Electrode/Organic Interfaces in Organic Optoelectronics

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy

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Abstract

Organic semiconductors have the advantage over traditional inorganic semiconductors, such as Si or GaAs, in that they do not require perfect single crystal films to operate in real devices. Complicated multi-layer structures with nanometer scale thicknesses can thus be easily fabricated from organic materials using low-cost roll-to-roll manufacturing techniques. However, the discrete nature of organic semiconductors also implies that they typically contain almost no intrinsic charge carriers (i.e., electrons or holes), and thus act as insulators until electrical charges are injected into them. In electrical device applications this means that all of the holes and electrons within a device must be injected from the anode and cathode respectively. As a result, device stability, performance, and lifetime are greatly influenced by the interface between the organic materials and the electrode contacts. Despite the fundamental importance of the electrode/organic contacts, much of the basic physical understanding of these interfaces remains unclear. As a result, the current design of state-of-the-art organic optoelectronic devices tends to be based on trial and error experimentation, resulting in overly complicated structures that are less than optimal.

In the present thesis, various electrode/organic interfaces relevant to device applications are studied using a variety of different techniques, including photoelectron spectroscopy and the
temperature dependent current-voltage characteristics of single carrier devices. The fundamental understanding gleaned from these studies has been used to develop new strategies for controlling the energy-level alignment at electrode/organic interfaces. A universal method for tuning the work function of electrode materials using a halogenated organic solvent and UV light has been developed. Application of this technique in organic light emitting diodes enabled the first highly simplified two-layer device with a state-of-the-art record breaking efficiency.
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1 Introduction

1.1 Motivation

Energy is a global concern. Lighting currently accounts for ~ 20% of global electricity usage. Compact fluorescent light bulbs (CFLs) and light emitting diodes (LEDs) have emerged as alternatives to incandescent light bulbs. However, neither technology is ideal for widespread global application, due to both their high manufacturing costs and negative environmental impact (e.g., CFLs contain toxic mercury). High efficiency light sources that are cheap to manufacture and that are also environmentally friendly are therefore key technologies in defining our energy future. Organic light emitting diodes (OLEDs), composed of environmentally friendly carbon-based organic compounds, are rapidly gaining momentum as high-end displays in portable electronics, due to their superior performance and thin form factor. OLEDs also have the potential to be used for high efficiency lighting. Although OLEDs can potentially outperform CFLs and be on parity with LEDs in terms of power efficiency, they are currently far more expensive to manufacture due to the complicated multi-layer structures that are required to achieve start-of-the-art efficiencies. New solutions are thus required to reduce the complexity, and hence lower the manufacturing costs, of state-of-the-art OLEDs if they are to become a viable mass produced alternative to CFLs and traditional LEDs.

1.2 Background

1.2.1 Organic Optoelectronics

Organic electronic devices are electrical devices, such as LEDs, photovoltaics (PVs), or thin film transistors (TFTs), in which the active materials consist entirely of organic materials with semiconducting properties. Since organic materials consist of discrete molecular units there is no need for long range order between adjacent molecules or polymer chains. Organic semiconductors therefore have the advantage over traditional inorganic semiconductors, such as Si or GaAs, in that they do not require perfect single crystal films to operate in real devices. Complicated multi-layer structures with nanometer scale thicknesses can thus be easily fabricated from organic materials using low-cost roll-to-roll printing or vacuum coating techniques. However, the discrete nature of organic semiconductors also implies that they typically contain almost no intrinsic charge carriers (i.e., electrons or holes), and thus act as
insulators until electrical charges are injected into them. In electrical device applications this means that all of the holes and electrons within a device must be injected from the anode and cathode respectively. As a result, device stability, performance, and lifetime are greatly influenced by the interface between the organic materials and the electrode contacts. Despite the fundamental importance of the electrode/organic contacts, much of the basic physical understanding of these interfaces remains unclear.

1.2.2 Organic Light Emitting Diodes

An organic light emitting diode (OLED) is an LED in which the active light emitting layer is composed of organic compounds that are electroluminescent, or in other words emit light in response to an electrical current. A typical OLED consists of one or more organic layers sandwiched between an anode and cathode. Typically the anode is made of a transparent conducting oxide (TCO) to allow light to exit the device. Under applied bias holes and electrons are injected from the anode and cathode respectively, and are transported through the various organic layers, until they recombine in the emissive layer to emit light. Typically the emissive layer is composed of either a fluorescent organic small molecule, or a phosphorescent transition metal complex doped into a fluorescent host. Although the first OLED demonstrated by Eastman-Kodak consisted of only a single organic heterojunction formed between two layers of an n- and p-type molecule, modern state-of-the-art OLEDs now consist of multiple n- and p-type layers to facilitate charge injection and transport from the electrode contacts. However, many of these additional layers that have been added over the years are needed, in part to compensate for the less than optimal energy-level alignment at the electrode/organic contacts. Thus, better understanding of these interfaces may provide new strategies for developing highly simplified OLEDs with state-of-the-art performance.

1.2.3 Problem with Existing Electrode Materials

TCOs, such as tin-doped indium oxide (ITO), are the electrode materials of choice in state-of-the-art organic photovoltaics (OPVs), OLEDs and flat-panel displays due to their unique combination of high electrical conductivity and high optical transparency across the visible spectrum. Despite the dominance of ITO in the flat-panel display industry, its surface electronic properties are less than ideal for organic devices. Organic electronic devices, such as OLEDs in particular, fabricated on bare ITO electrodes are usually problematic due to insufficient charge
injection and poor operational stability caused by the large mismatch between the work function of ITO (\(~4.7\) eV) and the highest occupied molecular orbital (HOMO) of the organic materials.\(^2\) Chemical modification of the ITO surface has been extensively studied to control its work function and surface energy for improved charge injection and interfacial stability with organic hole-transporting materials.\(^3\)\(^-\)\(^7\) Unfortunately, chemical surface treatments typically cannot increase the work function of ITO high enough for efficient charge injection into many organic hole transport layers (HTLs), particularly molecules with very deep HOMOs.\(^8\) Additional injection layers, such as copper phthalocyanine (CuPc),\(^2\) poly(3,4-ethylenedioxythiophene:poly(styrenesulfonate) (PEDOT:PSS)\(^9\) or transition metal oxides such as \(\text{WO}_3\),\(^10\) are therefore required to facilitate charge injection from ITO electrodes. However, these additional injection layers may complicate the device design and in some cases introduce additional problems with materials matching. For example, the high acidity of PEDOT:PSS tends to corrode the surface of ITO resulting in poor interfacial stability.\(^11\)

The goal of this thesis is therefore to solve these problems by first gaining a deeper understanding of the physics that governs electrode/organic interfaces, and then applying this new insight to engineering better organic optoelectronic devices that are simpler and cheaper to manufacture.

### 1.3 Outline

The remainder of this thesis is structured as follows: Chapter 2 details the experimental methods used in this work. Chapter 3 presents a comprehensive overview of the theories related to energy-level alignment and charge injection at electrode/organic interfaces. Chapters 4 through 10 presents the major experimental results of this work, each of which has been independently published in a peer-reviewed journal. Finally, Chapter 11 summarizes the major findings of this thesis and discusses relevant future work. Details of the academic contributions that have resulted from this thesis are summarized in Appendix A.
2 Experimental Methods

2.1 Materials

The organic materials used in this work were standard off-the-shelf organic semiconductors available from major suppliers, such as Lumtec.

![Chemical structures of organic materials used in this work](image)

**Figure 2.1:** Organic compounds used in this work.
2.2 Device Design

Two different organic devices were studied in this work, OLEDs and single carrier hole-only devices. For both types of devices a cross-bar structure similar to a passive matrix display was used. Layers of organic molecular are sandwiched between orthogonal anode and cathode lines. The intersection of each cathode (2 mm wide) and anode (1 mm wide) line yields one OLED or single carrier device, with 32 devices per substrate (see Figure 2.2). The active area for all devices was 2 mm\(^2\). A total of four different device structures were fabricated on a single substrate to eliminate possible run-to-run variability caused by subtle variations in process conditions.

Figure 2.2: Layout of OLED and single carrier devices on glass substrates, (a) schematic representation, and (b) picture of real device.

2.2.1 Green OLEDs

OLEDs are used as the primary test platform in this work, since the primary goal is to develop simplified OLEDs with state-of-the-art efficiency. Although most of this work focuses on green OLEDs many of the results are equally applicable to other colours of OLEDs and are also applicable to other organic electronic devices such as OPVs. The Alq\(_3\) device structure from Pioneer® was used as the baseline fluorescent OLED. The standard device structure is as follows: ITO/CuPc (25 nm)/α-NPD (45 nm)/Alq\(_3\) (45 nm)/LiF (1 nm)/Al (100 nm). With proper substrate preparation and deposition conditions the baseline OLED structure has a driving voltage (at 20 mA/cm\(^2\)) of 6 - 7 V, a current efficiency (at 10,000 cd/m\(^2\)) of 4 – 5 cd/A, and a maximum luminance (at 500 mA/cm\(^2\)) of 20,000 – 30,000 cd/m\(^2\). A standard Ir(ppy)\(_2\)(acac) device structure developed internally in the Organic Optoelectronics Research Group was used as the baseline phosphorescent OLED. The standard device structure is as follows: ITO/MoO\(_3\) (1
nm)/α-NPD (35 nm)/CBP:Ir(ppy)_2(acac) (15 nm, 8%)/TPBi (65 nm)/LiF (1 nm)/Al (100 nm). With proper substrate preparation and deposition conditions the baseline OLED structure has a driving voltage (at 1 mA/cm²) of 4 - 5 V, a current efficiency (at 10,000 cd/m²) of 45 – 50 cd/A, and a maximum luminance (at 500 mA/cm²) of > 100,000 cd/m².

**Figure 2.3:** Typically device structure for a multi-layer OLED. For Al cathode the most commonly used buffer layer is LiF. For bottom-emitting OLEDs typically ITO is used as the anode.

### 2.2.2 Single Carrier Devices

In order to accurately determine the inject/transport parameters of organic semiconductors the injection current of organic diodes as a function of voltage and temperature must be measured. However, since most organic semiconductors can transport both holes and electrons, care must be taken to ensure that the total measured current density originates from the contact under study (i.e., uni-polar injection). Hence, single carrier, hole-only or electron-only devices are required; a sufficiently high injection barrier must be present at the other electrode contact to prevent injection of minority carriers. This section will focus on hole-only devices as an example; however, the same concepts can be equally applied to electron-only devices.

In the case of hole-only device a large electron injection barrier is required at the cathode. For most organic semiconductors a high work function metal should be, in principle, sufficient to ensure a significantly large electron injection barrier. However, there are two important caveats to consider: i) if the injection barrier under study is large, then an even larger electron injection barrier is required, and ii) if the organic tends to pin the Fermi level of the electrode near its lowest unoccupied molecular orbital (LUMO) then even a high work function metal may be
insufficient to adequately block electron injection. Luckily, there is a relatively simple way to deal with both of these potential problems. By measuring the injection current as a function of increasing cathode metal work function, selection criteria for a given anode structure can be determined. The point, at which the injection current becomes independent of the cathode metal work function, represents the minimum required work function to sufficiently block electrons for an ideal contact. Au typically makes an excellent cathode for hole-only devices since it is non-reactive and has a high work function (5.1 eV).

![Figure 2.4](image)

**Figure 2.4:** Current density as a function of electric field for α-NPD single carrier hole-only devices with Ni/Ni$_2$O$_3$ anode and Ag cathode. The dashed curves represent the same data corrected for the built-in potential (~ 0.5 V). The electric field ($F$) is taken as $F = V/d$, where $V$ is the voltage and $d$ is the device thickness (98 nm or 443 nm).

Another consideration in the design of single carrier devices is the possibility of a built-in potential due to the difference in work function between the anode and cathode. This built-in potential must be subtracted from the externally applied bias prior to analyzing any experimental data. However, since an interfacial dipole often exists at metal/organic interfaces, the value of any built-in potential is unknown. An interfacial dipole tends to pin the Fermi level at a metal/organic interface, such that the effective work function of the metal is different from the pristine vacuum work function$^{12}$. Hence, the built-in potential cannot be taken as the difference in work function between the anode and cathode. Direct measurement of the built-in potential can be performed using various techniques, such as electro-absorption$^{13}$ (EA) or photovoltaic$^{14}$ measurements. However, the complexity of such measurements in terms of both experimental apparatus and data interpretation, combined with the additional constraints on the device design.
(e.g., semitransparent electrodes for optical techniques), in general preclude their general applicability in determination of the built-in potential. In order to overcome this challenge, the effect of any built-in potential can be minimized by increasing the thickness of the single carrier device. In doing so, the external applied bias can also be increased such that the built-in potential becomes negligible. For an organic semiconductor, such as α-NPD, a layer thickness in the range of 500-1000 nm is usually sufficient to negate the effects of any built-in potential at high electric field strength, within experimental error (see Figure 2.4).

The standard device structure for the single-carrier devices is as follows: anode (25 nm)/organic (~ 500 nm)/cathode (25 nm). Au and Ag were used as the different cathode materials to minimize electron injection.

### 2.3 Device Fabrication

OLEDs and single carrier devices were fabricated in a Kurt J. Lesker LUMINOS® cluster tool using stainless steel shadow masks to define the device structure. The cluster tool is comprised of five high vacuum (HV) process chambers, each with a base pressure of ~ 10⁻⁸ Torr, interconnected by an ultra-high vacuum (UHV) central distribution chamber, with a base pressure of ~ 10⁻⁹ Torr. The process chambers are equipped with independent vacuum pumping and each chamber is dedicated to a different type of thin film deposition or processing technique in order to minimize cross contamination. The process chambers are as follows: an organic chamber for the low temperature deposition of organic molecules, a metallization chamber for the high temperature deposition of metals and oxides, a sputtering chamber for direct current (DC) and radio frequency (RF) magnetron sputtering of refractory metals and ceramics, a “crazy” chamber for the deposition of high vapour pressure materials and hybrid organic-inorganic composites, and a load lock chamber with RF plasma treatment for loading and cleaning substrates and shadow masks.

Single carrier hole-only devices were fabricated in a Kurt J. Lesker LUMINOS® cluster tool using stainless steel shadow masks to define the device structure. Commercially patterned indium tin oxide (ITO) coated glass (50 mm × 50 mm) with a sheet resistance less than 15 Ω/□ was used for all the devices in this study. The ITO was patterned to provide under-pads at the contact points used to probe each device; the ITO only functions as an adhesion layer at the probe points and is not actually part of the device structure.
Substrates were ultrasonically cleaned with a standard regiment of Alconox®, acetone, and methanol followed by ultraviolet (UV) ozone treatment for 15 minutes. The standard device structure is as follows: anode (25 nm)/organic (~ 500 nm)/cathode (25 nm). ITO, Au and Ag were used as the different anode and cathode materials; α-NPD and m-MTDATA were used as the different organic layers. The various organic molecules were deposited from alumina crucibles in a dedicated organic ultra-high vacuum (UHV) chamber with a base pressure of ~ 10⁻⁸ Torr. The cathode lines (2 mm wide) were deposited orthogonally to the anode lines (1 mm wide) from alumina lined molybdenum boats, in a separate metallization chamber with a base pressure of ~ 10⁻⁸ Torr. Additional details of the OLED fabrication using ITO and Au anodes have been discussed elsewhere¹⁵. Film thicknesses were monitored using a calibrated quartz crystal microbalance (QCM). However, the thickness reading from a QCM often drifts with film thickness and time. Since the thickness of the organic layers is critical for injection/transport studies, the thickness of the organic layers were further verified (for each device) using both a stylus profilometer (KLA Tencor P-16+) and capacitance-voltage (CV) measurements (Agilent 4294A). The intersection of each cathode and anode line yields one pixel, with 32 devices per substrate. The active area for all devices was 2 mm².

2.3.1 Substrates

Corning® 1737 glass (50 mm × 50 mm) or commercially patterned (1 mm wide lines) indium tin oxide (ITO) coated glass (50 mm × 50 mm) with a sheet resistance less than 15 Ω/□ were used as substrates for all of the devices in this work. Corning® 1737 glass was used for OLEDs
with metal anodes and ITO coated glass was used for the baseline OLEDs. The ITO coated glass was also used for single carrier devices tested in the cryostat. For single carrier devices with metal anodes, commercially patterned ITO was patterned again to provide under-pads at the contact points used to probe each device; the ITO only functions as an adhesion layer at the probe points and is not actually part of the device structure. All substrates were ultrasonically cleaned with a standard regiment of Alconox®, acetone, and methanol followed by ultraviolet (UV) ozone treatment for 15 minutes.

2.3.2 Thin Film Deposition

The various organic molecules were deposited from alumina crucibles in a dedicated organic chamber. Alkali-metal fluorides (e.g., LiF) were deposited in the same chamber from dedicated pyrolytic boron nitride (BN) crucibles. Al was deposited in a separate metallization chamber from a pyrolytic BN crucible. Au, Ag, Cu, Ni and Co were deposited from the same chamber from alumina lined molybdenum boats. Mg was deposited in a separate chamber from a pyrolytic BN crucible (K-cell). Al₂O₃ was deposited using radio frequency (RF) magnetron sputtering in a separate sputtering chamber. HfO₂ was deposited using a similar procedure from a 99.95% pure HfO₂ target with an RF power of 140 W. V₂O₅ was produced by ex situ ultra-violet (UV) ozone oxidation of 1 nm thick sputtered V films. In all cases film thicknesses were monitored using a calibrated quartz crystal microbalance (QCM) and verified using a stylus profilometer (KLA Tencor P-16+).

2.4 Device Characterization

Current-voltage (IV) characteristics were measured in ambient air using an HP4140B picoammeter in a guarded two-point probe configuration. Luminance measurements were taken using a Minolta LS-110 Luminance meter. Temperature dependent IV characteristics were measured in a homebuilt closed loop He cryostat using an HP4140B picoammeter in a guarded two-point probe configuration. The frequency-dependent capacitance of the devices was measured using an HP4192A impedance analyzer in the variable temperature vacuum cryostat.
2.4.1 Variable temperature cryostat*

A custom homebuilt variable temperature cryostat was built to overcome the limitations of traditional cryostat designs for the rapid testing of organic electronic devices on inexpensive glass substrates. Since the electrical properties of most organic semiconductors tend to “freeze-out” below ~ 100 K, the cryostat does not need to operate anywhere near liquid helium temperatures (~ 4 K), which greatly simplifies the design. The design of the cryostat is modular in order to maximize its versatility and ease of maintenance. The main modules include the cold-finger, sample stage, heater, probe assembly and vacuum system. Each module can be modified or swapped out completely with minimal required changes to the rest of the system.

The cold-finger is based on a closed loop He cryo-cooler (CTI-Cryogenics Model 21 Refrigerator) with two stages of cooling. The first (lower) stage provides up to 8 watts of heat lift at 77 K, and the second (upper) stage provides useable heat lift below 10 K. A copper foil blackbody radiation shield, cooled by the first stage, surrounds the cryo-cooler cold finger and sample stage in order to absorb room temperature radiation from the vacuum chamber walls. The cold-finger and sample stage is schematically depicted in Figure 2.6.

![Diagram of the cryostat](image)

**Figure 2.6:** Schematic representation of the cryo-cooler cold finger and sample stage for the variable temperature cryostat.

The sample stage is a copper block coupled to the second cooling stage of the cold-finger using very ductile indium foil, and can accommodate arbitrarily sized and shaped samples up to 50 mm $\times$ 50 mm. In traditional cryostat designs, indium foil is the *de facto* standard used for mounting samples. However, indium foil requires a considerable compressive force to ensure reliable thermal contact between the sample and stage. In order to simplify the mounting of large or irregularly shaped samples Apiezon® N cryogenic grease is used to bond samples directly to the sample stage. This mounting technique ensures good thermal contact, even for samples with high surface roughness, such as glass substrates. The temperature of the substrates is monitored using a calibrated chromel-alumel (Type K) thermocouple bonded directly to the top of the substrate using the same cryogenic grease. The temperature differential between the stage and top of the sample ranges from 10 – 30 K depending on the operating temperature and thermal conductivity of the substrate. In any given operating range the temperature on the sample is stable to within $\sim$ 20 mK, which is more than sufficient for characterizing most organic semiconductor devices.

**Figure 2.7:** Temperature of the sample stage and substrate as a function of time for a typical cool down cycle in the variable temperature cryostat. The temperature is stable to within 50 mK in less than 45 minutes. The small bump in the curve for the sample temperature at around 35 min is due to a phase transformation in the Apiezon® N cryogenic grease.

The heater is comprised of a resistive heating coil (Manganin 30 AWG wire) wound around a copper block attached to the sample stage using indium foil. The heating coil is coated with silicon heat sink compound (Corning® 340) and encapsulated with UV-curable epoxy in order to maintain good thermal contact between the coil and copper block. The total power of the heater is rated at 25 watts, which is sufficient to maintain the cryostat temperature at 20 – 400 K; cryo-
cooler operating in a fixed cooling mode. The heater power, and hence the cryostat temperature, is controlled using a proportional-integral-derivative (PID) temperature controller (LakeShore 325). Figure 2.7 shows the temperature of the sample stage and a Corning® 1737 glass substrate as a function of time, during a typically cool down cycle from room temperature (300 K) to ~ 200 K.

The probe assembly is composed of several fixed point contact probes mounted directly on the sample stage and a micromanipulator probe arm with translational and rotational degrees of freedom. By employing a common anode or cathode for several devices (i.e. crossbar structure), allows a single probe arm to be used to contact multiple devices. Connections to each probe point are made with micro-coaxial cable, which allows electrical characterization to frequencies > 10 MHz. IV characteristics are measured using an HP4140B picoammeter in a guarded two-point probe configuration. Using this measurement configuration the leakage current for a typical Corning® 1737 glass substrate at room temperature is ~ 1 pA. Data acquisition is fully automated via LabVIEW® running on a general purpose interface bus (GPIB) attached computer.

The vacuum system consists of several vacuum pumps, pressure gauges and a stainless steel chamber that encloses the cryostat. In order to achieve a good insulating vacuum in the cryostat, a 60 l/s turbo-molecular pump station is first used to rough pump the vacuum chamber. After the desired base pressure is reached, typically < 10⁻⁶ Torr, pumping is switched over to a vibration free ion pump. The operating pressure is < 10⁻⁸ Torr at low temperature due to the cryo-pumping effect of the cryo-cooler cold finger (i.e. residual gases condense onto the cold finger). The pressure in the cryostat is monitored using a thermocouple gauge and Bayard-Alpert (ion) gauge.

### 2.5 Photoelectron Spectroscopy

Thin film characterization using photoelectron spectroscopy (PES) of ex situ prepared samples and in situ deposited organic films are performed in a Kurt J. Lesker multi access chamber (MAC) cluster tool with an attached PHI 5500 multi-technique surface analytical system. The cluster tool is comprised of five UHV process chambers, each with a base pressure of ~ 10⁻⁹ Torr, a PHI 5500 analysis chamber with a base pressure of ~ 10⁻¹⁰ Torr, and an interconnecting UHV central distribution chamber with a base pressure of 10⁻⁹ Torr. Similar to the LUMINOS® cluster tool the process chambers are equipped with independent vacuum pumping and each
chamber is dedicated to a different type of thin film deposition or processing technique in order to minimize cross contamination. The process chambers are as follows: an organic chamber for the low temperature deposition of organic molecules, a molecular beam epitaxy (MBE) chamber for annealing and the high temperature deposition of metals and oxides, a UV ozone treatment chamber for the \textit{in situ} oxidation and cleaning of samples, a “flipping” station for manipulating the sample holder, and a load lock chamber for loading samples. The PHI 5500 is equipped with a hemispherical electron energy analyzer, a monochromatic Al K\(\alpha\) (\(h\nu = 1486.6\) eV) source for X-ray photoelectron spectroscopy (XPS), a He I (\(h\nu = 21.22\) eV) discharge lamp for ultraviolet photoelectron spectroscopy (UPS), and an Ar\(^+\) sputter ion gun for cleaning samples and depth profiling.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{kurt_lesker_mac_cluster_tool_with_attached PHI 5500.png}
\caption{Kurt J. Lesker MAC cluster tool with attached PHI 5500.}
\end{figure}

\section*{2.6 Work Function Measurements\footnote{This section published as \textit{Appl. Surf. Sci.} 256, 2602 (2010).}}

\subsection*{2.6.1 Background}

Work function (i.e., the minimum energy required to remove an electron from the surface of a solid) is an important parameter in the study of surfaces and interfaces.\footnote{This section published as \textit{Appl. Surf. Sci.} 256, 2602 (2010).} Many interfacial chemical and electrical properties are related to the work function of a material. Hence, experimental determination of work function is critical to many scientific endeavours and
engineering applications. Photoelectron spectroscopy (PES) is one of the most commonly used techniques used to measure the absolute work function of a sample. Most reliable tabulated work function values are from PES measurements. However, despite the importance of this technique, there is relatively little discussion in the literature of how to properly perform work function measurements using PES. Arguably, PES is a mature enough technique that such discussion should be readily available in textbooks. However, the frequency of errors in reported PES work function measurements highlights the need for an up-to-date discussion of common pitfalls. By its very nature PES is extremely sensitive to subtle changes in the experimental conditions. As a result, there is significant disagreement in the literature over reported work function values, even for well controlled sample surfaces (e.g., Ag single crystal).

2.6.2 Theory

PES relies on the analysis of the kinetic energy of photoelectrons emitted from the surface of a sample upon irradiation by a mono-energetic photon source. The kinetic energy of the emitted electrons is typically measured using an electron energy analyzer (spectrometer), such as a spherical capacitance analyzer (SCA) equipped with an electrostatic lens system to more efficiently collect and focus the emitted photoelectrons. XPS uses soft x-rays as the photon source, such as monochromatic Al Kα (hv = 1486.7 eV). XPS is the most common embodiment of PES and is often used to study surface chemical composition. UPS is another commonly used variation of PES that utilizes lower energy vacuum ultraviolet (VUV) photons, such as He Iα (hv = 21.22 eV). UPS is more commonly used than XPS for work function measurements due to the superior line width and high photon flux from laboratory VUV sources, such as noble gas discharge lamps.

Before beginning the discussion of work function measurements, a review of the basic concepts concerning the electron work function is required. The work function of a uniform surface of a conductor is defined as the minimum energy required to remove an electron from the interior of the conductor to just outside the surface, where “just outside” refers to a distance that is large enough that the image force is negligible, but small compared to the physical dimensions of the crystal (typically ~ 10^{-4} cm). In other words, the work function is the difference between the electrochemical potential \( \mu \) of electrons in the bulk and the electrostatic potential energy \( -e\Phi_{\text{vac}} \) of an electron in the vacuum just outside the surface,
\[ e\phi_m = -e\Phi_{\text{vac}} - \mu \, . \] (2.1)

The energy-level corresponding to \(-e\Phi_{\text{vac}}\) is referred to as the *local* vacuum level \(E_{\text{vac}}\) and is not to be confused with the vacuum level at infinity \(E_0\), which represents an electron at rest at infinity (i.e., zero potential energy).\(^{36,37}\) Since the Fermi level \(E_F\) relative to the vacuum level at infinity \(E_0\) is the electrochemical potential of electrons in the conductor,\(^{38}\)

\[ E_0 - E_F = -\mu \, , \] (2.2)

the work function given by Equation (2.1) is equivalent to the difference in potential energy of an electron between the local vacuum level \(E_{\text{vac}}\) and the Fermi level,

\[ e\phi_m = E_{\text{vac}} - E_F \, . \] (2.3)

From Equation (2.3) it is clear that if the local vacuum level \(E_{\text{vac}}\) varies across a sample, as is the case for the different faces of a single crystal, the work function will also vary.\(^{35}\)

From the photoelectric effect the maximum kinetic energy of a photoelectron is given by,

\[ E_{K,\text{max}} = h\nu - e\phi_m \, , \] (2.4)

where \(E_K\) is kinetic energy and \(h\nu\) is the photon energy. This maximum kinetic energy occurs for a photoelectron emitted from the Fermi level. By varying the photon energy the work function in principle can be determined from the threshold photon energy required for the onset of photoemission. This was in fact one of the original methods used to measure work function.\(^{35}\) However, in PES measurements typically only a single photon energy is used and hence another methodology is required.

Based on Equation (2.4) the local kinetic energy of a photoelectron emitted from an energy-level with binding energy \(E_B\) below the Fermi level is given by,

\[ E_K = h\nu - E_B - e\phi_m \, , \] (2.5)
where $E_B$ is the binding energy of the electron referenced to the Fermi level. In PES measurements the sample is in electrical contact with the spectrometer, resulting in a contact potential difference $\Delta \phi = (\phi_m - \phi_s)$ due to a difference in local vacuum level between the sample and spectrometer, where $\phi_s$ is the work function of the spectrometer.\textsuperscript{33,34} The measured kinetic energy of a photoelectron in PES is therefore given by,

$$E_{K,\text{meas}} = h\nu - E_B - e\phi_m + \Delta \phi = h\nu - E_B - e\phi_s$$

(2.6)

As a result the measured kinetic energy $E_{K,\text{meas}}$ of a photoelectron in PES is independent of the sample work function. This effect is schematically depicted in Figure 2.9a. Nonetheless, the work function of the sample can still be determined by correcting for the built-in potential $\Delta \phi$ (i.e., by taking the width of the photoelectron spectrum),

$$e\phi_m = h\nu - (E_{K,\text{meas}}^{\text{max}} - E_{K,\text{meas}}^{\text{min}}),$$

(2.7)

where $E_{K,\text{max}}^{\text{meas}}$ is the maximum measured kinetic energy of an electron emitted from the Fermi level and $E_{K,\text{min}}^{\text{meas}}$ is the minimum measured kinetic energy in the photoelectron spectrum (i.e., the zero of the kinetic energy scale relative to the sample), as shown in Figure 2.10. For semiconductors the Fermi level typically falls in the band gap, which means that $E_{K,\text{max}}^{\text{meas}}$ must be determined from a metal sample in electrical contact (i.e., the Fermi levels are aligned) with the semiconductor sample.
Figure 2.9: Schematic energy-level diagram for a conductive sample in electrical contact with the spectrometer, (a) photoemission process for an electron excited from a core level with binding energy ($E_b$), and (b) the effect of an applied bias ($V_b$) between the sample and spectrometer. The Fermi level ($E_F$), local vacuum level of the sample ($E_{vac}$), sample work function ($\phi_m$), local vacuum level of the spectrometer ($E_{vac}^S$), spectrometer work function ($\phi_s$), photon energy ($h\nu$), kinetic energy of the emitted photoelectron ($E_K$), and measured kinetic energy of the emitted photoelectron ($E_{K,meas}$) are as shown.

Figure 2.10: He I\(\alpha\) ($h\nu = 21.22\,\text{eV}$) valence band spectrum of an Ar\(^+\) sputter cleaned Au film on Si(100). The spectrum was collected with a photoelectron take-off angle ($\theta$) of 90° and with a -10 V bias ($V_b$) applied to the sample. The kinetic energy scale has already been corrected for the applied bias. The high intensity peak at low kinetic energy corresponds to the SEC region of the spectrum. The energetic position corresponding to $E_{K,\text{max}}^{\text{meas}}$ (Fermi level) and $E_{K,\text{min}}^{\text{meas}}$ are as shown. The inset of the figure shows the corresponding schematic energy-level diagram for the sample and spectrometer.
The point of minimum kinetic energy in a photoelectron spectrum $E_{K,\text{min}}^{\text{meas}}$ occurs in the region of the spectrum typically referred to as the secondary-electron cut-off (SEC) since i) the majority of the signal is comprised of low kinetic energy secondary electrons, and ii) in this region the spectrum is suddenly “cut-off” due to the local vacuum level. In other words an electron leaving the sample with energy less than $E_{\text{vac}}$ has insufficient kinetic energy to escape, and hence does not contribute to the photoelectron spectrum. This implies that the electrons of interest leave the sample with zero kinetic energy. However, it is extremely difficult, if not impossible, to measure electrons leaving the sample with zero kinetic energy. Even electrons with near zero kinetic energy may have insufficient energy to make it into the spectrometer. Therefore, a small negative bias is typically applied to the sample when measuring the SEC region of the spectrum. This bias helps accelerate the lowest kinetic energy electrons into the spectrometer (and also helps to overcome the contact potential difference), as schematically shown in Figure 2.9b. Since an applied bias offsets all of the energy levels in the sample, Equation (2.7) is still valid.

### 2.6.3 Results and Discussion

Figure 2.10 shows a typical He Iα ($h\nu = 21.22$ eV) valence band spectrum for an Ar$^+$ sputter cleaned Au film. The high intensity peak at low kinetic energy corresponds to the SEC region of the spectrum. The positions of $E_{K,\text{max}}^{\text{meas}}$ (Fermi level) and $E_{K,\text{min}}^{\text{meas}}$ used in Equation (2.7) are indicated on the spectrum. The inset of the figure shows the corresponding schematic energy-level diagram for the sample and spectrometer. Using Equation (2.7) the calculated work function of the sample is $5.33 \pm 0.05$ eV, consistent with values in literature for Au.\textsuperscript{39}

As discussed above, measuring work function using PES relies on accurate determination of the energetic position of $E_{K,\text{min}}^{\text{meas}}$ at the low kinetic energy edge of the SEC region. However, since the SEC region of the spectrum is derived from electrons with near zero kinetic energy, its shape and position can be significantly influenced by subtle changes in the local electromagnetic field. Of particular importance is the direction of the electric field at the surface of the sample relative to the trajectory of an emitted electron. Since the electric field at the surface of a conductor (sample) is perpendicular to the surface, only electrons emitted normal to the surface will experience a purely tangential acceleration. As a result, the sample must be perpendicular to the
detector in order to prevent the lowest kinetic energy electrons from experiencing a normal acceleration away from the detector.

**Figure 2.11**: Measured work function of Ar\(^+\) sputter cleaned Au film using as a function of photoelectron take-off angle (\(\theta\)) and applied sample bias (\(V_s\)). The inset shows the geometry of the sample relative to the photon source (He discharge lamp) and spectrometer.

Figure 2.11 shows the measured work function of the same Au film from Figure 2.10 as a function of applied sample bias and photoelectron take-off angle. As expected the work function measurements deviate significantly (and are bias dependent) for photoelectron take-off angles less than 90° (see inset of Figure 2.11). For photoelectron take-off angles less than 90° the emitted photoelectrons experience a normal acceleration away from the spectrometer since the electric field at the surface of the sample points away from the spectrometer. The lowest kinetic energy photoelectrons are therefore swept away from the spectrometer due to the normal acceleration, resulting in \(E_{K,\text{min}}^{\text{meas}}\) shifting to higher kinetic energy, which incorrectly yields a higher work function value. This effect is schematically depicted in Figure 2.12. Also, for higher applied sample bias the electric field at the surface of the sample is also higher, resulting in an even more significant normal acceleration away from the spectrometer.
Figure 2.12: Finite element simulation of the electric field between a conductive sample and the grounded lens of the spectrometer, with an applied bias of -15 V. The electron trajectories (± 90°) from a point source at the sample surface are also shown. The angular distributions of the electron point sources are identical at the sample surface, however the trajectories of the slow (0.25 eV) electrons are severely distorted by the electric field, such that at a photoelectron take-off angle of 45° none of the slow electrons are directed into the lens. Note that the trajectories of the higher kinetic energy electrons are not significantly affected by the electric field.

Work function measurements using PES must therefore always be taken with the sample perpendicular to the detector (i.e., at a photoelectron take-off angle of 90°). This necessary condition has often been overlooked in previous discussions of PES work function measurements.
Figure 2.13: SEC region of the UPS spectrum of a laterally inhomogeneous “patchy” Au film. The sample was prepared by partially Ar⁺ sputter cleaning an air exposed Au film for several seconds. Reference spectra for air exposed Au (dirty) and Ar⁺ sputter cleaned Au (clean) is also shown. The spectra were collected with a photoelectron take-off angle (θ) of 90° and with a -15 V bias (V_b) applied to the sample. The kinetic energy scale has already been corrected for the applied bias. Three distinct peaks are observed in the spectrum corresponding to patches with different work functions, namely: εΦ₁ ≈ 4.9 eV, εΦ₂ ≈ 5.1 eV, and εΦ₃ ≈ 5.3 eV. The two lower work function values correspond to dirty Au, while the third value is for clean Au.

Based on Equation (2.7) it is clear that $E_{K,min}^{meas}$ scales with work function. Hence the signal from the SEC of a patch with lower work function will tend to bury the signal from a patch with higher work function. Therefore, PES measurements tend to yield the lowest work function patch on a non-uniform surface. Figure 2.13 shows the SEC region for a patchy Au film. The signal from the high work function (clean) patches is almost completely buried by that from the lower work function (dirty) patches. Since nearly all surfaces, including single crystals, exhibit some degree of patchiness this is an important point to consider, particularly when comparing PES work function measurements to values obtained by other techniques, such as Kelvin probe, which measure an average value of work function. As a result the shape of the SEC region of the spectrum is an extremely sensitive indication of surface cleanliness. Since adsorbed contaminates tend to lower the work function of clean metals, the presence of any low kinetic energy tail in the SEC region of the spectrum is an indication of residual contaminates, which may be below the
detection limit of other techniques such as XPS. Such tail features in the SEC region are often found in many spectra of apparently “clean” surfaces reported in literature, but have been largely ignored.
3 Background Theory*

3.1 Energy-level Alignment at Electrode/Organic Interfaces

Of particular interest for device applications is the energy-level alignment at the electrode/organic interfaces, or in other words the alignment of the molecular orbitals of the organic to the energy-levels of the electrode (typically the Fermi level). For traditional inorganic semiconductors the energy-level alignment at semiconductor/metal contacts is typically described by the Schottky barrier height, which is the potential barrier between the Fermi level of the metal and the conduction band or valence band edge of the semiconductor. Analogous to the Schottky barrier height at semiconductor/metal interfaces, the energy-level alignment at electrode/organic interfaces is also typically represented by an injection barrier height $\phi_B$. This injection barrier represents the potential barrier which must be overcome to move an electrical charge from the Fermi level of the electrode into the highest occupied molecule orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) of the organic (or vice versa). The operating voltage of a device is directly related to the magnitude of the injection barrier height. Since the injected current is typically exponentially dependent on the barrier height, even a small change on the order of ~0.1 eV can have a drastic effect on device performance. Matching the energy-levels of the organic materials to those of the electrodes is thus critical to achieving high efficiencies.

3.1.1 Work Function

The work function of a uniform surface of a conductor is defined as the minimum energy required to remove an electron from the interior of the conductor to just outside the surface, where “just outside” refers to a distance that is large enough that the image force is negligible, but small compared to the physical dimensions of the crystal (typically $\sim 10^{-4}$ cm). In other words, the work function is the difference between the electrochemical potential $\mu$ of electrons in the bulk and the electrostatic potential energy $-e\Phi_{vac}$ of an electron in the vacuum just outside the surface, $^{35}$

* This chapter published as Electrode organic interface physics in the book Encyclopedia of Nanotechnology (In press).
The energy-level corresponding to \(-e\Phi_{\text{vac}}\) is referred to as the *local* vacuum level \(E_{\text{vac}}\) and is not to be confused with the vacuum level at infinity \(E_0\), which represents an electron at rest at infinity (i.e., zero potential energy). 36 Since the Fermi level \(E_F\) relative to the vacuum level at infinity \(E_0\) is the electrochemical potential of electrons in the conductor, 38

\[
E_0 - E_F = -\bar{\mu},
\]

the work function given by Equation (3.1) equivalent to the difference in potential energy of an electron between the local vacuum level \(E_{\text{vac}}\) and the Fermi level,

\[
e\phi_{\text{m}} = E_{\text{vac}} - E_F.
\]

From Equation (3.3) it is clear that if the local vacuum level \(E_{\text{vac}}\) varies across a sample, as is the case for the different faces of a single crystal, the work function will also vary.

### 3.1.2 Schottky Contacts

The energy-level alignment at semiconductor/metal contacts has been extensively studied owing to their importance in microelectronics. In the Schottky-Mott limit the vacuum level of the semiconductor and metal align, forming a region of net space charge at the interface. No charge is transferred across the interface and hence the semiconductor bands are forced to bend to accommodate the potential difference. The Schottky barrier height for electrons is then given by the difference between the work function of the metal \(\phi_m\) and the electron affinity of the semiconductor \(\chi\) (i.e., the conduction band edge).
Figure 3.1: (a) Schottky-Mott limit and (b) pinning of the Fermi level by induced interface states.

However, the Shottky-Mott limit has been rarely observed so far at most metal/semiconductor interfaces due to charge transfer across the interface (i.e., an interfacial dipole). As a result the Fermi level cannot move freely in the band gap of the organic and thus tends to be pinned by the dipole layer. The interface slope parameter is a convenient parameter that quantifies this phenomenon, and is commonly defined in terms of the Schottky barrier height for an electron or hole,\textsuperscript{30}

\[
S_{\phi} \equiv \frac{d\phi_{Bn}}{d\phi_{m}} = -\frac{d\phi_{Bp}}{d\phi_{m}},
\]

where $S_{\phi}$ is the interface slope and $\phi_{Bn}$ and $\phi_{Bp}$ are the barrier heights for electrons and holes respectively. In the Shottky-Mott limit $S_{\phi} = 1$ (vacuum level alignment); and for Fermi level pinning $S_{\phi} = 0$ (interfacial dipole).

In the case of organic semiconductors many studies have experimentally demonstrated a strong correlation between the metal work function and the barrier height for holes or electrons. In analogy to inorganic semiconductors, in the Schottky-Mott limit the vacuum level of the organic and metal align, forming a region of net space charge at the interface. The barrier height for holes is then given by the offset between the HOMO of the organic $E_{HOMO}$ and the work function of the metal,

\[
e\phi_{Bp} = E_{HOMO} - e\phi_{m}.
\]

However, since organic semiconductors contain almost no free charge carriers, band bending in the organic cannot fully accommodate the potential difference. Hence, the Shottky-Mott limit is
rarely observed at metal/organic interfaces due to the formation of a strong interfacial dipole between the metal surface and organic molecules. Accounting for the effect of an interfacial dipole the injection barrier for holes is then given by the following,

$$e\phi_{Bp} = E_{\text{HOMO}} - e(\phi_m - \Delta).$$  \hspace{1cm} (3.6)

From the above equation it is clear that a negative dipole reduces the hole injection barrier, while a positive dipole enhances electron injection. From Equation (3.6) an effective metal work function can be defined as the difference between the pristine metal work function and the dipole,

$$\phi_{m,\text{eff}} = \phi_m - \Delta,$$  \hspace{1cm} (3.7)

where $\phi_{m,\text{eff}}$ is the effective metal work function.

### 3.1.3 Interface Dipole Theory

Deviation from the Shottky-Mott limit was first described by Bardeen\textsuperscript{41} as the result of a large density of surface states; charge transfer between the metal and these surface states acts to pin the Fermi level. In fact surface states were first postulated by Tamm and Shockley prior to the Schottky model, but were largely ignored. Heine\textsuperscript{42} later demonstrated that surface states do not exist in the gap of most metal/semiconductor interfaces, or at least not for modern devices produced by the high vacuum deposition of metal onto a clean semiconductor surface. In Bardeen’s time semiconductor/metal contacts were formed by laminating a piece of metal and semiconductor, which inherently results in a “dirty” interface. Heine postulated that for a “clean” interface, gap states are induced in the semiconductor as a result of the rapidly decaying tail of the electronic wave function from the metal. These gap states would also tend to pin the Fermi level same as for Bardeen’s surface states. Tersoff\textsuperscript{43} later identified the gap states as metal induced gap states (MIGs), which derive from the virtual gap states (VIGs) of the semiconductor complex band structure.

Regardless of their specific origin, interface states are independent of the energy levels in the semiconductor, and hence can either be donor-like or acceptor-like when close to the valence or conduction bands respectively. A charge neutrality level $\phi_{\text{CNL}}$ is defined as the point at which the interface states are equally donor- and acceptor-like (i.e., the transition point from donor to
acceptor states). Cowley and Sze\textsuperscript{44} applied this notion to derive the dependence of the Schottky barrier height upon the metal work function. They argued that at semiconductor/metal interfaces the charge neutrality level of the semiconductor will tend to align with the Fermi level of the metal as a result of charge transfer between the metal and the interface states, forming an interfacial dipole. In other words, the redistribution of charge at the interface (dipole) offsets the vacuum level of the metal and semiconductor, resulting in an effective metal work function that is different from the vacuum metal work function,

$$\phi_{m,\text{eff}} = \phi_{\text{CNL}} + S\phi (\phi_m - \phi_{\text{CNL}}).$$  \hspace{1cm} (3.8)

The interfacial dipole is then the difference between $\phi_{m,\text{eff}}$ and $\phi_m$.

$$\Delta = (1 - S\phi)(\phi_m - \phi_{\text{CNL}}).$$  \hspace{1cm} (3.9)

### 3.1.4 Interface Slope Parameter

In their analysis, Cowley and Sze assumed a constant continuum of interface states across the semiconductor gap. Based on this assumption, the interface slope parameter, which in this context represents the dielectric screening strength of the semiconductor, is given by,

$$S\phi = \frac{\epsilon_i}{\epsilon_i + e\delta D_s},$$  \hspace{1cm} (3.10)

where $\epsilon_i$ is the interface permittivity, $\delta$ is the characteristic thickness of the interface (atomic length) and $D_s$ is the density of interface states. However, since these parameters can only be measured indirectly, accurate determination of the interface slope parameter using Equation (3.10) is problematic at best. Luckily, Mönch\textsuperscript{45} empirically found that the interface slope parameter (for weakly interacting interfaces) is dependent on the optical dielectric constant,

$$S\phi = \frac{1}{1 + 0.1(\epsilon_{\infty} - 1)^2},$$  \hspace{1cm} (3.11)

where $\epsilon_{\infty}$ is the optical dielectric constant (high frequency limit of the dielectric function). One important caveat to consider for Equation (3.11) is that it only accurately describes the interface slope parameter for weakly interacting and laterally homogenous Schottky contacts. If interfacial
chemical reactions occur, or if the interface is patchy, then $S_\phi$ often deviates from the ideal theoretical dielectric value.

Recently it was shown that organic semiconductors also follow the same empirical relationship between $S_\phi$ and $\varepsilon_\infty$ described by Equation (3.11), same as for Schottky contacts with solid Xenon. However, many organic molecules either interact fairly strongly with clean metal surfaces or do not wet the surface of metals uniformly. The experimentally determined value of $S_\phi$ for clean metal surfaces, is therefore often different than the ideal theoretical value described by Equation (3.11). For example, the experimental value of $S_\phi$ for $C_{60}$ is nearly 0, while the theoretical value is 0.53 assuming $\varepsilon_\infty = 4$. In this case it is well known that $C_{60}$ interacts strongly with most clean metal surfaces, which results in complete pinning of the Fermi level (i.e., $S_\phi = 0$). For terminated surfaces, such as an oxidized metal surface (e.g., Al/Al$_2$O$_3$), the interaction between the metal and organic is screened by the adsorbed surface termination layer. In this case, $S_\phi$ approaches the ideal theoretical value for a weakly interacting interface. Metal oxides in particular form ideal contacts with most organics since the first layer of adsorbed molecules tends to wet the oxide surface, forming a laterally homogeneous contact. One important consequence of this is that a clean metal and oxide terminated metal will behave differently in contact with an organic semiconductor, even if the effective metal work function of the oxide terminated metal is the same as the work function of the clean metal surface. In general, the clean metal will pin the Fermi level stronger than the oxide terminated metal.

Since the interfacial dipole is indicative of charge transfer between the metal and semiconductor, electronegativity is often used in place of work function to describe the dependence of barrier height on the contacting metal. In this case a linear dependence of the injection barrier on the electronegativity difference of the metal and semiconductor is observed,

$$
\phi_{m,\text{eff}} = \phi_{\text{CNL}} + S_x (X_m - X_s),
$$

where $X_m$ and $X_s$ are the electronegativity of the metal and semiconductor respectively and $S_x$ is the electronegativity-based interface slope parameter given by,

$$
S_x = \frac{d\phi_{pm}}{dX_m} = -\frac{d\phi_{np}}{dX_m}.
$$
One important distinction between the two different interface slope parameters is that $S_{\phi}$ is a dimensionless quantity with an upper limit of 1, while $S_x$ on the other hand is not dimensionless and has an arbitrary upper limit depending on the units of electronegativity used. There have been several attempts to link the two interface slope parameters via a constant of proportionality,

$$S_{\phi} = A_x S_x,$$

where the value of $A_x$ varies depending on the electronegativity scale used. In the case of organic semiconductors there is no clear definition of electronegativity and hence previous attempts to relate injection barriers at metal/organic interfaces to electronegativity values are in general not very useful.

### 3.1.5 Metal/Organic Interfaces

Experimental determination of the interface slope parameter and charge neutrality level is usually done by fabricating Schottky junctions with different metals. The Schottky barrier height for holes or electrons is then plotted vs. the work function of the different metals. From Equation (3.13) the slope of a linear fit to this plot is the interface slope parameter. The charge neutrality level can be extracted from the intercept of the linear fit with the $y$-axis. Since the charge injection barrier height for holes or electrons is linearly related to the effective work function of the metal (e.g., $\phi_{bn} = \phi_{m,\text{eff}} - \chi$), the slope of a linear fit to a plot of effective metal work function vs. the pristine metal work function will also yield the interface slope parameter. The convenience with this approach is that the charge neutrality level can be directly read off as the intersection of the linear fit with a line of slope one (i.e., $\phi_{m,\text{eff}} = \phi_m = \phi_{\text{CNL}}$).
Figure 3.2: Effective work function for different work function anodes at metal/m-MTDATA contacts.

For organic semiconductors a similar experimental approach can be used by fabricating various single carrier devices with different metal electrodes. Figure 3.2 shows the effective metal work function vs. the pristine metal work function (of the anode) for m-MTDATA single carrier hole-only devices with different metal anodes. The slight scatter in the data is attributed to laterally inhomogeneous contacts at the metal/organic interface, which is not surprising given the difference in wettability of organic molecules on different metal surfaces. Nonetheless a clear trend in the data is observable. A linear fit to this data (solid line) yields a value of the interface slope parameter for m-MTDATA of \( S_\phi = 0.1 \); hence m-MTDATA is a strongly pinning material. The Schottky-Mott limit is also shown (dashed line) as the upper limit for a non-pinning materials (i.e., \( S_\phi = 1 \)). The charge neutrality level for m-MTDATA is then taken as the intercept of these two lines, namely \( \phi_{\text{CNL}} = 4.1 \text{ eV} \).

Once again it is important to distinguish the difference between the experimentally determined value of the interface slope parameter for m-MTDATA on clean metals, and the ideal dielectric value predicted by Equation (3.11). Taking the dielectric constant of m-MTDATA as \( \varepsilon_\infty = 3 \) yields a theoretical value of \( S_\phi = 0.71 \), which obviously significantly differs from the experimentally determined value of \( S_\phi = 0.1 \). As discussed above the theoretical value predicated by Equation (3.11) is for a weakly interacting lateral homogeneous interface. Many organic molecules, including m-MTDATA, interact strongly with clean metal surfaces resulting in a much reduced value of the interface slope parameter (i.e., stronger pinning). Hence, \( S_\phi = 0.1 \) is...
representative of strongly interacting metal/m-MTDATA interfaces, while $S_{\phi} = 0.71$ is representative at weakly interacting metal/dielectric/m-MTDATA interfaces.

### 3.2 Charge Injection at Electrode/Organic Interfaces

Up to this point only the barrier height at electrode/organic interfaces has been discussed. However, in real devices what is measured is the flow of current through the device as a function of applied bias. Therefore how the barrier height discussed above affects the injection and transport of charge in real devices is of interest. At traditional semiconductor/metal interfaces the process of charge injection is typically divided into two different regimes, space charge limited current (SCLC) and injected limited current (ILC).

#### 3.2.1 Space Charge Limited Current

The first regime, which represents the maximum current that a semiconductor can sustain in the bulk (i.e., the amount of carriers in thermal equilibrium), is called the SCLC. A semiconductor/metal contact capable of injecting enough charges to sustain the SCLC is called an Ohmic contact. In most traditional semiconductors an Ohmic contact is assumed to represent a zero barrier height. One significant feature of SCLC is that the spatial distribution of electric field is described by $F(x) \propto x^{1/2}$, where $x$ is the distance from the charge-injecting contact. The electric field at the interface of an Ohmic contact is therefore equal to zero. For uni-polar transport (i.e., transport of only one type of charge carrier) in a perfect insulator (no intrinsic carriers) without traps the SCLC is given by the Mott-Gurney law,

$$J = \frac{9}{8} \varepsilon_0 \varepsilon \mu \frac{V^2}{d^3},$$

where $V$ is the applied voltage, $d$ is the thickness of the film, and $\mu$ is the field-independent mobility.

With further consideration of an exponential distribution of trap states, the trap charged limited current (TCLC) based on Equation (3.15) follows,

$$J \propto \mu \frac{V^{l+1}}{d^{2l+1}},$$

(3.16)
where \( l \) is a parameter derived from the trap distribution. Notice that the injection of charge depends only on the mobility, thickness of the semiconductor and applied voltage as the barrier height is assumed to be zero.

In the case of organic semiconductors, however, the mobility typically depends on electric field. In disordered organic materials, it is believed that all electronic states are localized and participate in conduction through thermally activated hopping, which yields a Poole-Frenkel like field dependence of the mobility,

\[
\mu(F) = \mu_0 \exp(\beta \sqrt{F}).
\]  

Under the assumption of a Poole-Frenkel dependence, an approximation to the SCLC for a field dependent mobility is given by,

\[
J_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon \mu_0 \exp \left( 0.89 \beta \sqrt{\frac{V}{d}} \right) \frac{V^2}{d^2}.
\]  

There has been significant experimental evidence that this model does indeed describe the SCLC in many organic semiconductors. One interesting caveat however due to the hopping based transport in organic materials is that the barrier height for an Ohmic contact does not have to be zero in the typically operating electric field range of most device applications. Specific criteria for determining this critical threshold barrier height will be discussed in detail below.

### 3.2.2 Injection Limited Current

The second regime of charge injection in semiconductors represents the situation where a significant barrier height exists at the interface, such that the transport of charge in the semiconductor is limited by the injection of charge at the semiconductor/metal contact. The ILC at Schottky contacts has traditionally been described by one of two processes. For high electric field strength and large barrier heights, Fowler–Nordheim (FN) tunnelling, also known as field emission, dominates the injection current,

\[
J_{FN} = \frac{q^3 F^2}{8 \pi \hbar \phi_B} \exp \left[ \frac{-8 \pi \sqrt{\frac{2m}{q^3 \phi_B^3}}}{3qhF} \right].
\]  

where \( F \) is the electric-field strength, \( \phi_B \) is the barrier height, \( m^* \) is the effective mass of an electron or hole in the semiconductor, \( q \) is the electronic charge and \( h \) is the Planck constant. For
thermally activated processes at lower electric field, Richardson-Schottky (RS) emission, also known as thermionic emission, dominates the injection current,

$$J_{RS} = A^*T^2 \exp \left[ -\frac{\left( \phi_B - \sqrt{qF/4\pi\varepsilon} \right)}{k_BT} \right]$$  \hspace{1cm} (3.20)

where \( A^* \) is the modified Richardson constant, \( \varepsilon \) is the permittivity of the semiconductor, \( k_B \) is the Boltzmann constant and \( T \) is the temperature.

In the case of organic semiconductors, the ILC was early on modeled as diffusion-limited thermionic emission. However, both FN tunnelling and RS emission are derived for delocalized Bloch waves in the semiconductor, whereas the electronic states in most organic semiconductors are highly localized due to their discrete molecular nature. In addition, at room temperature FN tunnelling typically requires electric field strengths on the order of \( 10^6 \) V/cm, which are greater than what are observed in real organic devices (\( \sim 10^5 \) V/cm).

To overcome these deficiencies Scott and Malliaras\(^{48}\) have proposed a modified thermionic emission model for the ILC in organic semiconductors based on the original solution to the drift diffusion equation for injection into a wide band gap intrinsic semiconductor solved by Emtage and O’Dwyer.\(^{49}\) This model determines the equilibrium contributions to the current density for charge carriers recombining with their own image analogous to Langevin recombination of an electron-hole pair in the bulk,

$$J_{ILC} = 4N_0\psi^2 e\mu F \exp \left( \frac{-e\phi_B}{k_BT} \right) \exp(f^{1/2})$$  \hspace{1cm} (3.21)

where \( N_0 \) is the density of chargeable sites in the organic film, \( \phi_B \) is the barrier height, \( F \) is the electric field at the charge-injecting contact, \( \mu \) is the electric field dependent mobility, \( k_B \) is the Boltzmann constant, \( T \) is temperature, \( e \) is the electron charge and \( \psi \) is a function of the reduced electric field (\( f = e^3F/4\pi\varepsilon k_BT^2 \)),

$$\psi = f^{-1} + f^{-1/2} - f^{-1} (1 + 2f^{1/2})^{1/2}$$  \hspace{1cm} (3.22)

There has been significant experimental evidence that this model does indeed describe the ILC in many organic semiconductors. Also, under ILC conditions the spatial electric field distribution is
assumed to be uniform such that $F(x) = V/d$; whereas for SCLC the value of $V/d$ only gives the average value of the electric field. This suggests that SCLC can be distinguished from ILC by the electric field at the electrode/organic interface.
4 Energy-level Alignment at Metal/Oxide/Organic Interfaces*

4.1 Background

In the case of traditional semiconductors, such as Si or GaAs, it is widely accepted that interface dipole theory most accurately predicts the band alignment for Schottky contacts formed at metal/semiconductor interfaces. The theory describes the formation of an interfacial dipole due to the charging of intrinsic interface states, which tends to drive the band alignment towards a zero net dipole charge (see the previous chapter for further details). Recently, Mönch argued that this theory can also be used to describe metal/organic interfaces. However, despite the surprising accuracy of interface dipole theory in describing traditional metal/semiconductor contacts, there has been no direct experimental evidence to demonstrate its relevance to predicting injection barrier heights at electrode/organic interfaces in real organic electronic devices.

In this chapter it is demonstrated that the hole injection barriers predicted by the interface dipole theory are in excellent agreement with the barrier heights extracted from carrier transport measurements performed on single carrier hole-only devices for a variety of metal/organic and metal/oxide/organic archetype systems.

4.2 Methods

Single carrier hole only devices were fabricated on Corning® 1737 glass substrates (50 mm × 50 mm). The standard device structure is as follows: anode (20 nm)/oxide (0, 1 nm)/organic (500 nm)/Au (20 nm). The organic thickness was chosen as 500 nm in order to ensure that any built-in potential is negligible compared to the applied external potential (~ 20 V); given the interface dipoles at the metal/organic and metal/oxide/organic interfaces discussed in this work, the value of any built-in potential is unclear. Au and Ag were used as the different anode materials. Sputter deposited Al₂O₃ and HfO₂ were used as the different oxide layers. α-NPD and m-MTDATA were used as the different organic semiconductor layers. The Al₂O₃ films were deposited using radio

frequency (RF) magnetron sputtering as described elsewhere. The HfO$_2$ films were deposited using a similar procedure from a 99.95% pure HfO$_2$ target with an RF power of 140 W. Current-voltage (IV) characteristics were measured at room temperature (300 K) in the variable temperature vacuum cryostat.

### 4.3 Results and Discussion

Figure 4.1 shows typical IV characteristics for single carrier devices utilizing Au/Al$_2$O$_3$ bilayer as anodes and α-NPD and m-MTDATA hole transport layers. The dashed curves represent the estimated space charge limited current (SCLC) for α-NPD and m-MTDATA. The solid curves are the corresponding calculation results based on the well-known carrier injection model proposed by Scott and Malliaras (see the previous chapter for further details), and are used to extract the experimental injection barrier heights, $\phi_{Bp}$, by fitting the room temperature IV data.

![Figure 4.1: Current density as a function of electric field for single carrier devices utilizing Au/Al$_2$O$_3$ bilayer anodes with α-NPD and m-MTDATA hole transport layers. Experimental results (symbols) along with theoretical calculations (solid curves) are shown. The estimated space charge limited current (dashed curves) is also shown as the upper limit. The electric field ($F$) is taken as $F = V/d$, where $V$ is voltage and $d$ is the device thickness (~ 500 nm).](image)

In order to calculate the net effect of the oxide layer on the injection barrier treat the thin oxide as a surface modification layer on the metal. The interaction between the oxide and the metal creates an interfacial dipole layer that modifies the work function of the pristine metal surface. This results in the organic molecules deposited on top of the oxide modified metal experiencing an effective metal work function as given by Equation (3.8). In this case the morphology of the
oxide film on the metal surface plays a minor extrinsic role as compared to the intrinsic interface states that tend to dictate the band alignment\textsuperscript{45,56}. Treating the metal/oxide as a layered anode structure the effective metal work function can be plugged back into Equation (3.8) to extract the effective work function of the metal/oxide after consideration of the effect of the organic layer,

\[
\phi_{m,\text{eff}} = (1 - S^\text{org}_\phi) \phi^\text{org}_{\text{CNL}} + S^\text{org}_\phi \left[ \phi^\text{org}_{\text{CNL}} + S^\text{org}_\phi (\phi^\text{org}_{m} - \phi^\text{org}_{\text{CNL}}) \right], \tag{4.1}
\]

where \(S^\text{org}_\phi\), \(S^\text{org}_{\text{CNL}}\), \(\phi^\text{org}_{\text{CNL}}\) and \(\phi^\text{org}_{m}\) are the interface slope parameters and charge neutrality levels of the organic and oxide respectively, as shown in Figure 4.2.

**Figure 4.2:** Schematic energy level diagram of the band alignment at a metal/oxide/organic interface where the oxide interlayer is treated as a surface modification layer on the metal. Here, \(S_\phi\) is taken as the dielectric value given by Equation (3.11), since the oxide interlayer ensures a weakly interacting interface.

The hole injection barrier is then taken as the difference between this effective work function and the highest occupied molecular orbital (HOMO) in the organic. The HOMO of \(\alpha\)-NPD and \(m\)-MTDATA are taken as 5.4 eV and 5.1 eV respectively\textsuperscript{57}. The required material parameters to extract the theoretical barrier heights—namely the charge neutrality level, optical dielectric constant and interface slope parameter—are summarized in Table 4.1. The theoretical barrier heights along with the extracted experimental values for the different metal and metal/oxide bi-layer anodes are summarized in Table 4.2; the calculated effective metal work functions for the various anode structures are also shown. For all of the metal/organic interfaces considered in this study the insertion of a thin oxide layer dramatically reduces the hole injection barrier due to Fermi level pinning by the oxide. Remarkably the hole injection barriers predicted by interface dipole theory are in excellent agreement with the experimentally determined values; for nearly
all of the structures the agreement is better than 100 meV. Similar agreement between theory and experiment was also found based on photoemission\textsuperscript{58}, albeit with a larger error range due the limited resolution of photoemission. For the case of Au/Al\textsubscript{2}O\textsubscript{3}/m-MTDATA the high experimental current density near the SCLC (see Figure 4.1) combined with the low predicted injection barrier (0.29 eV) strongly suggest that the contact is already in the quasi-Ohmic injection regime described by Wolf \textit{et al.}\textsuperscript{59}, and therefore injection-based models may no longer be applicable in extracting the injection barrier. As a result the extracted experimental injection barrier (0.44 eV) is most likely an overestimate of the actual value.

**Table 4.1:** Material properties for the oxides and organics used in this study: charge neutrality level ($E_{\text{CNL}}$), optical dielectric constant ($\varepsilon_\infty$) and interface slope parameter ($S_\phi$). All energies are reported with respect to vacuum level in units of eV.

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_{\text{CNL}}$</th>
<th>$\varepsilon_\infty$</th>
<th>$S_\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>5.2</td>
<td>3.4</td>
<td>0.69</td>
</tr>
<tr>
<td>HfO\textsubscript{2}</td>
<td>4.8</td>
<td>4.0</td>
<td>0.52</td>
</tr>
<tr>
<td>$\alpha$-NPD</td>
<td>4.2</td>
<td>3.0</td>
<td>0.33</td>
</tr>
<tr>
<td>m-MTDATA</td>
<td>4.1</td>
<td>3.0</td>
<td>0.10</td>
</tr>
</tbody>
</table>

**Table 4.2:** Comparison of theoretical and experimental hole injection barriers ($\phi_{B_p}$) at metal/organic and metal/oxide/organic interfaces. The calculated effective metal work function ($\phi_{\text{m,eff}}$) of the anodes are also shown. All barriers are given in units of V.

<table>
<thead>
<tr>
<th>Anode</th>
<th>$\phi_{\text{m,eff}}$</th>
<th>Organic</th>
<th>$\phi_{B_p,\text{theory}}$</th>
<th>$\phi_{B_p,\text{experiment}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>5.1</td>
<td>m-MTDATA</td>
<td>0.90</td>
<td>0.86</td>
</tr>
<tr>
<td>Au/HfO\textsubscript{2}</td>
<td>4.96</td>
<td>m-MTDATA</td>
<td>0.41</td>
<td>0.46</td>
</tr>
<tr>
<td>Au/Al\textsubscript{2}O\textsubscript{3}</td>
<td>5.13</td>
<td>m-MTDATA</td>
<td>0.29</td>
<td>0.44</td>
</tr>
<tr>
<td>Ag/Al\textsubscript{2}O\textsubscript{3}</td>
<td>4.79</td>
<td>m-MTDATA</td>
<td>0.53</td>
<td>0.47</td>
</tr>
<tr>
<td>Au</td>
<td>5.1</td>
<td>$\alpha$-NPD</td>
<td>0.90</td>
<td>0.95</td>
</tr>
<tr>
<td>Au/HfO\textsubscript{2}</td>
<td>4.96</td>
<td>$\alpha$-NPD</td>
<td>0.68</td>
<td>0.60</td>
</tr>
<tr>
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<td>5.13</td>
<td>$\alpha$-NPD</td>
<td>0.56</td>
<td>0.55</td>
</tr>
<tr>
<td>Ag/Al\textsubscript{2}O\textsubscript{3}</td>
<td>4.79</td>
<td>$\alpha$-NPD</td>
<td>0.80</td>
<td>0.77</td>
</tr>
</tbody>
</table>

### 4.4 Summary

In summary, it is found that theoretically predicated hole injection barriers for various archetype metal/organic and metal/oxide/organic contacts are in excellent agreement with experimentally determined values based on transport experiments. It is further found that interface dipole theory not only explains why metal oxides act as universal hole injection layers, but can also be used to accurately predict the injection barriers.
5 Substrate Dependent Charge Injection at Metal/Oxide/Organic Interfaces

5.1 Background

Recently, transition metal oxides (TMOs), such as MoO$_3$, WO$_3$ and V$_2$O$_5$, have been proposed as alternative materials to the traditional organic hole injection layers (HILs), such as CuPc, due to their good stability, low cost, ease of processing and high work function (typically > 5 eV). However, despite numerous reports of enhanced device performance in organic electronics through the use of TMO buffer layer, few works have studied the charge injection from TMOs into organic molecules. As discussed in Chapter 3 and experimentally demonstrated in the previous chapter, interface dipole theory accurately predicts the energy-level alignment at metal/oxide/organic interfaces. Oxides typically have $S_\phi < 1$, which implies that the Fermi level is not completely pinned at most metal/oxide/organic interfaces. As a result, the barrier height at the interface is partially dependent on the work function of the underlying metal. To date this effect has been largely ignored and has yet to be demonstrated in organic devices.

In this chapter it is demonstrated that the charge injection properties at the anode/V$_2$O$_5$/α-NPD interface is dependent on the underlying metal anode. V$_2$O$_5$ does not completely pin the Fermi level, such that the underlying electrode (anode) can still significantly influence the energy-level alignment at the V$_2$O$_5$/α-NPD interface.

5.2 Methods

Single carrier hole-only devices were fabricated on commercially patterned indium tin oxide (ITO) coated glass ($50 \times 50$ mm$^2$) with a sheet resistance less than 15 $\Omega/$□. The standard device structure is as follows: anode/V$_2$O$_5$ (0 and 1 nm)/α-NPD (480 nm)/Au (25 nm). ITO, Au (25 nm) and Mg (50 nm) were used as the different anode materials. V$_2$O$_5$ was deposited from a tungsten boat at a rate of 0.1 Å/s. Mg was deposited in a dedicated chamber from a boron nitride crucible at $\sim 10^{-8}$ Torr.

* This chapter published as Appl. Phys. Lett. 95, 083301 (2009).
5.3 Results and Discussion

Figure 5.1 shows the room temperature (300 K) IV characteristics for ITO and Au (anode) single carrier devices with and without a thin (~ 1 nm) V$_2$O$_5$ layer. The low current density for Au is due to the large (~ 1 eV) interfacial dipole between α-NPD and Au$^{65}$. For both anode materials the thin V$_2$O$_5$ surface modification layer is found to dramatically improve the injection of holes into α-NPD; in the case of Au the current density is increased by nearly 7 orders of magnitude. In addition to the reduction in hole injection barrier, the V$_2$O$_5$ interlayer also significantly changes the temperature dependence of the injection current.

![IV Characteristics](image)

**Figure 5.1:** Current density as a function of voltage for ITO and Au (anode) single carrier devices with and without a thin (~ 1 nm) V$_2$O$_5$ hole injection layer. The inset shows the device structure.

Figure 5.2 shows the temperature dependent IV characteristics for Au single carrier devices with and without V$_2$O$_5$. For the Au devices without V$_2$O$_5$ the injection current is almost temperature independent below room temperature. This abnormal temperature dependence has also been reported for other large injection barriers and is attributed to temperature independent tunneling to interfacial trap states$^{66}$. Since the V$_2$O$_5$ interlayer significantly reduces the injection barrier height at the Au/α-NPD interface, it is expected that the temperature dependence should also be increased as the influence of interfacial trap states is reduced. Indeed, the injection current follows an exponential dependence (for Au/V$_2$O$_5$), which is consistent with a thermally activated (i.e., thermionic) injection process. No dramatic difference in the temperature dependence of the injection current was observed for ITO, which is consistent with the lower initial barrier height for ITO/α-NPD than for Au$^{66}$. 
Returning to the room temperature $IV$ characteristics (Figure 5.1), the driving voltage for the Au anode is $\sim$ 2 V lower (at 10 mA/cm$^2$) than that of ITO; this result has been confirmed for multiple devices on the same substrate and also for several repetitions of the same experiment. In all cases, the Au anode is found to have a lower driving voltage than ITO. In OLEDs, a similar finding for $V_2O_5$ modified Au and ITO was attributed to the higher series resistance for ITO than for Au. However, for our devices the measured difference in series resistance is only $\sim$ 100 $\Omega$, which cannot account for a 2 V difference in driving voltage; by Ohm’s law the voltage drop at 10 mA/cm$^2$ for a 100 $\Omega$ series resistance is only 20 mV. What is more, by re-plotting the $IV$ characteristics in semi-log form, as shown in Figure 5.3, the 2 V difference in driving voltage between ITO and Au is consistent across several decades of current density (see Figure 5.2), which confirms that our data is indicative of a difference in injection barrier and not due to series resistance. It appears that the electrode material (e.g., Au or ITO) can influence the energy-level alignment at the $V_2O_5/\alpha$-NPD interface.

Figure 5.2: Current density as a function of electric field over the temperature range of 300 – 150 K for single carrier devices with, (a) Au anode, and (b) Au/$V_2O_5$ anode. The electric field ($F$) is taken as $F = V/d$, where $V$ is voltage and $d$ is the device thickness (~ 500 nm).

If the electrode material can indeed influence the oxide/organic energy-level alignment then one would expect a significant difference in the injection barrier for an electrode material with a work function much less than that of either Au (5.1 eV) or ITO (5.0 eV). To demonstrate this
point the $IV$ characteristics for Mg (work function of 3.6 eV) with and without V$_2$O$_5$ are also shown in Figure 5.3. The Mg anode exhibits extremely low injection current, consistent with the large injection barrier for a low work function anode. Interestingly, at low electric field the $IV$ characteristics for Au and Mg overlap, which indicates that hole injection is dominated by tunneling to interfacial trap states$^{66}$. As expected the current density for Mg/V$_2$O$_5$ is much less than for Au/V$_2$O$_5$, which confirms that the hole injection barrier at the V$_2$O$_5$/α-NPD interface is influenced by the underlying substrate, or in other words V$_2$O$_5$ does not completely pin the Fermi level at the interface.

**Figure 5.3:** Current density as a function of electric field for ITO, Au and Mg (anode) single carrier devices with and without a thin (~ 1 nm) V$_2$O$_5$ hole injection layer. The estimated space charge limited current (SCLC) is also shown as the upper limit. The electric field ($F$) is taken as $F = V/d$, where $V$ is voltage and $d$ is the device thickness (~ 500 nm).

Examining the trend in the $IV$ characteristics in closer detail, the injection current (at a given electric field) is found to correlate with the work function of the underlying electrode (see Table I). This finding contradicts previous reports in the literature which suggest that the energy-level alignment at the oxide/organic interface should only depend on the work function of the oxide and the HOMO of the organic$^8$. The $IV$ characteristics shown in Figure 5.3 indicate that V$_2$O$_5$ does not completely pin the Fermi level and hence cannot fully screen out the effects of the underlying metal on the energy-level alignment at the oxide/organic interface$^{12}$. The interface slope parameter $S_\phi$ is a convenient parameter that quantifies the pinning strength of a material at metal/semiconductor interfaces. Mönch empirically found that $S_\phi$ (for weakly interacting
interfaces) is related to the optical dielectric constant \( \varepsilon_{\infty} \) (see Equation (3.11)).\(^{45}\) From spectroscopic ellipsometry studies of V\(_2\)O\(_5\) thin films \( \varepsilon_{\infty} = 5.22\)\(^{67}\), which yields a value of \( S_\phi = 0.36 \) (discussed in more detail below).

One important consequence of Equation (4.1) in the previous chapter that the energy-level alignment at a metal/oxide/organic interface will depend on the underlying metal if \( S_{\text{air}} > 0 \), which as discussed above is the case for V\(_2\)O\(_5\) (\( S_\phi = 0.36 \)). A similar effect has already been experimentally demonstrated for metal/organic/organic interfaces.\(^{68-70}\) Since the work function of clean Au is greater than that of ITO or Mg, it is clear from Equation (4.1) that the injection barrier for holes should be less for Au/V\(_2\)O\(_5\) than for ITO/V\(_2\)O\(_5\) or Mg/V\(_2\)O\(_5\), which is consistent with the experimental results (see Figure 5.3).

![Diagram of energy-level alignment at a metal/oxide/organic interface](image)

**Figure 5.4:** Schematic energy-level diagram of the band alignment at a metal/oxide/organic interface for a thin (~ 1 nm) transition metal oxide (TMO) interlayer. The hole injection barrier (\( \phi_{Bp} \)) is taken as the Fermi level (\( E_F \)) to highest occupied molecular orbital (HOMO) offset.

For the metal/oxide/organic interfaces considered in this work the only unknown parameter is the charge neutrality level of V\(_2\)O\(_5\); for \( \alpha \)-NPD \( \phi_{\text{avg}}^{\text{CNL}} = 4.2 \) eV\(^{12}\), \( \varepsilon_{\infty} = 3.6\)\(^{57\,71}\) (\( S_{\text{avg}} = 0.71 \)) and the HOMO is 5.4 eV\(^{71}\). The work functions of the pristine electrodes are summarized in Table I. The charge neutrality level of oxides is typically calculated using Tersoff’s method\(^{43}\) by taking the branch point of the complex band structure from the zero of the Green’s function. However, like most of the transition metal oxides the band structure of V\(_2\)O\(_5\) contains localized states\(^{72}\), which makes the application of Tersoff’s method problematic\(^{50}\). Alternatively the charge neutrality level can be determined from a self-consistent set of experimental data\(^{73}\). Using the well-
established modeling techniques described elsewhere\textsuperscript{9,12,74}, the hole injection barriers were determined from the $IV$ characteristics presented above, and are summarized in Table 5.1. From the hole injection barriers there are three equations, with one unknown, namely the charge neutrality level of V\textsubscript{2}O\textsubscript{5}. A least squares fit yields $\phi_{\text{CNL}}^{\text{ox}} = 5.35 \pm 0.15$ eV.

\textbf{Table 5.1}: Comparison of theoretical and experimental hole injection barriers ($\phi_{\text{bp}}$) at the metal/V\textsubscript{2}O\textsubscript{5}/\textalpha-NPD interfaces considered in this work. The pristine metal work function ($\phi_{\text{m}}$) and the calculated effective metal work function ($\phi_{\text{m,eff}}$) of the anodes are also shown. All barriers are given in units of V.

<table>
<thead>
<tr>
<th>Anode</th>
<th>$\phi_{\text{m}}$</th>
<th>$\phi_{\text{m,eff}}$</th>
<th>$\phi_{\text{bp}}$ Theor.</th>
<th>$\phi_{\text{bp}}$ Expt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/V\textsubscript{2}O\textsubscript{5}</td>
<td>5.0</td>
<td>5.2</td>
<td>0.47</td>
<td>0.51</td>
</tr>
<tr>
<td>Au/V\textsubscript{2}O\textsubscript{5}</td>
<td>5.1</td>
<td>5.3</td>
<td>0.45</td>
<td>0.49</td>
</tr>
<tr>
<td>Mg/V\textsubscript{2}O\textsubscript{5}</td>
<td>3.6</td>
<td>4.8</td>
<td>0.83</td>
<td>0.79</td>
</tr>
</tbody>
</table>

5.4 Summary

In summary, the charge injection properties at the V\textsubscript{2}O\textsubscript{5}/\textalpha-NPD interface on Au, ITO and Mg anodes have been compared using temperature dependent $IV$ measurements. It is found that the injection current at the V\textsubscript{2}O\textsubscript{5}/\textalpha-NPD interface is greater for Au than for either Mg or ITO. This result indicates that the energy-level alignment at the V\textsubscript{2}O\textsubscript{5}/\textalpha-NPD interface is dependent on the underlying metal, which contradicts previous reports in the literature. V\textsubscript{2}O\textsubscript{5} is found to incompletely pin the Fermi level, such that the work function of the underlying substrate can still influence the dipole between V\textsubscript{2}O\textsubscript{5} and \textalpha-NPD. The charge neutrality level of V\textsubscript{2}O\textsubscript{5} is also found to be 5.35 eV.
6 Effect of Electrostatic Screening at Electrode/Organic Interfaces*

6.1 Background

In the study of organic interfaces photoelectron spectroscopy (PES) has been extensively used to study the electronic structure of organic thin films deposited on various inorganic substrates. It is often observed that the PES spectra of very thin organic films differ from that of thicker bulk-like films. In particular, the binding energy shifts in molecular orbitals at metal/organic interfaces has been reported to vary as a function of the organic over-layer thickness. The spectral features of the organic over-layer are found to shift to higher binding energy with increasing film thickness.\(^75\text{-}^78\) The interpretation of these apparent thickness dependent organic over-layer spectra have, however, remained a source of contention.\(^79\text{-}^81\) More than two decades ago a similar debate was waged over the interpretation of PES spectra of the Si/SiO\(_2\) interface. Shifts on the order of \(\sim 1\) eV in the SiO\(_2\) spectral features were observed between thin and thick SiO\(_2\) layer films.\(^82\text{-}^84\) It is now well established that these apparent thickness dependent shifts are a result of electrostatic screening effects on the final-state relaxation energy.\(^85\text{-}^87\) However, in the case of metal/organic interfaces the effect of electrostatic screening on PES spectra has in general been overlooked.

In this chapter it is demonstrated that the experimentally observed binding energy shifts for a prototypical organic semiconductor on various conductive substrates are consistent with electrostatic screening. Although several authors have qualitatively discussed electrostatic screening at metal/organic interfaces,\(^88\text{-}^89\) this work provides detailed theoretical calculations quantifying the direction and magnitude of the apparent binding energy shifts, including valence band features, for an amorphous organic semiconductor. Good agreement between experimental results and theoretical calculations for a variety of different metallic and dielectric substrates strongly suggests that many of the reported thickness dependent energy-level shifts in organic over-layer spectra are a result of electrostatic screening. Therefore many models of the energy-

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level alignment at organic interfaces based on PES spectra of organic thin films need to be re-examined.

6.2 Methods

The substrates used in this study were selected to represent a range of dielectric properties. Au, Cu and Ag thin films were prepared on Si(100) as described elsewhere. H-terminated Si(100) was prepared by several cycles of UV ozone treatment and etching in 5% hydrofluoric acid. Highly orientated pyrolytic graphite (HOPG) was freshly cleaved prior to use. After sample preparation, substrates were immediately loaded into the PHI 5500 Multi-Technique system. The metallic substrates were Ar+ sputter cleaned until the C 1s and O 2p signals vanished and consistent work function measurements were obtained. UPS measurements were performed at a photoelectron take-off angle of 90° and with a -15 V bias applied to the sample. Peak positions were determined using a polynomial fit to the top 5% of the peak.

6.3 Theory

To calculate the effect of electrostatic screening on the final-state relaxation energy a classical dielectric continuum model was applied. A system of three dielectric layers is considered, with permittivities of $\varepsilon_1$, $\varepsilon_2$, and $\varepsilon_3$, in contact with each other as shown in Figure 6.1: a semi-infinite substrate slab ($z < 0$), an organic over-layer of thickness $d$ ($0 < z < d$), and the vacuum above the organic thin film ($z > d$). The reflection coefficients at the dielectric boundaries are defined as,

$$k_1 = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + \varepsilon_1} \text{ and } k_2 = \frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}. \quad (6.1)$$

A metal can be substituted for the dielectric substrate using a jellium slab, in which case $k_1 = -1$. 

\[ \text{\{special characters here\}} \]
Figure 6.1: Dielectric continuum model of an organic over-layer on a substrate with point charge $q = e$ in the organic layer. $\varepsilon_1$, $\varepsilon_2$ and $\varepsilon_3$ are the permittivities of each layer and $k_1$ and $k_2$ are the reflection coefficients at the dielectric boundaries. The image charges shown are from the $n = 0$ term of Equation (6.2).

The correction to the final-state relaxation energy can be calculated by solving Poisson’s equation. For an excitation in the second dielectric layer (i.e., the organic film),

$$\Delta E = -\frac{e^2}{16\pi\varepsilon_0\varepsilon_2} \sum_{n=0}^{\infty} (k_1k_2)^n \left[ \frac{k_1}{z + nd} + \frac{k_2}{(n+1)d - z} + \frac{2k_1k_2}{(n+1)d} \right], \quad (6.2)$$

where $e$ is the electron charge and $\varepsilon_0$ is the permittivity of free space. Equation (6.2) represents the binding energy shift due to an infinite series of image charges, reflected in the two dielectric interfaces; for a complete derivation see Ref. 94. A similar approach was used to describe the electrostatic screening at the Si/SiO$_2$ interface$^{85}$ and for physisorbed rare-gas multilayers$^{95}$ on various substrates.
Figure 6.2: Correction to the binding energy as a function of the position ($z$) in the organic film for different organic layer thickness ($d$) and substrate permittivity ($\varepsilon_1$). The permittivity of the organic was taken as $\varepsilon_2 = 3.0$.

Figure 6.2 shows the calculated correction to the binding energy as a function of the position $z$ in the organic over-layer for different film thicknesses $d$ and substrate permittivity $\varepsilon_1$. To calculate the net effect of the $z$ dependent binding energy shift on PES spectra of the organic over-layer the contribution to the measured signal from different depths in the organic are summed, following the procedure from Ref. 85. The sum includes the attenuation due to the electron mean free paths over the escape depth in the organic. The total shift in the binding energy for a thin organic over-layer is referenced to that of a thick over-layer. This approach avoids the energy artefacts due to the artificial divergence of classical electrostatics near the vacuum interface for the dielectric continuum model. 85 Similarly, the sum is terminated a finite distance near the substrate interface. The minimum distance was taken as the mean substrate-molecule separation of $\sim 2.5$ Å, 96-98 corrected by $\sim 0.5$ Å for metallic substrates 99,100 based on the overlap of charge density at the interface estimated from calculations for a jellium slab. Figure 6.3 shows the net correction to the binding energy as a function of organic film thickness $d$ for different photoelectron escape depths $\lambda$. The inset shows calculated model spectra for two different film thicknesses on a metallic substrate. Due to the exponential dependence of the signal intensity on the depth in the organic layer, the shifted peaks are only slightly asymmetrically broadened.
Typically, the Auger-parameter—the sum of the kinetic energy of the sharpest Auger line and the binding energy of the most intense photoemission peak—has been used to evaluate the effect of electrostatic screening on the final-state relaxation energy near dielectric interfaces. The Auger parameter has the advantage that it is independent of sample charging and energy scale referencing. However, for organic semiconductors shifts in the valence levels are a more useful metric, since the Auger features of C and N are in general too weak to accurately determine changes in the Auger-parameter, particularly for very thin organic films. In addition the prolonged exposure to x-rays required to accurately measure the core-level binding energies for very thin organic films using XPS can lead to additional binding energy shifts, which are difficult to correct for. Alternatively, changes in valence levels can be measured using UPS with much greater precision and without x-ray induced binding energy shifts. More importantly, it is the valence levels of organic molecules that are typically of interest in most studies.\textsuperscript{101-104} It is therefore not only more practical, but also more meaningful to evaluate the effect of electrostatic screening on the final-state relaxation energy of the valence levels for organic semiconductors. Most organic semiconductors are amorphous with highly localized electronic states, even for valence levels. The simple image-charge model assuming point-charges given by Equation (6.2) should therefore be applicable to both core- and valence level excitations.
6.4 Results and Discussion

Figure 6.4 shows the evolution of the He Iα ($h\nu = 21.22$ eV) valence band spectra and secondary electron cut-off of a Ag thin film during the layer-by-layer deposition of 2T-NATA to a total thickness of 25 Å. 2T-NATA was chosen since it is an amorphous organic semiconductor, which is representative of the most commonly used molecules used in devices.\textsuperscript{105,106}

![Figure 6.4: He Iα ($hv = 21.22$) valence band spectra of the Ag/2T-NATA interface showing the evolution of (a) the secondary electron cut-off, and (b) the HOMO of 2T-NATA. The 2T-NATA thickness is shown in (b) in nm. The molecular structure of 2T-NATA is shown in the inset.](image)

The highest occupied molecular orbital (HOMO) of the organic overlayer is found to shift to higher binding energy with increasing film thickness. The total shift between the first and last deposition is ~ 0.5 eV. Since the work function of the sample remained constant after the first deposition of organic molecules (see Figure 6.4a), it can be concluded that the interfacial dipole is confined to the first monolayer of molecules only, and hence cannot account for the thickness dependent shifts. No charging of the sample was also confirmed by comparing the work function measured by XPS and UPS.

Figure 6.5 shows the measured position of the HOMO for 2T-NATA as a function of layer thickness for substrates with different dielectric properties. Calculation results for the electrostatic screening induced binding energy shifts using Equation (6.2) are shown as solid lines in the figure. Good agreement between the experimental results and theoretical calculations
for a variety of different substrates strongly suggests that electrostatic screening plays an important role in the apparent thickness dependent binding energy shifts. Even more compelling is the good agreement between substrates with similar dielectric properties (e.g., the different metals).

Figure 6.5: Comparison of the experimental (symbols) and theoretical (lines) binding energy shift in the HOMO of 2T-NATA as a function of the organic film thickness \(d\) for various substrates. The photoelectron escape depth \(\lambda = 6.4\) Å was determined from the attenuation of the Fermi edge of the Ag substrate with film thickness, and is in good agreement with Ref. \(^{107}\). The permittivity of Si and HOPG were taken as \(\varepsilon_1 = 12\) and \(\varepsilon_1 = 6\) respectively.

One obvious implication of electrostatic screening is the measured ionization potential for an organic thin film. For the examples shown in Figure 6.5 the work function of the substrate remained constant after the first deposition of organic molecules (see Figure 6.4a). However, due to the effect of electrostatic screening the measured position of the HOMO varied with film thickness and dielectric constant of the substrate. As a result the measured ionization potential of the organic also varied from 4.55 – 5.0 eV depending on the substrate and film thickness. For film thicknesses > 2.5 Å the measured ionization potential of the 2T-NATA converged to a constant value of 5.0 eV, in good agreement with transport-based measurements.\(^{105}\) This finding explains the wide variation in reported ionization potential for the same molecule in literature (i.e., different studies use different substrates and film thicknesses), and also highlights the need for using consistent substrates and film thicknesses when measuring the properties of organic thin films.
In the present work the dielectric continuum model yielded satisfactory results since the molecule used, 2T-NATA, is amorphous with isotropic dielectric properties. However, this simple model may not be sufficient to describe electrostatic screening in well-ordered or polycrystalline organic thin films, such as phthalocyanines, where the dielectric properties are anisotropic.\textsuperscript{108}

### 6.5 Summary

In summary, it has been shown that the experimentally observed thickness-dependent binding energy shifts for a prototypical organic semiconductor on various conductive substrates are well explained by electrostatic screening. This finding demonstrates that the spectral shifts observed in PES spectra of organic semiconductors near metal/organic interfaces could easily be caused by electrostatic screening. This brings into question many models of organic interfaces based on PES spectra of organic thin films. In particular, the effects of electrostatic screening must be taken into account when measuring the properties of organic thin films, such as the ionization potential.
7 Effect of High Vacuum on Metal/Organic Interfaces*

7.1 Background

The metal/organic interfaces studied using photoelectron spectroscopy (PES) are almost always exclusively prepared in ultra-high vacuum (UHV), and therefore do not accurately represent the interfaces in actual devices, which are typically prepared in high vacuum (HV). Several authors have attempted to reconcile this discrepancy by studying metal/organic interfaces where the metal has been exposed to either air or oxygen prior to the deposition of the organic.\textsuperscript{65,109-112} The barrier height is usually significantly different, and in most cases lower, for air exposed metals due to the effect of adsorbed atmospheric contaminants. However, since most state-of-the-art devices are processed without breaking vacuum, air exposed metals are also not an accurate representation of the interfaces in actual devices.

In this chapter the effect of HV on the energy-level alignment at metal/organic interfaces is studied using single carrier devices and PES measurements. Although it has been well documented that low work function metals will adsorb significant amounts of residual gases in HV,\textsuperscript{113-116} thus altering the energy-level alignment with organic semiconductors, this issue has been largely overlooked for less reactive metals, such as the noble metals. As will be shown even the minute amounts of residual gases that are adsorbed on the surface of clean metals in HV can in general significantly alter the energy-level alignment at metal/organic interfaces. In light of this finding many models of the energy-level alignment at organic interfaces that attempt to reconcile device performance with PES measurements may need to be re-examined.

7.2 Methods

Single carrier devices were fabricated on Corning\textsuperscript{®} 1737 glass (50 mm × 50 mm) without breaking vacuum. The standard device structure is as follows: anode/2T-NATA (500 nm)/Au. Au, Ag and Cu where used as the different anode materials. All devices were fabricated on a single substrate to avoid any possible run-to-run differences in processing conditions. Current-voltage (IV) characteristics of the devices were measured in the variable temperature vacuum

cryostat. Samples were exposed to ambient air for ~1 minute while transferring from the cluster tool to the vacuum cryostat. This short ambient exposure does not alter the device characteristics. For PES measurements HV conditions were prepared by venting the organic deposition chamber attached to the PHI 5500 Multi-Technique system to air and pumping it down using a cryopump, without baking, to a base pressure of ~10^{-7} Torr.

![Graph](image)

**Figure 7.1**: (a) UPS valence band spectra of 2T-NATA deposited on UHV processed Ag, Cu, and Au. The inset shows the measured barrier height as a function of the metal work function. (b) Current-voltage characteristics of 2T-NATA single carrier devices with HV processed Ag, Cu, and Au anodes. The inset shows the device structure.

### 7.3 Results and Discussion

Figure 7.1a shows the UPS valence band spectra of 2T-NATA deposited on clean Au, Cu, and Ag prepared in UHV. Note that the morphology of organic films on UHV and HV prepared samples was the same. The inset shows the measured barrier height (taken as the offset between
the leading edge of the HOMO derived peak and the Fermi level) as a function of the metal work function. The barrier height is found to decrease linearly with increasing work function, consistent with previous reports in the literature. Figure 7.1b shows the room temperature (300 K) $IV$ characteristics of 2T-NATA single carrier devices with Au, Cu and Ag anodes prepared in HV. Surprisingly the trend in the $IV$ characteristics contradicts the UPS results as Ag is found to have the highest current density at a given voltage, which corresponds to the lowest barrier height. Also, Au and Cu are found to have nearly equivalent $IV$ characteristics. Clearly, the metal/organic interfaces in the devices must be different than those measured using UPS.

Figure 7.2: UPS valence band spectra of (a) Ag, (b) Cu, and (c) Au processed in HV and UHV showing the secondary electron cut-off (left), valence band of the metal (middle), and HOMO derived peak of 2T-NATA (right).
Since the devices were prepared in HV the residual gases in the vacuum system might have adsorbed to the surface of the metals, altering the energy-level alignment at the interface. To elucidate this possibility UPS measurements for metal samples exposed to HV conditions prior to deposition of the organic layer were performed. The samples were exposed to ~500 Langmuir of HV residual gases to replicate the exposure received by the samples during device fabrication.

Figure 7.2a shows the UPS valence band spectra of Ag processed in UHV and HV along with the valence band spectra of 2T-NATA deposited on the same samples. Surprisingly the work function of the HV processed Ag is 0.55 eV higher than the UHV processed sample. The barrier height with 2T-NATA is also found to be 0.65 eV lower for the HV processed Ag, which is in agreement with the device performance data. Silver oxides have a high work function of ~5 eV, which suggests that the Ag processed in HV might have an over-layer of oxide on the surface. However, the valence band of HV processed Ag is very similar to that of UHV processed Ag. The only difference is a ~8% attenuation of the $d$-band and loss of fine structure in the $s$-band.

To further investigate the chemical composition of the Ag surface high resolution XPS spectra of the Ag and O core levels were measured. Figure 3a shows the Ag $3d$ and O $1s$ core levels of Ag processed in UHV and HV conditions. A very minute amount of O (~0.5 at%) was detected on the HV sample only with a very long collection time of several hours. However, the Ag $3d$ peak indicates only a single chemical state of Ag (i.e., metallic Ag), which rules out a surface oxide layer. The attenuation of the $d$-band and Ag $3d$ core level suggests that the detected O is in the form of an adsorbed over-layer on the surface. Although the primary residual gas in HV is water, H$_2$O does not readily adsorb to clean Ag at room temperature and also decreases rather than increases the work function. Also, a small amount of C in addition to O was detected on the HV sample, which suggests that the over-layer could be adsorbed CO$_2$ and/or CO, both of which have been reported to adsorb to clean Ag at room temperature and to increase the work function. Since these gases are two of the primary residual gases in HV it is therefore likely that adsorbed CO$_2$ and/or CO is responsible for the high work function of Ag processed in HV conditions. Since the decrease in barrier height is ~ 0.1 eV larger than the increase in work function for HV processed Ag it is clear that another phenomena must also contribute to the lower barrier. In addition to increasing the work function, the adsorbate over-layer also shields the organic molecules from direct interaction with the electron tail from the metal, resulting in a lower barrier height.
Figure 7.3: XPS spectra of (a) Ag, (b) Cu, and (c) Au processed in HV and UHV showing the O 1s, Ag 3d, Cu 2p, and Au 4f core-levels.

Figure 7.2b shows the UPS valence band spectra of Cu processed in UHV and HV along with the valence band spectra of 2T-NATA deposited on the same samples. In contrast to Ag, the work function of Cu is not significantly different. However, the barrier height with 2T-NATA is still significantly lower for the HV processed Cu. Also, the d-band is attenuated by ~20% and there is a significant increase in the background signal above a binding energy of 5 eV, both of which suggest a significant oxide over-layer on the surface. Figure 7.3b shows the Cu 2p and O 1s core levels of Cu processed in UHV and HV conditions. Although no oxide peak is detectable in the Cu 2p core level, some O on the surface was observed. The O 1s core level can be resolved into
two separate peaks with binding energies of 529.9 eV and 531.3 eV, which correspond to CuO and Cu(OH)$_2$ respectively. For comparison the O 1s core level of Cu prepared in UHV and then exposed to ~500 Langmuirs of O$_2$ (99.9995%) was also measured. Only a single peak with a binding energy of 529.8 eV is observed in the O 1s core level of the UHV processed Cu exposed to O$_2$, and is consistent with the lower binding energy peak observed for the HV processed Cu. Although it is well known that bulk CuO forms a good contact with many hole transporting molecules, this find demonstrates that even a fraction of a monolayer coverage is enough to alter the interaction between metal and molecule.

Finally, in contrast to Ag and Cu there was no difference in the valence band, core levels or work function between the UHV and HV processed Au as shown in Figure 7.2c and Figure 7.3c. As a result the barrier height on both samples was identical. This finding is not surprising as Au is the least reactive of the noble metals, and is therefore the least likely to pick up any of the residual gases in HV. Table 7.1 summarizes the work function and barrier heights for the different metals processed in UHV and HV.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\phi_m$ (UHV)</th>
<th>$\phi_{Bp}$ (UHV)</th>
<th>$\phi_m$ (HV)</th>
<th>$\phi_{Bp}$ (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>4.32</td>
<td>1.46</td>
<td>4.87</td>
<td>0.81</td>
</tr>
<tr>
<td>Cu</td>
<td>4.56</td>
<td>1.34</td>
<td>4.49</td>
<td>0.96</td>
</tr>
<tr>
<td>Au</td>
<td>5.29</td>
<td>0.96</td>
<td>5.27</td>
<td>0.94</td>
</tr>
</tbody>
</table>

### 7.4 Summary

In summary, it was demonstrated that the energy-level alignment at metal/organic interfaces is strongly dependent on the vacuum conditions under which the samples are prepared. Even the minute amounts of residual gases that are adsorbed on the surface of clean metals in HV can in general significantly alter the energy-level alignment at metal/organic interfaces. In light of this finding previous attempts to reconcile the performance of devices fabricated in HV with the PES measurements performed in UHV may need to be re-examined.
8 Oxidized Gold Thin Film Electrodes*

8.1 Background

Thin film organic semiconductors—both small molecule and conjugated polymer—have the advantage over traditional inorganic semiconductors, such as Si or GaAs, in that they do not require epitaxial growth of perfect single crystal films to operate in real devices, and hence can be processed into flexible devices. This feature of organic semiconductors is a key requirement for future low-cost mass production using roll-to-roll processing on flexible plastic substrates. However, ITO, the de facto standard transparent anode in research and production, is incompatible with processing on plastic substrates due to the high annealing temperatures of ~300 °C required to achieve adequate conductivity. As a result, there is renewed interest in new electrode materials that can enable the roll-to-roll processing of next generation high performance organic electronics on plastic substrates.

As it turns out ITO is a difficult material to beat in terms of device performance and ease of processing. The dominance of ITO is largely in part due to its compatibility with a wide variety of different organic molecules, device structures and processing techniques. This is not surprising since most organic semiconductors and device architectures have been engineered around the properties of ITO. For example, the work function of ITO (~ 4.7 eV) has served as the guideline for developing new hole transporting molecules, such as α-NPD. As a result it is often difficult to find materials that work well with the standard structures developed for ITO.

Early on, metal thin films were proposed as alternative anodes in OLEDs due to several key advantages over ITO. First, the conductivity of many metals, in particular the noble metals, is nearly two orders of magnitude higher than that of ITO, which will be shown is of critical importance for large area devices. Second, metals are easily patterned using traditional photolithography and can be deposited using a variety of deposition techniques such as thermal evaporation, electron-beam evaporation and sputtering. Third, metals can be deposited onto large area flexible plastic substrates using roll-to-roll processing; this technique is already used in the low-cost production of thermal control coatings for windows (e.g., Pd, Pt, Au).

* This chapter published as Adv. Mater. 22, 2037 (2010).
Despite the obvious advantages of metals, a direct drop-in replacement for ITO has yet to be demonstrated. For example, a Lambertian emission from OLEDs is extremely difficult to achieve with metal anodes. The high reflectivity of most metals creates a strong optical microcavity between the anode and cathode, resulting in significant deviation from ideal Lambertian emission.\textsuperscript{128} Also, many of the currently used standard organic molecules form poor interfaces with metal anodes due to strong interfacial dipole effects.\textsuperscript{75}

In this chapter, oxidized Au (AuO\textsubscript{x}) thin films are demonstrated as a direct drop-in replacement for ITO in OLEDs, with superior device performance and ITO-like Lambertian (i.e., angle independent) emission. The unique combination of optical properties, high electrical conductivity, good chemical stability, and ease of processing make AuO\textsubscript{x} an interesting candidate for a new anode material in flexible OLEDs fabricated on plastic substrates.

### 8.2 Methods

Commercially patterned ITO coated glass (50 mm × 50 mm) with a sheet resistance less than 15 \(\Omega/\square\) was used for devices with ITO anodes. Corning\textsuperscript{®} 1737 glass (50 mm × 50 mm) was used for devices with Au and AuO\textsubscript{x} anodes. The standard device structure for C545T doped Alq\textsubscript{3} OLEDs is as follows: anode/CuPc (25 nm)/\(\alpha\)-NPD (45 nm)/Alq\textsubscript{3}:C545T [1 wt.%] (30 nm)/Alq\textsubscript{3} (15 nm)/LiF (1 nm)/Al (100 nm). Au anode lines (1 mm wide) for the Au and AuO\textsubscript{x} anodes were deposited in a dedicated metallization chamber from an alumina lined molybdenum boat. AuO\textsubscript{x} was produced from freshly deposited Au films by either UV ozone treatment in ambient air or O\textsubscript{2} plasma treatment for 30 minutes. Transmission spectra of the AuO\textsubscript{x} films were measured using a PerkinElmer Lambda 25 UV/Vis spectrophotometer. For photoelectron spectroscopy measurements samples were oxidized \textit{in situ} using UV ozone. Reliable electrical connection to the thin Au layers was made via ITO under pads at the probe points.

### 8.3 Results and Discussion

A suitable replacement material for ITO must possess adequate conductivity and transparency across the visible range. Au thin films are ideal candidates since they are highly conductive and semi-transparent across the visible with low absorbance. Figure 8.1 shows the transmission spectra of oxidized Au thin films deposited on glass as a function of film thickness. For the 15 nm thick Au film (i.e., the optimized thickness used in this work) the transmission at 540 nm is ~
60%, which is only 25% less than that of ITO (also shown in the figure). However, the sheet resistance measured by 4-point probe of the 15 nm thick Au film was 6.0 Ω/□, which is nearly 3 times lower than the corresponding value of 17.8 Ω/□ measured for ITO. As it turns out this lower sheet resistance is far more critical for device applications, since the reflectivity of the AuOₓ can be used to generate a weak optical cavity that can enhance device performance.\textsuperscript{129}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8.1.png}
\caption{Transmission spectra of oxidized Au thin films on Corning® 1737 glass substrates as a function of thickness; commercial ITO on glass is also shown as reference. Below the graph is a picture of the Au coated glass substrates on a sheet of graph paper, with film thickness increasing from left to right; the size of each substrate is 25 x 25 mm\textsuperscript{2}. The 1 nm and 3 nm thick films are pink and blue respectively, which is a characteristic of plasmonic effects from Au nanoparticles.\textsuperscript{130}}
\end{figure}

Figure 8.2a shows the x-ray photoelectron spectroscopy (XPS) core levels of a Au thin film oxidized using UV ozone treatment (similar results were obtained for oxygen plasma treatment). From the Au 4f peak it is clear that two chemical species exist in the oxidized sample, namely metallic Au in the bulk and Au oxides (high binding energy shoulder) at the surface.\textsuperscript{131-133} Angle resolved XPS measurements confirm that the Au oxides are localized to the surface of the film and are \textasciitilde{} 1 monolayer thick. The work function of the oxidized Au was found to increase from 5.3 eV (Au) to 5.7 eV (AuOₓ), which is in good agreement with literature.\textsuperscript{134} Due to the higher work function and surface layer of oxide, a more favourable energy-level alignment for hole injection into organic molecules is expected for AuOₓ.\textsuperscript{134} Figure 8.2b shows the He Iα (hv = 21.22 eV) valence band spectra of a 5 nm thick CuPc layer deposited \textit{in situ} on Au and AuOₓ. The valence band of clean Au is also shown as reference for the Fermi level position (i.e., zero
binding energy). The HOMO derived peak of CuPc is clearly resolved. However, for CuPc deposited on Au the Fermi edge and s-band of the substrate (i.e., Au) are also clearly resolved, while only over-layer features from CuPc are resolved on AuOₓ.

![Figure 8.2: XPS and UPS spectra of Au and AuOₓ with and without a 5 nm thick layer of CuPc, (a) Au 4f core-level spectra indicating the formation of AuOₓ after UV ozone treatment, and (b) He Iα (hν = 21.22 eV) valence band spectra showing the energy-level alignment of the CuPc HOMO.]

Since the probing depth of UPS is typically ~1 nm (much less than the CuPc film thickness) this indicates that CuPc grows as patchy islands on clean Au, in contrast to a closed packed film on AuOₓ. Since the electrical properties of organic semiconductors depend strongly on molecular packing and orientation, different charge injection properties are expected for Au and AuOₓ. From the UPS valence band spectra the injection barrier height for holes (φ_Bp) can be estimated from the offset of the leading edge of the HOMO to the Fermi level as indicated in the figure. The estimated injection barrier heights are 0.93 eV and 0.30 eV for Au and AuOₓ respectively. Results for ITO and other commonly used organic semiconductors are shown in Table 8.1.

**Table 8.1:** Hole injection barrier heights of commonly used HTL molecules on ITO, Au and AuOₓ substrates measured using UPS. All values are reported in units of eV.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>ITO</th>
<th>Au</th>
<th>AuOₓ</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuPc</td>
<td>0.35</td>
<td>0.93</td>
<td>0.30</td>
</tr>
<tr>
<td>α-NPD</td>
<td>0.60</td>
<td>0.88</td>
<td>0.53</td>
</tr>
</tbody>
</table>
The lower barrier height and uniform morphology for AuO$_x$ is due to a significant reduction in the interfacial dipole at the Au/organic interface as a result of the thin interlayer of Au oxides; this effect has been discussed in detail elsewhere.$^{12}$ Clearly, oxidation of Au significantly reduces the injection barrier and yields an interface similar to that of ITO (see Table 8.1).

![Figure 8.3](image)

**Figure 8.3:** Device performance characteristics of Alq$_3$ OLEDs with ITO and AuO$_x$ anodes, (a) current density and luminance as a function of voltage, and (b) current and power efficiencies as a function of luminance. The inset of (a) shows the device structure.

Figure 8.3a compares the current-voltage ($IV$) and luminance characteristics of OLEDs with AuO$_x$ anode in comparison to devices with a typical ITO anode. The device structure is shown in the inset of the figure. The driving voltage at a given current density for the AuO$_x$ anode is found to be less than that of ITO. However, it was found that this difference is due to the higher sheet resistance of ITO; this is evidenced for example by the difference in driving voltage increasing linearly with voltage (i.e., following Ohm’s law). After correcting for a $\sim$150 $\Omega$ higher series resistance for ITO (measured value), the driving voltage for the two electrodes was found to be similar, consistent with the injection barrier for CuPc measured by UPS. The lower series
resistance for AuO\textsubscript{x} is critical for large area device applications. In any event the luminance was also found to be increased; for example the maximum luminance of the devices with AuO\textsubscript{x} anode was 22,000 cd/m\textsuperscript{2}, while for ITO it was only 18,000 cd/m\textsuperscript{2}. As a result the efficacy of the devices with AuO\textsubscript{x} anode is superior to that of ITO. Figure 8.3b compares the electroluminescence efficiencies as a function of luminance for OLEDs with AuO\textsubscript{x} and ITO anodes. The current efficiency of the AuO\textsubscript{x} devices is 35\% higher than that of ITO. Since the driving voltage of the two devices is similar this improvement is attributed to a weak microcavity effect in the AuO\textsubscript{x} devices, which will be discussed in greater detail below. At high luminance (i.e., \( > 1,000 \) cd/m\textsuperscript{2} ) the current efficiency is 5.1 cd/A for AuO\textsubscript{x}, which is one of the highest reported values for Alq\textsubscript{3} based OLEDs with an un-doped emission layer\textsuperscript{135,136}. What is more, this result was achieved with only a simplified three layer OLED structure. Clearly, AuO\textsubscript{x} can be used as a direct drop-in replacement for ITO.

To demonstrate the versatility of AuO\textsubscript{x} in OLEDs devices with C545T-doped Alq\textsubscript{3} emission layer were fabricated. The maximum current efficiency of the ITO baseline device was 14 cd/A, which is comparable to literature values\textsuperscript{137}. The AuO\textsubscript{x} anode on the other hand had a maximum current efficiency of 16.9 cd/A, which represents a 20\% improvement over ITO, but which is slightly less than the improvement for Alq\textsubscript{3} devices. These results have been reproduced for multiples devices on the same substrate and for different substrates (i.e., different batches); in general a \( \sim 30\% \) improvement for Alq\textsubscript{3} devices and \( \sim 20\% \) for C545T devices is found. This difference in enhancement is attributed to the higher radiative lifetime of C545T when placed in an optical microcavity (discussed below).

Since Au thin films are semi-transparent, an optical microcavity will be formed with the highly reflective Al cathode. Microcavity OLEDs can exhibit significantly enhanced emission along the cavity optical axis (forward direction), as well as a much narrower emission spectrum\textsuperscript{129}. Although the microcavity effect can be beneficial for monochromatic emission, many applications (e.g., solid state lighting) require a broadband spectrum with Lambertian emission. To prevent narrowing of the emission spectrum, the spectral width of the cavity resonance should be larger than the natural emission spectrum of the emitter molecule\textsuperscript{138}. For an optical microcavity the spectral width of the cavity resonance is given by\textsuperscript{139}.
\[ \Delta \lambda = \frac{\lambda^2}{2L} \left[ \frac{1 - \sqrt{R_1 R_2}}{\pi (R_1 R_2)^{1/4}} \right], \]  

(8.1)

where \( R_1 \) and \( R_2 \) are the reflectivities of the mirrors and \( L \) is the effective cavity length. From Equation (8.1) it is clear that a large value of \( \Delta \lambda \) can be achieved by reducing the reflectivity of one of the mirrors (e.g., by using a semi-transparent electrode) or by reducing the cavity length (e.g., by removing the optically thick ITO layer). Taking \( R_1 = 0.9 \) for the Al cathode and \( R_2 = 0.25 \) for the AuO\(_x\) anode (measured values), the spectral width is \( \Delta \lambda \sim 150 \) nm at \( \lambda = 530 \) nm, which is greater than the natural emission spectrum of Alq\(_3\) (~ 100 nm). Thus there should be little or no spectral narrowing for the AuO\(_x\) anode.

![Figure 8.4: Optical characteristics of Alq\(_3\) OLEDs with ITO and AuO\(_x\) anodes, (a) EL spectra of ITO, (b) EL spectra of AuO\(_x\), and (c) normalized EL intensity as a function of emission angle indicating Lambertian emission.](image)

Figure 8.4 shows the EL spectra of Alq\(_3\) green OLEDs with ITO and AuO\(_x\) anodes at various emission angles. Other than a slight red-shift (~ 10 nm) of the EL spectra (relative to ITO) for AuO\(_x\), the spectra are very similar. The FWHM of the EL spectra is identical for both ITO and AuO\(_x\) (~ 90 nm), which confirms the weak microcavity effect predicted by Equation (8.1). What is more, the EL spectra is nearly independent of emission angle for the AuO\(_x\) anode (as well as ITO), which also confirms a weak microcavity effect. As a result the AuO\(_x\) anode exhibits a Lambertian emission profile (same as for the device with ITO), as shown in the polar plot of normalized EL intensity as a function of emission angle in Figure 8.4c.
Although the AuO\textsubscript{x} anode forms only a weak optical microcavity, the EL intensity is still enhanced relative to ITO. The emission enhancement factor relative to free space emission along the optical axis of a microcavity is given by,\textsuperscript{140}

\[
G_e = \frac{T_2}{1 - \sqrt{R_1 R_2}} \cos \left( \frac{4 \pi L_1}{\lambda} \right) \cos \left( \frac{4 \pi L}{\lambda} \right) \frac{1 + R_1 + 2 \sqrt{R_1} \cos \left( \frac{4 \pi L_1}{\lambda} \right)}{1 + \sqrt{R_1 R_2} \cos \left( \frac{4 \pi L}{\lambda} \right)},
\]

(8.2)

where \( T_2 \) is the transmittance of the second mirror, \( L_1 \) is the effective distance from the emission zone to the first mirror and \( \tau_{cav} \) and \( \tau \) are the radiative lifetimes in the cavity and free space, respectively. Using the above equation, Lin et al.\textsuperscript{128} recently calculated a cavity enhancement factor for microcavity OLEDs with two metal mirrors relative to a conventional OLED with ITO anode. Based on their calculations, the AuO\textsubscript{x} devices with \( R_1 = 0.9 \) (Al cathode), \( R_2 = 0.25 \) and \( T_2 = 0.6 \) (AuO\textsubscript{x} anode) have an enhancement factor of 1.35 for Alq\textsubscript{3} and 1.2 for C545T, consistent with the device performance (i.e., OLEDs with AuO\textsubscript{x} anodes had \(~30\%\) and \(~20\%\) higher efficiency for Alq\textsubscript{3} and C545T, respectively). The slight difference in enhancement factors for Alq\textsubscript{3} and C545T is due to the higher radiative lifetime of Alq\textsubscript{3} in the microcavity; \( \tau_{cav}/\tau \sim 0.9 \) for Alq\textsubscript{3}\textsuperscript{141} and \( \tau_{cav}/\tau \sim 0.8 \) for C545T\textsuperscript{128}.

A low sheet resistance is critical for large area OLED applications in order to minimize Ohmic losses in the electrode. Since the EL emission from OLEDs is dependent on applied bias, even a small drop in voltage across a large electrode will cause noticeable non-uniformities. Figure 8.5 shows large area (25 x 75 mm\textsuperscript{2}) OLEDs fabricated using ITO and AuO\textsubscript{x} anodes. For the device with ITO anode (Figure 8.5a) the emission is non-uniform across the length of the device due to the voltage drop in the ITO layer; notice that the device is brightest near the cathode contact at the left of the figure. In contrast the device with AuO\textsubscript{x} anode (Figure 8.5b) has significantly more uniform emission. Also, notice the bright halo around the left side of the ITO device (top); edge emission from the substrate is suppressed for the AuO\textsubscript{x} anode due to the elimination of the waveguide modes in the ITO layer.\textsuperscript{129} Since the sheet resistance of ITO deposited on plastic is typically 4-5 times higher than that of ITO on glass,\textsuperscript{124} non-uniformity is expected to be an even more significant problem for large area flexible OLEDs using ITO as anode. To demonstrate the versatility of AuO\textsubscript{x} as anode for large area flexible OLEDs devices were fabricated on plastic
substrates. Figure 8.5c shows a large area (50 x 50 mm$^2$) flexible OLED on plastic using AuO$_x$ anode. The device is free of defects and dark spots commonly found on ITO based devices. In addition the yield and reproducibility of the devices was very high, and on par with that of devices fabricated on ITO.

![Figure 8.5: Picture of operating large area green OLEDs fabricated on, (a) glass substrate with ITO anode, (b) glass substrate with AuO$_x$ anode, and (c) flexible plastic substrate with AuO$_x$ anode. The size of the devices in (a) and (b) is 25 x 75 mm$^2$ and in (c) the size is 50 x 50 mm$^2$.]

8.4 Summary

In summary, the use of oxidized Au as anode in OLEDs has been demonstrated. The unique efficacy of these devices was found to result from enhanced injection of holes (relative to Au) into commonly used hole transporting molecules due to a large reduction in the interface dipole at the metal/organic interface. Combined with the enhanced EL emission as a result of a weak cavity effect, high performance OLEDs with Lambertian emission were realized. Due to the ease of processing of Au thin films large area flexible OLEDs on plastic substrates with uniform emission were easily demonstrated. It is envisioned that AuO$_x$ will potentially provide a new platform for enabling the roll-to-roll processing of next generation flexible organic optoelectronics for applications such as solid state lighting.
9 Chlorinated Indium Tin Oxide Electrodes*  

9.1 Background  

Transparent conducting oxides (TCOs), such as ITO, are the electrode materials of choice in state-of-the-art organic OPVs, OLEDs and flat-panel displays due to their unique combination of high electrical conductivity and high optical transparency across the visible spectrum. Controlling the interface properties between ITO and organic materials is of great importance for device engineering since the performance, stability and lifetime of organic devices are greatly influenced by the electrode/organic contacts. Organic electronic devices fabricated on bare ITO electrodes are problematic due to insufficient charge injection and poor operational stability caused by the large mismatch between the work function of ITO (~ 4.7 eV) and the HOMO of the organic.  

Chemical modification of the ITO surface has been extensively studied to control its work function and surface energy for improved charge injection and interfacial stability with organic hole-transporting materials. Unfortunately, chemical surface treatments typically cannot increase the work function of ITO high enough for efficient charge injection into many organic HTLs, particularly molecules with very deep HOMOs. Additional injection layers, such as CuPc, PEDOT:PSS or transition metal oxides such as WO₃, are therefore required to facilitate charge injection from ITO electrodes. However, introducing additional injection layers complicates the device design and can often introduce additional problems with materials matching. For example, the high acidity of PEDOT:PSS tends to corrode the surface of ITO resulting in poor interfacial stability. The ability to tune the work function of ITO high enough to enable charge injection into organic materials with deep HOMOs, without the need for additional injection layers, is thus highly desirable.  

Early on it was discovered that UV ozone or O₂ plasma treatment could significantly increase the work function of ITO, resulting in enhanced device performance. Due to the high reliability and simplicity of these treatments, they are now standard practice in the ITO cleaning process. However, the work function of UV ozone or O₂ plasma treated ITO is often not high

* This chapter published as Science 332, 944 (2011).
enough for many device applications\textsuperscript{144} and also tends to rapidly decrease due to hydrolysis or desorption of the meta-stable surface oxygen species.\textsuperscript{145} Elaborate chemical treatments have therefore been developed over the years in an attempt to overcome these problems by functionalizing the surface of ITO with more stable electronegative species.

Halogen atoms are ideal candidates for functionalizing the surface of TCOs since they can be highly electronegative and form stable chemical bonds with In and Sn (the building blocks of most TCOs). Various chemical methods of functionalizing ITO with halogen species have been attempted. Most techniques involve exposing the ITO to a halogen acid (e.g., HCl) or elemental halogen in either the vapour phase or dissolved in an organic solvent.\textsuperscript{146-148} Treatment with halocarbon plasmas (e.g., CHF\textsubscript{3}) has also been shown to be effective in creating surface indium halide species.\textsuperscript{149-151} However, treating ITO with acids or elemental halogens tends to corrode the surface resulting in increased surface roughness and reduced conductivity.\textsuperscript{146} Halocarbon plasmas corrode the surface of ITO less, but often leave behind increased carbon contamination and require specialized equipment.\textsuperscript{152} What is more, none of these techniques have been able to achieve a work function much higher than what can be achieved with UV ozone or O\textsubscript{2} plasma.

In this chapter a simple method for tuning the work function of TCO thin films using a novel UV assisted halogenation technique is presented. It is demonstrated that decomposition of halogenated solvents using UV treatment can be used to functionalize the surface of TCOs with halogen atoms. Using this facile technique an unprecedented high work function of $> 6.1$ eV for Cl functionalized ITO (Cl-ITO) is achieved. The application of Cl-ITO in organic electronic devices allows efficient charge injection into organic materials without the need for additional injection layers, potentially simplifying device design and fabrication.
Figure 9.1: Picture of an Cl-ITO sample being treated in a Pyrex Petri dish with UV radiation. The distance between the low pressure mercury lamp and the Petri dish is ~5 cm.

9.2 Methods

9.2.1 Preparation of Cl-ITO

Samples were first pre-treated with UV ozone for 3 minutes to remove carbon residue left behind by the standard solvent cleaning process. The sample was then placed in a closed Pyrex Petri dish with a drop of 1,2-dichlorobenzene (~ 0.1 mL) and treated with UV for up to 10 minutes (see Figure 9.1). Finally the sample was treated outside of the Petri dish with UV ozone for an additional 3 minutes to fully remove any residual chloro-carbons. The Petri dish helps to contain and concentrate the solvent vapour and also limits the formation of ozone by blocking out the lower wavelength UV (see Figure 9.2). Since the cut-off wavelength of the Petri dish is similar to the C-Cl bond energy in many chlorinated solvents,\textsuperscript{153} decomposition therefore most likely occurs by direct photolysis.
9.2.2 Device Fabrication and Characterization

The standard device structure for the simplified OLEDs is as follows: anode/CBP (35 nm)/CBP:Ir(ppy)$_2$(acac) (15 nm, 8%)/TPBi (65 nm)/LiF (1 nm)/Al (100 nm). The luminous flux for calculating the EQE and power efficiency were measured using an integrating sphere with a silicon photodiode with NIST traceable calibration. The device under test was mounted on the entrance aperture of the integrating sphere (i.e., the sample was not placed inside the sphere) for all measurements (see Figure 9.3). Measurements with out-coupling enhancement used a 10 mm diameter BK7 half-sphere lens mounted on top of the device with index matching gel. The electroluminescence (EL) spectra were measured using an Ocean Optics USB4000 spectrometer. The angular distribution of the EL intensity was measured using a goniometer. All the measurements were conducted in ambient air. Transmittance measurements were taken using a PerkinElmer Lambda 1050 UV/Vis/NIR spectrophotometer. Surface roughness was measured using AFM with a Digital Instruments Dimension 3000. Conductivity was measured using a custom built 4-point probe with a Keithley 2400.
Figure 9.3: Schematic diagram of the measurement geometry using an integrating sphere.

9.2.3 Photoelectron Spectroscopy

All photoelectron spectroscopy measurements were performed with the electrostatic lens of the analyzer configured for an analysis area of 0.5 mm$^2$ (800 μm diameter circle) and a photoelectron acceptance angle of ±5°. XPS spectra were collected at a photoelectron take-off angle of 75°. All work function measurements (both XPS and UPS) and UPS spectra were collected at a photoelectron take-off angle of 90° (normal emission) with a -15V bias.

9.2.4 Efficiency Measurements

Calculation of the external quantum efficiency (EQE) and power efficiency (PE) require measurement of the total flux. For a Lambertian source the angular distribution of the emission intensity follows Lambert’s cosine law and hence the total flux can be determined from the forward intensity. However, since not all OLEDs are Lambertian sources$^{157}$ the EQE and PE should be calculated based on a measurement of the total flux. For our devices the intensity is side enhanced (Figure 9.4), and hence calculation of the EQE and PE from the forward intensity assuming a Lambertian source would be greatly underestimated.
Watanabe et al.\textsuperscript{158} have shown that the EQE and PE calculated assuming a Lambertian source can be either overestimated or underestimated depending on the device structure. Therefore, to avoid such uncertainty in the determination of the EQE and PE of our devices an integrating sphere was used to measure the total flux. The device was mounted on the entrance port of the integrating sphere. The efficiency measurements from the integrating sphere have been confirmed using two independent measurement techniques. First, the total flux was measured using a calibrated Si photodiode following the procedure of Forrest et al.\textsuperscript{154} Second, the total flux was calculated by integrating the angular distribution of the intensity measured using a goniometer. All three measurements are in excellent agreement with each other (Figure 9.5).

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig9_4.png}
\caption{Angular dependence of the EL intensity of Cl-ITO based OLEDs.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig9_5.png}
\caption{EQE as a function of current density measured using three different techniques.}
\end{figure}
9.3 Results and Discussion

X-ray photoelectron spectroscopy (XPS) was used to characterize the work function and surface composition of the Cl-ITO electrode. Figure 9.6a shows the secondary electron cut-off and Cl 2p core-level, respectively, of Cl-ITO as a function of increasing UV treatment time from 0 - 10 minutes. With increasing treatment time the secondary electron cut-off monotonically shifts to lower binding energy, indicating an increase in work function. The intensity of the Cl 2p peak also increases concurrently with treatment time, indicating an increase in the surface coverage of Cl. Beyond 10 minutes of treatment time the secondary electron cut-off and Cl 2p peak remain unchanged, suggesting that the surface is saturated with Cl.
Figure 9.7: Surface composition of Cl-ITO. a, C 1s, Cl 2s and Cl 2p core levels for $\Theta = 0$ (bare surface) and $\Theta \approx 1$ (saturated surface). The inset shows the Cl 2p core level of Cl-ITO compared to InCl$_3$. b, (left) valence band for $\Theta = 0$ and $\Theta \approx 1$, and (right) density of states at the Fermi level for $\Theta = 0$ and $\Theta \approx 1$.

To determine the distribution of Cl atoms in the sample angle resolved XPS (AR-XPS) measurements were performed on a sample treated for 10 minutes. Figure 9.6b shows the measured intensities of the Cl 2$p$ (from the overlayer) and In 3$d$ (from the substrate) core levels as a function of photoelectron take-off angle ($\theta$). The surface sensitivity of XPS is increased at low photoelectron take-off angles due to a reduced photoelectron escape depth. Hence the increase in signal intensity of the Cl 2$p$ core-level at low photoelectron take-off angles indicates that the Cl atoms are confined to the surface of the Cl-ITO. The AR-XPS data also indicate that the surface coverage of Cl is close to one monolayer for the Cl saturated surface.$^{159}$

Figure 9.6c shows the work function determined from the secondary electron cut-off as a function of surface coverage ($\Theta$) determined from the Cl 2$p$ signal intensity and AR-XPS results.
The work function of Cl-ITO is found to increase linearly with the Cl surface coverage, indicating that the work function can be tuned by controlling the amount of Cl on the surface. For the highest Cl surface coverage (\( \Theta \approx 1 \)), corresponding to a treatment time of 10 minutes, a work function of 6.13 eV was measured. This is an unprecedented high work function, particularly considering that the electrode is prepared in ambient air. As shown in Figure 9.6d the high work function was also found to be stable with time, there was no significant change after 24 hours.

![Figure 9.8: XPS spectra of Cl-ITO showing the Cl 2p core level. The spectra can be fit with a single doublet peak, indicating that only a single Cl species is present on the surface. The binding energy of the Cl 2p peak is 199.06 eV, consistent with an In-Cl bond.](image)

Figure 9.7a shows the C 1s, Cl 2s and Cl 2p core levels of Cl-ITO with \( \Theta = 0 \) (bare surface) and \( \Theta \approx 1 \) (saturated surface). The C 1s peak is essentially identical on the two samples, indicating that the Cl is not in the form of a chloro-carbon fragment. It has also been confirmed that the Cl is not from residual chlorinated solvent on the surface by measuring a sample dipped into chlorinated solvent; no Cl was detected. This finding suggests that the Cl is chemically bonded to the surface. To determine the nature of the Cl chemical bond high resolution XPS spectra of the Cl 2p core level were examined. The Cl 2p core level can be fit using a single doublet peak, indicative of only a single chemical species of Cl (Figure 9.9). The Cl \( 2p_{3/2} \) binding energy of
this species is 199.06 eV (Figure 9.8), which rules out chlorate and perchlorate, which have a much higher binding energy. The inset of Figure 9.7a shows the Cl 2p core level of Cl-ITO and InCl₃. The spectra are identical, which demonstrates that the Cl is bonded to In at the surface. A separate peak in the In 3d core level for the In-Cl bond could not be resolved due to the similarity in binding energies between In-O and In-Cl.

![XPS spectra of UV ozone treated ITO dipped in o-dichlorobenzene (DCB) showing the C 1s, Cl 2s and Cl 2p core levels. No Cl is detectable on the sample indicating that the Cl detected on Cl-ITO is not from residual DCB.](image)

**Figure 9.9:** XPS spectra of UV ozone treated ITO dipped in o-dichlorobenzene (DCB) showing the C 1s, Cl 2s and Cl 2p core levels. No Cl is detectable on the sample indicating that the Cl detected on Cl-ITO is not from residual DCB.

Figure 9.7b shows the valence band of Cl-ITO with Θ = 0 (bare surface) and Θ ≈ 1 (saturated surface) measured using XPS and UPS. The valence band maximum of both samples is located 3.1 eV below the Fermi level, indicating that the Cl does not alter the doping level. Since ITO is an n-type degenerate semiconductor the finite density of states (DOS) at the Fermi level is representative of the partially filled conduction band. The DOS at the Fermi level, which is a sensitive indication of surface electronic structure, is nearly identical on both samples. It is therefore clear that the high work function of Cl-ITO cannot be a result of a change in Fermi level (i.e., electrochemical potential), doping level, or surface electronic structure. By definition the work function of a uniform surface of a conductor is the difference between the electrochemical potential $\mu$ of electrons in the bulk and the electrostatic potential energy $-e\Phi_{\text{vac}}$ of an electron in the vacuum just outside the surface,

$$e\phi_m = -e\Phi_{\text{vac}} - \mu.$$ (9.1)
The Cl must therefore change the electrostatic potential just outside the surface. Our XPS data demonstrates that Cl is bonded to In at the surface. Due to the large difference in electronegativity between In and Cl (i.e., 1.78 compared to 3.16) the In-Cl bonds at the surface are polar, which is equivalent to introducing a layer of dipoles across the surface. These dipoles would increase the electrostatic potential energy just outside the surface (Figure 9.10).

Figure 9.10: Schematic energy-level diagram of Cl-ITO with (a) Θ = 0 (bare surface) and (b) Θ ≈ 1 (saturated surface) showing the effect of polar In-Cl bonds on the work function. The work function (ϕ_m) is taken as the difference between the local vacuum level (E_{vac}) and the Fermi level (E_F) as indicated.

9.4 Device Applications

To demonstrate the significant benefits of the tuneable high work function of Cl-ITO for device applications simplified phosphorescent OLEDs were fabricated using the high work function of Cl-ITO to enable direct injection of holes into CBP, the host material used for the phosphorescent emitter. A complex multi-layer hole injection/transport stack is typically required to match the deep HOMO of CBP (6.1 eV). Using Cl-ITO, however, allows us to tune the work function of the anode to match the deep HOMO of CBP without having to introduce any additional injection/transport layers, thus greatly simplifying the device design and fabrication. Such a simplified device design also has the potential to greatly improve device performance as it eliminates several of the heterojunctions in the device which can block carrier transport and contribute to exciton quenching. Figure 9.11 shows a schematic energy-level diagram of the simplified OLED using Cl-ITO as anode. Part of the CBP layer is doped with the phosphorescent emitter to form the emission zone.
Figure 9.11: Schematic energy-level diagram of simplified OLED.

Figure 9.12: Energy-level alignment between CI-ITO and CBP. b, UPS spectra of CBP deposited on CI-ITO with different work function. The inset shows a schematic energy-level diagram of the CI-ITO/CBP interface. c, Current density as a function of voltage for CBP based OLEDs fabricated on CI-ITO with different work function.
Figure 9.12b shows the HOMO derived peak of CBP deposited on Cl-ITO with different work functions measured using UPS. By tuning the work function of the Cl-ITO to match the deep ionization potential of the CBP the barrier height at the interface can be reduced by ~0.7 eV. Figure 9.12c shows current density as a function of voltage of OLEDs fabricated on Cl-ITO with different work functions. With increasing work function the operating voltage of the OLED is dramatically reduced due to the lower barrier height at the Cl-ITO/CBP interface.

Figure 9.13 shows a photograph of a Cl-ITO based OLED operating at high brightness as well as a large area prototype device. Figure 9.14b shows the current-voltage-luminance characteristics of an optimized device with Cl-ITO anode. A similar device fabricated on ITO exhibited an extremely high driving voltage and no visible electroluminescence (EL) due to the poor energy-level matching between ITO and CBP.

![Image of OLEDs](image.png)

**Figure 9.13:** Photograph of a device (1 mm × 2 mm) operating at a high brightness of 5,000 cd/m² and (right) a large area prototype device (50 mm × 50 mm).

Figure 9.14c shows the external quantum efficiency of the Cl-ITO device. The EQE reaches a record high 29.1% (93 cd/A) at 100 cd/m², 29.2% (94 cd/A) at 1,000 cd/m², and 25.4% (81 cd/A) at 10,000 cd/m². Although a similarly high efficiency can be achieved in a traditional device with α-NPD hole-transport layer and PEDOT hole-injection layer at low luminance (90 cd/A at 100 cd/m²), the efficiency is much lower at high luminance (50 cd/A at 10,000 cd/m²), as shown in Figure 9.15. The drastic efficiency roll-off in the traditional device (i.e., ITO/PEDOT/α-NPD) is due to the additional organic-organic heterojunctions in the device, which block carrier transport and contribute to exciton quenching. Even at an ultrahigh luminance of 100,000 cd/m², the EQE of the Cl-ITO device is still as high as 14.3% (46 cd/A).
Figure 9.14: Device performance of OLEDs with Cl-ITO electrode. b, Current density and luminance as a function of voltage. The inset shows the EL spectra as a function of current density. c, EQE and power efficiency as a function of luminance. The open symbols are without out-coupling enhancement and the solid symbols are with lens-based out-coupling enhancement.

The power efficiency of the Cl-ITO device reaches 97 lm/W at 100 cd/m², 79 lm/W at 1000 cd/m², and 51 lm/W at 10,000 cd/m², which is better than state-of-the-art p-i-n phosphorescent organic light-emitting diodes, which require six or more organic layers.158,163

The use of a simple lens-based structure to help out-couple trapped light at the glass-air interface155,156,164 can further enhance the device performance, and the EQE can be further increased to 54% at 1000 cd/m², 50% at 10,000 cd/m², and 35% at 100,000 cd/m². The maximum power efficiency is also increased to 230 lm/W. At 10,000 cd/m² the power efficiency is still as high as 110 lm/W, more than double the value of the best previously reported OLED.

Using a high index substrate instead of glass could further help to improve the efficiency by outcoupling more light trapped in the ITO modes.136,144
Figure 9.15: Effect of stepwise injection on device performance. Current efficiency as a function of luminance for devices with Cl-ITO anode in comparison to devices using a traditional stepwise injection structure. The ITO was coated with 5 nm of PEDOT, and the 35-nm-thick undoped region of CBP was replaced with a separate layer of α-NPD of the same thickness, yielding ITO/PEDOT (5 nm)/α-NPD (35 nm)/CBP:Ir(ppy)2(acac) (15 nm, 8%)/TPBi (65 nm)/LiF (1 nm)/Al (100 nm).

9.5 Summary

The facile tuning of the work function of Cl-ITO demonstrated in this work can also be applied to different materials systems, such as other halogen atoms or TCOs and should also be applicable in a variety of different organic optoelectronic devices, such as organic solar cells, and organic thin film transistors. Independent control of the work function of transparent electrodes up to unprecedented high values offers a new materials platform for the design of simplified high performance organic optoelectronics. No longer are complicated multi-layer charge injection and transport structures required to align the energy-levels of the organic materials with the low work function of the transparent electrode. As has been shown, tuneable high work function TCOs potentially can enable simplified high performance device structures, thus reducing manufacturing costs for next generation mass produced organic optoelectronic devices, such as OLEDs for solid state lighting.
10 Chlorinated ITO Electrodes for Admittance Spectroscopy*

10.1 Background

The carrier mobility of organic semiconductors is an important parameter for many aspects of device performance and design. Several techniques can be used to measure the carrier mobility of thin film organic semiconductors, such as time of flight (TOF), space charge limited current (SCLC), and admittance spectroscopy (AS). Although TOF is the most accurate and reliable method to measure carrier mobility, it is often not practical since it requires several micron thick films and specialized equipment. It is often difficult to replicate the morphology of the thin films used in devices, typically ~100 nm, in the micron thick films required for TOF measurements. What is more, TOF is not well suited to measure the carrier mobility of organic materials with highly dispersive transport. AS has recently drawn significant attention as a practical alternative to the TOF technique.165-170

AS is based on the measurement of the frequency-dependent capacitance of an organic thin film. The typical thickness of the organic layer is ~300 nm, which is much closer to the real thickness used in devices. What is more, AS is also capable of measuring the carrier mobility of organic materials with highly dispersive transport.171 However, AS requires an Ohmic contact between the charge injecting electrode and the organic material under study.172 Recently, transition metal oxides, such as WO₃ and MoO₃, have been proposed as charge injecting layers for admittance spectroscopy.8 Due to their high work function, typically > 6.0 eV, transition metal oxides can enable efficient hole injection into many organic hole transporting materials, even with deep highest occupied molecular orbitals (HOMOs).8 However, most transition metal oxides are insulators or semiconductors and may therefore introduce series impedance into the device structure. The use of a transition metal oxide charge injection layer can therefore alter the measured frequency-dependent capacitance of the organic layer, introducing error into the mobility measurement.

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In this chapter, Cl-ITO discussed in the last chapter is examined as a charge injection anode for AS. Cl-ITO is shown to be advantageous as a charge injecting anode for AS since it possesses a high work function of >6.1 eV, but does not introduce any series impedance into the device structure. The hole mobility of α-NPD measured using AS with a Cl-ITO anode is found to be closer to the value measured by TOF than for an equivalent measurement with a MoO₃ layer.

### 10.2 Methods

Single carrier devices for the AS measurements were fabricated on commercially patterned ITO coated glass with a sheet resistance less than 15 Ω/□. The standard device structure is as follows: anode/α-NPD (536 nm)/Ag. The anodes used in this work were bare ITO, Cl- ITO, and ITO coated with 0.75 nm of MoO₃. Cl- ITO was produced by treatment of pre-cleaned substrates with 1,2-dichlorobenzene vapour for 10 minutes in a sealed Pyrex Petri dish in UV photo surface processor (SEN Lights Corporation), followed by UV ozone treatment for 3 minutes. The frequency-dependent capacitance of the devices was measured using an HP4192A impedance analyzer in the vacuum cryostat.

### 10.3 Theory

The theory behind the AS technique has been extensively discussed in the literature. A very thorough summary of the technique complete with all derivations is provided in Ref. In short the AS technique is based on the measurement of the frequency-dependent capacitance of an organic thin film. The capacitance is found to exhibit a characteristic minimum as a function of frequency, which is indicative of the carrier transit time \( \tau_{dc} \) across the organic film. Typically the frequency-dependent capacitance is re-plotted as the negative differential susceptance,

\[
-\Delta B = -\omega \left( C - C_{geo} \right),
\]

where \( \omega = 2\pi f \) is the angular frequency, \( C \) is the capacitance and \( C_{geo} = \varepsilon A/d \) is the geometric capacitance. This plot typically yields a maximum in \(-\Delta B\) at a characteristics frequency \( f_r = \tau_1^{-1} \). Simulation results have shown that \( \tau_{dc} = 0.56 \tau_r \) for non-dispersive transport. The dc mobility is then given by,
\[ \mu_{dc} = \frac{d^2}{\tau_{dc} (V - V_{bi})}, \]  

(10.2)

where \( d \) is the device thickness, \( V \) is the applied voltage and \( V_{bi} \) is the built-in potential, which can be measured using photovoltaic measurements.\(^\text{14}\)

### 10.4 Results and Discussion

Figure 10.1 shows the room temperature (300 K) current-voltage (\(IV\)) characteristics of \(\alpha\)-NPD single carrier devices with ITO, ITO/MoO\textsubscript{3}, and Cl-ITO anodes. As expected the device with bare ITO anode has the lowest current density due a large injection barrier at the ITO/\(\alpha\)-NPD interface. The current density of the devices with ITO/MoO\textsubscript{3} or Cl-ITO anodes is \(\sim 2\) orders of magnitude higher than the device with bare ITO anode. Transition metal oxides, such as MoO\textsubscript{3}, have been reported to lower the injection barrier into HTL molecules due to their high work function.\(^\text{174}\) Cl-ITO also has a high work function of \(>6.1\) eV,\(^\text{175}\) which allows for a lower injection barrier into \(\alpha\)-NPD. The current density of the device with Cl-ITO anode is slightly higher than that of the device with ITO/MoO\textsubscript{3} anode, particularly at higher currents. This suggests that there is series impedance introduced by the MoO\textsubscript{3} layer. The mobility extracted from devices with ITO/MoO\textsubscript{3} anode using AS might therefore be influenced by this impedance.

![Figure 10.1](image-url)

**Figure 10.1:** Current density as a function of electric field for \(\alpha\)-NPD single carrier devices with ITO, ITO/MoO\textsubscript{3}, and Cl-ITO anodes. The inset shows the device structure. The electric field (\(F\)) is taken as 
\[ F = (V - V_{bi})/d, \]  
where \( V \) is the applied voltage, \( V_{bi} \) is the built-in potential determined from photovoltaic measurements and \( d \) is the device thickness (536 nm).
Figure 10.2 shows the frequency-dependent capacitance and conductance of α-NPD single carrier devices with Cl-ITO anode as a function of applied bias. At zero applied bias the capacitance is nearly constant with frequency and is representative of the geometric capacitance $C_{geo}$. The decline in capacitance at high frequency is due to the parasitic capacitance of the test fixture and does not affect the present analysis. With increasing applied bias the characteristic minimum in the capacitance curve shifts to higher frequency, indicative of the field dependent mobility of the organic. Figure 10.3 shows the negative differential susceptance $-\Delta B$ as a function of voltage for the same device. The characteristic frequency $f_r = \tau_r^{-1}$, indicated by the arrows, shifts to higher frequency with increasing applied bias.

![Figure 10.2: Admittance spectra as a function of bias for α-NPD single carrier devices with Cl-ITO anode showing (a) the frequency-dependent capacitance, and (b) the frequency-dependent conductance.](image)

Figure 10.4 shows the hole mobility as a function of electric field extracted from the negative differential susceptance of α-NPD single carrier devices with ITO, ITO/MoO$_3$, and Cl-ITO anodes. The mobility measured by TOF is also shown as reference.$^{71}$ As expected the mobility extracted from the device with ITO anode using AS is significantly lower than the value measured using TOF. What is more, the field dependence is also significantly different than the TOF results. This can be easily understood as there is a significant injection barrier of $\sim$0.6 eV at the ITO/α-NPD interface;$^{176}$ as discussed above AS requires an Ohmic contact at the electrode.
Figure 10.3: Frequency-dependent negative differential susceptance as a function of bias for α-NPD single carrier devices with Cl-ITO anode. The arrows indicate the characteristics relaxation time $f_r = \tau_r^{-1}$.

The mobility extracted from the device with ITO/MoO$_3$ anode using AS is much closer to the value measured using TOF, but is still noticeably lower. Since MoO$_3$ has been reported to form an Ohmic contact with α-NPD$^{61}$ this implies that the impedance of the MoO$_3$ layer does indeed affect the AS measurements. On the other hand, the mobility extracted from the device with Cl-ITO anode using AS is nearly identical to the value measured using TOF, since the Cl-ITO electrode does not introduce any series impedance into the device. Clearly, Cl-ITO is an advantageous charge injecting electrode for mobility measurements using AS.

Figure 10.4: The field dependent hole mobility as a function of the square root of electric field extracted from α-NPD single carrier devices with ITO, ITO/MoO$_3$, and Cl-ITO anodes using AS. The dashed line is the mobility measured by TOF shown as reference.$^{71}$
10.5 Summary

In summary, it has been shown that Cl-ITO can be used as a charge injecting electrode for mobility measurements using AS. The mobility extracted from devices with Cl-ITO anode using AS is found to be closer to the value measured by TOF than for devices with ITO/MoO$_3$ anode. The lower value of the mobility measured for the devices with ITO/MoO$_3$ anode is attributed to the effect of the series impedance introduced by the MoO$_3$ layer. Cl-ITO is therefore found to be an ideal charge injecting electrode for mobility measurements using AS since it possesses a high work function, but does not introduce any series impedance into the device structure.
11 Summary and Future Work

11.1 Summary

This thesis has addressed some of the fundamental characteristics of electrode/organic interfaces in organic optoelectronics. As a result of the insights gained a universal method of tuning the work function of a conductor was developed using halogenated organic solvents and UV light.

In Chapter 3, the fundamental theories related to energy-level alignment and charge injection at electrode/organic interfaces was discussed in the contact of interface dipole theory and traditional semiconductor transport equations.

In Chapter 4 the energy-level alignment at various metal/organic and metal/oxide/organic interfaces in real devices were examined. It was found that theoretically predicated hole injection barriers using interface dipole theory were in excellent agreement with experimentally determined values based on transport experiments. It was further found that interface dipole theory not only explains why metal oxides act as universal hole injection layers, but can also be used to accurately predict the injection barriers.

In Chapter 5 the effect of the metal substrate on the energy-level alignment at metal/oxide/organic interfaces was examined. The charge injection properties at the $V_2O_5/\alpha$-NPD interface on Au, ITO and Mg anodes were compared using temperature dependent $IV$ measurements. It was found that the injection current at the $V_2O_5/\alpha$-NPD interface is greater for Au than for either Mg or ITO. This result indicates that the energy-level alignment at the $V_2O_5/\alpha$-NPD interface is dependent on the underlying metal, which contradicts previous reports in the literature. $V_2O_5$ was found to incompletely pin the Fermi level, such that the work function of the underlying substrate can still influence the dipole between $V_2O_5$ and $\alpha$-NPD.

In Chapter 6 the effect of electrostatic screening on the apparent binding energy of peaks in photoelectron spectroscopy measurements of electrode/organic interfaces was examined. It was shown that the experimentally observed thickness-dependent binding energy shifts for a prototypical organic semiconductor on various conductive substrates are well explained by electrostatic screening.
In Chapter 7 the effect of residual gases in high vacuum on the energy-level alignment at metal/organic interfaces was studied. It was found that the energy-level alignment at metal/organic interfaces is strongly dependent on the vacuum conditions under which the samples are prepared. Even the minute amounts of residual gases that are adsorbed on the surface of clean metals in HV can in general significantly alter the energy-level alignment at metal/organic interfaces.

In Chapter 8 oxidized gold thin film was examined as an alternative electrode to ITO in flexible OLEDs. The unique efficacy of these devices was found to result from enhanced injection of holes (relative to Au) into commonly used hole transporting molecules due to a large reduction in the interface dipole at the metal/organic interface. Combined with the enhanced EL emission as a result of a weak cavity effect, high performance OLEDs with Lambertian emission were realized. Due to the ease of processing of Au thin films large area flexible OLEDs on plastic substrates with uniform emission were easily demonstrated.

In Chapter 9 the knowledge gained from the previous studies was synthesized to develop a universal method of halogenating the surface of a material using halogenated organic solvents and UV light. Independent control of the work function of transparent electrodes was demonstrated up to unprecedented high values for the case of chlorinated ITO. Using this new electrode material highly simplified OLEDs with a record high efficiency were demonstrated.

Finally, in Chapter 10 chlorinated ITO was studied as a new charge injection electrode for admittance spectroscopy for measure the mobility of organic molecules. The mobility extracted from devices with Cl-ITO anode using admittance spectroscopy was found to be closer to the value measured by time-of-flight than for devices with ITO/MoO$_3$ anode. The lower value of the mobility measured for the devices with ITO/MoO$_3$ anode is attributed to the effect of the series impedance introduced by the MoO$_3$ layer. Cl-ITO was therefore found to be an ideal charge injecting electrode for mobility measurements using admittance spectroscopy since it possesses a high work function, but does not introduce any series impedance into the device structure.

11.2 Future Work

The findings of this thesis are not only interesting, but were also demonstrated to have utility in real device applications. Highly simplified OLEDs with state-of-the-art efficiency were realized
for the first time as an outcome of this thesis. Indeed, the various inventions developed during the course of this thesis have attracted considerable interest from major flat-panel display manufacturers, and are currently in the process of being commercialized by a spin-off company, OTI Lumionics Inc. (www.otilumionics.com). Nonetheless there are still several avenues of future work that can be explored.

The most significant future work that should be performed is to continue development of the chlorinated ITO discussed in Chapter 9.

1. The detailed mechanism of the halogenation process should be explored, including possible catalytic behavior of the substrate surface, in order to better optimize the processing conditions and design better halogenated precursor molecules. Other organic solvents should be tested as well as further process developments such as plasma based halogenation. Intermediaries and additional volatile products produced during the halogenation process could be determined using gas chromatography mass spectrometry (GC-MS). Reaction products and intermediaries on the surface of the substrate can be studied using vacuum Fourier transform infrared spectroscopy (FTIR) and surface enhanced Raman spectroscopy (SERS). Different types of chlorinated organic compounds should also be investigated to determine the effect of molecular structure on the chlorination process.

2. The stability and lifetime of organic devices fabricated using Cl-ITO electrodes needs to also be examined. Due to the strong covalent bond between Cl and In the interface could likely be more robust than bare ITO. However, Cl is known to be deadly to many of the phosphorescent emitters currently used in OLEDs. In situ lifetime studies of Cl-ITO devices therefore need to be explored. The migration of Cl, if any, from the electrode into the organic layers could be studied using time of flight secondary ion mass spectroscopy (ToF-SIMS) on aged samples.

3. Integration of the Cl-ITO process with standard TFT backplanes needs to be examined. Certain wavelengths of UV light are known to cause pixel shrinkage in standard Si TFTs. Identifying the exact wavelengths of UV light required for the halogenation process would help in this endeavor.
4. Although only chlorinated ITO was demonstrated in this thesis, the same process and methodology should be applicable to other halogens and other substrate materials. These other systems should be explored and optimized. Interesting applications for altering the surface energy could arise from such studies. For example, UV halogenation could be used to deposit atomically thin layers of fluorocarbons.
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