to be periodically read and re-written, or refreshed, otherwise the data will be lost. It is further divided in to SRAM (Static random access memory) and DRAM (Dynamic random access memory).

2. Non-volatile memory:

This is further divided in to:

a. **Read only memory (ROM):** ROM is factory programmable only; data is physically encoded in the circuit and cannot be programmed after fabrication. ROM is further classified in to WORM (write-once read-many- times memory)and EPROM(Erasable programmable read only memory).

b. **Hybrid memory:** Hybrid memory allows data to be read and re-written at any time. It is further classified in to flash and EEPROM memory.

TYPES OF ORGANIC MEMORY MATERIALS

There are three classes of materials which can exhibit bistable states and are used in organic memory devices. They are:

1. Organic molecules,
2. Polymeric materials,
3. Organic- inorganic hybrid materials.

Under each category, lot of different types of molecules exhibiting memory effect are available. Few of them are described here:

I. ORGANIC MOLECULES

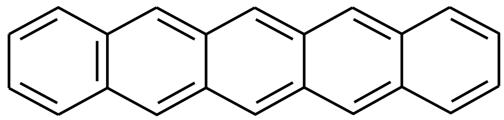
There are different category of organic molecules which show bistable or multistable states when external field is applied. When a threshold voltage is applied they undergo a transition from the OFF state to the ON state, or from the ON state to the OFF state. All these materials can be used in organic electronic memory devices. Few of them are mentioned here.

1. **Acene derivatives:** Acenes are the polycyclic aromatic compounds consisting of linearly fused benzene rings. They are the very first discovered organic memory devices because of their high charge carrier mobility.

Ex : pentacene, perfluoropentacene, naphthalene, anthracene, tetracene, etc.,

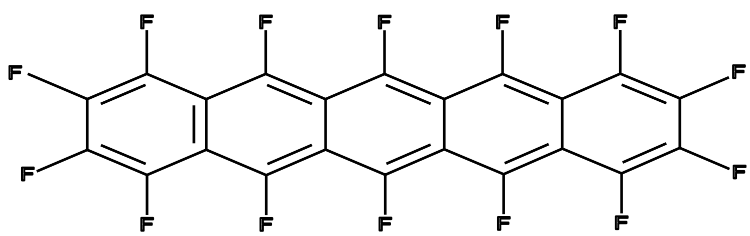
Pentacene :

The most important member of the acene family is pentacene. It is a linearly-fused aromatic compound with five benzene rings. It can be obtained in crystal and thin film form. Both forms exhibits a very good hole mobility and hence it behaves as a p-type semiconductor.



Perfluoropentacene :

When all the hydrogen atoms of pentacene are replaced by fluorine atoms the resulting molecules is perfluoropentacene. Strongly electron withdrawing nature of fluorine atoms converts this molecule in to n-type semiconductor.

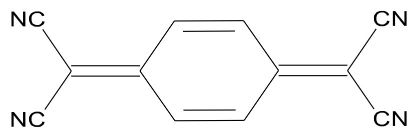


Pentacene and Perfluoropentacene, both have similar structure and similar crystal packing but former behaves as p-type semiconductor and latter behaves as an n-type Semiconductor. Therefore, these molecules together exhibit charge-transfer processes that are useful for memory applications.

2. Charge Transfer Complexes:

These molecules have 2 parts one is electron donor and second is electron acceptor. Donor is an organic molecule. Acceptor can be either metal or organic molecule. These devices exhibit two stable charge states which arise due to transfer of electrons from donor to acceptor under the influence of external field and this principle is used in memory device.

Ex: TCNQ (tetracyanoquinodimethane complex)

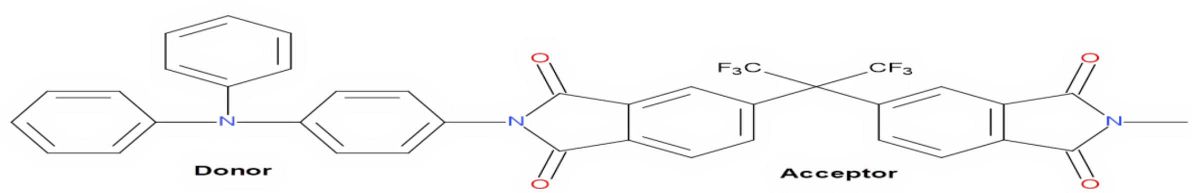


II. POLYMER MOLECULES

There are five classes of polymers which exhibit memory effect and are used in electronic memory devices.

1. Functional polyimides (PIs):

Functional polyimides (PIs) are one of the most commonly used polymeric materials for organic electrical memory applications. They have high thermal stability and mechanical strength and can be easily processed from solution. In functional PIs, phthalimide acts as the electron acceptor, and triphenylamine acts as an electron donor

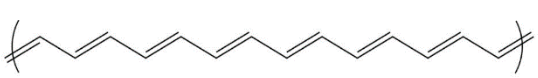


to form a Donor-Acceptor structure. They exhibit two stable charge states under applied electric field. These states arise due to transfer of electrons from donor to acceptor. This bistability is used to store data in memory device.

2. Conjugated Polymers

Conjugated polymers are rich in pi electrons and they can be made to show charge states by incorporating electron acceptor groups in their back bone. This induced charge transfer channel determines volatility of the memory device. D-A type conjugated polymers are used to fabricate different types of memory device, such as volatile DRAM and SRAM devices, and non-volatile WORM and Flash devices.

Ex: Polyacetylene



polyacetylene

iii. ORGANIC-INORGANIC HYBRID MATERIALS

Generally, organic-inorganic hybrid materials are composed of organic layers containing inorganic materials. Inorganic materials used are allotropes of carbon like fullerenes, carbon nanotubes, graphene and metal nanoparticles, semiconductor nanoparticles and inorganic quantum dots (QDs).

1. Organic-Carbon Allotrope Hybrid Materials

Polymers containing electron donors, such as thiophene, fluorene, carbazole and aniline derivatives can be combined with Fullerenes to obtain a charge transfer hybrid material with donor-acceptor ability and electrical bistable states. Fullerenes exhibit high electron-withdrawing ability, and can capture up to six electrons. They are used in WORM memory effect devices.

2. Organic-Inorganic Nanocomposites

These are the hybrid electronic memory devices in which organic polmer with appropriate functional group is clubbed with metal nanoparticles, quantum dots and metal oxide nanoparticles. An example is a composite of 8-hydroxyquinoline- containing polymer with gold nanoparticle sandwiched between two metal electrodes.

The advantages of organic and polymer molecules based electronic memory devices are:

a) They can be processed easily.

b) Structure of the molecule used can be design through chemical synthesis.

c) Device structure is very simple.

d) Dimension of the device can be decreased (miniaturized).

e) Cost of production is less & Power consumption during operation is low.

DISPLAY SYSTEM

LIQUID CRYSTALS

Introduction Liquid crystals (LC)

- The general classification of mater are Solids , liquids and gases
- Solids have definite orientation and positional order , Liquid do not have both orientation and

positional order. **Liquid crystal is a state of mesophase whose properties comes between conventional solids and liquids. Due to this unique property of Liquid crystal they play an important role in modern technology.**

- Liquid crystal flow like a liquid and have orientation order as that of solids
- A liquid crystal is a thermodynamic stable phase characterized by anisotropy of properties without the existence of a three-dimensional crystal lattice, generally lying in the temperature range between the solid and isotropic liquid phase, hence the term mesophase.
- Liquid crystals find application in the areas of science and engineering, particularly in display systems of modern electronic gadgets. Devices using liquid crystal displays have the advantage of low power consumption and hence are widely used in display devices of mobile communication appliances, aircraft cockpit, laptops and related electronic equipments.

Relation between chemical structure and liquid crystal

Substance to behave as liquid crystal they should process following properties

- Molecule should be elongated
- Molecules should have both flexible and rigid structure
- Solubility rate is different in different part of the molecule

Example: n-alkanes and n-alkanoic acid do not exhibit liquid crystal properties but when double bond is introduced within these structure the substance behave as liquid crystals

Classification

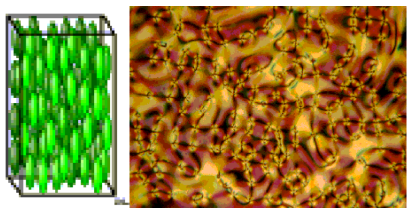
Liquid crystals can be first organized into

1.**Thermotropic (temperature dependent)** - The class of compounds that exhibit liquid crystalline behavior on variation of temperature alone are referred to as thermotropic liquid crystals.

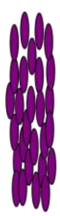
Example – Cholesteryl benzoate is solid but on heating it shos liquid crystal behaviour at temperature 145.5 ^{O}C to 178.5 ^{O}C

Thermotropic liquid crystals may be further classified as:

a. Nematic liquid crystals - Nematic (Greek nematos = thread like) liquid crystals are formed by compounds that are optically inactive. The molecules have elongated shape and are approximately parallel to one another. In this phase the molecules maintain a preferred orientational direction but positional order is completely absent and they can diffuse throughout the sample. An example of a nematic liquid crystal is para-azoxyanisole (PAA) which exhibits liquid crystalline behaviour in the temperature range of $118^{O}C$ to $135^{O}C$.



b. Chiral Nematic liquid crystals - **Chiral nematic** or twisted nematic liquid crystals are formed from optically active compounds having chiral centres. Compared to nematic phase where all the molecules are approximately parallel to one another, in chiral nematic phase, the molecules arrange themselves so as to form a helical structure.



Nematic phase

Helical pattern of Chiral nematic phase

c. Semectic liquid crystals - Substances that form semectic phases are soap-like. Infact, the soft substance that is left at the bottom of a soap dish is a kind of semectic liquid crystal phase. In semectic mesophase, there is a small amount of orientation order and also a small amount of positional order. The molecules are arranged in regularly spaced layers (positional order). Within the layer they tend to point along thedirector (orientation order).

2. **Lyotropic (concentration dependent) -** Some compounds transform to a liquid crystal phase when mixed with a solvent. They have both polar lyophilic and a non-polar, lyophobic end. They are amphiphilic compounds. Such amphiphilic molecules form ordered structures in both polar and non-polar solvents. They are usually obtained by mixing the compound in a slovent and increasing the concentration of compound till liquid crystal phase is observed. Such liquid crystals are called lyotropic liquid

crystals. The formation of lyotropic mesophases is dependent on the concentration of either the component or the solvent. Examples: (i) soap (soap - water mixture) molecules (ii) phospholipids which are biologically important molecules where each cell membrane owes its structure to the liquid crystalline nature of the phospholipid - water mixture.

Properties of Liquid crystals

- Liquid crystal show properties of both solids and liquids. Liquid crystal are anisotropic and the physical properties of the system vary with the average alignment with the director. If the alignment is large the material is very anisotropic. Similarly if the alignment is small the material is almost isotropic.
- Liquid crystal show some properties of liquid like they have flow like liquid, they have surface tension, and viscocity.
- Liquid crystal show some properties of solids such as orderly arrangement, optical and , electrical properties. Uses of Liquid crystals

Application of Liquid Crystals:

1. **In Display systems:**

Due to less consumption of power as compared to other display they are used in

i. Automobile dash boards indicators, traffic signals, advertisement boards and petrol pump indicators.
ii. Various analytical instruments like pH meter, conductometer, colorimeter, Potentiometer, etc.,
iii. Various electronic gadgets including watches, TV, calculators, mobile phones, laptops, desktops, etc.,

2. **Thermography:** Thermography measures surface temperatures by using infrared video and still cameras. These tools see light that is in the heat spectrum. Images on the video or film record the temperature variations of the skin, ranging from white for warm regions to black for cooler areas.

i. In Medical Thermography:

Used in the early detection or diagnosis of tumour or breast cancer besides orthopedic disorders such as arthritis and back pain etc. The basic principle is that heat changes produced in the affected skin are different from the healthy skin.

ii. In Radiation & pressure sensors:

Cholesteric liquid crystals have been used in versatile and inexpensive radiation sensors. These devices are based on the principle of conversion of radiation energy into heat energy and the measurement of the heat energy using a thermal transducer.

iii. In electronic industry

iv. In detection of air pollutants :

Used to detect the impurities in the atmosphere. The colour of the liquid crystals changes in the presence of impurities.

3. **Point of potential failure in electric circuit** - Liquid crystal are also sensitive to electric field so they are used in detection of point of potential failure in electric circuit.

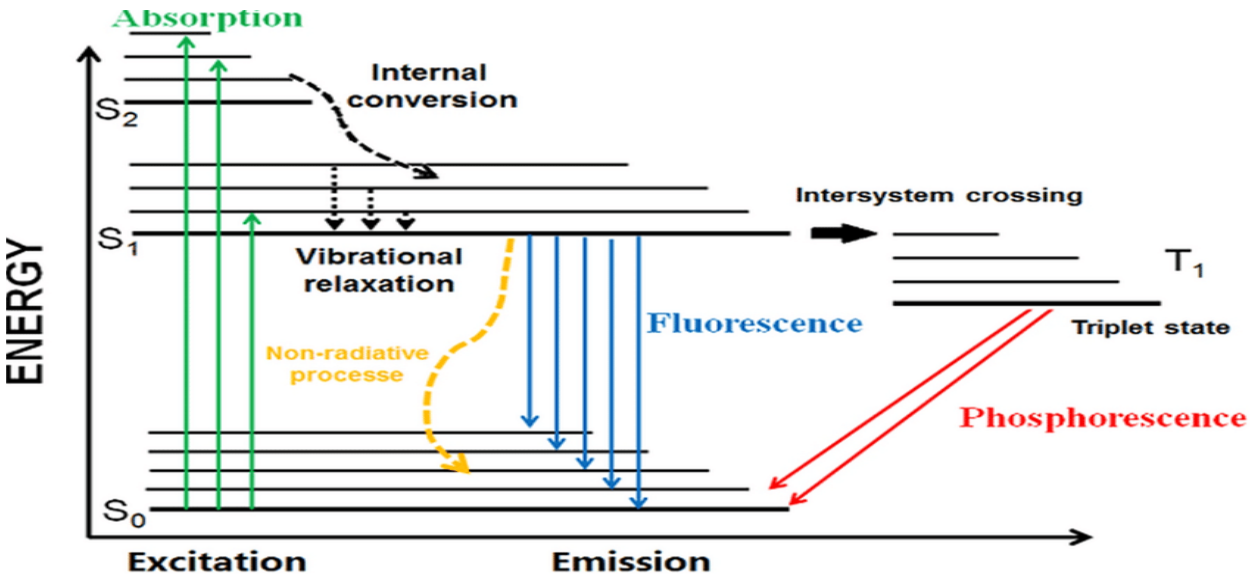
4. **In Research work :** Liquid crystals are employed as solvent in spectroscopic studies like NMR, IR and UV. It is used in pH meter, conductometer, colorimeter, potentiometer and other analytical instruments to detect the structure of various organic compound.

Other Applications:

- Cholesteric liquid crystal substances, when applied to the surface of the skin, have been used to locate veins, arteries, infections, tumors and the fetal placenta which are warmer than the surrounding tissues.
- Liquid crystals are widely used in cosmetic industry in manufacturing of liquid crystal makeup removers, lipsticks and lip glasses containing cholesteric liquid crystals.
- Liquid crystals are using extensively in pharmaceutical industries.
- Liquid crystal polymers also gained much interest on industrial applications. polyester liquid crystals were developed for fire resistant, and are used as coating for multifibre, optical cables due to good surface roughness, low coefficient of friction. Polyesters are used for moulding with improved elastic modulus.

Jablonski Diagram:

It is an energy diagram which describes about various emission pathways by the molecules after the absorption of light. These diagrams are common representations of the possible electronic states and transitions as molecules enter and leave the excited state. As Jablonski diagrams describe the electronic states of molecules, transitions and associated light emitting phenomena. **Horizontal lines in a diagram represent energy states of a molecule or system.**



Meaning of levels:

- S_0 is the ground state of the molecule.
- S_1 & S_2 are the first and second excited singlet states.
- T_1 & T_2 is the first and second excited triplet state.

The various processes are as follows:

1. **Absorption:**

   Absorption is represented by a vertical upward arrow, signifying the transition of an electron to a higher energy level upon absorbing a photon. It is very fast transition on the order of 10^{-15} seconds.

2. **Emission:**

   Excited molecule cannot stay in higher energy state for longer time thereby they come back to the ground state by emitting heat or light. Emission follows two pathways such as Non-radiative transitions(emissions) and Radiative transitions(emissions)

a. **Non-radiative transitions:**

Non-radiative transitions are pathways for excited molecules to return to their ground state that do not involve the emission or absorption of a photon. Instead, the energy dissipated as heat to the surrounding environment.

- **Internal Conversion (IC)**: It is a non radiative process where a molecule transitions from a higher to a lower electronic state without emitting a photon and these transitions takes place between two electronic states of the same spin multiplicity (singlet to singlet).
- **Inter System Crossing (ISC):** It is a non radiative or radiation less process, involving a transition between the two electronic states with different states spin multiplicity (Triplet to singlet or S2 toT2 or S1 toT1).

b. **Radiative transitions:**

Radiative transitions involve the absorption or emission of photons, leading to changes in a molecule's electronic state.

- **Fluorescence-** It is a radiative transition where a molecule in an excited singlet state (S_1) emits a photon and return to the ground state (S_0) or lower vibrational level. It is a faster process than phosphorescence, occurring within 10^{-9} to 10^{-7} seconds.
- **Phosphorescence-** This is also a radiative transition where a molecule in an excited triplet state (T_1) emits a photon and return to the ground state. It is slower than fluorescence, in the order of 10^{-3} seconds.

Uses:

- It is a tool used in molecular spectroscopy to illustrate the energy levels of a molecule and the transitions between them, particularly those involving absorption and emission of light.
- It helps to explain phenomena like fluorescence and phosphorescence. The diagram depicts electronic states, vibrational energy levels within those states, and the different radiative (light-emitting) and non-radiative (without light emission) transitions that can occur.

PHOTOACTIVE AND ELECTROACTIVE MATERIALS

Present day technological developments in the information – oriented society are mainly attributed to discovery of electronic, optoelectronic, and photonic devices which use inorganic semiconductors. In recent years, new organic materials which exhibit electro –

optical properties similar or superior to classical inorganic materials have been discovered. Accordingly, new fields of organic electronics, organic optoelectronics, and organic photonics using organic materials have emerged. Devices using organic materials have the following advantages over inorganic semiconductor-based devices:

a. They are lightweight.
b. They are flexible.
c. They can be easily synthesized by chemical methods.
d. Cost of production is less.
e. They can be used in novel thin-film flexible devices.
f. Properties can be fine-tuned by structure modification.

Hence, they are being used in Organic photovoltaic devices (OPVs). organic light-emitting diodes (OLEDS), and organic field-effect transistors (OFETS).

Organic materials used in optoelectronic devices are referred to as photo and electroactive organic materials. They are also called as organic semiconductors. When these materials are used in devices, they exhibit opto-electronic phenomena as:

a) Absorption and emission of light radiation in the wavelength region from ultraviolet to near infrared.
b) Photogeneration of charge carriers.
c) Transport of charge carriers.
d) Injection of charge carriers from the electrode.
e) Exhibit excellent nonlinear optical properties.

Organic compounds with extensive conjugation and π-electron systems are capable of exhibiting above mentioned set of properties. Those organic materials can be broadly classified in to three categories:

a) Small molecules
b) Oligomers with well-defined structures.
c) Polymers

Small organic molecules are crystalline in nature. Few examples for this class of molecules are, the metal and metal-free phthalocyanines, porphyrines, poly- condensed aromatic hydrocarbons, like anthracene, pentacene, and fullerenes.

Conjugated oligomers are a new family of organic π-electron systems, with well-defined structures, whose properties and functions can be controlled by varying the π - conjugation length. Few examples for this class are, pentacene, and oligothiophenes.

Polymers are bad conductors of electrons. But, conducting polymers with extensive conjugation and π – electron system exhibit above mentioned electro-optical behaviour and they are excellent functional materials. Examples of this class of polymers which find extensive application as organic semiconducting materials are, polyacetylene poly(p-phenylene), poly(p-phenylene vinylene), poly(9.9-dialkylfluorene),polythiophenes, polypyrroles, and polyanilines.

<u>Nanomaterials used in optoelectronic devices:</u>

There is a demand for miniaturization of electronic devices and integrated circuits. Even though the size silicon transistors have been reduced from 1000 nm three decades ago to about a few tens nanometres today, there are limitations to further reduce their size. Nanomaterials with electro-optical properties can help in size reduction of future opto-electronic devices. Graphene, fullerenes, carbon nanotubes (CNTs), are carbon based materials which show good electrical, electronic and optical properties. Quantum dots (QDs) with typical diameters as low as 0.5 nm of a large diversity of materials, including silicon, germanium, different III-V compound

semiconductors, such as GaAs, GaN, InN, GaP, InP, AlN, InAs, II-VI materials, such as CdS, CdSe, ZnS, ZnSe, and semiconducting oxides such as In_2O_3, ZnO, TiO_2, etc. show interesting properties. These materials along with low-dimensional structures also exhibit unique kind of light-matter interactions like surface plasmon resonance, spintronics, plasmonics etc. They can be used in future photonic and electronic devices.

Light Emitting Electrochemical cells:

A light-emitting electrochemical cell (LEC or LEEC) is a solid-state device that generates light from an electric current (electroluminescence). LECs are usually composed of two metal electrodes connected by (e.g. sandwiching) an organic semiconductor containing mobile ions. Aside from the mobile ions, their structure is very similar to that of an organic light-emitting diode (OLED).

LECs have most of the advantages of OLEDs, as well as additional ones:

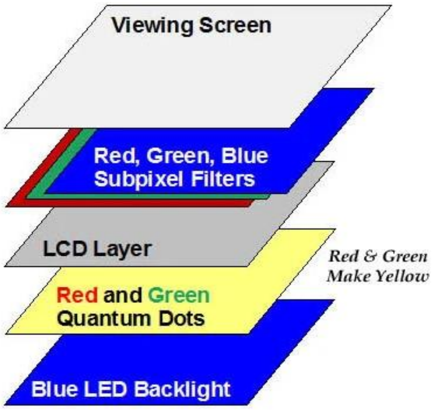
- The device is less dependent on the difference in work function of the electrodes. Consequently, the electrodes can be made of the same material (e.g. gold). Similarly, the device can still be operated at low voltages.
- Recently developed materials such as graphene or a blend of carbon nanotubes and polymers have been used as electrodes, eliminating the need for using indium tin oxide for a transparent electrode.
- The thickness of the active electroluminescent layer is not critical for the device to operate. This means that:
- LECs can be printed with relatively inexpensive printing processes (where control over film thicknesses can be difficult).
- In a planar device configuration, internal device operation can be observed directly.

Quantum Light emitting diodes (QLED's)

Over the past decade, organic light-emitting diodes (OLEDs) have been successfully launched in the display industry, dominating the flat panel display (FPD) market owing to the advantages of self-emissive devices including both performance and form factor metrics, such as high contrast ratio (CR) and substrate flexibility. However, despite the successful industrialization of OLEDs, the demand for higher color saturation and higher electrical stability has emerged for next-generation displays.

QLED (Quantum Dot LED) enhance picture quality by incorporating a layer of quantum dots within an LCD display. These dots, acting as tiny light filters, convert the light from a blue LED backlight into purer, more vibrant colors, resulting in a wider color gamut and higher brightness. Essentially, a QLED TV combines the established LCD technology with the advanced color capabilities of quantum dots.

Construction and working principle:



- Traditional LCD Panel: QLED utilize a standard LCD (Liquid Crystal Display) panel, which consists of liquid crystals that control the amount of light passing through to create an image.
- Blue LED Backlight: A blue LED backlight provides the light source for the LCD panel.
- Quantum Dot (QD) Layer: A thin film of quantum dots is placed between the backlight and the LCD panel.
- Quantum Dots: These are nanoscale semiconductor crystals that emit specific colors of light when excited. The color emitted depends on the size of the quantum dot; smaller dots emit blue/green light, while larger dots emit red light.

Working Principle:

Light Emission: The blue LED backlight shines onto the quantum dot layer.

Color Conversion: The quantum dots absorb the blue light and, based on their size, re-emit light of a different, more precise color (red, green, or blue).

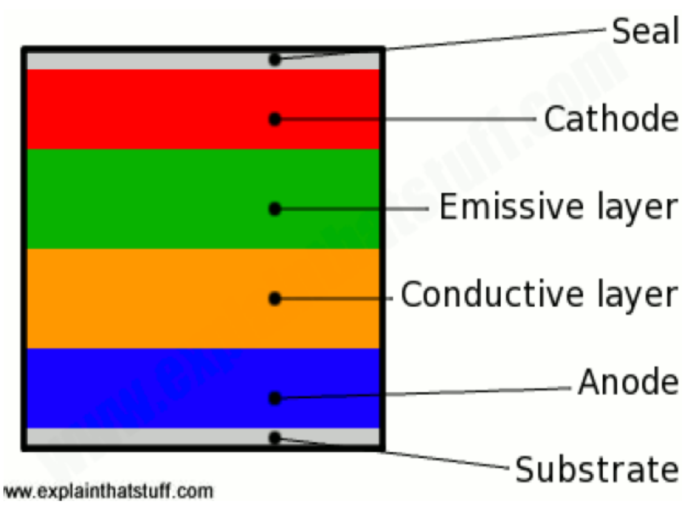
Color Filtering: The LCD panel then filters this light, creating the final image.

Improved Color Gamut: By using quantum dots to generate specific colors, QLED TVs can achieve a wider color gamut (the range of colors they can display) and a more accurate color representation compared to standard LED TVs.

Increased Brightness: The quantum dots also contribute to higher brightness levels, as they are more efficient at converting light than traditional phosphors used in LED backlights.

OLED – Organic Light Emitting Diode

- OLEDs work in a similar way to conventional diodes and LEDs, but instead of using layers of n-type and p-type semiconductors, they use organic molecules to produce their electrons and holes.
- A simple OLED is made up of six different layers. On the top and bottom there are layers of protective glass or plastic.
- The top layer is called the seal and the bottom layer the substrate. In between those layers, there's a negative terminal (sometimes called the cathode) and a positive terminal (called the anode).
- Finally, in between the anode and cathode are two layers made from organic molecules called the emissive layer (where the light is produced, which is next to the cathode) and the conductive layer (next to the anode).



Working principle OLED

1. To make an OLED light up, we simply attach a voltage (potential difference) across the anode and cathode.

2. As the electricity starts to flow, the cathode receives electrons from the power source and the anode loses them (or it "receives holes," if you prefer to look at it that way).

3. Now we have a situation where the added electrons are making the emissive layer negatively charged (similar to the n-type layer in a junction diode), while the conductive layer is becoming positively charged (similar to p-type material).

4. Positive holes are much more mobile than negative electrons so they jump across the boundary from the conductive layer to the emissive layer. When a hole (a lack of electron) meets an electron, the two things cancel out and release a brief burst of energy in the form of a particle of light—a photon, in other words. This process is called recombination, and because it's happening many times a second the OLED produces continuous light for as long as the current keeps flowing.

Application of OLED :

- Broadly speaking, you can use OLED displays wherever you can use LCDs, in such things as TV and computer screens and MP3 and cell phone displays.
- Their thinness, greater brightness, and better colour reproduction suggests they'll find many other exciting applications in future.
- Apple, originally dominant in the smartphone market, has lagged badly behind in OLED technology until quite recently.
- In 2015, after months of rumors, the hotly anticipated Apple Watch was released with an OLED display.
- Since it was bonded to high-strength glass, Apple was presumably less interested in the fact that OLEDs are flexible than that they're thinner (allowing room for other components) and consume less power than LCDs, offering significantly longer battery life.
- In 2017, the iPhone X became the first Apple smartphone with an OLED display.