# Study of oxidized aluminum anode and application thereof in organic light-emitting diodes

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science

School of Graduate Studies, Department of Materials Science & Engineering University of Toronto

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#### Abstract

Organic light-emitting diodes (OLEDs) have emerged as promising alternatives to conventional light-emitting diodes (LEDs) in microdisplay applications due to their low powerconsuming emissive nature which is specifically suited for solving view angle issues with a fundamentally low-cost manufacturing process. However, when OLEDs are coupled with a silicon backplane, the high optoelectronic performance is heavily hindered due to limitations on device configuration. In this thesis, we discovered an *ex-situ* fabrication method to utilize aluminum's electrical and optical properties to enhance the luminance characteristic of the OLED. By employing the UV-ozone oxidation of thermal evaporated aluminum thin films in conjunction with various transition metal oxides as part of the anode, highly efficient top-emitting OLEDs were fabricated. Given the large thickness of the aluminum oxide, we explored the possibility of a diffusion reaction between the transition metal oxide and the underlying aluminum to be responsible for enabling the emission of the OLED.

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# List of units:

eV	electron volt
K	degree Kelvin
nm	nanometer
°C	degree Celsius
Å/s	angstrom per second
Pa	Pascals
lm/w	lumens per watt
А	ampere
cd/m <sup>2</sup>	candela per meter squared
V	volts
J	current density
L	luminance
0	angle
cd/A	candela per ampere
mins	minutes
Arb. Unit	arbitrary unit
mA/cm <sup>2</sup>	milliampere per centimeter squared
Ω*cm	ohm per centimeter (resistivity)

# List of abbreviations:

Al/Al <sub>2</sub> O <sub>3</sub>	aluminum oxide on top of aluminum
ALD	atomic layer deposition
BEOLED	bottom-emitting organic light-emitting diode
CBP	4,4'-Bis(N-carbazolyl)-1,1'-biphenyl
CE	current efficiency
CVD	chemical vapor deposition
EA	electron affinity
E <sub>F</sub>	Fermi level
EIB (E <sub>e</sub> )	electron injection barrier
EL	electroluminescent layer
ETL	electron transport layer
HIB (E <sub>h</sub> )	hole injection barrier
НОМО	highest occupied molecular orbital
HTL	hole transport layer
IP	ionization potential
Ir(ppy) <sub>2</sub> (acac)	Bis[2-(2-pyridinyl-N)phenyl-C](acetylacetonato)iridium(III)
ITO	indium tin oxide
J-V-L	current density-voltage-luminance
LED	light-emitting diode
LUMO	lowest occupied molecular orbital
NPB	N,N'-di-[(1-naphthalenyl)-N,N'-diphenyl]-1,1'-biphenyl-4,4'-diamine
NTE	near-to-eye
OLED	organic light-emitting diode

OLEDoS	organic light-emitting diode on silicon
PE	power efficiency
PVD	physical vapor deposition
QCM	quartz crystal microbalance
SEM	scanning electron microscopy
TEM	transmission electron microscopy
TEOLED	top-emitting organic light-emitting diode
ТМО	transition metal oxide
ТРВі	2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)
UPS	ultraviolet photoelectron spectroscopy
UVO	ultraviolet ozone
Vac	vacuum
VBM	valence band maximum
WF	work function
XPS	X-ray photoelectron spectroscopy

# **Chapter 1**

# Introduction

#### **1.1 Motivation**

The recent sensation of organic emissive display technologies in academic research and industrial commercialization attribute its popularity to its ability to provide a captivating experience with its vibrant colours. Whether it be for biological, military, or for general entertainment, these upcoming electronic devices are comprised of organic semiconductors which have been garnering public and private interests largely due to their promise in flexible screens, near-to-eye (NTE) applications including wearable technologies such as smart-glasses, virtual and augmented reality displays and solid-state lighting [1-4]. However, in the past decade, these products have been limited to niche fields and small-scale research because of manufacturing demands, logistics issues, and hardware complications [5].

In particular, an organic light-emitting diode-on-silicon (OLEDoS) microdisplay is comprised of a hybrid stack of organic and inorganic layered thin film materials that currently play a vital role in NTE display applications. The use of a silicon backplane provides the circuitry required to support the millions of individual pixels emitted by the organic light-emitting diodes (OLEDs). In contrast to a conventional inorganic display, OLEDs have the capacity to minimize power consumption, provide sufficient backlight suppression for the removal of dark space between pixels, increase display lifetime, acquire a slimmer form factor, and lower the fabrication costs for future commercial adoption [6]. Collectively, these improved device performance parameters are expected to make significant impact in manufacturing processes of future OLED applications. Currently, one of the major challenges in the fabrication methods of an OLEDoS device is the natural degradation of its optical and device performance due to external exposure to oxygen and moisture. Previously, academic and industry researchers have hypothesized that metal surfaces which form insulating oxides are detrimental to device performance as it inhibits hole injecting properties of the OLED. For example, due to limitations on the anode portion of the device structure, the effect of moisture and oxygen from the natural environment can significantly hinder and decrease the luminance parameters up to 70% [5,7]. For prospective commercial NTE displays, these reduced values do not meet the minimum luminance requirement of 2,000 cd/m<sup>2</sup> [5]. In order to compensate for optical losses, the brightness expectations of OLED pixels are approximately ten-fold [5]. Given the configuration of an OLEDoS device, the anode architecture therefore plays a critical role in achieving high luminance and current efficiency [5,7]. By optically isolating the thin film transistors and the OLEDs from the electronic device, the luminance can be drastically improved [8].

An OLEDoS technology requires the silicon wafer to be assembled from a foundry where it is post-processed by patterning the anode layers on top. Subsequently, the silicon device is then transferred to a separate OLED fabrication facility. However, before the OLED layers can be deposited, the native insulating oxide layer forms on the metal or metal-based anode during and after the patterning process. This former technique can hinder the hole injecting properties of the anode leading to luminance and current efficiency degradation.

Modern solutions require expensive *in situ* fabrication procedures. Additionally, the methods include a removal or reduction step of the native insulating oxide layers from the metal anode. In the academic community, silver is primarily used as a viable alternative due to its high transmittance and conductivity while industry companies such as LG Chem Ltd. utilizes a metal

with a higher oxidation rate or whose metal surfaces are less reactive with oxygen on the cathode part of the OLED [9-12]. An alternative, cost-efficient configuration of materials for anode has yet to be disclosed, thus, in order to successfully reach the consumer level for microdisplay applications, the unmet requirements and a deeper understanding of its anode components must be addressed.

#### **1.2** Top-emission organic light-emitting diodes (TEOLEDs)

In today's modernized world, OLEDs have started to become a viable solution in commercialized television screens and phone displays. The majority of these products require circuitry on the backplane of its device architecture for programmable logistics and to acquire control over the emission of individual pixels. As a result, to improve the overall device performance of an organic emissive display, light must be emitted upwards. This type of organic electronic device is known as a top-emission OLED or TEOLED (**Figure 1.1**).





A TEOLED is usually comprised of a substrate, a hole injection structure defined by a reflective anode on top of the substrate, an electroluminescent (EL) layer made up of one or more

organic materials on top of said anode, and an optically transmissive or transparent cathode. In the EL layer, photons are emitted spontaneously in various directions. The use of a highly reflective anode allows to direct and guide the potential loss of photons towards the cathode, thereby increasing the luminance properties of the TEOLED. Additionally, the hole injection function of the anode allows positively charged carriers (holes) to move into the EL layer. Likewise, the cathode permits the injection of negative charged carriers (electrons) to the same EL layer. Under a power source or applied voltage bias, electrons and holes move by hopping between localized sites within the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO). Unlike the band transport of inorganic semiconductors, amorphous organic semiconductors are governed by hopping transport due to their natural energetic disorder (Gaussian distribution of states). In an amorphous structure, there is a different energy environment for each organic molecule. Therefore, through weak intermolecular interactions, charge transport of the electron and holes occurs through "hopping" between localized states (Figure 1.2). Conventional inorganic light-emitting diodes (LEDs) attribute their charge transport mechanism to the free charges moving in energy bands.



Figure 1.2: Exciton formation and spontaneous emission of photons in an OLED.

As the electrons and holes are injected from the cathode and anode respectively, the Coulombic attraction between the charges develop into a pair known as an exciton. The exciton forms within the EL layer, recombines and then decays radiatively, ultimately emitting a photon (light). Due to the radiatively relaxation of excitons, OLEDs heavily depend on the charge injection materials and charge balance. Both parameters can be characterized by current, voltage, and luminance, which is further explained in Chapter 3. At the organic and electrode interface, charge injection becomes a crucial parameter as it dictates the current density of the device. The current density of an OLED can increase by decreasing the hole or electron injection barriers. To help facilitate this, charge transport and charge injection layers are utilized. Hole and electron transport layers (HTL and ETL) assist in carrying charges from the anode and cathode respectively. The HTL blocks electrons from leaking at the cathode to the EL layer. On the other hand, ETL performs the opposite duties by transporting charges from the cathode to the EL layer while blocking holes from leaking into the cathode. This charge carrying mechanism is portrayed in **Figure 1.3**.



Figure 1.3: A band diagram outlining the emission mechanism in an OLED.

TEOLEDs continue to be commercialized as they are heavily employed in television, displays, stretchable and wearable electronic systems, and solid-state lighting technologies [13-17]. OLEDs also have several advantages over LEDs including but not limited to: wide viewing angle, capable of being deposited on thin and flexible substrates, high contrast, and high color gamut [18]. However, it is important to look at the modes of natural degradation of OLEDs due to the intrinsic properties of the material. To overcome some of the mentioned challenges, it is necessary to examine stable and efficient anode configurations of the TEOLED. The type of degradation this thesis plans to explore is the oxidation of the anode. In this study, an alternative anode for TEOLEDs has been examined. Furthermore, oxidized aluminum-based anodes (Al/Al<sub>2</sub>O<sub>3</sub> multi-layered material system) have been studied but have not been demonstrated in highly efficient TEOLED devices. This specific OLED reported in this thesis is superior than its counterparts and the conventional bottom-emitting OLED (BEOLED) composed of the same emissive host-dopant organic layers (Figure 1.4). At the time, Z. B. Wang et al. reported the highest current efficiency using a CBP:Ir(ppy)2(acac) host-dopant emissive layer for a green phosphorescent OLED [19]. The specific organic layers used will be reported in Chapter 3, Section 3.1, titled "Organic materials and TEOLED structure". Through the fabrication of a hole injection anode structure comprised of aluminum, the native insulating aluminum oxide, and a transition metal oxide (TMO), this new TEOLED structure has exhibited enhanced current efficiency and luminance properties, administering this device to be potentially commercialized. The deposition of the TMO layers on top of the multi-layered anode structure and its effect on the OLED will be further examined in Chapter 4 of this thesis.



Figure 1.4: A green phosphorescent OLED pixel fabricated in the lab using the mentioned host-dopant system.

#### **1.3** Aluminum and aluminum oxide

Aluminum (Al) is typically known for its natural formation of an oxide layer (alumina or Al<sub>2</sub>O<sub>3</sub>), that is usually deposited as a passivation or encapsulating layer for an OLED [**20-21**]. Al<sub>2</sub>O<sub>3</sub> naturally occurs in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (compact phase), and sometimes in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (porous phase) where the band gap of the respective phases varies from 7.0 eV- 8.7 eV [**22-24**]. Given this large band gap, it is commonly used as an electrically insulating material with high resistivity (~10<sup>14</sup> Ω\*cm) [**25**]. However, a thin layer of alumina can be porous as indicated by its  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and allow diffusion of other metallic ions and ultimately enable charge transfer through the interface.

As mentioned in the motivation section, a native insulating oxide layer forms on the aluminum metal anode during the fabrication procedure. The selection of aluminum is significant because aluminum is one of the most abundant elements on Earth. It is popularly used in many academic and industrial electronic applications but restricted in TEOLEDs in regard to conductivity because of its assumed incompatibility (in terms of interfaces and hole injection properties) with organic materials. Compared to conventional metal anodes used by OLED microdisplay manufacturers, aluminum thin films have excellent morphology and one of the highest reflectivity across visible, near-infrared, and ultra-violet light spectrums [10-12]. By enabling a highly efficient TEOLED using a hole injection structure comprised of a naturally insulating oxide material, the experimental studies presented in this thesis are expected to form a guiding principle for materials scientists and electronic engineers to explore this particular multilayered anode structure. The scientific exploration of oxide-oxide heterojunctions (Al<sub>2</sub>O<sub>3</sub>/TMO) may not only assist in manufacturing the next-generation OLED products but open up more industrial and academic opportunities for oxidized aluminum anodes to be utilized in future electronic technologies. To this day, the use of aluminum oxide, fabricated ex situ, have not been reported and have not been well characterized in highly efficient TEOLEDs. The primary goals of this work are to disclose an improved TEOLED structure with Al<sub>2</sub>O<sub>3</sub> and to create a solid understanding of the hole transfer process between the multi-layered oxidized anode and the organic layers.

#### **1.4** Introduction to transition metal oxides (TMOs)

In literature, a highly cited review paper by Greiner *et al.* reported the importance of TMO thinfilms in organic semiconductor devices [26]. Due to the nature of OLEDs requiring extrinsic charge injection from the electrodes, energy level alignment between the various organic and inorganic materials become a critical condition. By utilizing a buffer layer, namely TMOs, the electrode work functions may be modified to enhance hole injection properties at the anode. Though Greiner's paper solely focuses on the enhanced charge injection effect of the TMO/organic semiconductor interface, in this thesis, the hole injection properties at the Al<sub>2</sub>O<sub>3</sub>/TMO interface are studied. Given the fact that interfacial oxidation and reduction reaction may occur within the interface, there seems to be an avenue to explore oxide-oxide heterojunctions in organic electronic devices. This thesis plans to portray the understanding behind a highly efficient TEOLED and attribute its improved device performance to the multi-layered hole injection configuration utilizing an oxidized aluminum anode.

In case of an OLED, providing an Ohmic hole-injection contact between the anode and organic layers for high conductivity enhances the hole transfer between the electrode and the rest of the device. By employing charge-selective contacts, a buffer layer of high work function greater than the electrode, the Fermi level (E<sub>F</sub>) is pinned to the HOMO level of the organic layer [26]. This means, through the hopping transport mechanism, at the anode electrode, holes can efficiently transport through the TMO's valence band into the organic semiconductor material. As seen in Figure 1.5, given the HOMO level of an organic semiconducting layer, the hole injection barrier (HIB) is dependent on the work function (WF) of the buffer layer. The electron affinity (EA) is the energy released to add an electron while the ionization potential (IP) is the energy necessary to remove an electron from the neutral atom. Fermi level is defined as the energy required to add one electron to the system. The valence band of inorganic materials (metals and TMOs) or HOMO level of organic materials are filled with electrons up to this energy.

Because the OLED fabrication will be using a thermal evaporation system, the device architecture will want to include a TMO that has a relatively low sublimation temperature. For example, by exploiting a high work function TMO such as  $MoO_3$  (WF = 6.82 eV + or - 0.05 eV),  $WO_3$  (WF = 6.80 eV + or - 0.4 eV), ReO\_3 (WF = 6.70 eV) [26-27], the hole injection properties of the anode structure may be significantly improved. However, the idea of oxide-oxide

heterojunctions is still unclear as the thickness of the oxides tend to cause high or low-series resistance in a device. Thus, this thesis will examine the interfacial reduction reactions and the energy level alignment on the anode structure between the Al/Al<sub>2</sub>O<sub>3</sub>/TMO/Organic layers. The concept of energy level alignment and characterization of valence electronic structures will be further discussed in Chapter 4.



**Figure 1.5:** Example of an energy diagram where IP is the ionization potential, EA is the electron affinity, EIB is the electron injection barrier, HIB is the hole injection barrier, and  $E_{vac}$  is the vacuum level.

#### **1.5** Thesis structure

The purpose of this thesis is to provide experimental knowledge of the physics and materials science relevant to the oxidized aluminum anode structure comprised of oxide-oxide heterojunctions (Al/Al<sub>2</sub>O<sub>3</sub>/TMO). The use of an insulating oxide layer, grown *ex situ* reveals intriguing and interesting results at the oxide and organic interfaces. Through this thesis, the promising information in regard to interface science, thin film diffusion, and energy level

alignment will likely have an impact on the development of next-generation organic electronic devices.

- Chapter 2 will review the fabrication and characterization techniques used in this thesis, focusing on the physical vapor deposition system (thermal evaporation) and X-ray/ultra-violet photoelectron spectroscopy (XPS/UPS). The surface morphology is also mentioned using the scanning electron microscopy technique (SEM). This chapter will conclude with the *ex situ* growth and relationship of Al<sub>2</sub>O<sub>3</sub>.
- Chapter 3 shows the materials used to improve the device performance of the TEOLED utilizing the Al<sub>2</sub>O<sub>3</sub> as part of the multi-layered anode configuration. Here, the improved efficiency of the devices will be depicted.
- Chapter 4 concentrates and explores the in-depth physics and materials science behind the oxide-oxide heterojunction and organic interfaces. This chapter provides XPS/UPS evidence and theories behind the highly efficient TEOLED comprised of an insulating oxide layer.
- Chapter 5 presents the final findings of oxidized anodes in organic luminescent devices, and its future potential of exploiting oxide heterojunctions in organic electronics.

#### Chapter 2

# **Fabrication and characterization methods**

#### 2.1 Review of fabrication techniques and thermal evaporation

There are a variety of methods to produce thin film devices, including, but not limited to: chemical vapor deposition (CVD), atomic layer deposition (ALD), and physical vapor deposition (PVD). Though there are other types of deposition methods, for this thesis, PVD by thermal evaporation under vacuum was the primary fabrication technique of choice to form thin films (**Figure 2.1**).

Other fabrication procedures are not suitable for small-scale research of individual OLED pixels due to its inability to form accurate and precise nanometer (nm)-sized thicknesses [18]. Ion sputtering for example may damage the anode portion of the device or substrate from high energy bombardment of atoms [18]. Lastly, alternative deposition methods for fabricating efficient organic electronics are not capable of producing high quality thin films which are significantly dependent on the level of impurities and contamination [28-29]. Thermal evaporation under vacuum thrives in forming nm-sized thin films as it attributes its efficient (low energy consumption) deposition mechanism to relatively low heating temperatures (< 400°C). This is due to the nature of organic semiconductors' weak van der Waals interactions.

The thermal evaporation technique proceeds by heating a solid phase material above its sublimation temperature. Next, the vaporized material is guided through a high vacuum

environment and eventually condensed onto the sample substrate to create a solid thin film. This system process allows atoms to stick onto the surface of the substrate uniformly while being evaporated at a temperature above 200°C. Additionally, it keeps the substrate from contamination and prevents film oxidation. All the materials used in this work are of purity greater than 99%. The thin films were sublimated under a base pressure of 10<sup>-5</sup> Pa. The schematic diagram for this PVD mechanism can be seen in **Figure 2.2**.



Figure 2.1: The thermal evaporation PVD system used to fabricate the thin films in the lab.

In terms of small-scale production, the most fundamental fabrication technique of an OLED is therefore the thermal evaporation deposition method due its advantageous factor of film growth quality [18]. The precise and uniform film growth is monitored by a quartz crystal microbalance (QCM), where the density of the material is correlated with its resonant frequency. As the thin film grows, the mass or thickness of the materials can be calculated with the QCM. Each solid material has a specific tooling factor to take account for the geometric position of the deposition sources and individual evaporation rates in the vacuum chamber system. As a result,

the films can be deposited at a high rate precisely and leave the surface undamaged. However, the major disadvantage of PVD is its cost-ineffectiveness because as the devices are scaled up (> 100 nm), the deposition thickness drastically changes for large area substrates. This makes it difficult to monitor and control the quantity of materials within the vacuum system. Thus, for commercial applications, it is viable to use other fabrication techniques such as inkjet printing, roll-to-roll, or in-line production as the inefficient use of organic and inorganic materials in a thermal evaporation system may lead to large profit loss [**28-29**].



Figure 2.2: A schematic diagram of the thermal evaporation system.

#### 2.2 Characterization of materials and interfaces

In this work, two main types of surface analysis techniques were used to examine thin film characteristics. The XPS and UPS are part of a high vacuum system as seen in **Figure 2.3**. To generalize, this system works in a way where the main load lock acts as the oxidation chamber. As the pressure is lowered, or pumped down, the roughing pump is utilized. This particular pump

is connected to a turbo pump, where it further decreases the pressure in the load lock, organic deposition, and central deposition chamber.



**Figure 2.3:** A diagram of the vacuum systems which incorporates the XPS/UPS characterization techniques.

For XPS and UPS analysis, it is essential that the pressure is pumped down to ultra-high vacuum. This allows the study of thin films and *in situ* analytical measurements while being free of residual contamination. Additionally, there are ion and thermocouple gauges located on the deposition chambers to assist in monitoring the pressure levels. The cryogenic pump is also used to achieve ultra-high vacuum for the deposition chambers. Accordingly, in the organic deposition chambers, the k-cells hold the solid materials usually consisted of the host, dopant, and other organic layers. In the metal deposition chambers, aluminum and other TMOs are present. Finally, the flipping station is required because during the deposition of the solid materials, the substrate must be facing downwards as the materials condense from the bottom of the chamber. However, when utilizing the XPS and UPS systems, the sample must be facing upwards.

#### 2.2.1 X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS)

The XPS is setup with monochromated Al K $\alpha$  soft x-rays with an energy of 1486.7 eV. Due to the high energy of the x-rays, core-level electrons are emitted. This process allows the study of the interface and the surface of the thin film material. On the other hand, the UPS is equipped with a He I $\alpha$  plasma discharge lamp with a much lower energy of 21.22 eV. Though this limits the UPS to examine valence-level spectroscopy, in comparison with the XPS, it has a higher resolution and signal-to-noise ratio. Therefore, the UPS is highly sought out for the characterization of electronic valence structure, work function, and energy level alignment. The results of the photoelectron spectroscopies on the surface and interface of the oxidized anode structure is explained in further detail in Chapter 4.

#### 2.2.2 Scanning electron microscopy (SEM)

SEM (**Appendix A**) characterization of various  $Al_2O_3$  thin films deposited on SiO<sub>2</sub> terminated Si <100> wafers were performed. The Si wafer was used due to its smooth surface and to easily compare the surface morphology of the aluminum film. Similar to the glass substrate, the Si <100> wafer was cleaned with Alconox soap, then sonicated in acetone and methanol for 15 minutes respectively. After removal of the Si native oxide layer, the aluminum thin film was deposited the same way as the glass substrate. For analysis, the images were taken with Hitachi SU 5000 at 1.5 kV. In the characterization images, the smooth morphology of the Si <100> wafer can be seen. As the 150 nm Al is deposited on top of the Si, due to the low substrate temperature during deposition, the images portray distinct microstructural features of the aluminum film [**30**]. The porous pits and spaces between the microstructures can be portrayed in the SEM images. Given the surface morphology of the Al<sub>2</sub>O<sub>3</sub>, this supports the possibility of TMO diffusion to the

underlying aluminum anode layer. Additionally, both the UVO grown and natural grown Al<sub>2</sub>O<sub>3</sub> provide similar surface morphology.

#### 2.3 Ex situ growth and relationship of aluminum oxide

In literature, the use of Al<sub>2</sub>O<sub>3</sub> in organic optoelectronic devices have been reported. Nevertheless, many of the Al<sub>2</sub>O<sub>3</sub> thin films have been prepared using atomic layer deposition (ALD) or chemical vapor deposition (CVD) due to the assumption that *ex situ* fabrication of  $Al_2O_3$  will lead to low device performance as the films are exposed to moisture and oxygen [31]. For example, Zhou et al. reported a BEOLED employing alumina as the buffer layer on top of an indium tin oxide (ITO) anode. Given the relatively thin 1.4 nm thickness layer of *in situ* grown Al<sub>2</sub>O<sub>3</sub>, the paper attributes the increase in the hole injection process to the quantum tunneling effect and thermionic emission [32]. Furthermore, Lee *et. al* displayed an efficient TEOLED using a pure aluminum anode [33]. Nevertheless, the work provided in this thesis portrays a TEOLED comprised of an aluminum anode with a thickness of 150 nm. To mimic industry conditions, this thesis employs an ex situ process to grow the natural oxide layer on top of the aluminum anode upwards to a thickness greater than 2.6 nm by implementing ultraviolet ozone (UVO). Additionally, Al-MoO<sub>3</sub> diffusion through the  $Al_2O_3$  have been reported in literature for nanocomposites [34]. Thus, the high performance TEOLED fabricated in this work may be explained by the potential diffusion occurring through the oxide-oxide heterojunction.

The Al<sub>2</sub>O<sub>3</sub> was grown on an aluminum thin film with UVO (**Figure 2.4**). The formation of ozone and atomic oxygen occurs through the process of UV radiation absorption by atmospheric oxygen. In this work, the UVO treatment was carried out in a separate chamber equipped with a photo surface processor (model: PL16-110 Sen Lights corporation).



Figure 2.4: Diagram of the UV ozone technique used to grow the oxide layer of aluminum.

As noted in academia and industry, Al<sub>2</sub>O<sub>3</sub> grows naturally and quickly, upwards to 3 nm in approximately 10 minutes of exposure to ambient environment [**35**]. To confirm the formation of the oxide layer, XPS was performed. Ultimately, to resemble and mirror the industry fabrication process, the saturation time for the native oxide was studied. Through the Strohmeier Overlay equation [**36**], the following equation was used:

$$d = \lambda_o \sin \theta \ln \left( \frac{N_m \lambda_m I_o}{N_o \lambda_o I_m} + 1 \right). \tag{1}$$

In the equation above, d represents the XPS oxide thickness,  $\lambda$  signifies the inelastic mean free path accounting for the energy loss from the electron scattering, o and m subscripts defining the oxide and metal respectively,  $\theta$  being the photoelectron take-off angle, the variable I, displaying the peak area intensity, and N as the notation for atom volume density. The following parameters were also defined:  $\lambda_o = 2.8$ ,  $\lambda_m = 2.6$ ,  $\theta = 75^\circ$ , and  $\frac{N_m}{N_o} = 1.6$  [**37**]. All the XPS results are curvefitted using a combination of methods: Gaussian-Lorentzian, asymmetric peak, or Shirley-type background subtraction.

Thirteen XPS samples with an Al/Al<sub>2</sub>O<sub>3</sub> structure of 150 nm thick aluminum were fabricated to investigate their oxidation states. Nine of these samples were measured at 2, 4, 6, 8, 10, 15, 20, 25, and 30-minute intervals. Additionally, to compare with the naturally grown oxides,

four samples in ambient environment were examined at 1-day, 10-day, 15-day, and 6-month intervals. **Figure 2.5 (a) and (b)** show the XPS chemical composition of Al<sub>2</sub>O<sub>3</sub> and the Al 2p core-level. To help identify the chemical state of Al, pure Al is indicated the main feature peak at 73 eV. However, as the oxide is treated with UVO and naturally grown in ambient environment, the peak is located between 75 eV and 76 eV, indicating the presence of the oxide, Al<sub>2</sub>O<sub>3</sub>. The slight shift of the black line (1-day) is due to the charging effect. The shift to lower binding energy is due to the positive charged accumulation on the surface. The unoxidized peaks are also normalized to indicate the difference between the oxide peaks.



Figure 2.5: (a) XPS spectra of natural grown  $Al_2O_3$  in 1-day, 10-day, 15-day and 6-month intervals. (b) is the XPS spectra of UVO-treated  $Al_2O_3$  at various times.

**Figure 2.6 (a)** is displayed as a simplified XPS result utilizing equation 1 while **Figure 2.6 (b)** depicts the XPS analysis of the combined data from **Figure 2.5**. After 10 minutes of UVO treatment, the thickness was approximately 2.6 nm. The UVO thickness saturated around 3.7 nm after 20 minutes. On the other hand, the naturally grown oxide saturated at a similar thickness of 2.8 nm as outlined by the green line in **Figure 2.6 (a)**. **Figure 2.6 (b)** portrays the Al 2p XPS core-level spectra of Al<sub>2</sub>O<sub>3</sub> where the first peaks around 75 eV – 76 eV indicate the chemical state of Al<sub>2</sub>O<sub>3</sub> in the thin films.



**Figure 2.6:** (a) describes the UVO-treated sample thickness as a function of time in minutes. The green dashed lines show the band range of the native oxide saturation thickness. (b) portrays the Al 2p XPS spectra to compare the 10-minute UVO-treated sample to 10-day and 15-day native grown oxide samples.

**Figure 2.7** is displayed as a simplified XPS result of **Figure 2.5** (b) to obtain the native oxide saturation thickness. Quantitively, these experimental findings show that the oxide thicknesses for both the UVO-treated and naturally grown oxides are similar due to the analogous peaks. Therefore, to quicken the process, to imitate the natural grown oxide process, and to maintain consistency for experimental research purposes, the aluminum anode was UVO-treated for 10 minutes.



Figure 2.7: Natural grown Al<sub>2</sub>O<sub>3</sub> sample thickness as a function of time in days.

# Chapter 3

# Aluminum oxide as anodes for TEOLEDs

#### **3.1** Organic materials and TEOLED structure

The aluminum anode (99.999% purity) was first fabricated on a glass substrate, cleaned thoroughly with acetone, then methanol, followed by sonication and UVO for 15 minutes respectively. The pixel area was measured to be approximately 4.4 mm<sup>2</sup> while the deposition rates of the organics and host-dopant concentrations were controlled by an *in situ* calibrated QCM. After the deposition of the 150 nm thick aluminum thin film, the sample was taken out of the metal evaporation chamber, exposed to atmosphere, and transferred into the ex situ chamber for UVO-treatment. Next, the rest of the TEOLED layers were deposited in the order of the following: one of the TMOs, MoO<sub>3</sub>, ReO<sub>3</sub>, or WO<sub>3</sub> as the hole injecting layer, 4,4'-Bis(N-carbazolyl)-1,1'biphenyl (CBP) as the hole transporting layer, a co-deposition of CBP (host) and Bis[2-(2pyridinyl-N)phenyl-C](acetylacetonato)iridium(III) or Ir(ppy)<sub>2</sub>(acac) (dopant) as the emissive layer, 2,2',2''-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) or TPBi as the electron transporting layer, and lithium fluoride (LiF) as the electron injecting layer. To achieve a low work function cathode electrode, a co-deposition of magnesium and silver was used to form an alloy. The additional thin silver layer deposited on top of the alloy acts as the transparent cathode and the organic encapsulating layer was composed of N,N'-di-[(1-naphthalenyl)-N,N'-diphenyl]-1,1'-biphenyl-4,4'-diamine (NPB) to help increase the out-coupling efficiency. The device reported in this work used an efficient phosphorescent green BEOLED baseline structure due to its high industrial performance [19]. Thus, all the fabrication experiments regarding the TEOLED was comprised of the CBP:Ir(ppy)<sub>2</sub>(acac) host-dopant emissive layer (Figure 3.1). The device performance of the BEOLED can be found in Appendix B.



Figure 3.1: The TEOLED structure with various layer thicknesses.

#### **3.2 TEOLED device performance**

For the TEOLED device performance, in ambient conditions, the HP4140B picoammeter and Minolta LS110 luminance meter was used to measure current density-voltage-luminance (J-V-L) characteristics, including current and power efficiencies (CE and PE). To ensure data consistency and reproducibility, the measurements were taken on multiple pixels and devices of the same OLED configuration.

#### **3.2.1** Current density-voltage-luminance characteristics

J, V, L, CE, and PE parameters are the benchmark device characteristics of an OLED. The efficiency of the devices (CE and PE) have significant impact on a device's ability to be commercialized. PE provides information on the power consumption (lm/W) while CE indicates the ratio and relationship between the luminance and current density of the device. In this work, three different TMOs were fabricated: MoO<sub>3</sub>, WO<sub>3</sub>, and ReO<sub>3</sub>. It is important to note the microcavity effect in TEOLEDs as it is known to increase the out-coupling efficiency due to the high reflectively of the electrodes. Thus, this configuration forms the Fabry-Pérot optical resonator which may increase the overall current efficiency of the device [**38-39**]. In **Figure 3.2**, the OLED device without the TMO between the Al<sub>2</sub>O<sub>3</sub> and CBP layer seems to result in very low current density, approximately in the order of 10<sup>-5</sup> to 10<sup>-6</sup> mA/cm<sup>2</sup>. Thus, with the omission of a buffer layer, there seems to be a hole injection issue between the insulating alumina layer and the CBP organic layer. Furthermore, a pixel will be incapable of emitting any efficient light with current density values of 10<sup>-5</sup> mA/cm<sup>2</sup>. On the other hand, with OLED pixels that included a TMO layer, the hole injection efficiency of these devices drastically increased.



**Figure 3.2:** Current density as a function of voltage of the TEOLED with various TMOs including the omission of the MoO<sub>3</sub> layer.

Given multiple experiments with the same OLED configuration, with the addition of a TMO buffer layer, there is significant increase in hole injection properties. The driving and turn-on voltage are known to be dependent on the hole injecting properties of the anode. As seen in Figure **3.2**, though the different TMOs have relatively similar driving voltages ranging from 2.8 V - 3.2V, the MoO<sub>3</sub> exhibited the best results. Additionally, this is evident in Figure 3.3, where the MoO<sub>3</sub> device recorded a highly efficient OLED as high as 94 cd/A at 1000 cd/m<sup>2</sup>. This is consistent with its higher current density and hole injection properties. Mentioned in literature by Greiner et al. [26], in majority of OLED devices, there is an optimal TMO material and thickness for improved device performance. This can be further investigated through the deposition of different MoO<sub>3</sub> thicknesses. The thickness of the buffer layer correlates to the decrease of its work function and increase in conductivity until eventual saturation [26]. In terms of thermodynamic reactions, since there is no natural reaction between Al<sub>2</sub>O<sub>3</sub>-MoO<sub>3</sub>, there must be significant impact of the underlying aluminum layer. This means a reduction reaction between the underlying aluminum and MoO<sub>3</sub> may occur through the Al<sub>2</sub>O<sub>3</sub>. Subsequently, the aluminum metal anode sequesters oxygen anions as the potential reaction between aluminum and MoO3 can lead to the reduction of the oxidation state near the anode interface. This is mainly due to aluminum's higher oxidation potential in comparison with the reduction potential of MoO<sub>3</sub>. Given that the TMOs have different work functions, this work speculates better energy level alignment for the multi-layered anode structure utilizing MoO<sub>3</sub> between the Al/Al<sub>2</sub>O<sub>3</sub>/TMO/CBP interfaces. Though ReO<sub>3</sub> was evaporated without difficulty, the devices seem to be unstable when exposed to ambient air as some of the pixels could not be measured. This could have been due to ReO<sub>3</sub> sensitivity to moisture and air. The deposition of WO<sub>3</sub> was difficult due to its high evaporation and sublimation temperature and may have had significant impact on its device performance. Thus, MoO<sub>3</sub> was further studied due to its high work function, excellent conductivity, and improved J-V characteristics.



Figure 3.3: Current efficiency as a function of voltage of the TEOLED with various TMOs.

#### 3.3 Various MoO<sub>3</sub> thicknesses

In **Figure 3.4** (a), with the omission of the MoO<sub>3</sub> layer, the TEOLED's hole injection efficiency drastically decreases, which is fairly consistent with the results with other TMOs. The 4 nm buffer layer showed the highest CE, reaching the values of 94 cd/A at 1000 cd/m<sup>2</sup> as seen in **Figure 3.4** (b). As the buffer layer thickens, there seems to be a relationship between the efficiency of the device and its TMO properties. For example, there is a decrease in its work function and increase in conductivity until eventual saturation as mentioned in Greiner's work [**26**]. The highly cited review paper mentions there is an optimal thickness for a buffer layer as the performance of the OLED tends to degrade when the layer is too thick or too thin [**26**]. Accordingly, the 6 nm and 8 nm seem to be too thick of a layer as the device provides higher current density, but lower current efficiency compared to the 4 nm TEOLED. Therefore, the optimal MoO<sub>3</sub> thickness seems to be 4 nm.



Figure 3.4: (a) Current density as a function of voltage of the TEOLED with various  $MoO_3$  thicknesses including the omission of the  $MoO_3$  layer. (b) depicts the current efficiency of the TEOLEDs.

This is further evident in the total luminous PE and L-V curves in **Figure 3.5** (a) and **Figure 3.5** (b) respectively. The 4 nm MoO<sub>3</sub> device seems to be the most power efficient compared to the other thicknesses. Though it's more difficult to examine this on the L-V curve, the luminance and brightness capability at a relatively high current density gives an optimal device performance for the 4 nm buffer layer.



**Figure 3.5:** (a) The power efficiency as a function of luminance of the TEOLED device at various MoO<sub>3</sub> thicknesses. (b) portrays the luminance as a function of voltage of the same devices.

#### **3.4 Single carrier and short-circuit devices**

The highly efficient TEOLED device utilizing the Al<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub> heterojunction is the only condition enabling the efficient hole carrier transport through the alumina layer. In order for an OLED device to perform efficiently, the charge balance is a critical criterion. Creating a balance between the injection of the electrons from the LiF/Al cathode and the holes injected from the multi-layered anode is of much importance. The imbalance of the charges may lead to significant decrease in device performance and current efficiency. Therefore, to examine the hole injecting properties of the 4 nm MoO<sub>3</sub> in the TEOLED, the possibility of a low injection barrier due to the energy level alignment of the materials and the pinhole defects of the aluminum anode (Al<sub>2</sub>O<sub>3</sub>) may attribute to the valuable functionality of the oxide heterojunction. The pinhole defects may allow diffusion of the Al-MoO<sub>3</sub> through the Al<sub>2</sub>O<sub>3</sub>. Since the LiF/Al structure is commonly used in academia and industry as an efficient electron injection cathode, series of experiments regarding the J-V characteristics of a single-carrier device was performed. The single-carrier devices only consisted of hole-only materials as noted in **Figure 3.6**. Five of these devices were fabricated with different MoO<sub>3</sub> thicknesses.



Figure 3.6: Single carrier-device structure with different MoO<sub>3</sub> thicknesses.

As seen in **Figure 3.7**, the single-carrier device without  $MoO_3$  has a much lower current density in the order of  $10^{-4}$  to  $10^{-7}$ . Since the driving voltage and current efficiency of OLEDs are heavily dependent on injection contacts due to their limited intrinsic charge carriers, by eliminating the junction resistance and achieving Ohmic contact, the multi-layered hole injection anode used in this thesis may be further studied. Generally, at a certain voltage, a small hole injection barrier at the anode is correlated with the increase in current density.



Figure 3.7: J-V curves of the five single carrier devices of different MoO<sub>3</sub> thicknesses.

Qualitatively, in comparison with the 4 nm MoO<sub>3</sub>, the 2 nm MoO<sub>3</sub> may already start diffusing through the pinholes through the interface reaction with the aluminum anode. As the reaction occurs with the underlying aluminum, the oxidation state and work function of MoO<sub>3</sub> may be lowered. The decrease in work function may lead to the slight increase in hole injection barrier. In regard to the 8 nm thickness, its thicker layer may act as a dielectric, hence its slight decrease in current density when compared to the 4 nm and 6 nm device respectively. The 6 nm layer gives a marginally lower current density than the 4 nm layer as well. Consequently, the 4 nm MoO<sub>3</sub> exhibits the highest current density which enhances the hole injection into the CBP and evidently provides the optimal charge balance in the TEOLED. It is important to note that a higher current is not directly correlated to a higher current efficiency. The balance in the charge carriers

depends on the combination of organic and electrode materials. For example, an increasing current efficiency with a lower current density profile can mean the OLED may have different concentrations of hole and electron carriers [40].

To provide further evidence that the oxide-oxide heterojunction of Al<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub> enhances the hole injection, a series of experiments regarding the short-circuit device structure was examined. The short-circuit device included the aluminum and its native oxide layer, MoO<sub>3</sub> and aluminum as the cathode.



Figure 3.8: J-V curves of the following structure: Al/Al<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub>/Al.

First, the assumption was that the 2.6 nm Al<sub>2</sub>O<sub>3</sub> was sufficiently thin, and thus responsible for the hole transfer process which may be explained by the quantum tunneling mechanism [**41**]. However, given the structure of Al/Al<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub>/Al, this short-circuit device displays a forward current density-voltage curve (J-V) which is shown in **Figure 3.8**, having the characteristics of a resistor. Though detecting pinholes in dielectrics are very challenging to verify with electron microscopes [**42-43**], this specific sample shows a short-circuit device which can provide reasonable evidence to credit the potential existence of pinholes. Furthermore, even with a transmission electron microscope (TEM), it is quite difficult to locate the pinhole [44-45]. Nevertheless, the natural growth of the aluminum oxide can make samples more susceptible to pinholes [44-45]. The surface morphology of the anode structure can be seen in **Appendix A**.

In summary, the 0 nm MoO<sub>3</sub> J-V curve portray the characteristic of a short-circuit device, attributing its behavior to the pinholes in the Al<sub>2</sub>O<sub>3</sub>. In this device, the alumina acts as the dielectric insulator. Furthermore, the J-V curves of the various MoO<sub>3</sub> thicknesses depict further evidence of efficient hole transfer through diffusion. As the thicknesses increase, the device becomes increasingly hole deficient.

## **Chapter 4**

# Study of transition metal oxide and aluminum oxide interface

#### 4.1 Diffusion at the oxide heterojunction interface

If there is any indication of pinholes in the Al<sub>2</sub>O<sub>3</sub> layer, there must be molybdenum (Mo) or Al ions diffusing through the insulating native oxide. Therefore, thermodynamically, a redox reaction can occur, resulting in the formation of a Mo ion with lower oxidation states [**34**]. To provide supporting evidence on the underlying aluminum surface of the Al/Al<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub> multi-layered anode structure, *in situ* XPS was performed. The samples were examined to investigate the reduction of Mo<sup>6+</sup>.

#### 4.1.1 Molybdenum ion ratio

As seen in **Figure 4.1**, the existence of more than one Mo ion species is evident. This is vividly indicated by the asymmetric shape of the Mo  $3d_{3/2}$  and  $3d_{5/2}$  peaks. For both Mo 3d core level spectrums, curve fitting was conducted. The asymmetric part of both curve fittings indicates the presence of more than one peak. Semi-quantitatively, this means there is more than one oxidation

state. The slight shift for  $Mo^{5+}$  and the difference of the full width at half maximum in **Figure 4.1** can be attributed to the particular XPS system used. The difference in samples, the associated atomic sensitivity factor, and the slight deviation from a perfect stoichiometry can have an impact quantitatively. However, the significance of this figure is to see the presence of two different oxidation states. In addition, further information can be obtained in **Figure 4.1(a)** by identifying the higher ratio of  $Mo^{5+}$  in comparison to the  $Mo^{6+}$ . This ratio difference implies that there is a redox reaction between the underlying aluminum and the thin, 1 nm MoO<sub>3</sub> buffer layer. When the interface with thicker MoO<sub>3</sub> was studied in **Figure 4.1(b)**, the 4 nm thickness showed a much higher ratio of  $Mo^{6+}$  than  $Mo^{5+}$ . Thus, given this finding, on top of the underlying aluminum anode, there is significant diffusion of MoO<sub>3</sub> through pinholes. To help further support this statement, UPS was conducted on these samples. The observation of gap states on various UPS spectrums provide the presence of  $Mo^{5+}$  states. This additional evidence is in well accordance with past literature as the gap states are consistent with the XPS results reported in this work [**26, 46-47**].



**Figure 4.1:** (a) XPS spectra of 1 nm MoO<sub>3</sub> in the following structure: Al/Al<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub>. (b) XPS spectra of the same structure with 4 nm MoO<sub>3</sub>.

#### 4.2 Energy level alignment

From the information obtained from the XPS spectra of MoO<sub>3</sub> and the J-V-L characteristics of the single carrier devices, there is evidence of the superior hole injection structure of Al/Al<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub>. To analyze the electronic transport of the anode interfaces, the valence band maximum (VBM) for inorganics and highest occupied molecular orbital (HOMO) for organics can be obtained through UPS. UPS usually has two main regions, dictated by the secondary electron background and the valence level. Through inelastic collisions, the electrons travelling from the source to the surface form and generate a continuous background. Though this means that the information about the valence state the electrons originated from are no longer present, the data regarding the surface is still relevant. As a result, the secondary electrons provide data on the work function of the material. This is possible by linearly extrapolating the secondary electron spectrum which can be seen in Figure 4.2 (figure on the left side). Since hole injection barriers are heavily dependent on the conductivity of the materials, the value of the work function is of much importance. To measure the work function, a bias of -15 V was applied to the samples while the take-off angle was 88°. The VBM and HOMO can also be calculated by extrapolating the valence edge to the noise level and corresponding the Fermi level to 0 eV. For example, in Figure 4.2, the inorganic material of MoO<sub>3</sub> can help provide information to calculate the VBM. The gap state is shown as the additional edge and can also be calculated by linear extrapolation. The work function can be directly measured by the following equation:

$$\Phi = hv - E_{Sec}.$$
 (2)

Where  $E_{sec}$  is the binding energy of the secondary electron cut-off and hv is the photon energy of the UV radiation.



Figure 4.2: UPS spectra of  $MoO_3$  on top of  $Al_2O_3$ . The gap state at 0.5 eV and valence band maximum at 2.87 eV can be seen in the inset.

Similarly, in **Figure 4.3**, the VBM of  $Al_2O_3$  and its work function can be calculated. As expected, the work function of  $Al_2O_3$  is quite low at 3.18 eV, which represents a low-work function material.



Figure 4.3: UPS spectra of  $Al_2O_3$ , where the left represents the secondary electron cut-off and the right depicts the valence band spectra. The valence band maximum of 5.55 eV can be determined from the inset.

Lastly, the HOMO levels of CBP organic layer can be calculated by the same methods used for Al<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub>. However, to provide results for comparison between the use of the buffer layer in between the underlying aluminum anode and the CBP, the HOMO level of the



**Figure 4.4:** UPS spectra of CBP on top of Al<sub>2</sub>O<sub>3</sub> and MoO<sub>3</sub>. The HOMO levels of 2.99 eV and 0.39 eV respectively can be determined from the inset.

MoO<sub>3</sub>/CBP layer was much lower at 0.39 eV (**Figure 4.4**). Ultimately, after gathering the work functions, VBM for inorganics, and HOMO level for organics, the energy level alignment diagram in **Figure 4.5** is displayed. For CBP, 1 nm was deposited on top of the MoO<sub>3</sub>. The LUMO level was calculated by subtracting the band gap from literature [**47-49**].  $\Delta E_h$  represents the hole injection barrier while  $\Delta E_e$  is the electron injection barrier.  $\Phi$  is the work function of the particular material, Vac stands for vacuum level, and  $E_F$  is the Fermi level. As seen in the energy level alignment diagrams, with the omission of the MoO<sub>3</sub>, the hole injection barrier of CBP is calculated to be 2.99 eV. However, with the addition of the buffer layer, the same barrier decreases significantly to 0.39 eV. This implies that the Al/Al<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub>/CBP interface is responsible for the efficient hole transfer. Therefore, it can be said that this multi-layered anode structure can reduce the TMO from Mo<sup>6+</sup> to Mo<sup>5+</sup> to slowly reach the properties of its bulk state. Subsequently, the enhanced hole transfer and lower hole injection barrier can be explained by the potential diffusion of the MoO<sub>3</sub> through Al<sub>2</sub>O<sub>3</sub> to the underlying aluminum anode.



**Figure 4.5:** (a) Energy level alignment diagram of the  $Al_2O_3$  interface. (b) Energy level diagram of the  $Al_2O_3/MoO_3/CBP$  interfaces.

## **Chapter 5**

# **Conclusion and future work**

#### 5.1 Conclusion

The work provided in this study attempts to utilize an exposed Al<sub>2</sub>O<sub>3</sub>, grown to more than 2.6 nm in thickness, as an anode for TEOLEDs. This multi-layered anode comprised of an aluminum anode, a naturally thick insulating oxide layer, and a transition metal oxide displayed high device performance comparable to BEOLEDs of the same emissive layer. The current efficiency provided to be much higher than the reported BEOLEDs despite the *ex situ* process of the anode structure. The functionality of the device in this thesis is attributed to the oxide heterojunction of the Al<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub> interface. Given the J-V-L characteristics, the MoO<sub>3</sub> seem to be highly conductive in conjunction with the Al<sub>2</sub>O<sub>3</sub>. The examination of the MoO<sub>3</sub> diffusion through the pinholes into the underlying aluminum layer is portrayed through the use of energy level alignment (UPS) and XPS characterization of Mo ion reduction. This gives further evidence of the decrease in the hole injection barrier by creating potential pathways through the multi-layered anode, ultimately allowing for efficient hole transfer. Without the TMO, there is a drastic decrease in current density of the single carrier devices.

The UVO-treated Al<sub>2</sub>O<sub>3</sub> layer mimics the natural growing oxide problem during industry fabrication of OLEDoS devices. By growing the Al<sub>2</sub>O<sub>3</sub> outside of a vacuum environment, this

work provides a unique fabrication method. The new procedure shows TEOLEDs with an *ex situ* fabrication step of the anode structure can still operate efficiently. The low turn-on voltage and high device performance is competitive with devices utilizing other expensive and challenging reflective anodes.

To summarize the chapters, Chapter 1 displayed the importance of finding alternative anode structures to provide a cheaper manufacturing method of OLEDoS devices. The use of aluminum and its native oxide is assumed to be detrimental to a TEOLED. However, with the introduction to oxide-oxide heterojunctions, it is clear that there may be an efficient solution at hand. In Chapter 2, the fabrication and characterization methods of the multi-layered anode is shown. The purposes of using a PVD technique, the use of UPS/XPS to study the interfaces, and images of Al<sub>2</sub>O<sub>3</sub> surface morphology measured by SEM is described. The natural and UVO growth relationship of Al<sub>2</sub>O<sub>3</sub> is also explained. Then, in Chapter 3, the use of Al<sub>2</sub>O<sub>3</sub> and the TMOs in a TEOLED is shown. The impact on the performance of the TMO on top of the Al<sub>2</sub>O<sub>3</sub> is portrayed through J-V-L curves. To further explain the high performance of the TEOLED, the diffusion at the oxide heterojunction interface along with the energy level alignment of the different inorganic and organic materials are examined in Chapter 4.

#### **5.2** Future of oxide heterojunctions in organic electronics

Although the results of this work have proven to be successful, there remain some questions regarding the oxide-oxide heterojunction. In the near future, the work presented in this thesis will hopefully assist in how oxide heterojunctions function. With various TMOs, it has been shown that this particular structure can provide high conductivity and effective hole transfer through relatively thick insulating oxide layers. However, there needs to be a further understanding of

various TMOs and its working process with different oxide films. Therefore, there is a need to study the oxide-oxide structures for the use in organic electronics. It is possible that different TMO and oxide combinations may provide a more efficient device. The significance of using an *ex situ* process in creating a highly efficient OLED also provides the idea that an efficient organic device does not require perfect encapsulation from moisture and oxygen.

Additionally, a more rigorous study of the Al<sub>2</sub>O<sub>3</sub> and other oxide layer's surface morphology can help understand the hole transfer mechanism in these devices. Cross-sectional TEM can be challenging but provide the detection of pinholes. Optimization of the buffer layer thickness of the TMOs seem to have an effect on device performance. Additionally, the study of lifetime degradation may also be of interest. Lastly, the use of this oxide-oxide heterojunction and multi-layered anode is not limited to OLED devices. The use of this multi-layered structure may be utilized in polymer OLEDs, photovoltaic devices, photodetectors, and many more organic optoelectronic devices.

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# APPENDIX A: Scanning electron microscopy (SEM) of Al<sub>2</sub>O<sub>3</sub>



**Figure A1**. SEM image of a silicon <100> wafer.



Figure A2. SEM images of aluminum deposited on top of silicon <100> wafer. The native Al<sub>2</sub>O<sub>3</sub> is grown in ambient conditions.



**Figure A3**. SEM images of aluminum deposited on top of silicon <100> wafer. The Al<sub>2</sub>O<sub>3</sub> is grown by UVO.



Figure A4. SEM images of Al/Al<sub>2</sub>O<sub>3</sub>/MoO<sub>3</sub>. The Al<sub>2</sub>O<sub>3</sub> is grown by UVO.

#### **APPENDIX B: TEOLED comparison with BEOLED**



**Figure B1**. (a) Current density as a function of voltage which includes the TEOLED with various MoO<sub>3</sub> thicknesses compared to a BEOLED and a TEOLED omitting the MoO<sub>3</sub> layer. (b) Current efficiency as a function of luminance. (c) Power efficiency as a function of luminance. d) Luminance as a function of voltage.



**Figure B2**. Current density as a function of voltage which includes the TEOLED with various TMOs compared to a BEOLED and a TEOLED omitting the TMO layer.



**Figure B3**. Current efficiency as a function of luminance which includes the TEOLED with various TMOs compared to a BEOLED.

#### **APPENDIX C: Academic and research contributions**

#### Articles published in refereed journals:

1. P. Li, G. Ingram, J.-J. Lee, Y. Zhao, Z.-H. Lu, Communications Physics, 2, 2 (2019).

#### Articles to be published in refereed journals (accepted manuscript):

1. J.-J. Lee, P. Li, H. T. Kung, Z.-H. Lu, J. Appl. Phys., (JAP19-AR-00989), Accepted 27 March 2019.

#### Patents and copyrights

1. J. J. Lee, Z. H. Lu, "Multiple hole injection structure on oxidized aluminum and applications thereof in organic luminescent devices," U.S. Provisional Patent, 62/746,905, (17 October 2018).