

Organic Semiconductor Based Display Devices: Architecture, Materials and Fabrications

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Abstract

Although display technologies have been matured enough in most of the applications field but an effort to make more & more compact and precise display, the newly emerging Organic semiconductor based light emitting diode (OLED) technology are taking place. High contrast, self-emitting property, high luminous efficiency, full- colour capability, wide viewing angle, low power consumption, low weight, potentially large area colour displays, flexibility, low temperature fabrication, are some fantastic features, which makes organic semiconductor based OLED most promising for the upcoming future display Technology. The paper presents the review of OLED materials useful for flexible electronic applications and subsequent technological developments based on organic materials which have established a new discipline named as Organic Electronics. The fabrication of Organic semiconductor based devices comes up with nano-engineering for Macro-electronics application and transforms the electronics to excitonics.

Keywords: Organic Semiconductor, Display Devices Architecture, Materials, Fabrication

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1. Introduction

Merging of different fields most of the time gives fruitful results. As merging of “Electronics and Electricals” gives the very improved technologies for communications and still they are progressively improving. In similar manner merging of “Inorganic with Electronics”, which gives the backbone to the semiconducting industry. However, merging of organic with electronics has been growing as a discipline “organic electronics” to improve the semiconducting, conducting, and light-emitting properties of organics (polymers, oligomers) and hybrids (organic-inorganic composites) through synthesis and self-assembly techniques, Organic light-emitting diodes (OLED) technology is part of it. From the several past years Silicon & Gallium

Arsenide semiconductors, silicon dioxide insulators and metals such as aluminium and copper are proved as breakthrough in semiconductor industry. But now time for add new materials and their design to make more accurate & precise electronics industry. Some non-traditional materials such as conjugated organic molecules, short-chain oligomers, longer-chain polymers and organic-inorganic composites are being developed that emit light, conduct current and acts as semiconductors. The ability of these materials to transport holes and electrons (charge carriers) due to the π -orbital overlap of neighbouring molecules provides their semiconducting and conducting properties. The reason behind the improvement in carrier mobility is self-assembling property of these organic and hybrid materials which enhances, π -orbital overlap. Due to the recombination of the charge carriers under an

applied field, formation of an exciton occurred & radiative decay of exciton produce light emission.

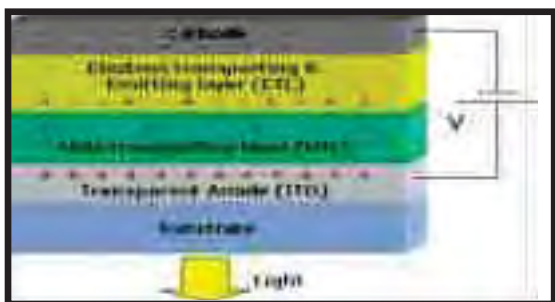


Figure 1: Schematics of typical organic light-emitting diode

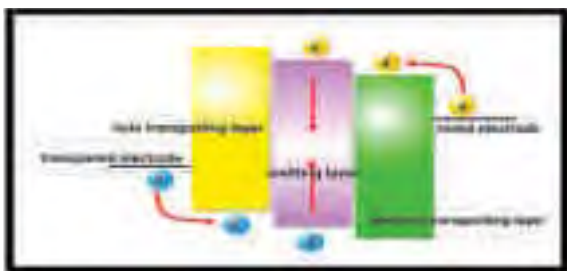


Figure 2: Electron Transport

Some of the thin-film materials possess good electronic, optical & mechanical properties (flexibility and toughness) and can be processed at low temperatures using techniques familiar to the semiconducting and printing industries, such as vacuum evaporation, solution casting, ink-jet printing, and stamping. These properties could lead to new form factors in which roll-to-roll manufacturing could be used to create products such as low-cost information displays on flexible plastic, and logic for smart cards and radio-frequency identification (RFID) tags.

2. Genesis of OLED

From the past few decades the role of lighting technology has been successfully driven by the CRT (CRT is still actively participated in laboratory and also in some experiments) LED

and LCD technology but in present scenario, emerging Technology of “Organic light emitting diode” is replacing the place. This technology is basically based on the principle of Electroluminescence. The first observations of the electroluminescence in organic material were occurred in 1950s by A. Bernanose and co-workers at the Nancy-Université, France on applying the high-voltage alternating current. This experiment was proved as the beginning of the electroluminescent property in organic material but to sort out the problem of the low quantum efficiency, new method of “Ohmic dark-injecting electrode contacts to organic crystals” was developed by Martin Pope and co-Workers at New York University in 1960. Pope's group also first observed direct current (DC) electroluminescence under vacuum on a pure single crystal of anthracene and on anthracene crystals doped with tetracene in 1963 using a small area silver electrode at 400V. Pope's group reported in 1965 that in the absence of an external electric field, the electro luminescence in anthracene crystals which consists of polycyclic benzene rings [1, 2] is caused by the recombination of a thermalized electron and hole, and that the conducting level of anthracene is higher in energy than the exciton energy level. But poor electrical conductivity of organic materials affected the device performance; this problem was vanished by the discovery and development of highly conductive polymers. Electro luminescence from polymer films was first observed by Roger Partridge at the National Physical Laboratory in the United Kingdom. The device consisted of a film of poly(n- vinyl carbazole) up to 2.2 micrometres thick located between two charge injecting electrodes. The results of the project were patented in 1975 and published in 1983. Replacing Technology of cathode ray tubes (CRTs) and Liquid crystal displays (LCDs) was firstly observed from single crystals of anthracene but the Superb work which was proved as milestone in organic electronics industry done by Tang and Van Slyke from

Kodak in 1987 on evaporated small molecules [3] and Another breakthrough of technological interest was the discovery of electro luminescence from polymers at the University of Cambridge in 1990 on solution-processed semiconducting polymers occurred [4].

3. Development of structure of OLED & associated materials

3.1 Basic Architecture of OLED & it's Working Principle

As per as Basic Architecture of OLED concerned, it is made up of by four major blocks. First is Substrate which is made up of Clear plastic, glass and foil, the role of substrate is to support the OLED, Second is Anode(which is may be or may not be Transparent ,depends on the application),it removes electrons(adds electron “holes”) when a current flows through the device. Indium tin oxide(ITO) was used as the anode in OLED. Third is Organic layers, this layer is combination of two layers:1.) Conductive layer (Hole Transport Layer)-Made up of polyaniline or metal-phthalocyanine (organic plastic polymer). This layer transport holes from the anode. 2.) Emissive layer(Electron Transport Layer):Made up of polyfluorene or metal chelates (organic plastic polymer but differs from the conductive one's)And Fourth one is Cathode- The cathode injects electrons when currents flow through the device, generally cathode is made up of Mg, Ca, Ba. Basic Architecture of OLED is shown below in Fig. 3.



Figure 3: Basic Architecture of OLED (reference)

On applying the external voltage of 2V- 10V across cathode to anode, then Current flows from cathode to anode and then electrons flow to emissive layer and electrons is removed from the conductive layer and leaving holes after that holes jump into emissive layer, on recombination of hole and electrons, light will produced. Working principle of OLED is depicted below in Figure (4).



Figure 4: Working principle of OLED

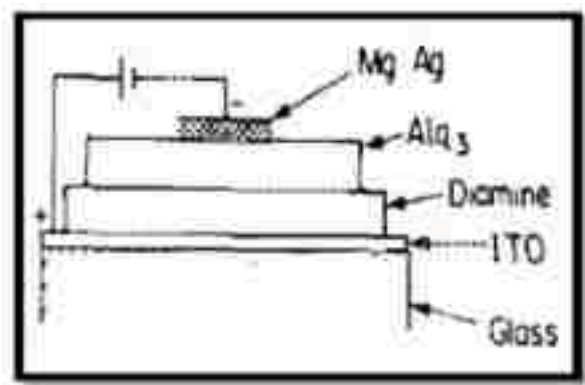


Figure 5: OLED Fabrication

Early thin film Organic device is shown in Figure 5. This was the beginning of such type of organic devices after that not only normal single layer but also multi-layer organic devices were came into the market and researcher are continuously working to improve the structure of Organic devices. Present researchers are

more focussed in multilayer designing of the Organic devices. As depicted in Figure 5, the first layer of cathode is made up by Mg and Ag in ratio of 10:1 then luminescent film of Alq₃ (which will be discussed in OLED materials) of 600Å, which is working as emissive layer or electron transport layer (ETL) in Organic device and Diamine of 750Å, which is working as conductive layer or hole transport layer (HTL) in Organic device, the anode layer is made up of Indium Tin Oxide (ITO). Lastly Glass substrate is used for giving support to the structure. Relative high voltage of 80-100 V applied which decrease the overall efficiency and efficacy of the Organic device. To overcome the drawbacks of this organic device, new multilayer structures and more polymer based materials were used to enhance the overall performance of the Organic device, and still research is on continuation.

3.2 Single and Multilayer OLEDs

On the basis of the device architecture, electroluminescent devices can be categorised into single layer and multilayer OLEDs. In general Single layer OLEDs consist of a metal cathode with a low work function (e.g. Mg, Ca, Al, Ba), an organic emissive layer and a transparent anode [e.g. indium tin oxide (ITO), which is a non-stoichiometric composite of SnO₂ & In₂O₃] immobilized on substrate such as glass or a flexible polymer [5]. Under action of a external voltage, electrons are injected from the cathode into the lowest unoccupied molecular orbital (LUMO) of the adjacent organic layer, while the anode injects holes into the highest occupied molecular orbital (HOMO) of the organic material. The molecular orbital theory better explain ligands, oligomer, polymer and metal chelates, similar to semiconductor band diagram where we study the basic of semiconductor materials in reference of two bands, one is conduction band and Second is valance band. The recombination

of hole and electrons leads to the formation of an “exciton”. exciton is considered as a quasi-particle, capable of migrating, it can be regarded as bounded electron-hole pairs, and also can be viewed as the excited states of molecules which emits light from going to its excited state to the ground state [6]. This process of electroluminescence is the basic working principle of OLEDs. An equally efficient injection but also equal mobility of electrons and holes in the organic material are very important, because it boost the recombination phenomenon in electroluminescent material which occurred in the emissive layer of the organic device. However, to achieve the balanced charge injection or carrier mobility in the simple device architecture of single layer OLEDs is difficult which resulting in decreased efficiencies because of exciton quenching processes close to the electrodes or non-radiative recombination of charges at the electrodes (reverse saturation current) [6].

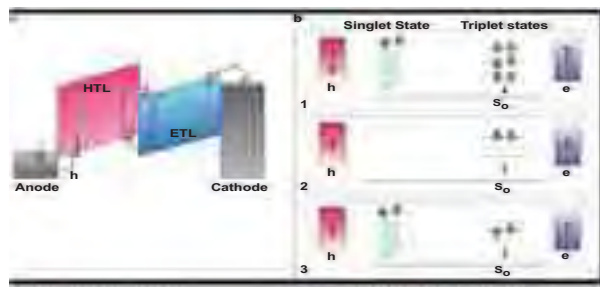


Figure 6: Multilayer Architecture

These problems can be sort out by the joining of additional layers giving multilayer OLEDs. In these type of organic devices the emitter is sandwiched between hole and electron transport layers (that is in between conductive layer and emissive layer) providing facilitated charge injection and increased the level of recombination of electrons and holes in the emissive layer and this leads to shifting the active zone roughly to the middle of the OLED structure. In nutshell OLEDs have range up to five layers, containing charge and exciton

blocking layers being essential for excellent device performance. Additionally, it should be mentioned that also doping of the transport levels can be used for increasing the efficiencies and efficacy of the corresponding light-emitting devices [7]. A normal single layer organic device is shown in Figure 5 and a multilayer architecture is shown in Figure 6.

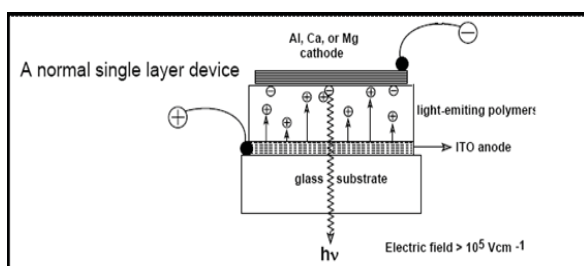


Figure 7: A normal single layer organic device

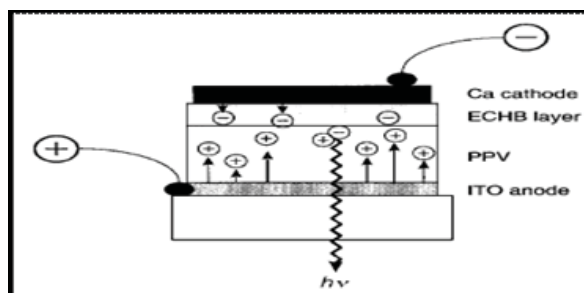


Figure 8: Multilayer Organic device

3.3 Small Molecule OLEDs (smOLEDs) & Polymeric Light-emitting Devices (PLEDs)

Conventional light-emitting devices available in today potential market are commonly made up from the inorganic crystals such as GaAs or GaN (direct band gap semiconductor material). Although these devices performance are good for many applications but their use in large area displays or on flexible substrates is limited or even impossible because of the brittle crystals grown by expensive epitaxial methods [8]. As to overcome all these problems organic

materials have soon be considered to be very promising alternatives to inorganic semiconductors, however, the practical application of OLEDs was unrealistic due to high operating voltages greater than 100 V until the fundamental breakthrough of Tang et al.(Kodak) in 1987 [9]. The milestone achievement of a double-layered architecture consisting of a hole transporting layer(HTL) and an emissive layer(ETL) of aluminum quinolinolate (Alq3) gave electroluminescence around $1,000 \text{ cd/m}^2$ at driving voltages of 10 V and is still the prototype setup for OLEDs [10]. Since that time enormous scientific progress has been made which resulting in numerous small molecules suitable for applications in OLEDs (commonly referred to as “small molecule OLEDs”, smOLEDs). Because thin films of these emitter materials are usually prepared by vacuum deposition methods, the interest in organic electroluminescence has further been highlighted by the incorporation of electroluminescence from conjugated polymers(aromatic conjugated polymers) providing the possibility of solution processing (commonly referred to as “polymeric light-emitting devices”, PLEDs) [11]. As a result of this progress, organic semiconductors (organic electronics) have developed rapidly and it is not only the topic of research interest but soon it becomes the field of different range of applications in display Technology. In this context, considerable advances concerning materials chemistry (e.g. the use of phosphorescent materials, polymer materials, hybrid materials to increase device efficiencies), device fabrication methods and device optimization [12] have been made giving OLEDs based on fluorescent small molecules, phosphorescent small molecules as well as polymeric materials (PLEDs) meeting industrial specifications. Although processing techniques are different for smOLEDs and PLEDs, but their working principle is basically the same.

3.4 Differences Between Polymer LEDs and Small Organic Molecule LEDs

In present scenario the all light emitting technology or we can say display technology deals exclusively with organic layers which is prepared in vacuum from low molecular weight organic semiconducting materials. The field of organic semiconductors includes also an additional field, namely polymeric semiconductors. The main difference between these two classes of materials from a designing point of view is that polymers are usually prepared by spin coating from a solution onto the desired substrate with following heating/drying cycles. This results in some differences, which are summarized in Table (1). Organic materials based on vacuum sublimable small molecules can be cleaned repeatedly until the purity shows the desired level. Furthermore, their storage and processing in vacuum conserves this purity. Whereas, polymer layers sometimes suffer from intrinsic impurities originating from their synthesis or remainders of the solvents. This is true for blue light emitting polymers. Furthermore, it is difficult to spin coat more than two polymer layers because of the demand for solution incompatibility among consecutive layers. To prevent this limitation, mixed layers of a matrix polymer and several transport molecules are sometimes used, but they suffer from decreased motilities'. Again, it is highly difficult to spin coat polymer layers uniformly on substrates greater than 5 inches and preserves their high quality. However, the operating voltage of polymer LEDs is usually lower than for comparable OLEDs. At the present, it is not clear which technology succeeds or if both technologies will co-exist. Both show some advantages and comparable device performances.

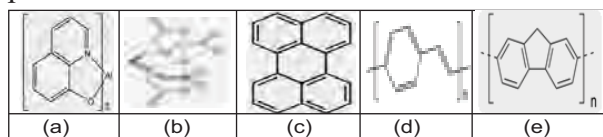


Figure 9: Small molecules material (a) Alq3Tris

(8-hydroxyquinolino) aluminum (b) chelate (c) perylene and PLED or LEP materials (d) poly (*p*-phenylenevinylene), (e) Polyfluorene

Table 1: Comparison of OLED & PLED

PROPERTIES	OLED	PLED
Preparation	Vacuum sublimation	Spin coating under atmosphere
Advantages	Control of purity & compatibility to CMOS technology	Low-cost (patterning by printing)
Disadvantages	Expensive vacuum system needed, mask positioning problems for multi-colour OLED-displays	Impurity & solubility incongruity
Conductivity	Undoped :<10 ⁻⁸ S/cm	same, but conducting polymers are possible by using chemical doping
Injection Behaviour	no level bending, interfacial dipoles favour electron injection	level bending assumed as easier injection
Mobilities (at around 1MV/cm, strongly field dependent!)	10 ⁻⁵ to 10 ⁻³ cm ² /Vs	Same order
Operating voltage	4.5-6 V (100 cd/m ²)	2.5-3.5 V (100 cd/m ²)
Lifetime	>10000 h	comparable except for blue

4. Synthesis and characterization of the Materials for OLED

4.1 Hole Transporting Materials (HTMs)

4.1.1 Biphenyl Diamine Group

There are various types of materials reported which show hole transporting characteristics, such as spiro compounds, tri-arylamines, starburst amine etc. As the early reports of bi-layer OLED structures, N,N'-diphenyl-N,N'-bis (3-methylphenyl) (1,1'-biphenyl)-4,4'-diamine (TPD) is a well known material and often used as hole transport material (HTM). But due to the poor thermal stability (glass transition temperature: T_g = 60 °C) of TPD, the

efficiency tends to reduce and the material leads to readily crystallize. So that, for improving the T_g , various derivatives of TPD have been examined by replacing the phenyl(3-methylphenyl)amino group (Figure 9). This contains the naphthyl substitution molecule N,N'-bis(1-naphthyl)-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB). This exhibited high stability in the OLEDs due to its higher T_g (95 °C) than TPD [13, 14]. However, NPB has an ionization potential of 5.7 eV [15, 16], indicating the state of existing of a high injection barrier at the interface of the ITO anode (~ 5.0 eV). Substitution of phenyl(3-methylphenyl)amino to carbazolyl in TPD, CBP (4,4'-di(N-carbazolyl)biphenyl), has high triplet energy level (2.56 eV) [16]. This is a good applicant material for green phosphorescent emitters that readily allows energy transfer [17, 18].

4.1.2 Spiro-linked Molecules

Upgrade thermal stability is achieved by linking two arylamine moieties via a spiro centre by introducing a 90° angle. These are so called spiro-linked compounds which generally exhibit a higher T_g . Several spiro-linked materials have been examined by the group of Salbeck. The spiro-linked molecules showed high hole mobility in field effect transistor devices and did not exhibit a significant change in the mobility after a storage for three months in air [18]. 2,2',7,7'-tetrakis(diphenylamino)-9,9'-spirobifluorene (Spiro-TAD) shows nearly a double T_g of 133 °C, compared to its parent molecule TAD ($T_g = 70$ °C). Combination of hole transporting Spiro-TAD with an electron transporting Spiro-PBD has been demonstrated and used in OLED device [19]. The device has exhibited a blue luminescence with a turn-on voltage of 2.7 V and a luminance of 500 cd/m² at 5 V. Different hole transport materials such as Spiro-TAD and NPB [20] were used to check and compared the thermal stability of OLED

devices. The device with the NPD showed significant degradation in efficiency whereas the device with Spiro-TAD exhibited stable characteristics even with annealing at 140 °C. The favourably hole transporting Spiro-TAD can be put to use as electron blocking layer in p-i-n type OLED as well [21, 22].

4.1.3 Starburst Molecules

Starburst molecules are non-planar geometry compounds having three identical branches from a central N atom or phenyl group and were originated by Shirota et al [23]. This type of materials is bulky. When m-methyl-4, 4', 4''-tris(diphenylamino)-triphenylamine (m-MTDATA) is used in the hole only device, trap free space charge limited current is provided by the ohmic interface which is established in between the hole transport material m-MTDATA & ITO anode at high currents [24]. The performance & analysis in the bi-layer OLED device using an ETL of Alq3 and a HTL of m-MTDATA exhibited higher current injection compared to that with HTL of NPD [25]. starburst materials such as m-MTDATA and 1-TNATA (4, 4', 4''-tris[1-naphthyl(phenyl)amino]triphenylamine) possess low ionization potential, they can be put to use as a hole injection layer by inserting between ITO and HTL, tending to high current injection and low operating voltage [26, 27].

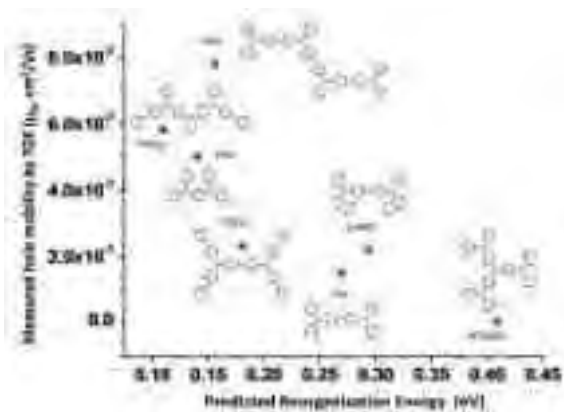


Figure 10: Graph of starburst molecules

4.1.4 Doped Highly Conductive Hole Transport Materials

Several methodology are used, for enhancing the hole injection from the anode. surface oxidation of ITO anode by UV ozone, O_2 plasma, Cf_4/O_2 plasma treatment [28, 29] or inserting a hole injection layer with low ionised potential such as copper phthalocyanine (CuPc) [30], polyaniline [31, 32] between ITO and HTL are some examples of the methodology which have been used. The purpose behind all these techniques is to reduce the energy barrier at the interface of ITO/HTL. another improvement of carrier injection was incorporated by HTMs doped with oxidizing agents such as $FeCl_3$ [33], iodine [34], tris(4-bromophenyl) a minium hexa chloroan-timonate (TBAHA) [35] or strong electron acceptor molecules 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4 -TCNQ) [9]. It was discovered that a meaningful improvement in the conductivity is obtained by combination of F_4 -TCNQ, as with various hole transport matrices, such as zinc phthalocyanine (ZnPc) [36, 37], m-MTDATA [38], MeO-TPD [22]. All these type of materials have an ionisation potential around 5.1 eV which is nearby the electron affinity of F_4 -TCNQ so that an easy charge transfer can established. Spiro-m-TTB is also a candidate for the matrix due to its low ionisation potential (~ 5.1 eV) and high mobility ($3\sim 4 \times 10^{-4} \text{ cm}^2/\text{Vs}$ [39]. It was discovered that the space charge layer between ITO and ZnPc was diminished by the doping of F_4 -TCNQ[40]. This implies that an Ohmic contact is formed by tunnelling injection from the anode, which is also discovered in inorganic semiconductors. The exhibition of the p-type HTL (p-HTL) in multi layered OLEDs [ITO/TNATA:2% F_4 -TCNQ(100 nm)/TPD(10 nm)Alq3(65 nm)/LiF(1 nm)/Al] revealed a very low operating voltage of 3.4 V for 100 cd/m², compared to OLEDs with un-doped HTL showing an operating voltage of 9.0 V for

100 cd/m² [38]. However, F_4 -TCNQ is not thermally stable (sublimation temperature is 90 to 100 °C) and it can diffuse in the organic layers. A new p-type dopant NDP2 was reported from Novaled AG, which has better thermal stability [41].

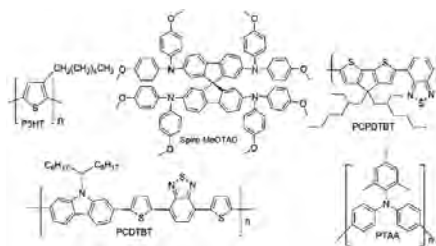


Figure 11: Doped highly conductive hole transport materials.

4.2 Electron Transporting Materials (ETMs)

Alq3 is still one of the most widely used electron transporting materials (ETMs) of OLED because of its thermal and morphological stability and easy synthesis. This material can be put into use both as a green fluorescent emitter and host matrix for green and red emitters [42]. Other ETMs include molecules containing electron accepting moieties such as 1,3,4-oxadiazole (OXD), triazole, triazine, pyridine etc. 2-(Biphenyl-4-yl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) has been used as an ETM in OLED device and exhibited outstanding electron transport and exciton confinement [43]. Although, this material is readily crystallised, tending to poor durability under continuous device operation due to the lack of electrochemical stability [44]. PBD derivatives (OXD-7) [45], spiro-linked (Spiro-PBD) [46, 47], were synthesised to improve morphological and thermal stability of the film. The triazole containing compound 3-phenyl-4-(1'-naphthyl)-5-phenyl-1,2,4-triazole (TAZ) has also been noticed to perform as an ETM [48].

ETMs showing a deep HOMO level such as bis-(2-methyl-8-quinolinolato)-4-(phenylphenolato) aluminum-(III) (BAIq), 2,9-dimethyl-4,7-diphenylphenanthroline (BCP) and 4,7-diphenylphenanthroline (Bphen) and TAZ can be put to used as HBL as well [49]. These materials capable to confine charges in the EML.



Figure 12: Electron transporting materials

4.2.1 Doped Highly Conductive Electron Transport Materials

To increase the efficiency of OLED devices, electron and hole injections are needed. As most of the OLEDs, having majority carriers as holes due to their higher mobility and easier injection. In the case of n-type ETLs (n-ETL), the ionisation potential of the n-dopant should be above the level of the LUMO of electron transport matrices. The LUMO level of the n-ETLs is normally around 3.0 eV, and a higher energy of the HOMO (< 3.0 eV) for a n-type dopant (n-dopant) is required. Feasible candidates for n-dopants include alkali metals such as Li [50, 51] and Cs [52] or high-lying HOMO molecules like Ru(terpy)2 [53]. ZnPc behaves as either p- or n-type by choosing the dopant F4-TCNQ or Ru(terpy)2, respectively. Very thin films of LiF can improve the electron injection into the devices, tending to an upgrade in efficiency for OLED applications [54 - 56]. Doping of Bphen with Cs results in more than 10^{-5} S/cm of conductivity in n-ETL [57, 58]. Finally, the p-i-n structure was realised by comprising both p-HTL and n-ETL [57]. For the n-ETL, Cs doped and non doped Bphen in

the p-i-n OLEDs using p-HTL (MeO-TPD:F4-TCNQ) were compared. The p-i-n-type OLED exhibited higher current injection compared to the p-i-i type OLED, and hence dramatically lower operating voltage. An electron transport molecule NTCDA (1,4,5,8-naphthalene-tetracarboxylic dianhydride) doped within has a very high conductivity (9.1×10^{-2} S/cm) and is very stable in air by time [58]. However, the LUMO of NTCDA lies rather deep level (~ 3.6 eV), thus its utilisation as n-ETL would be preferable for organic solar cells rather than OLEDs.

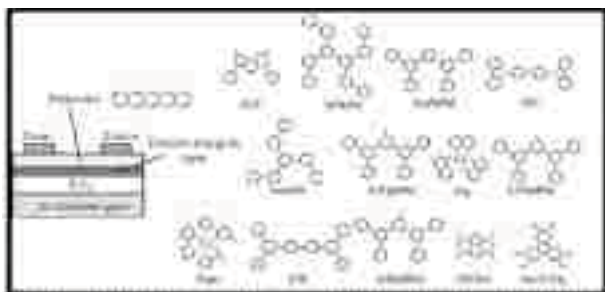


Figure 13: Doped highly conductive electron transport materials

4.3 Emitter Materials

The well selections of emitter materials are very important factor to complete the requirement of good display device. This emitter material allows the colour variety which is one of the features for OLEDs. The desirable emission colour can be obtained by selecting the emitter material, which is normally doped in an adequate host material to allow an efficient energy transfer. In the first report of OLEDs by Tang et al., a single layer of Alq3 was employed as an emitter (also as ETL). Later, the demonstration of doping with fluorescent dyes in OLED led to higher efficiency [59]. There has been two type of Emitter materials are reported 1. Fluorescent materials 2. Phosphorescent materials.

Assuming that balanced charge injection is

possible and that all injected charges recombine, considerations on quantum statistics are crucial for the realization of devices exhibiting high efficiencies [60]. In molecular orbital theory to understand the structure of small molecules OLED and polymer based OLED, the singlet and triplet states are used. Singlet excitons are states with an anti-symmetric spin and a total spin quantum number $S = 0$. The quantum mechanically allowed transition to the ground state gives rise to fluorescence within nanoseconds. Conversely, triplet states have an even symmetry with $S = 1$ whose transition to the singlet ground state is quantum mechanically forbidden resulting in phosphorescence with lifetimes in the microsecond to second regime. As a consequence of the corresponding multiplicities of the angular momentum states (i.e. $m_S = 0$ for $S = 0$ and $m_S = -1, 0, 1$ for $S = 1$) and the random nature of spin production in electroluminescent devices, simple statistics predicts that only 25% of the injected charges result fluorescence (from singlet states) whereas 75% give phosphorescence (from triplet states) in suitable device architectures. Thus, uncorrelated electrons and holes form triplet states with a threefold higher probability than singlet states. Here it should be mentioned, that recent studies on spin statistics suggest variations in the singlet-to-triplet-ratios. These findings have also been confirmed by quantum mechanical calculations [61]. The ground states of most luminescent materials are singlet states and the vast majority of luminescent compounds exhibit only weak spin-orbit couplings rendering these small molecules and polymers fluorescent with negligible radiative rates from triplet states. Competing non-radiative processes (e.g. triplet-triplet annihilation or vibronic relaxation) effectively quench the phosphorescence of the associated excited states clearly limiting the maximum quantum efficiency achievable with fluorescent small molecules and polymeric materials [62]. Since the pioneering work of Baldo et al. showing that phosphorescent dyes (transition

metal compounds with organic ligands or organometallic compounds) doped into appropriate host materials give improved OLEDs [63], considerable scientific efforts have provided numerous new materials for electro-phosphorescent devices reaching impressive external quantum efficiencies. Although these devices usually require elaborated multilayer structures, the fast and efficient intersystem crossing (ISC) (ISC: intersystem crossing is a radiation-less process involving a transition between two electronic states with different multiplicity), from excited singlet to light-emitting triplet states caused by strong spin-orbit couplings as well as the ability of triplet harvesting allow theoretically quantum efficiencies of 100% [64,65]. Today, a huge number of phosphorescent dyes are used in phosphorescent OLEDs utilizing different metal complexes containing transition metals such as iridium, platinum, osmium, ruthenium, etc. [66-68]. These transition metal complexes definitely exhibit a series of very desirable materials properties such as emission wavelengths covering the entire visible spectrum, high quantum yields and long lifetimes, however, severe concentration quenching is observed for most pure layers of phosphorescent dyes [69]. Consequently, phosphorescent dyes are usually blended into suitable host materials (small molecules or polymers) from which the excitation energy is transferred to the phosphorescent guest. Thus, basic knowledge about the energy transfer processes is required for understanding the working principle of phosphorescent OLEDs. As per as Charge recombination and efficiency are concerned, after carrier injection and transport, both electrons and holes can recombine. Holes and electrons recombination process is the basis of various excited states such as singlet excitons, triplet excitons and charge transfer excitons (according to the molecular orbital theory) In fluorescence devices, the emission is due to the radiative decays of singlet excitons (SEs), as radiative triplet exciton (TE) is forbidden. If we assume

that the probability of recombination of electron- holepairs in the singlet spin configuration to SEs is equal to the probability of recombination of pairs in the triplet spin configuration to TEs, then only a quarter of the pairs will recombine to the radiative SEs. So the internal EL efficiency or internal quantum efficiency will be limited to a maximum of 25% when there is no other quenching of SEs, and the hole-electron density is ideally balanced, i.e., equal to 1. Typically, SEs is quenched by various processes such as charge transfer to another molecule, traps and defects.

5. OLEDs Fabrication Methods

OLEDs are light emitting devices that have a thin film of organic compounds as its emissive electroluminescent layer. Physical Vapour Deposition, Screen Printing, Ink Jet Printing, In-line Fabrication, these are all OLED Fabrication methods. Substrate preparation is the first step in OLED fabrication, Device deposition is the next one where three steps are involved and these are as follows i) Deposit and pattern anode ii) Pattern organic layers iii) Vacuum deposit and pattern cathode. Finally the Encapsulation is last step which makes the OLED more robust to fight with environment adverse effect.



Figure14: fabrication process of OLED

Figure 14 demonstrated the step involved in fabrication process of OLED. As shown in Figure(15)Physical Vapour Deposition (PVD) are given. In this methodThermal vapor

evaporation of small molecules occurs in environment of 10^{-6} Torr or higher, It is usually carried out on glass substrate and Multicolor displays are made using properly matched shadow masks for depositing RGB emitting materials. As per as advantageous part of the PVD concerned, at first the Thickness can be easily controlled by using PVD method in OLED fabrication, secondly a two-dimensional arrays of OLEDs can be easily fabricated in a single deposition procedure and lastly PVD method uses the generally available vacuum equipment that exist in the semiconductor industry. But if we are utilizing this process in large scale of OLED production, this process is highly expensive and not flexible, in this process there is no control to direct the materials to deposit on the desired areas and also inefficient use of materials these are all factors leads to the less-popularity of this method.



Figure15: Physical Vapour Deposition (PVD)

Screen printing is the another approach in Fabrication of OLED, it is used for low information content displays such as logos and signs. In this process Thin films achieved which enhanced its efficiency. Elements of screen printing are screen, stencil, squeegee, ink, press bed, and substrate and Mesh materials can vary from polyester to stainless steel. Steps of screen printing are as follows: i) the mesh material is stretched across a frame. ii.) Hole transport layer prepared using a solution of diamine,

polycarbonate, and rubrene. iii) Squeegee is used to wipe solution through the open mesh. iv) Resulting film covers entire surface of ITO. v) Electron transport layer (ETL) and cathode are deposited by PVD. For patterned hole transport layer (HTL) devices, cathode is deposited in a block larger than the HTL pattern whereas for non-patterned HTL, cathode is deposited through a mask to create emitting regions of known area for device output measurement. Screen printing is more versatile. Comparatively these process possess lower cost and efficient usage of materials because materials are only directed to the printed areas. Screen printing is faster than the inkjet printing. But inkjet printing allows OLEDs to be printed on very large films, OLEDs are sprayed onto substrates like ink sprayed on paper during printing. Figure(16) illustrates the situation.

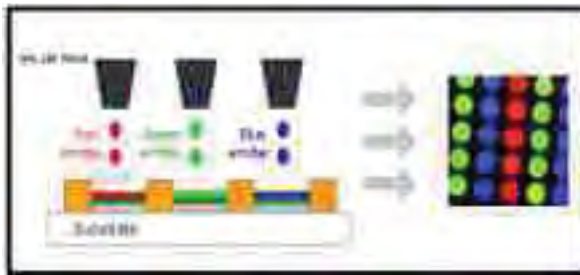


Figure 16: Ink-jet printing

Above discussed all methods are application dependent and possess some problem in large domain production. To overcome all problems, in-line fabrication process is adapted which is basically a mass production technique where vertical in-line tool operates with continuous substrate flow. Linear sources of depositing organic and metallic materials are used. In-line fabrication exhibits several advantages and these are as follows: i) Excellent thickness homogeneity ii) Excellent deposition stability iii) Complicated stack structures possible iv) High deposition rates/high throughput v) High material usage vi) Large substrate handling vii) Cheaper mass production technique. Figure (17) demonstrates the OLED Fabrication Roadmap.



Figure 17: OLED Fabrication Roadmap

6. Types of OLED

There currently are six types of OLED screens, each designed for a different type of use. The types are:

6.1 Passive Matrix OLEDs (PMOLEDs)

PMOLEDs have strips of cathode, organic layers and strips of anode. The anode strips are arranged perpendicular to the cathode strips. The intersections of the cathode and anode make up the pixels where light is emitted. External circuitry applies current to selected strips of anode and cathode, determining which pixels get turned on and which pixels remain off. Again, the brightness of each pixel is proportional to the amount of applied current. Designing of PMOLEDs is easy, but they consume more power than other types of OLED which leads to decrease in efficiency.



Figure 18: Passive matrix OLED

PMOLEDs are mostly used in designing for text and icons and are best suited for small screens (2- to 3-inch diagonal). Cell phones, PDAs and MP3 players are some examples where

PMOLEDs are used. Even with the external circuitry, PMOLEDs consume less battery power than the LCDs. A PMOLED display uses a simple control scheme in which you control each row (or line) in the display sequentially (one at a time). PMOLED electronics do not include a storage capacitor and so the pixels in each line are actually off most of the time. To make up for this you need to use more voltage to make them brighter. If you have 11 lines, for example, you have to make the one line that is on 11 times as bright (the real number is less than 11, but that's the general idea).

So while PMOLEDs are easy (and low cost) to fabricate, but it shows some disadvantages as they are not efficient as they possess lower lifetime (due to the high voltage needed from the external circuitry). PMOLED displays are also constrained in resolution and size (the more lines you have, the more voltage you have to use). The first OLED products in the market used PMOLEDs - these were MP3 players, sub-displays on cellphones and radio decks for automobiles. The displays were small and usually with just one or two colors. When AMOLED panels started to emerge in 2007 and 2008 we have seen these larger displays in mobile video players, digital cameras, mobile phones main displays and even OLED TV sets.

6.2 Active-matrix OLEDs (AMOLEDs)

AMOLEDs have full layers of cathode, organic molecules and anode, but the anode layer overlays a thin film transistor (TFT) array that constitutes a matrix. The TFT array itself is the circuitry that decides which pixels get activated to form an image. AMOLEDs belongs lesser power consumption than PMOLEDs because the TFT array claims less power than external circuitry, so that they can be put in efficient use for large displays. AMOLEDs also have rapid refresh rates which is suitable for video

applications. AMOLEDs are used in computer monitors, large-screen TVs and electronic signs or bill boards. AMOLED (active-matrix organic light-emitting diode) is a display technology for use in mobile devices and televisions. Table(2) demonstrate some AMOLED applications.

Table 2: Application of AMOLED

Term	Resolution	Size (Inches)	PPI	Pixel Layout	Used In
AMOLED Capacitive Touchscreen	640x380	3.2	229	RGBG PenTile	Nokia CB-01
Super AMOLED	800x480	4.0	233	RGBG PenTile	Samsung Galaxy S
Super AMOLED Advanced	980x540	4.3	256	RGBG PenTile	Motorola Droid RAZR
qHD Super Amoled	960x540	4.3	218	RGB S-Stripe	Samsung Galaxy S4 Mini
Super AMOLED Plus	800x480	4.3 (4.27)	218	RGB stripe	Samsung Galaxy S II
HD Super AMOLED	1280x800	5.3 (5.29)	285	RGBG PenTile	Samsung Galaxy Note
HD Super AMOLED	1280x720	5.0	295	RGB S-Stripe	Black Berry Z30
HD Super AMOLED	1280x720	4.7 (4.65)	316	RGBG PenTile	Samsung Galaxy Nexus
HD Super AMOLED	1280x720	4.7 (4.65)	316	RGB S-Stripe	Motorola Moto X
HD Super AMOLED	1280x720	4.8	306	RGBG PenTile	Samsung Galaxy S III
HD Super AMOLED	1280x720	5.6 (5.55)	267	RGB S-Stripe	Samsung Galaxy Note II
HD Super AMOLED Plus	1280x800	7.7	197	RGB Stripe	Samsung Galaxy Tab 7.7
Full HD Super AMOLED	1920x1080	5.0	441	RGBG PenTile	Samsung Galaxy S4
Full HD Super AMOLED	1920x1080	5.7	388	RGBG PenTile	Samsung Galaxy Note 3

An AMOLED display made up of an active matrix of OLED pixels that generate light (luminescence or electroluminescence) upon electrical activation, that have been integrated onto a TFT array, which functions as a series of switches to control the current flowing to each distinct pixel. Typically, this continuous current flow is regulated by at least two TFTs at each pixel (to trigger the luminescence), with one TFT to start and stop the charging of a storage capacitor and the second to provide a voltage source at the level needed to produce a constant current to the pixel, thereby removing the need for the very high currents needed for passive-matrix OLED operation.

TFT backplane technology is very important in the fabrication of AMOLED displays. The two primary TFT backplane technologies1.) Polycrystalline silicon (poly-Si) and 2.) Amorphous silicon (a-Si), are used today in AMOLEDs. These technologies express the potential for fabricating the active-matrix backplanes at low temperatures (below 150°C) clearly onto flexible plastic substrates for producing flexible AMOLED displays. Figure(19) demonstrate AMOLED.



Figure 19: Active- Matrix OLED

6. 3 Transparent OLEDs

This includes only transparent components (substrate, cathode and anode) and, when activated off, are up to 85% as transparent as their substrate. When a transparent OLED display is activated on, it allows light to go through in both directions. A transparent OLED display can be either active- or passive-matrix. Figure(19) demonstrate Transparent OLED.



Figure 20: Transparent OLED

6. 4 Top-emitting OLEDs

Top-emitting OLEDs have a substrate that is either opaque or reflective. They are best appropriate to active-matrix design. Designer may use top-emitting OLED displays in smart cards. Figure 21 illustrate the Top-emitting OLEDs.



Figure 21: Top-Emitting OLED

6. 5 White OLEDs

White OLEDs emit white light that is more luminous, more uniform and more energy efficient than that emitted by fluorescent lights. White OLEDs also have the true-color qualities of incandescent lighting. Because OLEDs can be made in large sheets, they can replace fluorescent lights that are currently used in homes and buildings. Their use could potentially reduce energy costs for lighting.



Figure 22: White OLED

6. 6 Foldable or flexible OLEDs

Flexible OLED is a newly emergent display technology that enables brighter and efficient display. Basically A flexible OLED is based on a flexible substrate which can be plastic, metal or flexible glass. The plastic and metal panels will be light, thin and very durable and they are also virtually shatter-proof. Figure (23) depicts the flexibility of OLED.



Figure 23: Flexible OLED

Second generation flexible OLED devices may be more flexible and more advanced. Finally, when the technology is ready, we may see OLED panels that you can fold, bend or stretch.

This may lead all sorts of exciting designs that will occupy large displays to be placed in a mobile device and only be opened when needed. After years of research, in October 2013, Samsung announced the world's first product to use a flexible OLED display - the Galaxy Round curved smartphone. This is an Android 4.3 smartphone similar to the Galaxy Note 3, with the major feature being the 5.7" Full-HD curved (400 mm curvature radius) flexible display (Samsung simply refers to it as a flexible Super AMOLED, strangely they are not using the YOUM brand)[70].

7. Electro-Optical Characteristics

7.1 Emission

Basically OLEDs are [71,74] Lambertian surface emitters, which means that they have the same apparent radiance when observed from any angle. This characteristic can be changed to some extent by modifying the composition of the micro-cavity. Effective beam shaping is only possible by means of additional external optical elements such as micro-lens arrays. The emission color of an OLED displays a notable angular dependency which can be deduced by applying a diffuser film on the emitting surface. The angular shift of the color in CIE space can be reduced by more than one order of magnitude by means of a diffuser, while enhancing the out-coupling efficiency up to 50 % at the same time.

7.2 Emission intensity

The Emission intensity of an OLED is generally characterized by its luminance, which is a measure of the luminous intensity per unit area of light propagating in a given direction. The unit for luminance is cd/m^2 , often also called "nit". Typical luminance values range from 300

cd/m^2 for mood lighting up to a few thousand cd/m^2 for general illumination. This translates into a luminous flux between 10 and 100 lumen for a device area of 100cm^2 . The efficacy (effectiveness) of OLEDs and other light sources is measured in lumen per watt and is called "luminous efficacy". Sometimes, specifications also include the external quantum efficiency, which relates the number of generated photons to the number of injected electron-hole pairs.

7.3 Current density-Voltage and Brightness-Voltage characteristics

Typical current density-voltage and brightness-voltage characteristics of OLED are shown in figure (25). In general, the luminance is directly proportional to the operating current. Stacked devices are driven at a multiple of the operating voltage of a simple device at the same luminance, depending on the number of emitting units. At the same time, the operating current is lower, so that the luminous efficacy is about the same for both device architectures. However, the differential resistivity, i.e. the slope of the voltage-luminance characteristics, is deduced, which makes stacked architectures (Figure 24) favorable for the fabrication of large-area devices.

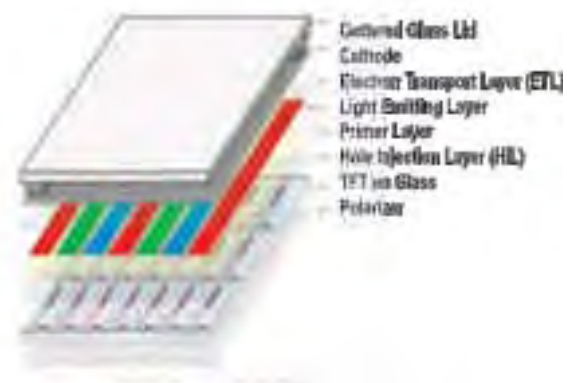


Figure 24: Stacked architecture of OLED

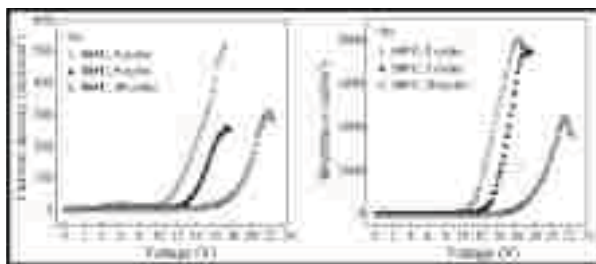


Figure 25: Current density-voltage and brightness-voltage characteristic

7.4 Color Rendering Index

The color rendering index (CRI) is a quantitative measure of the ability of a light source to reproduce the colors of various objects (similarly to a natural light source). A CRI of 100 means that the light source has the same illuminating properties as incandescent light (CCT < 5,000 K) or daylight (CCT > 5,000 K). It is very important electro-optical characteristics. Any value below 100 indicates a deficiency in some spectral region. The emission spectrum of an organic molecule is naturally broad and it is easy to achieve a CRI above 80 by combining a red, a green and a blue emitter. In addition, when looking at the spectrum, it becomes apparent that OLEDs emit neither UV nor IR radiation.

8. Advantages and Disadvantages of OLED

8.1 Advantages of OLED

LCD and LED are display technology in earlier days but now the display technology is shifted in new arena of OLED technology. But nevertheless to say LCD is also currently the display of choice in small devices and is also popular in large-screen TVs and Regular LEDs often form the digits on digital clocks and other electronic devices. OLEDs offer several unique features:

- They can be very thin, mainly limited by the thickness of the substrate and encapsulation, and therefore very light-weight that is compact in size.
- They are glare-free area light sources which can be transparent or have either a mirror-like or milky appearance when activated off.
- They possess high colour quality and activate quickly when current is applied.
- They have the potential to be equally or more efficient and long-living than fluorescent lamps, and being 100 % mercury-free.
- They emit neither UV nor IR radiation which makes it eco-friendly.
- Future products based on OLED technology may even be foldable or flexible.[72]

On moving through the Explanation of OLED Advantages, the very first point is its production and cost. As OLEDs can be printed onto any suitable substrate by an inkjet printer or even by screen printing, theoretically making them cheaper to produce than LCD or plasma displays. There is very strong anticipation that OLED will soon grab potential market and as well emerging market. However, fabrication of the OLED substrate is more costly than that of a TFT LCD, until mass production methods lower cost through scalability. Roll-to-roll vapour-deposition methods for organic devices do allow mass production of thousands of devices per minute for minimal cost. Next point is Lightweight and flexible plastic substrates as OLED displays can be fabricated on flexible plastic substrates tending to the possible fabrication of flexible organic light-emitting diodes for further new applications, such as roll-up display embedded in fabrics or clothing. As the substrate used can be flexible such as polyethylene terephthalate (PET), the displays may be produced inexpensively. Next point is Wider viewing angles and improved brightness as OLEDs can enable a greater artificial contrast ratio (both dynamic range and

static, measured in purely dark conditions) and a wider viewing angle compared to LCDs and LEDs because OLED pixels emit light directly. OLED pixel colours appear correct and unshifted, even as the viewing angle approaches 90° from normal. This feature is very useful to apply in upcoming display technology. Next point is better power efficiency and thickness asfirst; a larger production scale is needed, because OLEDs still somewhat are small products. When looking at top-emitting OLEDs, thickness also plays a role when talking about index match layers (IMLs). Emission intensity is increased when the IML thickness is 1.3–2.5 nm. The refractive value & the matching of the optical IMLs property, adding the device structure parameters, also increase the emission intensity at these thicknesses. And lastly Response time of OLEDs also can have a faster than standard LCD screens. Whereas LCD displays are capable of between 1 and 16 ms response time offering a refresh rate of 60 to 480 Hz, an OLED theoretically and practically can have a response time less than 0.01 ms, allow a refresh rate up to 100,000 Hz.. OLEDs also can be run as a flicker display, similar to a CRT, in order to eliminate the sample-and-hold effect that creates motion blur on OLEDs.



Figure 26: more clearly view in OLED

8.2 Disadvantages of OLED

OLED seem to be the very perfect technology,

although it is but it also poses some disadvantages, as OLED manufacture currently requires process steps that make it highly expensive. Specifically, it requires the use of low-temperature polysilicon backplanes; LTPS backplanes, in turn, require laser annealing from an amorphous silicon start, so this part of the manufacturing process for AMOLEDs starts with the process costs of standard LCD, and then adds an expensive, time-consuming process that cannot currently be used on large-area glass substrates. OLED also possess very limited lifespan. The biggest technical problem for OLEDs was the limited lifetime of the organic materials. In 2008 technical report on an OLED TV panel found that "After 1,000 hours the blue luminance degraded by 12%, the red by 7% and the green by 8%." In particular, blue OLEDs historically have had a lifetime of around 14,000 hours to half original brightness (five years at 8 hours a day) when used for flat-panel displays. This is lower than the typical lifetime of LCD, LED or PDP technology. Each currently is rated for about 25,000–40,000 hours to half brightness, depending on manufacturer and model. Degradation occurs because of the accumulation of non-radiative recombination centres and luminescence quenchers in the emissive zone. Colour balance issues, Is also a biggest problem in OLED , as the OLED material used to produce blue light which degrades significantly more rapidly than the materials that produce other colours, blue light output will decrease relative to the other colours of light. This variation in the differential colour output will change the colour balance of the display and is much more noticeable than a decrease in overall luminance. This can be avoided partially by adjusting colour balance, but this may require advanced control circuits and interaction with the user. More commonly, though, manufacturers optimize the size of the R, G and B subpixels to reduce the current density through the sub pixel in order to equalize lifetime at full luminance. For

example, a blue subpixel may be 100% larger than the green subpixel. The red subpixel may be 10% smaller than the green; this technique is somewhat able to sort out this colour balance issues.

9. Applications of OLEDs and Future Scopes

OLED technology is actualized in commercial applications such as flat-panel displays (FPDs) and solid-state lighting (SSL).

1) Flat-panel displays: I. Small screens: OLEDs used as small screens in mobile phones, portable digital media players, car radios, digital cameras, and others. Such portable applications favour the high light output of OLEDs for readability in sunlight and their low power drain. OLEDs are also used in many Motorola and Samsung cell phones, as well as some HTC, LG and Sony Ericsson models [73]. Recently, Nokia has also introduced some OLED products including the N85 and the N86 8MP, both of which based on an AMOLED display. OLED technology can also be found in digital media players such as the Creative ZEN V, the iriver clx, the Zune HD, and the Sony Walkman X Series OLED-TVs are commercially available now. DuPont stated in a press release in May 2010 that they can produce a 50" OLED TV in two minutes with a new printing Technology [72, 74].

2) Solid-state lighting: Applications in flexible and foldable signs and lighting are also being developed [73]. Philips Lighting has made OLED lighting samples under the brand name 'Lumiblade,' which are available for sale online [74], and Siemens Osram offers the Orbeus white OLED panels for sale. Figure (27) demonstrated the increment in demands of OLED display.

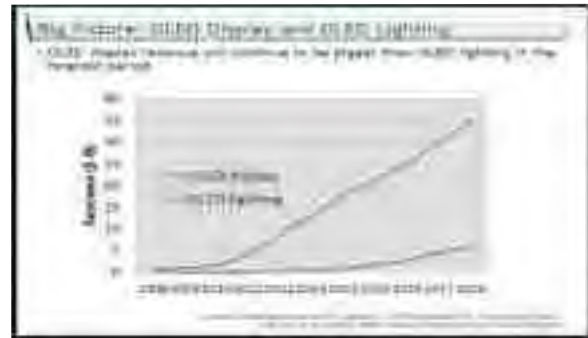


Figure 27: Graph of OLED display and OLED lighting

Table 3: Demonstrate the overall roadmap of OLED applications. [75]

	Thin light	Low power	Clear images	Fast response	Broad color gamut	Wide View	Long Life	Plastic substrate
Smart cards	H	H	H	L	L	L	M	H
Head-mounted displays	H	H	H	M	M	M	M	H
Car radios/dashboards	M	L	M	L	L	M	L	M
Voice phones	H	H	M	L	M	L	L	M
Data phones/PDA	H	H	H	L	M	M	L	M
Camera/camcorder viewers	H	H	H	L/M	H	M	L	M
Navigation aids in vehicles	M	M	H	L	M	H	L	M
Portable video phones/games	H	H	H	M	M	M	L	M
Portable DVD players	H	H	H	H	H	M	M	M
Handheld/notebook PC's	H	H	H	M	M	M	M	L
Desktop PCs/workstations	M	M	H	M	M	H	M	L
Transportable TV/DVD	M	M	H	H	H	H	H	L
Dynamic advertising	H	M	H	L	H	H	H	H
Diffuse lighting	H	H	L	L	L	H	H	H

In the lifetime column, an L indicates a nominal lifetime requirement of around 10,000 hours, M denotes about 20,000 hours and H requires over 40,000 hours.

As OLED technology facing some challenges like high cost (lack of the mass production and use of the high cost material comparatively), small lifespan, colour balance issues, efficiency of blue OLEDs, damage by water etc. And our researchers are continuously working to overcome all these problems.

But just imagine having high definition TV of 80 inches side, less than a quarter inch thick, consume less power and can rolled up when you are not using it is it possible? The displays of key board keys are fantastically visualize the respective commands, is this possible? You enjoy TV in a simple watch, is this possible? The answers of all questions are **yes** and these are going to be happen true very soon.



Figure 28: The prototype of a thin, roll-able, flexible OLED display by Universal Display Corp.



Figure 29: Near future keyboard by using OLED technology.



Figure 30: OLED used for external lighting in car in near future



Figure 31: OLED display in near future

10. Conclusions

Presently so many researcher have been working in so many issues for OLED such as Most efficient emitter, Voltage minimization, Light extraction. As OLEDs performance depends upon many parameters such as electron and hole mobility, magnitude of applied field, nature of hole and electron transport layers and excited life-times. Major electronics firms having good anticipation not only in OLED performance but also OLED usage at large scale. The Organic Electronics has been established as a discipline and holds enormous opportunity for the low cost and sometimes unexpectedly high performance offered by organic electronic devices. The physics of organic semiconductors may transform the electronics to excitonics. Organic Light Emitting Diodes are coming up as the light sources of the next generation & display technology and set a beautiful example of nanoengineering for macro electronics applications.

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