Transition Metal Oxides in Organic Electronics

by

Mark T. Greiner

A thesis submitted in conformity with the requirements
for the degree of Doctorate of Philosophy
Department of Materials Science and Engineering
University of Toronto

© Copyright by Mark Greiner 2012
Abstract

Transition metal oxide thin films are commonly used in organic electronics devices to improve charge-injection between electrodes and organic semiconductors. Some oxides are good hole-injectors, while others are good electron-injectors. Transition metal oxides are materials with many diverse properties. Many transition metals have more than one stable oxidation state and can form more than one oxide. Each oxide possesses its own unique properties. For example, transition metal oxide electronic band structures can range from insulating to conducting. They can exhibit a wide range of work functions. Some oxides are inert, while others are catalytically active. Such properties are affected by numerous factors, including cation oxidation state and multiple types of defects. Currently it is not fully understood which oxide properties are the most important to their performance in organic electronics.

In the present thesis, photoemission spectroscopy is used to examine how changes in certain oxide properties—such as cation oxidation states and defects—are linked to the oxide properties that are relevant to organic electronics devices—such as an oxide’s work function and electron band structure. In order to unravel correlations between these properties, we controllably change one property and measure how it changes affects another property. By performing such tests on a wide range of diverse transition metal oxides, we can discern broadly-applicable relationships.

We establish a relationship between cation oxidation state, work functions and valence band structures. We determine that an oxide’s electron chemical potential relative to an organic’s donor and acceptor levels governs energy-level alignment at oxide organic interfaces. We establish how interfacial reactivity at electrode/oxide interfaces dictates an oxide’s work function and electronic structure near the interface.
These findings demonstrate some of the very interesting fundamental relationships that exist between chemical and electronic properties at interfaces. These findings should assist in the future development and understanding of the functional interfaces of organic semiconductors and transition-metal oxides.
Acknowledgments

I thank my supervisor, Professor Zheng-Hong Lu for his excellent guidance throughout graduate school. He kept me on track, while still allowing my creativity to flourish. His advice helped me achieve my goals, and I am very appreciative for this.

I thank my lab-mates, Michael Helander, Zhi-Bin Wang, Wing-Man Tang, Jacky Qiu, Yi-Lu Chang, and Lily Chai. We have an excellent team dynamic. We work well together and drive each other to succeed. I enjoyed my time working with you all.

I thank my committee members, Professor Nogami, Professor Mims and Professor Walker for their positive support and guidance.

I thank all the administrative and technical staff who have helped me along the way, including Dr. Dan Grozea, Sal Boccia, Fanny Strumas-Manousos, Jody Prentice, Maria Fryman, and Luke Ng.

I also thank my family—my parents Waldemar and Violet—and my siblings—Michael, Stephen and Christina. They have kept my feet on the ground. They have also taught me that even when work is stressful and demands so much of me, there is always time for family.

I thank my father- and mother-in-law—Robert and Muriel D’Souza—for their warm hearted support. They have done so much to help Renita and I throughout our education.

Last and certainly not least, I thank my lovely wife Renita. She has always been understanding when I needed to work late hours, or when I was stressed over the load I was carrying. She has been supportive when I had difficulties. My achievements could not have been reached without her love and support.
# Table of Contents

Acknowledgments ....................................................................................... iv

List of Figures .............................................................................................. ix

1 Introduction ............................................................................................... 1
   1.1 Energy-Level Alignment at Interfaces in Organic Electronics .... 1
   1.2 Transition Metal Oxides in Organic Electronic Devices .......... 3
   1.3 Summary of Main Findings ........................................................ 5

2 Experimental Methods .............................................................................. 7
   2.1 X-ray Photoemission Spectroscopy: Background ...................... 8
   2.2 Ultraviolet Photoemission Spectroscopy: Background............. 10
   2.3 Characterization of Energy-Level Alignment at Organic Interfaces ................................................................................................ 15
   2.4 Sample Preparation ........................................................................... 18
      2.4.1 Metal Substrates........................................................................... 18
      2.4.2 Oxidation Procedure.................................................................... 19
      2.4.3 Oxidation Rates........................................................................... 19
      2.4.4 Growth of Organic Films........................................................... 20
      2.4.5 Substrate Morphology ................................................................ 21

3 Transition Metal Oxides .......................................................................... 24
   3.1 Background ....................................................................................... 24
      3.1.1 Electronic Structures .................................................................... 24
      3.1.2 Identifying Oxides Using Photoemission Spectroscopy ............. 30
   3.2 Metal Oxide Work Functions: The Effects of Defects and Cation Oxidation States ................................................................................................ 34
      3.2.1 Background ................................................................................... 34
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2.2</td>
<td>Methods</td>
<td>37</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Dilute Defects in d&lt;sup&gt;0&lt;/sup&gt; Oxides</td>
<td>38</td>
</tr>
<tr>
<td>3.2.4</td>
<td>Work Function, Donor States and Cation Electronegativity</td>
<td>41</td>
</tr>
<tr>
<td>3.2.4.1</td>
<td>Donor States</td>
<td>42</td>
</tr>
<tr>
<td>3.2.4.2</td>
<td>Electronegativity</td>
<td>45</td>
</tr>
<tr>
<td>3.2.5</td>
<td>Non-dilute Oxygen Vacancies</td>
<td>48</td>
</tr>
<tr>
<td>3.2.6</td>
<td>Reducing Other Transition Metal Oxides</td>
<td>50</td>
</tr>
<tr>
<td>3.3</td>
<td>Controlling Oxide Properties</td>
<td>51</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Controlling Oxidation State: Oxidizing in O&lt;sub&gt;3&lt;/sub&gt; and Reducing in Vacuum</td>
<td>51</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Effects of Air-Exposure on NiO</td>
<td>56</td>
</tr>
<tr>
<td>3.3.3</td>
<td>Effects of Air-Exposure on MoO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>61</td>
</tr>
<tr>
<td>4.1</td>
<td>Energy-Level Alignment</td>
<td>63</td>
</tr>
<tr>
<td>4.1.1</td>
<td>Background</td>
<td>63</td>
</tr>
<tr>
<td>4.1.2</td>
<td>Universal Trend</td>
<td>66</td>
</tr>
<tr>
<td>4.1.3</td>
<td>Charge-Transfer Model</td>
<td>68</td>
</tr>
<tr>
<td>4.2</td>
<td>Derivation of Energy-Level Alignment Equation</td>
<td>73</td>
</tr>
<tr>
<td>4.3</td>
<td>Appendix</td>
<td>82</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Band Gaps and Ionization Energies of Oxides</td>
<td>82</td>
</tr>
<tr>
<td>4.3.2</td>
<td>HOMO Binding Energy Profiles</td>
<td>82</td>
</tr>
<tr>
<td>4.3.1.1</td>
<td>Ionization Energy Profiles</td>
<td>84</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Oxide Film Thickness and Energy-Level Alignment</td>
<td>85</td>
</tr>
<tr>
<td>5.1</td>
<td>Background</td>
<td>87</td>
</tr>
<tr>
<td>5.1</td>
<td>Background</td>
<td>87</td>
</tr>
</tbody>
</table>
5.2 Methods ........................................................................................................... 92
5.3 Results .............................................................................................................. 92
5.4 Discussion ......................................................................................................... 97
  5.4.1 Thermodynamic Considerations .................................................................. 98
  5.4.2 MoO$_3$ on Au ............................................................................................ 100
  5.4.3 MoO$_3$ on Ni ............................................................................................. 104
  5.4.4 MoO$_3$ on Mo ........................................................................................... 105
  5.4.5 MoO$_3$ on V .............................................................................................. 105
  5.4.6 MoO$_3$ on Cu ............................................................................................ 106
  5.4.7 Work Function and Cation Oxidation State ................................................ 107
5.5 Summary .......................................................................................................... 107
6 Interfaces between Dissimilar Metal Oxides .................................................... 109
  6.1 Background ..................................................................................................... 109
  6.2 Methods ......................................................................................................... 111
  6.3 Results and Discussion .................................................................................. 111
7 Summary and Future Directions ...................................................................... 115
  7.1 Summary ........................................................................................................ 115
  7.2 Future Directions ......................................................................................... 116
References ............................................................................................................ 118
8 Appendices ........................................................................................................... 127
  8.1 Derivation of Equations Used to Calculate Oxide Thickness ....................... 127
  8.2 Discussion of Reference Levels ...................................................................... 134
  8.3 Measuring Work Function: Effect of Sample Orientation and Applied Bias .......................................................... 137
List of Figures

Chapter 1
1.1.1 Energy levels of a metal, molecule and metal/molecule interface 1
1.1.2 Energy levels in OLEDs 2
1.2.1 Oxide interfaces 3

Chapter 2
2.1.1 Chemical identification using XPS 9
2.1.2 High-resolution XPS of molybdenum oxides 9
2.2.1 UPS and valence band of gold 11
2.2.2 Work function from UPS spectra 12
2.2.3 UPS of an organic semiconductor 13
2.2.4 UPS reference spectra of several organic semiconductors 14
2.3.1 Determining energy-level alignment from UPS spectra 16
2.3.1 Illustration of the layer-by-layer process 16
2.3.3 Stacks of UPS spectra from a layer-by-layer characterization 17
2.4.1 Vacuum chamber layout 18
2.4.2 Oxidation rate of molybdenum 20
2.4.3 Organic Knudsen cells 21
2.4.4 AFM of metal surface morphology 22
2.4.5 Oxide film cross section 22

Chapter 3
3.1.1 Valence bands of transition-metal oxide classes 27
3.1.2 XPS spectra of transition metals and transition-metal oxides 30
3.1.3 UPS spectra of transition metals and transition-metal oxides 33
3.2.1 Work function and surface dipole of a solid 35
3.2.2 Valence bands of molybdenum oxides 37
3.2.3 UPS spectra of MoO$_3$ with increasing oxygen-vacancy concentration 38
3.2.4 XPS spectra of oxygen-deficient MoO$_3$ 39
3.2.5 Work function versus oxygen deficiency 40
3.2.6 Oxygen-deficient TiO$_2$ 41
3.2.7 Energy-level diagram of donor states in d$^0$ oxides 42
3.2.8 Electronegativity and Fermi level in a binary oxide 47
3.2.9 XPS, UPS and work function of non-dilute defects in MoO$_3$ 49
3.2.10 Work function versus oxidation state for several metal oxides 51
3.3.1 XPS and UPS spectra during TiO$_2$ annealing 52
3.3.2 XPS and UPS spectra during NiO annealing 53
3.3.3 XPS and UPS spectra during V$_2$O$_5$ annealing 54
3.3.4 XPS, UPS and energy alignment of NiO exposed to air 56
3.3.5 Work function versus air exposure for NiO 57
3.3.6 XPS, UPS and energy alignment of MoO$_3$ exposed to air 60
3.3.7 Comparison of XPS and UPS for Mo oxidized in O$_2$ and O$_3$ 61

Chapter 4

4.1.1 Universal energy-level alignment trend 66
4.1.2 Valence and conduction bands of oxides and organics 68
4.1.3 Origin of energy-level-alignment trend 69
4.1.4 Tuning energy alignment through electron chemical potential 72
4.2.1 Energy levels of floating and grounded solids 74
4.2.2 Energy levels as a molecule approaches a surface 75
4.2.3 Model of interfacial molecular ionization 76
4.2.4 Plot of energy alignment equations 82
4.3.1 Work function and HOMO binding energy profiles 84
4.3.2 Ionization energy profiles 85
4.3.3 Work function, XPS and UPS spectra for various MoO$_3$ thicknesses 86

Chapter 5

5.1 Valence bands of MoO$_3$, O-deficient MoO$_3$ and MoO$_2$ 89
5.2 Illustration of reactive and non-reactive interfaces 91
5.3 XPS spectra of reactive interfaces 93
5.4 Oxidation state and work function profiles for reactive interfaces 94
5.5 UPS spectra of reactive interfaces 96
5.6 Substrate XPS spectra for reactive interfaces 97
5.7 Energy levels at metal/MoO$_3$ interfaces 103
5.8 Plot of work function versus average oxidation state for reactive interfaces 108

Chapter 6

6.1.1 Work function profiles for reactive and non-reactive interfaces 110
6.3.1 Mo 3d XPS spectra for oxide/MoO$_3$ interfaces 112
6.3.2 UPS spectra for oxide/MoO$_3$ interfaces 113
6.3.3 Substrate XPS spectra for oxide/MoO$_3$ interfaces 113

Chapter 8

8.1 Illustration of photoemission procedure 127
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.2</td>
<td>Angle dependence of photoemission signal</td>
<td>128</td>
</tr>
<tr>
<td>8.3</td>
<td>Photoemission peak from infinite material</td>
<td>128</td>
</tr>
<tr>
<td>8.4</td>
<td>Illustration of a thin film</td>
<td>129</td>
</tr>
<tr>
<td>8.5</td>
<td>Illustration of XPS spectrum from a buried interface</td>
<td>130</td>
</tr>
<tr>
<td>8.6</td>
<td>Illustration of atomic structure and photoemission signal from an oxide film</td>
<td>132</td>
</tr>
<tr>
<td>8.7</td>
<td>Reference levels used in photoemission</td>
<td>135</td>
</tr>
<tr>
<td>8.8</td>
<td>Electric fields during work function measurements</td>
<td>137</td>
</tr>
<tr>
<td>8.9</td>
<td>Work function and irradiation time</td>
<td>139</td>
</tr>
<tr>
<td>8.10</td>
<td>Irradiation and core-level shifts</td>
<td>141</td>
</tr>
<tr>
<td>8.11</td>
<td>Irradiation effects during layer-by-layer characterization</td>
<td>142</td>
</tr>
<tr>
<td>8.12</td>
<td>UV irradiation and HOMO binding energy</td>
<td>145</td>
</tr>
<tr>
<td>8.13</td>
<td>UV irradiation and core-level shifts</td>
<td>146</td>
</tr>
<tr>
<td>8.14</td>
<td>Validating film thickness dependence of HOMO binding energy</td>
<td>147</td>
</tr>
<tr>
<td>8.15</td>
<td>3D illustration of TAE-cell</td>
<td>152</td>
</tr>
<tr>
<td>8.16</td>
<td>Schematic drawing of TAE-cell</td>
<td>153</td>
</tr>
<tr>
<td>8.17</td>
<td>Illustration of evaporation chamber</td>
<td>153</td>
</tr>
<tr>
<td>8.18</td>
<td>Chamber lay-out</td>
<td>154</td>
</tr>
</tbody>
</table>
1 Introduction

1.1 Energy-Level Alignment at Interfaces in Organic Electronics

The efficiency of an organic electronic device—such as an organic light-emitting diode (OLED) or an organic solar cell (OSC)—relies on the ability of charge to move from one material to another. For example, in organic light-emitting diodes (OLEDs), a semiconducting material is sandwiched between two electrodes. A bias is applied between the electrodes, and electrons move from one electrode, through the organic semiconducting material, to the opposite electrode. In this process, electrons must cross multiple interfaces. These interfaces can hinder charge transport and they often govern a device’s efficiency.

Charge transport across an interface requires that the donor and acceptor states of the materials on either side of the interface are closely aligned. Misalignment between donor and acceptor levels results in an energy barrier that inhibits charge transport. The alignment between the acceptor and donor levels on either side of an interface is termed energy-level alignment (ELA). In organic electronic devices, the interfaces between the electrodes and the organic semiconductors usually present the largest barriers in a device. Figure 1.1.1 illustrates how the ELA of a molecule on a metal to give rise to hole- and electron-injection barriers.

![Figure 1.1.1](image_url)

**Figure 1.1.1** – (a) Energy levels of a metal, indicating the Fermi level ($E_F$), the vacuum level ($E_v$), and the work function ($\phi$). (b) Energy levels of a molecule, indicating the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO), ionization energy (IE) and electron affinity (EA). (c) Energy-level alignment at a metal/molecule interface. The vertical scale represents energy.
A molecule’s donor and acceptor states are its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively. When a molecule contacts an electrode’s surface, the molecule’s orbital energies change relative to their gas-phase values. The change to a molecule’s orbitals can either enable or inhibit charge transfer with the electrode.

Energy-level alignment at interfaces in organic electronic devices affects device performance because interfacial energy barriers contribute to the amount of energy needed for charge to move through a device. When a device—such as an OLED—is in operation, a bias is applied between two electrodes, and electrons flow from the cathode to the anode, passing through several organic layers and across multiple interfaces, as depicted in figure 1.1.2. At each interface there is the possibility of a charge-injection barrier, and so it is necessary to optimize energy-level alignment.

![Figure 1.1.2](image_url) – Illustration of energy levels in an operating OLED. The red lines and blue lines indicate LUMO and HOMO levels, respectively. The arrows represent the path of electrons and V is the voltage applied between the two electrodes. The vertical scale represents energy and the horizontal scale represents distance.

Over the past two decades, there has been a large amount of research on ELA in the fields of organic electronic devices.4-6 A great deal of work has been devoted to a fundamental understanding of the interfacial interactions that control ELA. Several developments to the interfacial ELA model have developed, such as the interfacial pinning parameter,7-8 the concept of induced-density of interface states,9-10 interfacial dipoles,11 the push-back/pillow effect,12 the importance of the charge-neutrality level,10,12 and integer charge-transfer model.3,13 While these
concepts reconcile some of the initial discrepancies in the energy-alignment model, not all of these concepts are mutually consistent. Although significant progress has been made, many questions remain unanswered.\textsuperscript{14-17}

1.2 Transition Metal Oxides in Organic Electronic Devices

The present research focuses on interfaces in organic devices that involve transition metal oxides. Transition metal oxides were initially used in organic light-emitting diodes (OLEDs) when it was discovered that some oxides have the ability to decrease the hole-injection barrier at anode/organic interfaces.\textsuperscript{18} This discovery gave rise to decreased contact resistance in organic devices, resulting in vast improvements to device efficiency. Metal-oxides are now commonly used in organic electronic devices as buffer layers to enhance charge-transfer between electrodes and organic semi-conductors.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1_2_1.png}
\caption{(a) Illustration of a multi-layered organic electronic device. (b) Illustration of a metal-oxide buffer layer, demonstrating a typical thickness, and highlighting the oxide/organic and oxide/electrode interfaces. (c) Schematic energy-level diagram for a metal-oxide buffer layer.}
\end{figure}

Oxide thin films are usually coated onto electrodes—such as metals or transparent conductive oxides (TCO’s)—as thin buffer layers, as illustrated in figure 1.2.1. Note that most metals cannot be used as electrodes in organic devices without a charge-injection buffer layer because of the high charge-injection barriers that exist between metals and most organic semiconductors. Coating a metal electrode with a thin metal-oxide film can allow Ohmic charge injection. In fact, just about any conductive material can be used as an electrode once the appropriate oxide buffer layer is incorporated. Numerous metal-oxides have been used in organic electronic devices, some as hole-injectors (e.g. MoO\textsubscript{3}, WO\textsubscript{3}, V\textsubscript{2}O\textsubscript{5}, NiO, CuO),\textsuperscript{19-23} and others as electron injectors (e.g. ZnO, ZrO\textsubscript{2}, TiO\textsubscript{2}).\textsuperscript{24-26}
The low charge-injection barriers at metal-oxide/organic-semiconductor interfaces are believed to be caused by favourable ELA between metal-oxides and organic semiconducting molecules, which is largely affected by the metal-oxide’s work function. Hole-injecting metal oxides tend to raise an organic’s HOMO close to the Fermi level, while electron-injecting oxides tend to lower an organic’s LUMO close to the Fermi level.

Due to their wide range of energy-aligning capabilities, metal oxides are now used in all types of organic electronic devices—including dye-sensitized solar cells and organic photovoltaics—as well as low-power-consumption electronic devices—such as organic light emitting diodes and organic thin-film transistors. As transition-metal oxides exhibit a large diversity in physical, chemical, and electronic properties, they have great potential as materials that allow tuning of electron injection/extraction properties of electrodes.

As depicted in figure 1.2.1, metal-oxide buffer layers in organic devices generally involve two interfaces: an interface with a solid organic semiconductor, and an interface with an electrode material. In the present research we examine the chemical and electronic interactions that occur at these interfaces and affect energy-level alignment.

Given the broad diversity of transition metal oxides and the many factors that contribute to their properties, there are many possible factors involved in transition-metal-oxide/organic interfaces. Therefore, we take the approach of examining as many oxides as possible, in search of broad correlations. The oxides investigated herein span a wide range of electronic properties, and include: n-type wide-band-gap semiconductors, such as MoO₃, TiO₂, V₂O₅,WO₃ and Ta₂O₅; defective semiconducting oxides, such as MoO₃₋ₓ, TiO₂₋ₓ, V₂O₅₋ₓ; and CrO₃₋ₓ; p-type semiconductors, such as Cu₂O, Ag₂O, Cr₂O₃, and Co₃O₄; p-type Mott-Hubbard insulators, such as CuO, NiO, and CoO; and metallic oxides, such as MoO₂, WO₂, and TiO.

In order to have precise control over these oxides and their properties, all samples were prepared and analyzed in situ, and underwent thorough characterization. The primary technique used to characterize the oxides and their interfaces was photoemission spectroscopy. The oxide compositions were determined mainly using X-ray photoemission spectroscopy (XPS), while their valence electronic structures, work functions and ELA were determined using ultraviolet photoemission spectroscopy (UPS).
This report is broken up into the following sections: Chapter 2—Experimental Methods—where analysis techniques and the methods used to form well-defined oxides will be described. In Chapter 3—Transition Metal Oxides—we examine the electronic properties of oxides, their work functions and how their properties can be tuned through cation oxidation state. In Chapter 4–Organic/Metal-Oxide Interfaces—the causes of energy-level alignment between organic semiconductors and several transition metal oxides is discussed. In Chapter 5–Interfaces between Metals and Metal Oxides—we examine how interfaces between oxides and metal electrodes affect an oxide’s properties. In Chapter 6–Interfaces between Dissimilar Metal Oxides—we examine how oxide/oxide interfaces affect an oxide’s properties near the interface. And Chapter 7–Summary and Outlook—summarizes the main findings of this work and discusses potential directions for future research.

1.3 Summary of Main Findings

From the work on oxide electronic properties (Chapter 3), it was found that an oxide’s work function and electronic properties can be controllably tuned through defects and cation oxidation state. Defects can shift the Fermi level by acting as donor or acceptor levels. They can also cause major changes to an oxide’s electronic band structure—capable of changing an insulating oxide into a metallic oxide. Furthermore, low oxidation states tend to lower an oxide’s work function. A correlation between oxide non-stoichiometry and oxide work function is demonstrated, and mathematical formulations are developed to describe the observations.

From the studies of organic/metal-oxide interfaces (Chapter 4), it was found that organic semiconducting molecules tend to have non-reactive, physisorption interactions with oxides. Oxide electronic structure plays little role in energy-level alignment at these interfaces, as long as the oxide is sufficiently conductive. Instead, energy-level alignment is primarily governed by an oxide’s work function and an organic molecule’s ionization energy and electron affinity. When an oxide’s work function and organic’s ionization energy or electron affinity are appropriately matched, charge transfer between them becomes possible. Using this concept, a simple mathematical formalism is presented to predict energy alignment.

From the work on oxide/electrode interfaces (Chapter 5 and 6), it was found that electrode interfaces can affect an oxide’s defect density and cation oxidation state near-by the interface. Thus, oxide film thickness is an important factor governing an oxide buffer layer’s ability to
provide energy-level alignment. Metal/metal-oxide interfaces tend to be reactive, while oxide/oxide interfaces are more complex, and may or may not be reactive.

Overall, in this attempt to develop a comprehensive understanding of transition metal oxide interfaces in organic electronic devices, several interesting and unique relationships have been unveiled. These findings and the discussion that go with them should act as a springboard for future developments in the field of interfacial science.
2 Experimental Methods

The main purpose of this work was to discover relationships between transition metal oxide properties and interfacial interactions with organic semiconductors. The aim was to advance the theoretical understanding of such interfaces. The approach taken was to examine as many well-controlled and well-characterized interfaces as possible, such that broad-reaching conclusions can be drawn.

In reaching this end, photoemission spectroscopy (PES) is one of the most valuable tools. It is so useful because it can simultaneously provide structural information—such as film thickness and depth profiles—chemical information—such as oxidation state, elemental identity, and chemical environment—and electronic structure—such as valence band density of states, Fermi level, work function and energy-level alignment.

Core-level PES is capable of measuring chemical identity with a depth sensitivity of a few nanometers, making the technique ideal for measuring the chemical changes that occur within the first few nanometers of an interface. Valence-level PES is capable of measuring a material’s valence electronic structure, and is useful for observing any changes that are associated with interfacial interactions. It is also capable of comparing how one material’s valence states align with another material’s valence states, yielding information regarding the ease of charge transfer across an interface. For characterizing interfaces, we often employed a layer-by-layer technique (described further in section 2.3) where a thick film is built up in small incremental depositions and measurements are taken at each increment.

As analysis and sample preparation are both housed within the same vacuum system, a sample can be prepared and analyzed under well-controlled conditions. This affords us the ability to thoroughly characterize our samples prior to treatment, controllably alter some sample property, and then measure the effect the sample treatment had on the measureable properties; all performed without needing to expose the sample to the uncontrollable atmospheric conditions. Thus cleanliness, surface condition and composition were all well controlled and well characterized. By observing correlations between properties and treatments we can infer relationships, and through developing and testing hypotheses, we can use the findings to construct theories that explain the observed phenomena.
All photoemission measurements shown in this work were carried out on a PHI 5500 Multi-
Technique system, using monochromated Al $K\alpha$ radiation ($h\nu = 1486.7$ eV) for X-ray 
photoelectron spectroscopy (XPS) and non-monochromated He $I\alpha$ radiation ($h\nu = 21.22$ eV) for 
ultraviolet photoelectron spectroscopy (UPS). The spectrometer was calibrated using the Au 4f$_{7/2}$ 
peak at 83.98 eV, the Cu 2$p_{3/2}$ peak at 932.67 eV and the Fermi level (from UPS) at 0.00 eV.

2.1 X-ray Photoemission Spectroscopy: Background

Photoemission spectroscopy is an analytical tool that can be used to examine the composition 
and electronic structure of materials. It is a ‘photons in, electrons out’ technique, in which 
photons of a defined energy impinge on a sample’s surface. An impinging photon transfers its 
energy ($h\nu$) to an electron in the sample, causing the electron to be ejected with a quantity of 
kinetic energy (KE) that is indicative of the electron’s binding energy ($KE = h\nu - BE - \Phi$, where 
$\Phi$ is the spectrometer work function). Using an electrostatic analyzer, the kinetic energies of 
electrons are determined to construct a spectrum of counts versus binding energy.

X-ray photoemission spectroscopy (XPS) refers to PES that uses photons with sufficient energy 
to ionize core-level electrons. In an XPS spectrum, every occupied electron orbital of an element 
gives rise to a peak—as shown in figure 2.1.1 (a)—as well as additional peaks from multi-
electron emission processes (Auger electrons). An element’s core electrons have distinct binding 
energies. This allows for elemental identification. Generally, one can identify an element using 
binding energy values with a precision of $\pm 1$eV—as shown in figure 2.1 (b). Using higher 
precision binding energies ($\pm 0.1$ eV) one can also identify an element’s oxidation state and 
chemical bonding environment. Figure 2.1.2 illustrates how the Mo oxidation state can be 
identified from precise binding energies.

In general, peaks that are found at higher binding energies represent core electrons that are 
surrounded by lower electron densities (i.e. less shielded from the effective nuclear charge). 
Consequently, binding energy tends to be correlated to oxidation state—where a more positive 
oxidation state has a higher binding energy, and more negative oxidation state, a lower binding 
energy. Due to the correlation between oxidation state and binding energy, high-resolution XPS 
spectra are extremely useful in identifying metal oxides.
Figure 2.1.1 – (a) Electron configuration and XPS spectrum of metallic Cu. (b) XPS spectra and approximate binding energies of several elements.

Figure 2.1.2 – High-resolution XPS spectra of Mo metal and two Mo oxides (MoO$_3$ and MoO$_{2.5}$) illustrating how oxidation states can be distinguished.

Binding energy is also affected by chemical bonding. When an atom is bound to a more electronegative atom, the more electronegative atom pulls electron density away. Thus electrons remaining on the atom tend to have higher binding energies. The sensitivity to chemical environment makes high-resolution XPS useful for identifying when an interfacial chemical reaction has occurred.
While there are correlations between binding energies and oxidation state/bonding environment, many factors are at play and there is no simple way to accurately predict binding energies. Consequently, the binding energy of a species in a given oxidation state, or bound to a given atom, are known from measuring standards and are reported in the literature. Unfortunately, calibration methods differ from lab to lab, so there often a spread in the reported values greater than ± 0.1 eV. In this case it may be necessary to examine the qualitative features of an XPS spectrum or to use one’s “chemical intuition” to interpret a spectrum.

2.2 Ultraviolet Photoemission Spectroscopy: Background

Ultraviolet photoemission (UPS) is quite different from XPS in terms of the information it provides. In this work, we use UPS primarily to determine work function, ionization energy and the energy-level alignment at an interface. UPS has been widely used in catalysis and adsorption studies in the 1980’s and 1990’s. It has become an extremely popular technique for studying organic semiconductor interfaces in the past 15 years.

UPS uses lower energy UV-photons for photoemission. Consequently, these photons have only enough energy to photo-emit valence electrons. Although X-rays are also capable of photo-emitting valence electrons, UV-photons have a higher photo-ionization cross section with valence electrons (many orders of magnitude greater than X-rays). As a result, the photoemission signal from valence states when using UV-photons is much higher than when using X-rays.

UPS spectra, to a first approximation, represent the valence density of states of a material. Thus UPS is primarily used for measuring a material’s valence-band electronic structure. In contrast to core-levels—where electron orbital binding energies can be separated by tens to hundreds of eV—there are generally dozens of valence levels within only a few eV of one another. As a result, most UPS spectra are a dense convolution of peaks. Spectra are like a fingerprint, whose details can only be fully understood with the aid of molecular orbital calculations, and often requiring more sophisticated calculation methods such as density functional theory. Furthermore, in extended solids valence states are not localized and do not take on a Gaussian shape. In these cases, valence band structures can only be accurately interpreted using complex calculations of density of states.
In spite of the complexities of valence spectra, many simple interpretations are often possible, as in the UPS spectrum of Au shown in figure 2.2.1. This spectrum was measured using non-monochromated He Iα radiation \((hν = 21.22 \text{ eV})\), generated from a He plasma lamp. The zero on the binding energy scale represents the Fermi level of the sample, which is grounded to the spectrometer.

The figure on the left presents the general features of a UPS spectrum: the secondary electron background, the secondary-electron cut-off, the valence states and the Fermi level. The panel on the right shows an expanded view of the valence features, in which the Au s-band and d-band are highlighted to illustrate how a UPS spectrum represents electronic band structure. The spectrum matches well with theoretical density-of-states calculations. The Au valence band consists of a narrow d-band, and a broad s-band. The s-band crosses the Fermi level. One can also see that the electron density drops-off at the Fermi level, where the spectrum takes on the shape of the Fermi-Dirac distribution.

![Figure 2.2.1](image)

**Figure 2.2.1** – Illustration of the He Iα UPS spectrum of sputter-cleaned gold using binding energy as the x-axis. (a) spectrum showing the entire valence band as well as the secondary electron cut-off. (b) Expanded view of the shallow valence region, illustrating the contributions from various electron bands.

The secondary-electron cut-off is also a valuable feature of UPS spectra. It is used to determine a sample’s work function. Work function is important because it represents the energy required to remove an electron from a solid material’s surface. The secondary-electron signal arises from a
cascade of inelastically-scattered electrons. These electrons have lost much of their kinetic energy while passing through the sample, and their intensities no longer represent valence states. Figure 2.2.1 is re-plotted with the x-axis changed to kinetic energy, in figure 2.2.2.

The secondary-electron intensity increases rapidly towards low kinetic energy, and then cuts off abruptly at zero kinetic energy. This cut-off indicates that electrons have lost so much of their kinetic energy that they are no longer able to escape the surface of the sample. One can determine the vacuum level by drawing a line equal to the photon energy from the secondary electron cut-off, towards the high-kinetic-energy end of the spectrum. The work function is then the difference between the photon energy and the kinetic energy of electrons coming from the Fermi level.

![Figure 2.2.2 – Illustration of a He Iα spectrum of sputter-cleaned gold, with the x-axis plotted in kinetic energy.](image)

While the valence states of metals are delocalized and form bands that do not take the form of Gaussian-shaped peaks, organic semiconducting molecules are isolated entities with closed electron shells. Their valence states are more localized and are well-represented by Gaussian-shaped peaks. The UPS spectrum of a typical molecular organic semiconductor (α-NPD) is shown in figure 2.2.3. One can see that there is still a secondary-electron cut-off, and thus one can still define a work function for condensed molecular films.
Figure 2.2.3 – Illustration of the He $\text{I}_\alpha$ UPS spectrum of an α-NPD film. The in-set shows an expanded view of the HOMO level and shallow valence features.

While the UPS spectra of organic molecules can involve many peaks, the most important feature for energy-level alignment is the HOMO feature. The HOMO is always the valence feature that is closest to the Fermi level. It is the occupied state that is the easiest to ionize and therefore it is the state that is involved in electron transfer at an interface. Note that the binding energy of the HOMO level depends on the substrate the organic film is coated onto; however, the ionization energy of the HOMO (i.e. the sum of HOMO binding energy and work function) is a material constant.

A compilation of UPS spectra for several organic semiconductors is shown in figure 2.2.4. The horizontal axes of (a) and (b) is plotted in electron kinetic energy instead of binding energy because binding energy is substrate-dependant. As organic ionization energy is a constant, the kinetic energy scale is more appropriate. Figure 2.2.4 (c) shows an expanded view of the HOMO levels for each of these organics. The horizontal axis for these plots is converted to ionization energy (by subtracting the photon energy, 21.22 eV, from the kinetic energy scale). The HOMO ionization energies are shown for each organic.
Figure 2.2.4 – UPS valence spectra for several organic semiconductors. (a) Full spectrum, plotted in electron kinetic energy, (b) expanded view of valence features, plotted in kinetic energy, (c) expanded view of HOMO features, plotted in ionization energy. The numbers shown in (c) are the HOMO ionization energies. Molecular structures are shown in (d).
The UPS spectra of oxides can range from simple-to-interpret to complex-to-interpret. Generally, the more ionic the metal-oxygen bonding, the simpler the interpretation of the spectrum is. Oxide valence bands will be discussed in detail in section 3.1. In some cases one can clearly distinguish the valence features that are from oxygen states from those caused by metal states. In other cases, metal and oxygen states are more hybridized, and valence features represent a mixture of metal and oxygen states. Electron correlation further complicates spectrum interpretation in oxides with highly occupied d-bands.

In certain cases, where the valence-band spectra are relatively simple and easy to interpret, they can provide some unique chemical information. For example, the valence spectra of d⁰ oxides exhibit a distinct valence feature when oxygen vacancy defects are present. Furthermore, using a priori knowledge of a material’s electronic band gap, one can determine whether an oxide is n-type or p-type. If the oxide’s Fermi level is closer to conduction band than the valence band then it is considered n-type, and if the Fermi level is closer to the valence band than the conduction band it is considered p-type. Using work function and valence band positions, one can determine how an oxide’s the Fermi level changes with defect density and oxidation state. Furthermore, one can determine if an oxide has a metallic band structure.

2.3 Characterization of Energy-Level Alignment at Organic Interfaces

Ultraviolet photoemission spectroscopy (UPS) has become the technique-of-choice for measuring energy-level alignment (ELA) at organic interfaces. It is suitable for this purpose because one can measure a sample’s work function and valence states in a single spectrum. In ELA studies of organic molecules, one is primarily concerned with the binding energy of the HOMO because it is the shallowest electronic state, and thus it is the state involved in charge exchange. In an ELA measurement, one is generally interested in the following parameters: substrate work function (ϕ), HOMO binding energy (ΔE_H), and organic ionization energy (IE_{org}), as shown in the energy-level diagram in figure 2.3.1. Figure 2.3.1 (b) and (c) show how these parameters are extracted from UPS measurements (note that in figure 2.3.1 (b) and (c) the secondary electron cut-off is re-plotted 21.22 eV towards lower binding energy of the Fermi level because it represents the vacuum level, and plotting in this way makes the spectra more visually comparable to the energy-level diagram).
We generally use the layer-by-layer characterization method to determine energy-level alignment near an interface. This method involves sequentially depositing ultra-thin layers of organic molecules onto the substrates, with UPS measurements taken after each layer is deposited, as illustrated in figure 2.3.2.

The layer-by-layer measurement routine generates a stack of valence and secondary cut-off spectra. Example spectra of layer-by-layer depositions for the organic semiconductors CBP, α-
NPD, and 2T-NATA are shown in figure 2.3.3. The purpose for measuring HOMO binding energy and work function of the organic film in several steps, as opposed to using a single-point measurement is so a thickness profile can be created. The HOMO binding energy and work function of an organic film depends on the film’s thickness. We performed complete thickness profiles for each interface because we wished to determine whether there were any differences in the HOMO or work function profiles between the oxides. In general, it was found that HOMO binding energy is substrate-dependent, while organic ionization energy is substrate-independent. This is equivalent to saying the HOMO level referenced to the Fermi level is variable, while the HOMO level referenced to the vacuum level is constant.

Figure 2.3.3 – Examples of stacks of UPS spectra from layer-by-layer measurements of CBP (top) α-NPD (middle) and 2T-NATA (bottom) deposited onto various substrates. The substrates used in these examples are V$_2$O$_5$ for the CBP spectra, NiO for the α-NPD spectra and CuO for the 2T-NATA spectra.
2.4 Sample Preparation

2.4.1 Metal Substrates

Metal substrates were prepared by coating polished, degenerately p-doped Si wafers with 150 – 250 nm of a metal film. Metal films were deposited either by magnetron sputter deposition from metal targets (for high-temperature metals, such as W, V, Mo, Ta, Ti, Zr) or evaporating metal pellets (for low temperature metals, such as Au, Cu, Ni, Ag). Metal sources were high-purity (99.99 – 99.9999%). Depositions were performed in a Kurt J. Lesker Luminos Cluster Tool, which is designed for large area uniform film depositions. The wafers were positioned ~ 50 cm away from the deposition sources, and were constantly rotated to ensure uniform film coverage. The substrates were kept at room temperature during deposition.

We deposited each metal onto a 4” diameter silicon wafer and stored the wafer in ambient conditions until needed. Prior to use in an experiment, the metal-coated wafers were diced into ~ 1cm×1cm pieces, and loaded into the XPS vacuum system, shown in figure 2.4.1. Once loaded, the samples were sputter cleaned to remove the native air-formed oxide film using a Physical Electronics 04-303 Focused Sputter Gun. We used 3 kV Xe⁺ ions with a spot size of ~ 2mm diameter and a raster area of 8mm×8mm to clean the surface of the sample. The O 1s signal was monitored to determine when the oxide had been removed.

![Figure 2.4.1](image)

Figure 2.4.1 – (Left) Photo and (Right) schematic lay-out of the vacuum system used for sample preparation and photoemission characterization.
2.4.2 Oxidation Procedure

After the metal substrates were sputter-cleaned, they were transferred to an oxidation chamber. The oxidation chamber was attached to the XPS system via a central-distribution chamber (CDC), as shown in figure 2.4.1. All chambers were connected and kept under vacuum at a pressure between $1 \times 10^{10}$ to $5 \times 10^{-9}$ torr. Once the sample was moved to the oxidation chamber, the oxidation chamber was sealed off (by closing a gate valve between the CDC and oxidation chamber) and filled with ~ 760 torr of high-purity O$_2$. Faster oxidation rates and high-oxidation-state oxides were achieved by heating the substrates during oxidation using a 600 W halogen light bulb, positioned ~ 2 cm above the sample, and by generating ozone during oxidation by shining UV-light through a UV-transparent quartz window from an external UV-lamp.

Oxidation times and temperatures varied depending on the oxidation rate of the metal state, and the desired oxidation state. This procedure is capable of producing high-purity, high-uniformity oxide films with no detectible little surface contamination. The amount of surface contamination depends on the cleanliness of the oxidation chamber and the adsorption coefficient of the oxide. A well-baked and pre-oxidized oxidation chamber is capable of forming oxides with no detectible surface carbon contamination.

While oxidation at high temperature in relatively high-pressure ozone produces oxides in their high oxidation states, lower oxidation-state oxides can also be produced rather easily by heating these oxide films in vacuum. This was performed after oxidation, by pumping away all the oxygen, and heating an oxide film to ~ 400 °C in ~ $10^{-8}$ torr vacuum for 6 – 12 hours. During this process, oxygen is slowly removed from the oxide, and cations are reduced to lower oxidation states. This procedure was used for CuO $\rightarrow$ Cu$_2$O, MoO$_3$ $\rightarrow$ MoO$_{2.5}$, TiO$_2$ $\rightarrow$ TiO, Co$_3$O$_4$ $\rightarrow$ CoO, CrO$_{3-x}$ $\rightarrow$ Cr$_2$O$_3$, WO$_3$ $\rightarrow$ WO$_{2+x}$. In many cases, complete reduction to a stoichiometric oxide is not possible without higher temperatures. Also, some oxides decompose directly to metal rather than forming a lower oxide, such as NiO $\rightarrow$ Ni, and Ag$_2$O $\rightarrow$ Ag.

2.4.3 Oxidation Rates

We performed a systematic study of oxidation rate only with Mo. For other metals we would gauge the suitability of the oxide thickness from the XPS spectra, and re-oxidize if needed. In general, we preferred oxides thinner than 10 nm to ensure that the oxides are sufficiently
conductive. However, we have observed a general trend between oxide thickness and oxide work function—the thicker the oxide the higher its work function—so in some cases it was necessary to continue an oxidation until a desired work function was obtained.

Figure 2.4.2 – (Left) Plot of oxide thickness versus oxidation time for Mo oxidized in UV-generated O₃ at 25 °C. (Right) Mo 3d XPS spectra used to determine oxide thickness.

As shown in figure 2.4.2, the Mo oxidation rate follows a logarithmic trend, as predicted by the kinetics of diffusion (where the rate-limiting step is solid-state diffusion of ions through the oxide film). Note that at low temperature, a considerably long time is needed (~ 7.5 hours) in order to obtain an oxide film of only 3.5 nm thick. By increasing the oxidation temperature, the oxidation rate is greatly increased.

While oxidation rates differ from one metal to another, in most cases oxides could be grown thick enough to bury the metal substrate metal signal—indicating an oxide thickness of > 10 nm—by oxidizing a metal in 760 torr of O₂, with UV-generated ozone, at ~ 300 °C for 6 hours. However, this procedure is too aggressive for samples such as Cu and Ni, whose oxides tend to grow much faster, in which case a shorter oxidation time of 3 hours will suffice.

### 2.4.4 Growth of Organic Films

Organic films were deposited in a separate (but attached) organic deposition chamber, as shown in figure 2.4.1. Most organic thin films were evaporated from permanently mounted Knudsen cells (K-cells), as shown in figure 2.4.3. These K-cells are thermally shielded, and house 10cc
cone-shaped alumina crucibles. Each K-cell has its own independent, pneumatically controlled shutter, and the K-cells are isolated from one another by a 4-way shield.

Several organic molecules were investigated in this study. Layer-by-layer characterizations work best when the molecules form uniform amorphous films. One can detect island growth in the UPS spectra when the substrate signal does not disappear after several nanometres of organic are deposited. Generally, for uniform growth, the substrate signal becomes buried very quickly, after ~2nm of organic have been deposited. Uniform growth of these films has also been confirmed using AFM measurements. If island growth occurs, the layer-by-layer profiles will be inaccurate. Generally, only the rigid planar molecules, such as phthalocyanines, crystallize and form islands.

### 2.4.5 Substrate Morphology

The methods used to produce metal substrates gives rise to films that are composed of grains between 20 – 50 nm in diameter, with an average surface roughness of 0.6 nm, as illustrated in the AFM images of Cu in figure. 2.4.4. Note that when the AFM profile is plotted with a 1:1 scale (x:y) it is clear that the surface is very smooth, with an average vertical-to-horizontal feature ratio of ~60:1.

After oxidation, the gross features of the substrates remain the same, preserving the underlying metal grain structure. Oxide films were always grown to be between 2 – 10 nm thick, as determined using angle-resolved XPS measurements. Transmission electron microscopy profiles
of thin cross sectional samples would be necessary to accurately determine the morphology of such samples. However, determining the film morphologies with such accuracy is a rather large-scale and extremely expensive undertaking, and furthermore, outside the main scope of this work. We suffice to draw some logical conclusions regarding our oxide morphologies, using combination of AFM, XPS and previous TEM work on oxide thin films.

**Figure 2.4.4** – (a) AFM height image of a sputter-deposited Cu film. (b) Cross section from (a) using an x:y scale of 1:56. (c) Cross section from (a) using an x:y scale of 1:1.

**Figure 2.5.5** – (a) TEM image of 5 nm thick oxide film on Fe nanoparticle (from reference 35). (b) TEM image of a 5 nm thick oxide film on iron foil (from reference 36). (c) Proposed model of the typical substrate surface structure for the oxide films used in this study.

Previous studies of films grown in a similar manner have been shown oxides to grow as nano-sized grains (~ 3 nm) as shown in Fig. 2.4.5 (a),35, 37-38 and in some cases amorphous, as shown in Fig. 2.4.5 (b).36, 39 Thus, based on the knowledge of roughness and metal grain size as determined from AFM measurements, and from oxide film thickness determination from XPS, we propose our samples generally had morphologies as illustrated in Fig. 2.4.5 (c).
While there is essentially no preferred oxide orientation, we can assume that in all cases the most thermodynamically stable oxide face was the exposed face (with the inclusion of kinks and step edges). Therefore, the measured energy-level alignment in this study represents an average molecule-oxide interaction over all available oxide faces and molecular orientations. While admittedly, this approach washes over some details regarding molecule-substrate geometries, it is done so out of necessity of addressing a large number of oxides. However, by taking this approach we can provide a broader perspective by examining a large and diverse set of materials.
3 Transition Metal Oxides

3.1 Background

The study of transition metal oxides is a very rich field due to the wide variety of stable oxides. Most transition metals exhibit more than one stable oxidation state, and can form an oxide for each oxidation state. For example, vanadium has the following stable oxides: VO, V$_2$O$_3$, VO$_2$, and V$_2$O$_5$, with the corresponding formal oxidation states, +2, +3, +4, and +5. Other transition metals, such as nickel or copper have fewer stable oxides. Nickel has only one stable oxide; NiO, while copper can form either CuO or Cu$_2$O.

In addition to the multiple oxide stoichiometries which arise from the various oxidation states, there is also the possibility of oxides containing more than one oxidation state. For example, Fe$_3$O$_4$ contains both Fe$^{2+}$ and Fe$^{3+}$. Furthermore, some oxides exhibit non-stoichiometry, where vacancy defects give rise to cation-to-anion ratios that are not well defined. There are also structures which possess vacancy defects, but have a well-defined stoichiometry. For example, the two most stable molybdenum oxides are MoO$_2$ and MoO$_3$, however there are numerous stable, well defined oxides with stoichiometries between that of MoO$_2$ and MoO$_3$, such as Mo$_{18}$O$_{52}$, Mo$_{17}$O$_{47}$, Mo$_9$O$_{26}$, Mo$_8$O$_{23}$, Mo$_7$O$_{20}$, Mo$_6$O$_{17}$, Mo$_5$O$_{14}$, and Mo$_4$O$_{11}$.

The transition metal oxidation state, oxide stoichiometry and oxide defect density are all factors affecting the electronic structure of oxides. They are the factors determining whether an oxide is insulating, metallic or semiconducting. It is possible that any of these properties may affect organic energy-level alignment, so it is prudent to be aware of the oxide structures and properties. It is also essential, when trying to find relationships between oxide properties and organic energy-level alignment, to be able to identify and control which oxides are formed on the substrates. XPS is an extremely useful technique in this regard.

3.1.1 Electronic Structures

Transition metal oxides span a wide range of electronic properties, and include: n-type wide-band-gap semiconductors, defective semiconducting oxides, p-type semiconductors, p-type Mott-Hubbard insulators, and metallic conductors. Their electronic structures are governed by many factors, such as crystal structure, metal-oxygen bond length, valence electron populations,
electron correlation effects, and degree of ionic or covalent bonding. While an accurate quantitative description of oxide electronic structures often requires all of these factors to be considered, many simplifications can be made that are helpful in identifying important similarities among the oxides.

In general, the ionic radii of transition metal cations are smaller than the radii of $O^{2-}$ ions. As a result, most oxides consist of a close-packed lattice of $O^{2-}$ ions, with transition metal cations occupying the tetrahedral and octahedral interstitial lattice sites. This means that the bonding coordination between metal cations and oxygen anions is usually octahedral or tetrahedral (with octahedral coordination being more common). This generalization allows for a rather simple description of oxide valence states using crystal field theory and ligand field theory.

In crystal field theory one treats metal and oxygen atoms as ions, and uses this approximation to determine what happens to the metal $d$-orbitals when they are subjected to the electric field of negative point charges in an octahedral (or tetrahedral) coordination geometry. In a spherically symmetric electric field the $d$-orbitals are degenerate, however in an octahedral (or tetrahedral) electric field the $d$-orbitals are split in energy. In the case of an octahedral two of the five $d$-orbitals are destabilized (pushed up in energy) and the other three $d$-orbitals are stabilized (pulled down in energy). The two orbitals that are destabilized are given the point symmetry label $e_g$ and the three stabilized orbitals are given the point symmetry label $t_{2g}$. In effect, this splitting of $d$-orbitals creates a gap, such that the $t_{2g}$ orbitals are filled first, followed by the $e_g$ orbitals. So if the $t_{2g}$ is half full the oxide would be predicted to be a metal, while if the $t_{2g}$ states are full the oxide one would predict the oxide to be a semiconductor.

Ligand field theory is very similar except that the metal and oxygen atoms are no longer treated as ions. Instead linear combinations of atomic orbitals (LCAO) are used, with the appropriate overlap integrals to calculate the energies of molecular orbitals. The molecular orbitals computed from the combination of $d$-orbitals with $O 2p$ orbitals still have the same symmetry labels and splitting characteristics of $e_g$ and $t_{2g}$ orbitals found from crystal field theory. In fact, since metal oxides are often close to ionic, with weak overlap integrals between O2$p$ and metal $d$-orbitals due to the O2$p$ orbitals being lower in energy, the crystal field picture is often an adequate description of oxide valence levels.
Since oxides are usually quite ionic, the valence states can often be separated into O 2p and metal d contributions. In the ionic approximation, oxides are treated as though the metal has given its valence electrons to the oxygen atom, such that the oxygen is treated as an O^{2-} ion and the metal as an M^{x+} ion, where x is the formal oxidation state of the transition metal. In general the O 2p states have higher binding energies than the shallow metal d states. In the cases when hybridization between O 2p and metal d states is more significant, one can often still say that a certain state has more O 2p-character or more metal d-character using partial density of state calculations.

Crystal field theory and ligand field theory only address how a single metal cation interacts with its coordination environment, so the theories yield discreet energy levels. However, in extended solids these energy levels are broadened into bands in the same way that atomic orbitals of metals and semiconductors are broadened into bands in solids. However, oxides can have considerable ionic character, which can make their energy bands quite narrow. In these cases it is often more appropriate to use the ionic approximation rather than the electron band model of solids.

Aside from the fine details needed to accurately calculate a transition metal oxide’s electronic structure, one of the main factors controlling their electronic structures is d-band occupancy. In figure 3.1.1 various oxides have been divided into classes according to their d-occupancy. The left-hand column in figure 3.1.1 presents each oxide class’s schematic energy-level diagram, and the right-hand column presents their valence band photoemission spectra. For simplicity the band structures are described using crystal field theory, using as a first approximation, the ionic model of bonding. In general oxides have an energy gap in their d-bands from the non-spherical ionic coordination environments; however, for simplicity, we do not address the different cation coordination geometries and suffice to say that in general the d-bands have an energy gap.

The oxides with totally empty d-bands (d^0 oxides) constitute class 1. They are insulators in their stoichiometric forms, but tend to be n-type materials (i.e. the Fermi level is close to the conduction band) due to the presence of oxygen vacancy defects. Their conduction band minima are composed mainly of empty metal d-states, and valence band maxima are composed primarily of O 2p states, as shown in figure 3.1.1 (a). Oxides belonging to this class are: MoO₃, TiO₂, HfO₂, WO₃, ZrO₂, Ta₂O₅, V₂O₅ and CrO₃.
Figure 3.1.1 – (a) Schematic energy-level diagrams and (b) UPS spectra of valence bands for several transition-metal oxide classes.
A sub-set of class 1 oxides is the oxygen-deficient \(d^0\) oxides. Oxygen deficiency generates a high density of occupied defect states close to the Fermi level, as illustrated in figure 3.1.1 (a), ii, making these oxides n-type semiconductors. The defect states arise from filling of empty metal \(d\)-states and can be seen in the valence spectra of figure 3.1.1 (b) ii.

The oxides whose \(d\)-bands are partially occupied with a low number of electrons (e.g. \(d^1\), \(d^2\) and \(d^3\)) constitute class 2. These oxides tend to form when \(d^0\) oxides are chemically reduced. They are often metallic, as illustrated by the band diagram in figure 3.1.1 (a), iii and seen by the finite density of states at the Fermi level in the valence spectra level in figure 3.1.1 (b), iii. Oxides belonging to this call include, MoO\(_2\), V\(_2\)O\(_3\), Ti\(_2\)O\(_3\) and WO\(_2\).

The oxides whose \(d\)-bands are partially occupied with a high number of electrons (e.g. \(d^7\), \(d^8\) and \(d^9\)) constitute class 3. These oxides tend to be Mott-Hubbard or charge-transfer insulators due to strong electron correlation.\(^{41}\) Their valence spectra show states that die-off close to the Fermi level, as seen in figure 3.1.1 (b), iv. Oxides in this class include CuO, NiO, CoO, and Co\(_3\)O\(_4\).

Oxides with completely filled \(d\)-bands (\(d^{10}\) oxides) constitute class 4. They tend to be semiconductors due to the gap between the \(d\)-band and the next highest energy band (usually derived from metal s-orbitals). Oxides in this class include Cu\(_2\)O and Ag\(_2\)O.

The transition metal oxide electronic properties are summarized in table 3.1.1. The valence band numbers were determined from the UPS spectra (by summing valence band maximum binding energy with work function). The band gaps are from literature values determined by combined photoemission and inverse-photoemission. The work function values were determined from the secondary electron cut-offs. Some oxides can have wildly variable work functions, depending mainly on oxygen vacancy, oxygen interstitial and other defect concentrations.
Table 3.1.1 – Summary of transition metal and transition metal oxide electronic properties.

<table>
<thead>
<tr>
<th>Metal Structure</th>
<th>Band Structure</th>
<th>Metal Oxidation State</th>
<th>Valence Configuration</th>
<th>Ionization Energy (eV)</th>
<th>Work Function (eV)</th>
<th>Band Gap (eV)</th>
<th>Reference for Band Gap</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Titanium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>metal</td>
<td>0</td>
<td>(d^4)</td>
<td>4.0</td>
<td>4.0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>TiO</td>
<td>n-type</td>
<td>+4</td>
<td>(d^1)</td>
<td>8.0</td>
<td>5.2</td>
<td>3.4</td>
<td>42</td>
</tr>
<tr>
<td>TiO</td>
<td>metallic</td>
<td>+2</td>
<td>(d^2)</td>
<td>4.5</td>
<td>4.5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>+3</td>
<td>(d^1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Vanadium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>metal</td>
<td>0</td>
<td>(d^5)</td>
<td>4.2</td>
<td>4.2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>V_2O_5</td>
<td>n-type</td>
<td>+5</td>
<td>(d^0)</td>
<td>9.26</td>
<td>6.9</td>
<td>2.8</td>
<td>43</td>
</tr>
<tr>
<td><strong>Chromium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>metal</td>
<td>0</td>
<td>(d^6)</td>
<td>4.2</td>
<td>4.2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Cr_2O_3</td>
<td>p-type</td>
<td>+3</td>
<td>(d^3)</td>
<td>6.5</td>
<td>5.6</td>
<td>3.2</td>
<td>44</td>
</tr>
<tr>
<td>CrO_3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CrO_x</td>
<td>n-type</td>
<td>+6</td>
<td>(d^1)</td>
<td>9.0</td>
<td>6.9</td>
<td>2.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>+4</td>
<td>(d^2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Cobalt</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>metal</td>
<td>0</td>
<td>(d^9)</td>
<td>4.8</td>
<td>4.8</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Co_3O_4</td>
<td>p-type</td>
<td>+2, +3</td>
<td>(d^+, d^6)</td>
<td>6.4</td>
<td>6.1</td>
<td>1.6</td>
<td>46</td>
</tr>
<tr>
<td>CoO</td>
<td>p-type</td>
<td>+2</td>
<td>(d^8)</td>
<td>5.2</td>
<td>4.5</td>
<td>2.4</td>
<td>46</td>
</tr>
<tr>
<td><strong>Nickel</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>metal</td>
<td>0</td>
<td>(d^{10})</td>
<td>5.0</td>
<td>5.0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>NiO</td>
<td>p-type</td>
<td>+2</td>
<td>(d^8)</td>
<td>6.7</td>
<td>5.0-6.3</td>
<td>3.2</td>
<td>44</td>
</tr>
<tr>
<td><strong>Copper</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>metal</td>
<td>0</td>
<td>(d^{10}, s^1)</td>
<td>4.6</td>
<td>4.6</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Cu_2O</td>
<td>p-type</td>
<td>+1</td>
<td>(d^{10})</td>
<td>5.5</td>
<td>4.9</td>
<td>2.3</td>
<td>44</td>
</tr>
<tr>
<td>CuO</td>
<td>p-type</td>
<td>+2</td>
<td>(d^9)</td>
<td>5.7</td>
<td>5.6</td>
<td>1.4</td>
<td>44</td>
</tr>
<tr>
<td><strong>Molybdenum</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>metal</td>
<td>0</td>
<td>(d^6)</td>
<td>4.5</td>
<td>4.5</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>MoO_3</td>
<td>n-type</td>
<td>+6</td>
<td>(d^0)</td>
<td>9.4</td>
<td>6.9</td>
<td>3.0</td>
<td>47</td>
</tr>
<tr>
<td>MoO_{2.5}</td>
<td>metallic</td>
<td>+4</td>
<td>(d^2)</td>
<td>6.0</td>
<td>6.0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>+5</td>
<td>(d^1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Tantalum</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ta</td>
<td>metal</td>
<td>0</td>
<td>(d^5)</td>
<td>4.3</td>
<td>4.3</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ta_2O_5</td>
<td>n-type</td>
<td>+5</td>
<td>(d^0)</td>
<td>8.9</td>
<td>4.3-5.2</td>
<td>3.9</td>
<td>48</td>
</tr>
<tr>
<td><strong>Tungsten</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>W</td>
<td>metal</td>
<td>0</td>
<td>(d^6)</td>
<td>4.9</td>
<td>4.9</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>WO_3</td>
<td>n-type</td>
<td>+6</td>
<td>(d^0)</td>
<td>9.8</td>
<td>6.65</td>
<td>3.4</td>
<td>49</td>
</tr>
<tr>
<td><strong>Silver</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>metal</td>
<td>0</td>
<td>(d^{10}, s^1)</td>
<td>4.4</td>
<td>4.4</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Ag_2O</td>
<td>p-type</td>
<td>+1</td>
<td>(d^{10})</td>
<td>6.4</td>
<td>5.5</td>
<td>1.3</td>
<td>50</td>
</tr>
<tr>
<td><strong>Zirconium</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zr</td>
<td>metal</td>
<td>0</td>
<td>(d^4)</td>
<td>3.4</td>
<td>3.4</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>ZrO_2</td>
<td>n-type</td>
<td>+4</td>
<td>(d^0)</td>
<td>7.8</td>
<td>3.4 - 4.4</td>
<td>5.2</td>
<td></td>
</tr>
</tbody>
</table>
3.1.2 Identifying Oxides Using Photoemission Spectroscopy

The first major challenge of this study was the preparation and characterization of the oxide substrates. Oxide films were grown on metal substrates by means of controlled oxidation in-situ. The goal was to be able to grow oxides of various stoichiometries and metal oxidation states, determine their compositions using XPS, and draw correlations between their properties and energy-level alignment by eliminating extraneous factors related to ex-situ sample preparation.

By analyzing the high-resolution XPS spectra of the main core level emission features of the transition metals we could determine the composition of each oxide. High-resolution XPS spectra of the main transition metal photoemission peaks for all the oxides tested in this work are shown in figure 3.1.2.

![Figure 3.1.2 – XPS spectra of transition metals and transition metal oxides](image-url)
Oxide identification is usually accomplished by measuring the chemical shift of high resolution core-level photoemission peaks of the oxidized transition metal. In the majority of cases the core-level binding energy is positively correlated with the oxidation state of the element being measured. By comparing the binding energy of the oxidized metal core level with that of the non-oxidized metallic standard, and comparing with several consistent literature reports of the same, one can identify the oxide present in the sample.

The accepted literature values are generally taken from single crystal or polycrystalline samples whose compositions have been determined by x-ray diffraction. Very often however there is a significant spread in reported values of binding energies, which can be a result of differing sample preparation procedures, sample conditions, and calibration procedures. Sometimes the spread in reported values for one oxide is larger than the difference in binding energies between two different oxidation states. However this can generally be reconciled by retrieving the original literature reports and closely analyzing their spectra, calibration procedures and sample conditions.

In the cases where the binding energy values for different oxidation states are very similar, qualitative spectral features can sometimes be used to assist in identification of the oxide. For example, a number of oxides such as CuO, NiO, CoO and Cr₂O₃ exhibit satellite features caused by electron-correlation and relaxation effects. Satellite features may be present for one oxidation state of an element and absent for another, in which case it is easy to identify the oxide. Sometimes satellite features may be present for more than one oxidation state; however, the satellite features for each material have unique shapes, and binding energies which can allow one to distinguish oxides.

The O 1s photoemission peaks are not nearly as useful in identifying oxides as the main metal photoemission peaks are. The O 1s binding energies for all transition metal oxides are generally between 529.5 and 530.5 eV. Given this small range of binding energies oxides cannot usually be identified from the O 1s spectra. The reason for the small range of O 1s binding energies is that oxygen is invariably in the -2 oxidation state in all oxides.

A summary of the oxides observed in this study is shown in table 3.1.2, along with the binding energy of the main XPS metal peak, the oxidation state of the metal cation, and the valence electron configuration of the metal cation.
The compositions of the highly oxidized oxides are fairly straightforward and well-defined. Under the oxidizing conditions used, most metals oxidized into their thermodynamically most stable forms. As for the reduced oxides, a few cases form single oxidation state oxides (Cu, Co), other oxides contain multiple oxidation states (Mo, Ti), or cannot be reduced to a lower oxide at all and become reduced to metal instead (Ni).

<table>
<thead>
<tr>
<th>Table 3.1.2 – Summary of transition metal and transition metal oxide main core-level binding energies.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Binding Energy (eV)</strong></td>
</tr>
<tr>
<td>Ti (2p$_{3/2}$)</td>
</tr>
<tr>
<td>TiO$_2$</td>
</tr>
<tr>
<td>TiO$_{1+x}$</td>
</tr>
<tr>
<td>V (2p$_{3/2}$)</td>
</tr>
<tr>
<td>V$_2$O$_3$</td>
</tr>
<tr>
<td>Cr (2p$_{3/2}$)</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
</tr>
<tr>
<td>CrO$_{3-x}$</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
</tr>
<tr>
<td>V$_2$O$_4$</td>
</tr>
<tr>
<td>CrO$_3$</td>
</tr>
<tr>
<td>Co (2p$_{3/2}$)</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
</tr>
<tr>
<td>CoO</td>
</tr>
<tr>
<td>Ni (2p$_{3/2}$)</td>
</tr>
<tr>
<td>NiO</td>
</tr>
<tr>
<td>Cu (2p$_{3/2}$)</td>
</tr>
<tr>
<td>Cu$_2$O</td>
</tr>
<tr>
<td>CuO</td>
</tr>
<tr>
<td>Mo (3d$_{5/2}$)</td>
</tr>
<tr>
<td>MoO$_3$</td>
</tr>
<tr>
<td>MoO$_{2.5}$</td>
</tr>
<tr>
<td>Ta (4f$_{7/2}$)</td>
</tr>
<tr>
<td>Ta$_2$O$_5$</td>
</tr>
<tr>
<td>W (4f$_{5/2}$)</td>
</tr>
<tr>
<td>WO$_3$</td>
</tr>
<tr>
<td>Ag (3d$_{5/2}$)</td>
</tr>
<tr>
<td>Ag$_2$O</td>
</tr>
</tbody>
</table>

While the quantitative and qualitative features of high-resolution XPS spectra are extremely useful in determining the oxide composition, and can lead to conclusive identification most of the time, valence band spectra can also provide useful data to support the conclusions. The valence band UPS spectra of many of the metals and oxides tested in this work are shown in figure 3.1.3.
Analyses of valence spectral features are generally qualitative. This is due to several reasons. Firstly, the spectra most often do not consist of discrete Gaussian-Lorentzian shaped peaks. They are a convolution of numerous electron states, and occasionally some final-states effects as well. Secondly, these features are summed with a secondary electron background signal, which is weak at low binding energies, but increases rapidly at binding energies greater than \( \sim 6 \text{ eV} \) (when using He \( \text{I} \)\( \alpha \) radiation).

**Figure 3.1.3** – He \( \text{I} \)\( \alpha \) UPS spectra of select transition metals and their oxides. The upper-most spectrum in each panel is the high-oxidation state oxide, the lower-most spectrum in each panel is the parent metal, and in cases where a middle spectrum is present, it represents the reduced oxide.
The precise shape of the secondary electron background is strongly affected by the morphology of the substrate, and other subtle effects such as small quantities of adsorbates. Therefore the background signal cannot easily be subtracted from spectra. Lastly, the precise binding energies of the spectral features are also somewhat variable. This can be due to shifting of the surface Fermi level, caused by defects acting as dopant levels, and also by the presence of surface adsorbates.

Even though the quantitative features of UPS spectra are not extremely helpful in identifying compounds, the qualitative features can be very indicative of a particular oxide. For example CuO has very broad, washed-out valence features, while Cu$_2$O has very sharp and distinct valence features. Another example is MoO$_3$, which is a wide band gap semi-conductor, has no states near the Fermi level, however MoO$_2$ is a metallic oxide, and has a density of states that crosses the Fermi level. The real strength of UPS however is its use in examining the electronic structure of materials.

### 3.2 Metal Oxide Work Functions: The Effects of Defects and Cation Oxidation States

#### 3.2.1 Background

Work function is often considered to be one of the most important factors governing the energy-level alignment between molecular adsorbates and solid substrates. The reason why it is considered so important is that it represents the energetic requirements of removing or adding an electron to or from a substrate. Thus the energetic barrier to charge exchange at a metal/molecule interface is believed to be related to the solid’s work function and the molecule’s donor or acceptor levels. Differences in work function are also believed to determine which way electrons will flow when two materials are in contact.

The measured work function of a material (via photoelectron spectroscopy or Kelvin probe measurements) has two contributions: 1) electron chemical potential and 2) surface dipole. As illustrated in figure 3.2.1, the electron chemical potential ($\mu_e$) represents the Fermi energy ($E_F$) relative to the absolute vacuum level ($E_{\infty}$). The surface dipole ($\delta$) represents an additional energetic barrier to removing an electron from a solid surface. This barrier can be caused by the
electrostatic field formed by electron density spilling from the solid surface, but it can also be altered by adsorption of polar molecules to a surface.

Unfortunately, it is not currently possible to experimentally determine what portion of the measured work function is from surface dipole and what portion is from the solid’s electron chemical potential. As a result of the many things that can alter the surface dipole—such as crystal face, surface roughness, and presence of adsorbates—and the many things that can alter the electron chemical potential—such as doping concentration, chemical changes, oxidation state—reported work function values quoted for materials can fluctuate wildly. Thus work function cannot be considered to be a material constant.

Figure 3.2.1 – Illustration of electrostatic energies near the surface of a solid, indicating work function (\(\phi\)), Fermi level (\(E_F\)), surface dipole (\(\delta\)), electron chemical potential (\(\mu_e\)), local vacuum level (\(E_{V,\text{local}}\)), and absolute vacuum level (\(E_{V,\infty}\)).

However, under appropriate preparation conditions, reproducible work function values can be obtained. For example, poly-crystalline sputter-cleaned Au will reproducibly have a work function of 5.35 eV. Polycrystalline Cu will have a work function of 4.66 eV. Polycrystalline MoO₃ prepared by vacuum sublimation of MoO₃ and without exposure to adsorbates will have a work function between 6.8 and 6.9 eV.

So while at times it may seem like there is no rhyme or reason to the reported work function values for a given material, it is likely because work function is so sensitive to many factors. However, it is certainly advantageous to understand how each factor affects work function.
Transition metal oxides have recently attracted a large amount of interest as useful and versatile materials for catalysis, charge injection in organic electronics devices, dye-sensitized solar cells and electrodes in fuel cells, among many other potential applications. In these applications, a metal oxide’s work function is critical to its function.

Transition metal oxides have been reported to be capable of a broad range of work functions, from the extreme low of ZrO$_2$ ($\phi \sim 3$ eV) to the extreme high of V$_2$O$_5$ ($\phi \sim 7$ eV). Binary oxides are somewhat complex materials, with many intrinsic properties that can affect their work functions. For example, most oxides are prone to forming defects, such as oxygen vacancies and interstitials or cation vacancies and interstitials. Many oxide cations are also capable of exhibiting multiple oxidation states. In order to gain control over metal oxide properties, such that they can be optimized for use in various applications, we must understand how defects and cation oxidation states affect an oxide’s work function.

As mentioned in section 3.1, MoO$_3$ is from a class of binary oxides that are very common: the d$^0$ oxides. Other d$^0$ oxides include WO$_3$, TiO$_2$, ZrO$_2$, HfO$_2$, CrO$_3$, Ta$_2$O$_5$, and V$_2$O$_5$. These oxides contain d-block metal cations, in which the cation’s d-band is considered completely empty. Thus the metal centers are considered fully oxidized. These oxides all share similar valence band structures. Their valence-band maxima are composed of O 2p states, and their conduction-band minima are composed of metal d-states.

The d$^0$ oxides are also prone to forming oxygen vacancy defects, which results in partial filling of the metal d-band, and gives rise to gap states close to the oxide’s Fermi level, as illustrate in figure 3.2.2. In many cases, when these oxides are reduced—such that they contain lower-oxidation-state cations—their electronic band structures become metallic, with valence-band maxima intersecting the Fermi level.

We begin the discussion by examining d$^0$ oxides because the photoemission spectra of d$^0$ oxides are relatively simple to interpret. We later move on to show that other transition metal oxides—that do not have the d$^0$ configuration—also behave similarly.
We propose that the two main contributions to the drop in work function that accompanies oxygen vacancy defects and low-oxidation-state cations are: 1) occupied gap states that act as donor levels and cause a shift in the Fermi level position, and 2) the lower electronegativity of low-oxidation-state cations alters the oxide’s electron chemical potential.

We provide experimental examples to corroborate the theory, such as 1) measuring oxide properties, while intentionally introducing oxygen vacancy defects via ion sputtering, and 2) measuring oxide properties while various oxides are reduced to lower-oxidation-state forms via thermal annealing in vacuum.

Based on the experimental findings, we present a mathematical analysis to show how gap states and cation electronegativity affects an oxide’s work function.

### 3.2.2 Methods

Oxygen vacancy defects were induced by Xe$^+$ ion bombardment using a Physical Electronics 04-303 Ion Gun, using a Physical Electronics 11-065 controller. The ion beam was set to a 1 mm diameter spot size and raster area of 8 mm × 8 mm. For MoO$_3$ and TiO$_2$, a beam voltage of 0.5 kV was used. The ion current at the sample was ~ 0.5 μA.
3.2.3 Dilute Defects in d\textsuperscript{0} Oxides

The first test was to see how a d\textsuperscript{0} oxide, such as MoO\textsubscript{3}, behaves as O-vacancy defect concentration increases. We do this by measuring the MoO\textsubscript{3} valence band and work function while bombarding with oxide with 0.5 kV Xe\textsuperscript{+} ions in 5 second intervals. The sputter rate of O\textsuperscript{2-} is greater than that of Mo\textsuperscript{6+}, and the result is a gradual increase in O-vacancy concentration.

Figure 3.2.3 illustrates how the secondary electron cut-off (used to determine work function) and the UPS valence-band spectra progress as the O-vacancy concentration increases. The work function starts off at \( \sim 6.9 \) eV—for the nearly stoichiometric MoO\textsubscript{3}—and it decreases as O-vacancy concentration increases. Meanwhile, the valence-band spectra show a new feature appearing within MoO\textsubscript{3}’s band gap—labeled \( d \) in figure 3.2.3—which gradually increases in size as the vacancy concentration increases. This feature arises because, in order for charge neutrality to be maintained, Mo\textsuperscript{6+} is reduced to Mo\textsuperscript{5+} when an O\textsuperscript{2-} ion is removed. As a result, MoO\textsubscript{3}’s previously empty 4d band becomes partially occupied with electrons, giving rise to the defect feature seen in the valence spectra.

![Figure 3.2.3](image)

**Figure 3.2.3** – (a) Secondary-electron cut-off, (b) valence band and (c) expanded view of ‘defect’ feature for MoO\textsubscript{3} as O-vacancies are introduced.

The Mo\textsuperscript{5+} species are also evident in the Mo 3d XPS spectra, as shown in figure 3.2.4. The main Mo 3d peak (at 232.50 eV) is from Mo\textsuperscript{6+} species, and as the oxygen vacancy concentration increases, a shoulder from Mo\textsuperscript{5+} species appears at \( \sim 231.5 \) eV. Furthermore, as the O-vacancy concentration increases, the Mo\textsuperscript{5+} binding energy shifts slightly (0.15 eV) to higher binding energy, indicating that Fermi level position is changing.
We have used the Mo 3d and O 1s peak areas to determine the O-vacancy concentrations. Note that even ‘stoichiometric’ MoO₃ contains some O-vacancies, simply due to the thermodynamic equilibrium concentration of vacancies at ambient temperatures; however, the O-vacancy concentration of stoichiometric MoO₃ is too low to be detected with XPS.

As mentioned with the UPS spectra, the work function appears to decrease with increasing O-vacancy concentration. In figure 3.2.5 we show a plot of work function versus O-deficiency as determined from the UPS spectra. The trend shows an initial rapid decrease in work function, followed by a more gradual and almost linear decrease.

The initial work function decrease is believed to be caused by the increase in donor state density (labeled $d$ in the UPS spectrum of figure 3.2.3) and the gradual work function decrease is believed to be a result of the lower electronegativity of Mo⁵⁺ cations, and their effect on MoO₃’s Fermi level. We have modeled these effects and describe them in detail in the next section.
Figure 3.2.5 – (a) Experimentally-determined work function values as a function of O-deficiency, $x$. (b) Plot of equation 3.1, which calculates work function based on density of donor states and cation electronegativity.

The dashed line shown in figure 3.2.5 (a) is equation 3.1 fit to the experimental data by adjusting the parameters of O-vacancy formation energy and Mo$^{5+}$ electronegativity. The plot in figure 3.2.5 (b) shows equation 3.1 using estimates of O-vacancy formation energy and Mo$^{5+}$ electronegativity from the literature. One can see that equation 3.1 reproduces the observed trend; however, the equation is only effective in relatively low O-vacancy concentrations. At higher concentrations one can see the work function starts to decrease rapidly again. We attribute this deviation to the beginning of Mo$^{4+}$ formation.

We have performed a similar experiment using TiO$_2$, where O-vacancies were induced by bombarding stoichiometric TiO$_2$ with Xe$^+$ ions. Much like MoO$_3$, TiO$_2$ is a d$^0$ oxide, except in this case the cation is Ti$^{4+}$ and oxygen vacancy defects give rise to Ti$^{3+}$ cations. TiO$_2$ exhibits similar behavior to MoO$_3$ when oxygen vacancy defects are introduced, as shown in figure 3.2.6. There is a rapid initial decrease in work function, followed by a slower decline. A similar gap-state appears in the valence band spectrum, and its intensity increases with O-vacancy concentration. The O 2p-band shifts to higher binding energy with increasing O-vacancy concentration.
The XPS spectra also show that the Ti\(^{4+}\) peak shifts to higher binding energy, while a Ti\(^{3+}\) shoulder begins to appear at higher O-vacancy concentrations. Note the metallic Ti\(^0\) peak from the underlying Ti metal substrate can be seen in the Ti 2p XPS spectra. As the Ti\(^{4+}\) peak shifts to higher binding energy, the Ti\(^0\) peak remains unchanged. This peak shift indicates a shift in TiO\(_2\)'s Fermi-level position as O-vacancies are introduced.

**Figure 3.2.6** – Measurements from a TiO\(_2\) film with O-vacancies induced by Xe\(^+\) bombardment. (a) Secondary-electron cut-off, (b) UPS valence spectrum, (c) expanded view of the ‘defect’ band, (d) plot of work function versus intensity of ‘defect’ band, (e) O 1s XPS spectra, (f) Ti 2p\(_{3/2}\) XPS spectra and (g) plot of O 1s, and Ti 2p\(_{3/2}\) binding energies versus ‘defect’ band intensity.

### 3.2.4 Work Function, Donor States and Cation Electronegativity

From the experimental data in figure 2.3.5 (a)—demonstrating a relationship between \(\phi\) and O-deficiency (\(x\) in MoO\(_{3-x}\))—we propose that the two main factors contributing to the change in oxide work function are: 1) increased concentration of donor states, and 2) increased
concentration of cations with low electronegativity. Therefore, we have the following expression for work function:

\[
\phi = \phi_0 + \Delta \phi_{\text{donor}} + \Delta \phi_{e-\text{neg}}.
\]

\textit{equation 3.1}

Where \( \phi \) is the measured work function, \( \phi_0 \) is the work function of the stoichiometric oxide, \( \Delta \phi_{\text{donor}} \) is the change in work function caused by donor states, and \( \Delta \phi_{e-\text{neg}} \) is the change in work function caused by an increase in the concentration of low electronegativity cations.

As we explain below, the term \( \Delta \phi_{\text{donor}} \) accounts for the initial rapid decrease in work function with O-deficiency, and the term \( \Delta \phi_{e-\text{neg}} \) accounts for the gradual, almost linear, decline in work function.

\subsection{Donor States}

It is clear from the UPS valence-band spectra that when O-vacancies are introduced into a \( d^0 \) oxide the density of donor states increases. Increasing the density of donor states, will increase the density of carriers in the conduction band, and result in a shift of the Fermi level, as illustrated in figure 3.2.7.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure3_2_7.png}
\caption{Schematic energy-level diagram of a stoichiometric \( d^0 \) oxide (left) and an O-deficient \( d^0 \) oxide (right), illustrating how ionized donor states shifts the Fermi level (\( E_F \)) closer to the conduction vacuum level (\( E_{\text{vac}} \)), resulting in a decrease in work function (\( \phi \)). \( E_F \) and \( E_F^d \) are the Fermi levels of the stoichiometric and defective oxides. \( E_c \) and \( E_v \) are the conduction band minimum and valence band maximum energies, respectively.}
\end{figure}
Using classical semiconductor physics, we can write an equation relating the electron density in the conduction band to the position of the Fermi level (relative to the conduction band):

\[ E_F - E_c = -kT \ln \left( \frac{n^e}{N_c} \right) \]

\textit{equation 3.2}

Where \( E_F \) is the Fermi energy, \( E_c \) is the energy of the conduction band minimum, \( n^e \) is the concentration of electrons in the conduction band, \( N_c \) is the effective density of states of the conduction band minimum, \( k \) is the Boltzmann constant and \( T \) is the absolute temperature.

We will be concerned only with changes in work function. This way we can eliminate many unknown parameters. We are interested in calculating work function difference between “stoichiometric” MoO\(_3\) and defective MoO\(_3\). Note we write stoichiometric in quotes because there is always some concentration of O-vacancies. The change in work function is then:

\[ \Delta \phi = \left( E_F^d - E_c \right) - (E_F^0 - E_c) \]

\[ \Delta \phi = E_F^d - E_F^0 = -kt \ln \left( \frac{n_e^{(d)}}{n_e^{(0)}} \right) \]

\textit{equations 3.3 and 3.4}

Where \( \Delta \phi \) is the change in work function, \( E_F^d \) is the Fermi level of the defective oxide, \( E_F^0 \) is the Fermi level of the “stoichiometric” oxide, \( n_e^{(d)} \) is the carrier density in the defective oxide’s conduction band and \( n_e^{(0)} \) is the carrier density in the “stoichiometric” oxide’s conduction band.

We now need to relate the electron density in the conduction band with the donor state density. We can write an expression for the electron density in the conduction band as follows:

\[ n_{d}^e = \sqrt{N_d N_c \exp \left[ -\frac{E_g}{kT} \right]} \]

\textit{equation 3.5}
Where \( N_d \) is the effective density of states of the donor level, \( N_c \) is the effective density of states of the oxide’s conduction band, \( E_g' \) is the difference between the energy of the conduction band minimum and the energy of the donor state.

As the density of donor states, \( N_d \), will be proportional to the density of Mo\(^{5+}\) cations, we can substitute the expression for \([Mo^{5+}]\) for \( N_d \) in equation 3.5. We can then substitute equation 3.5 into equation 3.4 for an equation relating \( \Delta \phi \) with Mo\(^{5+}\) concentrations:

\[
\Delta \phi = -\frac{1}{2} kT \ln \left( \frac{[Mo^{5+}]^{(d)}}{[Mo^{5+}]^{(0)}} \right)
\]

\textit{equation 3.6}

Where \([Mo^{5+}]^{(d)}\) is the concentration of Mo\(^{5+}\) in the O-deficient oxide and \([Mo^{5+}]^{(0)}\) is the Mo\(^{5+}\) concentration in the “stoichiometric” oxide. Note that the terms \( N_c \) and \( E_g \) from equation 4 cancelled each other out in the above expression.

We now need an expression for \([Mo^{5+}]\), in order to: 1) determine the relationship between \([Mo^{5+}]\) and O-deficiency, and 2) determine the Mo\(^{5+}\) concentration in “stoichiometric” MoO\(_3\). We will start by writing a defect reaction equation, using Kröger-Vink notation:

\[
O^{\frac{x}{2}} + 2\text{Mo}^{6+} \rightarrow \cdot\cdot\cdot O^{2+} + 2\text{Mo}^{5+} + \frac{1}{2}O_2(g)
\]

\textit{equation 3.7}

Where \( O^{\frac{x}{2}} \) is an oxygen ion on its regular lattice site, \( \text{Mo}^{x} \) is a metal ion on its regular lattice and with the charge it would have in the stoichiometric lattice, \( \cdot\cdot\cdot O^{2+} \) is a doubly positive charged oxygen vacancy, and \( \text{Mo}^{5+} \) is a metal cation on its regular lattice site, but with an extra electron relative to what it would have in the stoichiometric oxide. In the MoO\(_3\) case, we can re-write this reaction as follows:

\[
O^{\frac{x}{2}} + 2\text{Mo}^{6+} \rightarrow \cdot\cdot\cdot O^{2+} + 2\text{Mo}^{5+} + \frac{1}{2}O_2(g)
\]

\textit{equation 3.8}
Therefore, for the oxide MoO$_{3-x}$, where $x$ represents the degree of oxygen deficiency, we get the relation $[\text{Mo}^{5+}] = 2x$.

Now, in order to determine the concentration of Mo$^{5+}$ in “stoichiometric” MoO$_3$, we will write the equilibrium constant for the above defect reaction:

$$
K = \frac{[\nu_0][\text{Mo}^{5+}]^2}{[O_0^x][\text{Mo}^{6+}]^2p_{O_2}^{1/2}}
$$

*equation 3.9*

In the case of dilute defects, the denominator of the above equation will be unity. Furthermore, we can use the relation $[\text{Mo}^{5+}] = 2[\nu_0^{••}]$ to get the following equation for Mo$^{5+}$ concentration:

$$
[\text{Mo}^{5+}] = 2^{1/3} \exp \left[ \frac{-\Delta H_{\nu_o}}{3kT} \right] p_{O_2}^{-1/6}
$$

*equation 3.10*

Where $\Delta H_{\nu_o}$ is the enthalpy of formation for oxygen vacancies, and $p_{O_2}$ is the equilibrium oxygen pressure of the oxide. As an estimate for $\Delta H_{\nu_o}$, we use the approximation proposed by Kofstad.$^{67}$ Using values of the Mo sublimation enthalpy and oxide formation enthalpy, we get a value of 0.38 eV. Using this value for $\Delta H_{\nu_o}$, using $T = 830$ K (which is the temperature that MoO$_3$ was evaporated onto the substrate in our experiments), and using the $p_{O_2}$ of MoO$_3$ at 830 K, we get a value of $x = 0.0095$ in the formula MoO$_{3-x}$. This is what we use as our Mo$^{5+}$ concentration for “stoichiometric” MoO$_3$.

### 3.2.4.2 Electronegativity

The increase in donor state density causes a logarithmic relationship between $\phi$ and O-deficiency ($x$). This accounts for the initial rapid decrease in work function when O-vacancies are introduced. However, the experimental plot of $\phi$ versus O-deficiency suggests that there is also a linear component in the relationship.

The linear relationship is a result the lower electronegativity of Mo$^{5+}$ compared to Mo$^{6+}$. But before we address this relationship, we will discuss why the Fermi level depends on electronegativity. We will start with the definition of Mulliken potential for gas phase atoms.$^{68}$
\[ M = \frac{1}{2} (IE + EA) \]

*equation 3.11*

Where \( IE \) is ionization energy and \( EA \) is electron affinity. Mulliken noted that in a binary compound Mulliken potentials will equilibrate. Pauling later expanded on this concept. In describing how electrons in a binary compound redistribute to reach equilibrium, Pauling came up with the idea of electronegativity. Electronegativity is related to Mulliken potential as follows:

\[ M = 2.86 \chi \]

*equation 3.12*

where \( \chi \) is electronegativity. To extend this concept to solids, it was noted that \( \chi \) is equivalent to the mid-gap position. For undoped semiconductors, the mid-gap is equal to a semiconductor’s Fermi level. Note, this is only strictly true when hole and electron effective masses are equal, but it remains a very good approximation even when hole and electron effective masses several orders of magnitude different.

In 1974, Nethercott used the postulate of geometric means (i.e. \( \chi(AB) = (\chi_A \chi_B)^{1/2} \)) to write the Fermi level of binary compounds, using electronegativity concepts.\(^{69}\) Accordingly, the Fermi level for the binary compound \( A_m B_n \)—where \( A \) and \( B \) represent elements and \( m \) and \( n \) represent stoichiometric coefficients—can be written as follows:

\[ E_F = (\chi_A^m \chi_B^n)^{1/m+n} \]

*equation 3.13*

This concept is depicted in figure 3.2.8. Recently, Campet et. al. applied this concept to metal oxides, and noted that the electronegativities of metal cations and oxygen anions depend on the oxidation states of the respective ions.\(^{70}\) For example, a cation in a low oxidation state has a lower electronegativity than its high-oxidation-state counterpart because the smaller effective nuclear charge of the low-oxidation-state cation.
Figure 3.2.8 – Illustration of (a) the Mulliken concept of electronegativity, (b) how the concept of electronegativity translates to the Fermi level in solids an (c) how the electronegativities of metal cations ($\chi_{\text{M}^{m+}}$) and oxygen anions ($\chi_{\text{O}^{2-}}$) give rise to an oxide’s Fermi level. $IE$ ionization energy, $EA$ is electron affinity, is $\chi$ is electronegativity, $E_{\text{vac}}$ is the vacuum level and $E_F$ Fermi level.

Based on these concepts one can see why introducing oxygen vacancies into MoO$_3$ causes its work function to lower. The O-vacancies result in Mo$^{6+}$ cations reducing to Mo$^{5+}$. As Mo$^{5+}$ has a lower electronegativity than Mo$^{6+}$, the work function of O-deficient MoO$_3$ should be lower than stoichiometric MoO$_3$.

Using the above concepts, we can write an expression for the Fermi level’s dependence on non-stoichiometry. We get the following equation for the Fermi level of MoO$_{3-x}$:

$$E_F = (\chi_{\text{M}^{6+}})^{1-2x}(\chi_{\text{M}^{5+}})^{2x}(\chi_{\text{O}^{2-}})^{3-x})^{1/4-x}$$

*equation 3.14*

Where $\chi_{\text{M}^{6+}}$, $\chi_{\text{M}^{5+}}$ and $\chi_{\text{O}^{2-}}$ are the electronegativities of Mo$^{6+}$, Mo$^{5+}$ and O$^{2-}$, respectively. This equation gives a linear relation between $E_F$ and O-vacancy concentration. After incorporating this relationship into the overall equation for work function (equation 3.1), we obtain the plot shown in figure 3.2.5 (b). Note: we used electronegativity values of 2.9 eV for Mo$^{6+}$, 2.7 eV for Mo$^{5+}$, and 11.0 eV for O$^{2-}$. 
3.2.5 Non-dilute Oxygen Vacancies

While dilute oxygen vacancies can cause an oxide’s work function to decrease, when large amounts of oxygen are removed from an oxide’s lattice, its structure can completely change. While dilute oxygen vacancies can be treated as isolated defects, at high concentrations defects can interact with one another. For example in MoO₃, high oxygen vacancy concentrations are result in the formation of line defects, which eliminate some of the reduced cations. However, as oxygen removal continues, eventually all cations become reduced and a new oxide phase is formed. Most d⁰ oxides become metallic once they are completely reduced to a lower oxidation state. Surprisingly, even though the oxide has a completely different valence structure, an oxide’s work function tends to decrease with lower oxidation state cations.

Figure 3.2.9 (a) and (c) show the Mo 3d XPS and He I valence-band spectra of MoO₃ as it is reduced to MoO₂.₅ via thermal annealing in vacuum. In the early stages of reduction (i.e. at lower annealing temperatures) the Mo⁵⁺ peak begins to appear (see spectrum for 75 °C). As the temperature increases the amount of Mo⁵⁺ overtakes Mo⁶⁺ (spectrum for 150 °C). Eventually, the Mo⁴⁺ peak begins to show, at ~ 200 °C. At higher temperatures, the Mo⁶⁺ peak continues to diminish, while the Mo⁴⁺ peak dominates the spectrum. The final oxide is not completely reduced to MoO₂, but also contains some Mo⁵⁺.

Figure 3.2.9 – (a) Mo 3d XPS spectra, (b) secondary-electron cut-off, (c) UPS valence spectra and (d) plot of work function versus average Mo oxidation state for MoO₃.
The valence-band spectra show that the appearance of Mo\(^{5+}\) coincides with the appearance of the donor state, labeled \(d_1\). As Mo\(^{5+}\) concentration increases, and with the appearance of Mo\(^{4+}\), a additional gap state appears (labeled \(d_2\)). Eventually, as the oxide becomes more MoO\(_2\)-like, the breadth and positions of the valence features—such as the O 2p peak and the \(d_1\) and \(d_2\) peaks—change. This is likely a result of the different crystal structure and Mo-O bond lengths of the MoO\(_2\)-like structure. As a result of the changes to the valence bands, the \(d_1\) feature actually intersects the Fermi level and gives rise to a ‘Fermi edge’ in the spectrum. Thus the oxide has become metallic.

In addition to these significant valence-band and structural changes, the oxide’s work function also decreases. The work function decrease appears to be related to the average oxidation state of the oxide, as shown in the plot of work function versus average oxidation state in figure 3.2.9 (d). Note the metal’s work function is also shown in this plot.

The actual relationship between oxygen deficiency and work function—when O-vacancies cannot be considered dilute—is not expected to be a simple one, because there are many factors at play. For example the binding energy of the donor state will change as the oxide’s crystal structure changes. Furthermore, when Mo\(^{4+}\) begins to appear, one must consider the Mo\(^{4+}\) electronegativity. The relationship between O-vacancy concentration and Mo\(^{4+}\) formation is unclear. Also, the O-vacancy formation energy is expected to change with high O-vacancy concentrations.

However, regardless of the complexities of such a model, it appears that a correlation between average cation oxidation state and oxide work function does exist. As expected based on the discussion of cation electronegativity, reducing MoO\(_3\) tends towards lower work function.

### 3.2.6 Reducing Other Transition Metal Oxides

So far, we have dealt only with d\(^0\) transition metal oxides, and the question arises whether other transition metal oxides also exhibit a decrease in work function when they are reduced. We have examined XPS and UPS spectra of several transition metal oxides (i.e. oxides of Cr, V, Co, Cu, Ni, Mo, V, W, Ag). The high- and low-oxidation-state forms of the metals’ oxides exhibit a wide range of electronic structures, including n-type semiconducting, p-type semiconducting,
insulating and metallic conductors. Their d-band occupancies range from completely empty \((d^0)\) partially filled \((d^2)\) to completely filled \((d^{10})\).

Although the relationships between these oxides’ properties (such as band gap, conductivity and Fermi level) are intimately related to the oxides’ crystal structures, it is found for many oxides, lower cation oxidation states generally have the effect of decreasing the oxide’s work function. This relationship is demonstrated in figure 3.2.10.

![Figure 3.2.10](image)

**Figure 3.2.10** – Plots of work function versus metal oxidation state for several transition metals and transition metal oxides.

Although one should not expect a simple relationship between cation oxidation state and work function in every case—given the many factors that contribute to an oxide’s electronic structure and to a cation’s electronegativity—it is reasonable to expect that metal oxidation state, and thus cation electronegativity should have a substantial effect on the electron chemical potential of an oxide.
3.3 Controlling Oxide Properties

3.3.1 Controlling Oxidation State: Oxidizing in O₃ and Reducing in Vacuum

Thin oxide films consisting of metal cations in their highest stable oxidation state can usually be made by oxidizing clean metal surfaces in a mixture of O₂ and UV-generated O₃ (UV-O₃) at atmospheric pressure, and temperatures between 25 °C and 300 °C. The oxygen activity of O₃ is about 10¹⁸ times greater than O₂ at room temperature.⁷¹ This causes oxides to grow faster and to consist of lower O-vacancy densities. Figure 3.3.1 shows the valence spectra of MoO₃ grown by oxidation in O₂ and O₃. When oxidized in O₂, there is a distinct defect feature from O-vacancies. When oxidized in O₂ at the same temperature and for the same time the defect feature is not present. In ozone it is also possible to oxidize noble metals, such as Au and Pt. However, only extremely thin oxide films appear to form.

![Figure 3.3.1](image)

**Figure 3.3.1** – Spectra of a Mo sample oxidized in O₂ at 150°C for 2 hours (grey dotted line) and in O₃ at 150 °C for 1.5 hours (black line). (a) Mo 3d XPS spectra, (b) secondary-electron cut-off, (c) UPS valence spectrum, (d) expanded view of shallow valence features.
Some other transition metal oxides require much higher oxidizing potentials and temperatures to form stoichiometric oxides, such as CrO₃. Even in O₃ and at the highest available temperature (300 °C) CrO₃ could only be formed with large O-vacancy concentrations, and is better described as CrO₃₋ₓ.

Oxides that do not easily form oxygen interstitials, such as MoO₃ and V₂O₅ tend to reach a plateau with their work functions once most of the O-vacancy sites become filled. Some other oxides have a propensity for forming O-interstitial defects, such as CuO and NiO. This can cause the work function to continue to increase with oxidation time and oxidizing potential. A peak due to O-interstitials can be seen in the as an additional O-peak in the O1s spectrum of NiO. As a result of variable interstitial oxygen concentrations, NiO can exhibit a wide range of work function values (5.0 – 6.7 eV).

Most oxides can be reduced to a lower oxidation state via annealing in vacuum. In some cases it is easy to obtain a relatively pure phase, such as CuO → Cu₂O. While in other cases, one tends to get mixed oxidation states, such as MoO₃ → MoO₂.₅, and TiO₂ → TiO₁₋ₓ. A series of spectra measured during TiO₂ annealing in vacuum are shown in figure 3.3.2. These were taken after a TiO₂ sample had been annealed at 300 °C for various times.

![Figure 3.3.2](image)

**Figure 3.3.2** – (a) Ti 2p XPS, (b) secondary-electron cut-off, (c) UPS valence spectra of a TiO₂ film annealed in vacuum for various times. Arrows indicate increasing annealing time.

One can see from the Ti 2p spectra shown in figure 3.3.2 (a) that the sample initially consisted of a thin TiO₂ film grown on Ti (there is a weak Ti⁰ peak visible at ~ 454.0 eV). The main peak of the stoichiometric film is from Ti⁴⁺ at 458.6 eV. As the film is annealed and loses oxygen, Ti⁴⁺
becomes reduced to lower oxidation states. One can see a Ti$^{3+}$ and Ti$^{2+}$ peak grow into the XPS spectrum at $\sim 457.6$ eV and $\sim 455.2$ eV, respectively.

The work function of the oxide initially exhibits a rapid decrease in work function, but the slowly increases again, as seen in figure 3.3.2 (b). The decrease is due to the presence of donor states and decreased electronegativity, as described in section 3.2; however, the subsequent increase in work function is likely due to the fact that the oxide becomes metallic. The valence band is shown in figure 3.3.2 (c) and (d). Reduction begins with an increase in the ‘defect’ state intensity (at $\sim 0.8$ eV). Eventually this state broadens and crosses the Fermi level. At this point, the valence band becomes pinned to the Fermi level and the arguments presented for dilute defects no longer apply.\(^72\)

While most transition metals exhibit multiple stable oxidation states and can have multiple stable oxides, in other cases a lower-oxidation-state form of an oxide is not possible, for example NiO. Since there is no stable nickel oxide with a lower oxidation state than NiO, O-vacancies give rise to Ni$^0$ atoms. Eventually the oxide reduces to metallic nickel. Figure 3.3.3 (a) shows the Ni 2$p_{3/2}$ XPS spectrum of NiO and vacuum annealed NiO (annealed for 4 hours at 180 °C in $1\times10^{-9}$ torr). One can see that the XPS peak of metallic nickel (binding energy = 852.7 eV) appears in the annealed NiO spectrum. Furthermore, the oxidized nickel peak of NiO shifts to higher binding energy by $\sim 0.7$ eV. The O 1$s$ spectra of the annealed and non-annealed NiO are shown in figure 3.3.3 (b). One can see that the main O 1$s$ peak is also shifted to higher binding energy, but by slightly less ($\sim 0.6$ eV). Also, the higher-binding-energy shoulder (at about 531.5 eV) decreases in intensity relative to the main oxide peak. This higher-binding-energy peak has been attributed previously to interstitial Ni$^{3+}$ cations.\(^73-74\) Its decrease in intensity is expected when the oxide becomes reduced, however even though some parts of the oxide had reduced all the way to nickel metal it is difficult to remove all the Ni$^{3+}$ defects.
The secondary electron cut-off and valence band UPS spectra of the annealed and non-annealed NiO samples are shown in figure 3.3.3 (c) and (d), respectively. The secondary electron cut-off shows that the work function decreases by 1.4 eV after annealing. The valence band spectrum of annealed NiO has also shifted to higher binding energy by ~ 0.7 eV, similar to the Ni $2p_{3/2}$ and O 1s main peaks. The valence features of the oxide are otherwise the same, indicating that the oxide did not change its electronic structure significantly upon annealing. The decrease in work function and shifting of the main Ni $2p_{3/2}$, O 1s and valence peaks is likely a result of a change in the position of the Fermi level of the oxide due to the presence of oxygen vacancies and removal of oxygen interstitials. While the electronic structure of the oxide does not appear very different in the annealed oxide, it is likely that its conductivity has changed.

When sufficient oxygen vacancies have been formed, nickel cations become reduced to metallic nickel. The valence spectrum of the annealed oxide shows evidence of metallic nickel. The expanded region of the spectrum, near the Fermi level, is shown the panel at the top right of figure 3.3.3 (d). Here the Fermi edge of nickel metal can be seen. The reduction of NiO directly to Ni metal, rather than forming an $n$-type defective oxide, is a manifestation of the doping asymmetry of transition metal oxides. NiO is known to be a $p$-type transparent conductive
oxide when oxygen interstitial or Ni\textsuperscript{2+} vacancies are present.\textsuperscript{77-78} NiO cannot be easily made (if at all) \textit{n}-type.\textsuperscript{76}

The \textit{n}-type TMO’s, such as the \textit{d}	extsuperscript{0} oxides (WO\textsubscript{3}, MoO\textsubscript{3}, TiO\textsubscript{2}, V\textsubscript{2}O\textsubscript{5}, CrO\textsubscript{3}), can easily form oxygen vacancies, which give rise to conductivity via \textit{n}-type states. By trying to induce oxygen vacancies in NiO however, the oxide is reduced directly to Ni metal. This reduction is likely a result of the instability of a Ni\textsuperscript{+} oxide. All the \textit{d}	extsuperscript{0} oxides, on the other hand, have stable lower-oxidation-state forms. The defective oxide, with its much decreased work function also gives rise to poor energy-level alignment with \(\alpha\)-NPD. The defective oxide has a work function of 4.26 eV, which is well below the ionization energy of \(\alpha\)-NPD, and results in a HOMO binding energy of \(\sim\) 1.15 eV.

Some oxides are capable of lower oxidation states, but are very stable in their high oxidation state forms, such as when annealing V\textsubscript{2}O\textsubscript{5} and ZrO\textsubscript{2}. Annealing these oxides at the temperatures we were able to achieve in our oxidation chamber left only O-deficient oxides. For example, the photoemission spectra of stoichiometric V\textsubscript{2}O\textsubscript{5} and V\textsubscript{2}O\textsubscript{5} after annealing in vacuum are shown in figure 3.3.4.

In the XPS spectra, one can see that there is no distinct peak for the lower-oxidation state of V, but rather, the oxidized beak becomes broadened and shifted to lower binding energy. This indicates reduction, but not well-defined reduction; most likely a disordered mixture of oxidation states.

The work function follows a constant decrease (from 6.8 eV to 4.9 eV) with increasing O-vacancy concentration. The UPS valence spectra show the appearance of a defect feature, similar to what can be found in any O-deficient \textit{d}	extsuperscript{0} oxide. However, unlike MoO\textsubscript{2} and TiO this feature does not cross the Fermi level, even after extended annealing at relatively high temperature. Therefore, the oxide does not become fully reduced to a metallic oxide. There is significant distortion in the O 2p part of the spectrum, likely indicating lattice re-structuring.
3.3.2 Effects of Air-Exposure on NiO

Nickel oxide films formed by *ex situ* oxidation, or having been exposed to air have been quoted as being composed of Ni$_2$O$_3$, based on the Ni 2$p_{3/2}$ binding energy from XPS spectra.$^{79-82}$ However, Ni(OH)$_2$ has nearly the same Ni 2$p_{3/2}$ binding energy as Ni$_2$O$_3$. We have found that NiO formed by *in situ* UV-ozone oxidation of nickel using dry oxygen, forms only NiO. Furthermore, air exposure of *in situ*-prepared NiO results in the appearance of the same peaks in the XPS spectra, which are commonly attributed to Ni$_2$O$_3$.

Figure 3.3.5 (a) shows the Ni 2$p_{3/2}$ XPS spectra of *ex situ*-oxidized nickel, *in situ*-oxidized nickel, and *in situ*-oxidized nickel, after exposure to air for 30 minutes. The *ex situ*-prepared sample contains a peak at ~ 855.3 eV, which is either Ni$_2$O$_3$ or Ni(OH)$_2$. The spectrum of the *in situ* sample is characteristic of pure NiO. It has a peak at ~ 853.9 eV and a lower intensity shoulder at ~ 855.6 eV. The spectrum of the air-exposed sample contains both the NiO peak at 853.9 eV, and the Ni$_2$O$_3$/Ni(OH)$_2$ peak at 855.3 eV. It is a convolution of the *in situ* and *ex situ* spectra.

The O 1$s$ spectra of the *ex situ*, *in situ* and air-exposed samples are shown in figure 3.3.5 (b). The *in situ* sample consists of a main peak at ~ 529.4 eV, which originates from the lattice O atoms of NiO, as well as multiple higher binding energy shoulders. These shoulders have been discussed extensively in the literature, and are believed to arise from defects and physisorbed oxygen.$^{74}$
Figure 3.3.5 - Photoemission spectra of ex situ-oxidized NiO (solid grey line), in situ-oxidized NiO (solid black line) and air-exposed NiO (dotted line). (a) Ni 2p$_{3/2}$ XPS spectra, (b) O 1s XPS spectra, (c) C 1s XPS spectra, (d) secondary electron cut-off, (e) He Ia UPS valence spectra of the substrates, (f) He Ia UPS valence spectra after 1 nm α-NPD was deposited on each substrate.\textsuperscript{75}

The ex situ sample also contains the peaks of NiO, but the most intense peak is at \(~530.6\) eV. Again, this peak can be attributed to either Ni$_2$O$_3$ or Ni(OH)$_2$. The air-exposed sample has the same set of peaks, but with the Ni$_2$O$_3$/Ni(OH)$_2$ peak being lower in intensity than the NiO peak. Based on these observations we conclude that in situ ozone treatment results in only NiO, while exposure of clean NiO to air results in chemisorption of water and the formation of Ni(OH)$_2$ at the surface. We also conclude that ex situ UV-ozone oxidation of nickel forms Ni(OH)$_2$-terminated NiO, not Ni$_2$O$_3$.

In fact, the existence of Ni$_2$O$_3$ has been a point of contention since the 1930’s.\textsuperscript{83-86} There is still no conclusive evidence in the literature to show that Ni$_2$O$_3$ is a thermodynamically stable compound. The only unambiguous evidence of the existence of an Ni$_2$O$_3$-like compound comes from XPS results of NiO samples which were bombarded with O$_2^-$ ions in vacuum.\textsuperscript{87} It this case, it appears that an oxide containing Ni$^{3+}$ was made, but whether a stable stoichiometry of Ni$_2$O$_3$
was achieved is uncertain. If Ni_2O_3 was formed it is clearly non-equilibrium, as it was made only by ion bombardment and likely not crystalline, nor stable under normal atmospheric conditions.

In addition to forming surface nickel hydroxide, \textit{ex situ}-prepared NiO also adsorbs carbonaceous species, such as CO_2. The C 1s spectra of \textit{in situ}- and \textit{ex situ}-prepared NiO are shown in figure 3.3.5 (c). Note that even though the \textit{ex situ}-prepared sample was loaded into the XPS vacuum chamber within 10 minutes of being oxidized; it still has a significant amount of carbonaceous species adsorbed.

The surface nickel hydroxide and adsorbed carbonaceous species affect the work function of the oxide. Figure 3.3.5 (d) shows the secondary electron cut-off (used to determine work function) for the \textit{ex situ}, \textit{in situ} and air-exposed samples. The work functions are 6.43 eV, 5.50 eV and 5.23 eV, respectively. From these measurements, we see that the \textit{in situ}-prepared oxide can have a very high work function. When prepared in a well-baked vacuum system we have observed values as high as 6.73 eV. However adsorbates stick very rapidly to NiO, and even trace amounts of background gases will cause the oxide work function to drop rapidly. After being exposed to air for only 10 minutes, the work function decreased by almost 1 eV.

The valence band UPS spectra of the \textit{in situ}, air-exposed, and \textit{ex situ} samples are shown in figure 3.3.5 (e). All three samples have similar features, arising from the NiO valence band. There is a peak at ~ 1.5 eV and one at ~ 4.5 eV. The air-exposed and \textit{ex situ} samples however have additional features, with peaks growing in at ~ 7 eV and 9 eV. These additional peaks likely result from oxygen states of the hydroxide.

In spite of the different work functions, and slight differences in valence bands of the three substrates, the energy-level alignment of \(\alpha\)-NPD was not severely affected. In fact the HOMO binding energy of \(\alpha\)-NPD is the same on \textit{in situ} and air-exposed samples, despite the 0.93 eV difference in work function. The HOMO binding energy on the \textit{ex situ} NiO however is slightly higher; about 0.15 eV further away from the Fermi level. The HOMO binding energies of \(\alpha\)-NPD and work functions of the three substrates are shown in table 3.3.1. More discussion of the relation between work function and HOMO binding energy will be presented below.

In this study, the work functions of \textit{in situ}-prepared NiO samples generally ranged from 6.2 to 6.7 eV, however the work function is extremely sensitive to adsorbate coverage and it rapidly
decreases even in a vacuum with $\sim 10^{-10}$ torr background pressure of water (other background
gasses such as He and H$_2$ were present in negligible quantities, as measured using a residual gas
analyzer). In device production of solution-processed devices, NiO electrodes would need to be
carried through air for a short duration before additional organic layers can be deposited. It is
important to know what kind of time budget one has before the work function of a freshly
prepared NiO electrode drops below an unacceptable level.

Table 3.3.1 - Summary of substrate work functions and α-NPD HOMO binding energies for in situ-
oxidized, ex situ-oxidized and air-exposed NiO films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\phi$ (eV)</th>
<th>HOMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>in situ</td>
<td>6.43</td>
<td>0.31</td>
</tr>
<tr>
<td>air exposed</td>
<td>5.50</td>
<td>0.32</td>
</tr>
<tr>
<td>ex situ</td>
<td>5.23</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Figure 3.3.6 - Plot of NiO work function versus background gas exposure in Langmuirs (1 Langmuir is 1
second of exposure at $10^{-6}$ torr). The expanded window shows data points taken in vacuum of $3 \times 10^{-10}$
torr. The three data points with the highest exposures represent samples exposed to atmospheric
pressure of ambient air for 10, 30 and 70 minutes, respectively.$^{75}$

Figure 3.3.6 shows a plot of NiO work function versus air exposure in Langmuirs (1 Langmuir is 1
second of exposure at $10^{-6}$ torr). The data points in the blow-up panel were taken from the
sample while kept in vacuum, while the other points were taken after the sample was exposed
briefly to air. The last three data points represent air exposure for 10 minutes, 30 minutes and 70 minutes.

One can see that the most rapid drop in the work function of NiO occurs during the first few Langmuirs of exposure. The work function drops by 0.75 eV during the first ~ 200 Langmuirs of exposure, and then drops only an additional 0.36 eV with ten orders of magnitude more exposure. It may appear from this figure that the work function of NiO levels-off at ~ 5.6 eV, however this is not the case. The work function of a sample left for 3 days in atmosphere had dropped to 4.7 eV (data point not shown). The continual drop in work function arises because the NiO surface continues to adsorb carbonaceous species and other atmospheric contaminants even after it has been fully hydroxylated.

3.3.3 Effects of Air-Exposure on MoO$_3$

MoO$_3$ is one of the most commonly used transition metal oxides for hole-injection buffer layers due to its extremely high work function. For low-cost organic electronics it is desirable to be able to process organic thin films via spin casting rather than high vacuum sublimation deposition. MoO$_3$ must be exposed to ambient conditions—or at least dry air—in order to spin cast a polymer onto it. However, oxide work functions can be affected by atmospheric adsorbates. It is important to understand one’s time budget available when processing MoO$_3$ substrates in ambient conditions before the oxide’s work function has decreased to the point that it no longer provides improved hole-injection. Here we examine the changes that occur to MoO$_3$ upon exposure to air. We examine its core levels, as well as its valence levels and work function. We find that a hole-injecting material with reasonably high ionization energy, such as $\alpha$-NPD, keeps its favorable energy level alignment with MoO$_3$ even after several hours of air exposure.

Figure 3.3.7 (a) shows the Mo 3d XPS spectra of an in situ-oxidized MoO$_3$ thin film, being exposed to ambient air. The spectra change very little with air exposure time. There is a slight decrease in the metallic Mo signal and a slight increase in the oxidized Mo signal. Figure 3.3.7 (b) and (c) show the O1s and C1s spectra of the same sample after various air exposures. There is no noticeable change in the O 1s spectra. However, the C1s spectra show that the in situ-oxidized MoO$_3$ had no detectible carbon signal prior to air exposure, and after air exposure the C 1s signal increases in intensity.
The secondary-electron spectra in figure 3.3.7 (d) show that air exposure causes the work function of MoO$_3$ to decrease. The work function of MoO$_3$ changes from 6.25 eV to 5.04 eV after 650 minutes of air exposure. This is likely due to a change in the MoO$_3$ surface dipole due to adsorbed polar molecules. The valence band spectra in figure 3.3.7 (e) show the appearance of a new feature at ~ 7 eV. This feature is likely caused by adsorbed atmospheric contaminants. The expanded view of the shallow valence features shows that the defect state in the oxide becomes buried under the signal from the atmospheric adsorbates. Due to the extreme surface sensitivity of UPS (IMFP of ~ 1 Å) buried signals diminish in intensity very rapidly with overlayer coverage.

**Figure 3.3.7** – Spectra collected after various air exposure times of an *in situ*-oxidized MoO$_3$ thin film. (a) Mo 3d XPS spectra, (b) O 1s spectra, (c) C1s spectra, (d) secondary-electron cut-off, (e) UPS valence spectra and (f) expanded view of shallow valence features. Note, the dotted line in (f) shows the HOMO level of α-NPD deposited onto the MoO$_3$ film after exposure to air for 650 minutes.

The HOMO level of α-NPD is shown in figure 3.3.7 (f). On *in situ*-oxidized MoO$_3$ the HOMO binding energy is 0.3 eV, while on air exposed MoO$_3$ the HOMO level moves away from the
Fermi level, and has a binding energy of 0.4 eV. The change in HOMO binding energy is likely due to the fact that the MoO$_3$ work function has dropped below $\alpha$-NPD’s ionization energy. This only causes an increase in HOMO binding energy of 0.1 eV; however, an increase in hole-injection barrier of 0.1 eV can have drastic effects on device efficiency.
4 The Interface between Transition Metal Oxides and Organic Semiconductors

4.1 Energy-Level Alignment

4.1.1 Background

This chapter is focused on the interactions between metal oxides and organic semiconducting molecules. In the previous chapter we examined the properties of transition metal oxides. We saw that transition metal oxides exhibit a large diversity in physical, chemical, and electronic properties, and these properties can be tuned in many ways. It is important to know which oxide properties most strongly affect energy-level alignment, in order to utilize transition-metal oxides to their greatest potential.

As mentioned in the introduction, transition metal oxides are used for efficient charge injection/collection between electrodes and organic molecules in several important technologies—such as dye-sensitized solar cells and organic photovoltaics, as well as low-power-consumption electronic devices like organic light emitting diodes and organic thin-film transistors. The property that makes transition metal oxides so useful to organic electronics is their ability to exchange charges with condensed molecules. This same property also allows certain oxides to photo-catalytically convert CO$_2$ into useful hydrocarbons; and permits oxides to be used as electrolytes in solid oxide fuel cells.

Oxides are able to shift an organic’s donor level close to the Fermi level for efficient hole injection, or move an organic’s acceptor level towards the Fermi level for efficient electron injection. Over the past several decades a great deal of work has been devoted to understanding energy alignment in organic devices. Metal-organic interfaces were the first to be considered. Researchers initially assumed that vacuum levels would align at an interface. Thus they expected that the difference between a metal’s work function and an organic molecule’s HOMO and LUMO levels would determine charge-injection barriers. Researchers soon realized that vacuum levels rarely align, and it became uncertain what role work function plays in energy alignment.
Several developments to the interfacial-energy-alignment model arose, such as the interfacial pinning parameter, the concept of induced-density of interface states, interfacial dipoles, the push-back/pillow effect, the importance of the charge-neutrality level, and integer charge-transfer model. While these concepts reconcile some of the initial discrepancies in the energy-alignment model, not all of these concepts are mutually consistent. Although many scientists and engineers routinely use work function as a ‘back-of-the-envelope’ evaluation of energy alignment, it is often taken for granted why this should be so. It is still uncertain how energy alignment is established, and a comprehensive and quantitatively predictive model has not been developed.

When metal oxides became the topic of research, work function was seen to affect energy alignment only in the sense that it determines an oxide’s valence and conduction band positions relative to the vacuum level. Many of the concepts developed for energy alignment at metal-organic interfaces do not necessarily hold for oxide-organic interfaces. For instance most oxides do not have electron states at the Fermi level to enable charge exchange with molecules, thus it is generally expected that charge transfer must proceed via an oxide’s valence or conduction bands. Indeed, several recent findings have shown convincing evidence that electrons can hop from an organic’s HOMO level into the low-lying conduction bands of certain $d^0$ oxides, such as MoO$_3$ and WO$_3$. These findings have led to the belief that MoO$_3$ and WO$_3$’s energy-aligning characteristics are a result of their low-lying conduction bands.

This charge-injection model is now frequently applied to a wide range of semiconductor-organic interfaces. However, this model is unable to explain why so many other oxides, having much different conduction and valence band positions than MoO$_3$ or WO$_3$, also work well as charge-injection layers. For example, NiO has a conduction band situated approximately 2 eV higher than the HOMO level of $\alpha$-NPD ($N,N'$-diphenyl-$N,N'$-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine), yet it still exhibits Ohmic hole-injection.

A global picture of oxide-organic energy alignment is not yet available. Although a Fermi-level-pinning transition was demonstrated by Fahlman et al., it was uncertain at the time whether this trend was actually universal, as it had only been demonstrated using a limited set of ex-situ-prepared samples. Here we demonstrate, using a large variety of in-situ-prepared oxides, that
such a Fermi-level-pinning transition is a universal trend, and is a result of an energy-alignment principle for non-reactive interfaces.

We have taken the approach of measuring a large set of diverse metal oxides because most current theories have been developed from small sub-sets of materials. The large variety of samples is very unique to this study, and illustrates the universality of the observed trend. The fact that this trend is observed for such diverse materials implies that substrate band structure does not affect the equilibrium energy-alignment position of adsorbed molecules. Rather, energy alignment is governed by the equilibration of a substrate’s electron chemical potential with an adsorbed molecule’s oxidation/reduction potentials. Using this concept, we present a simple mathematical formalism to predict energy alignment that is based on fundamental thermodynamic and electrostatic principles.

All samples were prepared in situ and characterized with core-level and valence-band photoemission spectroscopy. The oxides investigated here span a wide range of electronic properties, and include: n-type wide-band-gap semiconductors, such as MoO₃, TiO₂, V₂O₅, WO₃ and Ta₂O₅; defective semiconducting oxides, such as MoO₃-x, TiO₂-x, V₂O₅-x; and CrO₃-x; p-type semiconductors, such as Cu₂O, Ag₂O, Cr₂O₃, and Co₃O₄; p-type Mott-Hubbard insulators, such as CuO, NiO, and CoO; and metallic oxides, such as MoO₂, WO₂, and TiO.

Three different organic semiconductors were paired with these oxides and their parent metals in order to identify broadly applicable trends in energy-level alignment. The organic semiconductors are: 4,4′,4″-tris(N-2-naphthyl-N-phenyl-amino)triphenylamine (2T-NATA); N,N′-diphenyl- N,N′-bis(1-naphthyl)-1,1′-biphenyl-4,4′-diamine (α-NPD); and 4,4′-bis(carbazol-9-yl)-2,2′-biphenyl (CBP).

Energy-level alignment was determined by measuring the HOMO levels of the three organic semiconductors (CBP, α-NPD and 2T-NATA), which were condensed into thin films on the above-mentioned oxides and the oxides’ parent metals. While numerous possible correlations were investigated—such as correlations between the organic HOMO energy and an oxide’s valence band position, conduction band position, and work function—the only relationship that was found to affect energy alignment was the energy difference between a substrate’s work function and an organic’s ionization energy.
4.1.2 Universal Trend

The observed energy-alignment trend is shown in figure 4.1.1, where the HOMO off-set ($\Delta E_H$) for molecular monolayers is plotted against substrate work function. The data for CBP (a), $\alpha$-NPD (b), and 2T-NATA (c) are shown separately on the left. The data from separate molecules is combined into a universal plot in (d) by plotting HOMO off-set against the difference of substrate work function and organic ionization energy. The dashed lines in figure 4.1.1 (d) were determined by taking the average $\Delta E_H$ value for $\phi > IE$, and using linear regression for $\phi < IE$.

![Figure 4.1.1 - Universal energy-level alignment trends. a-c, Plots of HOMO off-set versus substrate work function for molecules CBP (a), $\alpha$-NPD (b), and 2T-NATA (c) on various transition-metal oxide and transition metal substrates (legend shown underneath). d, Universal plot of HOMO off-set ($\Delta E_H$) versus the difference of substrate work function and organic ionization energy ($\Phi - IE_{org}$) by combining plots (a)-(c). The dashed line for $\Phi > IE_{org}$ was determined by calculating the average $\Delta E_H$ value, and the dashed line for $\Phi < IE_{org}$ was determined using a least-squares regression fit, with the restriction that $\Delta E_H = 0.3$ when $\Phi = IE_{org}$.27 The trend in figure 4.1.1 (d) shows a distinct change in energy alignment when a substrate’s work function becomes equal to a molecule’s ionization energy. Once a substrate’s work...](image-url)
function has exceeded an adsorbed molecule’s ionization energy the HOMO off-set establishes a minimum value, and remains constant with further increases in work function. This trend is similar to that observed by Fahlman et al for polymer-coated and ex-situ-prepared substrates. Here, using well-defined oxides and metals prepared in ultra-high-vacuum, we find that this alignment principle is general and governs energy alignment of a wide range of materials.

What is especially interesting about this trend is that it is observed for such a diverse set of materials. The trend also implies that the HOMO off-set is independent of substrate electronic structure—this of course would only be true when there is no chemical reaction between the adsorbate and substrate, as is the case for each of the materials combinations examined here.

It is often thought that, in order for an electron to jump from an organic molecule to an oxide, the electron must move from the organic’s HOMO level into the oxide’s conduction band, and thus an oxide’s conduction band positions should be very important for energy alignment. However, the pinning trend shown in figure 4.1.1 implies that energy alignment can be established regardless of oxide conduction/valence band positions. A compilation of oxide energy-level diagrams is shown in figure 4.1.2, along with energy-level diagrams of TPBI, CBP, α-NPD, and 2T-NATA.

The band edges for the figure were determined from UPS spectra, and band gaps were taken from literature values, which are tabulated and referenced in the Chapter 4 Appendix. The oxides are placed in order of decreasing work function (left to right) and the organics placed in order of decreasing ionization energy (left to right).

A molecule’s HOMO level can become pinned to the Fermi level even if the HOMO level is far away from the oxide’s conduction or valence bands. For example, as shown in figure 4.1.2, α-NPD exhibits favorable energy alignment with numerous oxides—CuO, Cr₂O₃, MoO₂, Co₃O₄, NiO, WO₃, V₂O₅, CrO₃ and MoO₃—however, only MoO₃, V₂O₅, WO₃, CrO₃ and MoO₂ have conduction bands that are close enough to α-NPD’s HOMO level to permit thermal excitation of electrons into the oxides’ conduction bands.
4.1.3 Charge-Transfer Model

To understand why this occurs we have constructed an equation to describe the relationship between HOMO binding energy ($\Delta E_H$), substrate work function ($\Phi$), and organic ionization energy ($IE_{org}$). The observed trend implies that HOMO level pinning occurs when the organic’s ionization energy equals the substrate’s Fermi energy, so we will consider how a charge particle is affected by the Fermi level. From solid-state and semiconductor physics it is known that the formation energies of charged defects and ionized dopants depend on the Fermi level position.\textsuperscript{97,98} As adsorbed molecules are in intimate contact with a solid, they are coupled to the solid’s Fermi level, and so we will apply this concept to molecules adsorbed to a solid surface.

When an adsorbed neutral molecule becomes charged it gives (takes) an electron to (from) the Fermi level. Thus its formation energy is given by the following equation.

$$E_f (M^q) = E(M^q) - E(M^0) - qE_F - E_{rlx}$$

\textit{equation 4.1}
Here, $E(M^q)$ is the total energy of a molecule carrying a charge of $q$, $E(M^q')$ is the energy of the neutral molecule, $E_F$ is the Fermi energy, and $E_{rel}$ is the relaxation energy, which depends on the screening characteristics of the surrounding substrate and molecules. Neglecting for the moment relaxation effects, formation energy is simply the ionization energy for the $M^+$ state, plus an additional energy contribution from adding an electron to the solid’s Fermi level. Thus the Fermi energy has a direct influence on a charged molecule’s thermodynamic stability.

Figure 4.1.3 (a) shows a plot of the formation energy of molecules in the $M^0$ and $M^+$ states relative to the neutral molecule. When the Fermi energy becomes greater than the ionization energy of the molecule, the $M^+$ state becomes the thermodynamically favored species. When the Fermi energy lies within the energy gap of the molecule the neutral state is most stable.

![Figure 4.1.3 - Origin of energy-level-alignment trend.](image)

**Figure 4.1.3 - Origin of energy-level-alignment trend.** a, Formation energies of adsorbed molecular species $M^0$, and $M^+$ as a function of the substrate Fermi energy. The points on the formation energy plot correspond to two hypothetical oxides with band structures as shown to the right. b, Plot showing how the relative concentrations ($N_q/N$) of molecular species $M^0$ and $M^+$ in a monolayer change with the substrate’s Fermi level. c, Plot of HOMO off-set ($\Delta E_H$) versus the difference between substrate work function and organic ionization energy ($\Phi - IE_{org}$) calculated from equation 4.3.27.
The band diagrams of two hypothetical oxides with different work functions are shown to the right of the formation energy plot in figure 4.1.3 (a). Oxide 1, having the lower work function, has a Fermi level that sits above the point of transition from $M^0 \rightarrow M^+$. When adsorbed to the surface of oxide 1 the neutral molecule is most stable. Since oxide 2 has a higher work function, such that its Fermi level sits below the point of transition from $M^0 \rightarrow M^+$, the ionized molecule is the most stable form when adsorbed to oxide 2.

When a solid’s Fermi level falls below a molecule’s ionization energy, the number of ionized molecules rapidly increases. As the charged molecule’s stability is coupled to the Fermi level, Fermi-Dirac statistics must be used in calculating the equilibrium concentrations of charged molecules. Their relative concentrations are given by equation 2.

$$\frac{N^q}{N} = \left(1 + g(M^q) \exp \left(\frac{E_f(M^q)}{kT}\right)\right)^{-1}$$

*equation 4.2*

Where $N^q$ is the number of molecules of charge $q$ in the first monolayer adsorbed to the surface. $N$ is the total number of molecules in the first layer, $g(M^q)$ is a degeneracy factor, which accounts for the number of identical charged configurations of a molecule, and $E_f(M^q)$ is the formation energy of a molecule with a charge of $q$. The logarithm of the relative concentrations of each molecular species (equation 4.2) is plotted in figure 4.1.3 (b).

In order to model energy alignment we must consider how charged molecules affect the electric field at the interface. When the Fermi energy lies within the molecule’s HOMO-LUMO gap, essentially all of the adsorbed molecules are neutral, thus they do not generate an electric field and cannot counteract the Volta potential at the substrate surface (see the Appendix for more details of how a Volta potential arises at the substrate surface). Since the Volta potential increases linearly with substrate work function the HOMO binding energy shifts linearly with substrate work function.

As the Fermi energy moves below the adsorbed molecule’s ionization energy, the equilibrium concentration of ionized molecules rapidly increases. The presence of positively-charged molecules generates a positive electric field in the organic layer, which counteracts the negative
electric field from the substrate’s surface potential. As the work function increases further, the concentration of ionized molecules increases, such that the electric field and HOMO energy remain constant with increasing work function.

This scenario can be modeled by treating the adsorbed ionized molecules as a charged plane, where the charge on the plane depends on the concentration of ionized molecules in the plane. We can write an equation which calculates the HOMO-off-set as a function of ionization energy and substrate work function.

\[
\Delta E_H = IE + \delta - \alpha \phi + \frac{q^2 \rho d}{2\varepsilon_0} \sum_i \left(1 + g \exp \left[\frac{IE - (\phi - i\beta)}{kT}\right]\right)^{-1}
\]

\textit{equation 4.3}

Where \(IE\) is the molecule’s ionization energy, \(\delta\) is the interfacial dipole from the ‘push-back’ effect, \(\alpha\) is a proportionality constant based on the molecular layer’s ability to screen the potential of the substrate surface, \(\phi\) is the substrate’s work function, \(q\) is the elementary charge, \(\rho\) is the planar number density of molecules and \(d\) is the distance between the molecular plane and the substrate. The summation is taken over \(i\) molecular layers. Equation 3 is plotted in figure 4.1.3 (c), where one can see that it reproduces the observed relationship between HOMO off-set and substrate work function.

The above model implies that pinning only occurs because, when a molecule is adsorbed to a surface and coupled with the solid’s Fermi energy, the ionized form of the molecule becomes thermodynamically stable when the Fermi energy is greater than the molecule’s ionization energy. This implies that oxide band structure does not govern energy alignment because it does not govern the thermodynamic stability of charged molecules. Conduction bands and valence bands simply provide a convenient pathway for conduction, but the pathway for reaching equilibrium need not be well-defined in order for equilibrium to ultimately be reached.

While changing materials is one method of altering an electrode’s chemical potential, an oxide’s chemical potential can also be tuned by introducing oxygen defects. By removing oxygen atoms an oxide’s electron chemical potential can be decreased. Oxygen vacancies act as n-type dopants and raise the Fermi level, thus reducing the work function. Conversely, oxygen interstitials can
increase the oxide’s electron chemical potential. This principle can be used to tune the energy alignment of an oxide.

To illustrate this point, we have taken two oxides (NiO and MoO$_3$) and tuned their electron chemical potentials by inducing defects, then examined how $\alpha$-NPD’s energy alignment is affected, as shown in figure 4.1.4. NiO is known to form oxygen interstitial defects, while MoO$_3$ is known to form oxygen vacancy defects. NiO’s work function can be increased by growing the oxide under more oxidative conditions, such as higher temperatures, higher oxygen pressures or by using O$_3$ for oxidation. As shown in figure 4.1.4, when the work function of NiO increases $\alpha$-NPD’s HOMO off-set decreases until its ionization energy is reached and the HOMO level becomes pinned.

Figure 4.1.4 - Tuning energy alignment through electron chemical potential. a, Plot of HOMO off-set ($\Delta E_{\text{HOMO}}$) versus the difference between substrate work function and organic ionization energy ($\Phi - IE_{\text{org}}$) for $\alpha$-NPD on NiO and MoO$_3$, where the electron chemical potential of the oxides was tuned by inducing oxygen vacancy defects.$^{27}$

On the other hand, MoO$_3$’s work function can be decreased by annealing in vacuum. MoO$_3$ has such a high work function, that even a defective oxide has a work function greater than $\alpha$-NPD’s ionization energy. Therefore, $\alpha$-NPD’s HOMO binding energy stays pinned to MoO$_3$’s Fermi level over the whole range of work functions exhibited by MoO$_3$.

So if electron chemical potential is the driving force for energy-level alignment, what makes transition metal oxides so special? Oxides simply modify the surface potential of a substrate;
however, metal oxides are capable of a wide range of work functions from \( \sim 3 \) eV (ZrO\(_2\)) to \( \sim 7\) eV (V\(_2\)O\(_5\)). They can be made to position molecular levels close to the Fermi level for most organic semiconductors to enable efficient charge transfer. Their work functions and electronic structures can be tuned by inducing defects or changing the oxidation state of the metal cation. This versatility gives oxides a broad range of applications in organic electronics, as well as in heterogeneous catalysis.

### 4.2 Derivation of Energy-Level Alignment Equation

It has been shown that—for weakly interacting interfaces—HOMO binding energy is linearly related to substrate work function up until the work function reaches a threshold value. Once the threshold is reached, the HOMO level becomes ‘pinned’ to the Fermi level and is independent of substrate work function. In the previous section we proposed a model to describe this pinning behavior. The model implies that the concentration of ionized molecules at a substrate-organic interface depends on the substrate’s Fermi level.

We will start the discussion by addressing what happens just outside a solid’s surface when the solid is grounded. Figure 4.2.1 (a) shows a schematic energy-level diagram of a floating solid. The vertical scale represents energy and the horizontal scale represents distance. This is a hypothetical situation of a solid material completely isolated from any other material—i.e. floating in infinite space with no external electric fields. Here we have neglected surface dipole for simplicity, so the solid’s local vacuum level is aligned with the absolute vacuum level.

There is an energy level associated with ‘ground’ (\(E_{\text{ground}}\)). ‘Ground’ is the electrochemical potential of an infinite reservoir of electrons. Experiments have positioned this energy level at \( \sim 4.09\) eV below the absolute vacuum level. Figure 4.2.1 (b) shows the scenario where the solid becomes grounded. Assuming the solid has sufficient conductivity for electron chemical potentials to equilibrate, the solid’s Fermi level (\(E_F\)) aligns with ground.
Figure 4.2.1 – (a) Schematic energy-level diagram of the hypothetical situation for a solid, floating in infinite space, with no external electric fields. (b) Schematic energy-level diagram of the sample after being grounded, where the sample’s Fermi level equilibrates with the ‘ground’ energy level. The vertical scale is energy and the horizontal scale is distance. $E_{V,\text{local}}$ represents the local vacuum level, $E_{V,\infty}$ represents the absolute vacuum level, $E_{\text{ground}}$ represents the electron chemical potential of ‘ground’, and $E_{F}$ represents the solid’s Fermi level.

This results in an electrostatic field just outside the surface of the solid—highlighted in blue in figure 4.2.1 (b). This electrostatic field gives rise to a so-called local vacuum level, which is different from the absolute vacuum level ($E_{V,\infty}$). The absolute vacuum level is the energy associated with an electron at rest, with no external electrostatic fields, and infinite distance away from any other particle.

The electrostatic field outside the surface of a grounded sample affects an adsorbed molecule’s orbital energies. Figure 4.2.2 (a) shows an energy-level diagram for a molecule separated by infinite distance from a solid’s surface. The solid is grounded, so there is a surface electrostatic field. The molecule’s vacuum level aligns with the absolute vacuum level.

As the molecule comes close to the solid’s surface—depicted in figure 4.2.2 (b)—the molecule ‘feels’ the surface electrostatic field. This field shifts all of the molecular orbital energies upward. There is a drop in electrostatic potential at the solid/molecule interface, known as the interfacial dipole.
Figure 4.2.2 – (a) Energy-level diagram of a grounded solid (right) and an isolated molecule at infinite distance away from the solid. (b) Scenario where the molecule comes close to the solid’s surface. The surface electrostatic field pushes the molecule’s energy-levels upwards. (c) Scenario where the molecule is in contact with the solid’s surface. If the solid’s work function is greater than the organic’s ionization energy, then the HOMO will be above the Fermi level, and electrons will transfer from the molecule to the solid. $E_F$ is the Fermi level, $E_{v,\text{local}}$ is the local vacuum level, and $E_{v,\infty}$ is the absolute vacuum level.

Once the molecule is in intimate contact with the solid’s surface—and if the solid’s work function is greater than the molecule’s ionization energy—electrons will hop from the
molecule’s HOMO to the solid’s Fermi level. This will result in ionized molecules adsorbed to the solid’s surface.

**Figure 4.2.3** – (i) Illustration of the observed relation between HOMO binding energy and oxide work function, (ii) schematic energy-level diagram, and (iii) illustration of the microscopic picture of an oxide/molecule interface for four scenarios: (a) $\phi_{ox} < IE_{mol}$, (b) $\phi_{ox} = IE_{mol}$, (c) $\phi_{ox} > IE_{mol}$, and (d) $\phi_{ox} >> IE_{mol}$.

We will now describe how molecular ionization gives rise to the observed relationship between HOMO binding energy and oxide work function. Figure 4.2.3 illustrates how the observed trend
(a), is related to substrate and molecule energy-level alignment (b) and how this is interpreted microscopically.

In figure 4.2.3 (a) the oxide’s work function is less than the organic’s ionization energy. This corresponds to the linear region of the HOMO versus $\phi$ relationship. In this case there is no electron transfer at the interface, and essentially all the molecules in the film are un-charged.

In figure 4.2.3 (b) the oxide’s work function is equal to the organic’s ionization energy. This corresponds to the kink in the HOMO versus $\phi$ relationship. Electrons begin to transfer from the organic’s HOMO level toward the oxide’s Fermi level. This is the point where molecular starts to become significant.

In figure 4.2.3 (c) the oxide’s work function is greater than the organic’s ionization energy. This corresponds to the plateau in the HOMO versus $\phi$ relationship. Electron transfer, from the molecules to the substrate’s Fermi level, results in high concentrations of ionized molecules at the interface. The electrostatic field from the ionized molecules keeps the HOMO level pinned to the Fermi level.

In figure 4.2.3 (d) the oxide’s work function is much greater than the organic’s ionization energy. Molecules further away from the interface become ionized in order to keep the HOMO level pinned to the Fermi level.

Based on this model, we will now derive an equation for the HOMO binding energy. As a starting point, we will write an equation for the HOMO binding energy assuming perfect vacuum-level alignment between the organic molecule and the solid’s surface.

$$\Delta E_H \equiv E_H - E_F = (E_H - E_V) - (E_F - E_V) = IE - \phi$$

\textit{equation 4.4}

Where $\Delta E_H$ is the HOMO binding energy, $E_H$ is the energy of an electron in the HOMO, $E_F$ is the energy of an electron at the Fermi level, $E_V$ is the vacuum energy, $IE$ is the organic molecule’s ionization energy, and $\phi$ is the substrate’s work function.

We then incorporate an additional term for the so-called interfacial dipole ($\delta$) which is essentially a rapid change in electric potential at an interface. The origins of this term are still under debate.
in the literature, but it is often said to be due to polarization of the adsorbed molecule or possibly a result of electron repulsion between the molecule and the substrate’s surface dipole. Either way, we add it to equation 4.4 and treat it as an external electric field acting on the HOMO electrons. We will also include a term for the electric field caused by surrounding ionized molecules. This gives us the following equation:

\[ \Delta E_H = IE - \phi + \delta + E_{M^+} \]

\textit{equation 4.5}

Where \( \delta \) is the change in electrostatic energy caused by the interfacial dipole, and \( E_{M^+} \) is the change in electrostatic energy caused by any near-by ionized molecules.

We will treat the term \( E_{M^+} \) as the result of a uniformly charged plane. The electric field from a uniformly-charged plane is given by:

\[ E = \frac{\sigma}{2\epsilon_0} \]

\textit{equation 4.6}

Where \( \sigma \) is the planar charge density of the uniformly-charged plane, and \( \epsilon_0 \) is the permittivity of free space. The planar charge density is given by:

\[ \sigma = \frac{Q}{A} \]

\textit{equation 4.7}

Where \( Q \) is the total charge on the plane, and \( A \) is the area of the plane. In the case of organic molecules at an interface, the total charge on the plane depends on the number of ionized molecules in the plane. The total number of charged particles is given by the fraction of molecules in the plane that are charged, times the number of molecules in the plane, times the charge per molecule.

\[ Q = \left( \frac{n^+}{n} \right) \times (\rho \times A) \times q \]
Where \((n_+/n)\) is the fraction of charged particles in the molecular plane, \(\rho_A\) is the planar density of molecules, \(A\) is the area of the plane, and \(q\) is the elementary charge. Substituting this expression back into equation 4.5, we get:

\[
\sigma = q\rho_A \left(\frac{n_+}{n}\right)
\]

\(\text{equation 4.9}\)

And substituting this equation into equation 4.6, we get:

\[
E = \frac{q\rho_A}{2\varepsilon_0} \left(\frac{n_+}{n}\right)
\]

\(\text{equation 4.10}\)

Equation 4.10 represents the electric field from one molecular plane. But multiple molecular planes close to the interface can become charged. The net electric field is the sum of electric fields from multiple charged molecular planes close to the interface.

\[
E_{M^+} = \frac{q\rho_A}{2\varepsilon_0} \sum_{i=0}^{\infty} \left(\frac{n_+}{n}\right)
\]

\(\text{equation 4.11}\)

Note that the electric field is independent of distance away from the plane when the distances are negligible compared to the dimensions of the plane, as seen in equation 4.6.

In order to calculate the fraction of charged molecules in a plane, we use Fermi-Dirac statistics, as the number of charge molecules is coupled with the substrate’s Fermi level.

\[
\frac{n_+}{n} = \left(1 + g \exp \left(\frac{E_f (M^+)}{kT}\right)\right)^{-1}
\]

\(\text{equation 4.12}\)
Where $E_f(M^+)$ is the formation energy of a charged molecule, $g$ is a degeneracy factor, $k$ is the Boltzmann constant, and $T$ is the absolute temperature. As the molecules are in equilibrium with the substrate, the formation energy is the sum of the energy needed to ionize a free molecule ($IE$) plus the energy recovered when donating that electron to the substrate’s Fermi level. Thus the ion formation energy is:

$$E_f(M^+) = IE - \phi$$

*equation 4.13*

Where $IE$ is the molecular ionization energy and $\phi$ is the substrate work function. The expression for the fraction of ionized molecules in a plane is then:

$$\frac{n_+}{n} = \left(1 + g \exp \left[\frac{IE - \phi}{kT}\right]\right)^{-1}$$

*equation 4.14*

However, for molecular planes that are not in direct contact with the substrate surface, the formation energy is not directly coupled to the substrates Fermi level. We incorporate an additional factor ($\beta$) to account for the behavior that molecular planes further from the substrate do not become charged until molecular planes closer to the plane become charged first.

$$\frac{n_+}{n} = \left(1 + g \exp \left[\frac{IE - (\phi - i\beta)}{kT}\right]\right)^{-1}$$

*equation 4.15*

This expression implies that a molecular plane further away from the interface does not ‘feel’ the substrate because it is screened by the charged molecular layers in between. By combining equation 4.15 with equation 4.11, we get a complete expression for the electric field at the substrate-molecule interface as a result of the charged molecular planes in the molecular film.

$$E_{M^+} = \frac{q\rho_A}{2\epsilon_0} \sum_{i=0}^{\infty} \left(1 + g \exp \left[\frac{IE - (\phi - i\beta)}{kT}\right]\right)^{-1}$$
By incorporating equation 4.16 into equation 4.5, we get the completed equation for HOMO binding energy.

\[
\Delta E_H = IE - \alpha \phi + \delta + \frac{qP_A}{2\varepsilon_0} \sum_{i=0}^{\infty} \left(1 + g \exp \left(\frac{IE - (\phi - i\beta)}{kT}\right)\right)^{-1}
\]

The values for \(\alpha\), \(\delta\) and \(\beta\) are determined empirically. In fitting the above equation to our data (as shown in figure 4.1.1 of the previous section), we have used values of 1, 0.3 and 0.1, for \(\alpha\), \(\delta\) and \(\beta\) respectively.

The individual terms of equation 4.17 are plotted in figure 4.2.4. The red line shows the effect of the sum of all charged molecular layers (equation 4.16). The multi-colored lines show the electrostatic energy resulting from individual charge molecular planes (equation 4.15). The dashed grey line shows the effect of the increasing substrate work function on HOMO binding energy. The blue line shows the overall equation for HOMO binding energy (equation 4.17).

**Figure 4.2.4** – Plots of the individual contributions to HOMO binding energy equation (equation 4.17).
4.3 Appendix

4.3.1 Band Gaps and Ionization Energies of Oxides

The figure in the section 4.1 showing the valence bands and conduction bands of the oxides (Figure 4.1.2) was constructed using valence band maxima and work functions determined from ultraviolet photoemission measurements, and band gaps from the literature, taken from combined photoemission and inverse photoemission measurements. The values used to construct Figure 4 are shown in table 2.

Table 2 – Summary of oxide ionization energies, work functions, and band gaps used to construct Fig. 4 in the main manuscript. The references given in the final column are for the oxide band gaps, which were determined using combined UPS and IPES.

<table>
<thead>
<tr>
<th>Material</th>
<th>Ionization Energy (eV)</th>
<th>Work Function (eV)</th>
<th>Band Gap (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>8.0</td>
<td>5.2</td>
<td>3.4</td>
<td>42</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>9.26</td>
<td>6.85</td>
<td>2.8</td>
<td>43</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>6.5</td>
<td>5.6</td>
<td>3.2</td>
<td>44</td>
</tr>
<tr>
<td>CrO₂</td>
<td>9.0</td>
<td>6.9</td>
<td>2.25</td>
<td>45</td>
</tr>
<tr>
<td>Co₃O₄</td>
<td>6.4</td>
<td>6.1</td>
<td>1.6</td>
<td>46</td>
</tr>
<tr>
<td>CoO</td>
<td>5.2</td>
<td>4.5</td>
<td>2.4</td>
<td>46</td>
</tr>
<tr>
<td>NiO</td>
<td>6.7</td>
<td>6.3</td>
<td>3.2</td>
<td>44</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>5.5</td>
<td>4.9</td>
<td>2.3</td>
<td>44</td>
</tr>
<tr>
<td>CuO</td>
<td>5.7</td>
<td>5.6</td>
<td>1.4</td>
<td>44</td>
</tr>
<tr>
<td>MoO₂</td>
<td>9.4</td>
<td>6.9</td>
<td>3.0</td>
<td>47</td>
</tr>
<tr>
<td>MoO₃</td>
<td>6.0</td>
<td>6.0</td>
<td>0.0</td>
<td>47</td>
</tr>
<tr>
<td>Ta₂O₅</td>
<td>8.9</td>
<td>5.2</td>
<td>3.9</td>
<td>48</td>
</tr>
<tr>
<td>WO₃</td>
<td>9.8</td>
<td>6.65</td>
<td>3.4</td>
<td>49</td>
</tr>
<tr>
<td>Ag₂O</td>
<td>6.4</td>
<td>5.51</td>
<td>1.3</td>
<td>50</td>
</tr>
<tr>
<td>α-NPD</td>
<td>5.35</td>
<td>n/a</td>
<td>3.95</td>
<td>47</td>
</tr>
<tr>
<td>CBP</td>
<td>6.00</td>
<td>n/a</td>
<td>4.0</td>
<td>47</td>
</tr>
</tbody>
</table>

4.3.2 HOMO Binding Energy Profiles

It is interesting to note that, while the HOMO binding energy of a gas phase molecule is a material constant, when molecules coalesce to form a solid film their binding energies depend on the substrate to which they are adsorbed. This is exemplified by vertical off-set in the ΔE_H and Φ profiles of figure 4.3.1 (a) and (b).
The $\Delta E_H$ and $\Phi$ profiles also exhibit similar shapes regardless of the organic molecule used. There is always a rapid initial change in $\Delta E_H$ and $\Phi$, followed by a leveling off with thickness. The HOMO is generally closest to the Fermi level near the substrate/organic interface, and slowly moves to higher binding energy as the organic film thickens.

**Figure 4.3.1** – Work function and HOMO profiles for all substrates and all organics used in this study. These profiles were extracted from stacks of UPS spectra, such as the ones demonstrated in Fig. 1.5.2. The legend at the bottom indicated the substrates used for each profile.

Although $\Delta E_H$ and $\Phi$ are not material constants, the sum of them, that is, the ionization energy ($IE$) is constant. Figure 4.3.2 shows the $IE$ profiles of CBP, $\alpha$-NPD and 2T-NATA on all the various substrates.
The reason why HOMO binding energy is substrate dependant, while ionization energy is a constant is because the HOMO binding energy is measured with reference to the substrate Fermi level, while ionization energy is measured with reference to the vacuum level. The difference between the HOMO and the Fermi level is not a constant, and depends on charge transfer between the substrate and adsorbate. However, the difference between the HOMO and the vacuum level represents a property of the molecule, and is independent of the substrate.

Figure 4.3.2 – Ionization energy versus organic film thickness profiles for each organic on each substrate. These plots were constructed from the profiles shown in Fig. 4.3.1 by summing work function with HOMO binding energy.

4.3.1 Ionization Energy Profiles

The trend of ionization energy versus organic film thickness generally shows a reduction in ionization energy for extremely thin organic films. This is believed to be caused by distortion of the molecular orbital electron density due to polarization by the substrates. As the films thicken, the ionization energies quickly establish their constant bulk values. The bulk $IE$s for the three organics, as shown in Fig. 4.3.2, are 6.00, 5.35 and 4.98 eV for CBP, α-NPD and 2-TNATA, respectively.
4.3.2 Oxide Film Thickness and Energy-Level Alignment

Oxide film thickness affected energy-level alignment only to the extent that oxide work function depended on oxide thickness, and if oxides were too thick to allow electrical conduction, in which cases measurements could not be made using photoemission spectroscopy. In general, the work functions of very thin oxide films are lower than the bulk films, and work function increases as the films thicken, as shown in Fig. 4.3.3 (a). This happens because thin films have many defects at the substrate-oxide interface. For example, for MoO$_3$ grown on Mo metal, cations in lower oxidation states exist close to the Mo/MoO$_3$ interface, as shown in Fig. 4.3.3 (b) and (c). These lower oxidation state cations contribute occupied valence states within the oxide band gap and lower the oxide work function, as shown in Fig. 4.3.3 (d) and (e).

![Figure 4.3.3](image)

Figure 4.3.3 – (a) plot of work function versus oxide film thickness for a MoO$_3$ film grown on a Mo substrate. (b) Mo3$d_{5/2}$ XPS spectra of bulk MoO$_3$, clean Mo metal, a 0.6 nm thick MoO$_3$ film and the difference spectrum made by subtracting the Mo metal spectrum from the 0.6 nm spectrum. (c) Peak fit of the 0.6 nm MoO$_3$ spectrum, showing the Mo$^{6+}$ and Mo$^{4+}$ components. (d) Valence UPS spectrum of MoO$_3$ films of increasing thickness. (e) Expanded view of the defect features in the UPS spectrum, revealing two new states at the Mo/MoO$_3$ interface.

However, the oxide thickness does not affect energy-level alignment, so long as the oxide’s work function remains greater than the organic’s ionization energy. This is shown in figure 4.3.4. The left panel of this figure shows a plot of HOMO binding energy versus organic film thickness for $\alpha$-NPD grown on various MoO$_3$ thicknesses ranging from 0 to 3.5 nm. Note, the profile for Mo metal is also shown.
Figure 4.3.4 – (a) Plot of HOMO binding energy versus organic film thickness for α-NPD films grown on various thicknesses of MoO$_3$. (b) Plot of HOMO binding energy versus MoO$_3$ thickness.

One can see that the HOMO binding energy profiles overlap with one another (except for the profile on the clean metal film). The right panel in figure 4.3.4 shows a plot of HOMO binding energy versus MoO$_3$ thickness. One can see here that the HOMO binding energy is insensitive to oxide thickness. The reason why this is so, is that even though the oxide’s work function changes with thickness as seen in figure 4.3.3 (a), the oxide’s work function is always greater than α-NPD’s ionization energy. The only point for which the substrate’s work function is not greater than α-NPD’s ionization energy is the metal substrate, and this results in the expected HOMO binding energy shift.
5 Interfaces between Metals and Metal-Oxides: How Electrode Contacts Affect the Work Function and Band Structure of MoO$_3$

Transition metal oxides used in organic electronics and catalysis often must be in contact with a metal electrode. The interactions between a metal and metal-oxide at the interface can affect the oxide’s chemical and electronic properties for several nanometres away from the interface. In the present work, using a common oxide from organic electronics—MoO$_3$—we demonstrate how near-by metal interfaces can alter MoO$_3$’s oxidation states, valence band and work function for several nanometres away from the interface. We find that MoO$_3$ is generally reduced at metal interfaces, and the reduction causes MoO$_3$ to become semi-metallic and have a low work function near the interface. We attribute this behaviour to two separate causes: 1) charge transfer from the metal’s Fermi level into MoO$_3$’s low-lying conduction band, and 2) an oxidation-reduction reaction between the metal electrode and MoO$_3$. These results illustrate how near-by interfaces have important ramifications to an oxide’s capabilities to provide energy-level alignment.

5.1 Background

As mentioned in the previous chapter, the low charge-injection barriers at metal-oxide/organic-semiconductor interfaces are believed to be caused by favourable energy-level alignment between metal-oxides and organic semi-conducting molecules, which is largely affected by the metal-oxide’s work function. However, as oxide layers can also contribute electrical resistance to a device, the oxide’s electronic structure is also important to device performance, with metallic or semi-conductive oxides being preferred.

Over the past 15 years, the organic electronics research community has thoroughly examined the metal-oxide/organic-semiconductor side of this multi-junction, yet only relatively few papers have focused on the interfaces between metal-oxides and electrode materials.

While the interfaces between metal-oxides and metals have been studied for many decades—especially in the fields of corrosion science, catalysis and more recently inorganic semiconductor device research—such interfaces have not been thoroughly examined within the context of
organic electronics, and thus it has not been established how such interfaces affect the oxide properties that are most relevant to organic electronic devices—namely work function and electron band structure.

Oxide thin films can have strong interactions with their substrates. Catalysis research has shown that oxides in thin-film form can have enhanced catalytic activity compared to their bulk counterparts, due to charge-transfer interactions between the substrate and oxide on the nanometre length scale.\textsuperscript{104,105} Furthermore, in inorganic-semiconductor research, an oxide gate-dielectric’s leakage current can be affected by the near-by interface with the electrode. Interfacial chemical reactions and defects caused by lattice strain at the interface can lead to high leakage currents, making some material combinations unsuitable for such applications.\textsuperscript{106}

In organic electronics, oxide buffer layers should preferably be conductive. However, most of the oxides that provide favourable energy-level alignment are wide-band-gap semiconductors, and although they improve energy-level alignment, they also introduce a series resistance. Therefore, an oxide buffer layer’s thickness in a device is generally kept to no more than a few nanometres in order to retain high device efficiency. But, since research from catalysis and inorganic-semiconductors has shown that interfacial interactions can last several nanometres, these first few nanometres from the electrode interface may be very important to an oxide’s ability to improve organic device performance.

Indeed, research has shown that an oxide buffer layer’s thickness is critical to its ability to perform in a device. While this is partially due to series resistance, further research has shown that it is also due to changes in energy-level alignment with organic overlayers as an oxide thickens.

In this paper, we demonstrate how metal electrode interfaces can alter an oxide’s work function and electronic band structure. We focus on an oxide that is commonly used as a hole-injection layer in organic devices, MoO\textsubscript{3}. We have found that its work function and electronic structure, within the first few nanometres of a metal interface, depends on the choice of electrode material. The changes caused by an interface have ramifications that determine which oxide thickness should be used with a particular electrode material for the optimal balance of energy-level alignment and conductivity.
MoO$_3$ has been heavily studied over the past few years in the organic electronics community. Its very deep work function of ~ 6.8 - 6.9 eV, and its low-lying conduction band makes it very useful as a hole-injection layer and p-type dopant in organic electronics devices.

Although we have already discussed MoO$_3$'s electronic structure in Chapter 2, it will briefly be reviewed here because it is important for the results that follow. MoO$_3$ is a wide-band-gap semiconductor, with a band gap of ~ 3.0 eV. It is a $d^0$ oxide, meaning the Mo 4d-band is considered empty, and its valence band is composed primarily of O 2p states. Oxygen vacancy defects are the dominant type of defect, and MoO$_3$ can rather easily be reduced to the metallic oxide, MoO$_2$. Schematic energy-band structures and valence band photoemission spectra of stoichiometric MoO$_3$, oxygen-deficient MoO$_3$ and MoO$_2$ are shown in figure 5.1.

![Figure 5.1](image)

**Figure 5.1** – (a) Schematic energy-level diagram of MoO$_3$, O-deficient MoO$_3$ and MoO$_2$. (b) UPS valence band spectra and (c) expanded view of the ‘defect’ feature of MoO$_3$, O-deficient MoO$_3$ and MoO$_2$.

In stoichiometric MoO$_3$, the valence band is primarily of O 2p character and the conduction band is primarily of Mo 4d character. The Fermi level sits very close to the conduction band, and so it is an n-type semiconductor, but as oxygen vacancies act as n-type dopants and there is always some equilibrium concentration of vacancies, it is uncertain whether defect-free MoO$_3$ would be intrinsically n-type.

The cations in MoO$_3$ are Mo$^{6+}$, but oxygen vacancies cause Mo$^{5+}$ cations to form, and results in a partially occupied Mo 4d-band. The partially occupied d-band gives rise to valence states close to the Fermi level, as shown in the energy-level diagram for oxygen-deficient MoO$_3$ in figure 5.1.
(c). This defect state is clearly seen in valence-band photoemission spectra as a feature centered at \( \sim 0.8 \) eV below the Fermi level, as shown in figure 5.1 (b) and (c).

Additional removal of oxygen results in formation of MoO\(_2\), which contains mainly Mo\(^{4+}\) cations. The cations then have a partially-filled d-band, resulting in an additional valence feature centered at \( \sim 1.7 \) eV, as shown in figure 5.1 (c). The feature closest to the Fermi level, that was the defect feature in oxygen-deficient MoO\(_3\), becomes broadened and actually crosses the Fermi level, making MoO\(_2\) metallic—as seen in the UPS spectrum of figure 5.1 (b) and (c).

In the present work, we examine how interfaces between MoO\(_3\) and various metals affect MoO\(_3\)’s valence band structure, oxidation state and work function within the first few nanometres of the interface. We examine interfaces between MoO\(_3\) and metals of various work functions and reactivities—including a noble metal (Au), a high-work-function non-noble metal (Ni), the parent metal of MoO\(_3\) (Mo), and a reactive metal (V), and an alloying metal (Cu). We also examine the interface between MoO\(_3\) and the prototypical transparent conductive oxide, indium tin oxide (ITO).

We distinguish two types of interfaces: reactive interfaces, in which MoO\(_3\) is reduced near the interface, and non-reactive interfaces, where there is no evidence of MoO\(_3\) reduction. These scenarios are depicted in figure 5.2. At the reactive interfaces, reduction of Mo\(^{6+}\) to Mo\(^{5+}\) and/or Mo\(^{4+}\) causes a change in band structure that makes the oxide more metallic or semi-metallic near the electrode interface. With distance from the interface, the oxide becomes more stoichiometric and insulating. While increased conductivity near an interface may be beneficial to organic devices, and might suggest that one should always use the thinnest MoO\(_3\) film possible, the reduced cations also appear to lower the oxide’s work function. The reasons why an oxide should have a lower work function with lower oxidation-state cations will be addressed in the theoretical section.

For the non-reactive interfaces, MoO\(_3\)’s band structure is not altered by the presence of the substrate interface. In some cases, band bending in MoO\(_3\) may occur, but Mo\(^{6+}\) is not reduced to lower oxidation states near the interface, and MoO\(_3\) reaches its bulk work function and bulk conductivity closer to the substrate interface than in the case of reactive interfaces—as depicted in the bottom of figure 5.2.
The factors which influence reactivity and charge-transfer at an interface are the oxygen potential and electron chemical potential (i.e. Fermi energy) of the substrate relative to MoO$_3$. While a large discrepancy in oxygen potential between MoO$_3$ and the substrate material can cause an oxidation/reduction reaction, a large difference in electron chemical potential can also cause Mo$^{6+}$ cation to become reduced via charge-transfer with the substrate material. As a general trend, it is observed that metal substrates form reactive interfaces with MoO$_3$, while oxide substrates tend to form non-reactive interfaces; however, as seen with ZrO$_2$, an oxide with a sufficiently low work function can also form a reactive/charge-transfer interface with MoO$_3$. 

Figure 5.2 – Schematic layered structure of MoO$_3$’s oxidation states near an interface (top), schematic energy-band diagram for MoO$_3$ near an interface (middle) and plot of work function versus MoO$_3$ thickness and conductivity versus MoO$_3$ thickness (bottom) for reactive (a) and non-reactive (b) interfaces between MoO$_3$ and electrode materials.
5.2 Methods

All MoO$_3$ films were grown by vacuum sublimation. 99.99% pure MoO$_3$ powder was placed into 10cc cone-shaped alumina crucibles and placed in a Knudsen cell. MoO$_3$ was evaporated at a temperature of 550 °C to obtain a deposition rate of ~ 0.2 Å/s at the sample surface, as monitored by an oscillating quartz thickness monitor. The samples were ~ 1cm×1cm. The evaporation source was positioned 31 cm away from the sample, at an angle of 35° (K-cell axis relative to sample normal). The pressure during deposition was ~ 5×10$^{-9}$ torr.

Metal substrates were prepared by magnetron sputter deposition from 99.99% pure metal targets onto epi-polished, degenerately-doped Si substrates. Metal films were ~ 200 nm thick. All metal films were sputter cleaned in the XPS chamber to remove atmospheric contamination and native oxide films prior to MoO$_3$ deposition.

5.3 Results

Within the first few nanometres of each metal-MoO$_3$ interface, MoO$_3$ was found to contain lower oxidation states than Mo$^{6+}$. This is clear from the XPS spectra in figure 5.3, showing the Mo 3d spectra of thin MoO$_3$ films grown on each metal substrate. Note that the reduced cation states may be accompanied by oxygen loss in which case the molecular formula should be written MoO$_{3-x}$; however, for simplicity we will continue to use the notation MoO$_3$ but not to imply that the stoichiometry is strictly 1:3.

The metal substrates differ from one another in terms of the amount of reduction they cause to MoO$_3$—as gauged by the average oxidation state at the metal/MoO$_3$ interfaces. The average oxidation state, and relative peak areas, as determined from the peak fits for the thinnest films shown in figure 5.3 are summarized in table 5.1.

At interfaces with Au, Mo, and Ni substrates, MoO$_3$ contains Mo$^{5+}$ and Mo$^{6+}$, but when grown on V, Mo$^{4+}$ and Mo$^{5+}$ species are found at the interface. Cu is unique in that it forms a Cu-Mo-O alloy with MoO$_3$. The alloy contains Mo$^{6+}$ and Mo$^{5+}$. 
Figure 5.3 – (i) Mo 3d XPS spectra for MoO₃ films of various thicknesses deposited onto (a) Au, (b) Ni, (c) Mo, (d) V and (e) Cu substrates. (ii) Peak fits of the spectra in (i) showing the component from Mo⁶⁺, Mo⁵⁺ and Mo⁴⁺.

Table 5.1 – Summary of oxidation states present in MoO₃ films near the various metal interfaces.

<table>
<thead>
<tr>
<th>Substrate Material</th>
<th>Average Mo Oxidation State</th>
<th>Mo⁶⁺</th>
<th>Mo⁵⁺</th>
<th>Mo⁴⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>5.6</td>
<td>60%</td>
<td>40%</td>
<td>0%</td>
</tr>
<tr>
<td>Ni</td>
<td>5.5</td>
<td>50%</td>
<td>50%</td>
<td>0%</td>
</tr>
<tr>
<td>Mo</td>
<td>5.4</td>
<td>45%</td>
<td>55%</td>
<td>0%</td>
</tr>
<tr>
<td>V</td>
<td>4.5</td>
<td>7%</td>
<td>36%</td>
<td>57%</td>
</tr>
<tr>
<td>Cu</td>
<td>5.7</td>
<td>66%</td>
<td>34%</td>
<td>0%</td>
</tr>
</tbody>
</table>
Based on the average oxidation states of Mo at each metal interface, the amount of Mo cation reduction increases from Au→Ni→Mo→V. Coincidentally, this trend follows the trend of decreasing metal work functions: Au (5.3 eV) → Ni (5.0 eV) → Mo (4.5 eV) → V (4.2 eV). However, this trend also follows the trend of oxidation potentials for each of these metals: Au/Au_2O_3 (~ -9 kJ/mol) → Ni/NiO (-419 kJ/mol) → Mo/MoO_2 (-528 kJ/mol) → V/VO (-800 kJ/mol). But as metal oxidation potential and metal work function are expected to be related to one another, it is understandable why both these properties are similarly correlated with Mo oxidation. In the discussion section we will further discuss how metal work function and metal oxidation potential affect MoO_3 oxidation state at the metal/MoO_3 interface.

While Mo cations are reduced at the metal interfaces, the degree of reduction decreases with MoO_3 thickness. Oxidation-state profiles are shown in figure 5.4 (a). These profiles represent the relative Mo 3d peak areas for Mo^{6+}, Mo^{5+}, and Mo^{4+} peaks for each MoO_3 film thickness, as determined from the peak fitting shown in figure 5.3.

![Figure 5.4](image)

**Figure 5.4** – (a) Oxidation state profiles and (b) work function profiles for MoO_3 films grown on various metal substrates.

Note: due to the exponential dependence of XPS peak intensity with depth, and the fact some films are thinner than the probing depth, these plots do not quantitatively represent the composition of the film at each given thickness. However, even after taking the depth sensitivity of XPS into account, the plots do indicate that there is a gradient in average oxidation state with distance from the metal interface. Furthermore, comparisons between plots are meaningful.
Due to the Cu-Mo-O alloy that was formed, with Cu diffusing throughout the MoO$_3$ film, the oxidation state of Mo did not change with MoO$_3$ thickness, as shown in figure 5.4 (a), v. The Cu-Mo-O alloy and its composition will be addressed further in the discussion section.

In the oxidation-state profiles, one can see that the Mo$^{6+}$ signal eventually approaches 100% at MoO$_3$ film thicknesses between 7 - 10 nm. On the more reactive substrates, MoO$_3$ does not become fully stoichiometric until further away from the interface. As a figure of merit, we take the MoO$_3$ thickness for which Mo$^{6+}$ peak is 90% of the total peak area—represented by $d_{90\%}$ . Then from figure 5.4 (a) we get $d_{90\%}$ values of 6.4 nm for V, 6.0 nm for Mo, 3.3 nm for Ni, and 2.8 nm for Au. Note that the Cu-Mo-O alloy never reaches a stoichiometry of 90% Mo$^{6+}$.

The trend between MoO$_3$ work function and MoO$_3$ film thickness follows a similar profile to the cation oxidation state plots. Work function versus MoO$_3$ thickness plots are shown in figure 5.4 (b). These plots show that work function tends to increase away from the metal interface, eventually reaching a plateau at $\sim$ 6.85 - 6.9 eV. Note that the Cu-Mo-O alloy work function plateaus at $\sim$ 6.25 eV.

Again we assign a figure-of-merit as the thickness at which the work function reaches 6.0 eV—represented by $d_{6eV}$. We get $d_{6eV}$ values of 1.1 nm for V, 0.85 nm for Mo, 0.79 nm for Ni, and 0.28 nm for Au. Just as with the oxidation-state profiles, the MoO$_3$ work function reaches a high value closer to the interface on the less reactive metals. One can see why oxide thickness and substrate choice are important for energy-level alignment of molecular adsorbates.

Based on the similarity between work function and oxidation-state profiles, it appears that an oxide’s work function is correlated to cation oxidation state. This topic was discussed in Chapter 3.2.

While MoO$_3$’s cation oxidation state and work function are affected by metal interfaces, there are also significant changes to MoO$_3$’s valence band structure, which make it more metallic near a metal interface. As MoO$_3$ is a $d^0$ oxide, cation oxidation states lower than Mo$^{6+}$ result in excess electrons in the oxide conduction band, as illustrated in figure 5.1. These excess electrons occupy low-lying Mo 4d orbitals, and give rise to donor states within the MoO$_3$ band gap.
Figures 5.5 (a) and (b) show the UPS spectra taken for each MoO$_3$ thickness on each metal substrate. The MoO$_3$ thickness increases from top to bottom in the figure. Note: substrate reference spectra were subtracted from the spectra of the thinnest MoO$_3$ films to remove the substrate signal. The resulting spectra represent primarily the MoO$_3$ signal.

The O 2p band can always clearly be distinguished, seen at binding energies ranging from about 5 eV to 3 eV. For extremely thin MoO$_3$ films the O 2p band and higher-binding-energy features appear distorted by the interface. These distortions may be due to distortions to the Mo-oxide structure or due to changes in the substrate spectrum.

The most significant features of these spectra are the additional states present in the band gap (between binding energies of 0 eV and 3 eV) close to the metal/MoO$_3$ interface. These states are observed in every case. An enhanced view of these low-binding-energy regions are shown in figure 5.5 (b). There are two distinct features, labelled d$_1$ and d$_2$. These states, which have been found to arise in O-deficient d$^0$ oxides, are due to electrons occupying the previously empty metal d-band.$^{117}$ The d$_1$ feature resembles the feature seen in O-deficient MoO$_3$ and the d$_2$ feature resembles the feature seen in MoO$_2$ (compare with spectra shown in figure 5.1). The intensities of the two defect features diminish as the MoO$_3$ film thickens, indicating that the oxide becomes
less defective away from the interface. The higher-binding-energy feature, d$_2$, diminishes first, followed by the d$_1$ feature. Eventually, the valence spectrum of stoichiometric MoO$_3$ is obtained.

While stoichiometric MoO$_3$ does not contain either of these defect features, and oxygen-deficient MoO$_3$ always contains the d$_1$ feature, associated with Mo$^{5+}$, and MoO$_2$ contains both d$_1$ and d$_2$ features. This may indicate that the d$_2$ feature is associated with Mo$^{4+}$. However, by referring to the XPS spectra in figure 5.3, we can see that the d$_2$ feature can also be present when Mo$^{4+}$ is not detectible. Therefore, MoO$_2$ always has the d$_2$ feature, but the d$_2$ feature does not necessarily imply Mo$^{4+}$.

While it is clear that the interface affects MoO$_3$’s properties, it may also affect the substrate’s properties. Figure 5.6 shows XPS spectra of the substrate main peaks for clean substrate surfaces, spectra of substrates buried under ~ 2nm of MoO$_3$, and difference spectra (buried spectrum minus clean spectrum). One can see that the Au spectrum is not affected by the presence of MoO$_3$; however, Ni, Mo, and V show evidence of oxidation at the interface. The Cu spectra show that Cu is oxidized to Cu$^+$. 

Figure 5.6 – Core level XPS spectra of clean substrates and substrates buried under ~ 2 nm of MoO$_3$. (a) Au 4f, (b) Ni 2p$_{3/2}$, (c) Mo 3d, (d) V 2p and (e) Cu 2p$_{3/2}$

5.4 Discussion

In the following sections we discuss the causes of reactivity (or non-reactivity) at each interface, in terms of oxidation thermodynamics, and energy-level alignment. We address the importance of 1) substrate oxidation potential relative to overlayer oxidation potential, and 2) substrate Fermi level relative to energy levels in MoO$_3$. 
5.4.1 Thermodynamic Considerations

One can predict whether a metal is capable of reducing an oxide using classical equilibrium thermodynamics. For example, consider two metals, \( M^{(A)} \) and \( M^{(B)} \), and their oxidation reaction:

\[
M^{(A)} + \frac{1}{2}O_2 \rightarrow M^{(A)}O \hspace{1cm} \Delta G_{O_2}^{(A)} = x
\]

\textit{equation 5.1}

\[
M^{(B)} + \frac{1}{2}O_2 \rightarrow M^{(B)}O \hspace{1cm} \Delta G_{O_2}^{(B)} = y
\]

\textit{equation 5.2}

By writing and equation (5.1) – (5.2), we get the case where metal \( M^{(A)} \) reduces the oxide \( M^{(B)}O \):

\[
M^{(A)} + M^{(B)}O \rightarrow M^{(A)}O + M^{(B)} \hspace{1cm} \Delta G_{\text{rxn}} = x - y
\]

\textit{equation 5.3}

Thus we can see that metal \( M^{(A)} \) will spontaneously reduce oxide \( M^{(B)}O \) if the free energy of oxidation for metal \( M^{(A)} \) is more negative than the free energy of oxidation for metal \( M^{(B)} \).

Values for free energy of oxidation for various metals can be simply read from an Ellingham diagram. We have compiled the following reactions and free energies of oxidation for the reactions relevant to this work.

\textit{Table 5.2 – Chemical reactions and thermodynamic data for reaction relevant to the metal/MoO}_3 \textit{interfaces in this work.}

<table>
<thead>
<tr>
<th>Label</th>
<th>Cation transition</th>
<th>Reaction equation</th>
<th>( \Delta G_{O_2} ) (( \text{kJ/mol} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Au/Au_2O_3</td>
<td>0 ( \rightarrow ) +3 \hspace{1cm} 4/3 Au + O_2 ( \rightarrow ) 2/3 Au_2O_3</td>
<td>-2.3 to -8.7</td>
</tr>
<tr>
<td>b</td>
<td>VO_2/V_2O_5</td>
<td>+4 ( \rightarrow ) +5 \hspace{1cm} 4VO_2 + O_2 ( \rightarrow ) 2V_2O_5</td>
<td>-68.15</td>
</tr>
<tr>
<td>c</td>
<td>Cu_2O/CuO</td>
<td>+1 ( \rightarrow ) +2 \hspace{1cm} 2Cu_2O + O_2 ( \rightarrow ) 4CuO</td>
<td>-212.38</td>
</tr>
<tr>
<td>d</td>
<td>Cu/CuO</td>
<td>0 ( \rightarrow ) +2 \hspace{1cm} 2Cu + O_2 ( \rightarrow ) 2CuO</td>
<td>-253.12</td>
</tr>
<tr>
<td>e</td>
<td>MoO_2/MoO_3</td>
<td>+4 ( \rightarrow ) +6 \hspace{1cm} 2MoO_2 + O_2 ( \rightarrow ) 2MoO_3</td>
<td>-275.6</td>
</tr>
<tr>
<td>f</td>
<td>Cu/Cu_2O</td>
<td>0 ( \rightarrow )+1 \hspace{1cm} 4Cu + O_2 ( \rightarrow ) 2Cu_2O</td>
<td>-293.87</td>
</tr>
<tr>
<td>g</td>
<td>V_2O_3/VO_2</td>
<td>+3 ( \rightarrow ) +4 \hspace{1cm} 2V_2O_3 + O_2 ( \rightarrow ) 4VO_2</td>
<td>-368.4</td>
</tr>
</tbody>
</table>
The reactions in table 5.2 are arranged according to the free energy of the reaction. The lower the reaction is on the table, the more spontaneous the reaction is. Thus ZrO$_2$ is the most stable oxide and Au$_2$O$_3$ is the least stable one.

While the thermodynamic data in table 5.2 tells us whether a metal oxide is stable in the presence of another metal, it does not tell us what concentration of defects will be stable at a metal/metal-oxide interface. In the case of MoO$_3$ we are interested in oxygen vacancy defects and cation oxidation-state defects. Oxygen vacancy defects affect an oxide’s oxygen chemical potential. So we would expect that the oxygen vacancy concentration at the metal/MoO$_3$ interface would be such that the oxygen potential in defective MoO$_3$ equilibrates with the oxygen potential of the substrate metal.

The chemical equation for oxygen vacancy formation is (using Kröger-Vink notation):

$$O_O^\bullet + 2M_M^\chi = v_O^{\cdots} + 2M_M^{\prime\prime} + \frac{1}{2}O_{2(g)}$$

\textit{equation 5.4}

Where $O_O^\bullet$ represents an oxygen atom on its regular lattice site, $M_M^\chi$ represents a metal cation on its regular lattice site, $v_O^{\cdots}$ represents an oxygen vacancy with a 2+ charge relative to the neutral lattice, and $M_M^{\prime\prime}$ represents a metal cation in a lower oxidation state than it has in the stoichiometric lattice. In the case of MoO$_3$, we can write:
\[ O_0^x + 2Mo^{6+} = v_0^\cdot + 2Mo^{5+} + \frac{1}{2}O_{2(g)} \]

\textit{equation 5.5}

This equation shows that each oxygen vacancy gives rise to two reduced Mo cations. In the case of dilute defects, we can write the following equation relating Mo\(^{5+}\) cation concentration and vacancy free-energy of formation:

\[ [Mo^{5+}] = 2[v_0^\cdot] = 2^{1/3} \exp \left[ \frac{-\Delta G_{v0}}{3RT} \right] p_{O2}^{-1/6} \]

\textit{equation 5.6}

This equation shows that, no matter what the oxygen pressure, there is always some finite concentration of vacancy defects. An estimate on the enthalpy of formation for oxygen vacancies in MoO\(_3\) can be made using metal sublimation energies and oxide formation enthalpies,\(^{67}\) resulting in a value of ~ 36 kJ/mol for oxygen vacancies in MoO\(_3\).

\subsection*{5.4.2 MoO\(_3\) on Au}

According to the thermodynamic data in table 5.2—such as reactions e and i—Au is not expected to be capable of reducing MoO\(_3\) to either metallic Mo or MoO\(_2\). Furthermore, as oxygen potentials should equilibrate at a metal/metal-oxide interface, it is also not expected that the Au/Au\(_2\)O\(_3\) reaction could cause any more oxygen vacancy defects to form in MoO\(_3\) than are already present.

In agreement with the conclusion that MoO\(_3\) cannot oxidize Au, we see no evidence of chemical changes to Au at the buried interface, as shown in the Au 4f XPS spectra in figure 5.6 (a). The Au 4f spectrum exhibits no peak shift and no additional peaks in the buried spectrum.

Yet surprisingly we see from the XPS and UPS spectra for figures 5.3 (a) and 5.4 (a) that Au causes Mo\(^{6+}\) to be reduced to Mo\(^{5+}\) within the first few nanometres of the Au/MoO\(_3\) interface. While this is peculiar, it is not the first observation of this phenomenon. In fact there have been several reports of inert metals exhibiting charge-transfer with metal-oxides on the nano-scale,
such as Au nanoparticles on MgO supports, MgO films on Au surfaces, thin WO₃ films on Pt surfaces, MoO₃ films on Au surfaces, Au nano-particles an TiO₂, and V₂O₅ films on Au. Although this phenomenon has been modeled computationally, and lattice strain appears to be closely related to the charge-transfer process, this behaviour is still under debate. Nonetheless, it appears that, even though classical thermodynamics does not predict it, in nanoscopic systems charge transfer is possible between Au and various metal-oxides without necessary forming an interfacial chemical compound.

The Au/MoO₃ system has been examined before using photoemission spectroscopy (PES) scanning tunnelling microscopy (STM) supported with density-functional theory (DFT) calculations. The PES study also found evidence of Mo⁵⁺ at the interface, and it was suggested that electrons are donated to the Mo cations that have near-by oxygen vacancies. In the STM study, it was found that the MoO₃ lattice is strained at the interface. DFT calculations suggested that this strain allowed Au electron density to transfer to MoO₃. The DFT calculations also suggested that MoO₃ becomes semi-metallic near the Au/MoO₃ interface. From figure 5.4 (a) we can see that at the Au/MoO₃ interface, MoO₃ takes on a MoO₂-like band structure, due to the filling of the Mo 4d band.

Our findings are consistent with electron transfer from Au to Mo. But if Au transfers charge to Mo, without itself being oxidized, then what drives the charge-transfer process? MoO₃ is clearly reduced at the Au/MoO₃ interface. While the XPS and UPS spectra do resemble oxygen-deficient MoO₃, unless another material is being oxidized, the law of mass action does not allow for excess oxygen vacancies in MoO₃.

So how can this be understood? One possibility is that we do not need to consider oxygen vacancies in this case, and that the Mo⁶⁺ → Mo⁵⁺ reaction occurs without forming oxygen vacancies. This however would violate the charge neutrality requirement. But if we consider that an electron comes from the Au Fermi level, this may be possible. We therefore, consider another defect reaction (again using Kröger-Vink notation):

\[ e_{VB} + M^{x}_M = h_{VB} + M^/ \]

\[ equation 5.7 \]
Where $e_{VB}$ represents an electron at the metal Fermi level, $M_M^x$ represents a metal cation in the oxide on its regular lattice site, $h_{VB}$ represents a hole in the metal valence band, having a charge of +1 relative to the neutral metal, and $M_M^/$ is the a reduced metal cation in the oxide. In the case of the Au/MoO$_3$ interface, we can write:

$$e_{(Au)} + Mo^{6+} \rightarrow h_{(Au)} + Mo^{5+}$$

*equation 5.8*

Where $e_{(Au)}$ represents an electron at the Au Fermi level, and $h_{(Au)}$ represents a hole at the Au Fermi level. We then get the following equilibrium constant:

$$K = \frac{[h_{(Au)}][Mo^{5+}]}{[e_{(Au)}][Mo^{6+}]}$$

*equation 5.9*

As the denominator in this equation will be 1, and $[h_{(Au)}] = [Mo^{5+}]$, we can write the following equation for $[Mo^{5+}]$:

$$[Mo^{5+}] = [h_{(Au)}] = \exp\left[\frac{-\Delta G_f}{kT}\right]$$

*equation 5.10*

Where $\Delta G_f$ is the energy needed to move an electron from the Au Fermi level to a Mo$^{6+}$ site. Note: we use $kT$ in the denominator of the exponential here so that we can use units of eV for energy. We can approximate $\Delta G_f$ as the difference between the Au work function and the MoO$_3$ conduction band, resulting in the following equation:

$$[Mo^{5+}] = \exp\left[\frac{-(\phi_{Au} - EA_{MoO_3})}{kT}\right]$$

*equation 5.11*
This analysis implies that Au reduces Mo$^{6+}$ to Mo$^{5+}$ simply due to donation of electrons from the Au Fermi level. It also implies that Mo$^{5+}$ cations are not accompanied by oxygen vacancies, and that charge compensation is provided by the Au Fermi level. But the charge compensation will not persist as one moves further away from the Au/MoO$_3$ interface.

Figure 5.7 shows a schematic band diagram of the Au and MoO$_3$. The energy-level positions represent the valence bands, conduction bands and Fermi levels of each material prior to contact. Considering how the Au Fermi level sits above the MoO$_3$ conduction band (using vacuum-level alignment assumption), one can see how electron transfer from the Au Fermi level to the MoO$_3$ conduction band might occur.

Thus the oxide reduction is being driven by a difference in Fermi levels rather than a difference in oxidation potential. It therefore appears that Au can transfer electrons into the MoO$_3$ conduction band without Au oxidation. Note that the reason why Au does not exhibit a peak shift likely because any charge donated to MoO$_3$ is immediately replenished, as the Au sample is grounded. Au binding energy shifts have been observed previously when Au was present as nano-particles on an oxide support.$^{126,122}$ In these cases the Au particles become charged, but not oxidized or reduced.

Note that this interaction appears to affect MoO$_3$ only close to the Au/MoO$_3$ interface. The defect states in the valence spectrum become undetectable after about 2 nm of MoO$_3$ have been deposited. Likewise, the MoO$_3$ work function plateaus rather quickly.
5.4.3 MoO$_3$ on Ni

Nickel is similar to Au in that they are both high work function metals (Ni: $\phi = 5.0$ eV; Au: $\phi = 5.3$ eV). However, Ni can be oxidized much more easily than Au, with the formation enthalpy of NiO being $\sim -417$ kJ/mol, and the formation enthalpy of Au$_2$O$_3$ reported at $\sim -3$ to $-9$ kJ/mol. Therefore, there is the possibility of not only electron transfer from Ni to MoO$_3$ from the Ni Fermi level, but also the possibility of Ni becoming oxidized by MoO$_3$, and subsequent removal of oxygen from MoO$_3$.

At room temperature, the free energy of the reaction: $2\text{Ni} + \text{O}_2 \rightarrow 2\text{NiO}$, is $\Delta G_{\text{O}_2} = -419$ kJ/mol. While the free energy of the MoO$_3$ reduction reaction: $2\text{MoO}_3 \rightarrow 2\text{MoO}_2 + \text{O}_2$, is $\Delta G_{\text{O}_2} = +275$ kJ/mol. Therefore, Ni can reduce MoO$_3$ according to the reaction: $\text{Ni} + \text{MoO}_3 \rightarrow \text{MoO}_2 + \text{NiO}$, $\Delta G = -72$ kJ/mol. Thus there is an additional driving force for Mo$^{6+}$ reduction.

While Mo$^{5+}$ is certainly evident in the Mo3d spectra, there is no detectible Mo$^{4+}$. Thus it appears that Ni does not completely reduce MoO$_3$ to MoO$_2$ at the interface, but perhaps only oxygen vacancies are formed. Complete reduction of MoO$_2$ may be possible at higher temperatures, where solid-state diffusion becomes more rapid.

Although, it may be argued that the Ni/MoO$_3$ is like the Au/MoO$_3$ interface in that reduction occurs only due to electron transfer from Ni’s Fermi level, and that oxidation potentials have nothing to do with it. However, in contrast to Au/MoO$_3$, the Ni 2p$_{3/2}$ XPS spectrum shows evidence of Ni oxidation at the interface.

The Ni 2p$_{3/2}$ XPS spectrum shown in figure 5.6 compares a clean Ni surface with Ni buried under $\sim 2$ nm of MoO$_3$. By subtracting the clean Ni spectrum from the buried-interface spectrum, one can see that an additional peak is present at a binding energy of $\sim 853.0$ eV, as well as a possible satellite feature at $\sim 856.0$ eV.

5.4.4 MoO$_3$ on Mo

In contrast to the other interfaces examined in this work—where the cation in oxide is a different element than the metal substrate—in the case of Mo/MoO$_3$ the substrate is the parent metal of the oxide. This is the same type of interface that is relevant to metal oxidation and corrosion. However, in the present case we have grown MoO$_3$ on Mo by evaporating MoO$_3$ rather than
oxidizing Mo—simply for easy comparison with the other samples. We did also grow MoO₃ on Mo by oxidation (see supporting information) and the findings are essentially the same.

From corrosion studies it is known that, if a metal that has more than one stable oxide, a layered oxide structure is possible. For example, when Fe is oxidized in dry oxygen, the structure of Fe/FeO/Fe₂O₃/Fe₃O₄ is obtained. In this case, the layers are ordered according to increasing oxygen potential, from the metal outward. Layered structures can be predicted using metal-oxygen phase diagrams. If there is no boundary on the phase diagram showing equilibrium between an oxide and its metal, then that particular oxide will not equilibrate with the metal, and some lower-oxidation-state oxide must exist in between.

From the Mo-O phase diagram MoO₃ does not equilibrate with Mo. There are several Magnéli phases—with mixed oxidation states—that are stable in between MoO₃ and Mo. The oxide that will equilibrate with Mo is MoO₂. Although we cannot discern a Mo⁴⁺ peak from the XPS spectra, we cannot eliminate the possibility that it exists, because the intense metal substrate obscures the ability to peak-fit the spectrum.

We expect that the interfacial reduction is a consequence of both oxidation equilibrium and charge transfer from the Mo Fermi level.

**5.4.5 MoO₃ on V**

Vanadium is the most reactive metal that we examine in this study. It very easily oxidizes, first to VO, then to V₂O₃, VO₂, and V₂O₅. Based on the thermodynamic data, it is expected to reduce MoO₃. Indeed, the photoemission spectra show severe MoO₃ reduction at the interface. It is the only interface where we have seen significant amounts of Mo⁴⁺. In fact, very little Mo⁶⁺ is found at the interface.

The energy-level diagrams of V and MoO₃—shown in figure 5.6—suggest that electrons can transfer from the V Fermi level to the MoO₃ conduction band. However, it appears that the dominating cause of MoO₃ reduction in this case is the V oxidation reaction. The severe MoO₃ reduction at the V/MoO₃ interface causes MoO₃ to have a similar valence band to MoO₂. Therefore, we suggest that “MoO₃” is semi-metallic at the interface.
5.4.6 MoO$_3$ on Cu

The last case to address is Cu. While Cu is a good electrode material due to its very low sheet resistance and its relatively low optical absorbance, the fact that Cu alloys with MoO$_3$ restricts MoO$_3$’s ability as a buffer layer to provide energy-level alignment. The maximum work function that the Cu-Mo-O could achieve on Cu was $\sim$ 6.3 eV. This is likely due to the fact that the alloy always has a mix of Mo$^{5+}$ and Mo$^{6+}$ regardless of the oxide thickness.

The alloy that was formed is rather interesting. The Mo 3d spectra indicate that it contains Mo$^{5+}$ and Mo$^{6+}$, with binding energies of $\sim$ 231.1 eV and 232.0 eV, respectively. The Cu 2p$_{3/2}$ spectrum gives a peak centered at $\sim$ 932.0 eV, which is indicative of Cu$^+$. However, as the Cu 2p$_{3/2}$ peaks for Cu$^0$ and Cu$^+$ species are very close in proximity for copper oxides, we also examined the Cu LMM spectrum. This spectrum clearly shows a peak at 570.7 eV, which identifies the Cu species as Cu$^+$.23

On examining the UPS spectra, one sees that the bands d$_1$ and d$_2$—as seen at the reduced metal/MoO$_3$ interfaces—are present. The Cu-Mo-O alloy’s band structure resembles that of MoO$_2$ except, in contrast to metallic MoO$_2$, the valence band maximum of Cu-Mo-O does not cross the Fermi level, but sits $\sim$ 0.4 eV below the Fermi level.

We propose that when Cu is oxidized to Cu$^+$, it reduces of Mo$^{6+}$ to Mo$^{5+}$, thereby donating electrons to the MoO$_3$ conduction band, resulting in a partially filled Mo 3d-band. Thus, Cu acts similar to an n-type dopant in MoO$_3$.

Based on XPS peak areas, the alloy has an atomic composition of $\sim$ 71.4 % O, 3.5 % Cu and 25.1 % Mo. From these numbers, it appears that Cu$^+$ displaces O$^2$. But if one Cu$^+$ displaces one O$^2$, then the lattice becomes charged +3 relative to the neutral MoO$_3$ lattice. This would require three Mo$^{6+}$ $\rightarrow$ Mo$^{5+}$ reductions. Therefore, we propose the following general formula: 

$$\text{Cu}_x\text{Mo}^{(VI)}_{y-3x}\text{Mo}^{(V)}_{3x}\text{O}_{3y-x}.$$  

Using our atomic composition from XPS analysis, we get a formula of Cu$_1$Mo$_{2}$^{(VI)}Mo$_{3}^{(V)}$O$_{14}$. This composition is similar to composition ranges reported previously.128,129

Although this compound does not have the same high work function of stoichiometric MoO$_3$, its work function is still reasonably high and it has the added benefit that it’s valence band maximum is much closer to the Fermi level than MoO$_3$ (i.e. 0.4 eV for CuMo$_5$O$_{14}$ versus 2.5 eV
for MoO₃). Assuming a similarly-low conduction band, this would imply that the CuMo₅O₁₄ compound will be more conductive than MoO₃, and thus will not impart the same series resistance with large thicknesses.

5.4.7 Work Function and Cation Oxidation State

Based on the fact that the work function versus MoO₃ thickness plots and the oxidation-state versus MoO₃ thickness plots follow similar trends, we propose that work function affected by cation oxidation state in a rather simple way—i.e. that lower cation oxidation state results in lower work function. This has been proposed before, but not shown experimentally. The cause of the relationship is believed to be due to the fact that lower-oxidation-state cations are less electronegative than higher-oxidation-state ones, and electronegativity directly affects a solid’s Fermi energy. We are providing a follow-up paper to this one addressing in more theoretical detail how defect states and cation oxidation states affect an oxide’s work function.

Figure 5.8 shows plots of average cation oxidation state, versus measured work functions for the interfaces examined in this study. We show this simply to illustrate that there is a positive correlation between cation oxidation state and work function. Note, however that the average cation oxidation state was determined from XPS spectra, which have a deeper probing depth than photoelectric work function measurements.

5.5 Summary

We have presented photoemission characterizations of layer-by-layer MoO₃ growth onto various metal substrates. The metals differed from one another in terms of their work functions as well as their oxidation potentials. We find that when MoO₃ is grown on these substrates, the Mo⁶⁺ cations are reduced to lower oxidation states (Mo⁵⁺ and Mo⁴⁺) close to the metal interface. The degree of MoO₃ reduction differs from one metal to the next. We explain the interfacial MoO₃ reduction with two proposed mechanisms: 1) charge transfer from the metal Fermi level to the oxide conduction band, and 2) reduction of MoO₃ driven by oxidation of the metal substrate. With these mechanisms, we can explain why a noble metal, such as Au can reduce Mo⁶⁺ within the first few nanometres of the Au/MoO₃ interface.
The interfacial reduction also results in changes to the MoO$_3$ valence band structure, making the oxide semi-metallic close to the metal interface. These valence band changes are explained in terms of electrons filling previously-empty Mo 4d states, resulting in donor states close to the MoO$_3$ Fermi level.

The reduced MoO$_3$ also results in a lower work function close to the metal/MoO$_3$ interface. The work function increases as average cation oxidation state increases. This implies that more reactive interfaces will require thicker oxide buffer layers before the maximum work function is achieved; however, more reactive interfaces will also be more conductive near the interface. This finding has implications to organic electronic device design and choosing the right oxide buffer thickness for the optimal balance of work function and conductivity.
6 Interfaces between Dissimilar Metal Oxides

6.1 Background

As discussed in the previous chapter, metals can be used as electrodes in organic devices if an oxide buffer layer is used. However, quite often metal oxides, such as transparent conductive oxides (TCO’s) are used as electrodes. Oxide electrodes have the benefit over metal electrodes that they are generally more transparent. However, most TCO’s have lower conductivities than metals, and often one must trade-off conductivity for transparency, depending on the intended application.

The prototypical TCO is indium tin oxide (ITO), which is an indium oxide (In$_2$O$_3$) doped with about 2% Sn. Many alternative TCO’s are starting to become popular, such as fluorine-doped tin oxide (FTO) and aluminum-doped zinc oxide (AZO).

Oxide buffer layers are commonly used in conjunction with TCO’s to improve the electrode’s work function. In the present chapter, we examine the interfacial interactions between MoO$_3$ and several metal oxides. We only examine one TCO in this study, ITO. The other oxides that we examine are NiO, CuO, V$_2$O$_5$, and ZrO$_2$. We chose these oxides for academic purposes, to investigate how certain oxide properties affect MoO$_3$ at the interface.

V$_2$O$_5$ was chosen because it shares very similar properties with MoO$_3$. They are both n-type, d$^0$ oxides with very high work functions (~ 6.9 eV for MoO$_3$ and ~ 7.0 for V$_2$O$_5$). NiO and CuO were chosen because they are p-type oxides, so they are expected to form p-n junctions with MoO$_3$. They also have very different electronic structures from MoO$_3$; both NiO and CuO have highly occupied d-bands and are Mott-Hubbard insulators. ZrO$_2$ was chosen because of its extremely low work function of ~ 3 – 4 eV. Aside from its low work function it is very similar to MoO$_3$. They are both n-type, d$^0$ oxides, and have similar valence bands. However, ZrO$_2$ has a larger band gap than MoO$_3$ (5.1 eV compared to 3.0 eV) and is very insulating.

Unlike metal/MoO$_3$ interfaces, most of the oxide/MoO$_3$ interfaces are non-reactive. Most do not give rise to reduced Mo species near the interface, and do not change MoO$_3$’s band structure significantly. As a result, MoO$_3$ reaches its maximum work function closer to the electrode/MoO$_3$ interface than it does on metal electrodes. Figure 6.1 shows comparisons of the
work function versus thickness profiles for MoO$_3$ grown on various metal and metal oxide substrates.

![Graph: Work function versus MoO$_3$ thickness profiles for MoO$_3$ films grown on various reactive and non-reactive substrates.](image)

**Figure 6.1.1** – Work function versus MoO$_3$ thickness profiles for MoO$_3$ films grown on various reactive and non-reactive substrates.

While most oxides did not reduce MoO$_3$, the one observed exception is ZrO$_2$. This is somewhat surprising because ZrO$_2$ is one of the most thermodynamically stable oxides. It is not expected to react with MoO$_3$. The Mo reduction is likely due to ZrO$_2$’s low work function.

Oxide/oxide interfaces are more complex than metal/oxide interfaces. There is more to consider than chemical thermodynamics and simple charge transfer. As many oxides are semiconductors
one also needs to consider band bending in the oxides. Currently, using only the five interfaces examined in this study, the story is not complete, but reveals some interesting behavior.

6.2 Methods

ITO samples were commercially bought ITO films deposited onto glass. ITO samples were lightly sputter cleaned to remove atmospheric contaminants. The samples were then annealed and re-oxidized in an attached oxidation chamber by exposing the sample to ~ 760 torr of high purity O₂ at ~ 150 °C. Other oxides were grown by oxidizing sputter-cleaned metal films in an oxidation chamber at temperatures ranging from 100 to 300 °C, in ~ 760 torr high purity O₂. MoO₃ films were grown by vacuum sublimation of 99.99 % pure MoO₃ powder from a Knudsen cell.

6.3 Results and Discussion

The Mo 3d XPS spectra of the thin MoO₃ films grown on various oxide films are shown in figure 6.3.1. Raw spectra are shown (top) and normalized spectra with peak fits are shown (bottom). In most cases (V₂O₅, NiO, CuO and ITO) there is no evidence of MoO₃ reduction; however the peak for Mo⁶⁺ does appear to shift its binding energy with thickness in some cases. The magnitude and direction of the peak shift differs for each oxide. MoO₃ on V₂O₅, NiO and CuO experiences peak shifts toward higher binding energy of ~ 0.1 eV, ~ 0.1 eV and ~ 0.6 eV, respectively. While on ZrO₂ and ITO, the Mo 3d peaks shift toward lower binding energy of ~ 0.5 eV and ~ 0.2 eV, respectively.
Figure 6.3.1 – Mo 3d XPS spectra of MoO$_3$ thin films grown on various metal oxide substrates: (a) V$_2$O$_5$, (b) NiO, (c) CuO, (d) ZrO$_2$, (e) ITO and (f) sputter-cleaned ITO.

The only interfaces that show Mo reduction are ZrO$_2$/MoO$_3$ and sputter-reduced-ITO/MoO$_3$. The MoO$_3$ on ZrO$_2$ shows evidence of Mo$^{5+}$ species near the interface. The sputter-reduced ITO was prepared by bombarding ITO with 3kV Xe$^+$ ions to preferentially remove O and produce a reduced oxide surface. This surface caused MoO$_3$ to be severely reduced, giving rise to Mo$^{5+}$ and Mo$^{4+}$ species at the interface. This interfacial reaction occurs because In$_2$O$_3$ is more thermodynamically stable than MoO$_3$, so reduced In$_2$O$_3$ will take O away from stoichiometric MoO$_3$ in order to satisfy its own reduced cations.

The UPS valence band spectra of these interfaces are shown in figure 6.3.2. Here one can see that, in the cases where no Mo reduction was observed in the XPS spectra, the valence bands show no evidence of defect states. However, for ZrO$_2$ and sputtered ITO interfaces, defects states are observed.
Figure 6.3.2 – UPS valence spectra (top) and expanded view of the shallow valence features (bottom) of MoO$_3$ thin films grown on various oxide: (a) V$_2$O$_5$, (b) NiO, (c) CuO, (d) ZrO$_2$, (e) ITO and (f) sputter-cleaned ITO.

While MoO$_3$ showed peak shifting or reduction near the oxide interfaces, most of the substrates were unaffected. The XPS spectra of clean and buried oxide substrates are shown in figure 6.3.3. For oxides that did not cause Mo reduction (V$_2$O$_5$, NiO, CuO and ITO), no changes to the substrate spectra are observed. However, the reactive substrates (ZrO$_2$ and sputter-reduced-ITO) exhibit changes to the substrate spectra after the MoO$_3$ is deposited. The spectral changes appear to be rigid shifts rather than representing new chemical species. These shifts may imply changes in the substrates’ Fermi level positions.

Figure 6.3.3 – XPS spectra of the main photoemission peak from the substrate oxides. The black spectra represent clean substrates, and the grey spectra represent substrates buried under ~ 2 nm of MoO$_3$.

As mentioned in the previous section, the two main causes for Mo reduction at the interfaces were: 1) charge transfer from the substrate Fermi level and 2) an oxidation-reduction reaction between the metal and MoO$_3$. In the cases where substrates are oxides the picture is not so clear. Certainly sputter-reduced ITO reacts with MoO$_3$ due to an oxidation-reduction reaction, as In$_2$O$_3$
is more thermodynamically stable than MoO$_3$. O-deficient In$_2$O$_3$ will remove O from stoichiometric MoO$_3$ and leave MoO$_3$ O-deficient, according to the following reaction:

$$\text{In}_2\text{O}_{3-x} + \text{MoO}_3 \rightarrow \text{In}_2\text{O}_3 + \text{MoO}_{3-x}$$

However, the reason why ZrO$_2$ reduces MoO$_3$ is certainly different. ZrO$_2$ is already stoichiometric and fully oxidized. There is no thermodynamic force to drive further oxidation of ZrO$_2$ and cause reduction of MoO$_3$. But ZrO$_2$ has a work function of $\sim 3.5$ eV and MoO$_3$’s conduction band minimum is at $\sim 6.6$ eV below the vacuum level. It is likely, in this case, that charge-transfer is the cause of MoO$_3$ reduction.

After considering the other oxides—V$_2$O$_5$, NiO, CuO, and ITO—it is clear that having the substrate oxide’s Fermi level above MoO$_3$’s conduction band does not guarantee charge transfer. For instance, the work functions of the substrate oxides were 6.95 eV, 5.0 eV, 5.9 eV and 5.3 eV for V$_2$O$_5$, NiO, CuO, and ITO, respectively. The only oxide whose Fermi level is below MoO$_3$’s conduction band is V$_2$O$_5$. This observation suggests that some other factor is involved here. It is possible that there are barriers to moving charge across these interfaces that are not simply predicted by the difference between the substrate oxide’s Fermi level and MoO$_3$’s conduction band. Perhaps the substrate oxide’s Fermi level must be greater than this hypothetical barrier in order for charge transfer to occur, and thus the substrate oxide’s work function must be much less than MoO$_3$’s conduction band.

It is also uncertain what role band bending will play for these interfaces. As mentioned earlier, the V$_2$O$_5$/MoO$_3$ and ITO/MoO$_3$ interfaces are n-n junctions, while the CuO/MoO$_3$ and NiO/MoO$_3$ interfaces are p-n junctions. There is a possibility that band bending may play a role in these interfaces. At the moment it is uncertain, and additional interfaces must be examined in order to arrive at a reasonable conclusion.
7 Summary and Future Directions

7.1 Summary

This thesis has addressed some of the fundamental characteristics of transition metal oxides and their functional interfaces in organic electronic devices. Photoemission spectroscopy (XPS and UPS) was the primary analytical tool to examine these characteristics.

In Chapter 3, we have surveyed the electronic properties of transition metal oxides. The core-level photoemission spectra, valence band spectra and work functions of numerous \textit{in situ}-prepared transition metal oxides were measured. We found correlations between O-vacancy defects, cation oxidation state and oxide work function and electronic band structure. We surveyed the various methods one can use to tune an oxide’s electronic properties through oxidation and reduction.

In chapter 4 we examined interfaces between organic semiconductors and transition metal oxides. It was found that the energy-level alignment at these interfaces is primarily governed by a relationship between an oxide’s electron chemical potential and an organic’s ionization energy. A model was presented to describe the observed behaviour. This model used charge transfer and molecular ionization considerations to reproduce the experimentally observed energy-level alignment relationship.

In chapter 5 and 6 we examined interfaces between electrodes and a prototypical metal oxide, MoO$_3$. It was found that MoO$_3$ can form non-reactive and reactive interfaces with various electrode materials. MoO$_3$ was found to be reduced by each metal electrode, including the noble metal Au. The interfacial reactions affect MoO$_3$’s work function and electronic structure within the first few nanometres of the electrode interface, which affects MoO$_3$’s electrical conductivity and energy-level aligning capabilities. The Mo reduction observed at these interfaces was explained using two proposed mechanisms: 1) charge transfer from the metal’s Fermi level, and 2) oxidation-reduction reaction with the electrode metal.

In chapter 6 we dealt with metal oxide electrodes. Several different oxides were examined, including high work function n-type d$_0$ oxides, high work function p-type oxides, a transparent conductive oxide and a low work function n-type d$^0$ oxide. Most of these materials were found to
be un-reactive with MoO₃, with the exception of ZrO₂ and reduced ITO. When no Mo reduction was observed, the MoO₃ work function reached its maximum value very close to the electrode/MoO₃ interface, and MoO₃ retained its stoichiometric valence band structure even in contact with the interface. When reduction was observed, the MoO₃ work function requires several nanometres before it reaches its maximum value. MoO₃ also has a semi-metallic valence band at the reactive interface. The origins of these observations are not yet clear. As oxides are such diverse materials, the current sub-set of oxides is insufficient to draw conclusions. This study will require further investigation.

7.2 Future Directions

The findings of this thesis are both interesting fundamentally, and have broad-reaching implications for future work. In chapter 4 energy-level alignment was investigated for systems where substrate work function was greater than the molecular ionization energy and within the molecular band gap. The next step would be to investigate systems in which the substrate work function is smaller than the molecular electron affinity. In this case we would expect the molecule’s LUMO to become pinned to the oxide’s Fermi level.

For the interfaces we have examined in this study, we have seen a common value of HOMO/Fermi-level offset of ~ 0.3 eV. One question which arises is: What is the LUMO/Fermi-level offset? Furthermore, the value of 0.3 eV found in this study was for non-polar molecules. Would this value differ if polar molecules are used?

Regarding the properties of metal oxides, we demonstrated a relationship between dilute O-vacancies and oxide work function. It would be interesting to take this further and see how introducing oxygen interstitials into a stoichiometric oxide affects work function. New experimental techniques would need to be developed for such a study to controllably introduce O-interstitials. Perhaps an oxygen ion gun would work. Furthermore, one would need to find a suitable method for characterizing O-interstitials. It may be necessary to carefully choose the best oxide for such a study. NiO and CuO both have a propensity for forming O-interstitials, and one can detect these interstitials in the O 1s spectrum. Other future directions might be to find a way to introduce metal interstitials and see the effect these have on work function.
It would also be useful to more thoroughly characterize oxides when high concentrations of O-vacancies are present. We have developed a model for dilute O-vacancies and observed a rough correlation between cation oxidation state and oxide work function. It would be useful to more precisely understand and model this correlation.

Future directions for the electrode/oxide studies may include using a wider variety of oxide substrates, such as other low work function n-type d^0 oxides, and other p-type oxides. Furthermore, one could examine other transparent conductive oxides. Another alteration could be to use an oxide other than MoO_3 as the overlayer. While most oxides cannot be evaporated, some similar oxides such as V_2O_5 and WO_3 can be evaporated in a similar way to MoO_3.

8 Appendices

8.1 Derivation of Equations Used to Calculate Oxide Thickness

XPS is often said to be “surface sensitive”. This is because of the relatively small inelastic mean-free-path (IMFP) of electrons in solids. The probing depth of photoemission is determined by the IMFP of a given electron kinetic energy in a given material as well as the scattering properties of the material from which the electrons must travel before they escape the sample.

XPS produces a wide range of electron kinetic energies, and IMFP’s can often range from < 1 nm to > 3 nm. UPS however only produces low-kinetic energy electrons. As a result, IMFP’s are generally very short (~ 0.1 nm) and span a very narrow range. Consequently, UPS tends to be much more surface sensitive than XPS. UPS’s surface sensitivity often restricts its usefulness to ultra-clean, in-situ-prepared samples; however, XPS’s surface sensitivity can be used to perform non-destructive depth profiling and determine film thicknesses.

Here we will briefly go through the concept of electron scattering and how it affects XPS signal intensity. Then we will go through how XPS can be used for non-destructive depth profiling. These calculations were used extensively in this work to determine oxide film thicknesses.

When one measures a sample’s XPS spectrum, a large area of the sample is exposed to x-rays. X-rays penetrate several microns beneath a solid’s surface, and photoelectrons are generated
everywhere the X-rays hit; however, the electron analyzer collects electrons only from a small spot on the sample—as illustrated in figure 8.1 (a). While X-rays penetrate deep into a sample, the electrons that contribute to an XPS signal only come from the first few nanometers of the sample’s surface. This is because electrons can only travel a short distance through a solid before they collide inelastically with an atom. Due to the arbitrary energy loss accompanying a collision, the electron will lose the chemical information that it had carried via its kinetic energy.

**Figure 8.1** – Illustration of a sample being irradiated with X-rays, and the photo-emitted electrons being collected by an electrostatic lens.

Electron scattering follows the Beer-Lambert equation: $P = \exp \left( -\frac{z}{\lambda} \right)$, where $P$ is the probability of an electron being scattered, $z$ is the distance the electron travels, and $\lambda$ is the IMFP of the electron. A plot of this equation is shown in figure 8.2 (a). Here one can see that 65% of the total XPS signal comes from within a depth of $1\lambda$, 87% from within $2\lambda$, and 95% from within $3\lambda$. So, although XPS is surface sensitive, one can still detect a signal from an element buried 10 nm below the surface.

By tilting a sample relative to the electron collector, one can change the depth sensitivity. For example, given a sample coated with a thin oxide layer that is $\sim 1.5\lambda$ thick, the oxide will contribute to $\sim 78\%$ of the photoemission signal when the sample is tilted normal to the electrostatic lens is, and $\sim 94\%$ of the signal when the sample is tilted $35^\circ$ to the electrostatic lens. This is illustrated in figure 8.2 (b) and (c).
Here we will go through the derivation of the equations used to calculate oxide film thickness using XPS peak intensities. Consider the electrons from 1s orbitals of a material A. They give rise to a photoemission peak in an XPS spectrum as shown in the figure 8.3. Only the electrons that escape the sample surface without having an inelastic collision will contribute to the photoemission peak. The inelastically scattered electrons cause a background signal on the lower kinetic energy side of the photoemission peak.

Figure 8.2 – (a) Plot of number of electrons escaping a solid surface, versus depth from the surface, following the Beer-Lambert equation. (b) Illustration of measuring XPS from an oxide thin film at normal angle. (c) Illustration of measuring XPS from an oxide thin film at glancing angle.

Figure 8.3 – Illustration of a photoemission peak from an infinitely thick material, showing the elastically scattered background.
Using the Beer-Lambert equation for the probability of an electron escaping the sample without an inelastic collision, we can write an expression that represents the number of electrons from depth $z$ which reaches the electron detector.

$$
dI = I_0 \exp\left(-\frac{z}{\lambda \sin \theta}\right) dz
$$

*equation 8.1*

Where $I_0$ is a constant which represents the number of electrons generated at depth $z$, and $\theta$ is the angle between a vector parallel to the sample surface and the axis parallel to the XPS electrostatic lens column.

By integrating from $z = 0$ to $\infty$, we get...

$$
I_{\infty} = I_0 \lambda \sin \theta
$$

*equation 8.2*

At normal emission $\sin \theta = 1$. This equation represents the photoelectron intensity of an emission feature (e.g. the 1s electrons from element $A$) from an infinitely thick piece of material.

Now consider a thin layer of $A$, of thickness $d$ on substrate $B$ as shown in figure 8.4.

*Figure 8.4 – Illustration of a thin film of material A on material B.*

The XPS spectrum would look something like the figure 8.5. The intensity of the $A$ peak will usually be greater than the $B$ peak (but not always, depending on the thickness of $A$).
Note that the electrons from A and from B have different kinetic energies. This is generally the case when A and B are different elements. The consequence of the different kinetic energies is that the electrons will have different IMFPs. In this example, the kinetic energy of B electrons are higher than the A electrons.

The intensity of photoemission peak from $A$ can be obtained by integrating equation 8.1 from $z = 0$ to $d$. This yields the following equation.

$$I_A^d = I_{0,A}[1 - \exp(-d/\lambda_{AA} \sin \theta)]$$

*equation 8.3*

Where $\lambda_{AA}$ represents the IMFP of electrons from $A$ moving through $A$.

The expression for the intensity of electrons from $B$, buried under a film of $A$, of thickness $d$, is given by the following equation.

$$I_B = I_{\infty,B} \exp(-d/\lambda_{BA} \sin \theta)$$

*equation 8.4*

Where $\lambda_{BA}$ is the IMFP of electrons from $B$, moving through $A$, and $I_{\infty,B}$ is the photoemission intensity from an infinitely thick piece of pure $B$. 

---

**Figure 8.5** – Illustration of XPS spectra corresponding to the situation shown in figure 2.6
In principle we can know the thickness of \( A \) using equations 8.3 and 8.4 and by measuring the intensity of the photoemission peak from either \( A \) or \( B \). However, we do not always know the values of the constants \( I_0 \) or \( I_\infty \). They would have to be measured from standards, and measured under precisely identical conditions, which is not always feasible.

Alternatively, we can compare the intensity ratios of the \( A \) and \( B \) photoemission peaks to determine thickness. This gives us the following expression.

\[
\frac{I_A}{I_B} = R = R^\infty \left[ \frac{1 - \exp \left( -d / \lambda_{AA} \sin \theta \right)}{\exp \left( -d / \lambda_{BB} \sin \theta \right)} \right]
\]

\textit{equation 8.5}

\[
R = R^\infty \left[ \exp \left( \frac{d}{\lambda_{BA} \sin \theta} \right) - \exp \left( \frac{d}{\sin \theta} \left[ \frac{1}{\lambda_{BA}} - \frac{1}{\lambda_{AA}} \right] \right) \right]
\]

\textit{equation 8.6}

Once again, the ratio \( R^\infty \) requires measurements of standards. We can eliminate it by measuring the sample at two different angles.

When determining the thickness of an oxide on its parent metal, equation 8.6 can be simplified. An illustration of this scenario and an XPS spectrum of a typical oxide thin film is shown in figure 8.6.
**Figure 8.6** – (left) Illustration of the atomic structure of a thin metal oxide film on a metal, (right) schematic XPS spectrum of the main metal peak.

Note that the photoemission signal is coming from the same type of element (e.g. molybdenum), and same type of orbital (3d), however the metals in the oxide are in a higher oxidation state than the neutral metal (e.g. +6 compared to 0). The peak from the oxidized atoms will show up at slightly lower kinetic energy than the peak of the neutral atoms, usually a few eV away. These two types of electrons therefore travel through the solid with very similar kinetic energies, and we can approximate that they have the same IMFP.

Here we will change the subscripts from $A$ to $o$ (for oxide), and from $B$ to $m$ (for metal). For an oxide of its own metal however the electron kinetic energies are essentially equal, so $\lambda_{oo} = \lambda_{mo}$. This will change equation 8.6 to the following.

\[
R = R^\infty \left[ \exp \left( \frac{d}{\lambda_{mo} \sin \theta} \right) - \exp \left( \frac{1}{\sin \theta} \left[ \frac{1}{\lambda_{mo}} - \frac{1}{\lambda_{oo}} \right] \right) \right]
\]

*equation 8.7*

This can be reduced to...

\[
R = R^\infty \left[ \exp \left( \frac{d}{\lambda_o \sin \theta} \right) - 1 \right]
\]

*equation 8.8*

and by re-arranged to get...

\[
d = \lambda_o \sin \theta \ln \left[ 1 + \left( \frac{R}{R^\infty} \right) \right]
\]

*equation 8.9*

Once again we have the problem of $R^\infty$, however, we can use a simple expression for it.
\[ R^o = \frac{\rho_o \lambda_o}{\rho_m \lambda_m} \]

*equation 8.10*

Where \( \rho_o \) and \( \rho_m \) are the atomic densities of the metal atoms in the oxide and metal, respectively.

This gives us the following expression for oxide thickness:

\[ d = \lambda_o \sin \theta \ln \left[ 1 + \left( \frac{I_o \rho_m \lambda_m}{I_m \rho_o \lambda_o} \right) \right] \]

*equation 8.11*

### 8.2 Discussion of Reference Levels

Reference levels are an important consideration in interpreting photoemission spectra, and often a point of confusion.\(^9^9\), \(^1^3^0\)-\(^1^3^3\) In gas phase spectroscopy, binding energies are calibrated using optical methods. For example, the binding energy for a particular electron state can be determined by measuring the energy of the corresponding emission line in a Rydberg series. By doing so, the binding energy is calibrated with reference to the vacuum level (i.e. the energy of an electron at rest, infinite distance away from any other charged particles), such that the vacuum level is zero on the scale.

In solid state photoemission spectroscopy, the situation is more complicated. In general, when a sample contacts a spectrometer, the electron chemical potentials of the two equilibrate, resulting in Fermi level alignment. We will illustrate the concepts of reference levels in solid state spectroscopy using a step-wise example, as shown in figure 3.1.1. Part (A) represents the spectrometer and sample in complete isolation from one another, and from any other source of charge. Here, the two materials both have their own distinct Fermi energies defined by the energies of their highest filled electron states. These Fermi energies can in principle (although not in practice) be defined the absolute energy scale. The zero of this scale is indicated by the horizontal dashed line in figure 4.3.4, labeled “vac. level”. In this case, and neglecting surface dipoles of the sample and spectrometer, we can say their vacuum levels are aligned.
The next step to consider is grounding the spectrometer, as illustrated in (B). By grounding, we mean that the spectrometer is in electrochemical equilibrium with the electron reservoir known as “ground” or “earth”. In this case, the Fermi level of the spectrometer aligns with the Fermi level of ground, causing the ‘local’ vacuum level of the spectrometer to deviate from the absolute reference level. The energy of the Fermi level of ground on the absolute energy scale has been determined experimentally to be ~ 4.09 eV.\(^{99}\)

In the next step, we consider what happens when a sample contacts the spectrometer, as shown in (C). When contact is made, electrons will move in order to establish equilibrium between the sample and ground. In this case, we have shown a sample with a work function greater than the energy of ground. To establish equilibrium, electrons move from the spectrometer to the sample. The excess negative charge on the sample shifts its local vacuum level above the absolute vacuum level, and generates an electrostatic field outside the sample surface. The ‘local’ vacuum is very important because it is what is observed experimentally when one measures the secondary electron cut-off of a sample. One cannot directly measure the absolute vacuum level in solid state photoemission spectroscopy.

From the above description one can see why the Fermi level is more suitable as a reference level in solid state photoemission spectroscopy. The Fermi level remains constant due to the constraints of thermodynamic equilibrium. However, as a result of this equilibrium the local vacuum level (and only measureable vacuum level) becomes variable and sample dependent, and is thus not a suitable reference level.

We will now consider what happens when a molecule adsorbs to the sample surface. Figure 4.3.4 (D) shows the situation of the spectrometer and substrate at equilibrium, and the molecule in the gas phase at infinite distance away from the substrate. The molecule’s vacuum level is aligned with the absolute vacuum level, and the HOMO binding energy is the same as the gas phase ionization energy.

When the molecule comes close to the sample surface, as shown in figure 4.3.4 (E), it feels the electrostatic field of the sample’s local vacuum level. This field shifts all electron energy levels of the molecule upward. When the molecule adsorbs to the surface, a so called dipole, or shift in the sample’s vacuum level can occur, due to the push-back effect; however, this not shown in the figure for simplicity. If no charge transfer between the molecule and substrate occurs (i.e. when
the Fermi level of the substrate lies within the gap of the molecule) as shown in (E) then the binding energies of the molecular levels will shift in response to changes in the substrate’s local vacuum level. This is why the HOMO binding energy of molecules shifts linearly with substrate work function when the work function is less than the molecule’s ionization energy.

When the work function is greater than the molecule’s ionization energy, as shown in figure 4.3.4 (F), charge transfer from the HOMO of the molecule to the substrate occurs, allowing for equilibrium of the molecule with the Fermi level. As a result, the binding energies of the molecule are no longer dependant on the work function of the substrate.

When two metals come into contact, electrons are transferred from the metal with the low work function to the metal with the high work function. The result is a contact potential difference between the two metals, known as the Volta potential. A potential difference is established between any two materials in electrochemical equilibrium, in which charge transfer was required to reach equilibrium. A thin metal oxide film in contact with a metal will have a contact potential difference.

Since most oxides have work functions that are much higher than their parent metals, electron transfer goes from the metal to the oxide in order to align the two materials’ Fermi levels. This produces a negative potential on the oxide surface, which causes an upward shift of the oxide’s vacuum level. An upward shift in the oxide’s vacuum level is equivalent to saying that there is a negative electric field at the oxide/vacuum interface.

When a molecule approaches the oxide surface, the molecules ‘feels’ the negative field of the oxide surface. This field shifts all electron levels upward in energy, thereby moving their binding energies to lower values, closer to the Fermi level of the substrate.
Figure 8.7 – Energy-level diagrams illustrating how Fermi levels and vacuum levels align when (A) a spectrometer and sample are isolated, (B) a spectrometer equilibrates with ground, (C) a sample comes into contact and equilibrates with a grounded spectrometer, (D) a gas phase molecule not in contact with the grounded sample, (E) a molecule adsorbed to the surface of the grounded sample, where charge transfer cannot occur, (F) a molecule adsorbed to a grounded sample, where charge transfer can occur.

8.3 Measuring Work Function: Effect of Sample Orientation and Applied Bias

Measuring work function relies on the ability to detect slow electrons. The electrons that give rise to the secondary-electron cut-off leave a sample with essentially zero kinetic energy. There is generally a contact potential difference between a sample and the electrostatic lens, which results in a barrier for electron to enter the lens. Any electrons arriving at the lens that have
kinetic energies less than this contact potential difference will not be detected. When this is the case, the spectrum shows an artificial secondary electron cut-off, which does not actually represent the sample’s work function, but rather it is a property of the spectrometer. In order to overcome this problem it is necessary to ‘boost’ the secondary electrons by applying a negative bias to the sample. In all of our work function measurements we apply a -15 V bias to the sample, relative to the spectrometer.

However, due to this bias there is an electric field between the sample surface and the lens. This situation is illustrated in figure 8.8. Secondary electrons are very slow and their paths can be distorted by small electrostatic fields. As a result of non-symmetric electrostatic fields, work function values depend on the orientation of the sample relative to the electrostatic lens. Accurate work function measurements require the sample surface to be perpendicular to the electrostatic lens axis. This orientation ensures symmetrical electric field lines between the sample and the lens, and ensures that even slow electrons are detected.

**Figure 8.8** – Finite-element simulations of electron trajectories from a sample and a spectrometer, where the sample is biased -15 V relative to the spectrometer. Grey lines indicate electrostatic field lines and red lines indicate electron trajectories. (a) Electrons with 10 eV kinetic energies, with the sample normal to the lens. (b) Electrons with 0.25 eV kinetic energies, with the sample normal to the lens. (c) Electrons with 10 eV kinetic energies, and the sample tilted 45°. (d) Electrons with 0.25 eV kinetic energies, and the sample tilted 45°.
8.4 Effects of Measurement Radiation on Work Function and Binding Energies

As mentioned in section 2.3, the common procedure for measuring energy-level alignment (ELA) involves growing an organic thin film in a layer-by-layer fashion, with XPS and UPS spectra repeatedly measured on the same sample. Such procedures can take several hours to perform, during which time the sample accumulates significant doses of ultraviolet or x-ray radiation. A sample irradiated with about 1 - 50 mW/m² of $^{134}$ for thousands of seconds, absorbs $\sim 1 \text{ kJ/m}^2$. $^{135}$

The intention of such characterization procedures is to examine how the binding energies and work function of organic molecular films change with distance from an interface. Binding energy and work function shifts $> 0.5$ eV are routinely observed. Such profiles are often interpreted as electrostatic potential profiles close to the interface, $^{136-137}$ and explained as band bending, $^{17}$ molecular polarization $^{100-101, 138}$ or photo-hole screening. $^{139}$ However, binding energy and work function shifts can also be caused by the radiation used to measure these properties.

While radiation damage to polymers is well known, $^{140-144}$ subtle radiation damage is not always apparent in a spectrum. Subtle spectral changes may only become significant when accumulated throughout an experiment. Such subtle shifts can alter the observed binding energy or work function trends. Given the level of precision required of ELA data, there is a need to validate experimental procedures to ensure that radiation effects are insignificant.

We find that the typical radiation doses used in layer-by-layer PES procedures commonly can cause non-negligible work function and binding energy shifts, which can become a major source of error and variability. Although this source of measurement error is inevitable, minimizing the radiation exposure can reduce the error to below the levels of other sources of error so that reliable and reproducible interfacial energy level profiles can be obtained.

In order to validate our procedures and establish a suitable time budget for measurements we have examined the effects of collecting XPS and UPS spectra on the measured work functions, core level and valence level binding energies. We can reduce the sample-to-sample variability to $\pm 0.05$ eV by minimizing irradiation time. However, every material responds to radiation...
differently, which necessitates repeated data validation. We demonstrate a means of method validation for layer-by-layer PES procedures.

To demonstrate the effects of sample irradiation we have used a common hole-transporting organic semiconductor \( \text{N,N'}-\text{diphenyl-\text{N,N'}-bis-(1-naphthyl)-1-1'}-\text{biphenyl-4,4'}\)-diamine (\( \alpha\)-NPD), which has been used in many previous layer-by-layer PES studies, and several types of substrate relevant to current interface research, such as an inert metal (gold) and transition metal oxide substrates (MoO\(_3\) and CuO).

### 8.4.1 Validation Procedure

In order to establish whether radiation had induced changes or not, we always included a control sample. The control samples were placed next to the test samples (i.e. samples experiencing high radiation exposure), on a rotatable sample holder, such that the test sample could be irradiated without irradiating the control sample. The control samples otherwise experienced the same sample treatment (i.e. identical substrate, identical film thickness). The control samples were used to show that, without radiation exposure, peak shifts do not occur by having the sample sitting in vacuum for the same duration.

The typical XPS photocurrents in our system \( \sim 1\) nA, distributed over a 10 mm by 5 mm stripe. The photocurrents in UPS were \( \sim 20\) nA, distributed over an 8 mm diameter spot.

Three types of substrate were used: (1) gold, (2) molybdenum trioxide oxide, and (3) copper monoxide. The gold substrates were formed by magnetron sputtering of a 99.999 % pure gold target, onto a polished silicon wafer, to form a 100 nm thick gold film. The gold films were then cleaned \textit{in situ} via ion sputtering. The molybdenum trioxide substrates were formed by \textit{in situ} oxidation of 200 nm thick molybdenum films, formed by RF-plasma sputtering of molybdenum onto a polished silicon wafer. The copper monoxide substrates were formed by \textit{in situ} oxidation of 200 nm thick copper films, formed by RF-plasma sputtering of copper onto a polished silicon wafer. All organic film depositions were performed \textit{in situ}, by heating \( \alpha\)-NPD in a Knudsen cell, to obtain a deposition rate of 0.3 Å/sec.
8.4.2 Effects of X-ray Irradiation

Often in layer-by-layer PES characterizations, both core level XPS spectra and work function measurements are taken. Given that work function is so easily altered, it is important to know whether the radiation used to measure XPS spectra alters the work function value, and if so, how fast it occurs. To determine the effects of measuring XPS spectra on a sample’s work function, test samples were continuously irradiated by soft x-rays ($h\nu = 1486.7$ eV), with work function measurements taken at set intervals, and compared to control samples (i.e. samples not continuously exposed to x-rays).

![Figure 8.9](image)

**Figure 8.9** – Plots of work function versus irradiation time for samples continually irradiated with soft x-rays (solid lines) and control samples not irradiated with x-rays (dashed lines).

Two types of sample were examined: Sputter-cleaned gold, which is inert and expected to not be sensitive to chemical degradation, and a 3 nm thick $\alpha$-NPD film deposited on sputter-cleaned gold, which may or may not exhibit chemical degradation. Figure 8.9 shows a plot of work function with time for these two sets of samples.

When continuously irradiated with x-rays, both types of sample (clean Au and $\alpha$-NPD) exhibit a gradual decrease in work function, while the work functions of the control samples remained constant over the same course of time. The work functions of the irradiated samples decreased by 0.3 eV for the $\alpha$-NPD sample and 0.2 eV for the gold sample. This result demonstrates that collecting XPS spectra can significantly alter the work function of not only organic semiconducting samples, but also inert metal samples.

The rate of work function decrease however differs for the two types of sample. The work function of the $\alpha$-NPD film decreased more rapidly than gold. Since gold is inert, the decrease in
work function was not likely due to chemical changes. From the Au $4f$ XPS spectrum shown in figure 8.10 (b), one can see that the gold core levels were unaltered by x-ray irradiation, even though the work function decreased. Since there was no change in the peak shapes of the gold spectrum, one can infer that no chemical changes have occurred. Furthermore, since there were no changes in Au $4f$ peak positions, one can infer that the change in the work function was due to a change in surface dipole rather than a change in Fermi level position. This change in dipole may be due to adsorption of background gases,\(^{145}\) implying that x-ray irradiation enhances the rate of background gas adsorption.

Figure 8.10 – (a) The C 1s photoemission spectrum of a 3 nm thick $\alpha$-NPD film (i) before and (ii) after 30 minutes of continuous soft x-ray irradiation. A binding energy shift of 0.24 eV was observed after x-ray radiation. (b) Au $4f$ photoemission spectrum of a sputter-cleaned, 100 nm thick Au film (i) before and (ii) after 30 minutes of continuous soft x-ray irradiation. Irradiation did not result in any binding energy shift for Au.

In contrast to gold, $\alpha$-NPD is more susceptible to radiation-induced chemical changes. Chemical changes can be identified in XPS spectra by changes in the relative heights of photoemission features or by the appearance or disappearance of peaks.\(^{143-144}\) While no chemical changes were evident in the core level spectra of $\alpha$-NPD, the sensitivity of XPS is only parts per thousand (due
to the low photo-ionization cross section of C 1s electrons). Therefore, chemical degradation cannot be ruled out by this observation, as chemically altered α-NPD molecules could be present in amounts below the detection limit of XPS.

Figure 8.11 – (a) Work function data from a mock layer-by-layer PES characterization to demonstrate how collecting XPS spectra can affect the work function profile. XPS spectra, requiring 20 minutes of irradiation, were collected after each deposition. The work function measurements of irradiated sample are represented by solid diamond-shaped points. The points separated by vertical dashed lines indicate measurements taken before (upper data points) and after (lower data points) sample irradiation. The work function measurements of the control sample, from which XPS spectra were not collected, are represented by the un-filled circles. The overlayer was α-NPD and the substrate was CuO. (b) Shown here are the XPS spectra from the mock layer-by-layer PES characterization (C 1s, O 1s, N 1s, and Cu 2p3/2). The core levels of the overlayer (C 1s and N 1s) shift to higher binding energy as the film thickens, while the substrate peaks (Cu 2p and O 1s) remain constant.

Even though no gross changes to peak shape or peak area were found in the spectra, the C 1s spectrum does exhibit a shift towards higher binding energy during x-ray irradiation. This is shown in figure 8.10 (a), where the C 1s peak of α-NPD shifted by ~ 0.3 eV after 30 minutes of x-ray irradiation. Since both the peak position and work function shifted, one can infer that there has been a shift in Fermi level position. Although no chemical states of degraded molecules could be positively identified in the C 1s spectrum, concentrations of chemical states well below the detection limit of XPS can still significantly alter the Fermi level position. Photo-fragmented or cross-linked α-NPD molecules having ionization energies that differ from that of pristine α-
NPD could act as dopants to change the position of the Fermi level. Thus even though x-ray damage may not be obvious from the XPS peak shapes, minor damage can change the energy-level alignment characteristics of organic thin films.

The interpretation of layer-by-layer PES data can be altered by such irradiation-induced effects. Figure 8.11 (a) shows work function data of a mock layer-by-layer PES characterization in which core level spectra of all relevant peaks were collected after each deposition step. For both the irradiated and the control samples, the work function decreased rapidly upon the first α-NPD deposition. For the control sample, the work function plateaus after depositing about 16 Å of α-NPD. The work function does not plateau for the irradiated sample and continues to decrease as the film thickens. The points in figure 8.11 (a) connected by dashed vertical lines indicate work function measurements before and after collecting XPS spectra. Each time the sample is irradiated to collect XPS spectra, its work function drops by ~0.1 – 0.3 eV. If a potential energy profile were constructed using these measurements, it would appear that work function is largely dependent on α-NPD thickness, with a decrease of ~0.7 eV from 8 to 64 Å thick. Based on the control sample it is apparent that such a conclusion is false. In fact the work function does not change with thickness after about 16 Å of α-NPD have been deposited.

Very often, core levels are used for potential energy profiles. The core-level spectra measured throughout the mock layer-by-layer PES characterization are shown in figure 8.11 (b). The core levels of the overlayer (C 1s and N 1s) shift to higher binding energy as the film thickens, while the substrate core levels (Cu 2p and O 1s) are unaffected by the measurements. One might conclude that band bending exists in the organic layer, but not in the substrate.

However the organic semiconductor, which is capable of cross-linking and fragmentation, is likely more sensitive to irradiation effects than the oxide substrate. Based on the observed irradiation-induced work function shifts, any apparent thickness dependence of core level binding energies must be subject to scrutiny, and validated with a control sample. In the present case, the C 1s spectrum of the control sample was measured and compared to the C 1s spectrum of the irradiated sample, after the mock layer-by-layer characterization was complete. The C 1s spectrum of the control sample was found to be ~0.25 eV lower in binding energy. This confirms that the chemical shift observed in the full layer-by-layer XPS characterization was affected by irradiation, and does not accurately represent the potential profile of the interface.
8.4.3 Effects of UV Irradiation on UPS Spectra

While Al Ka x-rays can cause changes to work function and binding energies of organic thin films, not all layer-by-layer PES studies employ XPS. A potential energy profile can also be constructed from UPS valence band or work function measurements. It is therefore necessary to determine whether He Iα radiation has a similar effect on binding energies and work functions. Radiation damage occurs when electrons are excited into unoccupied states, either by photon absorption or by collision with other electrons, resulting in breaking of molecular bonds, cross-linking or radical formation. Both He Iα photons (hν = 21.22 eV) and Al Ka photons (hν = 1486.7 eV) are capable of causing radiation damage; however the rate at which they cause damage may differ.

In terms of photon absorption, He Iα photons only have sufficient energy to excite valence electrons into unoccupied states, while Al Ka photons can also photo-excite core electrons. Therefore, Al Ka photons have more pathways to radiation damage than do He Iα photons. However every photo-excitation pathway has a cross section that depends on photon energy. So depending on the cross section of the photo-degradation mechanism, one type of radiation may be more efficient at causing radiation damage than the other. Furthermore, photoelectrons and secondary electrons generated within the sample can collide with bound electrons to excite them into unoccupied states. All primary and secondary electrons generated by photoemission have kinetic energies less than hν. So even though the secondary electron intensity will be much greater when using a non-monochromated UPS source than when using a monochromated XPS source, the kinetic energies of electrons travelling through the sample will be much less for UPS than for XPS. While it is expected that He Iα irradiation is capable of causing radiation damage, the rate at which it does so is unknown, so it is necessary to determine whether He Iα from a non-monochromated light source will affect binding energies on the time scale of a typical measurement.

The effects of He Iα radiation on valence spectra are demonstrated in figure 8.12 (a). This figure shows a stack of UPS spectra for a 5 nm thick α-NPD film on MoO₃. The sample was continuously exposed to photons from a non-monochromated He discharge lamp, with an irradiance at the sample surface of about 1 - 5 mW/m². UPS spectra were collected every 5 minutes. One can see that the HOMO level shifts to higher binding energy and broadens with
UV irradiation time. Figure 8.12 (b) shows a plot of the binding energy of the HOMO feature versus UV irradiation time. The total binding energy shift after 45 minutes of irradiation is ~ 0.4 eV. This value would be considered large for an energy barrier, or band bending in a 5 nm film. A UPS spectrum however can generally be collected with less than one minute of irradiation time. As an estimate of time budget, the binding energy shifts by about 0.01 - 0.02 eV per minute. This time budget will also depend on the intensity of the light source, may differ for other material systems, may depend on film thickness, and may be affected by background pressure.

![Figure 8.12](image)

Figure 8.12 – (a) This figure shows a stack of UPS spectra of an α-NPD film while being continuously irradiated with UV radiation from a helium discharge lamp. Spectra were measured every 5 minutes. The film thickness was 5 nm, and the substrate was MoO₃. (b) This plot of the HOMO binding energy versus UV irradiation time shows the increase in HOMO binding energy with irradiation time, as determined from the spectra in figure 8.11 (a).

To confirm that the changes in the UPS spectra were caused by sample irradiation, and not other extraneous factors such as adsorption of background gases from the helium line, the UPS spectrum of the irradiated sample was compared to that of the control sample. Figure 8.13 (a)
shows the UPS spectrum of the irradiated sample at $t = 0$ min (i) and $t = 45$ min (ii) with the control sample at $t = 45$ min (iii). By comparing the control sample at $t = 45$ min with the irradiated sample at $t = 0$ min (compare spectra (iii) and (i) in figure 8.13) one can see that the UPS spectrum was unchanged when not irradiated. Spectrum (ii) however, shows that the features of the irradiated sample exhibited significant broadening and shifting higher binding energy.

---

**Figure 8.13** – (a) UPS valence spectra comparing (i) irradiated $\alpha$-NPD film before irradiation, (ii) after 45 minutes of UV irradiation, and (iii) an $\alpha$-NPD control sample. (c) C 1s XPS spectrum of (iv) the control sample, and (v) the irradiated sample after 45 minutes of UV irradiation.

Irradiating the sample with He $I\alpha$ also caused the $\alpha$-NPD core levels to shift to higher binding energy. Figure 8.13 (b) shows the C 1s spectrum of the control sample at $t = 45$ min (iv) and the irradiated sample at $t = 45$ min (v). Other than a shift of 0.4 eV to higher binding energy, UV-irradiation did not cause any other changes to the C 1s spectrum, just as was observed when the sample was irradiated with x-rays.

### 8.4.4 Establishing Thickness Dependence

The thickness dependence of binding energies in organic semiconductor thin films has often been debated in the literature. However, many of the arguments are based on layer-by-layer PES.
data. It is possible that the observed binding energy profile is dependent on the deposition routine. For example, if the film is deposited in steps which increase geometrically, and irradiation causes binding energy changes that increase linearly with time, then one could observe a geometric trend in the binding energy with thickness even if the binding energy is not truly thickness dependant. Alternatively, if the film is deposited in constant increments, then a different binding energy profile would result. If irradiation effects are adequately minimized then changes in the deposition routine should not alter the observed binding energy trend. Several HOMO binding energy profiles deposited using different deposition routines, are shown in Figure 8.14. Only UPS measurements were taken, and irradiation times were kept to a minimum.

![Figure 8.14](image_url)

**Figure 8.14** – Plot of HOMO binding energy versus α-NPD thickness, from several independent interfacial ELA measurements, demonstrating a true thickness dependence.

These profiles follow similar trends, regardless of the deposition routine, which indicates that irradiation is having a negligible effect. However, each sample accumulates radiation doses as the film thickens. In order be certain that HOMO binding energies truly are thickness dependent, the effects of irradiation must be isolated. The black data point in figure 8.14 represents a 50 Å-thick α-NPD film, which was deposited in a single step, and measured only once (i.e. it had no prior radiation exposure). The grey data points for the 8 Å-thick α-NPD films, likewise, were each deposited in a single step, and had no prior irradiation. The binding energy of the 50 Å-thick α-NPD film is 0.58 eV, while those of the 8 Å films are scattered between 0.2 to 0.25 eV. Since both film thicknesses experienced the same minimal irradiation times, the difference in binding energy represents true thickness dependence. This confirms the thickness dependant
binding energies of many previous reports; however, reports in which radiation time was not considered may have overestimated the thickness dependence of binding energy.

Irradiation-induced binding energy shifts also affect the detection limit of layer-by-layer PES measurements. In order for layer-by-layer PES interface characterizations to be useful for developing quantitative theories of organic interfaces, the detection limit must be better than 0.1 eV, that is, the technique must be capable of distinguishing between interfaces which differ in energy-level alignment by less than 0.1 eV. If a profile is not reproducible within 0.1 eV then this detection limit will not be attained. The measurements of the MoO$_3$/α-NPD interface shown in figure 8.14 were measured from separate samples. These profiles demonstrate that by minimizing acquisition time, interface binding energies can be reproduced to within ± 0.05 eV. Once irradiation effects have been minimized, other sources of variability, such as the measured film thickness, become the limiting factor for the energy-level alignment detection limit.

Although layer-by-layer PES technique can have sufficient sensitivity to distinguish small differences in ELA, due to the many spectra collected during a layer-by-layer PES characterization, considerations must be made to reduce irradiation doses wherever possible. In general, one must balance radiation time with signal intensity. This can be a problem for extremely thin films, and when photoemission cross sections are weak. Signal intensity is usually not a problem for non-monochromated UPS measurements, and UPS measurements tend to be the most reliable means for constructing energy-level profiles.

The HOMO level and work function can be measured in a matter of ~ 10 seconds; however excessive irradiation should still be avoided. For XPS measurements, signal intensities can be very weak when using monochromated sources, and when using the higher photon flux of a non-monochromated x-ray source, the rate of energy absorption by the sample is much higher, causing more rapid radiation damage. In order to obtain a profile using XPS peaks (e.g. the C 1s peak of an organic overlayer) it is advisable to collect only one core level per sample, using the narrowest spectral window needed. One can also sacrifice energy resolution for signal intensity by increasing spectrometer pass energy, and although peaks are slightly broadened, peak off-sets can still be accurately determined. Extremely high-resolution spectra, with very narrow peaks are only necessary when deconvoluting spectra, not when determining off-sets.
8.5 Transfer-arm evaporator cell for rapid loading and deposition of organic thin films

Described herein is a transfer-arm evaporator cell (TAE-cell), which allows for rapid loading of materials into vacuum for low-temperature sublimation deposition of thin films. This design can be incorporated with an existing analysis system, for convenient in situ thin film characterization. This evaporator is especially well suited for photoemission characterization of organic semiconductor interfaces. Photoemission is one of the most important techniques for characterizing such however it generally requires in situ sample preparation. The ease with which materials can be loaded and evaporated with this design increases the through-put of in situ photoemission characterization, and broadens the research scope of the technique. Here we describe the design, operation and performance of the transfer-arm evaporator cell.

8.5.1 Background

Progress in organic electronics research is often hindered by the difficulty of characterizing new materials. X-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) of in situ prepared organic thin films are among the most common techniques for characterizing organic interfaces. However, due to the complexity of instrument design, the research groups who have such equipment often restrict their characterizations to standard or commonly used organics, such as copper phthalocyanine (CuPc), aluminum tris hydroxy quinolinate (Alq3), N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1' biphienyl-4,4'diamine (α-NPD), etc. In order to characterize interfaces involving an alternative molecule, one would need to vent their vacuum chamber, fill a crucible often with a large amount of the desired evaporation material, followed by a lengthy pump-down and degassing of all the deposition sources. This procedure can require a week of equipment down time. Given the rate at which new semiconducting organic molecules are designed and synthesized, it is no wonder why in situ photoemission characterization has lagged behind. To make the technique more easily accessible, we have designed and constructed a deposition system that increases the through-put of in situ photoemission characterization (such as XPS and UPS) of organic semiconductors.

In situ XPS/UPS characterization is capable of measuring the energy levels of an overlayer, and determining how they align with those of a substrate. In early organic electronics research, the charge injection barrier across an interface was approximated by comparing the gas-phase
ionization potential of an organic material with the work function of a substrate. While this approximation can be a good starting point, it was soon realized that several concurring interface effects make this approximation inaccurate, and sometimes completely wrong. Such effects as solid-state polarization, charge screening by polarization of the substrate, and charge transfer across an interface or into interface states can cause the measured ionization potential of gas phase or even bulk organic material to become irrelevant at the interface. Therefore, measuring the valence band for a very thin film of an organic is important for an accurate picture of how energy levels align at an interface. In situ XPS/UPS characterization is one of the few, and arguably the most direct means of measuring energy-level alignment. An overview of how this experiment is performed can be found in the literature.

In the present work we describe an evaporator cell design where small amounts of molecules can be quickly loaded through a load-lock into an ultra-high vacuum (UHV) deposition chamber, which is attached to an XPS/UPS spectrometer. The deposition chamber contains permanently mounted Knudsen-cells filled with commonly used molecules, however with addition of this transfer-arm evaporator one can conveniently load, evaporate and characterize other less common molecules. The TAE-cell modification thereby expands the capability of the in situ photoemission technique to a large number of novel materials.

8.5.2 Construction

The TAE-cell involves a small aluminium fixture, which holds a tungsten heater and crucible, as illustrated in figure 8.15. The evaporator fixture is compact enough to fit through the standard 2.375" bore of a 4.5" gate valve to the evaporation chamber. The dimensions of the evaporator, as well as the top, side and bottom views are shown in figure 8.16. This fixture is attached to the end of a transfer arm to allow for the evaporator to be moved from the loading chamber to directly underneath the substrate during evaporation. The tungsten heater is electrically insulated from the frame by ceramic spacers. The heater is clamped to two copper contacts at either end of the fixture. Insulated copper rods are fastened along the side of the aluminium frame, and are in contact to the tungsten heater. Braided copper wire is attached to the ends of the copper rods via barrel connectors. The copper wire is insulated with braided fibreglass and coiled around the transfer arm rod. A coiled nickel wire is attached to the copper wire to add springiness, so that the wire will elongate when the transfer arm is extended, and recoil when the transfer arm is
retracted. The copper wire is then connected to an electrical feed-through. Thermocouples touching the bottom of the ceramic crucible are fed through a hole in the bottom of the aluminium fixture and are mechanically supported by a ceramic tube.

**Figure 8.15** – 3D illustration of the transfer-arm evaporator.\(^{154}\)

The transfer-arm evaporator is mounted on one side of a 4.5” 6-way cross with a quick-load door for easy re-loading of molecules, as illustrated in figure 8.17. The 6-way cross is mounted to a large evaporation chamber, and is isolated by a gate valve. The loading chamber also has an angle valve leading to a bellows and combination turbo-molecular/diaphragm pump for roughing. For *in-situ* transfer of the sample to an electron spectrometer our deposition chamber is attached to a central distribution chamber. The central distribution chamber is attached to several other process chambers and an analysis chamber equipped with an XPS/UPS photoemission spectrometer. The chamber lay-out and a photograph of the system is shown in figure 8.18. With this multi-chamber configuration we can quickly deposit new materials and analyze them *in-situ.*
Figure 8.16 – Top, side and bottom views of the transfer-arm evaporator, with approximate dimensions indicated.\textsuperscript{154}

Figure 8.17 – Illustration of a deposition system, which includes the transfer-arm evaporator and load lock.\textsuperscript{154}
8.5.3 Operation and performance

In order to perform a deposition, a small amount of the evaporation material is loaded into a crucible and placed into the tungsten heater through the quick-load door. The loading chamber is then pumped-down for two hours before opening to the main deposition chamber. The main deposition chamber has a base pressure of $\sim 10^{-9}$ torr. Once open to the load-lock, which has been pumped for only 2 hours, the pressure in the deposition chamber rises to only $\sim 10^{-8}$ torr, and slowly returns to the base pressure. The transfer-arm evaporator is then extended into the deposition chamber and de-gassed for several hours by passing a mild current through the evaporator. Once the materials are adequately de-gassed, and the desired pressure has been reached, the deposition can take place. Generally about four hours after initially loading in the material it can be deposited.

By extending the transfer arm, the evaporator is positioned directly below the sample, and the current is increased until the desired deposition rate is achieved. Typically around 30 A is needed to achieve deposition rates of $\sim 0.3$ Å/s for the present evaporator, for molecules that sublime at 250°C, however very high deposition rates of 10 Å/s have also be achieved using higher currents.

After the molecular film has been deposited the sample can be moved to the analysis chamber without ever being exposed to atmosphere. This point is essential for good quality UPS spectra, since UPS is extremely surface sensitive, and exposure to atmosphere will result in the
adsorption of a few monolayers of atmospheric gases, which can alter the work function and valence positions as well as bury the UPS signal of the material of interest.\textsuperscript{147}

An example UPS spectrum of a common organic material, \(\alpha\)-NPD, which was deposited from the transfer arm evaporator, is shown in figure 8.19. For comparison, a UPS spectrum using a thoroughly de-gassed Knudsen cell is also shown. One can see that the two spectra are identical, showing that the transfer-arm design can perform just as well as a high-end Knudsen cell for this type of application.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure819.png}
\caption{Comparison of UPS spectra of \(\alpha\)-NPD thin films evaporated from a high-end Knudsen cell and the transfer-arm evaporator.\textsuperscript{154}}
\end{figure}
References


134. Irradiance was calculated using photocurrents of 20 nA for UPS and 1 nA for XPS, and irradiated areas of 40 mm².

135. Note that the majority of the photon energy is absorbed by the sample, and not carried away by the photoelectrons. This is apparent when one considers that the majority of the photo-current arises from secondary electrons (i.e. photo-electrons which have transferred most of their energy to the sample via inelastic collisions).


8.6 List of Academic Contributions


**Conference Presentations**


*Oral presentation*: “Band alignment and charge injection at metal oxides and organic interfaces” SPIE Photonics Devices and Applications, San Diego, California, USA, August 2, 2010. (Presenter)