Formation of Interfacial Species by Deposition of MoO$_3$ on Organic Semiconductors

by

Robin T. White

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
Materials Science and Engineering
University of Toronto

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2014

Abstract

Transition metal oxides (TMOs), such as molybdenum tri-oxide (MoO$_3$), have been used in organic optoelectronic devices due to their effectiveness at providing excellent charge transport and reducing charge injection barrier at an interface. By utilizing an inverted device deposition order, whereby the TMO is deposited on-top of the organic semiconductor, as used in organic photovoltaic devices (OPVs) as well as inverted organic light emitting diodes (OLEDs), a full description of the physical and electronic interaction is resolved by use of photoelectron spectroscopy. Significant band bending by way of charge transfer from organic to MoO$_3$ and diffusion into the underlying organic film is observed. The relative extent of the diffusion is extracted by a simple electron attenuation by over-layer model. Universal energy level alignment rule is shown to be consistent even under inverted deposition order, indicating the significant role between TMO and organic semiconductor to form charge transfer species.
Acknowledgments

First I would like to thank Prof. Lu for giving me the opportunity to explore my interest in physics and materials science. I feel that he took a gamble and I could not be more grateful for his trust and guidance. Alongside him were my friends and group mates, always willing to give a helping hand or be involved in a lengthy discussion about what it is we are doing exactly. I need to give extra thanks to Kristine for helping me keep the XPS lab running, unfortunately I will really only know how much work that really is. Also to Michael for providing me with the knowledge so that I had some idea as to what I was doing as well as always being welcome to discuss any questions I might have had, I wish you the very best for your company and career and have no doubt toward your success. I would also like to thank Grayson for being a friend from day one, my enjoyment during my time here would not have been the same without you. Finally I need to say thank you to my family for providing me with emotional and financial support. I hope that you can be proud of the work I have done.

‘Till the next one…
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1 Introduction and motivation

Since the discovery of organic semiconductors in the mid-twentieth century[1], [2] and the demonstration of their use as an efficient light emitting device[3], OLEDs have moved from the research lab, into commercial products such as television screens and mobile displays. OLEDs also continue to show great promise towards applications for future device applications such as flexible displays and wearable electronics. The application of organic semiconductors have also made their way into the energy sector, providing a cheap and effective material for solar cell fabrication, increasing the availability of clean energy to a wider market.

The architecture and material use for any optoelectronic device has huge implications on the performance and lifetime. Over the years the complexity of device structure has increased, but so has efficiency, and each layer in a device has an important role to play in the performance.

The concept of an OLED is fairly straightforward. Under an applied bias, holes are injected from the anode and electrons from the cathode. The charge carriers move through the transport material and meet in the emissive layer.

![OLED device energy diagram](image)

**Figure 1-1: OLED device energy diagram showing charge transport direction. The horizontal scale represents distance**

Here, they interact to form an exciton, which has a probability to decay radiatively. Using an energy diagram approach, a device can be modeled simply, as shown in figure 1-1.
The efficiency of an organic optoelectronic device relies heavily on the ability of charge to move across an interface. At the interface a charge carrier is met by an energy barrier that it must overcome in order to move through to the next material before combining with its opposite in the emissive layer. Organic materials do not have intrinsic charge carriers and so they must be injected into the device from the electrodes. This is often a difficult task as the largest barrier resides typically between the electrodes and organic semiconductors. As a result, injection layers have been used to reduce the barrier height. These buffer layers enhance carrier injection, decreasing contact resistance, which has resulted in vast improvements in optoelectronic devices of all kinds. Since it was discovered that transition metal oxides provided the ability to decrease the hole-injection barrier, numerous metal oxides have now been employed as hole injectors (MoO$_3$, WO$_3$, V$_2$O$_5$, CuO) as well as electron injectors (ZrO$_2$, TiO$_2$) [4]-[6].

1.1 Molybdenum trioxide as an injection/buffer layer in optoelectronic devices

The present research focuses on the interface between MoO$_3$ and various organic semiconductors. MoO$_3$ has been researched quite thoroughly by the optoelectronic community and its values and behavior are well known[6]-[12]. MoO$_3$ has a very deep work function as well as a very low lying conduction band which make it extremely useful as a hole injection layer and p-type dopant for organic semiconductors.

In a typical device, a thin layer of only a few nanometers of MoO$_3$ is inserted between the transparent anode, typically ITO, which has too low of a work function to allow for efficient charge transfer into the organic semiconductor. Charge transport across an interface requires that the donor and acceptor states on either side of the interface be closely aligned. The addition of MoO$_3$ has been shown to act as a surface modification layer, aligning the energy values so that it is suitable to provide Ohmic contact between the electrode and organic material. It has been shown that electron transfer from ITO and the common HTL, NPB, to MoO$_3$ induces a shift in the Fermi levels leading to Ohmic hole injection at the ITO/MoO$_3$/NPB interface [9]. It has also been argued that an induced dipole at the surface of ITO by deposition of MoO$_3$, due to its large work function, ultimately reduced the injection barrier for holes from ITO to NPB. There was also an observation of energy gap state formation, which was attributed to charge transfer, and
could aid in the charge carriers being injected easily from ITO to NPB[13]. More information on the formation of these interface species will be discussed in later chapters, but for now it is suffice to say that the interaction with MoO$_3$ forms a complex system which still has not been fully catalogued.

![Energy level diagrams of an anode/ organic semiconductor interface with and without the insertion of MoO$_3$. The reduced injection barrier, $\Phi_B$, with the addition of MoO$_3$ is attributed to an induced surface dipole and formation of interface states.](image)

**Figure 1-2:** Energy level diagrams of an anode/ organic semiconductor interface with and without the insertion of MoO$_3$. The reduced injection barrier, $\Phi_B$, with the addition of MoO$_3$ is attributed to an induced surface dipole and formation of interface states

1.2 Deposition order – Transition metal oxides on organic semiconductors

Although the interface between these two types of materials has been studied quite extensively in the recent years due to the high performances achieved by devices, a detailed understanding of the interaction taking place is still widely debated. Over the past few years, much research has gone into studying what happens when an organic semiconductor is deposited on top of various substrates, such as metals and metal oxides. This research has mostly been driven by conventional optoelectronic design. There are, however, many designs for devices such as flexible displays, active matrix OLEDs (AMOLEDs) as well as organic solar cells (OSC) which require an “inverted” device architecture whereby the transition metal oxides are deposited on top of an organic semiconductor[5], [14]-[17] [18], [19]. This application of a transition metal
oxide shows improvement in device performance, as well as lifetime, by acting as a buffer layer to protect from high-energy electrode deposition. It also allows for more stable top-electrodes, such as gold and silver to be used, as well as opening the possibility for semitransparent electrodes. An inverted design also allows for n-channel amorphous Si thin film transistors to be used in AMOLEDs, which have shown to provide better performance for large area displays[16].

The interface between organic semiconductors and MoO₃ cannot be assumed to be symmetric. That is, deposition order matters. Although this has been a rule of thumb within the community, not enough detailed and generalized research has been conducted at the organic/MoO₃ interface for small organic molecules used in organic optoelectronic devices such as AMOLEDs, OSCs, flexible OLED displays and semitransparent solar cells and displays to formulate the proposition, which brings us to the point of this thesis. One question that would be particularly important to device performance is, what the extent of diffusion is that occurs with MoO₃ into the underlying organic semiconductor. MoO₃ would act as a p-dopant and create band bending, which has important implications in OSCs, for example. This measurement is quite difficult however, as the length may be quite small and would be difficult to determine using imaging measurements such as scanning electron microscopy (SEM) or atomic force microscopy (AFM), as well as only a physical model might be extracted. The electronic structure at the interface of small organic molecules and MoO₃ is also unknown in this deposition order but the energy alignment at an interface is arguably one of the most important questions in optoelectronic device physics. How charge transport is occurring, whether it be through chemical bond, defect states or simply charge redistribution is an important property that once identified can improve our knowledge of what materials would be best to use when configuring device architecture.

Before we begin to answer these questions, we will discuss some practical uses of this deposition order, which still have room for improvement if more knowledge on the organic/MoO₃ interface were known.
Figure 1-3: Illustration of an inverted optoelectronic device, consisting of the two electrodes, multilayer organic stack and transition metal oxide. This general architecture can be applied to many various devices such as Inverted Active Matrix OLED design and Organic solar cell design.

1.2.1 Lifetime improvement

Currently, Indium Tin Oxide (ITO) sputtered on glass is the standard substrate that is used in various types of organic optoelectronic devices such as OSCs and OLEDs and provides excellent light transmission and conductive properties. However, the novelty of organic materials is to provide flexible and lightweight devices. This can only be achieved if the substrates and electrodes exhibit the same properties. ITO and other similar substrates are brittle and so the possibility of using opaque or semitransparent metal foils instead of ITO for the bottom contact has been investigated. This device architecture also requires that a semitransparent top contact be used. The use of ITO in this architecture design is detrimental to performance since the standard sputtering process could destroy underlying organic molecules. For these reasons, the use of alternative top electrodes has been studied, which require the use of transition metal oxides between the organic layer and electrode to achieve superior performance. One such study looked at using silver as a top electrode. It was found that the best performance occurred in a standard ZnPc:C$_{60}$ OSC when an interlayer of MoO$_3$ was used compared to WO$_3$, V$_2$O$_5$, GeO$_2$, and Cu$_2$O due to improved hole collection and lower series resistance [18]. Without a MoO$_3$ interlayer, the sheet resistance of the silver electrode increased strongly with decreasing thickness. This suggests that diffusion of silver into the underlying organic semiconductor formed a non-conductive mixed layer. The use of MoO$_3$ as a capping layer also helped to improve the lifetime by 80%, this occurred only when the capping layer was in conjunction with the underlying MoO$_3$.
suggesting that MoO$_3$ acts as a buffer layer to greatly enhance lifetime by protecting the underlying organic material and the top metal electrode. This is shown in figure 1-4.

Figure 1-4: Normalized power conversion efficiency of an OSC at an elevated light intensity of 4 suns. As can be seen, the device efficiency lifetime increases with the use of MoO$_3$ sandwiched top electrode, as degradation occurs between metal and organic material which is reduced by the addition of 1nm of MoO$_3$ [18]

Although it was shown that device performance was improved over an extended lifetime, the electronic and physical interaction between organic semiconductor and MoO$_3$ was not investigated.

1.2.2 Fabrication improvement

As has been mentioned, many degradation problems arise in optoelectronic devices when using conventional electrode materials such as ITO and Al, which can be improved by the use of MoO$_3$ and inverted device structure. Oxygen diffusion through Al grain boundaries and degradation of ITO from the acidic nature of some hole transport layers such as poly(3,4-ethylene dioxythiophene):polystyrene sulfonic acid (PEDOT:PSS) in OSCs are two examples[20]. Also, PEDOT:PSS generally needs to be fabricated in an oxygen and moisture rich environment, typically outside the glovebox with baking, which is detrimental to the organic/polymer layer beneath. By using an inverted device structure and incorporating transition metal oxide, MoO$_3$, to replace such polymers as PEDOT:PSS, many problems can be avoided resulting in a fabrication process that is simplified and robust[15]. Transition metal oxide films can be deposited easily by
thermal evaporation, which is compatible with electrode deposition in polymer solar cells or the entire deposition process for small molecule OSCs and OLEDs.

Figure 1-5: Absorption spectra of MoO$_3$ on NPB, doped NPB with MoO$_3$ by co-evaporation and pure NPB film [14]

A recent study using absorption spectroscopy and current-voltage curves has also shown that the deposition of MoO$_3$ on organic semiconductors allows for diffusion of MoO$_3$ into the underlying organic material. This creates a film that is the same as doping by co-evaporation, which can be difficult to get the correct weight ratio. The deposition of MoO$_3$ on organic semiconductors significantly improved device performance, and the optimal performance was used to determine the extent of diffusion. The absorption spectroscopy, shown in figure 1-5, shows the p-type doping of NPB organic semiconductor, as well as indicating the importance of deposition order, where NPB on MoO$_3$ shows a similar absorption curve as pure NPB. The improvement of device performance is shown in figure 1-6, where the optimal performance occurred at 15nm which the authors contributed to the maximum diffusion length where MoO$_3$ reaches the ITO interface and improves hole injection [14].
Figure 1-6: *J-V* curves for the varying thickness of deposited MoO$_3$ on NPB. The optimal performance occurs at 15nm, which the authors attribute to the diffusion length [14]

### 1.2.3 Interface study

Although there have been many papers on the improved performance of OSCs and OLEDs by using an inverted device architecture, a limited amount of research has gone into studying the organic/MoO$_3$ interface to determine structural and electronic information. Only one such study has taken a scientific approach to understanding the interaction at the interface for MoO$_3$ deposited on an organic material. However, the researchers used a polymer poly(dioctylfluorene-alt-benzothiadiazole) (F8BT) as their organic semiconducting material as another research group (Morii et al.) showed improved lifetime and device performance when using F8BT/MoO$_3$ in polymer light emitting diodes (PLEDs)[19].

The research, led by Nakayama, used layer-by-layer deposition of MoO$_3$ on approximately 8nm of F8BT on ITO and subsequently measured XPS and UPS. There were several interesting results explaining the improved device performance by incorporating MoO$_3$ into the device structure. The first was seen by using UPS to observe the change in valence edge and secondary electron cut-off. The valence edge was seen to shift to lower binding energy toward the Fermi level until pinning occurred. The observed tail features were attributed to the formation of
Figure 1-7: (Left) UPS spectra of MoO$_3$ deposited on F8BT. The shift in valence edge can be seen and the formation of an interface state at around 1eV binding energy can be seen around 1nm of deposition. (Right) XPS core level spectra at thicknesses (i) 0nm ii) 0.05nm, iii) 0.19nm, iv) 0.68nm, v) 2.0nm, vi) 3.9nm, and vii) 7.5nm (C 1s only). Thick MoO$_3$ film is also shown in (viii) [21].

oxygen defects leading to an interface state that is occupied close to the Fermi level. This shift in valence edge was also seen by a change in the core level positions giving evidence for band bending by the spontaneous diffusion of MoO$_3$ into the film leading to doping. They concluded that the diffusion depth was approximately only 0.35nm based on the delay of attenuation of the C1s peak intensity. Figure 1-8 shows the summary of the energy value shifts. The continued change in the vacuum level position was associated with a dipole that formed at the interface as a result of charge transfer from F8BT to MoO$_3$. Although no devices were made, device performance improvement was attributed to the formation of interface states close to Fermi level, which allowed for efficient charge transport across the interface.
Figure 1-8: Summary of energy level shifts from the result of MoO$_3$ deposited on F8BT. Band bending is indicated by the shift in binding energy values of the C1s peak as well as the valence edge and the difference between C1s and Mo3d peaks shown in (b).

This thesis is organized into the following sections: Chapter 2 – Experimental methods – here analysis techniques as well as materials used will be described. In chapter 3 – Diffusion at the interface – we will examine how MoO$_3$ incorporates into the organic semiconductor film. In chapter 4 – Electronic interaction – we will examine how charge transfer is occurring between organic semiconductors and MoO$_3$. In chapter 5 – Energy Level Alignment – we will examine the change in the charge injection barrier with MoO$_3$ deposition. And lastly in chapter 6 – Summary and Outlook – the main findings are summarized and potential future directions are discussed.
2 Experimental Methods

The focus of this work was to better generalize our understanding of the interaction between MoO$_3$ and organic semiconducting materials. The aim was to better show how device architecture can have an impact by the interactions that take place under opposite deposition order.

To properly understand these interfaces, very high precision analysis is required. A common technique has been to use photoelectron spectroscopy (PES), which can provide structural, chemical and electronic information. The precision and diversity of this technique is what makes it so useful to better understand complex systems such as these.

2.1 Photoelectron Spectroscopy

Photoelectron spectroscopy techniques measure the kinetic energy of electrons that are emitted from matter as a consequence of the bombardment with electromagnetic radiation. Albert Einstein was the first to correctly describe an equation that relates the kinetic energy of an emitted electron with the incident light energy. This paper is what led to his Nobel Prize in Physics. It would take another 50 years before Kai Siegbahn and coworkers to develop a high-resolution photoelectron spectrometer, which would also earn him a Nobel Prize in Physics, and establish photoelectron spectroscopy as an important research and analysis tool.

The kinetic energy of the ionized electron can be described as:

$$E_K = h\nu - E_B - \phi_s$$ (1)

Where $h\nu$ is the incident light energy, $\phi_s$ is the work function of the spectrometer and $E_B$ is the binding energy of the electron. The work function of the spectrometer is often times a strange concept to be considered and is either left out of conversation or ignored completely, leaving it out of the equation all together. However the precise value must be known to properly calculate binding energy locations. Because the Fermi level of the sample and the spectrometer are aligned from charge transfer after contact occurs, we only need to know the work function of the spectrometer in order to determine the binding energy of core level electrons, since this will tell us the location of the Fermi level and vacuum level for the whole system. Sample work function can be calculated and will be discussed shortly. For a given atom, there is a range of binding
energy values possible, which correspond to the ionization of electrons from different inner and outer electron shells. What is also important is that these binding energy values are characteristic for each element. Measurement of $E_K$ (and therefore $E_B$) provides insight into the identification of atoms and their chemical environment.

**Figure 2-1:** Illustration of the emission of photoelectrons due to the bombardment by electromagnetic radiation. Inset shows the excitation of an individual electron from its energy level to above the vacuum level.

The energy distribution of emitted electrons is then plotted against the number of emitted electrons per energy interval that reach the detector. It is often plotted in terms of binding energy. Using a high-energy irradiation source, such as X-rays (XPS), enables the identification of elemental constituents within a sample. This is because the energy of electrons that can be probed can reside close to the nuclear core. The unique binding energy locations are due to these core level electrons having a unique configuration for every element. Generally speaking the binding energy locations of core level electrons are representative of their surrounding electron densities. That is, the lower the surrounding electron density, the higher the binding energy location. This is due to the shielding effect of the surrounding electrons on the nucleus, and therefore, effective nuclear charge. A heavier element will obviously have a stronger hold on its core level electrons, however for an element bonding to another electronegatively different element, a shift in electron density can be seen by it’s effect on core level electrons when using a higher precision scan, as shown in figure 2-2. This is known as chemical shift and will be discussed in later chapters. In this way we can determine the chemical environment of a sample.
Figure 2-2: XPS spectrum of a carbon based polymer showing the lower resolution scan where elemental constituents can be identified as well as a higher resolution scan where chemical bonding information can be resolved [22].

All photoelectron measurements were carried out using the PHI 5500 Multi-technique system, using monochromated Al Kα X-ray radiation (1486.7eV) and non-monochromated He Iα Ultraviolet radiation (21.22eV). The spectrometer was calibrated using the Au 4f7/2 peak, the Cu 2p3/2 peak and the Ag 3d5/2 peak which were set to 83.98eV, 932.67eV and 368.27eV, respectively. Curve fitting was carried out using PHI MultiPak 6.1A where a best fit for the deconvolution of core level peaks was done using a least-squares analysis. While there are correlations between binding energy locations, many factors are at play and it is difficult to precisely predict binding energy locations. However, binding energy locations can be determined based on standards and are reported in literature. Unfortunately, methods of preparation differ from lab to lab and so there is often a spread in reported values, often greater than ±0.5eV. It is thus up to the user to make use of his/her own intuition to best describe the qualitative features of an XPS spectrum.

As was mentioned, the radiation source is used to probe different energy level electrons, shown in figure 2-3. To observe valence level electrons it is best to use a lower energy irradiation source such as Ultraviolet (UPS). The use of UPS provides a measure of valence-level density of states of a material and can give valuable insight into electron exchange events. The delocalization of electrons forms the basis for the valence
Figure 2-3: Regions of binding energies accessible by using different radiation sources [23].

spectra we observe. In a typical metal solid, energy states are occupied all the way up to the Fermi level. The spectrometer is grounded and when the sample is mounted there is Fermi level alignment by charge transfer in order to maintain charge neutrality. This Fermi level position is set to 0.00eV as measured by a gold sample. The Fermi-Dirac function is plotted with the valence band maximum (VBM) of the gold spectrum shown in figure 2-4. The mid point is used as the reference Fermi level position as this would be the true Fermi level without the tail ends resulting from thermal fluctuation.
Figure 2-4: Valence band spectra collected using UPS of Au. Plotted in red is the Fermi-Dirac function at 298K.

Figure 2-5: UPS spectra of sputter cleaned gold, showing the calculation for vacuum level and work function, \( \Phi \). The secondary electron cutoff (SEC) marks the 0 kinetic energy reference.
In order to properly determine the energetic and electronic properties of a material, the distance between the Fermi level and the vacuum level of a material needs to be known. This value is known as the work function of a material. The work function is important because it represents the minimum energy required to remove an electron from a solid material’s surface. This value can be determined by studying inelastically-scattered, or secondary photoelectrons. These electrons have lost much of their kinetic energy due to collisions while passing through the sample. The secondary electron intensity increases as we move towards lower kinetic energy, and cuts off at zero kinetic energy. This cut-off indicates that electrons have lost all of their energy and can no longer escape the sample surface. By drawing a line equal to the radiation source energy, i.e. 21.22eV from the secondary electron cut-off toward higher kinetic energy, this will give a representation of the location of the vacuum level. By calculating the difference between the Fermi level position of the sample and the vacuum level, one can determine the work function of the material. This is shown in figure 2-5. Another important value which correlates strongly with device performance is the energy gap between the Fermi level and the valence band maximum. As will be discussed in later chapters, this value corresponds to the energy barrier, which must be overcome when injecting charge into a device.

In semiconductor physics, bands are a result of the delocalization of electrons by the broadening of energy levels as atoms are brought into close proximity with one another. Just like atoms have atomic orbitals with discrete energy values, energy bands also have allowed and forbidden energy ranges. The forbidden areas are what make up the band gap in a semiconductor. Similarly, in an organic molecule, molecular orbitals are also formed. These are a result of the delocalization of electrons that form bonds between atoms. The combination of bonding electrons within a molecule make up what is known as the highest occupied molecular orbital (HOMO), much like the valence band of a solid. While the valence states of an atomic solid are delocalized and form bands, organic semiconducting molecules are relatively isolated and represent the HOMO of a single molecule. These valence states can therefore be represented by Gaussian shaped peaks. A typical UPS spectrum of an organic semiconductor, C_{60}, is shown in figure 2-6. Although it might be expected that because of such localization, an organic molecule HOMO should be a narrow peak and not so dispersed as to form a Gaussian distribution, however variation of the molecular energy levels due to inhomogeneities of the local molecular environment and orientation of the molecules contribute to this broadening. Photoexcitation
allows for the dynamic delocalization of charge over at least a few molecules yielding a probability distribution that follows a Gaussian peak. The peak onset is taken as the HOMO value since this value corresponds to a relaxed ionic state and best corresponds with other experimental values[24].

![Normalized Intensity / Arb. Units vs. Binding Energy / eV](image)

**Figure 2-6:** UPS spectrum of an organic semiconductor C_{60}. Inset shows how the HOMO binding energy is measured

### 2.2 Film Deposition

All experiments, including data collection were carried out under ultra-high vacuum conditions. The deposition and measurement of samples were performed seamlessly without breaking vacuum by transfer through separate (but attached) vacuum chambers, as shown in figure 2-7. Growths of the organic and MoO3 films used in this study were performed by physical vapour deposition by either permanently mounted Knudsen cells (K-cells) or by the Transfer Arm Evaporator (TAE). The K-cells house 10cc alumina crucibles and have their own pneumatically actuated shutter as well as independently controlled and shielded heat source. The TAE allows for rapid loading of organic molecules without the need to open the chamber to atmosphere, keeping the contamination by atmospheric gases during deposition down to a minimum. The
TAE is composed of a ceramic crucible, which sits in a tungsten heater basket housed on an aluminum frame attached to a transfer arm. A separate load-lock chamber is used to load in the new molecules, which can then be inserted into the deposition chamber for sample preparation. A set-up of the organic deposition chamber is shown in figure 2-8.

Figure 2-7: (Top) Colourized photograph and (Bottom) schematic lay-out of the vacuum system used for sample preparation and photoelectron spectroscopy. Coloured red is the XPS/UPS system, green is the organic deposition chamber, yellow is the metal oxide deposition chamber and purple is the Central Distribution Chamber which allows *in situ* transfer of the sample to all other chambers.
A thickness calibration for each organic molecule was performed to ensure that there was no signal from substrate interaction. This was done by monitoring the work function and ionization energy of each organic molecule at increasing deposition amounts. UPS is an extremely surface sensitive technique due to the low kinetic energy electrons being able to escape from thicknesses of only a few angstroms up to one nanometer below the sample surface. XPS however, creates much higher kinetic energy electrons, which can have a much larger escape depth, up to a few nanometers. The thickness was then chosen based on saturation of work function and ionization energy, as well as the escape depth for electrons when using XPS was considered. Multiple measurements were taken at this chosen thickness, which gave a distribution within error of ±0.05eV for HOMO and work function measurements taken by UPS. Shown in figure 2-9 is the thickness calibration measurements done for NPB.
Figure 2-9: Thickness determination for consistent organic film measurement, shown here is the calibration done for NPB.

The thickness measurement was monitored using a Quartz Crystal Microbalance (QCM) for all depositions. A QCM outputs a deposition rate and thickness measurement based on the mass change of the crystal. This deposited mass induces a change in the frequency of oscillation of the Quartz crystal that is used to determine the deposition rate and thickness to a precision of 0.1nm. For these experiments it was not necessary to determine the exact thickness of the organic materials deposited, it was only required that we reached a consistent behavior regime where there was no influence from the substrate. For this reason, and to simplify the deposition process, an approximate value for the organic film density of 1.2g/cm$^3$ was used that applied to all the organic materials in this report, their true values varied by approximately $\pm 0.1g/cm^3$ [26]. The deposition of MoO$_3$ occurred in a separate chamber and therefore had its own QCM. The precise thickness of MoO$_3$ deposited was essential and so careful calibration using a profilometer was performed.
2.3 Light sensitivity

Although it is known that some light induced effects can result in misguided changes in photoelectron spectra, to the author’s knowledge, a clear and generalized trend has not been shown in reported literature. In this study, shifts in core level peaks show evidence for important interactions at the interface, as will be discussed in later chapters. It is imperative to know the origin of these shifts and to exclude any false interaction as a result of light induced effects over the course of the experimental data collection. To study this, each organic material was first subjected to constant illumination over a time period while monitoring changes in UPS and XPS measurements. Figure 2-10 shows the effects on work function for NPB under constant X-ray and Ultraviolet illumination. The control used UPS measurements over only a few seconds to obtain the information required, separated by the indicated time interval. As can be seen, the XPS illuminated and control samples show very little change of about 0.1eV over the time interval of 2 hours, which would be the same time as a typical experiment. The UPS constant illumination however shows a very radical change. This measurement was only done for analysis purposes and in reality the actual data collection for all other experimental data utilizes the control measurement procedure. Shift in the C 1s peak indicates that the work function change is a result of a change in the Fermi level and not just vacuum level change which may be due to the

![Figure 2-10](image-url)

**Figure 2-10:** (Left) Light sensitivity of NPB showing the effect of irradiation of both UPS and XPS on work function. (Right) The red peak shows the shift in core level to higher binding energy after 120min of X-ray irradiation. This shift is the same as that of the work function, showing a change in the Fermi level position.
physisorption of background gases. Although no chemical states of degraded molecules can be seen in the XPS spectrum, changes in concentration of chemical states can still have an effect on the Fermi level which are well below the detection limit of the XPS, which is sensitive only to parts per thousand. It is important to keep these changes in mind moving forward, however as will be seen, the changes shown here only justify our results further.

Based on our measurements of several organic molecules and correlating the slope parameter of the change in work function with irradiation sensitivity, it has been observed that the effect of X-ray irradiation is linear with an approximate change of -0.001eV per minute. Using our control procedure, the effect of UV irradiation for our data collection has a change of -0.002eV per minute. Shown in figure 2-11 is the summary of these results for all organic molecules used in this report, indicating consistency and possibly generalization to small organic molecules.

![Figure 2-11: XPS light sensitivity of organic molecules used in this report](image)

The effect of irradiation on MoO$_3$ was also monitored using NPB as the underlying organic. Here 1.2 nm of MoO$_3$ was deposited and the effect of UV and X-ray irradiation was monitored. As can be seen in figure 2-12, the effect on the work function is similar to that of just an organic film, with slope parameters of -0.001eV and -0.002eV for XPS and UPS control, respectively. Unlike a pristine organic film however, there is a no change in the core levels for either C1s or Mo3d. This indicates perhaps that a different interaction is producing the change in work
function here. This could be explained by a change in surface dipole from light irradiation, which caused a shift in the vacuum level changing the work function measurement. But with no chemical changes, the Fermi level remained unaltered as shown by the slight decrease in peak intensity but no change in the binding energy.

![Figure 2-12: (Left) Plot of the work function of 1.2nm of MoO₃ on 12nm of NPB under constant X-ray irradiation. (Right) Core level peaks of C₁s and Mo3d with and without X-ray irradiation](image)

Therefore core binding energy positions as measured by XPS can be assumed to provide accurate representation of the interaction between deposited MoO₃ and underlying organic semiconductor. Work function and HOMO location should be measured by the control UPS procedure, with ending values falling within error of ±0.05eV.

### 2.4 Materials Used

To try and get the most generalized view of transition metal oxides on organic semiconductors system, six commonly used but structurally different organic molecules were studied. The effect of size, glass transition temperature, formal oxidation sites as well as HOMO position were all considered by the choosing of these organic semiconductors. The structures of all these molecules are well known and are listed in Table 1.
Table 1: Structure and name of the organic compounds used in this work

<table>
<thead>
<tr>
<th>Molecular name</th>
<th>Abbreviation</th>
<th>Structure [27]-[29] [30]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N,N'$-Bis(naphthalen-1-yl)-$N,N'$-bis(phenyl)benzidine</td>
<td>NPB</td>
<td><img src="image1" alt="NPB Structure" /></td>
</tr>
<tr>
<td>$4,4'$-Bis($N$-carbazolyl) - 1,1'-biphenyl</td>
<td>CBP</td>
<td><img src="image2" alt="CBP Structure" /></td>
</tr>
<tr>
<td>Tris(4-carbazoyl-9-ylphenyl)amine</td>
<td>TCTA</td>
<td><img src="image3" alt="TCTA Structure" /></td>
</tr>
<tr>
<td>$4,4',4''$-Tris[phenyl$(m$-tolyl)amino]triphenylamine</td>
<td>m-MTDATA</td>
<td><img src="image4" alt="m-MTDATA Structure" /></td>
</tr>
<tr>
<td>1,3-Bis($N$-carbazolyl)benzene</td>
<td>mCP</td>
<td><img src="image5" alt="mCP Structure" /></td>
</tr>
<tr>
<td>9-[3-(3-carbazol-9-ylphenyl)phenyl]carbazole</td>
<td>mCBP</td>
<td><img src="image6" alt="mCBP Structure" /></td>
</tr>
<tr>
<td>1,3-Bis(triphenylsilyl)benzene</td>
<td>UGH 3</td>
<td><img src="image7" alt="UGH 3 Structure" /></td>
</tr>
</tbody>
</table>
Organic molecules were thermally evaporated at a rate of 0.3 Å/s. A thickness of approximately 14 nm using typical small organic molecule density of 1.4g/cm³ was used. The thickness was chosen such that the underlying substrate, highly ordered pyrolitic graphite (HOPG), had no effect on the organic semiconductor layer and could not be observed by XPS signal. The thickness still allowed for the sample to remain grounded and prevent charge build up during measurement as is shown in the thickness calibration of organic molecule by monitoring work function, discussed in the previous section of this report. Work function measurements were measured at a take-off angle of 88°. During UPS and work function measurements, the sample was held at a bias of −15 V relative to the spectrometer.

All MoO₃ films were grown by vacuum sublimation from 99.9% pure MoO₃ powder placed into a 10cc alumina crucible in a Knudsen cell. MoO₃ was evaporated at a temperature between 500 – 550°C to obtain a deposition rate of 0.1-0.2Å/sec. The evaporation source was positioned 31cm away from the sample, at an angle of 35° relative to sample normal [7]. The pressure during deposition was approximately 2x10⁻⁹ torr.
Figure 2-13: Energy levels as measured by UPS with band gap and LUMO positions from literature [11], [17], [29], [31], [30], [32]

The choice of using HOPG as a substrate was for convenience and consistency. HOPG is extremely easy to form a flat 1cm x 1cm surface by exfoliation using scotch tape to remove the top layer. This was done before each new sample run, right before the sample was put into vacuum. Other substrates such as Au could have been used, but it has been shown that there is often a large surface dipole associated with metals, HOPG does not generally form interface dipoles, the presence of typical ambient contamination does not change the work function significantly.
3 Diffusion at an interface

In a typical deposition, diffusion at an interface is not a concern. The reason for this is that typically a higher density and stability metal or metal oxide is the underlying layer with which we deposit an organic semiconductor on top. One of the unique aspects to this study is the effect of diffusion since the deposition order is reversed. The high temperature and heavy MoO$_3$ clusters have enough kinetic energy to penetrate into the underlying organic layer as well as diffuse through the low density amorphous film structure of typical organic semiconductor films. This can be a useful effect as the penetration allows for doping of the underlying organic film, aiding in charge transport and energy level alignment[10], [11], [14], [11]. The possibility of diffusion into underlying organic material has been discussed many times in literature[14], [21], [33], however the discussion is primarily based off device performance which gives indirect evidence of diffusion. Degradation mechanism of top-electrodes have also been studied in the past, with one possibility being diffusion of the metal into underlying organic material reducing the conductivity and also forming new chemical species[34]. Typically if further study is performed, researchers will use a sputtering process to determine whether diffusion has occurred and the possible length[35]. This sputtering process uses heavy Ar$^+$ or Xe$^+$ ions to erode the sample and could create diffusion when there may not be any or change the binding energy values of core level peaks by introducing ions into the film creating a false representation of the band alignment. Using a layer by layer approach and comparing the intensity of C1s to Mo3d core level peaks based on the known thickness deposited allows us to observe the bonding information with any amount of diffusion, without damaging the film, giving a more accurate description within a device.
Figure 3-1: Intensity ratio of core level peaks for element A and B as a function of the deposited amount as measured by a QCM for various growth modes. (Left to right) Layer-by-layer (Frank van der Merwe), layer + island (Stranski-Krastanov), islands (Volmer-Weber) [36]

3.1 Intensity attenuation

Figure 3-1 shows illustrations of different growth mode films that would produce the plots above. These modes are well known in the community and can be easily identified. The difficulty would be to determine, if there is some amount of diffusion taking place, how much and what model would it follow. The attenuation of signal intensity is based on the Beer-Lambert law which describes the probability that an electron which has been photoemitted at a certain depth, will escape to the surface without being scattered. This describes the collection depth for which electrons are emitted and reach the detector and is primarily based on the inelastic mean free path of an electron in the material, i.e.

\[ I_t^2 = I_o \int e^{-z/\lambda_l \cos \theta} \, dz \]  

(2)

Where \( \lambda \) is the inelastic mean-free path of an electron, \( I_o \) is the standardized intensity of a thick film with \( I_o = \sigma DLJT A \lambda \), which takes into account electron cross-section (\( \sigma \)), detection efficiency (D), angular asymmetry (L), x-ray flux (J), analyzer transmission (T) and analysis area (A) and take off angle, \( \theta \), which is measured to the surface normal.
If we now consider two films, one on top of the other, we simply need to integrate across appropriate thicknesses and using appropriate inelastic mean free paths, taking the ratio will yield:

\[
\frac{I_A}{I_B} = \frac{I_A e^{-d/\lambda_A \cos \theta}}{I_B \left(1 - e^{-d/\lambda_B \cos \theta}\right)}
\]

(3)

Generally the value of the constants \( I_A \) and \( I_B \) are unknown and would have to measured from standards, under precisely identical conditions. However much of this information is system dependent and so taking a ratio will cancel out any variation and we can use a simple expression that approximates the differences instead

\[
\frac{I_A}{I_B} = \frac{\rho_A \lambda_A}{\rho_B \lambda_B}
\]

Inelastic mean free paths are listed below for each organic molecule used in this study and have been calculated based on NIST Inelastic mean free path database [37]. The values used in these calculations are also shown below. The density was approximated as 1.5g/cm\(^2\) for all organics and 4.7g/cm\(^2\) for MoO\(_3\). The kinetic energy used was based on the X-ray light energy (1486.7eV) and core level binding energy peak location for C and Mo (~284eV and ~232eV).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Band gap (eV)</th>
<th>Valence electrons</th>
<th>Mass (g)</th>
<th>Inelastic mean free path ((\lambda)) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBP</td>
<td>3.3</td>
<td>178</td>
<td>484.59</td>
<td>3.285</td>
</tr>
<tr>
<td>NPB</td>
<td>3</td>
<td>218</td>
<td>588.74</td>
<td>3.296</td>
</tr>
<tr>
<td>mCBP</td>
<td>3.3</td>
<td>178</td>
<td>484.59</td>
<td>3.285</td>
</tr>
<tr>
<td>TCTA</td>
<td>3.2</td>
<td>272</td>
<td>740.89</td>
<td>3.297</td>
</tr>
<tr>
<td>mCP</td>
<td>3.7</td>
<td>50</td>
<td>408.49</td>
<td>3.427</td>
</tr>
<tr>
<td>MTDATA</td>
<td>3.2</td>
<td>296</td>
<td>789.02</td>
<td>3.326</td>
</tr>
<tr>
<td>MoO(_3)</td>
<td>2.8</td>
<td>19</td>
<td>143.94</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Table 2: Values used in the calculation of the inelastic mean free path.
3.2 Experimental results and discussion

For each organic molecule listed in table 2 above, MoO$_3$ was deposited layer by layer and the core peaks for carbon 1s (C1s) and molybdenum 3d (Mo3d) orbitals were observed using a high resolution XPS scan. The pass energy used was 5.95eV, which yielded accurate peak measurements with a FWHM of 0.8eV. The core peaks were then fitted using standard fitting procedures starting with a theoretical prediction of relative peak areas for the carbon bonds of C-C and C-N for a pristine film as mentioned in section 2.1. Since this is an intensity ratio calculation as described above and not atomic composition percent, sensitivity factors were not needed. The intensity ratio (total C area/ total Mo area) was then plotted as a function of deposited MoO$_3$ thickness and a “layer-by-layer” curve was observed, which consisted of no linear portion, suggesting that large islands did not form and the organic material was covered uniformly. The experimental data points were then fitted using a MATLAB non-linear fit algorithm using the equation described above, with an added fitting parameter associated with the thickness $g$. This parameter was associated with decreasing the over-layer thickness of MoO$_3$ that would attenuate the carbon signal. As $g$ approached 1, this would suggest a discrete boundary layer and as $g$ increased this would represent a more diffuse boundary layer. This simple model fit well with all organic semiconductors used and relative diffusion amounts are consistent with other reports by Zhao et al. [14]. The equation used for the fit in figure 3-2 is:

$$\frac{I_{C1s}}{I_{Mo3d}} = \frac{I_{C1s}e^{-(d/g)/\lambda_{C1s} \cos \theta}}{I_{Mo3d} \left(1 - e^{-(d/g)/\lambda_{Mo3d} \cos \theta}\right)}$$

(4)

Where $g$ is the fit parameter.

Below is the experimental data and fitted curves. The y-axis is in logarithmic scale to better show the values. The graph on the right shows a zoom in of the full curve on the left.
Figure 3-2: Experimental results and fitted curves for 6 organic molecules. The fit parameter, g, indicates the relative amount of diffusion occurring for each molecule and trends are consistent with expected literature values.
Previously in literature, the diffusion of MoO$_3$ has been suggested to be a result of the high sublimation temperature and heavy mass cluster that will have sufficient kinetic energy to penetrate into the underlying organic material [14], [21]. This model makes sense, especially when considering the conventional deposition order, where no diffusion is seen. It has been suggested by Zhao et al. that the amount of diffusion is dependent on the thermal stability of the organic molecule, i.e. their sublimation temperature. When comparing the molecules used in this study, CBP and it’s derivative molecules had the highest amount of diffusion, with larger molecules TCTA and MTDATA having the least amount. If the molar mass is plotted with the fit parameter $g$, a trend showing the relative diffusion with decreasing organic molecule mass is seen, shown in figure 3-3. This also supports the ‘diffusion by kinetic energy’ model.

![Figure 3-3](image)

**Figure 3-3:** The relationship between molecular molar mass of organic molecules and the relative diffusion amount by fit parameter $g$, derived from over-layer model.

The factor $g$, unfortunately does not give a direct physical quantity but represents the relative amount of diffusion based on the decrease in overlayer film thickness. The model fit is admittedly not the best for the more diffuse molecules at higher deposited MoO$_3$ thicknesses, which makes sense as this model was based on a discrete overlayer, providing further evidence for the diffuse interface formed. Further investigation into the concentration profile by use of Angle Resolved XPS is outlined in Appendix A. This procedure has been used in plasma treatments of polymers to determine the extent of oxidation in metals and is quite dependent on the model used but will yield actual diffusion length and could show a clearer picture of the concentration profile using XPS should this information be required for future work.
4 Electronic interaction

The use of transition metal oxides (TMOs) in optoelectronic devices is attracting much attention for their ability to improve device performance. Their application in inverted devices is even more pronounced as TMOs allow for the use of more stable top electrodes such as Au/Ag by allowing efficient charge injection into the underlying organic semiconductor. The mingling of TMOs such as MoO$_3$ into the organic hosts enhances hole-transport characteristics, acting as a p-dopant by forming charge transfer states [21], [31]. To date the interaction between MoO$_3$ and organic molecules used in inverted device structure has not been properly characterized, leaving many stones unturned in terms of degradation mechanisms, device performance and to enable the development of new materials. By observing the core level electrons one can determine changes in electronic properties as well as chemical environment. Because of carbon having a low photoemission cross-section [38], it is also useful to observe the interaction in the reverse deposition as this enhances the carbon signal. Below we will discuss the observations seen in core level peaks for the deposition of MoO$_3$ on various small organic molecules used in optoelectronic devices.

4.1 Background

4.1.1 Chemical Shift

The use of X-ray photoelectron spectroscopy to determine the bonding in chemical species has been practiced since its discovery by Siegbhan in the 1950’s when it was called Electron Spectroscopy for Chemical Analysis (ESCA) [23]. The reason for this is the high precision that can be obtained, which gives exceptional energy resolution. Ultimately this allows the user to very accurately determine the environment from which the electron being collected derived from. As was mentioned, XPS works by measuring the kinetic energy of an electron which is directly dependent on the binding energy. It is known that the binding energy of an electron is also dependent on the orbital, the nucleus, and therefore the element from which it originated. It is also known that the binding energy for various chemical configurations will also change. This energy change with varying chemical environments is known as chemical shift.

Chemical shift is a result from a change in electron density around an atom in bonding. This change can be approximated by differences in electronegativity between the two elements. The
The most common example is to use a metal and its oxide. As shown in figure 4-1. The reason for this shift is that the oxygen atoms present in MoO₃ have effectively removed valence electrons from the Mo atom, which reduces the shielding effect on other core electrons, yielding a higher binding energy, oxidized peak in the spectrum. Like wise, oxygen would have shifted to lower binding energy as now there is an increase in shielding having taken on more electrons.

![Figure 4-1: XPS curves for the growth of fully oxidized MoO₃ on Mo metal. Indicated are the neutral (Mo) and fully oxidized peak locations for Mo3d⁵/₂, with a binding energy shift of approximately 4eV. Not shown, but present are peaks for oxidation states Mo⁶⁺. [12]](image)

This same concept can be applied to organic molecules as shown in figure 2-2 with C1s core level shifts associated with different chemical environments by different electronegative neighbors in configuration. These shifts can also be a result due to changes in electron density around an atom by virtue of electronic interaction with nearby molecules. This does not necessarily require bonding where a new chemical species is formed, but charge transfer of a delocalized electron or shift in electron cloud could cause a similar change. This is observed by interaction with MoO₃ and Au where no oxidation of Au occurred, i.e. no new bond was formed [12]. However when Mo⁶⁺ is reduced, excess electrons occupy low-lying Mo4d orbitals which give rise to donor states with in the MoO₃ band gap, similar to oxygen deficient MoO₃. This charge transfer without interfacial chemical compound formation shows the same chemical shift and adds to the difficulty in determining the precise interaction present.
4.1.2 Band Bending

The term ‘band bending’ used in this context is analogous to inorganic interface structures which are used to explain XPS core level shifts, which result from Fermi level equilibrium between the substrate and over-layer redistribution of free carriers [39]. The energy of electronic levels of a solid with a finite energy gap show variation as a function of distance from the interface and correspond to changes in core level changes. This “energy level bending” is not governed by the type of wave function (delocalized Bloch or localized molecular orbital) but statistics of occupied energy levels [40]. When the concentration of free charge carriers is increased, the Fermi level moves towards the transport level. An illustration of the change in core level and HOMO energy levels can be seen in figure 4-2.

![Image of energy level bending diagram]

Figure 4-2: Changes in energy levels for the deposition of MoO₃ on F8BT as a function of overlayer thickness {Nakayama:2009ky}. This illustrates a summary for changes seen in core level shifts of C1s and Mo3d associated with band bending in conjunction with HOMO level changes from charge transfer.

The use of doping can be used to control the position of the Fermi level. In a practical sense, band bending induces an electric field in the space charge region, which can enable efficient charge separation. When this space charge layer is thin from heavy doping, carrier injection can be enhanced due to tunneling across the space charge layer [40].
4.2 Results and Discussion

Throughout this report, differences between the deposition order and the material system that is created at the interface has been discussed. Typically, researchers have been focusing on the deposition order that is involved with standard devices where organic material is deposited on-top of a metal or metal-oxide. This type of system is much simpler to study and is less convoluted. However, this may be because many of the detailed interactions are being overlooked because the amount of interaction that is taking place is less, due to the discrete boundary formed, as well as the fact that some experimental observations may be lost due to carbon having a small photoemission cross-section yielding a relatively weak signal for small deposition amounts, i.e. at the interface. This could have led to important interactions being missed. By doing a reverse deposition process however, there is already a strong carbon signal present and molybdenum yields a strong signal allowing for detailed interactions to be observed. Shown in figure 4-3 is a comparison between the two deposition processes and the core level spectra for carbon and molybdenum for the CBP/MoO$_3$ system. As can be seen there is a much larger band bending shift due to charge transfer and doping by injection of MoO$_3$ into the underlying CBP layer from diffusion. The shift in the Fermi level causes all energy levels to shift to lower binding energy after donating an electron to MoO$_3$. This is mirrored in the MoO$_3$ core peaks where the energy levels shift in the opposite direction from gaining charge as well as a clear formation of reduced Mo is seen. This is much more prevalent in the inverted deposition system. Also, a new carbon peak is observed, which is a result from the shift in C-C bonds by interaction with MoO$_3$, which is not observed in the other system or previously reported in literature, most likely due to the physical interaction at the interface and the resolution from high signal strength in the inverted deposition system. The origin of this new peak will be discussed below.
Figure 4-3: XPS high resolution scans of C1s and Mo3d peaks for MoO$_3$/CBP system (top left and right) and the CBP/MoO$_3$ inverted deposition system (bottom left and right).

In order to properly discuss the formation of new peaks and to get a clear understanding for the total interaction that is taking place to allow for charge transfer to occur, we must first look at all other elemental peaks present to determine their behavior. The core level peaks for oxygen and nitrogen are shown below for the deposition of MoO$_3$ on CBP as above.
Figure 4-4: XPS core level peaks for O1s and N1s for CBP/MoO$_3$. The Mo2p$_{3/2}$ peak convolutes the N1s peak.

As can be seen, a new peak from interaction with CBP is seen in the O1s spectra while N1s appears to only show a shift from Fermi level pinning by charge transfer. The other peak seen in the N1s spectra is the Mo2p$_{3/2}$ peak. This makes any deconvolution difficult for new nitrogen peak formation, however based on theoretical predictions such as HOMO electron density location and C/N bond ratio (see Appendix), no new nitrogen bonds form. The formation of the new oxygen peak, with its shift to higher binding energy is indicative of valence electrons being further away than in pristine MoO$_3$ bond formation. It is not expected that the oxygen will give up an electron, as it has a full outer shell and so is quite stable in its current configuration. However it is apparent that Mo is reduced to form Mo$^{5+}$ after gaining an electron due to its deep lying d-band. The new oxygen peak we observe could be resultant from this. The added electron could create more repulsion of valence electrons surrounding oxygen, which could cause a higher binding energy shift in core levels. The repulsion of electron density surrounding oxygen atoms is seen in a density functional theory (DFT) simulation that shows oxygen atoms repositioning themselves to avoid added electron density from interaction with a benzene ring, shown in figure 4-5. This simulation also shows that Mo does interact electronically with the delocalized electron ring and does not form a new chemical bond, agreeing with experimental results. The benzene ring was chosen to simplify the DFT calculation and since the HOMO
electron density is localized around the rings of the organic molecules this is most likely where an interaction would take place [31].

Figure 4-5: DFT simulation of MoO$_3$ interacting with benzene ring. From initial condition it can be seen that electronic interaction takes place by movement of oxygen atoms away from electron density around carbon ring and Mo being attracted. Final image shows converged solution.

The experimental results are consistent with all organic molecules used in this report, with the small exception of TCTA and MTDATA that show a similar but slightly different result. Shown below are the C1s and Mo3d XPS core level spectra for all organic semiconductors used in this study. The results for CBP are consistent with NPB, mCP and mCBP all of which show the same carbon peak formation, which only differ by the extent at which they are present owing to the amount of MoO$_3$ penetration taking place. TCTA and MTDATA also show the same new C peak however this peak is much larger than the other molecules. This makes sense when we consider the size of TCTA and MTDATA, and the number of rings present. The more locations that are available for MoO$_3$ to situate and interact, the higher the new carbon peak intensity should be. Another important observation is the shift in the C-N peak location, which moves to higher binding energy. This could be due to the fact that TCTA and MTDATA both have rings with two nitrogen atoms attached. The interaction with Mo at a C-N bond location will cause a shift to higher binding energy which may be more apparent in these two molecules.
Figure 4-6: C1s and Mo3d XPS high-resolution core level peaks for mCBP, mCP and NPB, which show similar interaction with MoO$_3$ forming charge transfer species. Shift in core level peaks indicate band bending as well as new peak formation from perturbation of electron density by interaction with MoO$_3$. 
Figure 4-7: C1s and Mo3d XPS high-resolution core level peaks for TCTA and MTDATA, which show similar interaction with MoO$_3$ forming charge transfer species. Shift in core level peaks indicate band bending as well as new peak formation from perturbation of electron density by interaction with MoO$_3$. 
5 Energy Level Alignment

As has been mentioned previously, the electronic structure at the organic/MoO$_3$ interface plays a very important role in device performance. The injection barrier of charge carriers for a given device architecture must be minimized, which will result in decreased contact resistance and lead to vast improvements in device performance[41]. When two solids are far away from one another, their vacuum levels can be considered to be in alignment. As they come into contact with one another, charge transfer is allowed to occur which forms a dipole layer at the interface, changing the vacuum level position and aligning the Fermi levels of both materials. This charge transfer can be a result from interfacial chemical reactions, redistribution of electron cloud or any other type of charge rearrangement[42]. The hole (electron) injection barrier is defined as the energy difference between the HOMO (LUMO) and the Fermi level. For our discussion we will stick with the movement of charges in the HOMO level, but similarly, this can be applied to the LUMO as well. Hole injection occurs relative to HOMO position, as it is electron extraction from the HOMO that produces a hole. It is appropriate to think in terms of holes moving when discussing device operation, as it is the hole that will later form an exciton when in conjunction with an electron, injected from the other electrode, that will combine to produce light in the luminance layer. However it is simpler, when looking at a single interface, to think in terms of electron exchange. MoO$_3$ is so often used because of its very low lying conduction band and work function of 6.7eV and 6.9eV respectively (see figure 2-14), this allows for electrons to occupy a more energetically favourable, lower energy state when compared to the molecules own HOMO position, which is generally much higher.
Upon charge transfer, the corresponding potential energy locally shifts the HOMO, LUMO and Vacuum levels by the same amount. The induced dipole, as a result of charge transfer, is sufficient enough to ‘pin’ the HOMO to the Fermi level minimizing the energy barrier. This is said to occur when the substrate work function is greater than the organic HOMO, and is seen consistently in literature [42], [44]-[46]. Besides this interfacial dipole model, there is also the existence of interface states, especially in MoO$_3$, as a result of oxygen vacancy defects. It has been shown by Greiner et al. that a reduced MoO$_3$ has defect states that lie very close to the Fermi level, which could become occupied upon charge transfer of electrons to MoO$_3$ [47]. The movement of the HOMO toward Fermi level is shown in figure 1-2 and has been extensively studied. The question remains however, what if the deposition order were flipped? Would the same models apply?

Figure 5-1: Change in energy level alignment (a) before and (b) after reducing the hole injection barrier by modification of anode substrate by deposition of metal oxide. (c) Device performance change with increased current density using V$_2$O$_5$ to reduce barrier height [43]

Figure 5-2: Schematic energy diagram of MoO$_3$ (Mo$^{6+}$), reduced MoO$_{3-x}$ (Mo$^{5+}$) and MoO$_2$ (Mo$^{4+}$). (b) and (c) show UPS spectra with defect states seen in O-deficient MoO$_3$ [7].
5.1 Conventional model

Typically energy level alignment is described by three categories: 1) chemically reactive/strongly interacting interfaces, 2) moderately interacting interfaces and 3) non-reactive/weakly interacting interfaces. For the majority of organic semiconductor molecules, the interface formed between the anode surface and the organic semiconductor is often of the third type. Various models have been proposed to explain the energetics of this type of interface. For example, Braun et al. [48] suggested that the most relevant parameters in energy level alignment at TMO/organic interface are TMOs work function and the energy level of molecular orbitals. In their model there exists a universal alignment trend that can be divided into three regimes: Fermi level pinning, slope equal to 0, to the highest occupied molecular orbital (HOMO) of the molecule, Fermi level pinning to the lowest unoccupied molecular orbital (LUMO), and vacuum level alignment, slope equal to 1. Based on this Fermi energy equilibrium principle, Greiner et al. [44] have demonstrated an universal energy level alignment (UEL A) rule at oxide/organic interfaces. Since then further revisions of this model have been presented taking into account capacitance effects for film thickness[46] and density of states of valence orbitals in organic semiconductors [45]. Each time however, the trend is the same. Shown in figure 5-2 is the full “z-curve” for energy level alignment with model fit. This data was presented in Physical Review B [49].

![Diagram](image-url)

**Figure 5-3:** Energy level alignment of C_{60} on various transition metal oxides with model fit [49]
The exact pinning position may vary with parameters such as the TMO layer capacitance, defect density and organic over-layer thickness. The pinning position is brought on by only a fraction (depending on coverage) of the organic molecules required to be in a charged state in order to create charge neutrality leaving a potential difference $\Delta \Phi$ across the TMO layer that moves the vacuum level up or down creating a pinning to the Fermi level. The amount of charge is based on Fermi – Dirac statistics and depends on the energy gap required for charges to move across. This is defined by $Q$, as:

$$Q = e\eta \left[1 + ge^{(IE - \Phi + \Delta\phi)/kT}\right]^{-1}$$  \hspace{1cm} (2)

Where $\eta$ is the molecular density, $\Phi$ is the work function of the substrate, $IE$ is the ionization energy of the organic molecule, $\Delta\phi$ is the potential drop across a charged interface and $kT$ and $e$ have their usual meaning. Since the potential drop is dependent on the amount of charge formed, there is a self-consistent equation, which must be solved numerically which is defined as:

$$\Delta\phi = \frac{e^2 \eta}{C_{ox}} \left[1 + ge^{(IE - \Phi + \Delta\phi)/kT}\right]^{-1}$$  \hspace{1cm} (3)

The HOMO offset $\Delta E_H$ (i.e. HOMO – Fermi) can then be calculated by:

$$\Delta E_H = IE - \Phi + \Delta\phi$$  \hspace{1cm} (4)

This model simplifies other models presented and reduces the number of variables required to fit to experimental data as well as can be expanded to included defect state effects and thickness effects. However, like all previous models, this describes a system consisting of thin TMO on conductive substrate with organic molecule deposited on-top. It may be that this model can still be applied with definitions changed around however.

5.2 Alignment under inverted structure

MoO$_3$ was deposited on eight different organic semiconductors and the valence states were observed using Ultraviolet photoelectron spectroscopy. Layer-by-layer deposition method was used to observe the change from organic valence states to occupied MoO$_3$ states. Since the electron kinetic energy of UV emitted electrons is low, the escape depth from within the sample
is also very small. In this way, UPS gives a very surface sensitive snapshot of the interface. Shown below is the complete catalogue of UPS spectra collected for this study.
Figure 5-4: UPS spectra of the 8 common organic molecules used in optoelectronic devices. Each figure is labeled to show thickness of MoO$_3$ deposited on each pristine organic film. Inset shows the position of the HOMO peak. Fermi level is calibrated to 0eV as described in section 2.

As can be seen in each UPS spectra, a similar trend appears where the work function progresses to values similar to pristine MoO$_3$ and the HOMO states get shifted close to the Fermi level. This shift is extremely important to see when considering device performance as this means there is a reduction in the energy gap for charge carriers to move through the interface. This minimization of the energy difference between Fermi and HOMO is known as Fermi level alignment or pinning, and as was discussed, has been shown to be dependent on the difference between the effective work function of the substrate and the organic molecule ionization energy. Because of the deposition order here, this definition does not really make sense, and instead it should be
considered that only the difference in the ionization energy and work function of MoO$_3$ matters such that charge transfer occurs. As is observed in the previous chapter, evidence for the formation of reduced MoO$_3$ is seen by the formation of Mo$^{5+}$ peaks. Although it is difficult to clearly see the defect states that must then be occupied, the pinning of the HOMO states suggests there must be charge transfer also forming the Fermi level pinning.

To summarize this data we plot the energy level alignment of approximately 1nm of MoO$_3$ deposited onto the various organic molecules in figure 5-4. This thickness is sufficient to form complete coverage of the underlying organic film and allow for sufficient charge transfer. As can be seen, the data follows the expected alignment curve shown in red, even for UGH 3, which falls in the Schottky-Mott regime with linear dependence on energy offset.

Figure 5-5: Energy level alignment curve showing the HOMO offset as a function of the difference between the ionization energy and work function
Although the trends are expected, if we directly compare the deposition order for 1nm of C\textsubscript{60} on MoO\textsubscript{3} and 1nm MoO\textsubscript{3} on C\textsubscript{60} we see quite a difference which is a result of the amount of charge transfer due to the increase in number of molecules interacting by penetration of MoO\textsubscript{3} into underlying organic film. In C\textsubscript{60} this leads to a reduced HOMO offset gap, which would have an impact on device performance. This is a major finding for the solar cell community as C\textsubscript{60} is used in most standard devices for its great charge transport properties and absorption spectrum. The UPS spectra of MoO\textsubscript{3} on C\textsubscript{60} is shown in figure 5-2, below is the spectra for C\textsubscript{60} on MoO\textsubscript{3}.

Figure 5-6: a) UPS spectra of C\textsubscript{60} on MoO\textsubscript{3}. b) Summary of work function and HOMO offset for deposition order. c) Spectra with 1nm of deposited material.

The fact that C\textsubscript{60} has the closest HOMO energy to that of MoO\textsubscript{3} work function may also be the cause for efficient charge transfer leading to a reduced gap at this interface. Although both deposition orders were not looked at for each molecule in this work, most other molecules showed similar HOMO offset values as expected from literature [44], [49]. It is clear however...
that assumptions on the symmetry of behavior for an interface cannot always be assumed. Since
the formation of charged states and their effect on the surrounding material has been shown to
have an impact on electronic states this is also expected to have an impact on device
performance.
6 Conclusions

This thesis has provided insight into the energetic and physical interactions between transition metal oxide, MoO$_3$, and various organic semiconductors used commonly in organic optoelectronic devices. The primary application for this work has been to properly determine the interfacial electronic structure for inverted OLED design in order to utilize the various lifetime and performance improvements over conventional OLED structure. The use of this work can also be expanded to OPV design, which frequently uses MoO$_3$ in this deposition order. Through the use of photoelectron spectroscopy (XPS and UPS) a complete understanding for the interfacial interaction has been illuminated.

It was found that the diffusion as a result of heavy MoO$_3$ clusters and high kinetic energy were able to penetrate into the underlying soft organic material. The relative amount of diffusion can be modeled based on a simple over-layer model with a fitting parameter related to the over-layer thickness was used. It was found that the results were consistent with previous reports in literature relating the amount of diffusion to evaporation temperature. Plotting the relative diffusion parameter, $g$, with mass of the molecules was also found to follow a trend, with the heavier and larger molecules approaching 1 for a discrete boundary, although saturating at 1.5. This could indicate a limiting parameter that is common with all organic molecule thin films, namely the amorphous nature of such films.

Analysis of high resolution XPS core level peaks showed that not only were there changes in binding energy in core level peaks from shift in Fermi level indicating band alignment, but we also elucidated the interaction leading to charge transfer between MoO$_3$ and organic semiconductor. This was shown to be unobservable when conducting the experiment in the conventional manner with organic deposited on-top of MoO$_3$ as the photoelectron cross-section for carbon is small and the interface boundary would be discrete, so by the time there is sufficient signal from C1s, the interface is no longer being observed by XPS due to inelastic mean free path of electrons. It was shown that the interaction of Mo$^{6+}$ with delocalized electron in the ring portion of the molecular structure led to the formation of reduced Mo$^{5+}$. The formation of a new carbon peak from the donation of an electron was also shown for the first time, confirming the proposed charge transfer mechanism. DFT analysis also confirmed these
results and showed that oxygen is repelled away from high electron density and so should not be
apart of the charge transfer process.

The formation of Mo$^{5+}$ from charge transfer was confirmed by UPS measurements which
showed the pinning of HOMO energy levels to the Fermi level. This is consistent with the
Universal Energy Level rule and the trend also was shown to extend to the linear regime when
the ionization energy of the organic is greater than that of MoO$_3$ work function indicating no
charge transfer. The pinning of the HOMO to Fermi level is vitally important for device
application as this forms an Ohmic contact providing efficient charge injection into the device. It
was also shown that variations in defect density and doping could lead to a reduced electron
barrier by inverted deposition as shown by results with the MoO$_3$/C$_{60}$ system.

6.1 Future direction

The findings in this thesis are both fundamental, and interesting from possible device point of
view. In order to further clarify some results single carrier devices could be fabricated and the
difference between deposition order could be examined. Taking into account for the possible
diffusion leading to doping which should improve charge transport. The addition of a metal top
layer would also be useful and the comparison between with and without MoO$_3$ interlayer could
also elucidated device degradation pathways and possible preventative measures. To better
illuminate the possibility of a kinetic energy model for diffusion, the effects of annealing should
be investigated. Penetration models based on ballistic transport of materials from high kinetic
energy could aid in the understanding of properties which dictate the diffusion length between
various organic materials, as has been initially described in this thesis. Comparison with the
above findings by XPS and an experiment with co-deposited MoO$_3$ would also be useful to
determine the consistency of the interaction forming charge transfer species. Another addition
could be to use other TMOs that can be easily deposited. While most oxides cannot be easily
evaporated, oxides such as V$_2$O$_5$ and WO$_3$ can be evaporated similar to MoO$_3$. Further and more
detailed DFT analysis using various initial conditions could also help to determine the exact
reason for the formation of second oxygen peak seen in XPS. Finally, outlined in the Appendix is
a possible procedure for determining a more detailed analysis on the extent of diffusion by
ARXPS. Determining the exact diffusion length and properties of the material such as
sublimation temperature or exact film density will aid in determining what material properties should be considered when choosing device materials.
Appendices

A.1 Summary of energy changes

Below are the combined energy changes for UPS and XPS measurements. Consistent changes in C1s and HOMO peaks indicates band bending with deviation from the work function, phi, resulting in dipole changes due to charge transfer. Grey boundaries indicate changes from interaction with MoO₃ to only observing MoO₃ film where a boundary has been established. Differences between Mo⁶⁺ and Mo⁵⁺ peaks are consistent indicating no other oxidation states possible.
Figure A-1: Summary of energy value changes with deposition of MoO$_3$ for all photoelectron peak measurements. Changes in grey background indicate approximate discrete boundary locations from changes of interacting organic/MoO$_3$ to bulk MoO$_3$. 
A.2 Bond ratio

In order to properly determine whether a new chemical species is present or new bonds have formed from bond rearrangement, it is useful to use XPS to determine the consistency of the bond ratio between regions of interest. This can be explained through an example. Let us consider the bond ratio between C-C bonds and C-N bonds for the molecule NPB. Based on its molecular structure this should have a bond ratio for C-N/C-C of approximately 0.16. This is based off of counting the number of C atoms which have a N bond and dividing by the number of C atoms with a C bond, i.e. 6/38. This is a better way to determine consistency over an older method of atomic concentration, as different sampling depths with elements that have core peaks far apart on the binding energy spectrum become difficult to properly determine correct atomic ratio as their inelastic mean free path must be taken into account. By using the same element this can be avoided, as the inelastic mean free path will be the same. By observing whether this ratio must change in order to properly fit to experimental data when doing curve fitting or by holding this ratio constant and observing the formation of new peaks can aid in understanding the interaction taking place. For this analysis the ratio between total C-C bonds was held constant against the number of C-N bonds. Because of the interaction with Mo being assumed to occur at the C-C bond in the ring end groups of the molecule, the total of C-C bonds was a sum of C\textsuperscript{X} and C-C peak areas. The existence of a new C peak was required to properly fit to experimental data and makes sense when combining with UPS and other core level spectra, which all show strong evidence for charge transfer which requires electronic interaction.

A.3 Angle Resolved XPS to determine concentration profile

The effect on the morphology of a deposited film is well known in the community. Layer by layer growth mode will obviously show a different signal representation than that of island growth as shown in figure 3-1. Due to possible error in the deposited thickness amounts however, especially at sub-nanometer thicknesses, the signal intensity may not be accurate enough to properly determine a diffusion length. It is then best to deposit a thick layer so the error is a small percentage of the overall thickness. ARXPS can then be used to probe different depths of the film by utilizing the Beer-Lambert Law, which states that the signal intensity (peak area) from a material, \(i\), at distance \(z\) from the surface will be\textsuperscript{50}, \textsuperscript{51}: 
which as can be seen is dependent on the x-ray incident angle, \( \theta \), measured to the surface normal. \( \lambda \) is the inelastic mean-free path of an electron and \( I_o \) is the standardized intensity of a thick film with \( I_o = \sigma D L J T A \lambda \), which takes into account electron cross-section (\( \sigma \)), detection efficiency (D), angular asymmetry (L), x-ray flux (J), analyzer transmission (T) and analysis area (A). Typically 95% of the signal intensity will come from \( 3 \lambda \cos \theta \), shown in figure 3-2. This shows how ARXPS can be used to probe different depths by changing the effective sampling depth when the angle \( \theta \) is varied.

Figure A-2: Schematic showing the premise for ARXPS, where the effective collection depth below the sample surface can be adjusted with the majority of the XPS signal coming from \( 3 \lambda \cos \theta \)

After a set of data consisting of intensities of core level peaks for various elements across a range of angles has been collected, a concentration profile can then be determined following the following mathematical derivations[51].

First it can be shown that for an element i, \( \sigma D L T \lambda \) is proportional to the sensitivity factor, \( S_i \), such that, \( QS_i = (\sigma D L T \lambda)_i \). Equation (2) can then be rewritten as:
\[ I_i(\theta) =QS_i(JA)\int_{z=0}^{\infty} N_i(z)e^{-z/\lambda_i \cos \theta} \, d\left(\frac{z}{\lambda_i}\right) \]  

(3)

We can also set \( s = 1/\cos(\theta) \) and \( t = z/\lambda \). This yields:

\[ I_i(s) = QS_i(JA)\int_{t=0}^{\infty} N_i(\lambda_i t)e^{-st} \, d(t) \]

\[ = QS_i(JA)\mathcal{L}[N_i(\lambda_i t); s] \]  

(4)

where \( \mathcal{L}[N_i(\lambda_i t); s] \) is the Laplace transform. Therefore using ARXPS data, which yields \( I_i(s), N_i(\lambda_i t) \) can be derived from the inverse Laplace transform. However, it has been shown that there is no straightforward method for accurately calculating the inverse Laplace transform from a set of experimental measurements, as the results are extremely sensitive to data error [51], [52]. Therefore the practice has been to guess a function for the concentration profile, taking the Laplace transform and perform a fit using sum of least-squares of these calculated values to experiment. This method was employed in this report, which to the author’s knowledge is the first time it has been used in an organic/transition metal-oxide system.

We can assume that experimentally determined intensities i.e. \( I_i(s)^{Exp} \) will vary from calculated intensities, \( I_i(s) \), by a loss factor \( F_{li} \) such that \( I_i(s)^{Exp} = F_{li}I_i(s) \). If we assume that the percentage loss is the same and standardized for a given system, then by taking the ratio of intensities of two elements, \( i \) and \( j \), we can eliminate \( F_{li} \) before fitting, that is:

\[ \frac{I_i(s)^{Exp}}{I_j(s)^{Exp}} = \frac{F_{li}I_i(s)}{F_{lj}I_j(s)} = \frac{I_i(s)}{I_j(s)} = \frac{QS_i(JA)_\theta \mathcal{L}[N_i(\lambda_i t); s]}{QS_j(JA)_\theta \mathcal{L}[N_j(\lambda_j t); s]} = \frac{S_i \mathcal{L}[N_i(\lambda_i t); s]}{S_j \mathcal{L}[N_j(\lambda_j t); s]} \]

This can be extended such that we consider atomic composition percentages to accurately reflect a complete concentration profile i.e.

\[ \frac{I_i(s)^{Exp}}{\sum I_i(s)^{Exp}} = \frac{S_i \mathcal{L}[N_i(\lambda_i t); s]}{\sum S_i \mathcal{L}[N_i(\lambda_i t); s]} \]  

(5)

Moving forward we will describe \( N_i(z) = Nc_i(z) \) where the total number of atoms \( N \) is assumed to be a constant. This is also another reason why ARXPS is a more accurate method to determine
information on the diffusion amount over layer-by-layer conventional XPS measurement as $N$ will vary in the second case.

A.3.1 Concentration gradients

In order to get an accurate description of the concentration profile and extract information such as possible diffusion length, it is best to use more than one concentration profile and compare the least squares fit. Ideally the one with the best fit will most accurately represent the system at hand. To this end, four different concentration profiles were considered; step, linear, exponential and diffusion from a finite source. The step and linear functions are easy to define and can be described as:

**Step**

$$ c_i(z) = \begin{cases} c_{B,i} + c_{S,i} & \text{when } 0 < z < \Lambda_i \\ c_{B,i} & \text{when } z > \Lambda_i \end{cases} $$

(6)

**Linear**

$$ c_i(z) = \begin{cases} c_{B,i} + c_{S,i} \left(1 - \frac{z}{\Lambda_i}\right) & \text{when } 0 < z < \Lambda_i \\ c_{B,i} & \text{when } z > \Lambda_i \end{cases} $$

(7)

Where $c_{S,i}$ is the difference between bulk concentration atomic percent ($c_{B,i}$) and surface concentration, in atomic percent. $\Lambda_i$ can be thought of as the diffusion length, or boundary position. The above-mentioned variables are the parameters to fit.

The exponential concentration profile is also relatively easy to consider, and can be defined by[53]:

**Exponential**

$$ c_i(z) = c_{B,i} + c_{S,i} e^{-z/\Lambda_i} $$

(8)

A more difficult consideration would be that of diffusion. In this case we will think of diffusion by a finite source as opposed to that of a infinite source, which will have an effect on the boundary conditions when solving the differential equation using Fick’s second law of diffusion, which for diffusion in one direction can be defined as:

$$ \frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial z^2} $$

(9)
where $t'$ is time. For finite source diffusion, the boundary and initial conditions are:

$$c_i(z \geq 0, t' = 0) = c_{B,i}$$

$$c_i(z \geq \infty, t' > 0) = c_{B,i}$$

$$\int_0^\infty [c_i(z, t') - c_{B,i}] dz = \frac{V_i}{N} = M_i$$

where $c_{B,i}$ is the bulk concentration of $I$ and $V_i$ is the total amount of $I$ that diffuses into the sample per unit area. $V_i$ is a constant for limited source diffusion. The solution for this differential equation with boundary conditions described above is:

$$c_i(z, t') = c_{B,i} + \frac{M_i}{\sqrt{\pi D_i t'}} e^{-\frac{z^2}{4D_i t'}}$$

To simplify the fitting we can combine terms such that

Limited source diffusion

$$c_i(z, t') = c_{B,i} + c_{S,i} e^{-\frac{z^2}{4D_i t'}}$$  \hspace{1cm} (10)$$

The choice of diffusion model is imperative in properly determining the concentration gradient and extracting a correct diffusion length. Various other models can also be formulated which could lead to a better fit with experimental data. The application of this method could turn out to be extremely helpful in determining film composition without the use of invasive techniques such as sputtering.
References


