

Review of Organic Light Emitting Diode Fabrication and Recent Progress

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Abstract — Light-emitting diodes (LEDs) have been encroaching on the long established domain of incandescent and fluorescent lighting due to their long life, intensity, and power efficiency. Certain limitations, however, have restrained LEDs from supplanting conspicuous application, particularly difficulty and cost of production. Organic Light Emitting Diodes (OLEDs) show promise of replacing liquid crystal displays (LCDs) and other lighting appliances, due to their low cost, ease of fabrication, brightness, speed, wide viewing angle, low power consumption, and contrast. The edge gained by OLEDs will facilitate further LED market permeation. This paper discusses the fabrication of OLEDs, and recent advances made in this area, as ease of fabrication is the singular most important benefit over alternative technologies.

Index Terms—OLED, fabrication, organic semiconductors, electro-luminescence

I. INTRODUCTION

THE current goal in optoelectronic engineering to replace conventional lighting sources such as incandescent and fluorescent lighting with more power efficient semiconducting light sources, has already had an impact. The benefits of LED lighting include a reduced ecological footprint on our environment in powering these devices, lower monetary expenditure on energy, self-sustainability, and lower fire risk. It will be shown that OLEDs can be developed to become a companion to LEDs in lighting applications, and eventually replace LCD display technology. The design choices pertinent to, and the fabrication of OLEDs is discussed herein.

In introducing fabrication specifics, it is helpful to present an overview of a basic fabrication process. Indium-tin oxide (ITO) is deposited onto a glass panel by some means, typically vacuum sputtering. The ITO substrate is subsequently cleaned by ultrasound, rinsed, dried, and cleaned by organic solvents. The substrate is then subjected to a surface treatment in which the work function is adjusted to the desired level by exposing to ozone or oxygen

plasma. In the next steps the semiconducting monolayer or heterostructure is either grown, printed, or deposited by some other means. In the case of a bi-layer diode layers of organic polymer or small molecules are deposited: the hole-transport layer (HTL), followed by the electron-transport layer (ETL). Other organic or metal layers may be present in other designs. Growth of these layers may take place in ultra high vacuum resistive heat evaporation chambers, electron beam deposition, solution dipping, or solution spin-coating. Each part of this process is discussed in the following sections.

II. SEMICONDUCTING MATERIAL

The basis for organic semiconductors as a whole revolves around the ability to develop the required material parameters, e.g. the desired lowest unoccupied molecular orbit (LUMO) and highest occupied molecular orbit (HOMO) energy bands. Weuss et. al. are credited with the discovery of perylene-iodine complex in 1952, the first semiconducting organic [1]. The first electroluminescence observed in organic materials followed shortly in the 1950s when acridine orange and quinacrine were subjected to high-voltage alternating current [2], though there is at least one other report from the time also claiming to be the first.

Semiconducting small molecule, oligomers, or conjugated polymer layers are typically deposited on top of a charge transport layer. Semiconducting materials may either be spin-coated in a conventional manner, chemical vapor vacuum deposited, or printed by a variety of technologies, such as ink jets, dry rolling and screen printing. The choice of organic film material is based on its charge transport, color, and luminance efficiency. Light is produced by the fast decay of excited molecular states, while the color of the light produced relies on the energy difference between the excited state and the molecular ground level.

A hole injection layer, or anode buffer layer can be used to increase efficiency by reducing the energy barrier between the ITO/HTL interface. A common hole injection layer material is poly (3,4-ethylenedioxythiophene) poly (styrenesulfonate) (PEDOT:PSS). As a hydrated gel, it has been shown to smooth the micro roughness in the ITO surface, reducing the possibility to incur a short [3]. The most common hole transport material is pyrimido-pentaphenylbenzene (NPB), due to its ease of manufacture, however its stability

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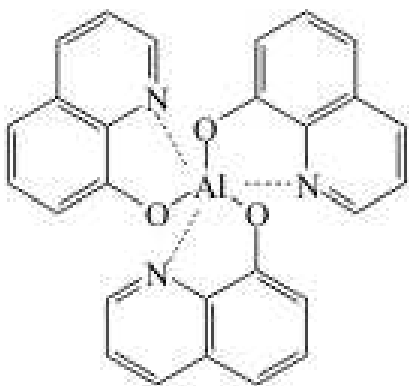


Fig. 1. tris(8-hydroxyquinolinato)aluminum Alq_3 is the most common electron-transport material in OLEDs, which is deposited before the light-emitting layer [10].

dependence on temperature is not ideal. NPB will decompose at 98°C , which is relatively cool for electronic components, particularly lighting elements. A paramount area of current research development involves finding new materials with high thermal film morphological stabilities. Materials of recent research are biphenyl diamine derivatives, and starburst amorphous molecules, which are named for their radically symmetric molecular arrangement [3, 8].

The most common and most important electron-transport material is Alq_3 , displayed in Fig 1. Other commonly used electron transport layers are TPD, and NPB. Engineering design decision for this layer must consider the work function of the metal contacts to be used. Typical contact metals and their work functions are discussed in the metal contact section.

The development of dopants has been key in increasing quantum efficiencies of OLEDs, and in adjusting color output. Fluorescent guest dopants interact with molecular valance bands to modify original electroluminescent properties to the desired color. One of the central attractive features of OLEDs is the wide color gamut which is made possible by these dopants. Dopants increase quantum efficiency by decreasing the probability of nonradioactive decay and enhance operational stability. Kanno, *et al.* have demonstrated effective strategies in co-doping OLED cells for full color displays [8]. Many other approaches to improving OLEDs have been investigated that do not fall under any of the previous categories already mentioned. Changes to the architecture of the OLED are particularly innovative. Chen reports a re-approach to the cathode, that is made possible by flipping the entire OLED upside down to an inverted structure [5]. This way, highly reactive metals are not needed, and reflective metals can be used. These preferred metals for the now bottom cathode are Al-Ag alloys. Inverted top-emitting OLEDs avoid the limitations of poor optical transparency of substrates, and improve the filling factor of pixels. The devices were fabricated on a glass substrate prepared with silver or aluminum films for the cathode.

III. PATTERNING TECHNOLOGY

Semiconducting materials may either be spin-coated in a conventional manner, or printed by a variety of technologies, such as ink jets, dry rolling, and screen printing. The true benefits of OLED manufacturing are realized by versatility of deposition.

Film coverage, uniformity, and general quality derived from spin coatings are heavily dependent on the mixture ratios and environmental conditions. Spin coating take place in sealed environments wherein temperature, ambient gases, humidity, and particulate contamination can all be kept in check. Film thickness is dependent on spin speed, ramp up time, and liquid viscosity.

D. Lee et al. report OLED fabrication by screen printing [7]. The argument is made that though multi-layer OLEDs are more power efficient, single-layer OLEDs have a place in low cost applications because they are inherently simpler to fabricate. To increase efficiency approaching the level of multi-layered devices, there may be phosphorescent dopants included. Screen printing is recommended because it is one of the most versatile, simplest, fastest, and cost-effective coating techniques. Furthermore, screen printing can be applied to a number of shapes and sizes of substrate. An interesting possible derivative of this technology could be OLED impregnated fabrics, or premade plastic products with illuminated, animated branding. Screen printing of organic films is not suitable for films less than 100nm. Pardo has investigated screen printing HTL and ETL layers as well for multi-layer devices [13]. Combining all organic layers into screen printing would greatly benefit manufacture simplification.

The processing procedure that Lee followed is strikingly similar to an ink and paper printing procedure. ITO glasses were cleaned then patterned using standard lithography techniques. After patterning with photoresist, the ITO layer was etched with HCL, and finally plasma treated. NPB, Alq_3 , and rubrene were dissolved in a solution of polystyrene in chloroform. The polystyrene acted as a host polymer to adjust the viscosity of the coating solution, in effect thickening the ink for screen printing. The screen itself was a 400-mesh stainless steel screen mask, though which the filtered coating solution was deposited onto an array of 49 pixels, each 3 mm x 3mm. The subsequent cathode metals, LiF and Al were deposited conventionally by sputtering in a vacuum chamber on top of the organic film structures. The findings relevant to increasing the knowledge of OLED fabrication was that the viscosity of the coating solution is directly related to the film thickness, and the thickness is extremely sensitive to a number of factors, including the mesh counts, and coating time.

Interestingly, the solution ratios of NPB, Alq_3 , and rubrene did not affect the viscosity because they are low-molecular weight molecules. The viscosity had to be adjusted by addition of polystyrene. Initially, the coating process was not



Fig. 2. Close up of housing and encapsulation of the first OLED "Future Lamp" by designer Ingo Maurer produces diffuse white light. Portions of the backplane are visible [15].

ideal, and many pinhole defects were created. Film quality was later improved by adjusting the wettability of the ITO. Wetting is an important factor in thin film processes including adhesion, lubrication, and printing. Pretreated ITO has contact angles from 50° - 60° , which must be adjusted to less than 20° by ozone or plasma treatment. Compared with conventional spin-coated OLEDs, the screen printed OLEDs have more materials issues of dark spots and reduced brightness and quantum efficiency, but they are still functional and can be improved in future research.

IV. METAL CONTACTS

At the point where either side of the p-n junction is joined to electrical connection, a specific metal is required. The work function of the metal is the integral decision that must be made based on the type of organic film to be used in the device. At the anode interface holes are injected, so there must be a high work function that matches the HOMO level of the semiconducting organic. ITO is the singular most popular choice unilaterally for anode contacts in OLEDs, though alternate metallurgies have been examined.

ITO has been an excellent choice for anode contacts in OLEDs for a number of excellent reasons. The anode is typically the top contact where light must escape, and ITO has excellent transmissive properties in the visible bandwidth of light. ITO has a low surface resistance from $15 - 100 \Omega / \square$ allowing for an ohmic contact electrically [3]. High transparency and conductivity are central to improving efficiency. Minimizing the reflection and maximizing the transmission of this thin film is a major focus of research in increasing efficiency of both inorganic LEDs and OLEDs.

ITO can be produced to have a work function with a range between 4.5eV and 5.0eV , which is convenient for a range of organic thin film choices. The transparency, conductivity, and work function can all be varied by deposition technique,

surface treatment, and thermal annealing. Surface treatments include using ozone or oxygen plasma to interact with the surface to increase the work function [3]. Thermal processing by rapid thermal annealing (RTA) under varying atmospheres causes changes in metal alloy phases, and thus transparency and conductivity can be tuned and optimized.

Seki, *et al.* report a novel method for ITO application by spray application [6]. This work leads way to an inexpensive deposition process, due to the fact that a vacuum chamber is not required. The spray chemical vapor deposition (CVD) was realized though a simple perfume atomizer with InCl_3 and SnCl_2 dissolved in ethanol. A total of 20mL of the solution was sprayed in ambient pressure in air 100 times from a distance of 15cm onto a substrate heated on a hotplate to 270°C . Seki, *et al.* were able to reduce this temperature from 350°C in an earlier experiment. For the semiconducting organic layer, Alq_3 was used with PEDOT:PSS as a hole injection layer and NPB as a hole transport layer. A chamber was used later in their process for typical cathode metal sputter deposition of an Al-Li alloy. Perhaps someday a spray CVD method can be developed to deposit the cathodes as well. Complete elimination of the need for deposition chambers would save considerable cost in manufacture. As this process currently stands, it is appropriate for glass substrates only, due to the high temperatures used. It is important to reduce this temperature for future use of alternate flexible substrates. Through these experiments, good conductivity and spectral transmission were achieved with values of $3.7 \times 10^{-4} \Omega\text{-cm}$ and nearly 85% for most visible wavelengths.

Cathode metals must match the LUMO of the organic materials, and thus a low work function is desirable. Mg-Ag is a common alloy used with work functions in the range of 3.66eV . Other alkali earth metals, such as Ca, may be used, but their reactivity presents yet another issue to the already problematic instability and lifetime of the device. Interestingly, room temperature liquid metal In-Ga alloys have been shown to work readily. Cathode films are typically vacuum evaporated by resistive heating on the substrate [3].

V. BACKPLANE

The backplane of a display refers to the addressing scheme and its supporting infrastructure. Passive and active addressing schemes are available for OLED displays, depending on the size of the display. Cheap passive displays such as alphanumeric displays have been the first devices available. Devices on the market today include an electric shaver, automotive instrument displays, and low cost cellphone sub-displays by Motorola and Sanyo. High resolution, high content graphics applications such as video, require active addressing and thus backplane circuitry. Pioneer, NEC, Eastman Kodak, Sanyo, and eMagin all have developed such active addressing displays for high resolution content for applications from GPS navigation systems to

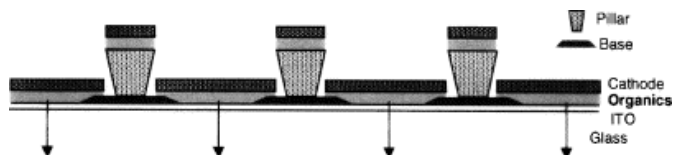


Fig. 3. Integral shadow mask structure used for cathode row isolation. [3], [11]

head-wearable microdisplays for the military.

Again, the backplane is an area where OLEDs can benefit over LEDs in their ease of manufacture. Costly lithography steps of large LCD screens, where huge pieces of glass are spun and developed, can hopefully be replaced entirely by roll printing technologies. In effect, the backplane can possibly be integrated into the OLED device itself and fabricated with the same process.

In passive-matrix displays, pixels are defined by the area held in common between ITO cathode columns and the metal anode rows. Patterning requirements may be achieved by use of familiar photolithography techniques, but on a larger scale. The spreading of photoresist and the subsequently applied caustic developer solution on the substrate can damage the underlying organic layer. Another way to form these metal patterns is to use a metal shadow mask during vacuum deposition. This method has its drawbacks as well, because shadow masks are fragile and have resolution limits, preventing fine patterns from being produced. One innovative method which mitigates both issues employs an integrated, or built-in shadow mask that self-aligns as the processing steps are completed. Fig. 3 illustrates a cut-away view of the integrated shadow mask pillars made from photoresist or organic polymer material. The thicker material protects the underlying organic layer 'base' in the diagram, while allowing metal to be anisotropically deposited through the windows [3], [11].

In an effort to simplify deposition of three different color-producing organic films in an RGB cell, one passive matrix device reported uses three white OLEDs, each with separate red, green, and blue filters. The luminances of the red, green, and blue subpixels within the cell were 400, 400, and 150 cd/m^2 . While this is a potentially cost effective method for production, much of the inherent power efficiency of the OLEDs are lost; at least $2/3^{\text{rds}}$ of the white light is lost due to absorption.

OLED displays can be processed conventionally using the same methods as LCD panels. The desire to gain uniform film thickness over the entire area of the display provides special concern, particularly with large displays. Conventional evaporation deposition from a point source requires large vacuum chambers and rotating components. Thus a new kind of source has been developed; rather than

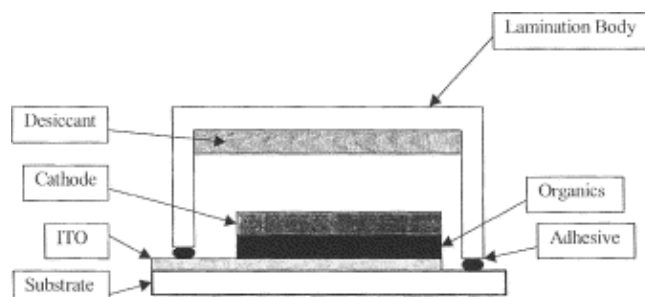


Fig. 4. Cross-sectional view of an encapsulated OLED displaying adhesive layer that moisture can diffuse through. [12]

using a point source in a crucible within the chamber, a linear boat or filament is used. Opposed to rotating the substrate in a planetary orbit around the source, the large panel is translated linearly across the source once, allowing for excellent coverage and uniformity [11].

TFT transistors for active addressing increase the multiplexability of high resolution displays by creating a sharp threshold operate at video frame rate operation. The inclusion options of TFTs is covered in the following section.

VI. ENCAPSULATION

Encapsulation is one of the most important areas of research concerned with improving OLEDs if they are to be viable for the market, unless highly stable organics can be found. Impermeability of encapsulation materials along with the development of stable organic polymers or molecules are the two solitary features that will lead to stable OLED displays with long lifetimes.

Encapsulation takes place at the end of device fabrication, after the organic and cathode layers have been deposited. A sheet metal canister is glued to the substrate glass or flexible plastic. An alkali earth oxide, such as CaO or BaO is included within the encapsulation to act as a getter desiccant. To seal the device, a UV-cured optical epoxy adhesive is used. The general array of each of these components is laid out in Fig. 4. The getter layer is important to absorb the moisture that will diffuse through the adhesive. Diffusion calculations show that $4\mu\text{g}$ of moisture can move through the sum of a perimeter lined with 1mm wide, $1\mu\text{m}$ thick adhesive optical epoxy over only 4 days [3]. This amount of water will react with an aluminum cathode, to form 3nm of sapphire (Al_2O_3). In the presence of a more reactive cathode, moisture diffusion worsens causing formation of even more oxide. These oxides form dark spots in the center areas of the OLED and grow inwards from the edge of the substrate, shrinking the light-emitting area, dimming the glow, and causing color drift.

Flexible displays are the most exciting trend in current development. They will enable displays to roll, bend into any shape, as well as attain very light weights. The issue of installing TFTs is problematic on the flexible substrate. The plastic layer has a low thermal budget because it will either burn or melt, thus the processing temperatures are limited to

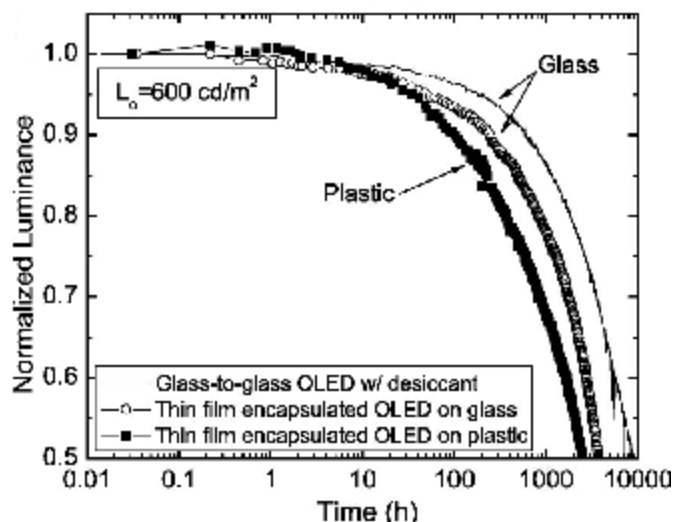


Fig. 5. Normalized lifetime for OLEDs tested in glass packages, and thin film flexible encapsulation [13].

150°C for PET and 200°C for PES [12]. The two obvious options are to fabricate the TFTs elsewhere, then transfer them to the flexible substrate, or directly fabricate them on the substrate. Two reports have shown that lasers have been used to “spot anneal” TFTs for crystallization, along with laser doping *in situ* which have been fabricated on the substrate [12]. Flexible displays open the possibility of roll processing, as is used in printing and textile industries. Considerable challenges persist in flexible display encapsulation in oxygen and moisture barrier solutions, but they will yield very low cost, even disposable products.

Chwang, *et al.* have described their advances in impermeable flexible displays [13]. Plastics normally present the worst problems in passing moisture and oxygen though, causing flexible display lifetimes to be much worse than glass substrates. Some displays coated with polyethyleneterephthalate (PET) have been shown to exhibit similar lifetimes to glass substrate devices, however use of a glass lid and epoxy sealants leave them rigid. A monolithic thin film encapsulant is presented by Chwang, which is grown on an 80 dpi PET. After OLED fabrication, the optically transmissive multi-layer barrier is deposited. To form the barrier, films of Al_2O_3 and polyacrylate are alternately deposited in pairs. The Al_2O_3 layers were reactively sputtered by energetic plasma, while the polyacrylate layers were deposited by flash evaporation of the monomer and then UV cured. UV curing serves to link up polymers into a rigid material. The entire process was carried out *in situ* within the same integrated vacuum chamber. It simplifies the process greatly to not have to change setup in between layer deposition steps. The Al_2O_3 inorganic oxide is the true diffusion boundary that prevents oxygen and moisture from migrating through to the device. The polyacrylate layer adds flexibility, as well as decoupling defects in between aluminum oxide layers. Solid sapphire would of course be a

rigid coating, if deposited monolithically, however thin layers are completely flexible. Consider the Al_2O_3 layer on a thin sheet of aluminum foil, for example, which is easily distortable. This device in effect is a composite material, which combines the best of both flexible organics, and impermeable inorganics. The entire multilayer encapsulation layer totals a thickness of 5 – 7 μm with 4 – 5 pairs of alternating layers. All of the devices were able to output a starting luminance of 600 cd/m^2 . The lifetime achievement of the thin film flexible encapsulated devices was 2,500 h, while the comparable conventional glass-encapsulated devices were 10,000 h. Lifetimes are measured by the amount of time passed to reach the half brightness

state of the OLED. Fig 5 represents the lifetime of OLED samples fabricated by the different available encapsulation methods, glass to glass, flexible on glass, and fully flexible encapsulation in logarithmic format. The devices’ performances rank as expected. The authors conclude that, though still much shorter than rigid encapsulations, this lifetime is still a significant improvement over previous flexible displays, considering they have lifetimes of only 600 h.

Dimming in OLEDs is characteristically observed by higher voltage and lower luminous efficiency for a current density point. Dark spot growth did occur in all of Chwang’s samples, but no new dark spots formed with aging. This indicates that initial dark spot formation was due to unintended exposure to particulate, oxygen, and moisture contamination during fabrication before the devices were sealed in the encapsulative material. The growth of the dark spots indicates the continuation of moisture and oxygen diffusion after device completion.

If Chwang *et al.*’s design can be improved upon by including desiccating gettering compounds, as described in the beginning of this section, the overall lifetimes could be further improved. It is probable that desiccants will come to be used in all OLED displays, unless they are truly only designed for short term use. By combining all of the aforementioned encapsulation technologies, truly robust, flexible, and useful products will emerge that can be efficiently produced.

VII. CONCLUSION

The fabrication methodologies of organic light-emitting diodes have been discussed. It is the ease of fabrication and introduction of established manufacturing technologies, not previously associated with the electronics industry that have gained OLEDs notable scientific attention.

OLEDs have attained long stability with bright non-drifting colors upwards of 10,000 hours. Many approaches to improving quantum efficiency have been explored and continue to require development. More effort is needed to push the upper limit of operating temperature stability so that organic films do not deteriorate through failure mechanisms

such as pin holes. Darkening of light areas attributed to oxide growth due to moisture diffusing has been dealt with by application of novel encapsulation materials and desiccants. We will continue to see better barriers that are durable and thin enough to function in flexible displays.

In the coming decade we will come to be failure with affordable flexible display and fabric technologies made possible by current and future diligent research. The true advantages will be realized when the individual advances discussed here are combined together in the same products.

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