Deposition and investigation of opto-electronic properties of organic semiconductor materials

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**DEPOSITION AND INVESTIGATION OF OPTO-
ELECTRONIC PROPERTIES OF ORGANIC
SEMICONDUCTOR MATERIALS**

**LEE CHEA BENG
SCHOOL OF MATERIALS SCIENCE AND ENGINEERING
2006**

Deposition and Investigation of Opto-Electronic Properties of Organic Semiconductor Materials

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School of Materials Science and Engineering

A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
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2006

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Abstract

In this project, electrical and optical characteristics, surface morphology, and nitrogen/carbon ratio of (Alq₃) were studied as the function of thermal evaporation rate. The results showed that the deposition rate of Alq₃ has direct influence on the surface roughness of the film and luminescence efficiency of device. A new approach to fit the Time-of-Flight measurements results has been proposed in order to estimate the carrier mobility instead of using graphical method (Scher-Montroll model). This new approach is based on the Gaussian distribution of carrier velocity. The trap depth Φ_B of trapping states of pure Alq₃ and the effectiveness of carriers escaping process from trapping states with temperature were calculated based on modified Poole-Frenkel (PF) model.

The polar dopants, 4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran (DCM) and Coumarin 6 (C-6), and extensive π conjugated dopant, 5,6,11,12-tetraphenylnaphthacene (Rub) were used to study the mean charge carrier mobility in doped Alq₃ films. The co-doped of Rub with DCM and Rub with C-6 into Alq₃ improved the carrier mobility compared to the single dye-dope organic Alq₃ films. The carrier mobility in single doped Alq₃: Rub, Alq₃: C-6 and Alq₃: DCM films did not follow the Poole-Frenkel (PF) model closely. Instead, the mobility was in agreement with the PF model at two different ranges of electric fields (F) separated by a critical field $\sqrt{F_c}$. The mobility in co-doped (Rub: C-6) and (Rub:DCM) into Alq₃ followed the linear relationship with the PF model. The exciton recombination rate γ_{ss} , diffusion coefficient D_s and the diffusion length L were estimated from the PL decay lifetime measurements and the exciton kinetic equation in these doped films. The transient EL measurements in pure and doped Alq₃ devices helped to estimate the EL onset time and carrier mobility in an indirect way. The EL onset was delayed

Abstract

before achieving the saturation in doped devices compared with pure Alq₃ device. An increasing delay time t_d and a slower rise of EL were observed with doping concentrations and the carrier mobility was found lower compared with TOF method because of the accumulation of space charges at interfacial barriers. The trap depth E_t of the doped films was found increase compared with pure Alq₃ from on the transient C-V measurements, which was modeled by considering the de-trapping of carriers from a discrete trap level to a Gaussian distribution model of carriers transport states.

Chapter 1 Introduction

1.1 Organic Light Emitting Diodes

Organic electronic materials are receiving widespread attention due to their potential application in micro- and opto-electronic devices, such as organic light emitting diodes (OLEDs), solar cells, thin film transistors, etc. [1-3]. Organic materials-based electroluminescent (EL) devices show great potential for use in display applications due to their high fluorescence quantum efficiencies in the visible spectrum [1-7]. Other advantages include ease of processing, robustness and almost infinite possibilities for modification, such as color tuning by suitable materials chemistry design and synthesis. Organic EL devices have also low operating voltages, lower power consumption, wide viewing angles, and high brightness and contrast ratio [8-11]. These electroluminescent properties of functional π -electron molecular and polymeric systems have been the subject interest of numerous studies [12-14].

Tang and VanSlyke [5] demonstrated that utilizing a basic bilayer structure could enhance the EL efficiency of organic light emitting diodes (OLEDs). The enhanced efficiency is presumably due to the spatial confinement of the recombination zone away from possible quenching sites such as regions near the electrodes. This can be achieved through a combination of differential carrier mobilities in the bilayers and injection/blocking characteristics at the interfaces between the organic layers and at the organic-metal interfaces.

Other methods have been used to further increase the efficiency of OLEDs by inserting buffer layers (SiO_2 , CuPc and H_2Pc) [15-17], hole transporting layers (TPD, NPB) [18-20], electron transporting layers (PBD, Alq_3 , TTF) [21], and thin layer of inorganic

materials (LiF, MgF₂, CsF) [22-23] in between the organic active layer and electrodes. A remarkable stability has been achieved for organic EL device using an emitter dopant in the host material to increase the device luminance life time and yield high quantum efficiency under low operating voltage [24-25]. The schematic structure of organic light emitting diode structure is shown in Fig. 1.

Figure 1 Schematic of organic light emitting diode structure

However, the short lifetime of the devices, low carrier mobility, the formation of non-emissive region (dark spots) in organic active layer, thermal instability and crystalline structures of organic material in the device are still preventing the commercial use of the devices [26-36]. The reliability and lifetime of OLEDs are still unsolved, unclear, and causing a bottleneck in OLEDs technology. Therefore, for the commercialization of OLEDs, these obstacles should be understood and solved.

1.2 Existing Problems

The carrier mobility in organic film is affected by the dopants because of the interaction between dopants and the surrounding host molecules in films [37]. This type of guest-host molecular system gives rise to the positional and energetic disorders in the film. The positional disorder is a temperature independent parameter related to the dispersion of the function jump over the spread of intersite distance of the local states. The effective drift mobility of the carriers is directly influenced by these positional and energetic disorders of

the film that is accompanied by more or less frequent capture of the involved charge carriers in localized states [38-39]. Since the interaction between guest-host molecules may result in the appearance of local states in the vicinity of the dopants, it is important to understand the temperature and field dependence, positional and energetic disorder parameters of local centers in order to estimate the carrier mobility in doped films. However, no work has been done on carrier mobility of organic doped films devices though many references can be found on the role of polar dopants on charge carrier transport are molecularly doped in polymer materials. These materials are working on polystyrene and bisphenol-A-polycarbonate as binders and several groups of donors and acceptors as charge transport materials [40-42].

In addition both energy transfer and carrier trapping in doped host (Alq_3) films are responsible for doping excitation, which is necessary to increase the luminance, lifetime, and producing full-color spectral emission [43-44]. To ensure the efficient energy transfer between host-guest, the overlap of the host emission and the dopant absorption is a key requirement, whereas for efficient hole or electron trapping, the Highest Occupied Molecular Orbital (HOMO) or Lowest Unoccupied Molecular Orbital (LUMO) energy levels of the dopant must fall within the energy gap of the host. Alq_3 luminescence originates from the radiative decay of singlet excitons or charge carrier injection in the case of photo-excitation and EL. Both EL and PL emissions from organic or polymers are thought to be related to the excitonic emission. However, the diffusion of excitons and its interaction with the trapping sites can lead to decrease in the PL and EL quantum efficiency.

The exact nature and kinetics of excitons in organic small-molecules or polymer materials are still debatable [45-48]. There is also little information on excitons lifetime and response time in doped organic materials [49-54]. The exciton response time is the time

between the formation and radiative decay of the excited state. Furthermore, the transport states for carriers to hop over the localized states (shallow levels and deep traps) in the doped film have important implications to the carrier transport and influences the efficiency of the devices [55]. No direct measurements of the distribution of transport states have been reported on doped organic (small molecules) semiconductor currently.

1.3 Motivation of Work

Therefore, the motivation of this study is to track carrier behavior in organic doped films in order to design high efficiency of optoelectronic and photonic devices with active organic layers. The fundamental understanding of the effects of doping on the charge carrier mobility and the transient PL and EL of excitons in Alq₃ at room temperature are focused and investigated. The doping influence on the trap depth, the diffusion coefficient, and the length of excitons for various concentrations of dopants in Alq₃ films are the motivation of this thesis. For this work, the effect of polar dopants **4-(diacynomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyan (DCM)**, **3-(2'-benzothiazolyl)-7-diethylaminocoumarin (C-6)** and non-polar molecular **5,6,11,12-tetraphenylnaphthacene (Rub)** were used as dopants in Alq₃.

1.4 Objectives of PhD study

- (i) Study of doping effects on the carrier transport properties in Alq₃ films.
- (ii) Develop a mathematical model for computation of carrier mobility in host material by simulating with Time-of-flight measurements results
- (iii) Study of doping effects on transient PL and EL of host material for different dopants at room temperature,
- (v) Estimate different parameters in the host materials for different dopants

1.5 Contributions and findings

- (i) A new mathematical model is developed based on charge velocity distribution in Gaussian function for the calculation of carrier mobility in host material. This is a modified approach to estimate the carrier mobility by simulating with TOF data instead of using a conventional graphical method (Scher-Montroll model). This new approach is justified by the carrier mean mobility of pure Alq₃ of $7 \times 10^{-5} \text{ cm}^2/\text{Vs}$, which is comparable to the reported results of 10^{-6} to $10^{-5} \text{ cm}^2/\text{Vs}$.
- (ii) A critical field barrier is observed for the first time in organic doped Alq₃ material from the TOF measurements. This critical field caused the carrier mobility not follow the linear relationship with the square root of applied electric field. The positional and energetic disorder parameters are first time calculated for doped films and found higher than pure Alq₃. The stronger dipole moment property induced higher positional and energetic disorders are observed from DCM and C-6 doped films. This is due to trapping states are broadened and deepened by these dopants in Alq₃.
- (iii) Interesting results are observed from the co-doping of Rub:DCM and Rub:C-6 (1 wt.%) in Alq₃ films. The positional and energetic disorders are reduced compare

with single doped films. The co-dopant improves the carrier mobility in the host film. This is due to the reduction of energetic disorder associated with the effect of strong dipole moments contributed from DCM and C-6 shielded from non-polar of Rub in the films. The strong Coulomb force interactions between polar molecules of DCM and C-6 to carriers are minimized by the introduction of Rub.

(iv) The PL decay time, diffusion coefficient and diffusion length of excitons are reduced with doping concentration compared with pure Alq₃ film. The DCM doped films showed the shorter diffusion length compared with Rub and C-6 in Alq₃. This can be attributed to higher dipole moments 26 D of DCM molecules compared to ~ 9 D for C-6, where induced higher attractive force facilitates the excitons diffusion from Alq₃. The shorter diffusion length in doped films can be caused by the trapping sites from the doping effect, which were created and distributed Gaussianly in films.

(v) The EL response time is found delay with doping concentration in OLED devices. This delay of response time can be due to the traps strongly affect the charge transport property at equilibrium conditions and most carriers will occupy those deep states. This leads to delay of slow recombination of electron and hole. The co-doped devices of Rub-C-6 and Rub-DCM at 1 wt.% showed the delayed time t_d is 16 % longer than pure Alq₃ device and at about the same level as compared with single doped of DCM, C-6 and Rub in Alq₃ devices. The heavily doped in Alq₃ active layer showed the longer delayed time t_d before the EL grows, where the delayed time t_d was increased to 150%, 100% and 34% for DCM, C-6 and Rub doped respectively. The redistribution of internal field due to the trapped charges is strong enough to affect the carrier mobility in doped active film.

- (vi) The trap depth is first time estimated base on transient capacitance-voltage model for organic doped films. The trap depth increased with doping concentration in Alq₃ films. This model confines the Gaussian width σ' to be 0.16 ± 0.02 eV for pure Alq₃ film, and increases to $\sim 0.30 \pm 0.04$ eV for the doped films. The estimated trap depth E_t is increased from 0.65 ± 0.05 eV to about 0.71 ± 0.15 eV as the dopant increased in the samples. The formation of deeper localized states located below the intrinsic DOS distribution of Alq₃ is due to the strong interaction of DCM and C-6 with Alq₃ molecules induced higher positional and energetic disorders.

1.6 Organization of report

This thesis is organized as follow: Chapter 2 is provided an insight to understanding the carrier behavior in organic doped films by a number of basic models that describe the charge transport, exciton kinetics and capacitance transients. The experimental methodology of samples preparation and fabrication is detailed in Chapter 3. The experimental results are summarized in Chapter 4-7. Chapter 4 deals with the basic study of Alq₃ related with the effect of deposition rate and carrier mobility. It demonstrates the importance of understanding the film quality, carrier behavior, and trap depth in pure Alq₃ film. Chapter 5 is devoted to mean carriers mobilities of the doped films. The co-doped of two dopants in Alq₃ are presented too. The positional and energetic disorders of these doped films are estimated. Then in chapter 6 the PL and EL decay of the excitons in doped films are investigated. The diffusion coefficient and diffusion length of excitons for various concentration of dopants in Alq₃ were estimated. Chapter 7 presents the observed capacitance transients that can be successfully modeled in terms of the de-trapping of carriers from a

discrete trap level to a Gaussian distribution of transport states. Chapter 8 concludes the report with a summary, and includes suggestions for continuous work in the future.

Chapter 2 Background and Fundamentals Aspects

2.1 Introduction

This chapter will introduce the structure of host-guest organic materials, basic theory of organic light emitting diodes, theories of time-of-flight measurements, mechanisms of photoluminescence and electroluminescence and capacitance-voltage measurements. The propose general function approach to simulate the time-of-flight measurements would be presented too.

2.2 Organic Semiconductor Materials

(a) Tris (8-hydroxyquinolato) aluminum (Alq_3)

Figure 2.1 The molecular structure of Alq_3 with pyridyl and phenoxide as acceptor and donor, respectively.

Alq_3 is the key electroluminescent material currently used in organic light emitting diodes based on “small molecules”, with stable and efficiency photoluminescence (PL) of 25-30% [55]. Alq_3 is well localized on the quinolate ligands but donor-acceptor characteristics are due to electron transitions between a phenoxide donor side-located HOMO and a pyridyl acceptor side-located LUMO of the quinolate ligands [56]. Under the field of about $4 \times 10^5 \text{ Vcm}^{-1}$, Alq_3 possesses a comparatively high mobility of electrons (about $1.4 \times 10^{-6} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) and low mobility of holes (about $2 \times 10^{-8} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) [57]. This difference of

mobility is attributed to the distribution of the electronic density on a neutral molecule of Alq₃. A nitrogen heteroatom possesses a higher electronegativity than a carbon atom, draws off onto itself a part of the electronic density of the π -electron system, and acquires a negative charge. Due to ionic bonding of aluminum-oxygen, a cloud of excessive electronic density forms on the oxygen. Then by virtue of Coulomb interaction some regions of deficient electron density are localized in the periphery of the molecule. Injected electrons repulsed from the negatively charged atoms of nitrogen and oxygen recompense the deficit of the electron density and are localized on the periphery of the molecule. A hole is localized preferentially in the vicinity of the oxygen anion and in the vicinity of nitrogen. Hence, the injected electrons are localized in the periphery of the molecules and their jumping conductivity is facilitated by Coulomb interaction with a positively charged periphery of the neighboring molecules. A hole is localized in the inner part of the aluminum complexes. So the jumping length for them is much longer and the Coulomb interaction creates the supplementary barrier for hole migration.

(b) Organic Dopants

(i) 4-(diacynomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyan (DCM)

DCM

Figure 2.2 The molecular structure of laser dye, DCM

Red emission by an OLED is usually obtained by doping red fluorescent dye into a host material that has a wider bandgap than the guest red dopant. DCM is one of the most commonly used red emitters in color OLEDs and has been intensely investigated [1-4]. The DCM is a very efficient arylidene laser dye with a dimethylamino [$-N(CH_3)_2$] electron donor group that is linked to dicyanovinyl [$=C(CN)_2$] electron acceptor groups by an effective π -conjugated pathway of alternating double and single bonds [58,59]. Electric field induced second harmonic (EFISH) measurements yielded a hyperpolarizability-dipole for DCM 1.6 times greater than the value of others. The lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energy level of DCM are located at 3.2 eV and 5.4 eV, which is well coupled within the energy band gap of Alq_3 . In fact, DCM is acting as a recombination center in Alq_3 because of its low reduction potential and good fluorescent efficiency [60]. These dyes possess a high concentration dependent emission. However, a desirable red color can only be obtained at high concentration, which dramatically reduces luminance efficiencies.

(ii) 5,6,11,12-tetraphenylanthracene or RB (Rub)

Rubrene

Figure 2.3 The molecular structure of Rub

Rubrene (Rub), a dopant with low ionization potential, has a good quantum efficiency of fluorescence, and the emitting layer doped with rubrene could impede formation of dark spots during device storage. The highest occupied molecular orbital (HOMO) state and the lowest unoccupied molecular orbital (LUMO) state of Rub and Alq₃ are (-5.51, 3.59 eV) and (-5.61, -2.91 eV), respectively, and are obtained by cyclic voltammetry. The HOMO and LUMO of rubrene are located within the energy gap of Alq₃ so that both electrons injected in the doped layer and holes diffused into the doped layer are bound into the rubrene molecules to form excitons. Another interesting aspect of Rub is that all by itself is a good charge transporter. In fact, it is known that in the crystalline state, Rub exhibits a large hole mobility of a fraction of $7\text{--}9 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Rub doped in host materials traps carriers, and emits light only when electrons and holes directly recombine on it [61-63]. Rub has been proved extremely stable in the reduction and oxidation process in a cyclic voltammetry measurement. This property directly assures that the radical species are stable in carrier transport process in both hole and electron transport, and contributes to the enhancement of the device stability.

(iii) 3-(2'-benzothiazolyl)-7-diethylaminocoumarin (C-6)

Coumarin 6

Figure 2.4 The molecular structure of C-6

Coumarin 6 (C-6) and its derivatives show sufficient fluorescence in the visible light range for it to be used in laser dyes and organic light-emitting diodes (OLEDs). Researchers have studied the photophysics of C-6 compounds since the 1940s due in part to the tunability of their absorbance and fluorescence. C-6 is a common green laser dye, used in green fluorescent OLEDs.

2.3 History of Organic Electroluminescence (EL)

Organic EL from anthracene crystals was observed by M. Pope et al. [64] and W. Helfrich et al. [65] in the early 1960s. The operating voltage ranging from several hundred to several thousand volts were needed due to the anthracene crystals thickness of $10\text{ }\mu\text{m} \sim 5\text{ mm}$. Due to these requirements, EL from anthracene and related crystals has long been of interest to basic research in optical characteristics and electrical transport mechanism rather than commercial applications. In 1982, P.S. Vincett et al. [66] achieved bright blue EL from vacuum-deposited $0.6\text{ }\mu\text{m}$ thick anthracene crystal films with an applied bias of less than 100 V. C.W. Tang and S. A. VanSlyke [1] made a breakthrough to fabricate 100 nm thin bilayer organic devices. The devices were made of evaporated small molecular weight organic materials including N,N'-diphenyl-N, N'-bis(3-methylphenyl) 1-1'-biphenyl-4,4' diamine (TPD) and tris (8-hydroxyquinoline) aluminum (Alq_3). They achieved a very high brightness of more than 1000 Cd/m^2 and high external quantum efficiency of 1 % (photons/electrons) at an applied bias of less than 10 V. The thin organic structure reduced the operating voltage to a manageable range of displays and the bilayer structure increased the luminous efficiency. Following this achievement, Adachi et al [6] succeeded in fabricating the stable multi-layer devices by inserting hole, emitting and electron transport layers between the two electrodes. In 1989, Tang et al. [5] developed a laser-dye doped Alq_3 multilayer structure, in which the

fluorescent efficiency was improved, and the emission color varied from the original green color of Alq₃ to the dopant emission color.

Another achievement in organic EL was the discovery of polymer EL in 1990 by J.H. Burroughes et al. [67]. Polymer light-emitting devices (PLEDs) have several potential advantages, such as fabrication by spin-coating [67,68] or inkjet-printing [69,70] from solutions, and subsequent thermal treatments. In general, small molecule and polymer OLEDs make use of the fluorescent emission of singlet excitons. If the injected hole and electron carriers recombine randomly, then the probability of forming spin-singlet and spin-triplet states is 25 % and 75 %, respectively. The ideal maximum fluorescent yield is therefore limited to 25 % by spin statistics. To overcome this limitation, M.A. Baldo et al [71,72] suggested and demonstrated phosphorescent OLEDs, where the EL is due to triplet emission, by doping phosphorescent molecules into a fluorescent host layer. Thus, this increased the molecular EL efficiency from 25 % to 100 %. Recently, P.W.Wang et al [73] and J.N.G. Pillow et al. [74] developed macromolecular EL devices, based on dendrimers, which composed of a luminescent core and branching dendrons that protect the exciton in the core. However, the transport properties of dendrimer films worsen with increased branching or dendrimer generation [75].

2.4 Advantages and disadvantages of OLEDs

OLEDs are already commercialized, and making inroads into liquid crystal display (LCD) markets. Currently, most of the commercialized OLEDs are used in low information displays with limited size such as mobile phones, digital cameras, and some palmtop computers. OLEDs have several advantages over LCDs. They are as follow:

- Self-luminous: Backlighting, diffusers and polarizers are not needed, so the overall efficiency is better than LCDs

- Low cost and easy fabrication: Inkjet printing and screen-printing are possible.
- Color selectivity: A variety of organic materials have been developed for blue to red emission.
- Light weight, compact and thin devices: The total thickness of the organic layers is only about 100 nm.
- Flexibility: It is easy to fabricate OLEDs on flexible plastic or on curved substrates
- High brightness and high resolution
- Large emissive displays
- Wide viewing angle (up to 160 degrees)
- Fast response (decay time $< 1 \mu\text{s}$)

The disadvantages of OLEDs are mainly related to their lifetime. The organic materials are sensitive to oxygen and moisture, so encapsulation is required to protect the devices from degradation agents. With proper encapsulation, lifetime exceeding 10,000 hours has been demonstrated [37,76]. The disadvantages are as follow:

- The relatively short lifetime is due to sensitivity to air and moisture
- Low glass transition temperature T_g for small molecular devices ($> 700^\circ\text{C}$). The operating temperature cannot be beyond T_g .
- As low mobility requires high-applied bias: to inject and transport charge carriers in dispersive organic media, very high electric fields (0.1-2 MV/cm) are needed.

2.5 Basic OLED structure

Figure 2.5 Schematic diagrams of Devices Structure of multi-layers device of OLEDs with electron transport layer (ETL), electron emission layer and hole transport layer (HTL)

Small molecular OLEDs are typically fabricated on glass or flexible plastic substrates coated with a transparent conducting anode such as indium tin oxide (ITO). The organic layers are thermally evaporated on the anode substrate with a total thickness of about 100 nm, and then a low work function metal cathode is deposited on the organic layers. If a forward bias is applied to this structure, holes are injected from the anode, and electrons from the cathode. The injected electron-hole recombine to form excitons, and some of these decay radiatively. Normal operating voltage is about 5-20 V, corresponding to average electric fields of 0.1-2 MV/cm, which are very high compared to the typical fields ~ 10 kV/cm in inorganic semiconductor devices. Besides, the resistivity ρ of the devices ranges over more than eight orders of magnitude, with very high values of 10^5 - 10^{13} Ωcm in forward bias. In reverse bias, ρ is also very high (10^9 Ωcm). Therefore, the OLEDs generally exhibit poor rectifying properties.

ITO is generally a wide band-gap amorphous semiconductor with $E_g = 3.5\text{-}4.3$ eV [77] composed of indium oxide (In_2O_3) and a small amount of tin oxide (SnO_2) (~ 5 wt%). Most OLEDs use ITO as the anode because of its relatively high work function and its unique transparent-conducting characteristics, high work function [78], low electrical resistivity, and good efficiency for hole injection into organic materials as well as ease of patterning [26,79-81]. The conductance and transparency of ITO are mostly dependent on the film thickness and the composition ratio of the two components. The resistivity of 200 nm thick ITO is about $\rho \sim 10^{-3}$ Ωcm with mobility $\mu \sim 10$ cm^2/Vs [77]. With increasing ITO thickness the conductance increases, but the transparency decreases. The ITO transparency is normally quite high in the visible range; typical transmission is more than 90 % for 150 nm thick ITO [77]. Another very important ITO parameter is its work function (ϕ) or Fermi energy (E_f) relative to the organic materials. Because the highest occupied molecular orbital (HOMO) energies of organic materials are typically $E_{\text{HOMO}} = 5\text{-}6$ eV, a ϕ is needed for the anode to enable efficient hole injection into the organic layer.

The surface electrical properties of ITO are expected to directly influence the characteristic of the OLEDs device as the organic material is coated directly onto ITO. The surface roughness morphology of ITO may produce localized electric fields, which can end-up with microscopic short circuits [82-85]. Hence, to overcome these existing problems, many solutions which involved changing the properties of the organic materials or introducing an intermediate stabilization layer with proper carrier injection/transport characteristics between the ITO and the active luminescent layers have been suggested [83,86-90]. The alternative way is to modify the ITO surface itself through chemical and mechanical treatments [80,90-93]. Many different techniques exist for the surface treatment

of ITO samples such as mechanical [94,95], chemical [96], UV-ozone and O₂ plasma treatments [97-99].

To control of surface morphology roughness, electrical properties and work function of ITO, many researchers proposed dry (oxygen-plasma) and / or wet (aquaregia) cleaning processes both alone and in combination, one after the other [95,100]. Surface of ITO treated *in situ* by oxygen plasma possesses a higher work function of 5.2 eV compared to untreated of ~4.7 eV. Besides, it also yields smoother surface morphology and the lowest surface resistance [85,101-102]. Chemical absorption of nitric acid on ITO, which is used to protonate the surface of ITO, also yields work function shifts as high as 0.7 eV compared to the nontreated ITO [103,104]. Due to this treatment, the contact between the protonated hole injecting oxide electrode and organic material becomes ohmic facilitating the hole injection. The efficient injection of holes produces a positive space charge in the organic layer, which enhances the emission of electrons from the cathode. Hydrogen peroxide is also used to oxidize the surface of ITO, and many have reported that this treatment has slightly increased the ITO work function, as well as In/Sn ratios to 8-12.7 compared to ultrasonification in organic solvents only range between 7-9.6.

These surface morphology treatments of ITO contributed to the final value of the work function, and this can be attributed to several factors. These include the concentration of the different species forming the ITO (namely, metallic In and Sn, SnO, SnO₂ and In₂O₃), and also the relative amount of the crystalline and the amorphous phases, as reported by others [105]. The variation of the oxygen concentration on surface of ITO after the treatments also affected work function as reported in [86,97].

Hole transport layer (HTL) is the first layer after the ITO substrate. Since most of the low molar mass emitters are electron transport materials, there is a need to provide hole carriers in the device to achieve higher quantum efficiency and increasing lifetime. HTL also

acts as an electron-blocking layer. There is a large number of hole transporting low molar mass organic materials, where a whole series of aromatic diamines have been synthesized and used as HTL in OLEDs. Aromatic diamines use is attributed to their low ionization potential, high hole mobility of $10^{-3} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and low electron mobility $\ll 10^{-8} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [8]. Another advantage is their capability for forming uniform, amorphous layers free of pinholes upon deposition under high vacuum. However, the glass transition temperature, T_g for aromatic diamines is often not high enough to avoid posing problems during high-temperature fabrication steps or to completely inhibit crystallization at moderately high operating temperatures, where crystallization is accelerated [106,107]. To overcome this low T_g problem for hole transporting layer, non-planar structures are used and triarylamine molecules with dendritic, spiro and asymmetric structures have been designed and synthesized [108]. These hole-transporting materials have higher thermal and morphological stability than aromatic diamines. There are some common used examples of HTL, such as N,N'-diphenyl-N,N'-(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD), N,N'-di(naphthalene-1-yl)-N,N'-diphenyl-benzidine (NPB), 4,4',4''-tri(N-dibenzo[a,g]carbazolyl)triphenylamine (TDCTA) and tetrafluoro-tetracyano-quinodimethane (F4-TCNQ) [26].

The majority of electron transport layer (ETL) materials are also good emitters. But there are some classes of organic materials that are used as non-emissive, combined electron transport and hole blocking layers. Some typical examples of ETL are 2-(4-biphenyl)-5-phenyl-1,3,4-oxadiazole (PBD), bis (benzimidazolyl) perylenedicarboximide (PV), Alq₃ and tetrathiafulvalene (TTF) [54]. The molecular structure of PBD has nitrogen in heterocycles ring, and due to N is higher electronegatively to carbon atom, draws off onto itself a part of the electronic density of the π -electron system, to acquire a negative charge. So, some regions of deficient electron density are localized in the molecular structure. This

would repulse injected electrons from the negatively charged atoms of nitrogen and recompense the deficit of the electron density, which is localized on the periphery of the molecule [109]. Hence, ETL provides electron-transporting paths in OLEDs.

The organic active layers are inserted in between ETL and HTL of multilayer structure of organic LED devices. Holes and electrons injected from electrodes and transported through HTL and ETL respectively and recombined in organic active layer, have to keep far away from electrodes to avoid or reduce the quenching of luminescence. The relaxation of singlet excitons in the organic active layer gives rise to electroluminescence. The wavelength and bandwidth of the emitted light depends on bulk physical material properties, and can be influenced by the design and synthesis of suitable organic molecules and their subsequent combination of single and multilayer OLEDs.

Low work function materials such as Ca ($\phi \sim 3$ eV), Mg ($\phi \sim 3.7$ eV) and Al ($\phi \sim 4.3$ eV) [110] are used as cathode to minimize the energy barrier for electron injection from E_f of the cathode to the lowest unoccupied molecular orbital (LUMO) level of organic materials (typical $E_{LUMO} = 2-3$ eV). The problem of many low work function metals is extreme reactivity to oxygen and water, so Ca and Mg should be protected by an additional layer such as Al. Another way to reduce the barrier for electron injection is to insert a very thin (~ 1 nm) insulating layer of LiF, CsF, or AlO_x [110-124] between the top organic layer and the Al cathode; in general LiF and CsF are more effective than AlO_x . These buffer layers apparently generate a dipole layer, and thus reduce the barrier for electron injection like the dipole layer on the ITO by surface treatments. A photoelectron spectroscopy study [125] has shown that CsF is decomposed by Al metal deposition; the F atoms react with Al to form AlF_3 . The dissociation likely results in Cs^+ and n -doped organic layer, and probably improves the electron injection from the Al cathode.

The lifetime and external quantum efficiency of OLEDs can be further enhanced by adopting the guest-host emitter system [126]. Shi and Tang [24] reported that the external quantum efficiency increased to 4-5 % and device life-time was prolonged to over 7500 h by adding fluorescent dye (DMQA) into active host material (Alq_3). Kido and Iizumi [127] also achieved remarkable improvement by doping C-6 into Alq_3 . This is due to the energy transfer from the excited host molecules to the dopant molecules or the direct recombination of the dopant molecules resulting from carrier trapping or both [40]. Kalinowski et al. [128] provided a thorough explanation on the mechanism of how electric field assisted the energy transfer from host to guest.

2.6 Molecular doped guest-host system

Normally, the active region of the OLED was prepared by a mixture of molecules, polymers and dye-doped organic materials [1,129]. Sometimes the active layer is doped with dye material in order to increase the emission intensity, select the emission color, provide both good charge transporter and reduce unwanted self-absorption effects. In general, the HOMO-LUMO energy gap of the guest molecule is smaller than that of the host, and at least one of the HOMO or LUMO levels of the guest material is located inside the host HOMO-LUMO gap. If the HOMO or LUMO level of the doped molecules is inside the host energy gap, then the dopant generates extrinsic trap-sites. The current density will consequently be reduced by these traps at a given applied bias. With increasing trap density net mobile charge density decreases. The energy transfer theory for molecular guest-host system will be discussed later.

2.7 Carrier Transport in Organic Devices

The transport mechanisms in organic solids are not well understood. The difficulties and complications of the transport processes are due mainly to the trap states in these organic materials. Without comprehensive knowledge of the distribution and characteristics of these traps, it is not possible to comprehend the exact current-voltage properties of OLEDs. Basically, there are two types of traps, intrinsic and extrinsic [130-132]. Intrinsic traps are due mostly to the amorphous structure of the organic film. They include conformational defects, and molecular structural defects. Even in the perfect molecular crystal, the carrier can be localized in a specific molecule due to the molecular crystal characteristics of relative weak interaction between molecules. Extrinsic traps are typically generated by chemical impurities, somehow unavoidable due to the nature of the synthesis or device fabrication processes, or by intentional doping. These traps and the localized states generated are closely related to the transport mechanisms and EL properties of OLEDs. Almost all organic devices show trap-related transport behavior. Before discussing the localized states in crystalline molecular solids, remarks on the difference between molecular and inorganic crystals may help clarify not only some of the transport properties but also some of the electro-optic characteristics of OLEDs.

Inorganic semiconductors are composed of regular arrays of unit cells, in which continuous conduction and valence bands are generated. Thus the electrons in the conduction bands are free to move without passing through any localized state. The carrier transport is then described by a band structure mechanism. In particular, the carrier mobility is independent of the electric field. In case of excited states, the excitons of inorganic semiconductors are very loosely bound Mott-Wannier excitons, with binding energies ~ 10 meV [133], i.e., smaller than room temperature thermal energy.

In contrast to inorganic crystals, the molecular crystals are made of discrete molecules generally held together by van der Waals forces [134]; the molecule itself consists of atoms bounded to each other by strong covalent bonds [135,136]. The van der Waals interaction between neighbor molecules is relatively weaker compared to the strong interaction between the unit cells in inorganic crystals. The most peculiar feature of the structure is the spatial localization of the valence and conduction bands with narrow bandwidths (0.1 eV) [137]. Due to localization, these levels are labeled as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), rather than valence and conduction bands. The transport properties of carriers are affected by the localization of the HOMO and LUMO states, as the localized carriers move from site to site either by thermal- or electric field-assisted hopping. Hence, typical carrier mobilities in molecular crystal are only $\sim 1 \text{ cm}^2/\text{Vs}$ [138,139]. The mobility may be calculated using either a hopping or a band mechanism, depending on the degree of localization. If localization is strong, then the mobility is explained by a hopping model; if it is weak, then it exhibits band-like characteristics [140].

The carrier transport in disordered molecular solids is strongly dependent on the temperature and applied electric field. Due to the positional and energy disorder of the molecular system, the carriers are trapped very easily. The presence of positional disorder inevitably gives rise to the energy disorder via dependence of the potential energy of interaction upon the distance between interacting particles [141,142]. Thus, the transport properties in organic amorphous solid are analyzed by hopping models [143]. In disordered hopping systems, both positional and energy disorder affect the carrier jump rate. The mobility μ of the carrier in this model is assumed to follow an Arrhenius dependence on the temperature T and applied field as shown below:

$$\mu(F, T) = \mu_{\infty} \exp[-(\frac{2\sigma}{3kT})^2] \exp[\beta\sqrt{F}] \quad (2.1)$$

where T is the absolute temperature, k is the Boltzmann constant, μ_{∞} is the high temperature limit of the mobility, and $\beta = C[(\frac{\sigma}{kT})^2 - \Sigma^2]$; where C is a temperature and field independent constant related to the intersite distance, σ is energetic disorder of the film, Σ is a temperature independent parameter related to positional disorder. Equation (2.1) shows that the carrier mobilities in organic films depend exponentially on $\sqrt{F}$ at a fixed temperature. However, in inorganic semiconductors, the carrier mobility is independent of the applied field. If a carrier is trapped in a potential well (the symmetry dotted lines in Fig. 2.6), then it needs activation energy E to jump out of the well. When a field F is applied (the linear line in Fig. 2.6), the potential is deformed into the asymmetric curved lines: one side of the potential barrier increases, and the other side decreases. Thus, the actual decrease of the potential barrier or activation energy is proportional to $\sqrt{F}$.

Figure 2.6 The potential barrier is plotted against the square root of applied electric field. When an electric field F is applied (linear line), the symmetric potential well (dotted-lines) transforms to the asymmetric well (curve line). Hence the field lowers the energy barrier and the actual activation energy, increasing the escape probability of a trapped charge.

2.8 Time-of-Flight Measurement

The time-of-flight (TOF) measurement was first described by Haynes and Shockley [144] and Lawrence and Gibson [145]. Kepler [146] and LeBlanc [147] first used TOF to study organic solids. Vannikov [148] was the first to measure mobilities of polymers using this method. Initially, the TOF method was mainly used to study transport properties of inorganic solids. As interest grew in the applications of polymers to xerography in 1970s, and in OLED and Field Effect Transistor devices in the 1990s, TOF was more often employed to measure the mobility of semi-conducting organic materials [149,150]. TOF measurements have become the conventional method for studies of transport phenomena in organic and polymers in the past several decades. The schematic diagram of TOF is illustrated in Fig. 2.7. A sample with thickness d is sandwiched between two planar metal electrodes.

Figure 2.7 A typical experimental setup for measuring mobility using TOF

The top electrode is semitransparent and should be a non-injecting or blocking electrode for the carrier transport across the sample. The two electrodes are connected to an external circuit via a resistor with resistance R and an applied voltage. The carriers are then generated with a short flash of laser pulse absorbed in a thickness δ , with $\delta \ll d$. The light pulse duration t_e should be short, i.e., $t_e \ll t_T$, with t_T the transit time. The light exposure creates bound electron-hole pairs near one of the electrodes. Under the influence of the applied electric field, a fraction of the pairs separate and then drift in a sheet across the sample, inducing a time dependent photocurrent in the external circuit. The transient photocurrent is recorded with a high-resolution digital oscilloscope. By switching the polarity of the battery, one can measure either hole or electron photocurrent. The first condition for TOF is that the amount of charge generated should be small enough so that space-charge effects do not change the internal field strength significantly. This will be true as long as the injected charge q_0 satisfies,

$$q_0 \ll CV \quad (2.2)$$

where C is the sample capacitance. The shape of the drift leading edge with current can broaden as a result of the mutual repulsion of the carriers within the generation volume. It has been shown [134] that the error in transit time due to this mutual repulsion is given by

$$\frac{\Delta t}{t_T} \approx \frac{q_0}{CV}. \text{ On the other hand, } q_0 \text{ should be large enough to give unequivocal signals.}$$

The second condition for conventional TOF is that the circuit reaction time $\tau = RC$ is much smaller compared with the average drifting time of the charges. A small value of τ can be realized by choosing small R or C . But R has some lower bound so that the oscilloscope has enough precision. As the device capacitance is directly proportional to the area and inversely proportional to thickness, a smaller value of C can be realized with a higher thickness and a smaller cross section.

A third condition requires that the dielectric relaxation time $\tau_0 = p\varepsilon_0\varepsilon$ be long enough compared to the transit time, and with p as the dark resistivity. This is the time required for the insulator to restore itself to the state of neutrality after a small change in the carrier population. The intrinsic concentration of carriers is very small for materials with small dielectric relaxation time [134]. Organic and polymer solids have dark resistivities such that this condition for TOF is readily satisfied in most materials of potential interest for xerography, field effect transistor and LEDs.

2.9 Scher-Montroll Model

In an ideal case for the photocurrent transient, the photocurrent pulse should display a rectangle-like shape when the circuit reaction time is negligible assuming all the charges propagate in a plane wave manner as shown in Fig. 2.8. There should be a sharp decrease at the time when the carriers exit the sample ideally. The time corresponding to this decrease is

usually known as the transit time. A small tail decaying exponentially should be observable if the circuit reaction time is not zero.

Figure 2.8 ideal situations when charges drift in a plane wave. The tail is observed due to circuit reaction time is not zero.

The measured tail is longer than an exponential decay that can be explained by the existence of traps. Traps are localized states for electrons or holes. When the trap density is not high, the majority of the charges will drift in a thin plane. An explanation in terms of density-of-states is illustrated in Fig. 2.9 [151]. In a perfect crystal, the free electron states form bands separated by gaps with sharply defined edges, as shown in Fig. 2.9(a). In the presence of a single localized imperfection, the band edges will not be disturbed if there is no interaction between the impurity state and the crystal state. Then a carrier will move essentially as if it were in a perfect crystal. The impurity level will be sharp, as shown in Fig. 2.9(b). But if the impurity or defect level does interact with the lattice, then the energy levels of the impurity and the crystal will be affected. Fig. 2.9(c) showed the interaction between the impurity level, and the valence or conduction bands form a band of localized states. A carrier moving in the crystal can be trapped or scattered by these localized states, exhibiting a transient photocurrent shape as shown in Fig. 2.10 [152]. In the presence of translational or compositional disorders, the localized states in the gap can trail off in a continuous tail from the valence and conduction bands. The states are so numerous that transport is possible from

one defect site to another. Since the motion of the carrier is wavelike in the extended states forming the conduction band, and is that of phonon-assisted hopping in the localized states, the mobility displays a gap [153].

In the case of amorphous materials with an almost continuous trapping center extending deep into the forbidden gap, the shape of the transient photocurrent is as shown in Fig. 2.10 [152]. There is a sharp spike followed by a rapid decay to a plateau that tails off gradually so that it is difficult, and sometimes impossible to determine the transit time. This type of transport is referred as dispersive transport, which is characteristic of most amorphous inorganic solids, organic, and polymeric solids.

Figure 2.9 Density of electronic states $n(E)$ as a function of energy E . (a) a perfect crystal, (b) a crystal containing only one localized imperfection, and (c) a crystal containing a low concentration of localized imperfection.

According to Scher and Montroll, the effect of disorder can be described by a power distribution for response time given by,

$$\psi(t) \sim t^{-(1+\sigma)} \quad (2.3)$$

where σ is a disorder parameter that has values between zero and unity. The more disordered the material, the smaller the value of σ and the more dispersive the transport. One way to look at this distribution function is that in $\psi(t)$ decreases with increasing time. Thus, at shorter times there is a greater fractional change than at longer times. A key prediction by Scher-Montroll model is that the transient photocurrent will decay as,

$$i(t) \sim \begin{cases} t^{-(1-\sigma)}, & t < t_T \\ t^{-(1+\sigma)}, & t > t_T \end{cases} \quad (2.4)$$

This relation is sometimes called “power law”, in which the tail current obeys the power relation. Following this relation, one can easily obtain the transit time by plotting the current and time in log-log scale. The point of interaction of the two branches in Eq. (2.4) defines the transit time. According to this model, the transit time is,

$$t_T \sim \frac{C}{W_0} \left| \frac{L}{l(F)} \right|^{1/\sigma} \exp\left(\frac{\Delta_0}{kT}\right) \quad (2.5)$$

where C is a constant of order unit, W_0 is a scaling factor, Δ_0 is a zero field activation energy, and $l(F)$ is the mean displacement in the field direction per hop. At low field, it may be assumed that $l(F) \propto F$ [154], thus, the transit time varies with thickness and field as $(L/F)^{1/\sigma}$.

The most important assumption in Scher-Montroll model is the power response time distribution $\psi(t) \sim t^{-(1+\sigma)}$, which is the reason for its success in amorphous inorganic solids. However it fails to be applicable to a lot of materials especially dispersive organic and polymeric solids. Bassler [143] argued that the response time distribution $\psi(t) \sim t^{-(1+\sigma)}$ in Scher and Montroll’s model is realized in materials where the multiple trapping within an

exponential distribution prevails, but organic glasses and molecularly doped polymers do not fall into this category. In most cases, the charge distribution can be well approximated by a Gaussian, which is not consistent with Scher-Montroll model. Furthermore, Godson and Hirsh [155] had earlier observed that in 1:1 TNF.PVK, the tail of the photocurrent were closer to an exponential than a power law.

In order to apply Scher-Montroll's power relation, one requires that the circuit reaction time $\tau = RC$ be much smaller than the transit time t_T so that the measured photocurrent is the same as the drifting current in the sample. Another requirement is that the quantity of charge produced by the laser is much less than the product of the sample capacitance and applied voltage ($q_0 \ll CV$), so that the drifting charges perturb the external electric field as little as possible. But at the same time, the quantity of charge carrier should be large enough to give unequivocal signals. However, in many low mobility organic and polymeric materials, these conditions are sometimes difficult to be satisfied simultaneously, a case which has limited the applicability of Scher-Montroll's method in these materials. A lot of efforts have been put to solve this problem, yet it has not been successfully solved [143].

As mentioned earlier, the majority of charges do not drift uniformly due to the effect of traps. Scher-Montroll model [153] and other studies [143] reported that the transit time for dispersive transport is a function of sample thickness. As a result, an interpretation in terms of charge carrier mobility is not meaningful. Scott et al. [156] have described a method to obtain the mean carrier mobility by a carrier velocity distribution. In the framework of Scher-Montroll model, they found that the velocity distribution could be described by a Gaussian function. Then the mean mobility is the average of the mobilities of all the carriers.

2.10 Propose: General Functional Approach to Fit TOF Photocurrent

This model is based on a simple assumption that the sample can be well approximated as a two-parallel capacitance. The capacitor is symmetric so that it is treated as one dimension here. Suppose that a single short laser pulse (the width of pulse is negligible) produces many electron-hole pairs or excitons in the organic layer, and then the external electric field successfully separates a total amount of charges (negative and positive) by applying negative bias drift across the sample through the external circuit, the charges inside the sample would follow a random walk with different hopping probabilities in forward and backward directions [157]. All the negative charges will drift uniformly to the other side in a plane if there is no trap in the sample and the charge density is a delta function. If traps exist, the charges will be trapped and repeatedly released many times during their drift. $\rho(x,t)$ is used to describe the line charge density for those charges drifting in the sample at position x and time t . This function is continuous and differentiable. On the basis of all these macroscopic assumptions, we have derived a differential equation describing the dynamic behavior of photocurrent in TOF as shown below.

$$\tau \frac{d}{dt} i(t) = -i(t) + \overline{i_{in}}(t) \quad (2.6)$$

where

$$\overline{i_{in}}(t) = \frac{1}{d} \int_0^d i_n(x,t) dx \quad (2.7)$$

$$i_{in}(x,t) = \frac{\partial}{\partial t} \int_0^x p(x,t) dx \quad (2.8)$$

where $\overline{i_{in}}(t)$ is the average drifting current, $i_{in}(x,t)$ is the drifting current at position x and time t inside the sample, and $\tau = RC$, which is the circuit characteristic constant. The differential equation has a general solution

$$i(t) = \exp\left(\frac{-t}{\tau}\right) \left[\int_0^t \overline{i_n}(t') * \exp\left(\frac{t'}{\tau}\right) d\left(\frac{t'}{\tau}\right) \right] \quad (2.9)$$

This solution depends on the average drifting current, which in turn depends on the charge density function. Furthermore, after neglecting some unimportant terms, one can obtain an expression for the photocurrent as:

$$i(t) = \frac{q_0}{d} \exp\left(\frac{-t}{\tau}\right) \left[\int_0^t \exp\left(\frac{t'}{\tau}\right) \left[\int_0^{d/t} v f_v(v, t) dv \right] d\left(\frac{t'}{\tau}\right) \right] \quad (2.10)$$

where $f_v(v, t)$ is the charge velocity distribution, i.e.,

$$q(x, t) = q_0 \int_0^{x/t} f_v(v, t) dv \quad (2.11)$$

Finally, if the distance between the locations, where charges are photo-induced, and the electrode is much smaller than the thickness of the sample, then the velocity distribution can be well approximated as Gaussian function,

$$f_v(v, t) = \frac{1}{\sqrt{2\pi \frac{\alpha_0^2}{t}}} \exp\left(-\frac{(v - v_0)^2}{2\left(\frac{\alpha_0^2}{t}\right)}\right) \quad (2.12)$$

where $\frac{\alpha_0^2}{t}$ and v_0 are the variance and the mean for Gaussian distribution function, respectively, d is the sample thickness, τ is the carrier drift time, and t is the time. In terms of physical meaning, α_0 is giving the width of the velocity distribution of carriers and v_0 is the mean diffusion velocity of carriers in the film. By fitting the simulated photocurrent to the experimental one, four parameters, τ , α_0 , v_0 and q_0 could be obtained. The Gaussian distribution for drifting velocity in TOF has also been observed and used in other studies [156,158,159]. After obtaining these values from fitting, the average velocity can be estimated by the following expression,

$$\langle v \rangle = \frac{\int_0^\infty dt \int_0^\infty v f_v(v, t) dv}{\int_0^\infty dt \int_0^\infty f_v(v, t) dv} \quad (2.13)$$

and the average mobility can be found by

$$\langle \mu \rangle = \frac{\langle v \rangle}{F} \quad (2.14)$$

2.11 Fundamentals of Luminescence

Luminescence occurs when an excited molecule returns to the ground state with the emission of a quantum of light. There are many ways in which the excited molecules may be produced. The simplest one is by prior absorption of light (photo-pumping), recombination of electrical injection of electrons and holes.

2.11.1 Photoluminescence (PL)

In organic molecules interactions with UV and visible light can lead to the absorption of photon energy by localized molecular units, called chromophores. The energy diagram for electrons in chromophores that can vary often is approximated in a way that resembles the electronic energy structure for atoms. The ground state S_0 corresponds to an electron configuration with the lowest possible energy. After excitation the molecule resides in the first or higher excited state S_n for certain duration. It can then relax back to a lower vibrational and/or electronic manifold without changing its spin state by emitting a photon with an energy $\Delta E = h\nu$, which equals the energy difference between S_0 and S_1 . Normally, this internal relaxation is fast, and thus virtually all of the luminescence emitted by the molecules occurs from the lowest excited singlet state, S_1 . Through interaction with photons, the molecule that can also enter long lasting triplet states are quantum-mechanically

forbidden when spin interactions are ignored. Therefore, intersystem crossing rates as well as deactivation rates of triplet states are about two orders of magnitude lower than rates for radiative relaxation from singlet states.

Jablonski established the illustration of absorption and emission processes as depicted in Fig. 2.12.

Figure 2.12 Jablonski diagram [160]: Absorption and emission processes are depicted as excitation from a ground to the first or second excited electronic state. Each electronic state is split into various vibrational states, which are populated according to a Boltzmann-distribution. Relaxation from electronic states can be due to fluorescence, intersystem crossing to long-lived triplet state, followed by phosphorescence, or non-radiative processes like internal conversion, quenching by and energy transfer to near-by molecules.

In this scheme additional pathways that cause non-radiative relaxation processes and reduce the number of excitations contributing to the fluorescence signal can easily be visualized. This fluorescence emission is shifted relative to the absorption spectrum by the so-called Stokes shift. Each excitation into an excited electronic state S_1 is followed by vibrational relaxation into the vibration ground state of S_1 . As shown in Fig. 2.12. The energy is converted from Coulomb energy into vibrational energy and eventually dissipated into heat. Vibrational relaxation occurs on time scales in the order of picoseconds (10^{-12} s). Since

the lifetime of an excited electronic state is in the order of nanoseconds (10^{-9} s), contributions from vibrational relaxation to fluorescence lifetime are negligible. Furthermore as fluorophores usually decay to excited vibrational levels of the electronic ground state S_0 more energy is lost to vibrations causing an even larger Stokes shift.

A third general feature of emission spectra in most fluorophores is expressed in the so-called mirror rule. This rule expresses that the emission spectrum representing the $S_1 \rightarrow S_0$ transition generally is a mirror image of the corresponding absorption spectrum. It can be explained by the similarity of vibrational energy levels in the ground and excited electronic state.

2.11.2 Electroluminescence (EL)

EL and PL are two related physical phenomena. EL from organic semiconductor materials is the process whereby light is emitted from a layer of an organic material is the passage of a current of electricity through it. Under a forward bias radical anions are generated by injection of electrons into the organic material from a low-work function cathode. At the same time holes are injected as radical cations into the organic material from the anode. The electrons and holes travel through the organic material in opposite directions towards the electrode of opposite polarity under the influence of an electric field. The electrons and holes may collide on route and then form an excited state, called an exciton. Upon relaxation of the excited state to the ground state, light is emitted. This process is similar as to PL mechanism.

2.11.3 Energy Transfer Mechanisms

The energy transfer is a direct process in PL or EL. This direct transfer of electronic energy to another molecule takes place without the mediation of collisions. For this to occur some kind of coupling between donor and acceptor is necessary. Several mechanisms are possible depending on the distance separating the two molecules; such mechanisms can be classified as (a) radiative transfer, (b) resonance transfer and (c) exciton transfer.

Radiative transfer is the emission of a photon by the donor, which is subsequently reabsorbed by the acceptor molecule. The conditions for transfer are simply that the absorption of the acceptor overlaps the fluorescence spectrum of the donor and that the medium between the donor and acceptor be transparent to the wavelengths of the radiation involved.

Resonance transfer has been shown by Forster [161] that, where resonant transitions exist in donor and acceptor molecules, a nonradiative coupling can occur via the electromagnetic field. The Coulomb interaction occurs, which can be dealt as a multipole series and usually the dipole-dipole coupling predominates. By this process, it is possible for energy to be transferred to an unexcited molecule over distances ranging up to 50 or 100 Å. The two molecules need not be identical. The condition for efficient transfer is that the fluorescence spectrum of the donor D be overlapped by the absorption spectrum of the acceptor A . This is the same condition as for radiative transfer.

Once the molecules are excited, the excited state is not confined to one molecule but may embrace several hundred or even several thousands of molecules. Such a delocalized excited state is called exciton. The theory of excitons was first developed for inorganic lattices by Frenkel [162] and subsequently applied to organic crystals by Davydov [163]. The energy of interaction is great enough that the time for the excitation energy migrates to a

neighboring molecule is comparable with the time required for the act of absorption. This model is dealing with a double molecule with its own excited states rather than with energy transfer between the excited states of two separate molecules. For a pair of molecules the interaction leads to a splitting of the single-molecule energy level into a pair of levels. The stronger the coupling, the greater is the splitting. The interaction can be extended from two molecules to n molecules, and in this case the original single-molecule level is split into a band of n levels. Because of exciton splitting, the lowest excited state of a molecular crystal is usually an exciton state, which lies lower than the lowest state of a free molecule. This leads to the appearance of new bands at longer wavelengths in the fluorescence spectrum.

2.11.4 Lifetimes Measurements

This time resolved fluorescence methods give the kinetic information on the various processes involved in the deactivation of the excited state. With the advent of lasers as excitation light sources, it is possible to have the time resolution of the order of femtoseconds for the excited processes under investigation. The typical fluorescence intensity decay is a plot of fluorescence intensity as a function of time. For a simple system having a single fluorophore the fluorescence intensity decay, $I(t)$, is a single exponential and is given as

$$I_t = I_0 \exp\left(\frac{-t}{\tau}\right) \quad (2.15)$$

where I_0 is the initial intensity and τ is the fluorescence lifetime. The fluorescence lifetime τ represents the average time spent by the fluorophore in the excited state before coming to the ground state. The fluorescence lifetime is related to the radiative and the nonradiative rates. The fluorescence quantum yield of the excited state is given as

$$\tau = \frac{1}{k_r + k_{nr}} = \frac{\phi}{k_r} \quad (2.16)$$

Generally, complex systems may have multiple fluorescent species and hence the fluorescence intensity decay cannot be fitted to one exponential function. One needs to use a multi-exponential function. In that case, the fluorescence intensity decay equation becomes

$$I(t) = \sum_{i=1}^n \alpha_i \exp\left(\frac{-t}{\tau_i}\right) \quad (2.17)$$

where α_i and τ_i are i_{th} pre-exponential factor (amplitude) and the lifetime is in the multi-exponential decay respectively. Pre-exponential factors are generally positive but can be negative whenever there is an excited state kinetics. A negative pre-exponential factor indicates the formation of an emissive species in the excited state reaction. In the case of multi-exponential decays the average lifetime, which is proportional to the total area under the fluorescence decay curve, is defined in the following equation 2.18.

$$\tau_{av} = \frac{\sum_i \alpha_i \tau_i}{\sum_i \alpha_i} \quad (2.18)$$

Also, there is another method of analysis for the fluorescence intensity decays of complex systems. Here, one obtains a continuous distribution of lifetimes using maximum entropy method (MEM) [164]. MEM analysis gives the lifetime distribution in a model independent manner. The fluorescence decay function with a continuous distribution of lifetimes is represented by equation 2.19.

$$I(t) = \int_0^\infty \alpha(\tau) \exp\left(\frac{-t}{\tau}\right) d\tau \quad (2.19)$$

where $\alpha(\tau)$ represents the amplitude of the lifetime τ . Recently, there is another new method of analysis for systems having continuous distribution of lifetimes, especially for the fluorescence lifetime imaging microscopy (FLIM) data, where a Stretched exponential

function (also known as Kohlrausch-Williams-Watts function) [165] is used for the data analysis. Stretched-exponential function is defined as in equation 2.20.

$$I(t) = I_o \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right) \quad 0 < \beta \leq 1 \quad (2.20)$$

where β is known as heterogeneity parameter. It is worth noting that the stretched-exponential becomes a single exponential for $\beta = 1$. Stretched-exponential function is widely used to describe the dielectric relaxation in polymers and glassy materials. None of the above methods, the discrete exponential method, MEM and the stretched-exponential analysis gives any information on the number of emissive species present in the sample under study. Information on the number of emissive species is very important for the correct interpretation of the experimental data for complex systems. A new model-free analytical method has been devised using wavelength dependent fluorescence intensity decays to determine the number of emissive species.

2.12 Capacitance-Voltage (CV) measurement

Direct CV measurement is a technique traditionally used to study traps in inorganic devices. This transient C-V measurement can also apply to study traps in electroluminescence organic and polymers semiconductors. This measurement provides more useful detail information on dielectric constant ε of the organic film, transport and trap properties of the organic materials.

$$\varepsilon = \frac{C * d}{8.85 \times 10^{-12} * A} \quad (2.16)$$

where C is the measured capacitance value in Farad, d the thickness of the film is meters, A is the cross sectional area in square meters. The loss factor values can be directly measured from the impedance analyzer and the values of ε can be calculated using Eq. (2.16). Based on a single relaxation model, the real part of dielectric constant ε in a solid is given by [166]

$$\varepsilon = \varepsilon_U + \frac{\varepsilon_R - \varepsilon_U}{1 + \omega^2 \tau_E^2} \quad (2.17)$$

ε_U represents the unrelaxed dielectric constant at higher frequencies; ε_R the relaxed dielectric constant at low frequencies and τ_E is the dielectric relaxation time. Thus, ε decreases with increasing frequency ω from a value of ε_R to ε_U .

The observed capacitance transients for organic materials can then be modeled in terms of de-trapping of carriers from a discrete trap level to a Gaussian distribution of transport states. Thus, the transient results have been modeled by considering the de-trapping of carriers from a discrete trap level to a Gaussian distribution of negative carriers transport states. This model is developed from Ref. [167]. As $N_t > N_A$, the change of the depletion width $x_d(t)$ with time is calculated from [167]

$$\frac{2\varepsilon}{q} (V_d - V_{appl} + V^*) = N_A x_d(t)^2 + N_t f(t) (x_1(t)^2 - x_2^2) \quad (2.18)$$

where V_{appl} is the applied bias and V^* is a fitting parameter that allows for charge stored in fast interface states, or fast bulk traps, or spatial variations in N_t . $x_I(t)$ is the distance from the cathode to the point at which the trap level intersects the quasi Fermi level when the device is held at applied bias as shown in Fig. 2.13. x_2 is the same distance during the filling of bias. $f(t)$ is the variation with time of the trapped charge between $x_I(t)$ and x_2 [168]. $x_I(t)$ and x_2 are calculated from the depletion width by subtracting the parameter λ where

$$\lambda^2 = 2\epsilon \frac{(E_t - E_F)}{qN_A} \quad (2.19)$$

Figure 2.13 The model of depletion region assumed in analysis.

Chapter 3 OLEDs Device Preparations

3.1 Introduction

This chapter will discuss the methods of OLEDs device preparation involves preparation of indium-tin oxide (ITO) substrate and fabrication of organic doped devices. Properties of surface treated ITO and surface morphology of doped OLEDs would be discussed.

3.2 Device Preparation

The device preparation involves a few important steps in the procedure namely, the treatments for indium-tin-oxide (ITO) substrate, thermal evaporation rate of organic materials, and vacuum of chamber condition.

3.2.1 Indium-tin-oxide (ITO) Substrate

An organic device consists of a sandwich structure with one or several thin organic layers deposited onto an Indium-tin-oxide (ITO)-coated glass substrate and with a top metal cathode. It serves as the anode contact and is easy to pattern [26,169,170]. Many device problems have been localized to the contact interface between the organic layer and the ITO. A high interface barrier potential (presumably from carbon contamination), limits the hole injection into the molecules [171]. It has been suggested that diffusion of indium, tin or oxygen into the organic layer causes quality degradation [172]. A rough ITO surface produces localized electric fields, which may result in microscopic short circuits [82,83]. Hence, to overcome these problems, many solutions, which involve chemical and mechanical cleaning [84,91,92], changing properties of the organic materials or introducing an intermediate stabilization layer with proper carrier injection/transport characteristics between

the ITO and the active luminescent organic layer have been suggested [173,174]. Treating the ITO glass substrates at room temperature in an oxygen-plasma and an aquaregia solution improved the driving voltage from above 20 to below 10 V and significantly increased the external electroluminescence quantum efficiency (from 0.28 % to 1 %) of OLEDs [169]. Treatment with hydrogen peroxide [91] or nitric acid onto the ITO thin-film electrode [103] led to an increase in the ITO work function and thus improved hole injection from the oxide electrode. The surface conditions and electrical properties of ITO directly influence the performance of the OLEDs due to the ITO work function. The work function of ITO should fit the highest occupied molecular orbit (HOMO) in the molecule to facilitate hole injection, and is strongly affected by the carbon containing contaminants. Therefore, cleaning is the first step in the preparation. Since the ITO is a complex compound there is no unique surface preparation method and the surface is not well defined even if the surface is in ultra high vacuum and cleaned by Ar bombardment. Preparation methods on technical surfaces include chemical (organic solvent) cleaning, UV-ozone or oxygen-plasma exposure, Ar-sputtering, or other treatments. In summary, the strongest effects in terms of reducing OLED turn-on voltages are believed to be (in order of appearance): oxygen deficiency, carbon removal and Sn concentration.

3.2.2 ITO Preparations

The ITO coated glass substrate (from Shenzhen Southern Float Glass Co. China), had a film thickness and resistivity of 40 nm and $\sim 30 \Omega/\text{sq}$, respectively. After cutting into $1 \times 1 \text{ cm}^2$ pieces, ITO samples were prepared by different chemical cleaning methods. The ITO surface was first cleaned in isopropyl alcohol ($\text{C}_3\text{H}_8\text{O}$) for 30 minutes, dichloromethane (CH_2Cl_2) for 30 minutes, and finally 60 min in a solution of hydrogen peroxide/ammonia/de-ionized water, $\text{H}_2\text{O}_2/\text{NH}_4\text{OH}/\text{H}_2\text{O}$ (1:1:5). Then it was exposed to UV light for 1 hour at

room temperature for oxidation. Finally, it was soaked for 3 minutes in nitric acid (HNO_3) and dried with an air gun. The wet cleaning procedures were performed in an ultrasonic bath. After the surface preparations, the ITO films were studied by various techniques before deposition of the organic Alq3. The physical results showed the comparison of treated with untreated (reference) ITO substrates. The surface morphology was studied by atomic force microscopy (AFM).

3.2.3 Properties of surface treated ITO

The surface morphology is an important parameter, especially when the layer thickness is similar to the surface roughness. The surface morphology is expected to affect the interface properties and also the organic active layer. ITO-surface roughness may cause local variations of the electric fields within an organic over layer [103]. The surface roughness was characterized by AFM. Figure 3.1 shows the tapping-mode AFM images of all four ITO samples, designating that the morphology of each sample was characteristic for its chemical treatment. These roughness values are shown in Table 3.1. Samples of untreated ITO had the roughest surfaces, 10 ± 4 nm, and additionally have large features compared to the smooth morphology of the treated samples. The AFM system was also used to measure the average grain height of the ITO surfaces. These values are shown in Table 3.1, for all samples.

Figure 3.1 AFM scanning images ($4\ \mu\text{m} \times 4\ \mu\text{m}$) of ITO surface profiles for samples (a) untreated, and (b) treated. The scale along the z direction is greatly expanded with respect to the scales along the x and y directions.

Table 3.1. The root mean square roughness ($R_{\text{r.m.s.}}$) and the average grain height of ITO surface for all samples. The table shows that the untreated samples have the most rough surface morphology and also have higher grain-height than treated samples.

Samples	Untreated samples	Treated samples
$R_{\text{r.m.s.}}$ (nm)	10 ± 4	4 ± 2
Average grain height (nm)	12 ± 5	7 ± 3

It can be concluded from the surface root mean square ($R_{\text{r.m.s.}}$) values that the chemical cleaning by hydrogen peroxide and ammonia, UV light treatment and protonate (ITO-H^+) of nitric acid provided the smoother surface morphology compared with untreated ITO.

3.2.4 XPS study: Surface composition

The XPS measurement is used to calculate the chemical surface composition from the peak area. Table 3.2 shows the estimated atomic concentration (%) of each step of treatments from the core level peak areas by assuming homogeneous surface composition. Based on the reference sample (without treatment), we can see that the compositional variations are relatively small. After the hydrogen peroxide treatment, the atomic concentration of In(3d) increased, and the concentration of O(1s) decreased while the In/Sn-ratio was the same. It is clear that the H_2O_2 reduced the surface oxide and effected the O(1s). However, exposure of the ITO to UV light, increased the relative concentration of O(1s). A new oxide was created on the In- compound. The sample 4 soaked in nitric acid further increased the O(1s) concentration, and sharply reduced both In and Sn concentrations. The UV light exposure reduced the In/Sn-ratio in sample 3 due to the reduction of indium from the ITO surface. Further treatment with nitric acid increased this ratio due to the reduction of Sn by further oxidation. This indicates an intense interaction of the ITO with nitric acid. Our results are concurrent with other works on ITO surface treatments [102, 105]. Normally, tin is substituted for indium as Sn^{4+} in tin-doped indium oxide gives rise to an additional electron for conduction. There are some tin ions not efficient in generating conduction electrons. Tin is observed to exist in two possible valence states, Sn^{2+} and Sn^{4+} in ITO films, and the preferred valence-state depends upon the deposition conditions. The resistivity of the ITO film will decrease if tin exists as Sn^{4+} with generation of free electron, and will increase if it becomes Sn^{2+} ion, which acts as an electron trap center.

Table 3.2 Atomic concentrations (%) of elements In, Sn and O on ITO surface are estimated from the XPS measurements for untreated and serial treatments samples. [1: treated with hydrogen peroxide and ammonia, 2: UV light treatment and 3: protonated with nitric acid]

Elements	Atomic concentration (%)			
	Ref. Sample (untreated)	1	2	3
In	21.1	30.3	23.0	19.1
Sn	2.2	2.9	2.6	2.1
O	76.7	66.8	74.4	78.8
In/Sn	9.6	10.4	8.8	9.1
O/(In+Sn)	3.3	2.0	2.9	3.7

From the results we suggest that the chemical and physical treatments on ITO surface have improved the OLED driving voltage and device performance. Hydrogen peroxide, UV light and nitric acid treatments have accelerated or promoted the oxidation and defect forming process on ITO-surface. It is believed that the ITO composition in bulk remained is unchanged [101]. Oxygen incorporated to the quasi-anion site by this process of the oxidation, would substitute Sn ions to form neutral SnO_2 and thus the carrier concentration reduced. This may be the reason for observing higher resistance after the serial of chemical treatments. This oxidation process is also changing the ITO surface Fermi level, causing the shift towards the middle of the band gap, but the Fermi level in the bulk remains unchanged. Thus, due to this band bending, the work function will increase accordingly [101]. The mechanism of changing the surface Fermi energy may be attributed to the oxygen and other surface ions, or defects that repel the free electron in the conduction band of ITO. This leads to form a surface depletion region and shifts the ITO surface Fermi level towards the upward

bend, thus helping to reduce the holes injection barrier between ITO and HOMO, and the bias voltage of OLEDs.

3.3 Devices Fabrication

Organic low molar-mass materials designed and synthesized for use in OLEDs must be capable of being deposited as a pure, uniform, thin solid film by vapor deposition under high vacuum environment. The individual layers exhibited high glass transition temperatures in order to inhibit crystallization during the lifetime of the device.

Organic thin film deposition requires a vacuum environment to eliminate or minimize the contamination. The quality and consistency of the final device depend on the vacuum conditions ($\leq 10^{-6}$ torr) during the deposition. Low pressure of the deposition chamber provides the mean free path for evaporation atoms or molecules, eliminates the presence of gases that could react with the deposition material, reduces the vapor pressure, thus lowering the evaporation temperature of the materials, and provides a clean deposition environment. With these parameters there may be an effect of the vacuum pressure. A deposition rate of 1 Å/s at 1×10^{-6} torr corresponds to a molecule arrival rate, which is similar to the impact rate of molecules from the residual vacuum. This effect of deposition rate of organic Alq₃ will be discussed in the next chapter in detail. Changing the deposition rate will merely change the ratio of vacuum species to deposition molecules. However, it is unclear what the detailed role of the H₂O, CO, N₂, O₂, etc. molecules in the residual gas may have on the molecular film and how much of them are incorporated, if any. Each organic layer (NPD, Alq₃ or Alq₃:dye laser dopants) was thermally deposited onto the ITO surface at room temperature in a vacuum of $\sim 3 \times 10^{-6}$ torr. The dopants were doped in host Alq₃ at their wt.% respectively by co-evaporation. The distance between the boat source and substrate was 25 cm. The Alq₃

growth rates were varied between 0.3 and 1.5 Å/s, and each organic layer thickness was fixed to 60 nm. Crystal oscillator (Edward) is used to monitor the film thickness and is further confirmed by Alpha-Step profilometer. In the final step a 200 nm thick aluminum film was deposited onto the Alq₃ surface as shown Fig. 3.2. The ITO and Al layers were used as anode and cathode, respectively, in current–voltage and luminance–current measurements. All measurements on the layers were performed in air on non-encapsulated devices.

Figure 3.2 The typical structure of OLED

3.4 OLEDs Doped Devices

For this study, two types of devices have been fabricated. They are single and double doped in Alq₃ as shown in table 3.3.

Table 3.3 Sample structures of doped devices

(1) ITO/NPD/Alq ₃ /Al	Standard reference
(2) ITO/NPD/Alq ₃ :DCM/Al	Single dopant
(3) ITO/NPD/Alq ₃ :Rub/Al	Single dopant
(4) ITO/NPD/Alq ₃ :C-6/Al	Single dopant
(5) ITO/NPD/Alq ₃ :Rub: DCM/Al	Two dopants
(6) ITO/NPD/Alq ₃ :Rub:C-6/Al	Two dopants

For each type of single doped devices, the dopant concentrations are varied from 0.5, 1, 3, and 24 wt.% with respect to Alq₃. While for co-doped devices, the ratios 1:1 and 1:2 of dopants (Rub:DCM and Rub:C-6) were prepared. However, their total wt.% was the same and remained as 1 wt.% with respect to Alq₃.

3.5 Equipment use for characterizations

Atomic Force Microscopic (AFM: Digital Instruments Dimension 3000 scanning microscope) was used to characterize the surface morphology of organic active layer.

3.5.1 Surface Morphology of Doped OLEDs

Figure 3.3 AFM scanning images (10 μm x 10 μm) of organic materials surface profiles for samples (a) pure C-6, (b) pure Rub, (c) pure DCM and (d) pure Alq₃

The surface morphology is expected to affect the interface properties. Organic layers roughness may cause local variations of the electric fields within an organic over layer and hence affect the carrier mobility within them. The surface roughness was characterized by AFM. Figure 3.3 shows tapping-mode AFM images of all organic guest-host materials on silicon substrates designating that the morphology of each sample was characteristic of its evaporation properties, being evaporated into a smooth thin film (average roughness < 2 nm).

This characteristic is also noticed in doped films, either single or double dye dopants in Alq₃. Fig. 3.4 shows the few surface morphology samples of doped films. The doped films show homogeneous morphology although it consists of two different materials. The DCM doped Alq₃ films have spike morphology and slightly more rough than C-6 and Rub. The Rub doped Alq₃ films depicted the small island morphology while C-6 doped films showed the smoother surface morphology. As the dopant concentration increases in doped films, the surface roughness increases as well. The average roughness of each single doped film versus the concentrations is shown in Fig. 3.5.

Another phenomenon is the morphology of the two dopants doped in Alq₃ films on silicon substrates. Co-doped of Rub:DCM or Rub:C-6 in Alq₃ films show the average roughness below 1 nm but slightly higher than single dopant in Alq₃ films. These films also depicted the spike-morphology and island-morphology if the ratio of DCM and rubrene dominated in the films, respectively. The surface morphology is smoother if the ratio of C-6 is higher in these co-doped films. The average roughnesses of these co-doped films are ranged between 0.5-1 nm. Few AFM scanning images for these co-doped films are shown in Fig. 3.6.

Figure 3.4 Surface morphology for single-doped guest-host films. (a) Alq₃:DCM (24 wt. %), (b) Alq₃:C-6 (12 wt.%) and (c) Alq₃:Rub (3 wt.%)

Figure 3.5 The average surface roughness (R_a) versus dopant concentrations in single doped films

Figure 3.6 The surface morphology of co-doped of two dopants in Alq₃ films. (a) Alq₃:Rub:DCM (2:1) shows the ‘spike’ morphology and (b) Alq₃:Rub:C-6 (1:2) shows the island-morphology feature.

The surface morphology of the thin films is the important feature as it may have an effect via the contact electrodes or at organic-organic interfaces. The existence of such rough surface features may lead to the formation of electrical shorts, non-emissive dark spots, and eventually reduce the device performance. Thus, though the doping technique is useful to increase the emission intensity and variable emission colors, there must be care that the dopant used does not induce the rough surface morphology feature. As the investigation has shown, the single-doped or co-doped of dye laser dopants in this study did not induce obvious changes to the surface morphology of the thin films. The average grain height is estimated from all these AFM scanning images. The laser dye dopant of DCM in Alq₃ films showed a higher grain height compared to other two dopants, as shown in Fig. 3.7. The grain height of the single-doped films increased as the dopants’ concentration increased. The grain height of co-doping of the two dopants in Alq₃ ranged between 2.5-7.5 nm.

Figure 3.7 The grain height of single-doped organic films. The Alq₃:DCM films showed the higher grain height compared to the others.

Chapter 4

Study of thermal evaporation rate and carrier mobility of Alq₃ film

4.1 Introduction

This chapter is divided into two sections; the first will discuss the effect of deposition rates of Alq₃ on OLED devices. Analysis would show that the deposition rate of Alq₃ is directly influence the luminance efficiency, and the film surface roughness. The decomposition of Alq₃ and surface roughness seems to be responsible for the reduction of OLEDs performance when the Alq₃ deposition rate is reduced from 1.5 Å/s.

The second section will discuss the temperature and electric field dependence charge carrier mobility in pure Alq₃ films by TOF measurements. Analysis would show a new approach to estimate carrier mobility based on the Gaussian distribution instead of using conventional graphical method (Scher-Montroll model). The trap depth Φ_B of trapping states of pure Alq₃ and the effectiveness of carriers escaping process from trapping states with temperature would be discussed as well. Both discussions are based on modified Poole-Frenkel (PF) model.

4.2 Study of Thermal Evaporation Rate of Alq₃

The OLEDs samples were prepared as stated in chapter 3. The ITO glass substrates were treated and loaded into thermal evaporator. Each Alq₃ layer was thermally deposited onto the ITO surface at room temperature in a vacuum of $\sim 3 \times 10^{-6}$ torr. The distance between the boat source and substrate was 25 cm. The Alq₃ growth rates were varied between 0.3 and 1.5 Å/s and each organic layer thickness was fixed to 50 nm. With these

parameters there may be an effect of the vacuum pressure. A deposition rate of $1 \text{ \AA/s}$ at 1×10^{-6} torr corresponds to a molecule arrival rate, which is similar to the impact rate of molecules from the residual vacuum. Changing the deposition rate merely changes the ratio of vacuum species to deposition molecules. However, it is unclear what the detailed role of the H_2O , CO , N_2 , O_2 , etc. molecules in the residual gas may have on the molecular film, and how much of them are incorporated. In the final step, a 200 nm thick aluminum film was deposited onto the Alq_3 surface. The ITO and Al layers were used as anode and cathode, respectively, in current–voltage and luminance–current measurements. All measurements on the layers were performed in air on non-encapsulated devices. For studies of the Alq_3 surface morphology a tapping mode AFM instrument was used on organic layers deposited on silicon substrates. The reason was to avoid any influence of the ITO surface roughness on the morphology of the Alq_3 layer as we consider silicon surface to be smoother than ITO.

The variations of atomic nitrogen and carbon concentration with the Alq_3 deposition rate were analyzed by XPS in ultra-high vacuum (UHV) at the pressure $\sim 10^{-10}$ torr. These measurements were carried out using a Kantos Ultra or a PHI 5500 system. Both systems were equipped with a monochromic Al K_α source with the photon energy 1486.6 eV. The overall energy resolution was about 0.5 eV. The data were collected at a photoelectron take-off angle of 90° . All the XPS spectra reported here are referred to the C 1s peak at 280.5 eV.

4.3 Effect of Thermal Evaporation Rate

Figure 4.1 shows the current-voltage characteristics of single organic layer OLEDs with the device layer structure in the inset. The current has a strong almost exponential, increase with bias. It is also evident that the deposition rate has a pronounced effect on the I-V characteristic. As the rate increases, the current density shifts to higher values for a constant bias voltage. The turn-on characteristics of OLEDs are controlled by the majority carrier injection from the electrode [102]. Since the electron is the majority carrier in the present devices, the turn-on characteristic is mainly determined by the Al/Alq₃ interface barrier. At higher operating voltages, the contribution of the minority carrier current to the total current becomes more significant [102]. The current increases with the field dependent electron mobility in an Alq₃ layer. The bulk-limited current density can be defined as [175]

$$J = ne\mu F, \quad (4.1)$$

where n is the injected carrier density, e is the carrier charge and F is the applied electric field. The field dependent electron mobility [176] is

$$\mu = \mu_0[\exp(\alpha F^{1/2})], \quad (4.2)$$

where μ_0 is the low field mobility and α the constant for a given sample. As the free charge density in organic materials is low it is the injected space charge that determines the electric field under the bulk transport limit. For voltage values above 12 V, the current density sharply increased as shown in Fig. 4.1. The shape of the current density above 12 V is characteristic of an insulator material with traps, expected for a disordered system, such as a polymer material [177]. The I-V characteristic using Eqs. 1 and 2 provided $\mu_0 = 3.53 \times 10^{-14}$ cm²/Vs and $\alpha = 0.73 \times 10^{-2}$ (cm/V)^{1/2} for the Alq₃ deposition rate 1.5 Å/s [178]. The estimated mobility was $\sim 2.08 \times 10^{-6}$, $\sim 3.74 \times 10^{-6}$ and $\sim 9 \times 10^{-6}$ cm²/Vs, for 0.3, 1 and 1.5 Å/s, respectively at the applied field of 2.6×10^3 (V/cm)^{1/2}. These estimated results is comparable

with giving electron mobility between 10^{-6} to 10^{-5} $(\text{V}/\text{cm})^{1/2}$ under typical operating conditions from Ref. [178] .

Figure 4.1 The I-V characteristics of OLEDs with the deposition rates of Alq₃ on an ITO substrate as parameter. The inset is the structure of a single layer device. The current density sharply increases with deposition rate of Alq₃.

The luminescence as a function of current density is shown in Fig. 4.2 for three deposition rates of Alq₃. The maximum efficiency increases about three times when the deposition rate increases 5 times as shown in Fig. 4.2(b). The maximum intensity also shifts to lower current density with increasing deposition rates. The ratio between luminescence and current density is a measure of the efficiency. The reason for the lower current density and emission intensity at low deposition rates is the presence of the higher number of defect centers in these layers. The development of a luminescence maximum can be explained by the field dependent electron and hole mobilities. The electron mobility sharply increases with the electric field as compared to the hole mobility. At high current density most of the

electrons cross the active region before recombination. That is why the luminance efficiency is reduced with increasing current density. We can make an empirical description of the relation in Fig. 4.2 (a). First there is a relatively slow increase, $\sim I^{1/2}$, until another mechanism reduces the luminescence efficiency, exponential decrease. This may be described by two competing processes L_1 and L_2 giving the resulting efficiency, $L=L_1L_2/(L_1+L_2)$, where

$$L_1 = L_{10}\sqrt{J-J_{10}} \quad L_1 = 0 \text{ for } I \leq I_{10} \quad (4.3)$$

$$L_2 = L_{20} \exp\left(-\frac{J}{J_{20}}\right) \quad (4.4)$$

This is shown for the upper experimental curve in Fig. 4.2 (a). The parameters (L_{10}, J_{10}) and (L_{20}, J_{20}) are $(4.62, 0.02)$ and $(1.95, 0.76)$ respectively for the upper curve 1.5 A/s . The physical meanings of them are related to the mobility change with the electric field in the layers. The reason for the structure (reduction), which is observed before the maximum in all curves, is not known but may come from a field dependent parameter.

Figure 4.2 (a) Luminance – current characteristics of OLEDs for different Alq₃ deposition rates. In (b) is the maximum luminance intensity shown versus the deposition rate of Alq₃. The maximum luminance efficiency increases about three times when the deposition rate increases from 0.3 to 1.5 Å/s.

It has been suggested that the higher deposition rate decomposes the Alq₃ molecular structure, where it tends to release N-containing species with other hydrocarbon, as the decomposition energy of Alq₃ is smaller than its sublimation energy [179]. This nitrogen-hydrocarbon is the contaminant in Alq₃ molecule. If the deposition rate is slow (low temperature) the effect of molecular decomposition can be ignored. This was studied by XPS, using the N 1s peaks at 395, 397, 399 and 403 eV. The atomic concentration of nitrogen (N) and the atomic nitrogen/carbon (N/C) ratio were found to decrease as the deposition rate increased from 0.3 to 1.5 Å/s as shown in Table 4.1. For a rate of 1.5 Å/s, the N/C ratio was close to the theoretical value, 0.09, of the Alq₃ molecule, while it was 80 % higher, 0.16, at 0.3 Å/s. Thus, the N/C ratio decreased with deposition rate. One reason may be the incorporation of nitrogen species at lower evaporation temperatures.

The changed atomic N/C ratio with deposition rate of the Alq₃ may have an effect on the electrical and optical properties. Slower deposition rate releases less N-containing species from the Alq₃. The sources of them are the vacuum or contaminants in the evaporation charge. The loss of N with deposition rate certainly changes the charge transfer in the molecules, which we observed in the electrical and optical properties. For a neutral Alq₃ molecule, the distribution of the electronic density for a nitrogen atom has higher electronegativity than a carbon or oxygen atom [175]. Electrons, injected from the cathode into the Alq₃, are repelled by the negatively charged nitrogen atoms in the molecules. This Coulomb interaction reduces the carrier hopping conductivity between the neighboring molecules in Alq₃. However, as there is a release of N-atoms with deposition rate, the injected electrons experience less repulsive force from the negatively charged nitrogen atoms to facilitate their hopping conductivity. The hopping distance and frequency of electrons increase with deposition rate. This affects the current density across the device as well as the electroluminescence efficiency as shown in Figs. 4.1 and 4.2.

Table 4.1 The nitrogen, N, atomic concentration and nitrogen-to-carbon ratio, N/C, in Alq₃ films estimated from the XPS measurements. The observed N 1s peaks are shown.

Deposition rate (Å/s)	N concentration (%)	N/C ratio	N 1s peaks (eV)
0.3	8.0	0.18	395, 397, 399 & 403
1.1	6.6	0.12	
1.5	5.9	0.09	395 & 397

Another phenomenon is the morphology of the film that may have an effect via the contact metal. Figure 4.3 shows the AFM surface morphology of Alq₃ films deposited on silicon substrates. The average surface roughness, (RMS-root mean square average), are 4.4, 2.4 and 1.0 nm for deposition rates 0.3, 1.1 and 1.5 Å/s, respectively, [Figs. 4.3a–c]. The film

surface in Fig. 4.3 (a) has most island-like morphology while the surface in Fig. 4.3 (c) is the smoothest. One reason may be the incorporation of nitrogen species with other hydrocarbon at lower evaporation rate to form rougher surface morphology. It has been suggested that the higher deposition rate decomposes the Alq_3 molecular structure, where it tends to release N-containing species. If the deposition rate is slow the effect of molecular decomposition can be ignored. The density of the island-like morphology is significantly higher ($\sim 10^7 \text{ cm}^{-2}$) in Fig. 4.3 (a) compared to (b) and (c). It is evident that the increased deposition rate generated a smoother surface morphology with less island-like features extending from the rest of the smoother surface. The existence of such features may lead to the formation of electrical shorts, non-emissive dark spots, and eventually reduces the device performance.

Figure 4.3 Surface morphology of Alq_3 layers deposited on Si substrates, measured by tapping mode AMF. The average surface roughness of the Alq_3 films are 4.4, 2.6 and 1.1 nm for the deposition rate of (a) 0.3 Å/s, (b) 1.1 Å/s and (c) 1.5 Å/s, respectively.

4.4 Temperature and electric-field dependence charge-carrier mobility in Alq₃ films

The carrier mobility of Alq₃ film was measured by the photo-induced TOF method. The sample was attached vertically to precise temperature controlled heater plate. A NG-YAG laser ($\lambda=355$ nm) with a 5 ns pulse width was used as the excitation source for the generation of carriers. The sample was exposed to laser light through the ITO electrode. The ITO electrode was biased negatively with respect to Al electrode. The dark current was found to be negligible under the bias condition indicating that ITO and Al act as non-injecting electrodes of electron or hole. The photocurrent was recorded in the single shot regime. The intensity of the laser was kept sufficiently low to avoid space charge effects. The response time of the circuit was kept well below the transit time. The resistor chosen for this TOF method was 1 k Ω . The voltage drop across the resistor produced by the photocurrent was measured with a HP oscilloscope with a frequency of 100 MHz. The measurement was considered invalid if the duration of the photocurrent was shorter than ten times of the system time constant ($= RC$, where R is the series resistance and C the sample capacitance). All ten samples on the same substrate were found to exhibit similar TOF traces. The sample was attached vertically to a precisely temperature controlled heater plate where the temperature of the samples could be changed from room temperature to 400 K to study the temperature effect to carrier mobility in doped-films devices.

Figure 4.4 The TOF photocurrent measurement set-up

4.5 Modified PF Model

The electric field E dependence electron potential is given as $[qFx - \{q^2 / \{4\pi\epsilon_s/x\}]\}$, where q is the electron charge, x is the distance between two charges and ϵ_s is permittivity of the material [179]. By maximizing the potential with $x > 0$, the barrier is lowered by $\beta E^{1/2}$. The Poole-Frenkel law of mobility μ is given as [180]

$$\mu(E, T) = \mu_0 \exp(\beta F^{1/2} / k_B T) \quad (4.5)$$

where μ_0 is zero field mobility, k_B is the Boltzmann constant, T is the temperature and β is defined as PF factor. The general current density equation is

$$J = n_{eff} q v, \quad (4.6)$$

where $n_{eff} = \frac{n_{tot} N_c \exp[\frac{-\Phi_B}{\delta_\infty k_B T}]}{N_t + N_c \exp[\frac{-\Phi_B}{\delta_\infty k_B T}]}$ is the effective carrier density and v is the electron drift

velocity, where N_c is the density of states in the conduction band, N_t is the density of trap

states, n_{tot} is the total electron density, Φ_B is the trap depth and δ_∞ is the carrier escape effectiveness from the trapping center. By definition drift velocity $v = \mu F$. Now combining equations (4.5) and (4.6), it can be written as

$$J(E, T) = n_{eff} q \mu_o \exp [\beta F^{1/2} / (k_B T)] E \quad (4.7)$$

The carrier density n_{eff} can be estimated if J , μ and F are known.

For the evaluation of μ_o , we assume that the carrier transport between trap states and the waiting time in the traps will reduce their mobility. The current density can be rewritten for trap states with a trap depth of Φ_B in the form of:

$$J(E, T) = n_{eff} q \mu' \exp [(-\Phi_B / (k_B T) \delta_\infty)] F, \quad (4.8)$$

where μ' and δ_∞ are the unknown constants. Physically, Φ_B can be defined as the average energy required for a carrier to escape from the trap. The larger value of δ_∞ will enhance the escape of the trapped carriers. In the presence of space charge near the trap, it is possible to include a barrier height modulation term due to the nearby space charge which would reduce Φ_B (in Eq. 4)) to $\Phi_B - \Delta\Phi$, where $\Delta\Phi = q(\frac{qF}{4\pi\epsilon_s})^{1/2}$. Then the Eq. (4.8) can be written as

$$J(F, T) = n_{eff} q \mu' \exp [(\frac{-\Phi_B}{k_B T \delta_\infty})] \exp [q(\frac{qF}{4\pi\epsilon_s})^{1/2} / (\delta_\infty k_B T)] F, \quad (4.9)$$

and can be simplified as

$$J(F, T) = n_{eff} q \mu_o \exp(\beta F^{1/2}) F, \quad (4.10)$$

where $\beta = q(\frac{q}{4\pi\epsilon_s})^{1/2} \frac{1}{\delta_\infty k_B T}$ and $\mu_o = \mu' \exp[\frac{-\Phi_B}{\delta_\infty k_B T}]$.

The trap depth Φ_B and δ_∞ were estimated from the Eq. (4.10).

4.6 Results and Discussions

The electrical and optical characteristics, surface morphology and nitrogen/carbon ratio in Alq₃ film were studied as a function of thermal evaporation rate in our previous paper [181]. The deposition rate of 1.5 Å/s was chosen for this study as the film had less N-containing species, and the surface roughness of film decreased to 1.0 nm and gave better transport and luminance performances. The shape of the transient photocurrent is shown in Fig 4.5. This type of TOF photocurrent decay was treated as dispersive transport and was the characteristic for most amorphous materials [182]. In dispersive transport, the current is not constant for a short time and the spread of carrier arrival times at electrodes is much broader than expected of Einstein relationship between mobility and diffusion [153]. This is due to wide variations in site-to-site non-uniform hopping rates of carriers. Normally, the conventional Scher-Montroll model is used to extract the carrier flight time τ' to estimate the carrier mobility $\mu = \frac{d^2}{V\tau'}$ from the transient photocurrent decay spectrum, where d is the film thickness and V is the applied bias. However, this method of determining the mobility is not parallel with its definition of drift velocity, as we know the carriers do not move uniformly in the sample. The interpretation of carrier mobility in amorphous materials is not meaningful. Instead we used the carrier mean mobility from the carrier velocity distribution to describe the dispersive mobility of carriers. The inset in Fig. 4.5 shows the double logarithm plot to determine the transit time τ' for Alq₃ bulk film at room temperature. The crossing point of the two lines at the shoulder was taken as the transit time for the calculation of carrier mobility. The estimation of transit time may be varied for different researchers even from the same raw data.

We used carrier's average mobility to simulate TOF photocurrent. The model was modified from Ref. [156], by assuming the carriers hopping velocity, v across the Alq₃ bulk film follows a random walk with different hopping probabilities in forward and backward directions. The carriers were trapped and repeatedly released many times during their hop to cause the photocurrent falls. We assumed that this function was continuous and differentiable. The photocurrent was dependent on the carriers average drift velocity and density. The carrier velocity distribution was approximated as Gaussian function. We modified the photocurrent $i(t)$ proposed in Ref. [156]. The modified photocurrent is given in chapter 2, Eq. 2.6-2.14. By fitting the simulated photocurrent to the experimental one, four parameters, τ , α_0 , v_0 and q_0 could be obtained. The integration of Eq. (2.13) in the numerator is the carrier hopping velocity v weighted by the Gaussian distribution function $f_v(v,t)$ within the time dt . The denominator is the probability of finding a carrier with a hopping velocity v . It is the total number of carriers with hopping velocity in the system. Then, the average mobility was calculated from the relation from Eq. (2.14).

Figure 4.5 shows the fitted curve of the simulated photocurrent (dot line) from equation (7) to the observed curve (hollow circle) from the TOF measurements. The simulated curve is well fitted. The estimated values of four constant parameters were found as $\tau = 5.97 \pm 0.5 \mu\text{s}$, $\alpha_0 = 0.09 \pm 0.03 \text{ m/s}$, $v_0 = 0.099 \pm 0.001 \text{ cm/s}$ and $q_0 = 538 \pm 25 \text{ pC}$.

Figure 4.5 The plot of photocurrent versus decay time at room temperature in Alq₃ bulk film for the applied field of 6.25×10^4 V/cm. The simulated photocurrent (dot line) is well fitted with the experimental data (hollow circle). The inset shows the double logarithm plot of photocurrent and decay time. The cross of the two lines at the ‘shoulder’ was taken as the transit time for the estimation of carrier mobility.

The carrier hopping velocity can be defined as $v = \frac{l_i \cos \theta_i}{\tau_r}$, where l_i is the length of

the i th hop, making an angle θ_i with the applied field, and τ_r is the residence time preceding the hop [156]. The distributions of l , θ , τ_r and v obey the central limit theorem when summed over a large number of hops and the large number of carriers. Therefore, the effective velocities have a normal distribution.

The relative width of the velocity distribution $w_v = \sigma/\langle v \rangle$ was obtained by fitting the simulated photocurrent to our experiment data and the estimated value was within 0.2 to 0.9 in Alq₃. This result indicates that some carriers either never reached the electrode or presumably recombined at the illuminated electrode. Some carriers might hop out from shallow trapping states, and re-trapped in the deeper localized states. Some carriers might perform random walks within the bulk of the film until they reached the collecting electrode.

The carrier mobility was calculated in Alq₃ as a function of temperature at different applied electric fields by estimating the carrier mean velocity from the measured photocurrents as a function of external electric fields and temperatures as shown in Fig. 4.6. The carrier mobility increased with temperature and applied fields. As the temperature increased over 360 K, the mobility curve shows nearly a saturation behavior. At the field of 1.63×10^5 V/cm, the higher curve slope indicates the carrier mobility was more sensitive to thermal energy. The observed behavior of mobility is due to the carriers drift across the localized states in Alq₃ with different hopping probabilities. The generated free carrier concentration increased with temperature and applied field. However, the mobility of electrons achieved saturation above 360 K if the applied field was lower than 1.63×10^5 V/cm. This indicates that the trapping states controlled the carrier mobility at lower temperature and field. At the higher temperature the activation of electrons from the trapping states were increased as we observed in Fig. 4.6. The thermal energy helped the carriers to overcome the trapping barriers. We re-plot the Fig. 4.6 (a) as a function of $\ln\mu$ versus $1/T$. We observed the relationship of $\ln\mu \propto 1/T$ at low electric field as shown in Fig. 4.6 (b).

Figure 4.6 (a) The plot of carrier mobility versus temperature under different applied electric fields in Alq₃. The carrier mobility increased with temperature as well as with applied fields. (b) The curves are re-plotted as $\ln \mu$ versus $1/T$.

Figure 4.7 shows the $\ln\mu$ plot as a function of $\sqrt{F}$ at various temperatures. The mobility μ increased exponentially with $\sqrt{F}$ for all temperatures, which obey the Poole-Frenkel model $\mu(E,T) = \mu_0 \exp(\beta F^{1/2}/k_B T)$. However, at high temperature (>340 K), the $\ln\mu$ increased faster with $\sqrt{F}$. The increase of carrier mobility with temperature in Alq_3 is contradictory with inorganic semiconductors such as Si, GaAs, etc. The mobility of carriers in inorganic semiconductor reduces with temperature due to increasing phonon scattering [183]. The mobility increased in Alq_3 with temperature mainly due to its controlled by the trap centers. Electrons in Alq_3 hop from one molecule to another within the irregularly spaced nearest neighbors of distance ~ 1.0 nm [184]. The mobility of electrons rely on thermal activation and the external electric field to hop from molecule to molecule. At low temperatures such as 250 K, the carriers localized in traps without thermal assistance, which results in low density of carriers hopping in Alq_3 . At low temperature the transient time was longer.

Figure 4.7 The plot of estimated carrier mobility μ as a function of $F^{1/2}$ at different temperatures. The lines show the linear relation of $\ln\mu \sim \sqrt{F}$.

We estimated the zero field mobility μ_0 and Poole-Frenkel (PF) factor β as a function of temperature by extrapolating the mobility in Fig. 4.7 (not shown in Fig. 4.7). The changes of μ_0 and β with temperatures are shown in Fig.4.8. The zero field mobility μ_0 was changed from $2.2 - 1.9 \times 10^{-9} \text{ cm}^2/\text{Vs}$ for temperature range of 250 – 400 K. Our estimated results are also agreed with other reported values [178]. The factor β was increased linearly from $\sim 3.0 - 5.7 \times 10^{-3} (\text{cm/V})^{1/2}$ for a temperature range of 250 - 400 K. The results suggest that the temperature has affected the disorder as β is related to the degree of disorder in the bulk film. The carrier mobility change with temperature may also relate with the change in the ordering of Alq_3 film. The effective charge carrier density n_{eff} was estimated from the measured photocurrent. For example $n_{\text{eff}} = 4.5 \times 10^{14} \text{ cm}^{-3}$ at 400 K which was decreased to $2 \times 10^{14} \text{ cm}^{-3}$ at 250 K at $F = 1.4 \times 10^5 \text{ V/cm}$.

Figure 4.8 Zero field mobility μ_0 and Poole-Frenkel factor β are plotted as a function of temperature in Alq_3 .

We used the Eq. (4.10) to estimate the δ_∞ and trap depth Φ_B for the trapping states in Alq_3 . We used β values to compute δ_∞ to estimate the changes of trap depth of the trapping states with temperature and applied field. As we defined earlier, β is a barrier height modulation term due to the image effect, which would reduce the trap depth Φ_B of the trapping states. Figure 4.9 (a) shows the plot of $\ln\mu_0$ versus $1/\delta_\infty k_B T$. The $\ln\mu_0$ plot decreased linearly with $1/\delta_\infty k_B T$ in Alq_3 . The carrier escape effectiveness δ_∞ shows the linear relationship with temperature as shown in Fig. 4.9 (b). The escape effectiveness of carriers increased with temperatures. At low temperature, carriers were trapped in localized states and only a low density of carriers was able to reach the electrode by random walks. This has been proven by the low photocurrent generation at 250 K compared to the higher temperatures.

The trap depth Φ_B of the trapping states was estimated as 70 ± 5 meV from the slope of line in Fig. 4.9 (a). The trapping states were due to the disorder structure. The energy of interaction of an Alq_3 molecule with surrounding molecules can be locally modified and split into manifold of trapping states. These trapping states will be Gaussianly distributed in Alq_3 film. Some of these trapping states can be integrated to form deep traps if they are not perfectly split. Here, we assume the trapping states are associated with the energy bands of Alq_3 . The estimation of trap depth needs further confirmation. It is assumed that the trap depth Φ_B for the trapping states is stable with temperature.

Figure 4.9 (a) The plot of estimated $|\ln \mu_0|$ as a function of $1/\delta_a k_B T$. The trap depth, Φ_B is estimated from the slop of the line. (b) The trapped carrier escape effectiveness δ_a is plotted as a function of temperature. The plot shows the linear relationship between δ_a and temperature.

4.7 Summary

The OLED performance of an ITO/Alq₃/Al structure on the Alq₃ deposition rates was investigated. When the deposition rate increased 5 times from 0.3 to 1.5 Å/s, the luminance efficiency increased about a factor of three. XPS data showed that the N/C ratio decreased with increasing deposition rate. The Alq₃ film surface roughness was 4.4, 2.4 and 0.1 nm for deposition rates of 0.3, 1.1 and 1.5 Å/s, respectively. The decomposition of Alq₃ and surface roughness seems to be responsible for the reduction of OLEDs performance when the Alq₃ deposition rate is reduced from 1.5 Å/s.

Thus, 1.5 Å/s of Alq₃ was used for the rest of experiments. The temperature and electric field dependence charge-carrier mobility in Alq₃ film was measured by TOF measurements. A new approach to calculate the carrier mobility to simulate with the experimental data was proposed. The carrier mobility was calculated from the Gaussian distribution of carrier velocity. The observed and simulated carrier mobility at different temperatures and electric fields were explained. The carrier mobility increased with temperature and applied electric field. The mobility of electron in Alq₃ was controlled by the trapping states. We estimated the temperature and field dependence carrier density. The trap depth Φ_B of trapping states of 70 ± 5 meV was estimated from the modified PF model.

Chapter 5

Time-of-Flight (TOF) Measurements: Carrier Mobility Properties in Organic Doped Films

5.1 Introduction

In this chapter, the temperature and field dependence positional, and energetic disorder parameters of local centers would be discussed and examined to estimate the carrier mobility in doped films. Doping of molecular solids with a small amount of suitably chosen guest molecules may give rise to a dramatic reduction of the effective drift mobilities due to trapping of charge carriers. The effect of polar and non-polar molecular dopants on charge carriers in Alq_3 is still unknown. Hence, the carrier mobility in dope organic Alq_3 films by time-of-flight (TOF) measurement would be analyzed. For this study, DCM, Rub and C-6 would be used as dopants in Alq_3 .

5.2 Experimental

The highly pure (99.9%) Alq_3 , Rub, C-6 and DCM chemicals were purchased from Aldrich-Sigma for this experiment. The pure Alq_3 device was fabricated as the standard reference sample for these TOF measurements. The devices fabrication method was discussed in chapter 3. Two kinds of doped-films devices were fabricated: (1) single-doped and (2) co-doped of (Rub:DCM) and (Rub:C-6) in Alq_3 films. The dopants concentration of DCM, C-6 and Rub were varied from ~ 0.5 to ~ 24 wt.% in Alq_3 films. For co-doped samples, the total wt.% was maintained at 1 and the ratios of Rub to DCM and C-6 were changed according to 1:1 and 2:1. The film thickness was ~ 1 μm . Ten samples were prepared at a time on a substrate for each doped-film device; each with an active area of 32

mm². The carrier mobility was measured by the photo-induced TOF method as discussed in chapter 4, section 4.4.

5.3 Results and Discussion

First this section will present the results and discussions of the TOF photocurrent measurements in single-doped films, and later it will be compared with the results of co-doped of two dye dopants in Alq₃.

Figure 5.1 shows the typical TOF curves measured at room temperature in bulk films for each device of (a) Alq₃:DCM (b) Alq₃:C-6 and (c) Alq₃:Rub, at an applied electric field $F \approx 6.25 \times 10^4$ V/cm. In case of single-doped film devices the carrier mobilities obtained from the transit times were strongly field and temperature dependent in all the film compositions. The TOF transient of these doped films was regarded as dispersive transport. We used the carrier's average mobility to simulate the TOF photocurrent instead of graphical method (Scher-Montroll's model, $\mu = \frac{d^2}{(V\tau')}$) to extract the transient time of carrier. The photocurrent depended on the carriers average drift velocity and density. The carrier velocity distribution was approximated as Gaussian function. This modified photocurrent $i(t)$ simulation is well described in chapter 2.

Figure 5.1 The typical transient photocurrent curves in single-doped films as, (a) in Alq₃:DCM, (b) in Alq₃:C-6 and (c) in Alq₃:Rub films for various concentrations. The dotted lines are the simulated curves fitted with experimental data at RT

The simulated photocurrent from Eq.(2.10) was fitted to the experimental curves as shown in Fig. 5.1. The simulation curves fitted well with the experimental results. The velocity distribution of the charge carriers is the Gaussian form. The measured photocurrents have indicated that the heavily doped (12 and 24 wt.%) films generated lower conductivity than lightly doped. This could be due to the increase of trapping of carrier electrons in heavily doped bulk films. The electrodes are negatively bias to prevent external carriers being injected into bulk films. The carriers generated from lasers may be trapped and repeatedly released many times during their hop to cause the photocurrent falls. The photo-generated electrons and holes in doped films would diffuse or drift across the bulk film assisted by the external electric field to reach the opposite electrodes. The generated carriers that drift across the bulk film are also temperature dependent too. The characteristic of these photocurrent curves does not show a plateau region but is continuous with time and then decreases sharply. It is attributed to the carriers trapped before they started to drift across the

doped-films. Based on the Eqs. 2.10-2.14, the average carrier mobilities for each doped-film were estimated. The electron mobility in each doped-films were estimated. The estimated carrier mobility is electrical field and temperature dependent. The electric field dependence of electron mobility at different temperatures for each single-doped film is summarized in Fig.5.2.

5.3.1 Single Doped Films

The field dependence of electron mobility at various temperatures of dopants (DCM, C-6 and Rub) in Alq_3 films with various concentrations is presented here. The increase of carrier mobility with temperature in doped films is contradictory with inorganic semiconductors such as Si, GaAs, etc. The mobility of carriers in inorganic semiconductor reduces with temperature due to increasing phonon scattering [183]. The mobility in Alq_3 increased with temperature mainly due to its control by the trap centers. A local potential well where carrier trapping occurs is modified by temperature due to the increased lattice vibrations and the electron can hop more easily out of the barrier to another site.

(i) ITO:Alq₃:DCM/Al

Figure 5.2 The plot of electron mobility versus $\sqrt{F}$ at various temperatures (a)-(e) in Alq₃:DCM films for various concentrations. The arrow marks at each figure showed the critical electric field $\sqrt{F_c}$ of electron mobility. The $\sqrt{F_c}$ increased as the DCM concentration increased in Alq₃.

Figure 5.2 shows that the carrier mobility is not closely followed the Poole-Frenkel (PF) model of $\mu \propto \exp(\beta\sqrt{F})$, where F is the applied electric field, and β is a constant at a fixed temperature [180,185]. The field dependence electron mobility was separated into two discrete regions of square root field ($\sqrt{F}$), which is indicated by an arrow in each curve as shown in Fig. 5.2 (a) to (e). This discrete region phenomenon was observed even in lightly doped 0.5 wt.% Alq₃:DCM film. The carrier mobility is only in agreement with the PF model at two different ranges of square root fields. The electron mobility characteristic in single doped films into two discrete regions can be defined as $\mu_{1,2} \propto \exp(\beta_{1,2}\sqrt{F_{1,2}})$. Two values of β (the gradient of the linear line) were observed as the square root of field increased from 250 to 460 (V/cm)^{1/2} in each doped film. The electron mobility in doped films was increased faster after $\sqrt{F_c}$. We observed the values of $\beta_2 > \beta_1$. This phenomenon is supported by the

findings of Borsenberger and Baessler, where they found polar additives doped polycarbonate that the main effect of the polar additives is the enhancement of disorder, both energetic and positional [186].

. We noted that the values of $\sqrt{F_c}$ shifted to the higher values as the concentration of DCM was increased in Alq₃:DCM films and saturated as the concentration of DCM ≥ 3 wt.% in Alq₃ films. The results were summarized and shown in Fig. 5.5. The saturated $\sqrt{F_c}$ values may be attributed to the maximum polarity effect of DCM on Alq₃ molecules when the biasing field is parallel to the orientation of the dipole in the films [38]. This phenomenon is also observed for energetic σ and positional disorders Σ , which was discussed in later parts of this report.

(ii) ITO/Alq₃:C-6/Al

Figure 5.3 The arrow marks at each figure showed the critical electric field $\sqrt{F_c}$ of electron mobility at various temperatures in Alq₃:C-6 films for various concentrations. The $\sqrt{F_c}$ increased as the C-6 concentration increased in Alq₃.

Figure 5.3 shows the carrier mobility of single-dopants of C-6 in Alq₃ films with various concentrations. The carrier mobility in these doped films is $0.3\text{--}1 \times 10^{-4}$ which is slightly higher than DCM doped films of $0.1\text{--}0.8 \times 10^{-4}$ ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$). The discrete regions phenomenon was observed in these doped films. Two different ranges of square root fields were noted, and the curves' gradients were obtained as the square root of field increased from 250 to $460 (\text{V/cm})^{1/2}$ in each film. The gradients of the curves were marked as β_1 and β_2 for before and after the critical field of $\sqrt{F_c}$. The electron mobility in doped films was increased faster after $\sqrt{F_c}$. We observed the values of $\beta_2 > \beta_1$.

(iii) ITO/Alq₃:Rub/Al

Figure 5.4 The arrow shows the critical electric field $\sqrt{F_c}$ of electron mobility of Alq₃:Rub films at various temperatures for various concentrations. The $\sqrt{F_c}$ increased as the rubrene concentration increased in Alq₃. The similar trend of carrier mobility versus square root field was obtained in rubrene doped Alq₃ films as the dopants of DCM and C-6 in Alq₃.

The carrier mobility in Rub doped Alq₃ films was also influenced by this dopant although Rub has non-polar molecular structure as DCM and C-6. The carrier mobility of these rubrene-doped films shows a similar trend with applied electric-field and temperature as the two discrete regions separated by square root critical field ($\sqrt{F_C}$) were observed. The critical field was shifted to higher values as the Rub concentration increased in doped films. This is the property observed for the carrier mobility in small-to-small molecule of guest doped in the host despite the homogeneous quality of the film.

Temperature and applied field are the two parameters to lower the trap depth, and also increase the carrier mobility. However, the experimental results showed the critical field is still remain the same as temperature increased. Critical field is seemed related with dopant types and its concentration in Alq₃, which it was not observed in pure Alq₃. Critical field increased as the dopant concentration increased in Alq₃. If the energy of the dopant-induced Coulomb traps (higher dipole moments of dopant) is larger than the thermal activation energy, most carriers will localize within Coulomb potential wells of ionized dopants and in the deep tail states below activation energy. The temperature increased in this case may not help to reduce the critical field. The alignment of the dipoles to the externally applied field should dominate the geometric disorder than the fluctuation in intermolecular separation. At the higher field, Alq₃ and dopant molecules may be polarized and well aligned with each other, reducing the effect of dipolar contribution in the DOS function. Thus, $\sigma^2 = \sigma_{vdW}^2 + \sigma_{dip}^2$ will dominate on van der Waals component. The effect of van der Waals will be weaker to trap the carriers

The carrier mobility in these doped-Alq₃ films is slower compared to the pure Alq₃ film. Figure 5.5 shows the statistical box-chart plot for the average carrier mobilities of doped devices under the influences of electric-field and temperature. The average carrier

mobilities for doped-films are grouped in a statistical box-chart according to their type and concentration. The carrier mobility was reduced when the dye dopants doped in Alq₃ film. The carrier mobility in Rub doped films is higher compared with C-6 and DCM-doped films, while the DCM doped films show the lowest mobility. The role of the polarity of dopants in molecular materials indicates the presence of dipolar and manifests itself in modifying the carrier mobilities. This effect introduces a dipoles contribution in the DOS function and broadens the width of DOS. The dipole moments of DCM is the highest at ~ 6 D (at ground state) and ~ 26 D (at excitation state) [187] compared with C-6, which has a moment of 7 D (at ground state) and ~ 9 D (at excitation state) [188]. However, the dye dopant of Rub has a non-polar property because of the symmetry of the molecular structure. Hence, the introduction of polar dopants (DCM and C-6) results in enhancement of the dipolar disorder σ_{dipolar} , and consequently to a decrease of the carrier mobilities. The non-polarity of Rub induced the disorder of DOS due to van der Waals component σ_{vdW} with Alq₃ molecules, but this van der Waals effect is weak compared to σ_{dipolar} . Therefore, the carrier mobility is higher than DCM and C-6.

Figure 5.5 The statistical box-chart plot shows the average carrier mobilities of doped-films compared to pure Alq₃ device. The average carrier mobilities of Rub-doped devices are higher than the C-6 and DCM-doped devices due to polar properties of C-6 and DCM broaden the width of DOS.

Based on the carrier mobility results shown in Fig. 5.2-5.4, the values of critical fields $\sqrt{F_c}$ were shifted to higher values as the concentration of dopants increased in Alq₃ films and saturated as the concentration of these dye dopants ≥ 3 wt.%. The results were summarized and shown in Fig. 5.6. The saturated critical fields are found as $\sqrt{F_{Dc}} > \sqrt{F_{Cc}} > \sqrt{F_{Rc}}$, where the notations of *D*, *C* and *R* indicated DCM, C-6 and Rub, respectively. The DCM doping induced higher critical field values compared to C-6 and Rub. This may be attributed to the strong dipole moments property of DCM compared to C-6 and Rub.

Figure 5.6 The plot of critical field F versus the dopants concentration in Alq_3 films. DCM doped induced highest critical field compared to C-6 and Rub. However, the dopants doped-films show the saturation trend as the concentration > 3 wt.%.

The doping of small molecules gives rise to a reduction of the effective drift mobilities due to trapping of carriers. The polarity of dopants plays a role to enhance the dipolar disorder σ_{dipolar} of the films to broaden the width of DOS. The width of the DOS is assumed to be a superposition of van der Waals and dipolar components. Then

$$\sigma^2 = \sigma_{\text{vdW}}^2 + \sigma_{\text{dipolar}}^2 \quad (5.1)$$

with the dipolar component related to the permanent dipole moment of the species (m) and its concentration, where

$$\sigma_{\text{dipolar}} = \frac{Kx^b m}{\epsilon a_0^2}, \quad (5.2)$$

where K and b are constants, ϵ is the relative electric permittivity of the medium, and a_0 is the inter-site distance, which m is the dipole moments of the dopants and x is the mole fraction. Consequently, the σ of the doped-films is determined via an empirical equation, where σ is defined as energetic disorder in a modified PF model. This equation is given as [143]:

$$\mu(E, T) = \mu_{\infty} \exp[-(\frac{2\sigma}{3kT})^2] \exp[\beta\sqrt{F}], \quad (5.3)$$

where T is the absolute temperature, k is the Boltzmann constant, μ_{∞} is the high temperature limit of the mobility, and $\beta = C[(\frac{\sigma}{kT})^2 - \Sigma^2]$; where C is a temperature and field independent constant related to the intersite distance, σ is the energetic disorder of the film, and Σ is a temperature independent parameter related to positional disorder. The presence of positional disorder gives rise to the energetic disorder via the dependent of the potential energy of interaction upon the distance between interacting particles. This potential energy is further enhanced if the molecules have polar properties as mentioned above. Equation (5.3) predicts that the electron mobilities in doped-Alq₃ bulk films depend exponentially on $\sqrt{F}$ at a fixed temperature. The constant parameter values were obtained by fitting the simulated curve from Eq. (5.3) with experimental results. The constant parameters values are also dependent on the nature of the charge-transporting material and the polarity of the organic material. The charge carrier transport in disordered molecular solids is changed with field and temperature due to the local (random) modifications of the polarization energy.

Figure 5.7 (a) shows the zero-field mobility vs $(1/T^2)$ in pure Alq₃ bulk film (reference sample) as derived from Eq. (5.3). The linear curve was extrapolated for each temperature and revealed the linear dependence predicted by Eq. (5.3). We plotted the zero-field mobility $\mu(F=0,T)$ vs $(1/T^2)$ curve for each concentration of dopants doped in Alq₃ bulk film, but only 1 wt.% concentration for each dopant shown in Fig. 5.7 (b)-(d). From the slope of $\mu(F=0,T)$ vs. $(1/T^2)$ plot, the energetic disorder σ was estimated for each doped film. The results were summarized in Fig. 5.8. This energetic disorder σ was estimated as σ_1 and σ_2 according to two discrete linear lines separated by $\sqrt{F_c}$ in each doped film.

Figure 5.7 The plot of μ_{∞} versus temperature to estimate the energetic disorder σ from the slope of the curve for (a) the pure Alq₃ bulk film and (b)-(d) 1 wt.% of doped-films.

The energetic disorder σ_1 ($> \sigma_2$) is higher in each doped film. The energetic disorder σ_2 was reduced tremendously at $\sqrt{F} > \sqrt{F_c}$ due to the higher fields. When a high field F was applied, this lowers the energy barrier and the actual activation energy, increasing the escape probability of a trapped charge. Thus, the actual decrease of the potential barrier or activation energy is proportional to $\sqrt{F}$. The carrier mobilities in doped-films may be turned-up as strong field dependent because of the alignment with external field of the dipolar moments. Non-polar molecules such as Rub incorporated in Alq₃ host results in the creation of traps in the same way as polar molecule as DCM and C-6. However the overall critical field of F_c is smaller (Fig. 5.6), indicating that the quick response to the applied external field to escape from the localized states is due to the weak van der Waals force between the molecules.

The energetic disorders of σ_1 and σ_2 of these doped films are summarized and shown in Fig. 5.8.

Figure 5.8 The summary of energetic disorders of doped films for DCM, C-6 and Rub in Alq₃ bulk films before and after the critical fields.

The higher doping concentration in Alq₃ films showed higher energetic disorder compared to lightly doped films. The energetic disorder in the doped bulk film was increased from 0.02 eV (in pure Alq₃ film) up to 0.1 eV, 0.08 eV and 0.06 eV for DCM, C-6 and Rub with doping concentration of 24 wt.% in Alq₃ bulk films, respectively. Therefore, we can conclude that the electron mobility increased with the higher rate due to lower σ_2 after the critical field when the polar effect was depressed by higher applied electric field. Similar observations were also made in Ref. [38] as the energetic disorder has a smaller influence on charge carrier mobility when the higher electric field was applied in amorphous film. The effect of the applied field lowered the trap depth to release the carriers from localized states. At the highest dopant concentration of 24 wt.%, the polar nature of molecules (DCM and C-6) contributed strong electrostatic interactions with a carrier to cause the localization, whereas the non-polar structure of Rub induced much more lower interactions via a van der

Waals force within the molecules in bulk films. If the applied field is greater than the critical field for each type of doped film, the energetic disorder σ_2 was reduced further to the level of pure Alq₃. Thus, the presence of dopants, necessary to disturb the electrostatic interactions between carriers and the molecules is likely to create the local states even though the guest molecules themselves do not act as traps.

There is a tendency of DCM and C-6 molecules to aggregate due to the asymmetrical molecular structure of strong dipolar interactions [12]. For highly doped films (such as 12 and 24 wt.%), the molecules may have arranged themselves in an anti-parallel manner due to stronger attraction within the DCM and C-6 molecules to reduce distance. Besides, the DCM and C-6 molecules also have strong interactions with surrounding Alq₃ molecules due to their strong dipole characteristic. This is because the DCM molecules, comprising arylidene laser dye with a dimethylamino [-N(CH₃)₂] electron donor group linked to dicyanovinyl [=C(CN)₂] electron acceptor groups [61] have strong interaction with phenoxide donor and pyridyl acceptor in the quinolate ligands of Alq₃ molecules. The C-6 possesses benzothiazolyl and diethylamino group, which have strong electron affinities to form localized states to trap carriers. However, rubrene (C₄₂H₂₈) is a molecule comprised of tetracene with four additional phenyl rings attached at the center positions, which is a good charge transporter. In fact, it is known that in the crystalline state, Rub exhibits a large hole mobility of a fraction of cm² V⁻¹ s⁻¹. Rub doped in host materials can still trap carriers, and acts as recombination center for hole and electron. Rub has been proved inducing the energetic disorder of the doped in Alq₃ as the concentration increased but σ values are lower compared to DCM and C-6 doped films.

The dopant interaction gives rise to positional and energetic disorders in the doped films. Thus, the dipole orientation dominates the geometric disorder than the fluctuation in intermolecular separation. At the higher field, Alq₃ molecules and DCM molecules may be polarized and well aligned between each other, reducing the effect of dipolar contribution in the DOS function. Thus, $\sigma^2 = \sigma_{vdW}^2 + \sigma_{dip}^2$ will dominate on van der Waals component. Based on Eq. (5.1 and 5.2), σ^2 versus m^2 was plotted, where m is dipole moments of the dopants.

Figure 5.9 Influence of the dipole moment of the dopant on the energetic disorder of the DOS function.

The energetic disorder of the dopants based on the influence of the dipole moments properties of the dopants in Alq₃ host is plotted in Fig. 5.8. This figure shows the energetic disorder increased rapidly ($> 20 D^2$) when the dopants' with low dipole moments were introduced in Alq₃ and achieved plateau at highest dipole moments. This may be due to the point dipole approximation breaking down in the case of sufficiently large molecules, or the differences in molecular packing in doped films resulting in differences of the van der Waals component and influencing the effective dipole moments of the molecules in doped films.

The σ is incorporated in DOS to observe the change of the width. The distributions of intersite distances and site energies are in Gaussian form and hopping mechanism is incoherent in doped films. Therefore, the shape of the density-of-states (DOS) function is given as [13],

$$N(E) = \frac{N_{tot}}{(2\pi\sigma^2)^{1/2}} \exp\left(-\frac{(E - E_m)^2}{2\sigma^2}\right), \quad (5.4)$$

where N_{tot} is the total density of states, E_m is the energy of the maximum distribution, and the dispersion σ is a measure of the energetic disorder. The N_{tot} was assumed as 10^{19} cm^{-3} and E_m as 0.24 eV for this simulation [189]. The curve was plotted as $N(E)$ versus $E(\text{eV})$ as shown in Fig. 5.10.

Figure 5.10 The DOS function versus the energy E (eV) of the hopping sites under the factor of energetic disorder of the doped films.

The interaction of polar dopant molecules widened the total density of states, induced the local electric fields, and increased the intermolecular interaction forces in the films. The polarity of DCM and C-6 molecules doped in Alq_3 may induce the formation of deeper localized states and normally located below the intrinsic DOS distribution of Alq_3 [190]. These traps can strongly affect the charge transport property at equilibrium conditions and most carriers will occupy those deep states. This phenomenon is strongly reflected from single-doped films of the relationship $\mu_{1,2} \propto \exp(\beta_{1,2}\sqrt{E_{1,2}})$ as shown in Fig. 5.11.

Figure 5.11 The examples of the plot of corresponding β vs. $(\sigma/kT)^2$ of (a) Rub, (b) C-6 and (c) DCM (1 wt.%) in Alq₃ films. The constant C and position disorder Σ were estimated from these plots.

The positional disorder Σ in the doped films was obtained by plotting β against $(\frac{\sigma}{kT})^2$ as shown in Fig. 5.11. β has a linear relationship with $(\frac{\sigma}{kT})^2$. The temperature and field independence constant C was estimated from the slope of the linear curve. The linear line was extrapolated to obtain the positional disorder, Σ . β as a function of $(\frac{\sigma}{kT})^2$ was plotted for different dopant concentrations in Alq₃ films to estimate the constant C and positional disorder Σ . C is a function of the intersite distance and assumes the value of $2.9 \times 10^{-4} \text{ (cm/V)}^{1/2}$ for the distance equal to 0.6 nm [191]. The Σ is a temperature independent parameter related to the dispersion function describing the off-diagonal disorder in distribution of intersite distances. The distribution site energies are often due to diagonal disorder.

Higher electron mobility ($\beta_2 > \beta_1$) was observed when the bias field was greater than the critical field. Figure 5.12 shows the summary results of positional disorders for each doped film. The Σ is assigned to Σ_1 and Σ_2 for before and after the critical field, respectively. The values of Σ_1 were found higher than Σ_2 . Before the critical field, the positional disorder in doped films presented the geometric disorders associated with randomness both in dipole orientations and intermolecular separations. The Σ_1 values were changed from 0.3 to 6.5 with DCM doping concentration of up to 24 wt.% in Alq₃. The Coulombic interaction between the random distributions of the stronger polar DCM molecules with Alq₃ molecules has increased the positional disorder. This leads to broadening the effective density of states distribution. The positional disorder Σ_2 values were changed tremendously from 0.3 to 1.9 with DCM doping concentration of up to 24 wt.% in Alq₃, respectively after the applied field exceeded the critical point. The positional

disorders were saturated at the higher doping concentration of DCM as shown in Fig. 5.12. Therefore, the polarity of dopants' molecules in Alq₃ is proven as one of the factors enhancing the positional disorders of the doped films.

Figure 5.12 The plot of positional disorders before and after the critical field $\sqrt{F_c}$ in doped-films for various concentrations in Alq₃.

The presence of positional disorder gives rise to energetic disorder due to the positional molecular dependence of potential energy of interaction. This has been proven from the above result of energetic disorders σ ($\sigma_{\text{van der Waals}}$ and $\sigma_{\text{dipole-dipole}}$), which were estimated higher as (i) the doping concentration of dopants increased but gradually achieved plateau situation as the concentration increased > 3 wt.%, (ii) DCM and C-6 which possessed higher dipole moments presented higher values of Σ compared with rubrene, and thus induced the higher σ as has been discussed above, (iii) the bias field exceeded the critical field $\sqrt{F_c}$ in each doped-film and depressed the traps depth in the films to enhance the carrier mobility.

This positional disorder is related to the dispersion function of the disorder films and described the off-diagonal disorder in distribution of intersite distances for carriers hopping across the localized states. The spread of these intersite distances inevitably influences the respective transfer rate of carriers from one state to another. C is a constant independent from the influence of temperature and electrical field, and is a factor of intersite distance. However, based on the results as shown above, two discrete regions of carrier mobilities are found related with the applied field in doped-films and this is in contrast to the PF model of Eq. (5. 3). C was estimated for these doped films and found ranged at $2.6-7.8 \times 10^{-4} \text{ (cm/V)}^{1/2}$ and $5.6-3.5 \times 10^{-3} \text{ (cm/V)}^{1/2}$ at before and after the critical field of the doped films. Thus, C is believed influenced by the “alien” molecules in the host film and the possibility of dynamic disorder on the transport of carriers. This part needs further investigation before drawing any conclusion.

The energetic disorder controls the charge carrier transport in amorphous organic materials. Previous studies have shown that, the energetic disorder has two components in a molecular amorphous solid. One component comes from the van der Waals interaction among molecules. The other originates from the dipole-dipole interaction. However, it is found that the net dipole moment of Rub is vanished. Thus, the van der Waals component in Rub is the only contributor in energetic disorder. The geometric disorders are generally associated with randomness both in dipole orientations and in intermolecular separations. The fluctuation in intermolecular separation should dominate the geometric disorder in Rub. Normally Rub is not used as a hole-transporting layer in an OLED due to the tendency of Rub to form crystals. Rub is used as a dopant to adopt a guest-host approach in Alq₃.

However, the DCM has the highest dipole moment compared to C-6. The dipole-dipole interaction dominates the energetic disorder more than van der Waals component in DCM and C-6. Thus, the stronger Coulomb attraction force between these polar molecules is

stronger than the weak van der Waals force in Alq₃ film. The dipole moment of Alq₃ was estimated at about 5 D at room temperature. The energetic disorder of Alq₃ is contributed from dipole-dipole interaction and van der Waals components. The interaction of polar molecules broadened the total density of states, induced the local electric fields, and increased the intermolecular interaction forces in the films. The polarity of molecules doped in Alq₃ may induce the formation of deeper localized states normally located below the intrinsic DOS distribution of Alq₃. These traps can strongly affect the charge transport property at equilibrium conditions and most carriers will occupy those deep states. Thus, the effect of doping on an intrinsically Gaussian DOS distribution generates a large number of deep states. Therefore, one can expect that the doping-induced change in DOS distribution would immediately affect the carrier hopping mobility in Alq₃.

5.3.2 Two dopants doped in Alq₃ Films

The presence of Rub with polar (DCM or C-6) dopants in host material Alq₃ interacted with and modified the carrier mobility. Rub co-doped with DCM or C-6 into Alq₃ in the bulk film reduced the energetic and positional disorders of these doped films compared to the results presented above. The co-doped of Rub with polar dopants of DCM or C-6 into Alq₃ films was the ratios of 1:1 and 2:1, and the total concentration of both dopants set at 1 wt.%.

Two discrete regions of carriers mobilities in single-doped films of temperature and external applied fields dependents phenomenon is strongly reflected in of the relationship $\mu_{1,2} \propto \exp(\beta_{1,2} \sqrt{F_{1,2}})$ as discussed above. However, the co-doped of non-polar Rub with polar dopants into Alq₃ has eased these phenomena. The critical field regions disappeared as Rub incorporated with DCM in Alq₃ films. The electron mobility followed the Poole-Frenkel

dependence in co-doped films. The position and energetic disorders were significantly reduced. The Rub molecular structure may be responsible for these reductions.

(i) Co-doped of Rub with DCM into Alq₃ Films

Figure 5.13 shows the photocurrent versus decay time of co-doped of non-polar Rub with DCM into Alq₃ films with the ratios of 1:1 and 2:1 at a field F of 6.25×10^4 V/cm.

Figure 5.13 The typical TOF measurement curves of doped-films. Co-doped of Rub-DCM with ratio 1:1 and 2:1 in Alq₃ bulk films. The simulated dotted lines are fitted with experimental data to estimate the average carrier mobility of μ .

The typical photocurrent measurement in co-doped films was the same as in single-doped films, and simulation of the photocurrent to estimate the average carrier mobility in these co-doped films were based on Eq. (2.13). The carrier mobility, μ versus the $\sqrt{F}$ under the factor of temperature was plotted in Fig. 5.14.

The critical field divided the electron mobility characteristic in single doped DCM in Alq₃ films into two discrete regions. However, this critical field in the co-doped films was not observed as shown in Fig. 5.14. The linear relationship was obtained and the Poole Frenkel model was obeyed.

Figure 5.14 The plot of electron mobility versus $\sqrt{E}$ at various temperatures. (a) Ratio 1:1 (b) Ratio 2:1, co-doped of Rub-DCM in Alq_3 films. No discrete regions of carriers mobilities are observed in single-doped of DCM in Alq_3 films have observed.

Two phenomena were observed based on Fig. 5.14. First, the electron mobility moved faster in co-doped of Rub-DCM in Alq₃ bulk film in the ratio of 1:1 than in Alq₃:DCM doped film (1 wt.%) especially when $\sqrt{F} > \sqrt{F_c}$ [≈ 372 (V/cm)^{1/2}]. Second, when the ratio of Rub:DCM increased to 2:1, the electron mobility was found higher than the ratio of 1:1 and single doped films. It can be concluded that the addition of Rub into Alq₃:DCM film will help to increase the electron mobility. We attribute this phenomenon to the molecular structure of Rub and it has greater influence than dipole-dipole and Coulomb force interactions among the molecules to favor the electron mobility.

The curves of zero-field mobility $\mu(E=0, T)$ vs $(1/T^2)$ are shown in Fig. 5.15 for both ratios derived from Eq. (5.3). The energetic disorder σ was found as ~ 0.030 eV and 0.039 eV for two ratios of 1:1 and 2:1 in co-doped of Rub-DCM in Alq₃, respectively. The energetic disorder was lowered once the Rub was introduced. This can be proven from Fig. 5.15 (a) and (b) where the energetic disorder σ for both ratios was about the same as ~ 0.037 eV. The co-doping of Rub with DCM reduced the energetic disorder σ of the films and thus enhanced the carriers mobilities compared to single doped of DCM in Alq₃.

Figure 5.15 The plot of zero field mobilities vs $1/T^2$ for different samples. (a) and (b) are for co-doped of Rub:DCM in Alq_3 films for two ratios. The energetic disorder and zero field mobilities were estimated from these plots.

The positional disorder Σ was estimated for different doped films by plotting β as a function of $(\frac{\sigma}{kT})^2$ as shown in Fig. 5.16. The values of Σ and constant C are recorded in Table 5.2 for different samples before and after the critical electric-field. The values of Σ in co-doped Rub-DCM in Alq_3 films were found as 1.09 and 1.54 for two ratios of 1:1 and 2:1 respectively, compared to the positional disorder values of ~ 4.2 for single dopant films of Alq_3 :DCM at $\sqrt{F} \leq 372 \text{ (V/cm)}^{1/2}$. The positional disorder correlated with the energy disorder within the molecules in the films. It can be concluded that the increase of electron mobility in co-doped films compared to Alq_3 :DCM film is due to the reduction of energetic disorder associated with the effect of strong dipole moments contributed from DCM shielded from non-polar of rubrene in the films. The strong Coulomb force interactions between polar molecules of DCM to carriers are minimized by the introduction of Rub.

Figure 5.16 The plot of β vs. $(\sigma/kT)^2$ for different samples. (a) and (b) are for co-doped of Rub:DCM in Alq_3 films for the two ratios. The constant C and positional disorder Σ were estimated from these plots.

The interaction of polar DCM molecules widened the total density of states, induced the local electric fields, and increased the intermolecular interaction forces in the films. The polarity of DCM molecules doped in Alq_3 may induce the formation of deeper localized states, normally located below the intrinsic DOS distribution of Alq_3 . These traps can strongly affect the charge transport property at equilibrium conditions and most carriers will occupy those deep states. This phenomenon is strongly reflected from single-doped films of the relationship $\mu_{1,2} \propto \exp(\beta_{1,2} \sqrt{E_{1,2}})$ as shown in Alq_3 :DCM. However, the co-doped of Rub with DCM into Alq_3 has removed this phenomenon. The critical field regions also disappeared in co-doped films. The electron mobility followed the Poole-Frenkel dependence in co-doped films. The positional and energetic disorders were significantly reduced. The Rub molecular structure may be responsible for these reductions. The Rub molecules were formed with 8 benzene rings with abundance pi-conjugated bonding and interacted with polar molecules of DCM to: (i) reduce the Coulomb and dipole-dipole interactions between

DCM and Alq₃ molecules, (ii) shift the charge distribution from centers on DCM molecules (due to dipole moments of DCM) to distribute more randomly in doped molecules in the film and (iii) provide channeling to electron and thus facilitate the hopping mechanism of electron carriers by anti- π conjugation of benzene rings.

(ii) Rub Co-doped with C-6 into Alq₃ Films

The non-polar Rub was also co-doped with C-6 in Alq₃ films to investigate the carriers mobilities with applied field at different temperatures. The C-6 possesses the dipole moment of 8.6 D, which is lower compared to DCM of 26.3 D. The addition of rubrene is expected to further reduce the energetic and positional disorders as compared to co-doped of Rub-DCM in Alq₃ films. Figure 5.17 showed the TOF photocurrent measurements of these co-doped films for the ratios of Rub:C-6 at 1:1 and 2:1. These photocurrents were simulated based on Eq. (2.13) to estimate the average carrier mobilities. The results of carriers mobilities versus the $\sqrt{F}$ is presented in Fig. 5.17.

Figure 5.17 (a) The typical TOF measurement curves of co-doped-films of Rub:C-6 with ratio 1:1 and 2:1 in Alq_3 bulk films. Equation 2.13 was used to simulate the photocurrents to obtain the average carriers mobilities. (b) and (c) showed the summary results of carriers mobilities versus the $\sqrt{F}$, where the relationship obeyed the PF model and no discrete regions divided by critical field were observed.

The results shown in Fig. 5.17 (b) and (c) indicated that the co-doped of Rub with C-6 in Alq_3 eased the discrete regions of carriers mobilities via the square root of external bias fields. This phenomenon was also noticed in Rub:DCM co-doped in Alq_3 films. The carriers mobilities are averagely higher in Rub:C-6 film compared to Rub:DCM co-doped films. The curves of zero-field mobility $\mu(E=0, T)$ vs $(1/T^2)$ are plotted as shown in Fig. 5.18 (a) to estimate the energetic disorders of the films. The energetic disorder σ was found as ~ 0.032 eV and 0.034 eV for two ratios of 1:1 and 2:1 of co-doped of Rub:C-6 in Alq_3 , respectively. This indicated that the energetic disorder was further lowered once the Rub co-doped with C-6 was due to lower polar effects C-6, when compared to DCM molecules. The introduction of Rub reduced the energetic disorder σ of the films and thus enhanced the carriers mobilities, when compared to single doped polar molecules in Alq_3 .

Figure 5.18 (a) The plot of zero field mobilities vs $1/T^2$ for different samples. Co-doped of Rub:C-6 in Alq₃ films for two ratios. The energetic disorder and zero field mobilities were estimated from these plots. (b) The plot of β vs. $(\sigma/kT)^2$ for different samples. The constant C and positional disorder Σ were estimated from these plots.

The positional disorder Σ was estimated for different doped films by plotting β as a function of $(\frac{\sigma}{kT})^2$ as shown in Fig. 5.18 (b). The values of Σ Rub:C-6 in co-doped films were found as ~ 1.7 and ~ 1.9 for the two ratios of 1:1 and 2:1 respectively. The positional disorder values of ~ 2 and ~ 1 was found in single-doped films of Alq₃:C-6 and Alq₃:Rub at $\sqrt{F} \leq \sqrt{F_c}$ (V/cm)^{1/2}, respectively. However, the co-doped of Rub with C-6 showed no significant change on the positional disorder in the films compared to single-doped films. This may be due to the minimum contribution of Rub and C-6 to the dispersion of off-diagonal disorder of the co-doped films. This means the distribution of intersite distance in Rub:C-6 co-doped of film has not altered even though the ratio of Rub increased to 2:1 with respect to C-6.

Table 5.1 shows the comparison of energetic disorders of each doped film. Rub molecules co-doped with polar dopant DCM and C-6 have significantly minimized the energetic disorders of the films especially the σ values before the critical field in single-doped film, respectively. Nevertheless, there is no significant change of energetic disorder compared to co-doped films at bias field higher than critical field in each single doped film. The higher applied field depressed the effect of the polarity of the molecules to carriers. Two discrete regions of carriers mobilities phenomenon was eased once the rubrene co-doped with polar molecules of DCM and C-6.

Table 5.1 The energetic disorders σ for each doped film were estimated.

Samples (1 wt. %)	$\sigma_{\text{bef. crit.}}$ (eV)	$\sigma_{\text{af. crit.}}$ (eV)
Pure Alq ₃	0.013	
Alq ₃ :DCM	0.064	0.037
Alq ₃ :C-6	0.055	0.027
Alq ₃ :Rub	0.047	0.023
Alq ₃ :(Rub:DCM) (1:1)	$\sigma=0.030$ eV	
Alq ₃ :(Rub:DCM) (2:1)	$\sigma=0.039$ eV	
Alq ₃ :(Rub:C-6) (1:1)	$\sigma=0.032$ eV	
Alq ₃ :(Rub:C-6) (2:1)	$\sigma=0.034$ eV	

Table 5.2 showed the comparison of positional disorders in single-doped and co-doped films. The DCM single doped films induced highest positional disorders compared to C-6 and Rub. The reason was attributed to highest dipole moments of DCM compared to others. The co-doped of rubrene with DCM in Alq₃ films significantly reduced the positional disorders. However, for the case of Rub:C-6 in Alq₃ was not giving the same results, where the positional disorder is still maintained at ~ 1.7 slightly lower than the single doped of C-6 before the critical field of ~ 2 . The C-6 has much lower dipole moments of 8.6 compared to DCM. This means the polar effect contribution to Coulomb attraction force upon the free carriers is lower. Thus the local electric fields and the intermolecular interaction forces in the films are lower. The polarity of C-6 may not induce the formation of deeper localized states as DCM. Hence, the addition of Rub molecules with 8 benzene rings with abundance pi-

conjugated bondings provided the alternative way for carriers to hop across the disorder films.

Table 5.2 The positional disorders Σ were estimated for each single-doped film before and after the critical field compared to co-doped films of ratios 1:1 and 2:1.

Samples (1 wt. %)	$\Sigma_{\text{bef. cri t.}}$	$\Sigma_{\text{af. cri t.}}$
Pure Alq ₃	0.378	
Alq ₃ :DCM	4.4	0.6
Alq ₃ :C-6	2.0	0.4
Alq ₃ :Rub	1.1	0.3
Alq ₃ :(Rub:DCM) (1:1)	1.1	
Alq ₃ :(Rub:DCM) (2:1)	1.5	
Alq ₃ :(Rub:C-6) (1:1)	1.7	
Alq ₃ :(Rub:C-6) (2:1)	1.9	

5.4 Summary

The carriers mobilities in doped amorphous Alq₃ films were measured by TOF measurements. The doped films were divided into single-doped and co-doped films. The single-doped films were prepared as the dopants of DCM, C-6 and Rub with different concentrations from 0.5 - 24 wt.% in Alq₃ films, respectively. The co-doped films were fabricated by the co-evaporation of Rub:DCM and Rub:C-6 in Alq₃ with the ratios of 1:1 and 2:1 respectively. The electron mobility in co-doped films ($0.5 - 9.0 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) was higher than the single-doped films. The carriers mobilities were averagely higher in the co-doped Rub:C-6 films compared to co-doped Rub:DCM films. The energetic disorder was estimated as ~ 0.037 eV and ~ 0.032 for the co-doped Rub:DCM and Rub:C-6 in Alq₃ film, respectively which was ~ 0.047 - 0.064 eV in single doped films. This indicated the energetic disorder was further reduced once the Rub co-doped with C-6 and DCM molecules in Alq₃ films. The lower values of energetic disorders in co-doped films could be due to the ease of

$\sigma_{\text{van der Waals}}$ and $\sigma_{\text{dipole-dipole}}$. The values of positional disorder Σ were found as 1.09 and 1.54 in co-doped Rub:DCM ratios 1:1 and 2:1 respectively in Alq₃ films. The values of Σ in co-doped Rub:C-6 films were found as ~1.7 and ~1.9 for the two ratios of 1:1 and 2:1 respectively. The positional disorder values were ~2 and ~1 in single-doped films of Alq₃:C-6 and Alq₃:Rub, respectively. However, the positional disorder values were increased tremendously to ~ 4.2 in single dopant films of Alq₃:Rub and Alq₃:DCM at $\sqrt{E_c} \leq 372(V/cm)^{1/2}$. Thus, the co-doped of Rub and DCM into Alq₃ significantly affected the energetic and positional disorders in DOS model.

Chapter 6

The Transient Photoluminescence (PL) and Electroluminescence (EL) in Doped Films

6.1 Introduction

This chapter is divided to two sections; the first will discuss the influence of polar and non-polar dopants in amorphous organic films on transient photoluminescence (PL). This study would be analyzed by the PL decay measurement in doped films. due to there is little information of excitons lifetime in doped organic devices. The dependence of the transient PL lifetime of exciton behaviors in doped Alq₃ would be presented. The diffusion coefficient D_s and diffusion length L of excitons for various concentrations of dopants in Alq₃ would be estimated from the exciton kinetic equation.

The second section will discuss the transient electroluminescence (EL) of bi-layer doped OLEDs. This investigation would be studied by driving the devices with short, rectangular voltage pulses. In this study, the EL decay behavior would be investigated in order to clarify the influence of dopants on the EL onset. Analysis would show that the EL onset time for DCM, C-6 and Rub doped devices has been delayed before achieving saturation. This EL onset is governed by the growth of the interfacial charge densities and the concomitant redistribution of the electric field inside the sample rather than by charge-carrier transport [192].

6.2 Experimental

Highly pure 99.9% of Alq_3 , DCM, C-6 and Rub were purchased from Aldrich-Sigma for this experiment. The doped films were deposited by the co-evaporation of Alq_3 and dopants on pre-cleaned silicon wafer substrates for the transient PL measurements. The wafer substrates were cleaned by a serial of sonication in chemicals and deionized water baths to remove contaminations. Subsequently, the organic doped films were deposited by vacuum sublimation at 10^{-6} torr in the thermal evaporator chamber. Single doped films of Alq_3 :DCM, Alq_3 :C-6 and Alq_3 :Rub with various concentrations from 0.5 to 24 wt.% were prepared. The co-doping of Rub:DCM and Rub:C-6 in Alq_3 films were prepared. The ratios of each Rub:DCM and Rub:C-6 co-doped film is fixed at 1:1 and 2:1 and the total dopants concentration is maintained at 1 wt. % with respect to Alq_3 in each co-doped film. The film thickness ~ 70 nm was monitored by a crystal oscillator, which was also measured by Alpha-Step profiler. Three samples were prepared on a substrate, each with an active area of 100 mm^2 .

Figure 6.1 The schematic of experimental set-up for transient PL measurements

The experimental setup for the transient PL decay measurement is shown in Fig. 6.1. The switch is excited by 5 ns pulses at 355 nm with a repetition rate at 20 Hz of an active-passive model locked, Nd-YAG laser. The 355 nm optical beam is focused onto the active area of the samples. The transient PL was measured by an ORIEL Photomultiplier tube (PMT) with the filter lens set to filter out any wavelength < 500 nm to avoid the capture of laser beam. The signal measured by PMT was amplified and recorded in the single shot regime by a HP oscilloscope (500 MHz). All measurements were conducted at room temperature.

For the transient EL experiments, the samples of bi-layer OLEDs consist of glass substrates covered with a patterned ITO anode, followed by a 70 nm thin NPD layer as hole transport layer (HTL) and a 70 nm thin Alq₃ doped with dopants (DCM, Rub, C-6) as the active material and finally a Al metal top cathode. The dopants concentrations of 0.5, 1 and 24 wt.% were set with respect to Alq₃. The concentration of co-doped devices of Rub:DCM and Rub:C-6 in Alq₃ layer was set at 1 wt.% with the ratios of 1:1 and 2:1 for each of them.

The experimental setup for the transient EL decay measurement is shown in Fig. 6.2. This typical set-up was modified from transient PL as the laser pulse was replaced by a dc pulse/function generator (50 MHz, rise time ~ 7 ns, decay time of 10 ns) to apply rectangular voltage pulse to our OLEDs devices. The repetition rate of the pulse was 1 kHz, and the pulses length varied between 5 and 10 μ s. The devices were fixed in a holder together with an ORIEL Photomultiplier tube (PMT) located directed to the device's emitting area to detect the EL intensity. The signal measured by PMT was amplified and recorded in the single shot regime by a HP oscilloscope (500 MHz). The oscilloscope was connected to a personal computer for the transfer and evaluation of the experimental data. All measurements were conducted at room temperature.

Figure 6.2 The Schematic set-up of Transient EL measurement

6.3 Results and Discussion

6.3.1 Single-Doped Films

The spectral overlapping of Alq₃'s PL spectrum with these dye dopants' absorption spectra is indicated in Fig. 6.3 (b)-(d). There is a good overlapping of the dopant absorbance spectra with the emission spectra of the Alq₃, which is necessary to maximize the probability of energy transfer from Alq₃ to dopants. This is the basic requirement for efficiency energy transfer based on resonance dipole coupling [193-195] model between the donor-guests molecules. The excitation wavelength was 355 nm as a suitable excitation source since the maximum absorption peak of Alq₃ is at 390 nm. The excited electrons from HOMO to LUMO will either decay directly or transfer the excitation to dopants' molecules.

Figure 6.3 The absorbance and PL spectra for (a) Alq₃, (b) DCM, (c) Rub and (d) C-6. The overlapping area (shaded area) between PL spectrum of Alq₃ with the dopants' absorbance spectra indicated the requirement for efficiency of energy transfer.

Fig. 6.4 shows the PL peak energy (eV) with different concentration of dopants in Alq₃ films. The inset shows the normalized PL properties versus the emission wavelength of doped films. The emission wavelength red-shifted in the doped films as the dopant's concentration increased. The energy transferred between Alq₃ and dopants by exciton diffusion, as described in Forster resonance transfer model [46,61,193,196].

The PL properties of Alq₃:Rub films with various concentrations of Rub are shown in Fig. 6.4 (c). The PL emission wavelength from these doped films are identical with Alq₃ emission at lower doping concentration. At the higher Rub concentration in the films the PL peak red-shifted to ~ 560 nm. The PL emission of Alq₃ is not observed in DCM and C-6 doped films even at the lowest dopant concentrations of 0.5 wt.%.

Figure 6.4 The PL peak energy (eV) versus dopants concentrations in doped-films as (a) Alq_3 :DCM, (b) Alq_3 :C-6 and (c) Alq_3 :Rub. The inset showed the PL properties versus the emission wavelength (nm) of each respective doped-films.

The Alq₃ fluorescence lifetime is 15 ns [197]. The Alq₃ molecules are “three dimensional,” and they do not aggregate densely and thus suffer little excimeric concentration quenching. The rapid decay is well explained as a singlet–singlet exciton annihilation process [197]. The excited Alq₃ molecules can pass most of their energy to dopants acceptors. Bimolecular singlet annihilation between Alq₃ molecules cannot be the primary relaxation mechanism in dopants doped samples. The excitation decay is doping concentration dependent [197]. This indicates that the de-excitation follows the processes as (1) an electron in Alq₃ molecules, which absorbs an excitation laser photon, exciting it from the HOMO to the LUMO. (2) This electron relaxes to the bottom of the LUMO via a Stokes shift within the Alq₃ excited state. (3) The excitation transfers from the Alq₃ to a dopant molecule. (4) The newly excited dopant electron relaxes energetically via another Stokes shift. (5) The dopants’ electron transfers back to the HOMO via radiative or nonradiative decay. The transfer energy from Alq₃ to dopants is attributed to Forster energy transfer as mentioned above. This dipole–dipole interaction is a fast, long-range (tens of angstroms) process, which exhibits a r^{-6} dependence, where r is the donor/acceptor separation [193]. Since concentration quenching restricts the acceptable percentage of dopant molecules, long-range transfer is important in this context.

6.3.2 Co-Doped Films: The PL Spectra in Co-doped Films

Figure 6.5 shows the PL spectra for each co-doped films of (a) Rub:DCM (1:1 and 2:1) (b) Rub:C-6 (1:1 and 2:1) in Alq₃ films. The total concentration of dopants was maintained at ~1 wt. % with respect to Alq₃ for both ratios of co-doped films. Few phenomena were noted from Fig. 6.5 as:

- (i) The PL peak was red-shifted to 600 nm for the ratio of 1:1 (Rub: DCM in Alq₃) compared to 585 nm of Alq₃:DCM (1 wt.%) film
- (ii) The PL peak was further red-shifted to ~610 nm due to higher ratio of Rub in co-doped film.
- (iii) The PL peak of Fig. 6.4 (b) shifted from 520 nm (Alq₃:C-6) to ~ 560 nm with a small doped of Rub in Alq₃:C-6 films. As the ratio of Rub:C-6 changed to 2:1 in the films, the PL peak was not further shifted from the peak position of 560 nm. However, a small peak from Rub emission component was seen at 600 nm shoulder for the higher Rub ratio of 2:1 in the film. This indicated that the photo-excited spectrum was entirely dominated by the concentration of C-6 and Rub in the films.

Hence, the addition of Rub in doped films resulted in a longer emission wavelength compared to single doped-films. With increasing the ratio of Rub to 2:1 in both cases of Rub:DCM and Rub:C-6, the Rub domination is more obvious as shown in Fig. 6.5.

Figure 6.5 The normalized PL intensity versus the emission wavelength of (a) co-doped of Rub:DCM in Alq₃ films and (b) co-doped of Rub:C-6 in Alq₃ films. Both cases red-shifted the emission wavelength compared to single-doped films

6.3.3 The PL Time Evolution in Doped Films

The PL time evolution of light emission from optically excited Alq₃ films with different concentrations of single doped and co-doped dopants is shown in Fig. 6.6. The fast initial rise time and emission lifetime for their transient PL decay was simulated from the equation:

$$y = A * (1 - \exp(-\frac{t}{t_1})) \exp(-\frac{t}{t_2}) \quad (6.2)$$

where A is constant, t_1 and t_2 are the fast initial rise time and exciton lifetime respectively. t_1 indicates the efficiency of energy transfer from Alq₃ to dopant molecules. t_1 decreased significantly (1 order) after pure Alq₃ lightly doped with dopants, indicated higher efficiency of energy transfer to dopant from Alq₃ molecules. As the dopant concentration increased in

Alq₃ films, t_1 showed an increase, indicated that the inefficiency of energy transfer from Alq₃ molecules to dopant molecules. This is due to too high concentration lead to exciton quenching, the emission would be smeared due to exciton concentration quench. t_2 is the exciton lifetime or decay time. As the dopant concentration increased, the exciton decay time t_2 decreased and the singlet excitation recombination rate constant γ_{ss} increased. Based on the results obtained, diffusion length of singlet exciton decreased with increasing dopant concentration. This indicated higher recombination rate of singlet exciton increases when dopant concentration is higher. The recombination of singlet exciton increases, the higher decay rate was obtained. It is possible to attribute the fast initial rise to the Forster energy transfer in Alq₃ doped films. Eq. (6.2) was used to simulate the results from Fig. 6.6 to obtain t_1 and t_2 for the transient PL decay. Figure 6.6 (a) showed the dotted lines from Eq. (6.2) to fit experimental results.

The PL decay time for single dopants with 3 different concentrations in Alq₃ films are compared to pure Alq₃ in Fig. 6.6 (a)-(c). The PL transient decayed faster as the dopants' concentrations increased in the films. The co-doped films in Fig. 6.6 (d) and (e) show faster decay compared with the single doped films. The excited carriers in Alq₃ may decay directly or it may transfer its excitation to the dopants. It can immediately be seen that the time-resolved relaxation of these doped-films is dopant-level dependent.

Figure 6.6 The time evolution of light emission from optically excitation on different concentrations of single doped and co-doped of dopants in Alq_3 films. (a) DCM doped, (b) Rub doped and (c) C-6 doped. Figures (d) and (e) show the co-doped films of Rub:DCM and Rub:C-6 in Alq_3 respectively. These doped films show the faster decay compared to pure Alq_3 film

Figure 6.7 summarized the t_1 and t_2 versus the dopants concentration. The initial rise time is t_1 and decay rate is t_2 for doped films in (a) and (b) respectively. Figure 6.7 (b) showed the fast decay rate of transient PL in the order of the faster of $\text{Alq}_3\text{:DCM} > \text{Alq}_3\text{:C-6} > \text{Alq}_3\text{:Rub}$ in doped films. The PL in co-doped films of $\text{Alq}_3\text{:Rub:DCM}$ is decayed with slightly faster rate compared to $\text{Alq}_3\text{:Rub:C-6}$. The insert in 6.7 (b) shows the comparison of transient PL decay t_2 between $\text{Alq}_3\text{:Rub:DCM}$ and $\text{Alq}_3\text{:Rub:C-6}$ films. The initial behavior of the doped sample is same as pure Alq_3 where the photo-excitation predominantly populates the excited states of Alq_3 . The excitons in excited states of Alq_3 suffer little excimeric concentration quenching and pass most of their energy to dopants acceptors in doped films. Therefore, the excitation decay of the doped films depends upon the doping percentage [198].

Figure 6.7 The plots showed the summarized of the t_1 and t_2 versus the dopants concentration for fast initial rise time and transient PL decay time in figures (a) and (b), respectively. The inset of figure (b) showed the comparison of decay time in co-doped films of Alq₃:Rub:DCM and Alq₃:Rub:C-6

The fast initial rise time t_1 between Alq₃ and dopant molecules are the fast transfer of exciton energy from Alq₃ diffused to dopants molecules, indicating that the diffusion is within the ‘capture’ distance for dopants molecules. The energy transfer from Alq₃ is facilitated by to the strong dipole-dipole resonance coupling induced by polar DCM and C-6. On the other hand, the capture of free charges from Alq₃ is dependent on weak van der Waals force between the extensive pi-conjugated and non-polar molecular structure of Rub. The Coulomb attraction force is too weak to attract the charges initially, but strong Coulomb interaction greatly increases the capture cross section of a second carrier of the opposite polarity once the molecule of Rub becomes charged upon the capture of a first charge carrier. The initial rise time t_1 of Rub-doped films is longer than DCM and C-6 molecules doped in Alq₃ films. This phenomenon is observed in co-doped films of Rub-DCM and Rub-C-6 in Alq₃ for both ratios. When the ratio of Rub increased to 2:1, the initial rise-time also increased in both types of doped films. This indicated that the dipole-dipole resonance coupling mechanism between DCM (C-6) and Alq₃ is depressed in Rub co-doped films. One of the reasons is the low polar dopants of DCM and C-6 concentration in these doped films. Thus, the fast initial rise-time of transient PL was delayed in co-doped films. Once the energy transferred to dopants, the recombination with hole to form excitons occurred directly in the dopants. Thus, the recombination rate in these doped films were estimated based on the kinetic equation [69,199].

The bimolecular recombination rate constant of singlet excitons in single doped Alq₃ films are quantitatively estimated, and compared to co-doped films by fitting to PL data with the kinetic equation describing the concentration of singlet molecular excitons $[S_1]$ [60,199]

$$\frac{d[S_1]}{dt} = \alpha I(t) - k[S_1] - f\gamma_{ss}[S_1]^2 \quad (6.3)$$

where α is the absorption coefficient, I is the excitation intensity ($\sim 10^{29}$ photon/cm²), k is the rate of the monomolecular decay of singlet excitons ($\frac{1}{t_2}$), γ_{ss} is the rate constant for bimolecular recombination, and f is a parameter that takes into account losses due to autoionization and direct nonradiative relaxation to the ground state (S_0) from states above the singlet exciton state. The recombination rate of doped films was estimated from Eq. 6.3. We can compare the differences between DCM, C-6 and Rub individually in Alq₃ films as well as the co-doping of both dopants in Alq₃. The diffusion coefficient D_s and diffusion length L were also estimated for the doped films.

This estimation of singlet molecular excitons is assumed that all the energy was transferred and there was no de-excitation from Alq₃. The values of k and f were determined before extracting γ_{ss} . The k was estimated from PL measurements at excitation intensities where bimolecular recombination is not a factor. The f parameter varies around the values of 0.5, when auto-ionization and direct nonradiative decay to the ground state is negligible [200,201]. Upon the optical pumped, the auto-ionization of Alq₃ molecules is an inefficient process, and excited singlet states relax primarily into charge transfer states and/ or the lowest excited singlet state (S_1). Thus, f is taken as 0.5 for our simulation.

The γ_{ss} for pure Alq₃ and doped films were estimated from the theoretical fits of equation (6.3). The results are shown in Fig. 6.8. The inset figure shows the recombination rate for co-doped films of Alq₃:Rub:DCM and Alq₃:Rub:C-6. The results show that the recombination rate in doped films range between $2.1\text{--}3.5 \times 10^{-12}$ cm³s⁻¹ which is $\sim 5 \times 10^{-12}$ cm³s⁻¹ in pure Alq₃. The co-doped films showed the recombination rate between $2.8\text{--}3.6 \times 10^{-12}$ cm³s⁻¹, slightly higher than other doped films. The recombination rate decreased as the concentrations of dopants increased in the films. The dopants are acting as a recombination center in the doped films. The dopants are highly planar [198] and have the tendency to

aggregate when the concentration is high, and are particularly susceptible to this type of concentration quenching. However, the co-doped films of $\text{Alq}_3\text{:Rub:C-6}$ showed higher recombination rates: (1) The addition of Rub in doped Alq_3 films with DCM and C-6 induced higher recombination rate compared at the same concentration of 1 wt.% for single-doped in Alq_3 films; (2) The additional Rub in $\text{Alq}_3\text{:C-6}$ showed higher recombination rate compared with $\text{Alq}_3\text{:Rub:DCM}$, and (3) as the ratio of Rub increased in the co-doped films, the recombination rate increased as well.

Now the diffusion coefficient D_s for singlet excitons was estimated from the following equation [187]

$$\gamma_{ss} = 8\pi D_s R + 8\pi R^2 (D_s k)^{1/2} \quad (6.4)$$

where R is the spherical reaction radius, and have taken as $R=10 \text{ \AA}$, to get D_s for different doping concentrations. The results of D_s were shown in Table 6.1. The value of D_s is estimated as $(1.2 \pm 0.3) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ in pure Alq_3 film and it is comparable to the reported values of $(3 \pm 1) \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [201] and $(1.2 \pm 0.8) \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [200]. The discrepancy is due to the film thicknesses used in their study. The diffusion coefficient D_s were reduced to $3\text{-}7 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ in both single and co-doped films, which is about one order smaller than in pure Alq_3 film. The diffusion length of singlet excitons, L was estimated from the equation,

$$L \cong \sqrt{Z t_2 D_s} \quad (6.5)$$

where Z is equal to 6, 4 or 2 for three-, two- or one-dimensional diffusion, respectively [200]. The t_2 is the singlet exciton lifetime where we have measured. The L and D were plotted as shown in Fig. 6.8 by assuming that the exciton diffusion was three-dimensional in Alq_3 and doped films. The diffusion length of exciton in doped films was reduced 11-22 $\text{\AA}$ from 36 $\text{\AA}$ in pure Alq_3 film.

Table 6.1 The diffusion coefficient D_s was estimated for pure Alq_3 and doped films

	$\text{Alq}_3\text{:DCM}$	$\text{Alq}_3\text{:Rub}$	$\text{Alq}_3\text{:C-6}$	$\text{Alq}_3\text{:Rub:DCM}$		$\text{Alq}_3\text{:Rub:C-6}$	
	$D_s (\text{cm}^2\text{s}^{-1}) \times 10^{-7}$	$D_s (\text{cm}^2\text{s}^{-1}) \times 10^{-7}$	$D_s (\text{cm}^2\text{s}^{-1}) \times 10^{-7}$	(1:1)	(2:1)	(1:1)	(2:1)
				$D_s (\text{cm}^2\text{s}^{-1}) \times 10^{-7}$	$D_s (\text{cm}^2\text{s}^{-1}) \times 10^{-7}$	$D_s (\text{cm}^2\text{s}^{-1}) \times 10^{-7}$	$D_s (\text{cm}^2\text{s}^{-1}) \times 10^{-7}$
0	12 ± 3						
0.5	5.3 ± 1.0	6.4 ± 1.5	5.8 ± 1.2				
1	4.5 ± 0.8	4.6 ± 1.2	4.6 ± 0.9	4.5 ± 1.2	5.2 ± 1.5	6.2 ± 1.5	6.6 ± 1.2
24	2.9 ± 0.6	3.2 ± 1.1	3.1 ± 1.2

Figure 6.9 The diffusion length of singlet excitons, L was estimated from the equation based on the diffusion coefficient for doped films, assuming that the exciton diffusion is three-dimensional in Alq_3 and doped films

The dopants in both single and co-doped films are acting as a capture center for recombination of excitons. A fraction of excitons from Alq_3 undergoes immediate transfer within Alq_3 -dopants nearest neighbors. The exciton diffusion length may influence the

efficiency of transfer in Alq₃. The exciton diffusion was reduced at the higher doping concentrations in doped films, due to the increase of dopants density in Alq₃, and the dipole–dipole interaction was enhanced due to r^{-6} reduced dependence, where r is the donor/acceptor separation according to Forster energy transfer model. The DCM doped films showed the shorter diffusion length compared to Rub and C-6 in Alq₃. This can be attributed to higher dipole moments 26 D of DCM molecules [187] compared to ~ 9 D for C-6 [188], where induced higher attractive force facilitates the excitons diffusion from Alq₃. However, the shorter diffusion length in doped films can be contributed the trapping sites from the doping effect, which were created and distributed Gaussianly in films. The effect of dopants broadens the total density of states, induces the local electric fields, and increases the intermolecular interaction forces in the films. These can induce the formation of localized states, normally located below the intrinsic density of state distribution of Alq₃. These traps can strongly affect the diffusion of excitons. The diffusion length is slightly different from each other for doped films. This is due to the dopant becoming strong recombination centers and there is immediate decay of excitons to the ground state without further diffusion. This indicates that the electron transfer is a short-range non-dipole coupling.

6.3.4 Transient EL Decay Measurements

Figure 6.10 presents the transient behavior of the EL of the doped bi-layer OLEDs devices upon applying a rectangular voltage pulse of 11 V. The pulse length was 5 μ s, the repetition rate at 1 kHz, and the EL signal was obtained over these doped samples. Figure 6.10 (a) shows that the EL onset occurred with a delay time of 0.7-1.9 μ s, in pure Alq₃ to heavily doped DCM in bi-layer devices. The resultant t_d for pure Alq₃ is compatible with the findings of Ref. [192]. For $t > t_d$ the EL signal increased and tended to saturate after ~ 1.2 -2.8 μ s, as defined by the intercept of the tangents. Figure 6.10 (b) and (c) show the transient EL

for ITO/NPD/Alq₃:C-6/Al and ITO/NPD/Alq₃:Rub/Al devices, respectively; where the concentrations varied from 0.5 - 24 wt.%. These C-6 and Rub doped bi-layer devices showed the sign of the delay time of EL onset, but smaller than DCM doped before achieving the saturation. Figure 6.10 (c) and (d) depicted the behavior of transient EL in co-doped OLEDs devices of the active layer as Alq₃:(Rub:DCM) and Alq₃:(Rub:C-6), respectively. The EL onset is delayed the other single doped devices. The t_d is ranged 0.8-0.9 μ s compared to pure Alq₃ of 0.7 μ s.

Figure 6.10 Comparison between time response of EL in single doped: (a) pure bi-layer Alq₃ and ITO/NPD(70 nm)/Alq₃:DCM (~ 70 nm)/Al, (b) ITO/NPD(70 nm)/Alq₃:C-6/Al and (c) ITO/NPD(70 nm)/Alq₃:Rub/Al, co-doped devices: (d) ITO/NPD(70nm)/Alq₃:(Rub:DCM)/Al and (e) ITO/NPD(70nm)/Alq₃:(Rub:C-6)/Al upon application of a rectangular voltage pulse of 11 V with a pulse length of 5 μs and a repetition rate of 1 kHz.

For comparison, these EL onset t_d and t_r of OLEDs devices are summarized in Fig. 6.11. The t_r indicated with increasing the doped concentrations, an increase of delay time t_d and a slower rise of the EL was observed, equivalent to a slower response time of the doped OLED. Note that t_d and t_r for doped Alq₃ bi-layer devices exceeded the values measured with the pure Alq₃. Based on these results shown, both t_d and t_r of bi-layer devices are influenced by the dopants in Alq₃. For the co-doped devices of Rub:DCM and Rub:C-6 in Alq₃ devices, the EL onset time t_d was ranged between 0.8-0.9 μ s and was noted lower than the single dope of DCM and C-6 in Alq₃ with the same doping concentration at 1 wt.%, indicating fast response time of the co-doped OLED. The results t_r for doped OLEDs are summarized in Fig. 6.12.

Figure 6.11 Summary of the transient EL onset t_d versus the dopant concentrations (wt.%) for single doped OLEDs devices. The t_d was delayed as the dopant concentrations increased in the devices

Figure 6.12 Summary of the transient EL t_r of single doped devices. t_r indicates the time until electron and hole distributions have interpenetrated the bulk films. t_r increases with the doped concentrations; where an increase of delay time t_d induces a slower rise of the EL, which is equivalent to a slower response time of the doped OLED

The time-resolved behavior of EL in an ITO/NPD/Alq₃/Al bilayer OLED clearly proves the existence of energy barriers for both electrons and holes at the NPD/Alq₃ interface. This result was known at Ref. [192]. Therefore the observed green emission from this device was due to the recombination of accumulated holes and electrons at the interfacial layer of NPD/Alq₃. It has been known that the transient EL behavior is related to this interfacial charging especially at lower electric fields. The delay time t_d is limited by space charges due to the time to accumulate a space charge layer at the internal NPD/Alq₃ interface of holes and electrons. Holes are found responsible for the accumulation of charge carriers at this interface. However, at higher electric fields the accumulated charges (hole) at this interface play a minor role, and thus the t_d is controlled by charge-carrier (electron) transport.

We noted that the EL onset delay time t_d for DCM, C-6 and Rub doped devices was longer than the pure Alq₃ at a constant electric field of $F^{1/2} = 868 \text{ (V/cm)}^{1/2}$. The dopant DCM has the longest delay time t_d , followed by C-6 and Rub in Alq₃ devices. Therefore, it has

been shown that longer time is taken before the EL grows compared to pure Alq₃ bilayer devices. For lightly doped devices (0.5 to 1 wt.%), the thickness of active layer increased slightly, but the t_d was influenced and delayed about 40%, 21% and 15% for DCM, C-6 and Rub doped devices, respectively. This indicates that the charge carrier transport behavior determines t_d for doped OLEDs.

The electron injection from Al into doped active layer may be localized by these dopant molecules. The role of polarity of dopants in molecular materials indicates the presence of dipolar properties to manifest itself in modifying the carrier mobilities. This effect broadened the width of DOS. The dipole moments of DCM is the highest as ~ 6 D (at ground state) and ~ 26 D (at excitation state) [202] compared to C-6 of 7 D (at ground state) and ~ 9 D (at excitation state) [203]. However, the dopant of Rub has non-polar properties due to the symmetry of molecular structure. Hence, the introduction of polar dopants (DCM and C-6) results in enhancement of the dipolar disorder σ_{dipolar} , and consequently, to a decrease of the carrier mobilities. The non-polar of Rub induced the disorder of DOS due to van der Waals component σ_{vdw} with Alq₃ molecules, but this van der Waals effect is weak compared to σ_{dipolar} ; therefore, the carrier mobility is higher than DCM and C-6 [204]. The interaction of polar dopants (DCM and C-6) broadened the total density of states, induced the local electric fields and increased the intermolecular interaction forces in the films; thus the deeper localized states below the intrinsic DOS distribution of Alq₃ [198] may be formed. These traps can strongly affect the charge transport property at equilibrium conditions and most carriers will occupy those deep states. This leads to delay of EL due to slowly recombine of electron and hole [205]. We believe some of the injected electrons accumulate at the NPD/Alq₃ interface, as the dopant concentration is low between 0.5 and 1 wt.%, thus this may lead to a redistribution of the electric field inside the device in such a way that the

field in the electron-transport (Alq_3 :dopants) increases and the field in the hole-transport layer (NPD) decreases.

The co-doped devices of Rub-C-6 and Rub-DCM at 1 wt.% showed the delayed time t_d is 16 % longer than pure Alq_3 device and at about the same level as compared to single doped of DCM, C-6 and Rub in Alq_3 devices. The heavily doped (24 wt.%) Alq_3 active layer showed the longer delayed time t_d before the EL grows, where the delayed time t_d was increased to 150%, 100% and 34% for DCM, C-6 and Rub doped respectively to accumulate the trapped charges. The redistribution is strong enough to affect the carrier mobility in doped active film. The entire electrical field drops across the doped film.

In principle, t_d reflects the time when the two leading fronts of injected carriers – electrons and holes meet in the doped active layer. t_r indicates the time until electron and hole distributions have interpenetrated. The 1 kHz frequency of the voltage pulses drive the electrons to recombine radiatively with holes from dopants, which penetrated more deeply into the Alq_3 doped layer during the preceding voltage pulse on phase, resulting in a delayed EL signal. Based on Fig. 6.10, the slope for heavily doped devices increased slowly as compared to lightly doped devices, indicating the strong controlled by the dopant properties inducing the slow carrier motion into the bulk of the device. In other words, the dopant possibility formed the thin interfacial layer in Alq_3 film.

This approach of transient EL in pure and doped Alq_3 devices enables the carrier mobility to be estimated in an indirect way based on the equation of:

$$\mu = \frac{L}{t_d F} \quad (6.6)$$

with $F = \frac{(U - U_{bi})}{d}$, where F is the electric field, d is the device thickness, L is the thickness of the active material, U is the voltage applied to the device, and U_{bi} is the built-in voltage

calculated from the difference of the work function of ITO and Al ($U_{bi} \sim 0.7$ eV). The t_d is used to determine the buildup of space charges inside the devices, and / or the charge-carrier transport behavior. The electric field $F < 10^6$ V/cm, and the obtained carrier mobility of these single-co doped devices are shown in Fig. 6.13 (a) and (b), respectively. The carrier mobilities decreased as the dopants increased in the devices for single doped of DCM, C-6 and Rub. The carrier mobilities are consistent though the different ratios of Rub, DCM and C-6 co-doped in the devices, where the carrier mobility is ranged at $1 \times 10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ as shown in Fig. 6.13 (b). Generally, the estimated carrier mobility is lower than the values obtained through TOF method [198]. The estimated carrier mobility of single doped films by TOF method is shown in Fig. 6.14. This discrepancy is because the accumulation of space charges at interfacial barriers, which have a major effect on t_d in time-resolved EL experiments. The dopants in Alq_3 film have formed interfacial barriers and trapped the charges to accumulate space charges; hence redistributing the electric field inside the sample and affecting the motion of carriers. The carrier mobility obtained through TOF method [198] is with thick (μm) film, and the morphology of thin and thick films can be varied, and their transport is expected to be dispersive.

Figure 6.13 The transient EL for pure and doped Alq₃ devices enables the carrier mobility which can be estimated in an indirect way based on the equation of: $\mu = \frac{L}{t_d F}$. The applied electric field F is less than 10⁶ V/cm, and the obtained carrier mobility are shown in (a) single and (b) co-doped OLEDs devices. The carrier mobilities decreased as the dopants increased in the devices for single doped of DCM, C-6 and Rub.

Figure 6.14 TOF method estimated the mean carriers mobilities of the doped films for various concentrations as a comparison to transient EL method.

6.4 Summary

The doping effects on transient PL were studied in Alq₃ at room temperature. The dopant DCM, C-6 and Rub were used in different concentrations in Alq₃ films. We measured the decay lifetime of transient PL in these doped Alq₃ films. The decrease of transient PL decay lifetime in doped films in both single and co-doped films was attributed to the polar molecular structure of DCM and C-6, the charge capture from Alq₃ to extensive pi-conjugated and non-polar molecular structure of Rub. We also quantitatively estimated the bimolecular recombination rate constant of singlet excitons in doped films via the kinetic equation. We also estimated the recombination rate γ_{ss} of excitons in doped films and obtained the diffusion coefficient D_s and diffusion length L of singlet excitons.

We also showed the transient EL measurements in doped Alq₃ films bilayer OLEDs devices. In these bilayer devices, the EL onset was limited by accumulation charges at dopants molecules which formed interfacial barriers in Alq₃ films for $F = 7.36 \times 10^5$ V/cm. It

was known that the pure Alq₃ bilayer device accumulated holes and electrons at interfacial layer of NPD/Alq₃, where the t_d was limited by the space charges. For the doped bilayer devices, the t_d was influenced and delayed compared to pure Alq₃. This indicates that the charge carrier transport behavior determines the t_d for doped OLEDs. This may lead to a redistribution of the electric field inside the device in such a way that the field in the electron-transport (Alq₃:dopants) increases and the field in the hole-transport layer (NPD) decreases. The carrier mobility in pure and doped Alq₃ devices can be estimated in an indirect way based on transient EL. The estimated carrier mobility is lower than the values obtained through TOF method. This is because the dopants in Alq₃ film have formed interfacial barriers and trapped the charges to accumulate space charges; hence redistributing the electric field inside the sample and affecting the motion of carriers. The carrier mobility obtained through TOF method was with thick (μm) film, and the morphology of thin and thick films can vary, and their transport is expected to be dispersive.

Chapter 7

Transient capacitance measurements for the transport and trap states distributions in doped organic light emitting diodes

7.1 Introduction

In this chapter, the discussion would be focused on the study of charge traps induced by the dopants, which can be determined by transient capacitance measurements. This transient capacitance measurement can also be used to determine the material's transport states distribution. Analysis would show that the observed capacitance transients could be successfully modeled in terms of the de-trapping of carriers from a discrete trap level to a Gaussian distribution of transport states. These dopants may tailor the local field within the film resulting in the appearance of local states to trap the charges. No direct measurements of the distribution of transport states have been reported on doped organic (small molecules) semiconductors.

7.2 Experimental

The doped films were prepared on pre-cleaned and etched p-type silicon wafer substrates for the transient PL measurements. The wafer substrates were cleaned by a series of sonication in chemicals and deionized water baths to remove contaminations. Subsequently, the organic doped films were deposited by vacuum sublimation at 10^{-6} torr in the thermal evaporator chamber. Single doped films of Alq₃: DCM, Alq₃:C-6 and Alq₃: Rub with various concentrations from 0.5 to 24 wt.% were prepared. The co-doped of Rub and DCM and Rub-C-6 in Alq₃ were prepared. The ratios of each Rub:DCM and Rub:C-6 co-doped film are fixed at 1:1 and 2:1 and the total dopants concentration is maintained at 1 wt.

% with respect to Alq_3 at each co-doped film. The film thickness was ~ 100 nm monitored by a crystal oscillator and confirmed by Alpha-Step profiler. The sample preparation was completed by the deposition of a $\sim 1\mu\text{m}$ thick aluminum (Al) layer. The thick Al is used to protect the probe from penetrating into the organic active layer. The structure of the sample was: p-type Si wafer/doped organic active layer/Al. We prepared 20 samples at a time on a substrate, each with an active area of 0.78 mm^2 .

The typical structure of the device is: p-type Si wafer/doped organic active layer/Al as shown in Fig. 7.1. Twenty samples were prepared each time on a substrate, each with an active area of 0.78 mm^2 . The HP 4284A LCR meter was used with a station probes to carry out the transient capacitance measurements. The small AC signal oscillation amplitude was set at 10 mV throughout the whole experiments. The frequency of AC was set from 1 MHz to 40 kHz. All measurements were carried out in room temperature. The DC bias was applying from -15 to $+13$ V for all the doped samples with a small step of 0.2 V. This HP 4284A was connected to computer, where all the measurements were controlled and the capacitance normalized with area was recorded together with the DC bias voltage.

Figure 7.1 The typical structure of transient CV device

7.3 Results and Discussion

The transient C-V measurements from negative to positive bias were able to fill any traps within the organic film and at the electrodes-organic interfaces. The capacitance equation with a material medium between two parallel plates is given by

$$C = \frac{\epsilon_r \epsilon_0 A}{d} \quad (7.1)$$

where d is the film thickness in meters, A is the cross-sectional area (m^2) of the film and ϵ_0 is the permittivity of free space. ϵ_r is called the dielectric constant of the material medium or its relative permittivity. The capacitance of the organic film was increased due to the polarization of the medium in which positive and negative charges were displaced with respect to their equilibrium positions. Figure 7.2 shows the few examples of C-V measurement that were from pure and doped samples of the doping concentration at 1 wt.%.

Figure 7.2 The C-V measurements of organic film sandwiched between p-Si and Al electrodes for (a) pure Alq₃, (b) DCM doped, (c) C-6 doped and (d) Rub doped

The doped organic film sandwiched between p-Si and Al was polarized by applied bias. The carriers displacement was a factor to influence the capacitance under the bias fields. Carriers were hopping across the localized states in the doped films due to the applied electric field. The dielectric constant ϵ_r of the doped film is directly proportional to the capacitance, and estimated from Eq. (7.1). The dielectric ϵ_r versus frequency measurements were summarized for each sample and is shown in Fig. 7.3.

The dielectric constant of each film decreased as the frequency increased at low frequency region (< 300 kHz). At the high frequency region (> 400 kHz) the dielectric of organic layer became frequency independent. The dielectric constant was doping concentration dependent. The ϵ_r was increased with doping concentration increased in Alq₃ film. At low frequency, the dielectric constant increased with applied bias due to the increased charge separation. The lower dielectric constant at higher frequency was also due

to the incomplete dielectric relaxation occurring. Based on a single relaxation model, the real part of dielectric constant ε in a solid was given by [206]

$$\varepsilon_r = \varepsilon_U + \frac{\varepsilon_R - \varepsilon_U}{1 + \omega^2 \tau_E^2} \quad (7.2)$$

where ε_U represents the unrelaxed dielectric constant at higher frequencies; ε_R the relaxed dielectric constant at low frequencies and τ_E is the dielectric relaxation time. The ε_r decreases with increasing frequency ω from a value of ε_R to ε_U . These data indicate the possibility of the presence of an interfacial polarization [207-211]. Such distortion causes an increase in capacitance of the sample [207].

Figure 7.3 The dielectric of each sample is frequency and dopant dependent: (a) the typical device of pure Alq₃, (b) DCM doped, (c) C-6 doped, (d) Rub doped and (e) co-doped of dopants. The trapping states of these doped organic films can also strongly affect the charge transport property at equilibrium conditions and most carriers will occupy those deep states to increase the capacitance.

The polar dopant molecules such as DCM and C-6, which possessed higher dipole moments induced stronger polarization compared to Rub in Alq₃ film. Thus, when carriers are impeded in their motion by polarization of DCM and C-6, it results in space charges and macroscopic field distortions. When the carriers hop under the influence of an electric field, it is possible to be localized or trapped in doped films in the electrode-doped films interfaces. This is observed in the higher value of ϵ_r in DCM and C-6 doped films. This is because the polar properties of the dopants interaction of polar dopants' molecules widened the total density of states, induced the local electric fields, and increased the intermolecular interaction forces in the films. These traps can strongly affect the charge transport property at equilibrium conditions and most carriers will occupy those deep states.

However, Rub doped in the Alq₃ film showed lower dielectric constant as compared to pure, DCM and C-6 single doped films in Fig. 7.3 (d). The co-doped of Rub-DCM and Rub-C-6 in Alq₃ films have reduced ϵ_r of the films as compared to single doped films of DCM and C-6 of 1 wt.% in Alq₃ as shown in Fig. 7.3(e). This is because the position and energetic disorders were significantly reduced as the Rub doped in films. The Rub molecular structure may be responsible for these reductions. Rub molecules were formed with 8 benzene rings with abundance pi-conjugated bondings and interacted with polar molecules of DCM and C-6 to: (i) reduce the Coulomb and dipole-dipole interactions between DCM and Alq₃ molecules, (ii) shift the charge distribution from centers on DCM and C-6 molecules (due to dipole moments of DCM and C-6 are higher) to distribute more randomly in doped molecules in the film and (iii) anti-pi conjugation of benzene rings provides channeling to electron, thus facilitating the hopping mechanism of electron carriers.

The DCM molecules have arylidene laser dye with a dimethylamino [$-N(CH_3)_2$] electron donor group linked to dicyanovinyl [$=C(CN)_2$] electron acceptor groups have strong

interaction with phenoxide donor and pyridyl acceptor in the quinolate ligands of Alq₃ molecules. But C-6 possesses the benzothiazolyl and diethylamino groups, which have strong electron affinities to form localized states to trap carriers. Thus, as the concentrations of these dopants increased in Alq₃ films, the stronger interaction will be felt by Alq₃ molecules to trap carriers in doped film for higher capacitance. However, Rub (C₄₂H₂₈) is a molecule comprised of tetracene with four additional phenyl rings attached at the center positions, to provide good charge transporter and non-polar structure compared to DCM and C-6 to induce weaker capacitance in Alq₃. Rub doped in host materials still can trap carriers, and acts as recombination center for hole and electron.

Figure 7.4 shows the variation of the dielectric loss factor with respect to frequency. The dielectric loss factor for different concentration was averaged in doped films. There is no effect of relaxation observed in the variation of $\tan\delta$ in this frequency range.

$$\tan \delta = \frac{\varepsilon_r''}{\varepsilon_r'} \quad (7.3)$$

where ε_r' is the real part and ε_r'' is the imaginary part from $\varepsilon_r = \varepsilon_r' - j\varepsilon_r''$, both being frequency dependent. The $\tan \delta$ has to minimize from the smaller of ε_r'' , and the dielectric constant of ε_r is dependent on the real part of ε_r' only.

Figure 7.5 Typical Mott-Schottky plots for (a) pure Alq₃, and single-doped of (b) DCM, (c) C-6, (d) Rub, and (e) co-doped films of Schottky barrier at 40 kHz. Inverse capacitance squared, $1/C^2$ against applied bias, V_{appl} of ~ 70 nm thick of pure and doped in Alq₃ films of the devices. Each of the curves from figure (a)-(c) shows two distinct slopes as a function of bias. This behavior is the characteristic for a Schottky diode that has the majority of carrier traps. For the single and co-doped of Rub in Alq₃ films, the slope changes slightly, indicating the presence of (a single) deep level.

The transient is very typical as observed in Fig. 7.5. The figures show the doped samples in different concentrations. Each of the curves shows two slopes as a function of bias, but this is only noted in Fig. 7.5(a)-(c). The slopes indicate that the traps act as acceptors in the film. For the reverse-forward bias, the slope changes slightly for Rub doped in Alq₃ films which are either single or co-doped in the films, indicating the presence of a single abundant deep level. The slope in a Mott-Schottky plot reveals the acceptor concentration, N_A in each sample.

The presence of deep trap levels can cause the slope to change with the bias voltages. The positive bias voltages put the Fermi level below the deep level somewhere in the depletion region. The larger gradient of slope at negative bias arises from the density of acceptor N_A for all doped films and is proportional to $1/N_A$. Note that this slope increased

significantly when the polar dopants doped in Alq₃ films. The polar dopants of DCM and C-6 showed a higher gradient of slope. The single doped of Rub and co-doped of Rub with DCM and C-6 in Alq₃ films have lower slopes compared to DCM and C-6 doped in Alq₃ films. The smaller gradient at negative bias arises from the combination of the acceptor dopants, N_A , and those traps that can empty on the time scale of the experiment, $N_t(\omega_{\text{expt}})$.

This gradient is proportional to $\frac{1}{N_A + N_t(\omega_{\text{expt}})}$, where ω_{expt} is determined by a sweep

rate of the measurement (0.5 s per data point) and is the order of the fastest trap emptying rates found in the measured capacitance transients. $N_t(\omega_{\text{expt}})$ therefore, gives a lower limit to the true trap density. As expected, $N_t(\omega_{\text{expt}})$ decreases with increasing measurement frequencies and increasing experimental sweep rates. The bias at which the slope changes (V_t) is that, with increasing negative bias, the traps pull below the Fermi level at the interface, and become effectively permanently filled. They can then no longer respond in the experiment. Devices with large N_A also have large $N_t(\omega_{\text{expt}})$, so that some of this scatter is almost certainly due to variations in the active devices of area A. The measured values of the acceptor density N_A reveals a large acceptor concentration of $0.4\text{-}1.4 \times 10^{18} \text{ cm}^{-3}$ for DCM and C-6 doped films compared to pure Alq₃ as $0.3\text{-}0.6 \times 10^{18} \text{ cm}^{-3}$ and Rub doped of $6.3 \times 10^{17} \text{ cm}^{-3}$. The detail results are shown in Fig. 7.6 in the statistical box-chart. If the trap states were to lie at the interface, the values of V_t should give the trap depth from $E_t = q(V_t - V_d) + E_F$, however, the estimated values of E_t are larger than $E_g/2$, suggesting that the trap density varies with depth, where N_t increases with distance from the Al/organic layer interface. If assumed $N_t > N_A$, then one might expect all the free extrinsic carriers to be trapped so the devices would be permanently fully depleted.

Figure 7.6 The acceptor concentration of N_A for each sample. Single doped of DCM and C-6 in Alq_3 show the larger deep levels compared to Rub doped and pure Alq_3 films. Co-doped of Rub with DCM and C-6 show the single abundant deep levels where the bias voltage changes slightly for the slope from the typical Mott-Schottky plots.

Figure 7.7 shows the slight change of the capacitance with time for each sample on a log-linear plot. The data were recorded at room temperature for an applied bias of -8 V after being stored in nitrogen for 4 h at 0V. This transient is very typical. The sign of the transients shows that the amount of negative charges in the depletion region decreases. The length of the transient shows the traps carriers are still escaping after 4 hours, indicates that part of the traps are very deep within the energy gap. This indicated that $N_t > N_A$ with the C-V results.

Figure 7.7 Log-linear plot of transient capacitance C , against time, t for the pure and doped samples

If $N_t > N_A$, then one might assume all the free extrinsic carriers to be trapped so that the device would be permanently fully depleted. However, the depletion region must be present, which has been proven from the C-V measurements. The formation of deeper localized states located below the intrinsic DOS distribution of Alq₃ is due to the polarity of DCM and C-6 molecules. Therefore, these trapping states are in the forbidden gap and strongly affect the charge transport property at equilibrium conditions and most carriers will occupy those deep states. The traps themselves being of the acceptor type capture and release the carriers depending on the trap depth. The cathode of Al forms an Schottky contact with the organic layer as negative carriers have a large barrier of about 1.3 eV [172]. Such a contact limited the negative carriers injected into the organic film. Hence, these limited negative carriers are captured or emptied from the traps. All of the observed transients are non-exponential and expected from a disordered organic film in the transport states, the traps, or both and are believed to distribute in Gaussian energy [179].

Thus, the transient results have been modeled by considering the de-trapping of carriers from a discrete trap level to a Gaussian distribution of negative carriers transport states. This model is developed from Ref. [167]. As $N_t > N_A$, the change of the depletion width $x_d(t)$ with time is calculated from [167]

$$\frac{2\epsilon}{q}(V_d - V_{appl} + V^*) = N_A x_d(t)^2 + N_t f(t)(x_1(t)^2 - x_2^2) \quad (7.4)$$

where V_{appl} is the applied bias and V^* is a fitting parameter that allows for charge stored in fast interface states or fast bulk traps or spatial variations in N_t . $x_1(t)$ is the distance from the cathode to the point at which the trap level intersects the quasi Fermi level when the device is held at applied bias as shown in Fig. 2.13 (page 44). x_2 is the same distance during the filling of bias. $f(t)$ is the variation with time of the trapped charge between $x_1(t)$ and x_2 [203]. $x_1(t)$ and x_2 are calculated from the depletion width by subtracting the parameter λ where

$$\lambda^2 = 2\epsilon \frac{(E_t - E_F)}{qN_A} \quad (7.5)$$

This model assumes the depletion region approximation and N_A does not change with distance from the cathode as shown by the linear of $1/C^2$ versus V plots of the devices [212]. At the average field in the depletion region, V_d/x_d , the carriers mobility in these doped films are determined by TOF measurements to be of the order $10^{-5} \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature [213,214]. Thus, the average transit time of a carrier across the depletion region should then be in the order of $10\mu\text{s}$. No re-trapping occurs on the time scales of the experiment. The decay function $f(t)$ is calculated by integrating at different times t over a normalized Gaussian distribution $N(g_t)$ of trap depths $g_t + E_t$,

$$f(t) = \int N(g_t) \times \exp\left\{-\chi \exp\left(\frac{-(g_t + E_t)}{kT}\right)t\right\} dg_t \quad (7.6)$$

This is an energetically disordered organic in which the trap capture cross-section is defined by the physical size of the trapping site, the density of states N_{DOS} is the molecular density and conduction is by hopping transport, and given as

$$N(g_t) = \frac{N_{DOS}}{(2\pi\sigma'^2)^{1/2}} \exp\left(\frac{-g_t^2}{2\sigma'^2}\right) \quad (7.7)$$

where χ is the hopping rate frequency and has a field and temperature dependence. $f(t)$ was calculated for a range of different E_t , and Gaussian width σ' . The relative permittivity of each sample was taken from Fig. 7.3 at 40 kHz. N_{DOS} was taken as 10^{19} cm^{-3} .

Figure 7.8 shows the fit of the model to the transient shown in Fig. 7.7. The simulation model is well fitted to the experimental data at room temperature. This model confines the Gaussian width σ' to be $0.16 \pm 0.02 \text{ eV}$ for pure Alq_3 film, and increases to $\sim 0.30 \pm 0.04 \text{ eV}$ for the doped films. The inset in Fig. 7.8 (a) shows the N_{DOS} of different E_t and σ based on the Gaussian distribution model. This estimated Gaussian width for pure Alq_3 film is in agreement with Ref. [202]. The value of N_A used at each sample was measured directly from the corresponding C-V plots. The estimated trap depth E_t is increased from $0.65 \pm 0.05 \text{ eV}$ to about $0.71 \pm 0.15 \text{ eV}$ as the dopant increased in the samples. The details of the results are shown in Fig. 7.9. The trap depth deduced for pure Alq_3 is higher than the Ref. [215,216] of 0.2-0.4 eV from thermally stimulated current measurements. No comparison can be made for the DCM, C-6 and Rub doped in Alq_3 films.

suggesting that the traps are deep within the energy gap for all types of dopants in Alq₃ films. The activate-motion energy of detrapping processes depended on the trap depth E_t since the depth is dominating the trap level.

7.4 Summary

The transient C-V measurements were used to estimate the trap depth in doped organic films. These transient C-V measurements results have been modeled by considering the de-trapping of carriers from a discrete trap level to a Gaussian distribution model of carriers transport states. The estimated trap depth E_t is increased from 0.65 ± 0.05 eV of pure Alq₃ film to about 0.71 ± 0.15 of doped devices. These estimated trap depth were based on the confined Gaussian width σ' to be 0.16 ± 0.02 eV and $\sim 0.30 \pm 0.04$ eV for pure and doped Alq₃ films, respectively. Based on the Mott-Schottky plots of these transient C-V measurements, the estimated values of the acceptor density N_A reveal a large acceptor concentration ranged between $0.3\text{--}1.4 \times 10^{18} \text{ cm}^{-3}$ for the pure and doped films devices. The dielectric versus frequency measurements showed that the dielectric constant of each film increased as the frequency was reduced.

Chapter 8

Conclusions and Recommendations for Future Work

8.1 Conclusions

OLED devices with electron transport layer (ETL) Alq₃ doped with laser dyes such as DCM, Rub, and C-6 have been studied rigorously. The thickness and deposition rate of Alq₃ is optimized for the highest luminance efficiency output. When the deposition rate increased from 0.3 to 1.5 Å/s, the device luminance efficiency is increased by a factor of 3. XPS analysis showed that the N/C ratio decreased with increased deposition rate. The Alq₃ film surface roughness was 4.4, 2.4 and 0.1 nm for deposition rates of 0.3, 1.1 and 1.5 Å/s, respectively. It is found that the decomposition of Alq₃ small molecules and high surface roughness is responsible for the reduction of OLED performance when the Alq₃ deposition rate is below 1.5 Å/s.

A thorough experimental investigation on behavior of carrier transport in the dye-doped organic Alq₃ films by time-of-flight (TOF) measurements was established. We examined the dependence of temperature and electric field on the positional and energetic disorder parameters of local centers and subsequently estimated the carrier mobility in doped films using Alq₃ as the host material. We used a new approach to calculate the carrier mobility to simulate with the experimental data instead of using the conventional graphical method (Scher-Montroll model) to determine the carrier drift time. The carrier mobility in pure Alq₃ film was $\sim 7 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ as calculated from the Gaussian distribution of carrier velocity at room temperature, and was comparable with other results. The effectiveness of the carrier escape process δ_{∞} and the trap depth Φ_B ($70 \pm 5 \text{ meV}$) of trapping states were also calculated from the modified PF model for the pure Alq₃ films. We observe that the carrier

mobility for both the pure and doped films increase with temperature and this is in contrast to the carrier transport in semiconductors where the carrier mobility decreases with temperature due to increase scattering from impurity centers. Hence we have shown that the mechanism of transport in these organic films is by phonon assisted hopping. Due to the increased lattice vibrations with temperature, a local potential well where carrier trapping occurs is modified and the electron can hop out of the barrier to another site more easily. The carrier mobility decreases in doped amorphous Alq₃ films due to increased disorder in the Alq₃ films induced by the molecular structures of the dopants. The electron mobility in co-doped films ($0.5 - 9.0 \times 10^{-4} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) was higher than the single-doped films. The carrier mobility of the co-doped Rub:C-6 films are generally higher than the co-doped Rub:DCM films. The observed and simulated carrier mobility at different temperatures and electric fields have been explained.

Both the energetic and positional disorder of the system are reduced once a non-polar dopant is introduced to a polar doped Alq₃ films. The energetic disorder is estimated to be $\sim 0.037 \text{ eV}$ and ~ 0.032 for the co-doped Rub:DCM and Rub:C-6 in Alq₃ film, respectively as compared to $\sim 0.047\text{-}0.064 \text{ eV}$ in single doped films. The lower values of energetic disorders in co-doped films may be due to the reduction of $\sigma_{\text{van der Waals}}$ and $\sigma_{\text{dipole-dipole}}$ between the molecules. The values of positional disorder Σ for co-doped Rub:DCM in Alq₃ films are 1.09 and 1.54 for the ratios 1:1 and 2:1 respectively. For Alq₃ films co-doped with Rub:C-6, Σ are determined to be ~ 1.7 and ~ 1.9 for the two ratios of 1:1 and 2:1 respectively, which is between the Σ values of ~ 1 for Alq₃:Rub doped films and ~ 2 for Alq₃:C-6 films at $\sqrt{F} \leq \sqrt{F_c} \text{ (V/cm)}^{1/2}$. However the Σ values are field dependent and there exists a critical field condition $\sqrt{E_c} \leq 372 \text{ (V/cm)}^{1/2}$, at which Σ increases tremendously to ~ 4.2 for both Alq₃:Rub and Alq₃:DCM singly doped films.

Carrier dynamics of the doped organic thin films have been studied via transient photoluminescence (PL) and electroluminescent (EL). The doping effects on transient PL were studied in Alq₃ at room temperature. The concentrations of the dopants are found to be varied in the Alq₃ films. The decrease of transient PL decay lifetime in both single and co-doped films is attributed to the polar molecular structure of DCM and C-6, the charge capture from Alq₃ to extensive pi-conjugated, and the non-polar molecular structure of rubrene. We have also quantitatively estimated the bimolecular recombination rate constant of singlet excitons in doped films via the kinetic equation. The diffusion length of exciton reduced for doped films to the range of 17-25 Å compared to pure Alq₃ film of 36 Å due to the molecular structure of dopants. The transient EL measurements from doped Alq₃ films bilayer OLEDs devices show that the EL onset is limited by accumulated charges at dopants molecules which form interfacial barriers in Alq₃ films for $E = 7.36 \times 10^5$ V/cm. For the doped bilayer devices, the delay time (t_d) is influenced by dopants and the delayed is compared to pure Alq₃. This indicates that the charge carrier transport behavior has a dominant effect on t_d for doped OLEDs. The dopants will cause a redistribution of the electric field inside the device in such a way that the field in the electron-transport in doped Alq₃ increases and the field in the hole-transport layer (NPD) decreases. It may be due to the aggregation of dopant molecules, hence forming a thin interfacial layer in Alq₃ film. This will cause the redistribution of the electric field inside the sample and affects the motion of carriers. The estimated carrier mobility from transient EL measurements is lower than the values obtained through TOF method due to differences in the thickness and morphologies of the films characterized.

Lastly transient capacitance measurements were carried out to observe the presence of charge traps induced by the dopants in the doped organic active layer. Subsequently we extended our study to determine the material's transport states distribution. The observed

capacitance transients were successfully modeled in terms of the de-trapping of carriers from a discrete trap level to a Gaussian distribution of transport states. The dielectric versus frequency measurements show that the dielectric constant of each film increases as the frequency is reduced. The dielectric is concentration and dipole moments dependent. The Mott-Schottky plot indicated the traps act as acceptors in the film. The transient results have been modeled by considering the de-trapping of carriers from a discrete trap level to a Gaussian distribution of negative carriers transport states. The N_{DOS} at different E_t and σ of the Gaussian distribution have also been estimated.

8.2 Recommendations for Future Work

We have presented a thorough experimental investigation on the behavior of carrier mobilities, transient PL, EL, and transient capacitance in the dope organic Alq₃ films with the conventional dopants of DCM, C-6 and Rub. Though we have shown that the co-doped of Rub either with DCM or C-6 in Alq₃ could further improve the mean carrier mobilities and reduce the disorders in films, these are still not enough to achieve the stability and commercialization for multi-color OLED in the display market. This organic doped-system is also not able to tune the color emission with the dopant's concentration due to quenching if it is too concentrated in the film. Therefore, a few suggestions are listed here for further understanding and clearer information to break through the existing problems in OLEDs.

Proposal for future work

- (i) Thermal stimulated current (TSC) experiment, which is the alternative method to further confirm the trap depth in these doped films

- (ii) Incorporate the inorganic nano-particles, such as CdSe(ZnO) to further improve the emission colors and tune the emission wavelength with the size of CdSe(ZnO)
- (iii) Tailor the organic molecular structure of host-guest in order to reduce the interactions and local fields within the fields. The generated local fields will redirect the motion of carriers in films and possibly reduce the recombination of holes and electrons
- (iv) Investigate the substrate temperate effects on the electrical and optical properties of organic films.

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- [213] C.B. Lee, A. Uddin and X.Y Zhao "Temperature and electric-field dependence charge-carrier mobility in amorphous tris-(8-hydroxyquinolinolato) aluminum films: Time-of-flight measurements and simulation" (submitted to *Physical Review B*)
- [214] C.B. Lee, A. Uddin and C.C. Teo "Effect of Polar Dopant on Energetic and Positional Disorders in tris (8-hydroxyquinolinato) aluminum (Alq3)" (submitted to *Applied Physics A*)
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List of Publications

Journal Publications

1. A. Uddin, C.B.Lee, X. Hu and T.K.S.Wong "Interface-injection limited carrier transport properties of Alq₃", Appl. Phys. A 78, (2004)401-405.
2. C. B. Lee, A. Uddin, X. Hu and T. G. Andersson "Study of Alq₃ thermal evaporation rate effects on the OLED", Mat. Sci. & Eng. B 112, 14 (2004)
3. X. Hu, XiongYan Zhao, A. Uddin and C.B. Lee "Preparation, characterization and electronic and optical properties of plasma-polymerized nitriles", Thin Solids Film 477, 81 (2005)
4. A. Uddin, C.B.Lee, X. Hu and T.K.S.Wong "Effect of doping on optical and transport properties of charge carriers in Alq₃", Journal of Crystal Growth 288, 115 (2006)
5. A. Uddin, C.B. Lee and X. Hu "Study of interface properties of electrodes for the Alq₃-based OLEDs", SPIE, vol. 5648, pg. 114-123 (2005)
6. C.B. Lee, A. Uddin and C.C. Teo "Effect of Polar Dopant on Energetic and Positional Disorders in tris (8-hydroxyquinolinato) aluminum (Alq₃)", Appl. Phys. A 83, 115 (2006)
7. C.B. Lee, A. Uddin and X.Y. Zhao "Temperature and electric-field dependence charge-carrier mobility in amorphous tris-(8-hydroxyquinolinolato) aluminum films: Time-of-flight measurement and simulation", J. Applied Physics, (resubmitted)
8. C.B. Lee and A. Uddin "Doping effect on charge carrier mobility in tris (8-hydroxyquinolinato) aluminum (Alq₃)" Physical Review B, (submitted)
9. C.B. Lee, A. Uddin, C.C. Teo and Javier Wong "Study of exciton behaviors in doped in tris(8-hydroxyquinoline) aluminum (Alq₃)", Journal of Luminescence, (resubmitted)
10. C.B. Lee, A. Uddin and T. G. Andersson "Investigation of charge carrier mobility in 5,6,11,12-tetraphenylnaphthacene (rubrene) and coumarin 6 doped Alq₃ films", Mat. Sci. & Eng. B, (submitted)
11. C.B. Lee, A. Uddin, C.C. Teo and Javier Wong "Study of emitting assist dopant: 5,6,11,12-tetraphenylnaphthacene (rubrene) in doped organic light emitting diodes", Journal of Materials Science, (submitted)
12. C.B. Lee, A. Uddin and C.C. Teo "Study of transient electroluminescence in doped Alq₃ thin films from bilayer organic light emitting diodes", Appl. Phys. A (submitted).
13. C.B. Lee, A. Uddin and C.C. Teo "Measurement of transient capacitance for doped organic light emitting diodes", Thin Solids Film (to be submitted)

Conferences and Workshop Presentation:

1. A. Uddin, C.B.Lee, L.C.Wai, X. Hu and T.K.S.Wong; "Investigation of carrier injection from Al and LiF/Al cathodes in Alq₃", 7 – 12 December, ICMAT2003, Singapore, (oral presentation).
2. C.B. Lee, A. Uddin, X. Hu and X.Y.Zhao, "Indium-tin-oxide anode surface treatment effects on hole injection in Alq₃", 7 – 12 December, ICMAT2003, Singapore, (poster presentation) .
3. X. Hu, X.Y. Zhao, C.B.Lee and A. Uddin, "Preparation and characterisation of electric and optical properties of plasma polymerized nitriles", 7 – 12 December, ICMAT-2003, Singapore, (oral presentation).
4. A. Uddin, C. B. Lee and X. Hu, "Study of interface properties of electrodes for the Alq₃ base OLEDs" SPIE International Conference on Smart Materials, Nano- and micro-smart Systems, 12 – 15 December 2004, Sydney, Australia, (oral presentation).
5. C. B. Lee, A. Uddin and X. Hu, "Investigation of Alq₃ Film Quality for Different Thermal Evaporation Rates", Workshop on Thin Films organized by MPE/NTU, 8 – 9 January 2004.
6. A. Uddin, X. Hu and C. B. Lee, "Organic semiconductor materials for advance foldable display", CoE technology exhibition, 8 – 13 March 2004.
7. C.B. Lee, A. Uddin, C.C. Teo and Javier H.S. Wong "Study of emitting assist dopant: 5,6,11,12-tetraphenylanthracene (rubrene) in organic light emitting diodes" ICMAT 4-8 July, 2005 , (oral presentation).
8. A. Uddin, C.B.Lee, X. Hu and T.K.S.Wong "Effect of doping on optical and transport properties of charge carriers in Alq₃", ICMAT 4-8 July, 2005, (oral presentation).
9. A. Uddin and C. B. Lee "Investigation of Doping Effect on Charge Carrier Transport in Tris (8-hydroxyquinolino) Aluminum (Alq₃)", The 89th Annual Meeting of Optical Society of America, 16-20 October 2005, Tucson Arizona, USA, (oral presentation).