

CHAPTER 1

INTRODUCTION

1.1 Overview

Prof Shirakawa and co-worker have successfully synthesized the first semi-conducting polymer in 1977 [Shirakawa *et al.*, 1977]. Since then, many reports on organic semiconductor have been published to date, especially in relation to their application. In 1987, Tang and VanSlyke have reported the first OLED with high efficiency using a small molecule of tris(8-hydroxyquinoline) aluminium (Alq_3) [Tang & VanSlyke, 1987]. The research and development of OLED technology expanded from display application towards lighting application. OLEDs have drawn intensive interest for the next generation of flat-panel displays due to their great response time, high contrast, wide viewing angle, low power consumption and low cost. However, the objective to have a high-performance, long life and low-cost device is still yet to be fully achieved. Thus this work will be focusing on enhancing the performance on single layer OLED by adopting the new dopant system.

Recently, multilayer or hetero-junction OLEDs are widely fabricated in order to improve the performance of the device [Huang *et al.*, 2009; Yang & Zhuang, 2011]. In multilayer OLEDs, the layers consist of various layers, including electron injection layer (EIL), hole injection layer (HIL), electron transporting layer (ETL), hole transporting layer (HTL) and emissive layer (EML). These layers assist to maintain approximately equal balance of electron and hole concentration in the recombination

zone [Leising *et al.*, 1997]. Usually the device was fabricated by using a vacuum or thermal evaporation technique [Adachi *et al.*, 2000], which is relatively expensive. Fig. 1.1(a) shows a typical structure of a multilayer OLED.

Single-layer OLEDs have attracted considerable interest, mainly due to their ease in solution processing and low cost fabrication [Hebner *et al.*, 1998]. In contrast, as compare to a multilayer OLEDs, the layers of a typical single-layer OLEDs are constructed to have three layers only, which are EIL, HIL, and EML. On the other words, it was a basic definition of OLED, which is a thin film made from an organic emissive material that is sandwiched between two electrodes. The light will emit when electricity is passed through it. In order to produce a good single-layer OLED, two approaches need to be considered: (1) a suitable organic emissive material must be selected or synthesized to obtain a high efficient transporting charge carrier and high luminescent properties or (2) a commonly used organic emissive material can be blended with a suitable organic dopant material and act as ETL and HTL for enhancing the transfer of charges to the emissive material [Divayana *et al.*, 2011]. Fig. 1.1(b) shows a typical structure of a single layer OLED.

In this work, an emissive material, Alq₃, was mixed with TPD:PBD blend thin film to enhance the luminance and efficiency of the single layer OLED. Particularly, *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) is used as hole transporting molecules and 2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole (PBD) as electron transporting molecules while Alq₃ remains as emissive molecules. It was expected that by introducing these transporting molecules, performance of Alq₃ based single layer OLED will be enhanced. The device structure was ITO/PEDOT:PSS/Alq₃:*x*/Al, where *x* is the dopant molecules. The device was

constructed based on ITO/PEDOT:PSS for the anode and Al for the cathode, which has been used to study the influence of molecular organization of OLED device [Aubouy *et al.*, 2007]. The annealing process was then applied in order to optimize the performance of the new blend OLEDs.

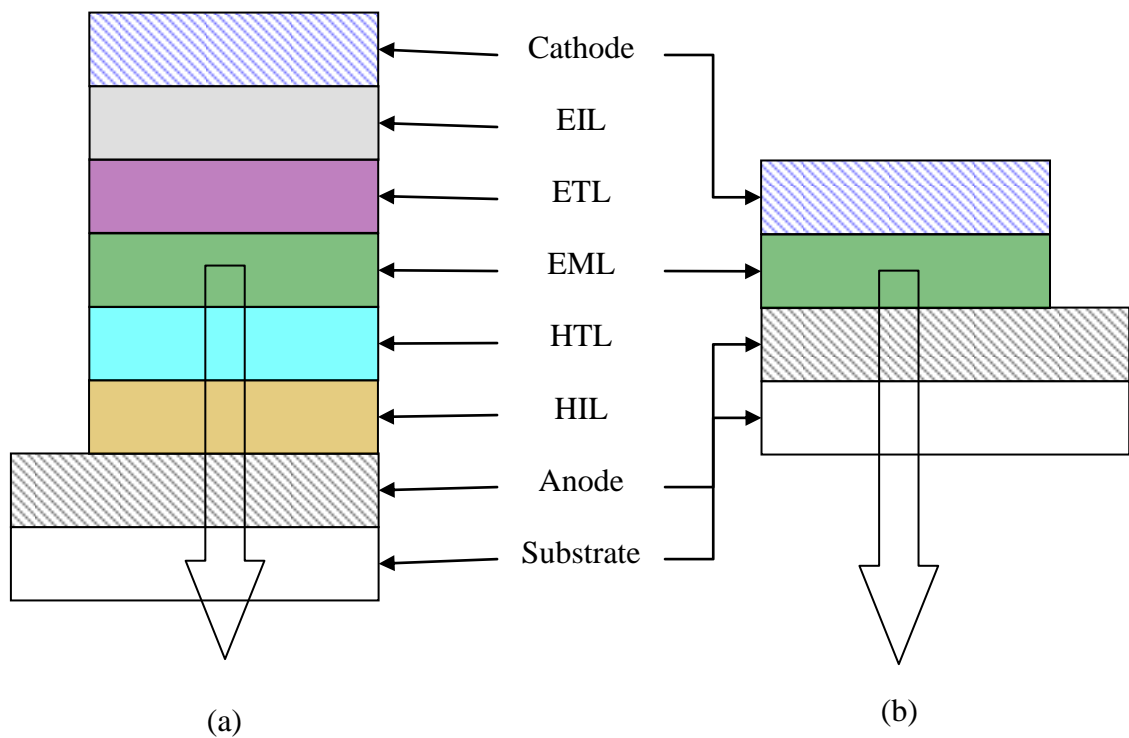


Figure 1.1: Typical structure of (a) multilayer and (b) single-layer OLEDs. The organic active layer are consisted of electron injection layer (EIL), electron transporting layer (ETL), emissive layer (EML), hole transporting layer (HTL) and hole injection layer (HIL). The arrow indicates the direction of light emission from the OLED devices.

1.2 History of Organic Light Emitting Diode (OLED)

The history of organic light emitting diode (OLED) started when the first semi-conducting polymer has been successfully synthesized by Prof. Shirakawa and his co-worker by controlling the chemical doping in the polymer in 1977 [Shirakawa, *et al.*, 1977]. Based on this finding, Prof Shirakawa was honored with the Noble Prize in Chemistry in the year 2000. The story continued by C. W. Tang and S. A. VanSlyke in 1986 from research and development (R&D) group of Eastman Kodak based in USA [Tang & VanSlyke, 1987]. They successfully fabricated the first OLED with a double layer structure, which consisted a small molecule Alq₃ and an aromatic diamine. Surprisingly, their main objective is to fabricate an organic solar cell at that time and eventually found that the device is more to convert electrical energy to light rather than converting light into electrical energy. Four years later, the first electroluminescence device based on conjugated polymer namely poly(para-phenylene vinylene) (PPV) has been successfully fabricated by Burroughes and his group [Burroughes *et al.*, 1990]. Then in 1995, the first single layer white OLED based on a dye-dispersed poly(N-vinylcarbazole) was reported by J. Kido *et al.* [Kido *et al.*, 1995], which was intensively studied further by S. R. Forrest *et al.* [D'Andrade *et al.*, 2004]. These magnificent achievements have encouraged many research groups either from academics or industries to conduct further investigation on OLED for various display applications.

Due to the low mobility and disordered structure of organic semiconductors, further experiments have been performed to enhance the efficiency of OLED via designing more efficient device architecture, e.g. multilayers devices. This kind of device structure may assist to maintain approximately equal balance of electron and hole accumulation in the recombination zone [Leung *et al.*, 2009]. In 1997, S. Tasch and his group research have produce electroluminescence of blue light based on

paraheaxaphenyl as the active layer inserted in the multi hetero structure [Leising, et al., 1997]. Additionally, the efficiency of OLED as reported by M.A. Baldo et al. [Baldo et al., 1998] can be enhanced in magnitude in order of four by introducing the phosphorescent dye into an OLED device.

In terms of commercial product, the first OLED display was produced by Pioneer Corp. in November 1997 for an automotive application [Tokoru,1997]. Ten years later, Sony Corp. introduced the first OLED TV called XEL-1 with an astonishing thickness of approximately 3mm in October 2007 [Sony, 2007]. In 2008, OSRAM has announced the first OLED lamp that used 10 OLED panels with 132 x 33 millimeters in size [OLED-Info.com]. In 2011, Samsung has announced the hand phone which is the world first product designed with a transparent super AMOLED display [Samsung, 2011]. Fig. 1.2 shows several products based on OLED technology.



OLED TV XEL-1 from Sony



OLED table lamp from OSRAM



OLED audio player from Pioneer



OLED hand phone display from
Samsung

Figure 1.2: Several commercialize device based on OLED technology

1.3 Motivation for this Research

Recently, the world is facing global environmental issues that are reflected from high technology industries. The reduction of an energy source such as natural gas and petroleum gas to generate the electricity from power plant may be a considerable issue. Most people who lived in developing countries tend to use a lot of products, daily. High usage of these products could lead to consuming a lot of electrical energy every day. Among of these product is the display device. In order to sustain the world environment, a solution is needed. “Green technology”, which is a technology that is environmental friendly, is required. One of the criteria of the green technology is a technology that can produce a product that consumes less electrical energy. Thus, OLED display is one of the best solutions as their production and usage can be categorized as green technology.

There are several advantages of OLED as a display device compared to that of a recently liquid crystal display (LCD). OLED display has a slimmer thickness with the size of a few millimeters, thus applicable to small size products such as mobile phone, visual media player (MP4) and hand watch. They also can be fabricated on plastic for flexible display application (refer Fig. 1.3). OLED displays also consume less energy compared to other displays which helps to reduce uses of batteries. Not like the LCD, OLED displays do not need the backlight, which reduce the electrical consumption. On top of that, they are possible to be fabricated as transparent displays (see Fig. 1.4). The display also produces their own emission which provide wider viewing angle about 170 degrees (refer Fig. 1.5). This property could give better picture and avoid an image destruction that usually occurred in commercial displays. Finally, this technology is relatively low in cost. The cost might be high now, however when OLED is widely used, the cost will be reduced due to an established of synthesizing method of the organic materials.



Figure 1.3: Flexible Active Matrix OLED (AMOLED)



Figure 1.4: Samsung AMOLED laptop with transparent display



Figure 1.5: Comparison of image destruction between other display and OLED display

In terms of marketing, OLED technology is believed to be expanding the next 10 years. According to the report by Jennifer Colegrove [2009], director of display technologies at Display Search, this green technology will have an uptick from small sample to mass production which are lead by Phillips and GE company as shown in Fig. 1.6. The other companies such as OSRAM, KONICA MINOLTA and Lumiotech are also competitively using this technology. Colegrove also mentions that hundreds of millions of dollars have been invested in OLED especially in Europe, US and Japan. Even though OLED display product has been released for a decade, OLED lighting has just started in sampling and small volume of production. The reports also state that more than 130 companies and universities are involved in the supply chain of OLED technology. The technologies of OLED in structures, materials, efficiency and manufacturing line also tend to be improved year by year.

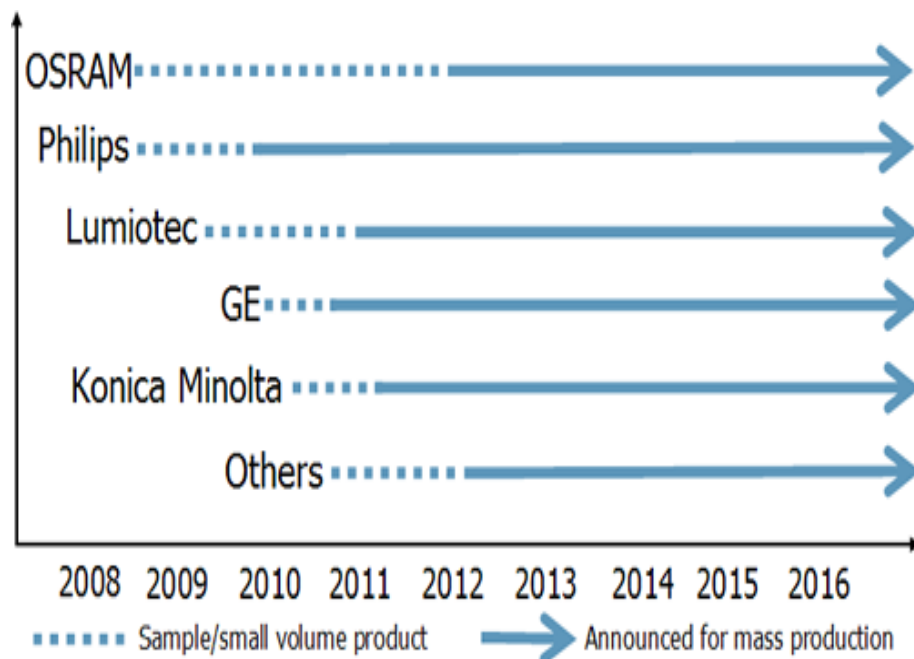


Figure 1.6: OLED Lighting Manufacturing Participant Roadmap [Colegrove, 2009].

1.4 Research Objective

Even though there are many reports on OLED are published to date, the objective to achieve a reasonable high efficient performance and an ease in the fabrication process are still yet researched. By considering the huge prospect of the technology in display application, an effective cost in OLED fabrication should be the pursued. This research work was aligned on three major objectives:

- 1) The first objective is to study the single-layer OLED based on Alq₃ molecule fabricated in an open-air environment. The OLED device was fabricated by using a solution process of spin-coating and characterized without encapsulation. This investigation provides fundamental knowledge on the OLED fabrication.
- 2) The second objective is to study the effects of doping TPD and PBD molecules to the emissive layer of Alq₃ on the optical and electroluminescence properties.
- 3) The third objective is to investigate the effects of an open-air annealing process to the new blend OLED in optimizing the performance.

1.5 Organization of the Dissertation

Chapter 2 presents the literature reviews on organic semiconductors and organic light emitting diode (OLED), and some theories in such device. In this chapter, the organic semiconductor theory will be explained in terms of atomic orbital, chemical bonds and their energy levels. Also included in this chapter is the basic principle of operation of OLED which covers topic such as charge injection, charge mobility, space-charge limited current (SCLC), traps-charge limited current (TCLC), Langevin recombination and light emission. The sub chapter is proceeds with explanation on the

spectroscopy impedance theory in organic semiconductor. Then, general introduction on the materials used in this work is presented at the end of this chapter.

Chapter 3 focuses on the experimental methods which divided into six subtopics. There are introduction, substrate preparation, solution preparation, thin film and OLED fabrication, thin film characterization and OLED characterization setup. Here, details on samples preparation and characterization will be discussed including some the theoretical background.

Chapter 4 presents the results and discussion on the single-layer OLED based on Alq₃ molecule fabricated in open-air environment related to optical and electroluminescence properties. This elementary study presents a robust fabrication and characterization technique of OLEDs.

Chapter 5 presents the results and discussion on effect of doping on the performance of Alq₃ based-single layer OLED. In this chapter, a novel blend OLED is introduced based on small molecules material.

Chapter 6 present the results and discussion on the effect of an open-air annealing process to the new blend OLED on optical, structural and electroluminescence properties. Optimum annealing condition is discussed in detailed.

Finally, Chapter 7 presents the summary and suggestions for future works related to this dissertation. Fig. 1.7 shows the flow chart of research methodology in this work.

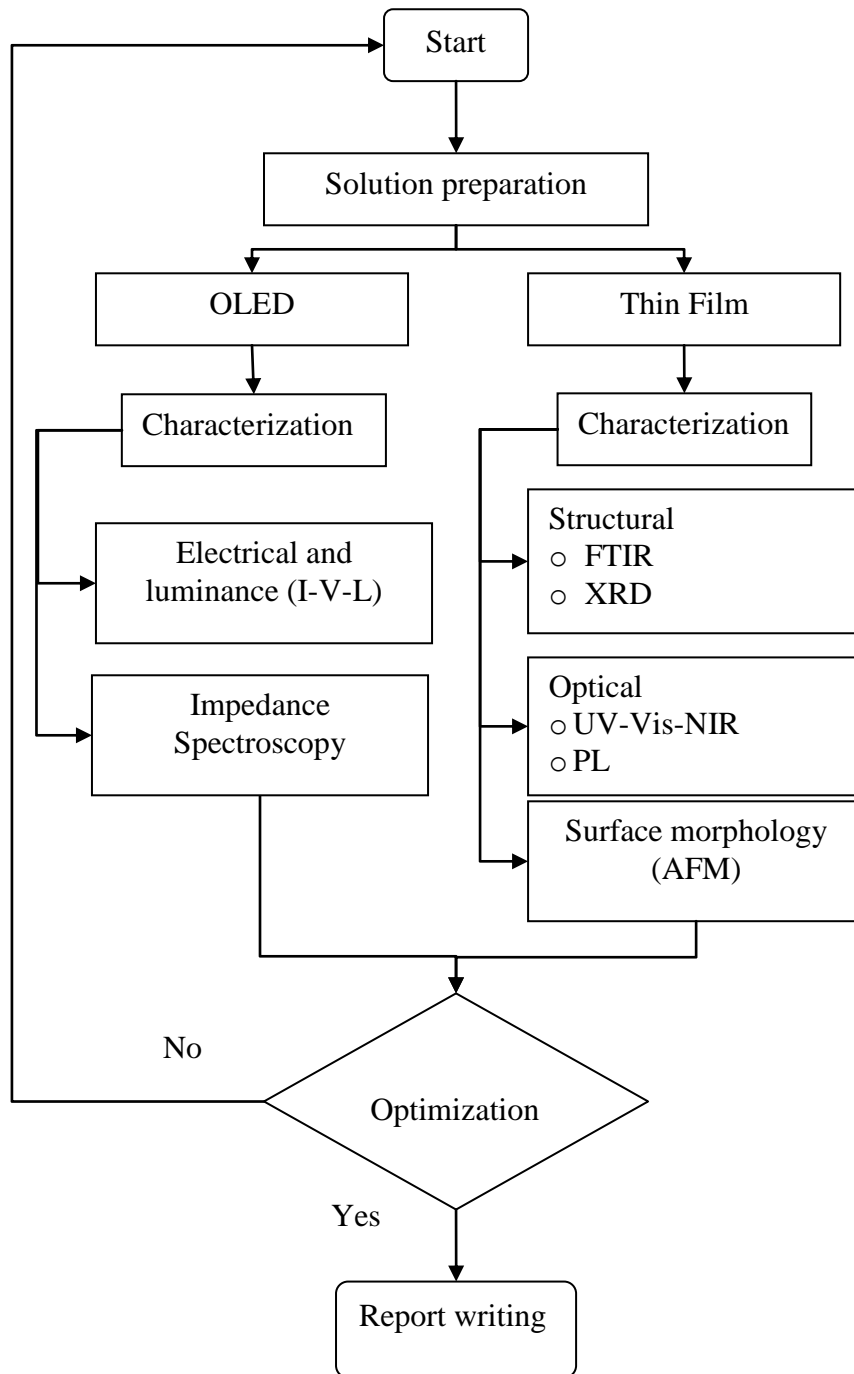


Figure 1.7: Research flow for this work

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