DEPARTMENT OF CHEMISTRY

RV COLLEGE OF ENGINEERING

Chemistry of Smart Materials and Devices

UNIT-III Notes

[Materials for memory and display technology]

Materials for memory storage: Introduction to materials for electronic memory, classification (organic, polymeric and hybrid materials), manufacturing of semiconductor chips. Green computing: Bio-composite based memory devices.

Fabrication of smart materials and devices: Photo and electro active materials for memory devices, materials for display technology (Liquid crystals display, organic light emitting diode and light emitting electrochemical cells).

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Chemistry of Smart Materials and Devices

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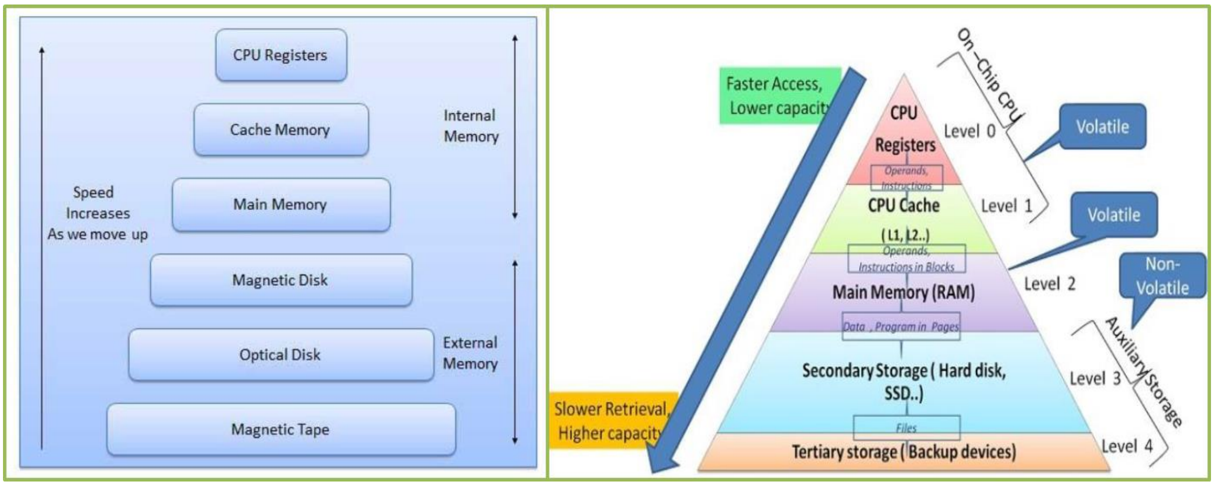
Introduction:

Memory is the electronic holding place for the instructions and data a computer needs to reach quickly. It's where information is stored for immediate use. Memory is one of the basic functions of a computer, because without it, a computer would not be able to function properly. New, high-performance memory is urgently required to keep up with the growing demands of information technology. Fortunately, new memory technologies are expected to increase memory performance and accelerate the information revolution. Electronic materials are the key elements of continued scientific growth and technological advances in the new millennium. The electronic materials are discussed in this unit include conducting polymers, organic conductors and hybrid conductors.



Characteristics of Memory Devices:

Location: The memory can either be stored externally with the help of some devices or internally.

Capacity: The amount of data a device can store is called capacity. It is measured as a byte (1 byte = 8 bits, 1 bit is either 0 or 1).

Access Method: The way of searching the storage devices is called the access method.

Unit of Transfer: The measure of data is different in internal and external devices

Performance: The performance of any memory device depends upon the rate at which data is transferred, the time taken by the device to carry out the process and the access time.

Basic Concepts of Electronic Memory

The basic goal of a memory device is to provide a means for storing and accessing binary digital data sequences of “1” and “0”, as one of the core functions (primary storage) of modern computers. 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).

Electronics using conventional silicon have been developed and are the core of various forms of modern electronic circuitry. In conventional silicon-based electronic memory, data are stored based on the amount of charge stored in the memory cells. An emerging category of electronic devices using polymers has attracted considerable attention, and extensive efforts have been made for the practical applications of electronic devices. Among various electronic devices, memory devices, such as flash memory, dynamic random-access memory (DRAM), and static random-access memory (SRAM), have permeated most applications. Organic/polymer electronic memory on the other hand, stores data in an entirely different way, for instance, based on different electrical conductivity states (ON and OFF states) in response to an applied electric field. Over the past 15 years, efforts have been directed towards the development of functional memory implementation using polymers as critical parts in various memory devices, including floating-gate memory, ferroelectric memory, filament-induced memristors, and charge-trapping memory. Organic/polymer electronic memory is likely to be an alternative or at least a supplementary technology to conventional semiconductor electronic memory. (https://doi.org/10.1039/9781782622505-00001)

Memory Devices: History of organic/polymer electronic memory devices

Since the 1940s, many storage forms based on diverse natural phenomena have been documented. A computer system often has many types of storage, each with a specific function. Due to their unusual electrical characteristics, amorphous semiconductors and disordered structures attracted a lot of attention in the 1960s.

- In 1968 - Pb/polydivinylbenzene/Pb bistable electrical switching device as an information storage device.
- In 1969 - Tetracene films sandwiched between metal electrodes.
- In 1970 - Phthalocyanines and polystyrene - bistable switching materials.
- In 1970 - Polymer thin films prepared by glow-discharge polymerization.

- In 1980 - Thin films of ferroelectric materials began exhibiting non-volatile memory effects.

- In 1995- Fabrication of ferroelectric films by the Langmuir–Blodgett (LB) technique. Polymer ferroelectric random access memory (FeRAM) as a promising memory technology has been achieved
- In 2001- An organic transistor memory device using a sexithiophene oligomer as the conductor and an inorganic ferroelectric material as the gate insulator were demonstrated.

  Ferroelectric organic and polymer materials have also been utilized as gate insulators in field-effect transistors (OFETs).

  High performance all-organic or polymer transistor memory devices have been demonstrated
- In 2003-A WORM type memory device based on polymer fuses was demonstrated

  The memory element consists of a thin film p–i–n silicon diode and a conductive polymer fuse, composed of poly (ethylene dioxythiophene) (PEDOT) oxidatively p-doped by poly (styrene sulfonic acid) (PSS).

  Polymer memory devices based on charge transfer effects from doping of a polymer matrix by electron donors, such as 8-hydroxyquinoline (8HQ), tetrathiafulvalene (TTF), polyaniline (PANI), poly-3-hexylthiophene (P3HT), or electron acceptors such as gold nanoparticles, copper metallic filaments and phenyl C61-butyric acid methyl ester (PCBM), have been reported.
- In 2005-Multilevel conductance switching in poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) films.
- In 2011-A polymer memristor was first reported in cobalt(iii)-containing conjugated (CP) and non-conjugated (NCP) polymers with an azo-aromatic backbone.

  Single crystals of a cyclodextrin-based metal–organic framework (MOF) infused with an ionic electrolyte and flanked by silver electrodes can act as memristors.
- Recent; organic-based resistive memory materials, biodegradable memory devices

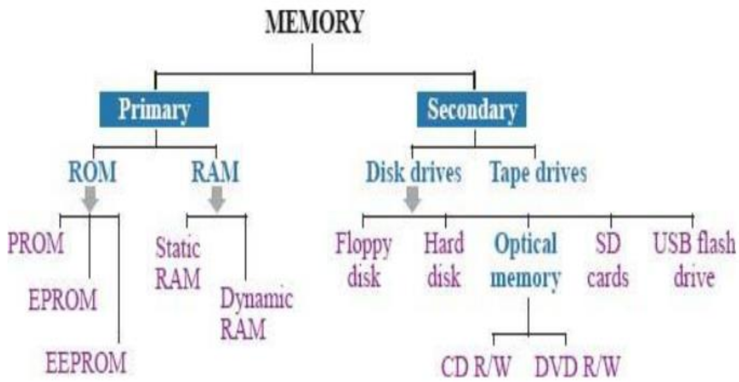
I. Electronic Memory and its classification:

A memory unit is a collection of storage cells with associated circuits needed to transfer information in and out of the device. The binary information is transferred for storage and from which information is available when needed for processing. When data processing takes place, information from the memory is transferred to selected registers in the processing unit. Intermediate and final results obtained in the processing unit are transferred back to be stored in memory.

I. Classification of Electrical Memory: In general, memory is of three types:

1. Primary memory or Internal memory (RAM, ROM, Cache)
2. Secondary memory or external memory (SSD, CD, Floppy disk, magnetic tape)
3. Cache memory (It is part of primary or internal memory)

Primary memory	Secondary Memory
1) Primary memory is the memory that is directly accessed by the CPU.	1) Secondary memory is a storage device that is not accessible directly by the CPU.
2) It is known as main memory. 3) A computer cannot run without primary memory	2) It is known as backup memory. 3) A computer can run without secondary memory.
4) It is faster than secondary memories.	4) It is slower than primary memories.
5) Example: ROM, RAM	5) Example: floppy disk, CD, DVD, USB flash drive



1. Primary Memory: It is also known as the main memory of the computer system. It is used to store data and programs or instructions during computer operations. It uses semiconductor technology and hence is commonly called semiconductor memory. Primary memory is of two types:

(i) RAM (Random Access Memory):

It is a volatile memory. Volatile memory stores information based on the power supply. If the power supply fails/ interrupted/stopped, all the data & information on this memory will be lost.

RAM is of two types: i) SRAM (Static RAM),
ii) DRAM (Dynamic RAM)

(ii) ROM (Read Only Memory):

It is a non-volatile memory. Non-volatile memory stores information even when there is a power supply failed/ interrupted/stopped. ROM is used to store information that is used to operate the system. As its name refers to read-only memory, we can only read the programs and data that is stored on it.

ROM is of following types:

1. MROM (Masked ROM), 2. PROM (Programmable Read Only Memory),

3. EPROM (Erasable Programmable Read Only Memory),
4. EEPROM (Electrically Erasable Programmable Read Only Memory)
5. ROM Flash

2. Secondary Memory: It is also known as auxiliary memory and backup memory. It is a non-volatile memory and used to store a large amount of data or information. The data or information stored in secondary memory is permanent, and it is slower than primary memory. A CPU cannot access secondary memory directly. The data/information from the auxiliary memory is first transferred to the main memory, and then the CPU can access it.

Characteristics of Secondary Memory:

- It is a slow memory but reusable.
- It is a reliable and non-volatile memory.
- It is cheaper than primary memory.
- The storage capacity of secondary memory is large.
- A computer system can run without secondary memory.
- In secondary memory, data is stored permanently even when the power is off.

3. Cache Memory: It is a type of high-speed semiconductor memory that can help the CPU run faster. Between the CPU and the main memory, it serves as a buffer. It is used to store the data and programs that the CPU uses the most frequently.
Advantages of cache memory:

- It is faster than the main memory.
- When compared to the main memory, it takes less time to access it.
- It keeps the programs that can be run in a short amount of time.
- It stores data in temporary use.

Disadvantages of cache memory:

- Because of the semiconductors used, it is very expensive.
- The size of the cache (amount of data it can store) is usually small.

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

i) Volatile and ii) Non-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. As shown in Figure, electronic memory can be further divided into sub-categories, as read only memory (ROM), hybrid memory, and random access memory (RAM).

- ROM is factory programmable only; data is physically encoded in the circuit and cannot be programmed after fabrication.
- Hybrid memory allows data to be read and re-written at any time.

- RAM requires the stored information to be periodically read and re-written, or refreshed, otherwise the data will be lost.

Among these types of electronic memory, write-once read-many-times (WORM) memory, hybrid non-volatile and rewritable (flash) memory, static random access memory (SRAM) and dynamic random access memory (DRAM) are the most widely reported polymer memory devices.

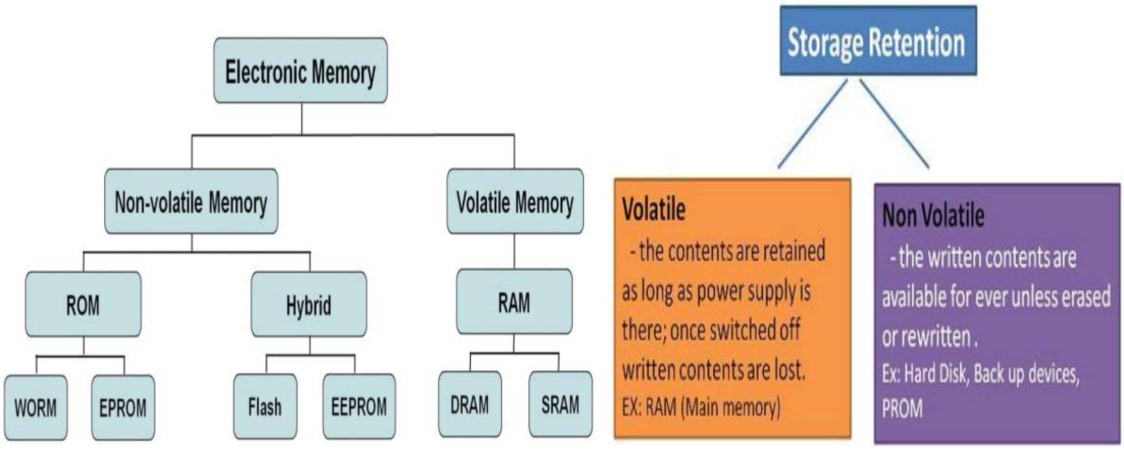


Figure: Classification of electronic memories into volatile and nonvolatile devices.

II. Classification of Electrical Memory Devices:

According to the device structure, electronic memory devices can be divided into three primary categories: transistors, capacitors and resistors.

Memory Devices: Classification of memory devices;

1. Transistor-Type Electronic Memory
2. Capacitor-Type Electronic Memory
3. Resistor-Type Electronic Memory

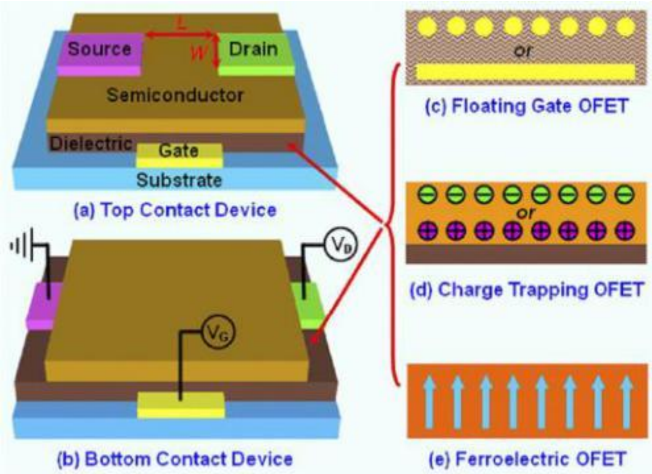
I. Transistor-Type Electronic Memory

Inorganic transistors are widely used in conventional semiconductor memory
Ex; SRAM cell, flash memory cell.

Organic (including polymer) transistors are also of great potential for memory applications
Ex; OFET type memory devices.

Organic field-effect transistor (OFET) memory device: The organic transistor inherits its design features from inorganic MOSFET (metal-oxide-semiconductor field-effect transistor.) precursors. It is composed of three main components: source, drain and gate electrodes, a dielectric insulator layer and an active semiconductor layer, as illustrated in below Figure.

The electrodes can be n- or p-Si, ITO, PEDOT:PSS, TaN, Au, Pt, Al, Cu, Cr or other metals. An OFET memory device consists of at least one polymeric material either in its dielectric insulator layer or active semiconductor layer or both. The device is usually supported by a glass, wafer, or plastic substrate.



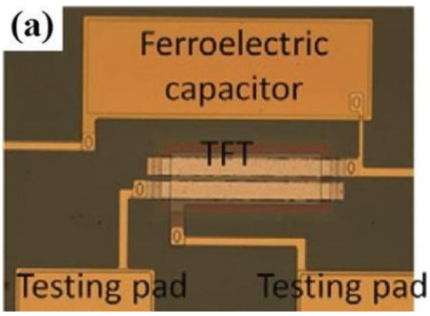
II. Capacitor-Type Electronic Memory

Capacitors can store charges on two parallel plate electrodes under an applied electric field. Based on the amount of charge stored in the cell, the bit level (either "0" or "1") can be encoded accordingly. When the medium between the electrodes is merely a dielectric, the stored charge will be lost eventually.

Example;

DRAM using a dielectric capacitor is volatile memory
ferroelectric capacitors (FeRAM) is non-volatile memory

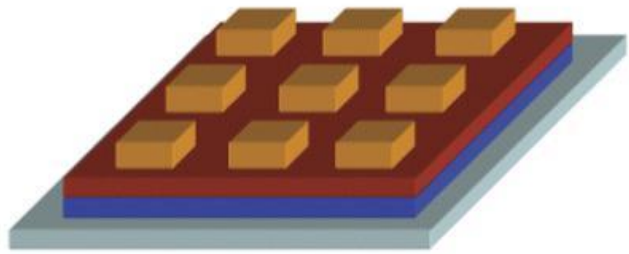
Figure shows an image of a 1T1C FeRAM device. The upper electrode of the capacitor is made of Pt, Ir or Ru, and the lower electrode is Pt/Ti. The local interconnect between the access transistor and the storage node of the capacitor is TiN.



III. Resistor-Type Electronic Memory

Resistor-type memory is based on the change of the electrical conductivity of materials in response to an applied voltage (electric field). Devices incorporating switchable resistive materials are generically classified as resistor-type memory, or resistive random-access memory (RRAM).

Resistor-type electronic memory usually has a simple structure with an organic/polymer thin film sandwiched between two electrodes on a supporting substrate (glass, silicon wafer, plastic or metal foil). The configuration of the top and bottom electrodes can be either symmetric or asymmetric, with aluminum, gold, copper, p- or n-doped silicon, and ITO being the most widely used electrode materials.



I. Electrical memory devices based on organic molecules

Types of Organic-Based Electrical Memory Devices

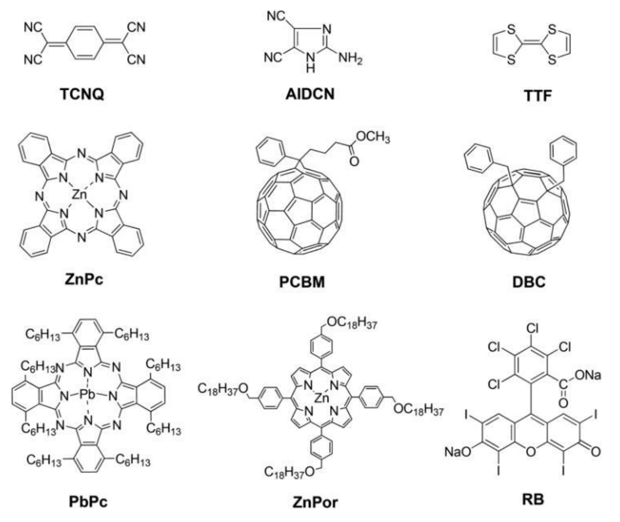
a) **Organic molecules:** Organic electronic memory devices based on organic molecules were first reported in several acene derivatives including naphthalene, anthracene, tetracene, pentacene, perylene, p-quaterphenyl and p-quinquephenyl.
Ex: Device with the structure of a single layer of N,N′-di(naphthalene-l-yl)-N,N′ diphenyl-benzidine (NPB) embedded between ITO and Ag electrodes.

b) **Organometallic and all-organic charge transfer (CT) complexes:** They have been explored for use in organic memory. Examples;

i. Electrical memory phenomena of Charge Transfer complexes were first reported in a copper and 7,7,8,8-tetracyanoquinodimethane (TCNQ) complex (Cu-TCNQ)- device with the structure Cu/Cu-TCNQ/Al.

ii. CT complexes consisted of methanofullerene 6,6-phenyl C61-butyric acid methyl ester (PCBM) as the organic electron acceptor, and tetrathiafulvalene (TTF) as the organic electron donor. Electrical bistability was demonstrated in devices with a sandwich structure.

Figure: Chemical structures of the molecules used for organic memory devices.



II. Electrical memory devices based on polymeric molecules

Polymer memory refers to memory technologies based on the use of organic polymers. The molecular structure of polymeric materials can be tailored using electron donors and acceptors. The properties of polymer memory are low-cost and high-performance, and have the potential for 3D stacking and mechanical flexibility.

a) **Functional Polyimides:** Functional polyimides (PIs) are one of the most attractive polymeric materials for organic electrical memory applications. In functional PIs, phthalimide acts as the electron acceptor, and electron donors (triphenylamine or carbazole moieties) are introduced to form a D–A structure (first reported in 2006). Example;

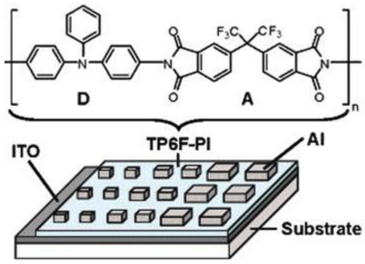
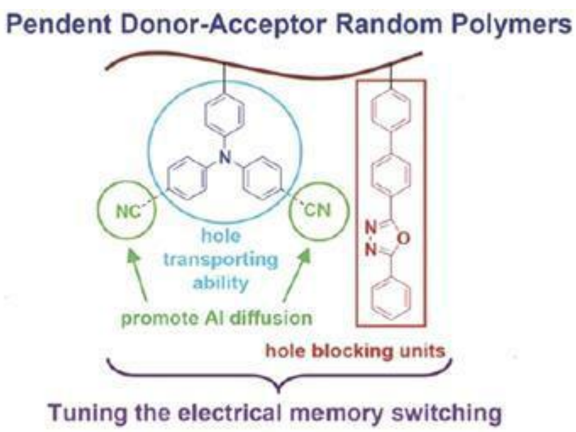


Figure: Molecular structure (top) of functional PI (TP6F-PI) and schematic diagram (bottom) of single-layer memory device.

b) **Non-Conjugated Polymers with Pendants:** Non-conjugated polymers with pendent electroactive donors, acceptors and chromophores are another kind of polymer material favorable for electronic memory.
Ex; Al/polymer/ITO, polymer-PVK-AZO-2CN and PVK-AZO-NO2(PVK- polyvinyl carbazole, AZo- azobenzene)



III. Electrical memory devices based on inorganic/organic nanocomposites

Generally, organic–inorganic hybrid materials are composed of organic layers containing fullerenes, carbon nanotubes, graphene, metal nanoparticles, semiconductor nanoparticles or inorganic quantum dots (QDs).

Non-volatile memory devices based on hybrid inorganic/organic nanocomposites have emerged as excellent candidates for promising applications in next-generation electronic and optoelectronic devices. The simplest structure for a hybrid memory device fabricated utilizing the solution method is a single-polymer layer embedded with inorganic nanomaterials and sandwiched between two metal electrodes, as shown in below Figure.

Generally, the hybrid nanocomposites are formed by dissolving inorganic nanomaterials and a polymer matrix simultaneously in a certain organic solvent with a relatively high volatility. Fabrications of single-layer-structured nonvolatile memories based on various organic/inorganic hybrid nanocomposites have been reported.

a) **Organic–Carbon Allotrope Hybrid Materials:** For organic electronic memory applications, Fullerene and its derivatives have been widely used as electron acceptors to form charge transfer (CT) complexes with polymer-containing electron donors, such as thiophene, fluorene, carbazole and aniline derivatives.
   Ex; rGO/P3HT:PCBM/Al, Al/Polystyrene:C60/Al

b) **Organic–Inorganic Nanocomposites:** Hybrid electronic memory devices have been reported in some organic composites containing metal nanoparticles, quantum dots and metal oxide nanoparticles. Inorganic species used in these memories include, semiconductor nanoparticles (ZnO, CdSe, Si, CuO and so on) and metal nanoparticles (Au, Ag, FeNi and so on).
   Both insulating polymers, such as polyimide (PI), poly(methylmethacrylate) and polystyrene, and conducting polymers, such as poly(N-vinylcarbazole) and poly(2-methoxy-5-(2-ethyhexoxy)-1,4-phenylene vinylene), are used as a matrix for the inorganic nanoparticles.

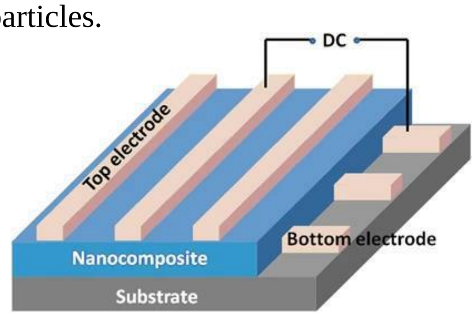


Figure: Schematic of a single-layer hybrid memory device.

Bio-composite based memory devices

With the wave of digitization, the volume of data produced by people is increasing dramatically. The manufacturing of electronic components is massive and the iterative updating pace is quick due to the tremendous amount of data that must be processed in order to fulfil the demands of human data services. Additionally, there is also a significant quantity of electronic garbage produced. Green electronics must become commonplace technology in order to decrease e-waste; as a result, natural biological materials that are environmentally benign and biodegradable are the greatest option for achieving the sustainable growth of the electronics sector.

Natural biomaterials are potential candidates for the next generation of green electronics due to their biocompatibility and biodegradability. The application of bio composite systems in information storage has further promoted the progress of environmentally benign bioelectronics. Certain organic materials and biomacromolecules possess great potential for application in biocompatible, low cost and disposable electronic devices. Devices using sericin protein, natural regenerated silk fibroin protein as the functional material are examples of used for the fabrication of memory devices.

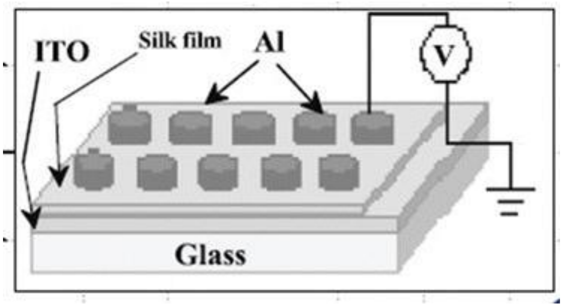
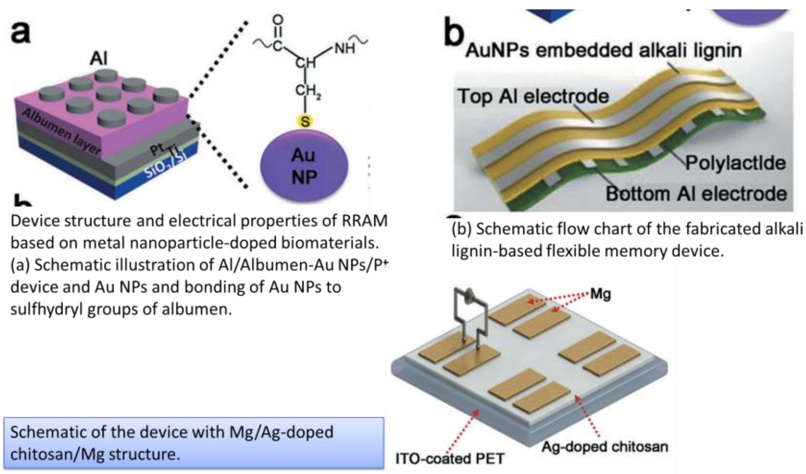


Figure: Schematic of the fabricated memristor device ITO/silk/Al device



Disadvantages: Biomaterials have a weak electron transfer function and are not compatible with traditional semiconductor device manufacturing processes; therefore biomaterial-based degradable electronic products have many difficulties to overcome in order to achieve industrial feasibility.

Researchers have actively tried to improve the electrical function of composite materials through combining biological materials with various functional materials. In combination with other advantages, electronic devices based on biological composite materials are expected to compete with traditional silicon-based devices.

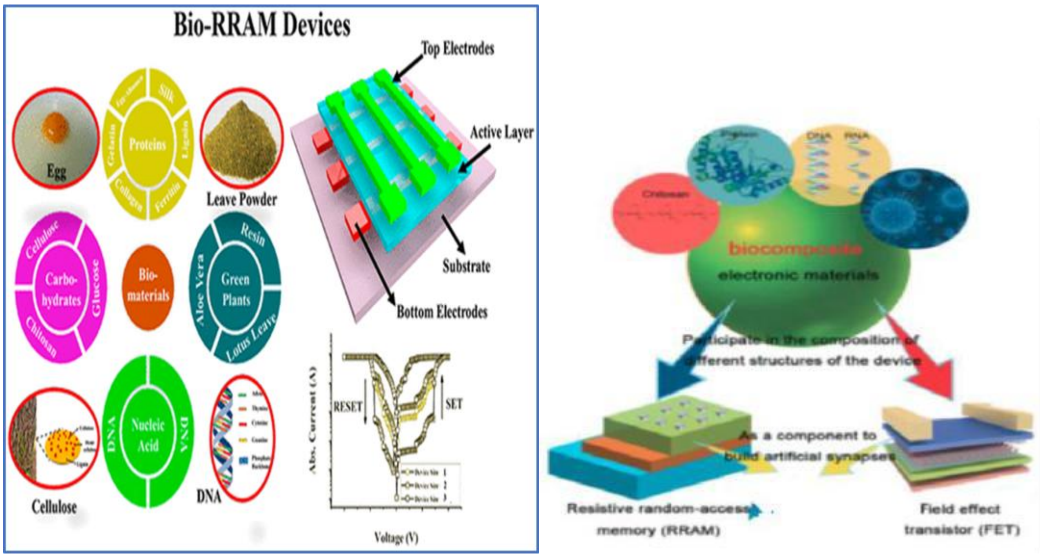


Fig: Outline of building memory devices from bio composite electronic materials: different kinds of biocomposite materials will participate in the construction of memory devices with different structures and properties. (Ref https://doi.org/10.1080/14686996.2020.172539)

Manufacturing of semiconductor chips

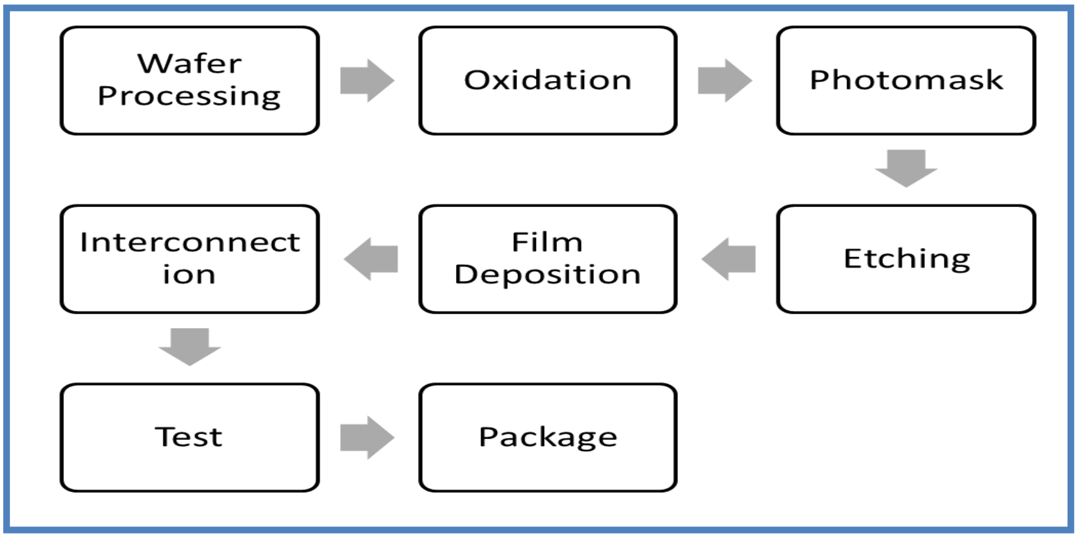
A semiconductor chip is an electric circuit constructed on a semiconductor wafer containing several components such as transistors.

Semiconductor device fabrication is the process used to manufacture semiconductor devices, typically integrated circuit (IC) chips such as modern computer processors, microcontrollers, and memory chips that are present in everyday electrical and electronic devices. Silicon is almost always used, but various compound semiconductors are used for specialized applications.

A semiconductor chip is an electric circuit with many components such as transistors and wiring formed on a semiconductor wafer. An electronic device comprising numerous these components is called "integrated circuit". The layout of the components is patterned on a photomask (reticle) by computer and projected onto a semiconductor wafer in the manufacturing processes described below. Entire manufacturing process takes time, from start to packaged chips ready for shipment, at least six to eight weeks.

Fabrication Steps: It is a multiple-step sequence of photolithographic and chemical processing steps (such as surface passivation, thermal oxidation, planar diffusion and junction isolation) during which electronic circuits are gradually created on a wafer made of pure semiconducting material.

Entire manufacturing process can be divided into 8 steps.

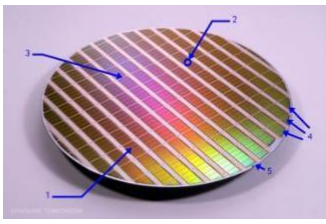


1. Wafer Processing

A wafer, also called a disc, is a thin round glossy slice of a silicon rod (or Germanium) that is cut using specific diameters for the fabrication of integrated circuits. Most wafers are made of silicon extracted from sand.

Once silicon is extracted from sand, it needs to be purified before it can be put to use. First, it is heated until it melts into a high-purity liquid then solidified into a silicon rod, or ingot, using common growing methods like the Czochralski (chokh-RAL-skee) process or the Floating Zone process. In these process, a cylindrical ingot of high purity monocrystalline semiconductor, such as silicon or germanium, called a boule, is formed by pulling a seed crystal from a melt. These ingots are then sliced into wafers about 0.75 mm thick. The thin slice obtained through cutting process is called "die" that is an unprocessed "raw wafer". The die surface is uneven and polished to remove surface defects through grinding and chemical etching processes then to smooth surface trough polishing to obtain mirror-smooth finish. The flawless surface allows the circuit patterns to print better on the wafer surface during the lithography process.

Once the wafers are prepared, many process steps are necessary to produce the desired semiconductor integrated circuit. Donor impurity atoms, such as boron, phosphorus, arsenic, or antimony in the case of silicon, can be added to the molten intrinsic material in precise amounts in order to dope the crystal, thus changing it into an extrinsic semiconductor of n-type or p-type.

 Si wafer  finished wafer

In general, the steps can be grouped into two areas:

- Front end processing
- Back end processing

2. Oxidation

The role of oxidation process is to form a protective film on the surface of wafer. It can protect the wafer from chemical impurities; prevent leakage current from entering circuit, diffusion during ion implantation and the wafer from slipping off during etching.

3. Photomask

A photomask is basically a “master template” of an IC design. Photomask is the use of light to print circuit patterns onto wafer. A photomask is an opaque plate with holes or transparencies that allow light to shine through in a defined pattern. (Previously, photomasks used to be produced manually by using rubylith and mylar).
The wafer is then covered with a light-sensitive coating called 'photoresist'. There are two types of resist: positive and negative. The main difference between positive and negative resist is the chemical structure of the material and the way that the resist reacts with light. With positive resist, the areas exposed to ultraviolet light change their structure and are made more soluble – ready for etching and deposition. The opposite is true for negative resist, where areas hit by light polymerize, meaning they become stronger and more difficult to dissolve. Positive resist is most used in semiconductor manufacturing because its higher resolution capability makes it the better choice for the lithography stage.

Several companies around the world produce resist for semiconductor manufacturing, such as Fujifilm Electronics Materials, The Dow Chemical Company and JSR Corporation.

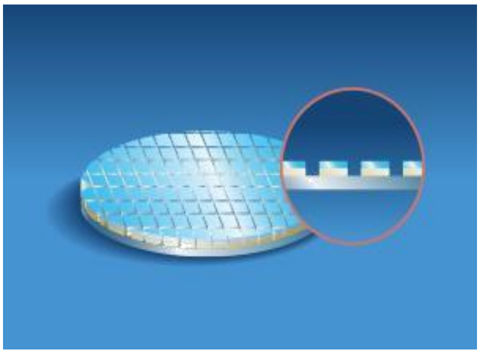
4. Etching

The next step is to remove the degraded resist to reveal the intended pattern. During 'etch', the wafer is baked and developed, and some of the resist is washed away to reveal a 3D pattern of open channels. Etch processes must precisely and consistently form increasingly conductive features without impacting the overall integrity and stability of the chip structure.

Removal is any process that removes material from the wafer; examples include etch processes (either wet or dry) and chemical-mechanical planarization (CMP).
(Wet etching uses chemicals solutions to remove oxide films. In wet etching, the exposed thin film on the surface layer is dissolved using chemicals, such as hydrofluoric acid or phosphoric acid, and removed. This forms the pattern. Advantages are low cost, fast etching speed and high productivity. Wet etching is not suitable for fine circuit diagrams. There is

also a dry etching method in which the wafer surface is bombarded with ionized atoms to remove the film layer. Now dry etching ***has been widely used for fine circuit diagrams. Dry etching has three different types:***

i. ***Chemical etching -which uses gas (Hydrogen fluoride),***
ii. ***physical sputtering****-ions in the plasma are used to strike and remove the excess oxide layer*
iii. *Reactive ion etching)*



5. Film deposition

To create the micro devices inside the chip, deposit layers of thin films and remove excess parts by etching and add some materials to separate the different devices. Thin film layers of silicon oxide, aluminium and other metals that will become the circuit materials are formed on the wafer. Thin films of conducting, isolating or semiconducting materials – depending on the type of the structure being made are deposited on the wafer to enable the first layer to be printed on it. This important step is commonly known as 'deposition'.

6. Interconnection

Implantation of Impurities

Once patterns are etched in the wafer, the wafer may be bombarded with positive or negative ions to tune the electrical conducting properties of part of the pattern.
Raw silicon – the material the wafer is made of is not a perfect insulator or a perfect conductor. Silicon"s electrical properties are somewhere in between. In order to give the silicon substrate semiconducting properties, impurities, such as phosphor or boron ions, are implanted in the wafers.

7. Test

The main goal of the test is to check whether the quality of the semiconductor chip meets a certain standard, thereby eliminating the defective products and improving the reliability of the chip. Electronic Die sorting (EDS) is a testing method for wafers.

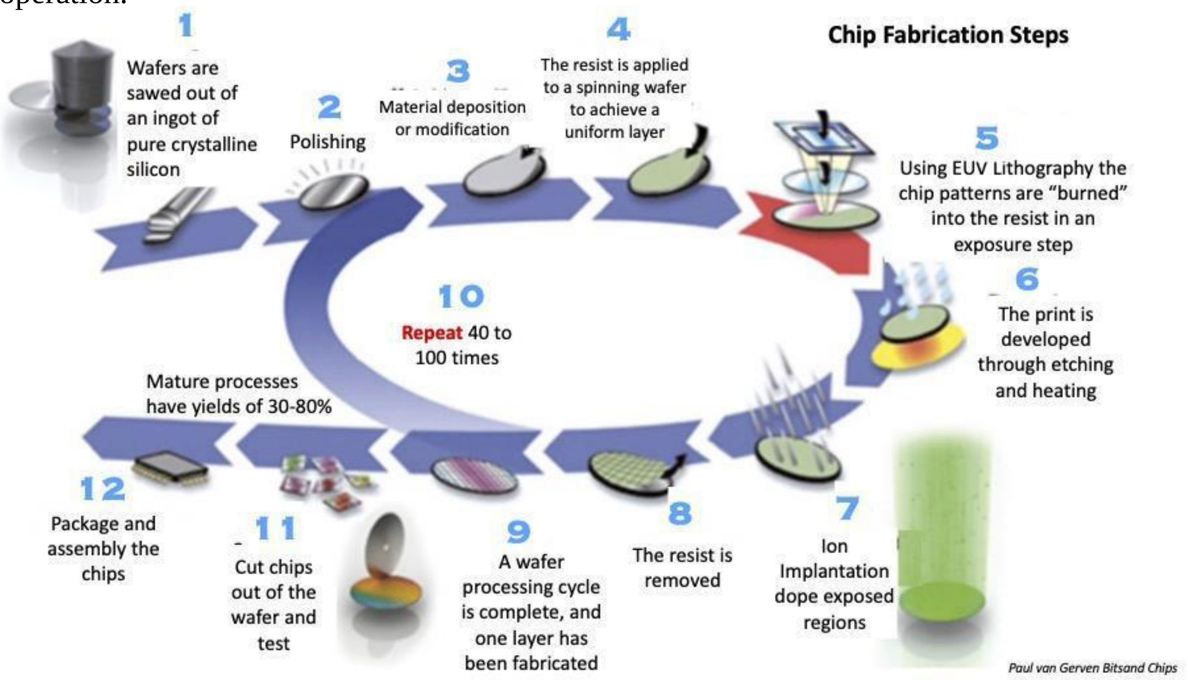
Once the front-end process has been completed, the semiconductor devices or chips are subjected to a variety of electrical tests to determine if they function properly. The percent of devices on the wafer found to perform properly is referred to as the yield.

8. Package

Single wafers are cut into individual chips by cutting. The entire packaging system is divided into five steps. Namely wafer sawing, single wafer attachment, interconnection, molding and packaging.

The entire process of creating a silicon wafer with working chips consists of thousands of steps and can take more than three months from design to production. To get the chips out of the wafer, it is sliced and diced with a diamond saw into individual chips. Cut from a 300-mm wafer, the size most often used in semiconductor manufacturing, these so-called 'dies' differ in size for various chips. Some wafers can contain thousands of chips, while others contain just a few dozen.

The chip die is then placed onto a 'substrate'. This is a type of baseboard for the microchip die that uses metal foils to direct the input and output signals of a chip to other parts of a system. And to close the lid, a 'heat spreader' is placed on top. This heat spreader is a small, flat metal protective container holding a cooling solution that ensures the microchip stays cool during operation.



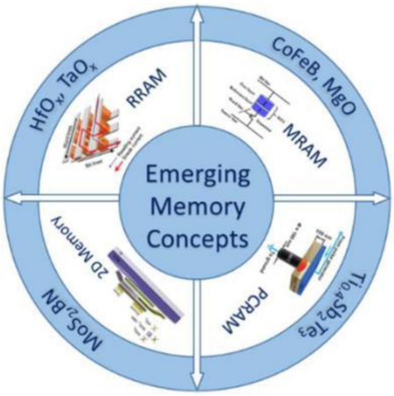
Display Systems: Photoactive and electroactive materials

• Definition and principle for photoactive and electroactive

Photoactive materials belong to the huge field of photonics, where materials that actively interact with light are tuned and optimized to achieve effects such as;

- light emission (LEDs and lasers, just to name the most common ones)
- light detection, with related signal amplification (e.g., in photomultipliers) and processing operations.
- Alternatively, they can be used to develop light-sensitive circuits and switches (such as with photoresistors),
- Generally, they convert light into an electrical signal (photodiodes – PV Cells) photo and electro active materials for memory devices

Memory cells have always been an important element of information technology. With emerging technologies like big data and cloud computing, the scale and complexity of data storage has reached an unprecedented peak with a much higher requirement for memory technology.



In the past few decades, modern information technology has developed rapidly. Memory is an important pillar supporting the development of integrated circuits, aerospace, defence, and military fields. With emerging technologies, such as cloud computing and big data, memory has greatly improved the quality of human society. In the meantime, the scale and complexity of data storage has reached an unprecedented peak.

Optoelectronic memories have attracted tremendous attention owing to its unique capability of accumulating and releasing photo-generated carriers under electrical stress and light irradiation. The great potential of optoelectronic memories in image capturing, confidential information recording, and logic data processing. Last decades have witnessed the exponential advances of silicon-based nonvolatile optoelectronic memories. However, the continued device miniaturization and the feasibility of integration into flexible, wearable, and transparent circuits greatly restrict the development of conventional silicon-based optoelectronic memories

Two-dimensional (2D) thin layered materials have been considered as promising building blocks for the next-generation electronic and optoelectronic devices due to their extraordinary and unique properties. The 2D thin layered structure enables their immunity against the short channel effects, while the mechanical strength and structural flatness allow their integration into flexible and wearable circuits.

Mechanically exfoliated few-layer copper indium selenide (CuIn7Se11) was firstly applied in 2D thin layered optoelectronic memory, however, the short retention time (approximately 50 s) and low current switching ratio (less than 10) hindered its application in image sensing. Monolayer molybdenum disulfide (MoS2) optoelectronic memory was reported to possess long retention time (approximately 104 s), while suffering from moderate switching ratio (approximately 4700) and limited data storage capacity (8 storage levels). Besides the memory devices fabricated by single 2D crystals, graphene/MoS2 vertical heterostructure was also realized with low switching ratio (less than two). Recently, the 2D materials-based semifloating-gate field-effect-transistor and metallic gold nanoparticles/crosslinked poly(4-vinylphenol)/MoS2 heterostructure memories have been reported, demonstrating high switching ratio, which are promising candidates for thin layered multibit optoelectronic memory. In order to enhance the data storage capability of a single optoelectronic memory, it is essential to increase the number of storage level, which is typically reflected by the difference of reading currents between a programmed state and an erased state1. Nonvolatile optoelectronic memory-based on a hybrid structure of thin layered tungsten diselenide (WSe2) and boron nitride (BN). The storage current of the WSe2/BN optoelectronic memory can be effectively modulated by backgate, resulting in a memory switching ratio approximately 1.1 × 106. This large switching ratio coupled with the optically tunable characteristic ensures over 128 distinct storage levels (7 bit storage). The device is also highly reliable, as reflected by its long retention time and large number of program-erase testing cycles.

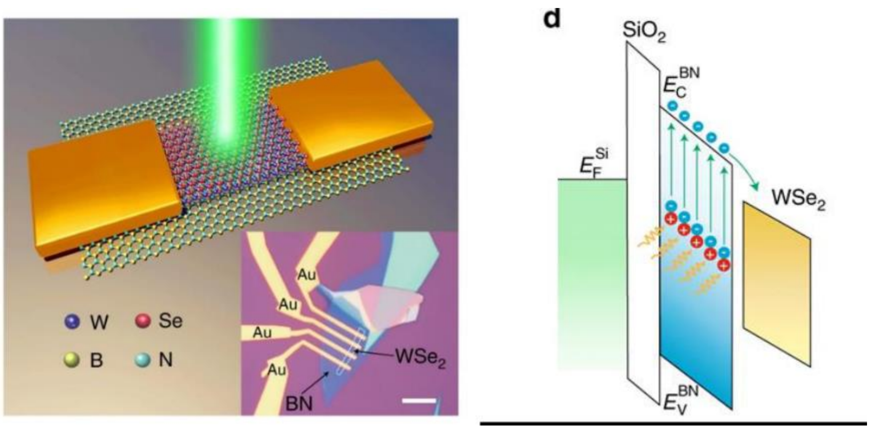


Figure shows the schematic of the hybrid WSe2/BN optoelectronic memory fabricated in a field-effect-transistor (FET) structure, in which monolayer WSe2 flake is transferred on top of a BN flake.

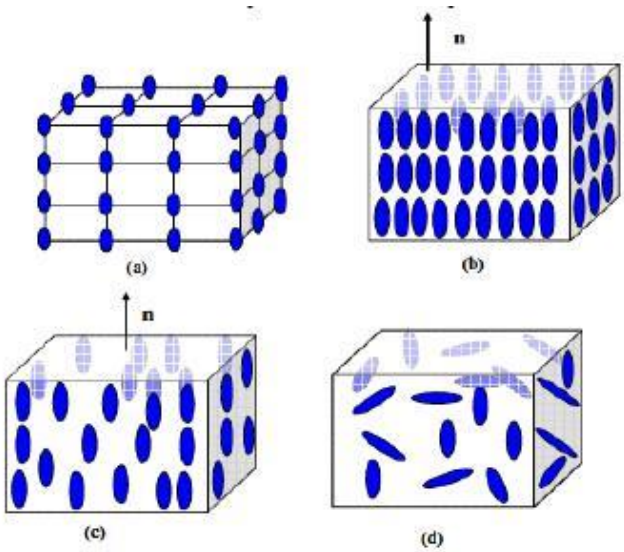
Materials for display technology

Liquid crystals display

Introduction:

Liquid crystals are state of matter which has properties between those of conventional liquids and those of solid crystals. There are many different types of liquid –crystal phases, which can be distinguished by their different optical properties (such as textures).

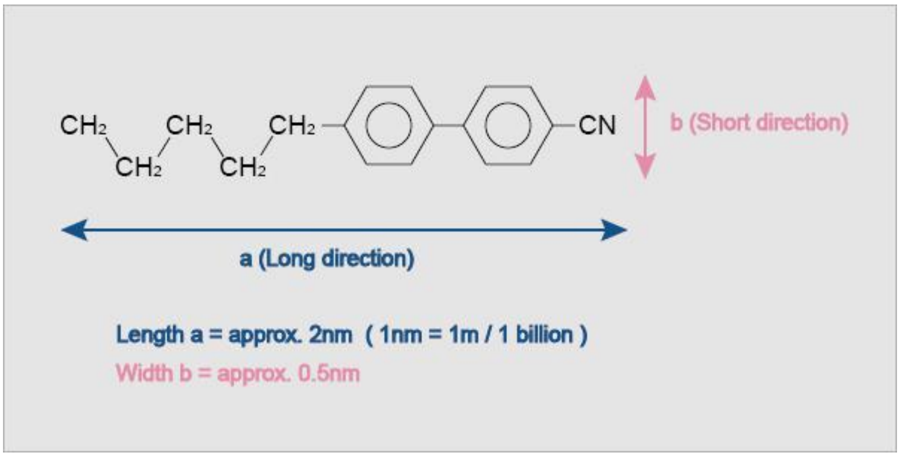
Liquid crystal (LC) phases represent a unique state of matter characterized by both mobility and order on a molecular and at the supramolecular levels. This behaviour appears under given conditions, when phases with a characteristic order intermediate to that of a three dimensionally ordered solid and a completely disordered liquid are formed. Molecules in the crystalline state possess orientational and three dimensional positional orders. That is the constituent molecules of highly structured solids occupy specific sites in a three dimensional lattice and points their axes in fixed directions as illustrated in Fig.



Schematic representation of molecular packing in the a) Crystals, b) & c) liquid crystals and d) liquid state

Liquid crystal refers to the intermediate status of a substance between solid (crystal) and liquid. When crystals with a high level of order in molecular sequence are melted, they generally turn liquid, which has fluidity but no such order at all. However, thin bar-shaped organic molecules, when they are melted, keep their order in a molecular direction although they lose it in molecular positions. In the state in which molecules are in a uniform direction, they also have refractive indices, dielectric constants and other physical characteristics similar to those of crystals, depending on their direction, even though they are liquid. This is why they are called liquid crystal. The diagram below shows the structure of 5CB (4-pentyl-4‘‘-Cyanobiphenyl) as an example of liquid crystal molecules.

An example of liquid crystal molecule.



Types of Liquid crystals:

Liquid crystals can be divided into

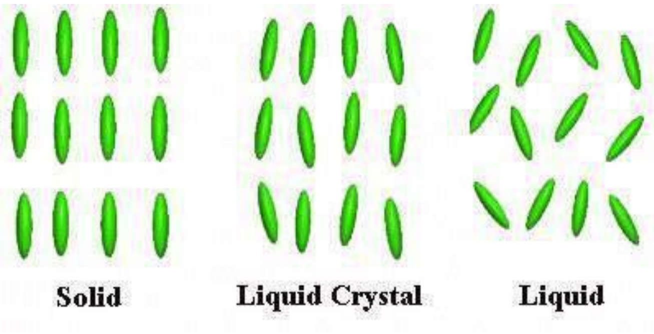
I. thermotropic, II. lyotropic and III. metallotropic.

Thermotropic and lyotropic liquid crystals consist mostly of organic molecules, although a few minerals are also known. Thermotropic LCs exhibit a phase transition into the LC phase as temperature changes.

Lyotropic liquid crystals exhibit phase transitions as a function of both temperature and concentration of molecules in a solvent (typically water).

Metallotropic liquid crystals are composed of both organic and inorganic molecules; their LC transition additionally depends on the inorganic-organic composition ratio.

The distinguishing characteristic of the liquid crystalline state is the tendency of the molecules (mesogens) to point along a common axis, called the director (the molecular direction of preferred orientation in liquid crystalline mesophases). This is in contrast to molecules in the liquid phase, which have no intrinsic order. In the solid state, molecules are highly ordered and have little translational freedom. The characteristic orientational order of the liquid crystal state is between the traditional solid and liquid phases and this is the origin of the term mesogenic state, used synonymously with liquid crystal state. Note the average alignment of the molecules for each phase in the following diagram. A mesogen is rigid rodlike or disclike molecules which are components of liquid crystalline materials.



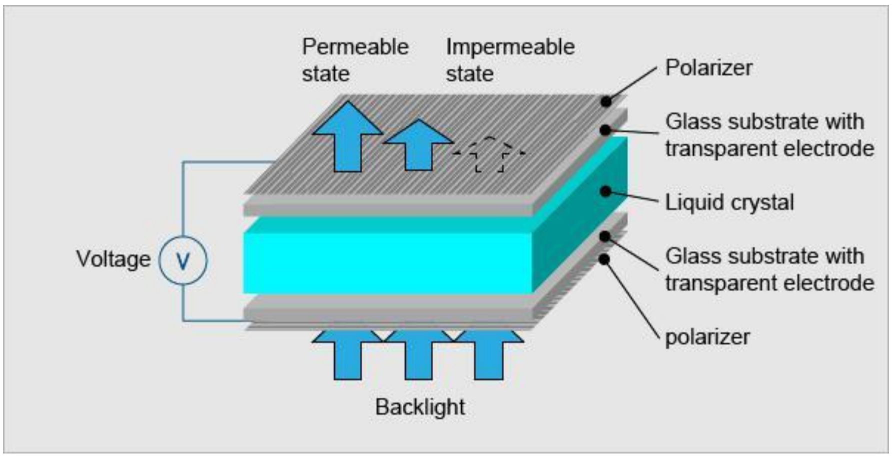
Application of Liquid crystals in display: Liquid Crystal Display (LCD)

Liquid crystals find wide use in liquid crystal displays, which rely on the optical properties of certain liquid crystalline substances in the presence or absence of an electric field. This field has grown into a multi-billion dollar industry, and many significant scientific and engineering discoveries have been made.

Principle of liquid crystal display

A liquid crystal display (LCD) has liquid crystal material sandwiched between two sheets of glass. Without any voltage applied between transparent electrodes, liquid crystal molecules are aligned in parallel with the glass surface. When voltage is applied, they change their direction and they turn vertical to the glass surface. They vary in optical characteristics, depending on their orientation. Therefore, the quantity of light transmission can be controlled by combining the motion of liquid crystal molecules and the direction of polarization of two polarizing plates attached to the both outer sides of the glass sheets. LCDs utilize these characteristics to display images.

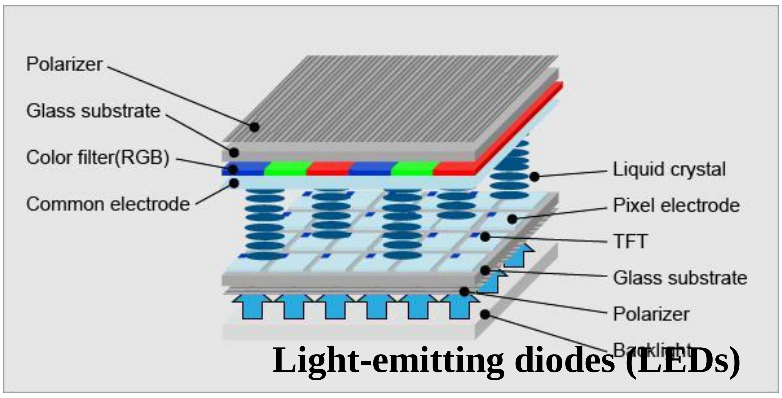
Working principle of an LCD



TFT LCD

An LCD consists of many pixels. A pixel consists of three sub-pixels (Red/Green/Blue, RGB). In the case of Full-HD resolution, which is widely used for smartphones, there are more than six million (1,080 x 1,920 x 3 = 6,220,800) sub-pixels. To activate these millions of sub-pixels a TFT is required in each sub-pixel. TFT is an abbreviation for "Thin Film Transistor". A TFT is a kind of semiconductor device. It serves as a control valve to provide an appropriate voltage onto liquid crystals for individual sub-pixels. A TFT LCD has a liquid crystal layer between a glass substrate formed with TFTs and transparent pixel electrodes and another glass substrate with a color filter (RGB) and transparent counter electrodes. In addition, polarizers are placed on the outer side of each glass substrate and a backlight source on the back side. A change in voltage applied to liquid crystals changes the transmittance of the panel including the two polarizing plates, and thus changes the quantity of light that passes from the backlight to the front surface of the display. This principle allows the TFT LCD to produce full-color images.

Structure of a TFT LCD



Light-emitting diodes (LEDs)

Light-emitting diodes (LEDs) are solid-state devices that use semiconductors and electroluminescence to create light. Essentially, LEDs convert electric energy directly into light, which differs from traditional incandescent lighting, which uses heat energy to generate light, which typically result in a significant waste of energy through heat loss. In comparison, LED technology is often referred to as „cold light technology‟, due to the lower heat output from LEDs, and the fact they don‟t waste energy in the form of non-light producing heat.

LED technology should not be confused with LCD (liquid crystal display) technology. LED screens are a completely different technology to LCD screens.

Advantages of LEDs:

1. Very low voltage and current are enough to drive the LED.
   Voltage range – 1 to 2 volts. Current – 5 to 20 milliamperes.
2. Total power output will be less than 150 milliwatts.
3. The response time is very less – only about 10 nanoseconds.
4. The device does not need any heating and warm up time.
5. Miniature in size and hence lightweight.
6. Have a rugged construction and hence can withstand shock and vibrations.
7. An LED has a lifespan of more than 20 years.

Organic light emitting diode (OLED)

Organic light emitting diode: Organic Light Emitting Diode popularly known as OLED is a solid-state device that consists of thin films of organic molecules that generate a bright light on the application of electric current. They are made by a series of organic thin films placed between two conductors. Organic LED or OLED technology is now established and being used in many forms of display. OLED technology is now being used for many applications from televisions to mobile phone displays. In view of the level of performance, organic LED, OLED display technology is being used increasingly in many areas.

Organic LED, OLED technology has many of the properties of a traditional organic LEDs. It utilises a PN junction and light emanates from this when a current flows in the forward direction. The different between traditional LEDs and organic LED display technology is that OLEDs utilise organic compounds for the PN junction rather than inorganic ones used for traditional LED technology. The organic LED materials include a variety of substances, including Aluminium 8-hydroxyquinoline and diamene. However many other substances can also be used for OLED technology.

OLED technology advantages:

- **Flexible:** It is possible to make OLED displays flexible by using the right materials and processes.
- **Very thin:** OLED displays can be made very thin, making them very attractive for televisions and computer monitor applications.

- **Colour capability:** It is possible to fabricate OLED displays that can generate all colours.
- **Power consumption:** The power consumed by an OLED display is generally less than that of an LCD when including the backlight required. This is only true for backgrounds that are dark, or partially dark.
- **Bright images:** OLED displays can provide a higher contrast ratio than that obtainable with an LCD.
- **Wide viewing angle:** With many displays, the colour becomes disported and the image less saturated as the viewing angle increases. Colours displayed by OLEDs appear correct, even up to viewing angles approaching 90°.
- **Fast response time:** As LCDs depend upon charges being held in the individual pixels, they can have a slow response time. OLEDs are very much faster. A typical OLED can have a response time of less than 0.01ms.
- **Low cost in the future:** OLED fabrication are likely to be able to utilise techniques that will enable very low cost displays to be made, although these techniques are still in development. Current costs are high.

OLED technology disadvantages:

- **Moisture sensitive:** Some types of OLED display can be sensitive to moisture.
- **Limited life:** The lifetime of some displays can be short as a result of the high sensitivity to moisture. This has been a limiting factor in the past.
- **Power consumption:** Power consumption can be higher than an equivalent LCD when white backgrounds are being viewed as the OLED needs to generate the light for this which will consume more power. For images with a darker background power consumption is generally less.
- **Lifespan:** The lifespan of the OLED displays is a major problem. Currently they are around half that of an LCD, being around 15 000 hours.
- **UV sensitivity:** OLED displays can be damaged by prolonged exposure to UV light. To avoid this a UV blocking filter is often installed over the main display, but this increases the cost.

Types of OLED technology

Organic LED, OLED technology can be divided into two main categories:

- **Passive-matrix OLED, PMOLED:** PMOLEDs are one form of OLED technology that has become a popular. The OLED display is made using strips of cathode, organic layers and strips of anode.
  Normally PMOLED displays are used for relatively small screens, up to around 6 or 7 centimetres diagonal and also for the display of text and icons. Consume more power.

- **Active-matrix OLED, AMOLED:** In the display, the AMOLEDs have full layers of cathode, organic molecules and anode, but the anode layer overlays a thin film transistor, TFT array matrix. The TFT array itself determines which pixels are activated to form the image.
  AMOLEDs consume less power than PMOLEDs. Another advantage of AMOLED display technology is that they have a faster refresh rate and this makes them suitable for video. AMOLEDs are typically used in applications like computer monitors, large-screen TVs and electronic signage.

- **Transparent OLEDs:** Transparent OLED display utilise all transparent components. The substrate, cathode and anode are all transparent enabling light to pass through the whole assembly. In this way, when a transparent OLED display is turned on, it allows light to pass in both directions. This makes this form of OLED technology ideal for applications like head-up displays. They can use either active matrix or passive matrix technologies.

Construction: The multilayer stack consists of a hole injection layer (HIL), a HTL, an electron-blocking layer (EBL), an emission layer (EML), a hole-blocking layer (HBL) and an electron transport layer (ETL). The various blocking and transport layers ensure effective injection of electrons and holes, as well as their subsequent transport to the EML, where they recombine radiatively. The iridium complex is a phosphorescence emitter that allows for highly efficient emissions by harvesting the energy of both singlet and triplet excitons.

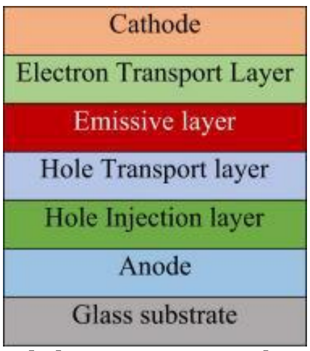
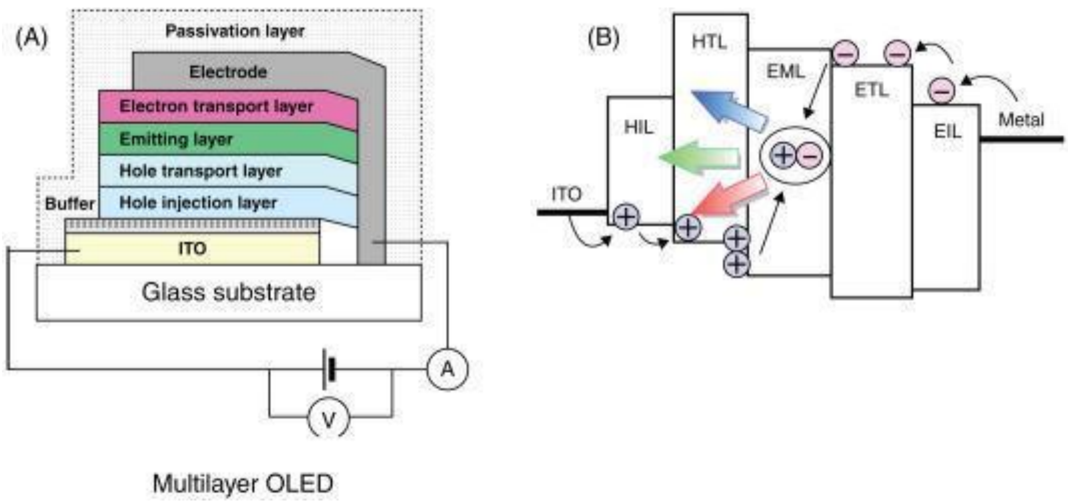


Fig: The general structure of a multilayer OLED is sketched.

OLEDs are based on certain organic small molecules or polymers that behave as diode semiconductors with an applied current. The organic materials derive their semiconducting properties from their highly conjugated pi-bond molecular structures that allow electrons to flow within or across the molecular bonds. Whether single molecules or polymers, they consist of aromatic structures having alternating single and double bonds. Examples of polymers include polyanilines, polyethylenedioxythiophene, and derivatives of polyphenylene vinylene. Examples of small molecules are bis-biphenyl anthracene, pentacene, and metal complexes of aromatic compounds such as copper phthalocyanine.



Light-emitting electrochemical cell (LEC)

Three important solid-state lighting technologies include: light-emitting diodes (LEDs), organic light-emitting diodes (OLEDs) and, most recently, light-emitting electrochemical cells (LECs). The last few years we have seen a tremendous progress in this field with the commercial introduction of the energy-efficient light-emitting diode (LED) lamp and the high-contrast organic LED display. These high-end technologies are, however, produced using costly and complex processes.

The light emitting electrochemical cell (LEC) is a newly invented illumination technology. The LEC was invented by Pei and co-workers in 1995. The LEC is a solid-state thin-film device, which comprises an active material sandwiched between a cathode and an anode (p-n junction doping structure) as its key constituent parts. Those large-area devices emit light when powered by a battery. LEC can be thin, flexible, and light-weight and be driven to essentially any emission color by the low voltage of a battery. It can also be extremely low cost, since it can be fabricated with low-cost printing and coating methods similar to how newspapers are fabricated.

An active-material film sandwiched between two charge-injecting electrodes, one of which must be transparent in order to let the light generated in the active material escape the device structure, as schematically shown in Figure. The active material contains a mixture of a semiconducting and luminenscent conjugated compound and mobile ions, and when a sufficiently large voltage is applied between the two electrodes, an electrochemical doping process is initiated in the active material. Eventually, light-emission is generated within a thin layer, the p-n junction zone, in the active material.

LECs contain ionic compounds in the light-emitting layer, have attracted considerable interest for their solid-state lighting and next generation display applications. Compared with conventional organic light-emitting diodes (OLEDs), LECs contain simple device architecture (generally only one light- emitting layer), and can use air-stable metals (e.g. Al, Ag and Au) as the cathodes directly. In particular, LECs based on ionic transition metal complexes (iTMCs) have received more attention because of their several advantages over conventional polymer-based LECs.

Solid-state light-emitting electrochemical cells (LECs) show the advantages of a simple fabrication process, low-voltage operation, and compatibility with inert electrodes. Employment of air-stabile materials for both electrodes and the use of a thick and uneven active material and hence cost-effective all-ambient solution-based fabrication of LEC devices.

The operation of a light-emitting electrochemical cell

The LEC differs from the OLED by the presence and action of mobile ions. These ions are intermixed with a luminescent organic semiconductor in the active material, which is sandwiched between an anode and a cathode. The organic semiconductor is characterized by a highest occupied molecular orbital (HOMO), a lowest unoccupied molecular orbital (LUMO), and an energy gap between the LUMO and HOMO. The energy gap defines the emission colour of the luminescent organic semiconductor.

When a voltage is applied between the cathode and anode, the mobile ions (being positive cations and/or negative anions) redistribute within the active material toward the electrode/active material interfaces (Figure). The cations and anions form electric double-layers (EDLs) at the cathodic and the anodic interfaces, respectively. These EDLs will screen the bulk of the active material from (most of) the external voltage and confine a large electric field within the EDLs. If the applied voltage is equal to, or larger than, the energy gap of the organic semiconductor, the high electric fields in the EDLs will facilitate for balanced electron and hole injection into the LUMO and HOMO levels, respectively, of the organic semiconductor.

The initially injected electrons and holes are electrostatically compensated by a further redistribution of the mobile ions in order to preserve electroneutrality in the bulk of the active material. At the cathode, the electrons injected on the organic semiconductor will be compensated by cations and at the anode; the injected holes will be compensated by anions (Figure 4(a)). This process is termed electrochemical doping, specifically n-type doping at the cathode and p-type doping at the anode, and the organic semiconductor increases its conductivity significantly during the doping process. With time, the highly conducting p- and n-type doping regions grow in size and eventually make contact under the formation of a p-n junction. Subsequently injected electrons and holes can recombine at the p-n junction under the formation of electron-hole pairs (excitons), which can either decay radiatively (as light) or nonradiatively (as heat) (Figure 4(b))