Dipole Engineering for Conducting Polymers

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A DISSERTATION
PRESENTEED TO THE FACULTY
OF PRINCETON UNIVERSITY
IN CANDIDACY FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY

RECOMMENDED FOR ACCEPTANCE
BY THE DEPARTMENT OF CHEMISTRY

ADVISOR: PROFESSOR JEFFREY SCHWARTZ

September 2014
Abstract

A method for the growth of a TiO₂ adhesion layer on PEDOT:PSS (poly[3,4-ethylenedioxythiophene]: poly[styrenesulfonate]) and for further functionalization with self-assembled monolayers of phosphonates (SAMPs) was developed. The TiO₂ adhesion layer was grown via chemical vapor deposition using a titanium(IV) t-butoxide precursor, and was characterized by goniometry and X-ray photoelectron spectroscopy. TiO₂ grown on a model system, H-terminated silicon, indicated that the surface was t-butoxide terminated. Phenylphosphonic acids were synthesized with a variety of molecular dipoles and were used to change the work function of PEDOT:PSS through the formation of an aggregate surface dipole. Good correlation was found between the z-component of the molecular dipole and the change in work function, indicating that the film was well-ordered and dense. The magnitude of the changes in work function and goniometry measurements were similar to measurements on ITO, a substrate on which phosphonates form well-ordered monolayers. As-grown PEDOT:PSS/TiO₂ electrodes showed a lower work function compared to PEDOT:PSS, which is attributed to residual t-butoxide groups on the TiO₂ surface. UPS measurements revealed that reductions in work function in the modified electrodes lowered the difference in energy between the Fermi energy (E_F) of the conducting polymer and the LUMO of PCBM ([6,6]-phenyl-C₆₁-butyric acid methyl ester). A reduction of this energy difference should translate into increased electron injection in electron-only diodes; however, devices with modified electrodes showed decreased current densities. UPS/IPES measurements show that TiO₂ grown using this method has a much larger band gap than bulk or nanocrystalline TiO₂, which is likely responsible for this decrease in device currents. At high bias, device currents increase dramatically, and the effects of the phosphonates or t-butoxide terminated TiO₂ vanish. This is attributed to a reduction of the TiO₂
to conducting TiO$_{2-x}$ and the phosphonates to non-binding phosphinates, which is facilitated by the acidic protons in PEDOT:PSS.
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<th>Meaning</th>
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<tr>
<td>OLED</td>
<td>Organic light-emitting diode</td>
</tr>
<tr>
<td>HTL</td>
<td>Hole-transport layer</td>
</tr>
<tr>
<td>ETL</td>
<td>Electron-transport layer</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>E_F</td>
<td>Fermi energy</td>
</tr>
<tr>
<td>E_g</td>
<td>Band gap</td>
</tr>
<tr>
<td>Φ</td>
<td>Work function</td>
</tr>
<tr>
<td>α-NPD</td>
<td>(N,N'-\text{Bis(naphthalen-1-yl)}-N,N'-\text{bis(phenyl)benzidine})</td>
</tr>
<tr>
<td>Alq_3</td>
<td>(\text{Tris}(8\text{-hydroxyquinolinato})\text{aluminium})</td>
</tr>
<tr>
<td>PTCDA</td>
<td>Perylene-3,4,9,10-tetracarboxylic dianhydride</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-assembled monolayer</td>
</tr>
<tr>
<td>SAMP</td>
<td>Self-assembled monolayer of phosphonates</td>
</tr>
<tr>
<td>T-BAG</td>
<td>Tethering by aggregation and growth</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>UPS</td>
<td>Ultraviolet photoelectron spectroscopy</td>
</tr>
<tr>
<td>IPES</td>
<td>Inverse photoelectron spectroscopy</td>
</tr>
<tr>
<td>PEDOT</td>
<td>Poly[3,4-ethylenedioxythiophene]</td>
</tr>
<tr>
<td>PSS</td>
<td>Poly[styrenesulfonate]</td>
</tr>
<tr>
<td>H-Si</td>
<td>Hydrogen-terminated silicon</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>MEH-PPV</td>
<td>Poly[2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene]</td>
</tr>
<tr>
<td>PCBM</td>
<td>[6,6]-\text{Phenyl-C}_6\text{1}-butyric acid methyl ester</td>
</tr>
<tr>
<td>J-V</td>
<td>Current-voltage</td>
</tr>
<tr>
<td>F-N</td>
<td>Fowler-Nordheim</td>
</tr>
<tr>
<td>SCLC</td>
<td>Space-charge limited current</td>
</tr>
</tbody>
</table>
Acknowledgments

I’d like to acknowledge everyone I’ve worked with over these past five years. In particular, I’d like to acknowledge Prof. Jeffrey Schwartz for being a great advisor, teacher, and mentor. Jeff has provided me with many opportunities to collaborate with others, and this interdisciplinary experience has been truly enriching.

I’d like to thank all the members of the Schwartz, Bernasek, and Bocarsly labs, including Steve Bandini, Esther Frederick, Steve Wulfsburg, Liz Bailey, Matt Frith, Matt Vallon, Colleen Richardson, Girija Sahasrabudhe, Zach Detweiler, Sean Edington, Aahana Ganguly, Travis Shaw, and Jake Herb (the last two being honorary group members). I’d especially like to thank Pat Donnelly and Conor Thomas, with whom I worked the most closely. It was nice to have people to bounce ideas back and forth with, especially when the ideas weren’t related to chemistry.

I’ve had many wonderful opportunities to collaborate with other groups during my time at Princeton. In particular, I would like to acknowledge Prof. Sturm, Prof. Wagner, Sushobhan Avasthi, Gabriel Man, Janam Jhaveri, and Ken Nagamatsu. It was a pleasure working with all of you on the DOE Sunshot Project. I’ve had a lot of fruitful collaboration with Prof. Kahn and Andrew Shu, who have both helped me tremendously with my project, for which I am thankful. I’d also like to thank Prof. Loo and Luisa Whittaker-Brooks; it was great collaborating with them. I’m especially indebted to Prof. Loo for finishing her reader’s report on such short notice.

I would like to thank my family. My mom and dad have always been there when I needed someone to talk to, and provided me with a lot of advice. I’d like to thank my brothers, Mike and Jim, who are also in graduate school for chemistry. It’s nice having brothers with whom you can
talk about your work, practice talks, and hang out. I’d also like to thank June Yeung and Ziggy for being with me these past three years. You’ve both been wonderful, and helped me through when things were rough.
Chapter 1

Introduction:

A Method for Controlling Organic/Organic Energy Level Alignment
Energy Level Alignment in Electronic Devices

There has been much interest in the past decade in organic electronic devices for a variety of applications, including thin-film transistors, photovoltaics, and optoelectronic devices. In these devices, π-conjugated organic small molecules or polymers act as the active semiconductor, in contrast to traditional inorganic semiconductors such as silicon, GaAs, and metal oxides. There are several purported advantages of organic electronics including low-cost processing using spin-coating, roll-to-roll fabrication, or inkjet printing, the ability to scale processing to large area devices easily, and the possibility of manufacturing thin, flexible devices.

Inorganic semiconductors can be extrinsically doped to increase the concentration of electrons in the conduction band (n-type) or of holes in the valence band (p-type). Often, the same semiconductor can be doped n-type and p-type, and a device can be made using this single semiconductor material; in this case, the junctions between n- and p-type regions are called homojunctions. Unlike inorganic semiconductors, organic semiconductors are typically undoped, and, moreover, typically exhibit desirable charge-transport properties for one charge carrier type (electrons or holes). As a result, homojunctions are not typically employed in organic optoelectronic devices; instead, heterojunctions between two organic semiconductors are used. Usually, one semiconductor allows the conduction of electrons through its lowest unoccupied molecular orbitals (LUMO); this material is called the electron transport layer (ETL). Meanwhile, another allows the transport of holes through its highest occupied molecular orbitals (HOMO); this material acts as the hole transport layer (HTL). Whether a material preferentially transports holes or electrons depends on the HOMO and LUMO energy levels of that material relative to the Fermi energy ($E_F$) of the device electrodes. Devices such as organic light-emitting
diodes (OLEDs) may also employ a third semiconductor that serves as the emissive layer (EL), which is an organic semiconductor layer where electrons and holes radiatively recombine. An example of the working principle of an OLED using an emissive layer is in Figure 1.

**Figure 1:** Working principle of an OLED under applied bias (ΔV). Holes are injected from the anode (left) into the HOMO of the HTL (green). Holes are transferred from the HOMO of the HTL to the HOMO of the EL (blue). Meanwhile, electrons are injected from the cathode (right) into the LUMO of the ETL (red). From there, electrons are transferred to the LUMO of the EL. Electrons and holes in the EL can recombine, giving off radiation. Differences in the HOMO energies inhibit hole transfer from the EL to the ETL, and electron transfer from the EL to the HTL (red arrows).

Much research has gone into understanding charge transport and efficiency in organic electronic devices, and a key finding is that the relative energies of the HOMO, LUMO, and Fermi energy of the device electrodes have large impacts on device performance.\(^1\) In order to develop efficient devices, it is advantageous to be able to manipulate \(E_F\) and the organic semiconductor HOMO and LUMO energies relative to each other in order to avoid the problems that undesirable energy level alignment can cause, such as potential barriers that inhibit desired charge transfer or result in undesired charge transfer between materials.
Figure 2: Left: A potential barrier between $E_F$ of an electrode and the HOMO of the organic semiconductor can inhibit hole injection into the semiconductor. Right: A potential barrier between $E_F$ of an electrode and the LUMO of the organic semiconductor can inhibit electron injection.

The HOMO and LUMO are measured experimentally using photoelectron (PE) spectroscopy. Ultraviolet photoelectron spectroscopy (UPS) allows quantification of the HOMO energies relative to $E_F$, while inverse photoelectron spectroscopy (IPES) allows quantification of LUMO energies. In the case of organic/organic interfaces, PE spectroscopy is used to determine the relative differences in the HOMO and LUMO energies of the two organic semiconductors. To determine the relative positions of these energy levels, PE spectra of the substrate (electrode or semiconductor) are taken and compared to PE spectra after depositing the organic semiconductor. The HOMO-$E_F$ and LUMO-$E_F$ energy difference can be calculated using the relative energies of the HOMO and LUMO peaks. Analogously, the relative HOMO and LUMO energies of two organic semiconductors can be determined by comparison of two PE spectra.

The use of UPS for determining the energetics of organic electronic devices is as follows. Ultraviolet radiation with a fixed energy is used to ionize the occupied molecular orbitals of the sample, freeing electrons, which travel to the detector. At the detector, the electron kinetic energy ($E_{kin}$) is measured. The detector and sample share a common ground (Figure 3), so electrons *en route* to the detector gain or lose kinetic equal to the differences in the work
function of the sample and the detector. The work function (Φ) is the difference between the Fermi energy and the vacuum energy; the vacuum energy (E_{vac}) corresponds to the energy of a free electron with no kinetic energy. The measured kinetic energies are translated into binding energies using Equation (1), which states that E_{kin} is equal to the energy of the ionizing radiation (hν) minus the binding energy (E_B), plus the energy gained or lost due to the difference in work functions between the sample and detector (Φ_s – Φ_{detector}). The binding energy is typically reported as the energy relative to E_F, which is simply Φ_s - E_B. The work function of the detector is determined using a standard with a known work function, typically a sputtered metal such as Au or Ag. Observation of the Fermi edge (E_B = Φ_s) allows the calculation of Φ_{detector}, which is assumed to be constant for subsequent measurements. An example calibrated UPS spectra is shown in Figure 4. Φ_s can be calculated using the cutoff of the secondary electron tail; this tail results from scattered electrons with near-zero kinetic energy, and the cutoff is the extrapolation to E_{kin} = 0. The ionization potential (IP) of the organic is the difference between the HOMO and E_{vac}, and can be determined from the HOMO onset. The barrier for hole injection into the organic is simply the energy of the HOMO onset with respect to E_F; barriers for electron injection are determined from UPS spectra using the difference in HOMO-LUMO energies of the semiconductor or using IPES.

\[ E_{\text{kin}} = h\nu - E_B + \Phi_{\text{sample}} - \Phi_{\text{detector}} \]  \hspace{1cm} (1)
Figure 3: Illustration of a metal/organic sample in electrical contact with the detector, showing the difference in the $E_{\text{vac}}$.

Figure 4: An example UPS spectrum, showing the secondary electron cutoff, HOMO, and determination of $\Phi$ and the IP of the organic.

Some general trends on the energy level alignment of metal/organic interfaces have been established from PE spectroscopy studies. When $E_F$ of the electrode is higher in energy (closer to $E_{\text{vac}}$, “higher” here refers to a less negative potential energy) than the LUMO or lower in energy than the HOMO of the organic semiconductor, there is electron transfer to the LUMO or hole transfer to the HOMO of the organic semiconductor, respectively. This charge transfer results in an electric field and a corresponding change in the relative energies of $E_F$ and the HOMO and LUMO energies. The end result is $E_F$ is “pinned” near the HOMO or LUMO.
When \( E_F \) is between the HOMO and LUMO, there is essentially no charge transfer to/from the organic for undoped semiconductors, although rigid shifts of the HOMO and LUMO relative to \( E_F \) are often observed. In most cases, the \( E_F \)-HOMO/LUMO energy difference typically asymptotes after a very thin layer (10 Å) of the organic semiconductor is deposited; the relative energies do not change with additional deposition of material, suggesting that this is a purely interfacial effect. Metal/organic interfaces commonly show large reductions of the effective work function of the electrode (~1 eV). This is attributed a suppression of the metal electron density that normally extends into free space by the organic semiconductor, and is often referred to as the “pillow effect.” By contrast, organic/organic interfaces typically exhibit small, but not negligible, shifts in energy level alignments (< ±0.1 eV). This shift is more pronounced (±0.3eV) when combining strong electron donors and acceptors, which is attributed to polarization, or, in some cases, charge transfer between compounds.

The difference in mechanisms of energy level alignment at organic/organic and metal/organic interfaces often explains differences in device performance. For example, organics deposited on the conducting polymer PEDOT:PSS (poly[3,4-ethylenedioxythiophene]: poly[styrenesulfonate]) show small increases and decreases in the effective work function (±0.3 eV) compared to the reductions in work function observed with metal electrodes. While PEDOT:PSS and gold have similar work functions, simple diodes made using the HTL material \( \alpha \)-NPD \( (N,N'\text{-Bis(naphthalen-1-yl)}-N,N'\text{-bis(phenyl)}\text{benzidine}) \) show current densities four orders of magnitude greater using PEDOT:PSS vs. Au electrodes due to this pillow effect (Figure 5).
Figure 5: Left: The pillow effect results in an energy-level mismatch between $E_F$ of an Au electrode (gold) and the HOMO of the HTL (green). This results in a barrier to hole injection ($E_b$). Right: The use of PEDOT:PSS (blue) eliminates the pillow effect and decreases the barrier to hole injection.

In addition to polarization, relative changes in energy alignment can result from chemical reactions at the surface, reduction or oxidation of the surface, including free-radical formation, and the introduction of molecules with a permanent molecular dipole. A dipole is the separation of charge across some distance. This separation of charge results in an electric field; Integrating this electric field over distance yields a change in electrical potential energy across the molecule, which results in a rigid shift of the relative energies.

Controlling Energy Level Alignment

Common methods for improving energy level alignment at metal/organic and/or inorganic/organic interfaces includes substituting or developing new organics/inorganic semiconductors and using different metals. Another well-explored method for the modification of energy level alignment is the introduction of oriented, permanent dipole between the metal electrode and the device active layer.\(^5\) The introduction of dipoles is accomplished by physisorption or chemisorption of molecules with permanent dipoles, or by chemisorption of strongly electron-donating or electron-accepting materials on the electrode surface. The chemisorption of molecules with a permanent dipole is typically accomplished using a functional
group that reacts preferentially with the surface, forming a covalent bond. This can lead to monolayer formation via self-assembly. The formation of a SAM with permanent, oriented dipoles results in a change in the electrode work function ($\Delta \Phi$); the magnitude of this change is given by Equation (2), and is a function of the $z$-components of the SAM molecular dipole ($\mu_{z,\text{SAM}}$), the induced dipole ($\mu_{z,i}$), the surface loading ($N$), and the dielectric constant of the SAM and the induced dipole ($\varepsilon_{\text{SAM}}$, $\varepsilon_i$). Self-assembled monolayers can reduce the barriers to charge carrier injection, as shown in Figure 6.

$$\Delta \Phi = N \left( \frac{\mu_{z,\text{SAM}}}{\varepsilon_0 \varepsilon_{\text{SAM}}} + \frac{\mu_{z,i}}{\varepsilon_0 \varepsilon_i} \right)$$

Figure 6: Modifying energy level alignment using dipoles. Center: an unmodified electrode, with a work function $\Phi$. Left: the barrier to hole injection (red) can be reduced by increasing the effective electrode work function ($\Phi_{\text{eff}}$). Right: the barrier to electron injection (red) from the electrode can be lowered by reducing the effective work function.

*SAMS of disulfides/thiols on gold*

The formation of self-assembled, covalently-bound monolayers has been well-studied using disulfides and thiols on gold and silver surfaces. Samples have been characterized by electron energy loss spectroscopy (EELS), infrared (IR) spectroscopy, cyclic voltammetry (CV). The effect of the monolayer on the work function of Au and Ag has also been
studied. A thorough comparison of thiols on Au and Ag determined the induced dipole of the S-Au bond is similar to noninteracting adsorbates (e.g. Xe), while S-Ag bond formation results in a 0.9 eV increase in the work function relative to the clean substrates. Au/SAM electrodes have been used to improve carrier injection in devices such as diodes and thin-film transistors (TFTs) through choice of the tail-group functionality.

**SAMs of Phosphonates (SAMPs)**

Much work has focused on metal oxides, which are used as transparent conducting electrodes (e.g. ITO) or as dielectrics or active layers in TFTs. SAMPs have been formed and characterized on a variety of metal oxides including mica, TiO$_2$, ZrO$_2$, Al$_2$O$_3$, the native oxide of titanium, SiO$_2$, and ITO. Infrared spectroscopy and XPS have been used to study binding modes of the phosphonate, and it has been determined that a bidentate or tridentate binding mode is observed on most surfaces. The orientation of SAMPs relative to the surface has been studied using *in situ* and *ex situ* AFM. Tilt angle was determined by comparing the observed AFM thickness to the molecular thickness: The alkyl chain tilt angle varies with Lewis acidity of the metal oxide, and typically ranges from 20-40° from the surface normal across a variety of metal oxides. QCM has been used to directly measure the surface loading, which is typically in the range of 0.3-1 nmol/cm$^2$. SAMPs with permanent dipoles have been studied for use in optoelectronic devices: SAMPs on ITO have been shown to improve carrier injection in OLEDs, while SAMPs on TFT dielectrics result in threshold voltage shifts; the mechanism by which this change occurs is likely change of the effective gate work function.
Using an Organometallic Metal Complex or an Adhesion Layer

As discussed in the previous section, there are many well-developed methods for controlling energy level alignment at metal/organic and inorganic/organic interfaces. However, controlling energy level alignment at the organic/organic interface remains a challenge. One approach includes doping of organic semiconductors through the use of extrinsic dopants or irradiation.\textsuperscript{6,32,33} For this work, self-assembled monolayers were explored as a means to systematically modify energy level alignment of the organic/organic interface. Based on previous work in this group, it was proposed that an organometallic complex or a thin film of metal oxide could bind to ligating groups at the surface of organic semiconductors and serve as an adhesion layer to allow the subsequent attachment of phosphonic acids.\textsuperscript{34-36} It was hypothesized that organometallic complexes or thin (~1 nm) metal oxide films would not have a deleterious effect on device performance due to their thinness; previous work in this group has demonstrated that organometallic complexes on ITO allowed improvement of device performance.\textsuperscript{37}

PEDOT:PSS was chosen as a model organic semiconductor for this work. Earlier, it was noted that PEDOT:PSS/organic interfaces show energy level alignment similar to other organic/organic interfaces.\textsuperscript{3} Because PEDOT:PSS is highly-doped, it can be used as an electrode in electronic devices. This allows the fabrication of simple PEDOT:PSS/organic semiconductor/metal devices, instead of more complicated heterojunction devices with two active organic semiconductors. Concurrently, ITO was studied as a model system in order to allow comparison of SAMP-derivatized PEDOT:PSS interfaces to a surface on which SAMP formation and use in organic electronic devices is well-studied.\textsuperscript{24,25,38}
References Cited


Chapter 2

Thin-Film Growth and Functionalization
Formation of Metal Oxide Complexes on Metal Oxide and Polymer Surfaces

Extensive research in the Schwartz group has examined the formation of zirconium and tin complexes on metal oxide surfaces. The hydroxyl content of the substrate is important to determine stoichiometries of the resulting organometallic complexes, which were measured by X-Ray photoelectron spectroscopy (XPS). For example, exposure of lightly hydroxylated aluminum to Zr(IV) t-butoxide yields the [O]_1 adduct (1) at low temperatures, which decomposes at 30-80 °C to yield ZrO_2. On more heavily hydroxylated aluminum, ligand substitution competes with decomposition and yields the [O]_2 adduct (2), which is stable up to ~150 °C, at which temperature it decomposes to yield ZrO_2.\(^1\) By contrast, the tin analog on heavily hydroxylated aluminum rapidly yields the [O]_3 adduct at room temperature with reduction to Sn(0) at elevated temperatures.\(^2\) This experiment was also done on the titanium native oxide surface, which is not easily hydroxylated.\(^3\) The [O]_1 adducts (1) were obtained for Zr(IV) an Sn(IV) t-butoxide, and the [O]_1 Sn adduct could be heated to give the [O]_2 (2) and [O]_3 (3) adducts.

![Scheme 1: Reaction of Zr(IV) t-butoxide on a hydroxylated aluminum surface. Lightly hydroxylated surfaces yield the [O]_1 adduct (1), while heavily-hydroxylated surface yield stable [O]_2 adduct (2) at room temperature.](image-url)
Scheme 2: Reaction of Zr(IV) \( t \)-butoxide with a lightly-hydroxylated aluminum surface, which thermalizes at low temperatures (30-80 °C) to form ZrO₂.

Scheme 3: Reaction of Sn(IV) \( t \)-butoxide with a fully-hydroxylated aluminum surface. Decomposition of the ligand gives an Sn-OH bond, which can react with the metal oxide surface, yielding the [O]₃ adduct.

The [O]₂ and [O]₃ Sn and Zr adducts could be exposed to phenols, hydroxyquinolines, phenylacetylenes, carboxylates, and phosphonates to yield coordination complexes (Scheme 4).\(^7\) Phenols were used both to quantify the stoichiometry of the Zr and Sn adducts using XPS and to introduce functionality for electronic devices. For the latter, Zn and Sn phenol complexes were used to improve the electronic properties of indium tin oxide (ITO) for optoelectronic devices.\(^8,9\) Ferrocene-containing carboxylic acids were attached to a proposed [O]₂ Zr adduct on the surface of ITO (Scheme 5). The surface loading was determined by chronocoulometry to be 0.1 nmol/cm² of the ferrocene-carboxylate, implying a surface loading of the zirconium complex of
0.05 nmol/cm\(^2\); this surface loading is comparable to ferrocene-carboxylates on ITO attached by other methods.\(^5\)

Scheme 4: Exposure of the \textit{bis}-alkoxide Zr(IV) complex with phenol results in formation of the \textit{bis}-phenolate.

Scheme 5: Modification of \([\text{O}]_2\) Zr adduct with ferrocene-carboxylic acid to form the ferrocene-carboxylate.

The mechanism of metal-organic complex and metal oxide formation was also studied. The kinetic isotope effect was measured with Zr(IV) \(t\)-butoxide on hydroxylated and deuteroyxylated Al and Si surfaces; the rate of mass addition over time was measured by quartz crystal microbalances (QCMs), and was an order of magnitude faster for Zr(IV) \(t\)-butoxide than for tetraneopentylzirconium. The kinetic isotope effect for Zr(IV) \(t\)-butoxide (\(k_H/k_D = 1.7\) for Al, \(k_H/k_D = 1.5\) for Si) was small compared to that observed for tetraneopentylzirconium (\(k_H/k_D = 8.4\) for Al, \(k_H/k_D = 5.3\) for Si).\(^10\) The smaller kinetic isotope effect observed with Zr(IV) \(t\)-butoxide was either due to the observation of a secondary isotope effect, in which coordination of Zr(IV) \(t\)-butoxide was rate limiting, or a rate of desorption of the alkoxide species from the
surface that was comparable to the rate of proton transfer (Scheme 6). For tetraneopentylzirconium, proton transfer is kinetically unfavorable due to a lack of ligand lone pairs, which results in the larger kinetic isotope effect. Temperature-programmed desorption, mass spectrometry, and XPS were used determine the stoichiometry and oxidation states of the Sn and Zr t-butoxide complexes and detect the decomposition products.\textsuperscript{1-3,11} Mass spectrometry revealed that in addition to the presence of t-butanol, \textit{iso}-butylene was also formed as a major product. This suggests that the alkoxide ligands decompose \textit{via} $\beta$-hydride elimination (Scheme 7). $\beta$-Hydride elimination results in a hydroxyl group on the organometallic complex that can coordinate to further metal alkoxides or react with other hydroxyls to eliminate water and form a bridging oxygen bond, resulting in the formation of ZrO$_2$.

\begin{center}
\textbf{Scheme 6:} Proposed mechanism for coordination of Zr(IV) t-butoxide species to a hydroxylated surface and ligand loss.
\end{center}

\begin{center}
\textbf{Scheme 7:} Thermolysis of Zr(IV) t-butoxide \textit{via} $\beta$-hydride elimination, resulting in the release of \textit{iso}-butylene and the formation of ZrO$_2$.
\end{center}
Functional groups in polymers that can serve as ligating groups to the Lewis acidic organometallic complexes were found to coordinate to the metal center of Zr(IV) \( t \)-butoxide, allowing functionalization of polyketones with ZrO\(_2\), and polyamides, and polyurethanes with organometallic complexes.\(^{12-14}\) The metal oxide layer thickness is a function of the surface’s exposure time to the precursor, and has been characterized by XPS, QCM, and SEM. This metal oxide can serve as an adhesion layer that allows the formation of a self-assembled monolayer of phosphonates, which has been used for alignment of cells on silicon, glass, and polymer surfaces.\(^{15,16}\)

**Choice of Metal Oxide for this Work**

For this work, charge transport through the metal oxide layer will depend on the thickness of the metal oxide adhesion layer as well as the position of the metal oxide conduction band/valence band relative to the PEDOT:PSS work function. Many metal oxides are insulating; the large band gaps would most likely result in large \( E_F \)-HOMO and \( E_F \)-LUMO offsets that would inhibit charge transfer. The formation of Zr(IV) \( t \)-butoxide complexes has been accomplished under UHV with controlled dosing. Under “normal” conditions employed for rapid fabrication of samples, Donnelly showed that exposure of SiO\(_2\) surfaces to Zr(IV) \( t \)-butoxide resulted in the formation of thick films (5- 50 nm).\(^{17}\) The difficult control of film thickness when using Zr(IV) \( t \)-butoxide seems to preclude its use in organic electronic devices, as tunneling is thickness dependent. Moreover, the insulating nature of ZrO\(_2\) could be detrimental to device performance, as there are large offsets between \( E_F \) of PEDOT:PSS and both the valence and conduction band of ZrO\(_2\) (Figure 7).\(^{18}\) SnO\(_2\) films or Sn(IV) organometallic species formed using Sn(IV) \( t \)-butoxide are another possibility. SnO\(_2\) has a smaller band gap, which leads to more favorable energy level alignment. The band alignment of TiO\(_2\) suggests that tunneling of
electrodes through the adhesion layer into a device would not limit device performance.\textsuperscript{19} PEDOT:PSS has a large work function (5.1 eV), and is generally used for hole injection. The possibility to use thin, transparent PEDOT:PSS films with a TiO\(_2\) adhesion layer for electron injection is advantageous, as there are very few transparent conducting electron-injecting materials.

![Band alignments of TiO\(_2\), SnO\(_2\), and ZrO\(_2\) with PEDOT:PSS.](image)

**Figure 7:** Band alignments of TiO\(_2\), SnO\(_2\), and ZrO\(_2\) with PEDOT:PSS.

While Ti(IV) t-butoxide has previously been used by members of this group for growth of multi-layer systems with bisphosphonic acids,\textsuperscript{20} no work on polymer surfaces has henceforth been demonstrated. The following chapter focuses on the development of a procedure for the growth of TiO\(_2\) on PEDOT:PSS and characterization of the resulting surface.
References Cited


Chapter 3

Growth of Thin, Conformal TiO$_2$ Films on PEDOT:PSS Substrates:

Comparison to Si Substrates
TiO₂ Growth on PEDOT:PSS

Previous studies using Zr(Ot-Bu)_4 for chemical vapor deposition showed that the organometallic species decomposed at low temperatures (∼30° C) to give either a surface alkoxide-containing species or ZrO₂ with minimal residual carbon-containing species.¹⁻⁵ This was initially demonstrated on aluminum, titanium, and ITO surfaces, and was eventually translated to polymer substrates that contained ligating groups (e.g. polyketones, polyurethanes, and polyamides) that could coordinate to the metal center in the alkoxide precursor.⁶⁻⁸

For this work, it was hypothesized that PEDOT:PSS could serve as an appropriate substrate for analogous metal oxide growth as it contains ether functional groups. Initial studies using the Ti(IV) analog and the same experimental procedure did not lead to any evidence of a surface-bound titanium species or TiO₂. Since the Ti(IV) alkoxide is smaller than its Zr(IV) analog, it is possible that steric congestion around the metal center could limit coordination with the ligating groups, leading to a low binding probability. It was proposed that cooling the substrates would lead to condensation of the precursor on the surface, promoting coordination of the alkoxide to the ligating groups. Cooling the samples to -10° C proved successful, and XPS spectra unambiguously confirmed the presence of titanium, sulfur, oxygen and carbon. Because the inelastic mean free path of electrons is on the order of nanometers, the presence of sulfur suggests a film thickness of the order of the inelastic mean free path.⁹

XPS spectra were taken of multiple samples prepared simultaneously in order to determine whether the TiO₂ film coverage was uniform over multiple samples. Because of the deposition chamber design, it is possible that a pressure gradient or temperature gradient could result in uneven deposition. In order to determine whether this occurred, a sample at the precursor side of the chamber was compared to a sample at the vacuum side of the chamber.
each sample, the ratio of S(2p) peak area was compared to the Ti(2p) peak area; the ratio was corrected for the atomic relative sensitivity factor (RSF). As this ratio gives information about the thickness of the TiO$_2$ layer, comparison between samples makes it possible to ascertain whether a thickness gradient is present. Initial tests revealed that a gradient was present (Table 1), and it was speculated that this temperature gradient was responsible for influencing the rate of precursor condensation; on one end, condensation would readily occur, while on the other end, condensation would not occur. As a result, there would be different TiO$_2$ thicknesses along the temperature gradient. The difference in peak ratios between the samples was reduced significantly by replacing the glass slide sample holder with a 1/8 in. piece of copper metal, which presumably reduced temperature variation among the samples (Table 1).

**Figure 8:** PEDOT:PSS/TiO$_2$ XPS survey, showing unambiguous presence of titanium, oxygen, carbon, and sulfur.
Table 1: PEDOT:PSS/TiO2 Ti(2p)/S(2p) peak area ratios, RSF corrected. The average and standard deviation of this ratio for the vacuum and precursor side samples are shown.

<table>
<thead>
<tr>
<th></th>
<th>Vacuum side</th>
<th>Precursor side</th>
<th>Avg.</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass slide</td>
<td>0.38</td>
<td>0.72</td>
<td>0.6</td>
<td>0.2</td>
</tr>
<tr>
<td>Copper</td>
<td>2.1</td>
<td>2.2</td>
<td>2.15</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The Ti(2p) XPS region of PEDOT:PSS/TiO2 (Figure 9, left) shows Ti(2p\textsubscript{1/2}) and Ti(2p\textsubscript{3/2}) peaks at binding energies of 464.8 and 458.9 eV, respectively. The binding energies and spin-orbit splitting of 5.7 eV indicate that Ti is present in the +4 oxidation state. This oxidation state remains unchanged from the precursor, which is expected based on the proposed mechanism of oxide growth. It is difficult to establish whether this is stoichiometric TiO\textsubscript{2} (as opposed to a species containing residual alkoxides), because background oxygen and carbon from the polymer support make quantification difficult. Compared to the XPS of pristine PEDOT:PSS samples, the S(2p) peak is attenuated by a large factor, and attenuation increases with increasing exposure time. Both these observations suggest that the thickness of the Ti-containing film is much more than a monolayer. It was hypothesized that if residual t-butoxide groups were present, they would inhibit coordination of further alkoxides, limiting the film thickness to a monolayer. Combined with previous observations by members in this group that the Zr(IV) t-butoxide can decompose fully to ZrO\textsubscript{2} on some substrates, the Ti(2p) peaks were tentatively attributed to TiO\textsubscript{2}.\textsuperscript{2-4}
**Figure 9:** PEDOT:PSS/TiO$_2$ Ti(2p) region (left) and S(2p) region (right). The Ti(2p$_{3/2}$) and Ti(2p$_{1/2}$) peaks indicate Ti is in the +4 oxidation state. Deconvolution of the S(2p) region shows S(2p$_{3/2}$) and S(2p$_{1/2}$) peaks for the PEDOT and PSS polymers.

The S(2p) region contains two distinct peaks that are easily deconvoluted into doublets (Figure 9, right): a low binding energy doublet with (2p$_{3/2}$) and (2p$_{1/2}$) peaks at binding energies of 163.7 and 165.2 eV, and a high binding energy doublet with (2p$_{3/2}$) and (2p$_{1/2}$) peaks at binding energies at 167.9 and 169.3 eV.$^{10}$ The lower binding energy doublet is assigned to the sulfur in the thiophene rings in the PEDOT copolymer, and the higher binding energy doublet is assigned to the oxidized sulfur in the sulfonic acid functional groups in the PSS copolymer. The absolute binding energies and spin-orbit splittings are in good agreement with literature values for PEDOT:PSS.$^{10}$

Since PEDOT:PSS consists of PEDOT and PSS domains at the surface, it is conceivable that TiO$_2$ could preferentially bind to one domain. The two PEDOT and PSS peaks are easily differentiated, so PEDOT to PSS S(2p) ratios can be examined as a function of TiO$_2$ thickness to determine whether preferential binding occurs. If it did occur, the PEDOT to PSS S(2p) ratio
would change with increasing thicknesses of TiO$_2$, as either the PEDOT or PSS S(2p) signal will be selectively attenuated by the titanium dioxide overlayer. However, the ratio remains essentially constant for varying thicknesses of titanium dioxide (Figure 10), suggesting that TiO$_2$ growth on PEDOT and PSS domains occurs at the same rate.

![Graph](image)

**Figure 10:** Comparison of Ti(2p)/PEDOT S(2p) and Ti(2p)/PSS S(2p) RSF-corrected area ratios. The red line corresponds to a PEDOT/PSS S(2p) ratio of pristine PEDOT:PSS. As the Ti(2p) peak area increases, the PEDOT/PSS S(2p) stays close to the ratio of pristine PEDOT:PSS, suggesting even coverage of both domains.

This analysis does not answer the question of whether the titanium dioxide overlayer covers the domains *fully*. AFM was used to compare the morphologies of the pristine PEDOT:PSS and PEDOT:PSS/TiO$_2$ (Figure 11, Figure 12). If TiO$_2$ growth fully covered the polymer domains, the AFM phase would remain essentially constant across the PEDOT:PSS/TiO$_2$ surface, as the overlayer should be homogenous. The phase image PEDOT:PSS contains distinct bright and dark domains, which have been attributed to PSS and PEDOT domains by Crispin, *et al.*$^{10}$ The phase image of PEDOT:PSS/TiO$_2$ samples do not show
this phase segregation. Quantitatively, this difference in phase distributions is reflected in RMS phase deviations, which are 2° and 1°, respectively. The height image shows no evidence of islanding, and furthermore, the height profiles are similar, with similar RMS height deviations (2 nm for pristine PEDOT:PSS and PEDOT:PSS/TiO$_2$), which suggests that the film does not alter the height morphology of the underlying surface. These combined height and phase data suggest that the TiO$_2$ layer is a thin, conformal film that fully covers the underlying PEDOT:PSS.

**Figure 11:** AFM Height (left) and phase (right) images for PEDOT:PSS.

**Figure 12:** AFM height (left) and phase (right) Images for PEDOT:PSS/TiO$_2$. Note the differences in scale for the height image and phase image compared to Figure 11.
**TiO\textsubscript{2} Thickness Quantification**

AFM and XPS data suggest that the TiO\textsubscript{2} overlayer is conformal and covers the entire surface. Based on these assumptions, it is possible to calculate the thickness of the TiO\textsubscript{2} layer using XPS. There are two well-established methods to do this: absolute ratios of a single peak before and after deposition, or the relative ratios of two peaks in a single spectrum.\textsuperscript{11} Calculation of thickness using the absolute ratio compares the intensity of a peak from the pristine sample ($I_{u,\infty}$) to the same peak in a sample with the overlayer grown on top ($I_u$). As the thickness of the overlayer increases, the signal is attenuated according to Equation (3), where $t$ is the overlayer thickness and $\lambda_u$ is the mean free path of the core level electrons from the underlayer in the overlayer, which is a function of electron kinetic energy. The absolute ratio method has a drawback, as it uses measurements from multiple samples, and the total signal depends on chamber pressure, channeltron voltage, and other factors that can vary from measurement to measurement.

$$I_u = I_{u,\infty} \exp\left(-\frac{t}{\lambda_u}\right)$$  \hspace{1cm} (3)

The relative ratio method compares the peak intensity of an underlayer to an overlayer signal to determine the overlayer thickness. For an overlayer of thickness $t$, the intensity $I_o$, is given by Equation (4), where $\lambda_o$ is the mean free path of the core level electrons of interest from the overlayer in the overlayer. Taking a ratio of the underlayer intensity (3) and the overlayer intensity (4) yields Equation (5). In the case where the core level electrons in the overlayer and overlayer are of similar kinetic energies, and thus have similar mean free paths, this reduces to Equation (6).
\begin{align}
I_0 &= I_{0,\infty} \left[ 1 - \exp\left( -\frac{t}{\lambda_0} \right) \right] \\
\frac{I_0}{I_u} &= \frac{I_{0,\infty}}{I_{u,\infty}} \left[ 1 - \exp\left( -\frac{t}{\lambda_0} \right) \right] \exp\left( \frac{t}{\lambda_u} \right) \\
\frac{I_0}{I_u} &= \frac{I_{0,\infty}}{I_{u,\infty}} \left[ \exp\left( \frac{t}{\lambda_0} \right) - 1 \right]
\end{align}

In order to be able to compare samples without using a pristine PEDOT:PSS standard for each set of measurements, it is possible to determine the thickness using the absolute ratio with a pristine PEDOT:PSS sample and a PEDOT:PSS/TiO$_2$ sample sequentially. From these measurements, it is possible to determine the parameters for the relative ratio measurements and use this to determine the thickness for subsequent samples. Using an experimental inelastic mean free path for electrons from the S(2p) peak in TiO$_2$ of 1.7 $\pm$ 0.1 nm yields a calculated thickness of 0.46 $\pm$ 0.07 nm for a sample using Equation (3).\textsuperscript{12} Using the Ti(2p)/S(2p) RSF-corrected ratio of 0.71 and the calculated thickness for this sample, it is possible to numerically solve for the thicknesses of further samples using relative peak intensity ratios, a literature value for the mean free path of Ti(2p) electrons in TiO$_2$ (1.2 $\pm$ 0.1 nm), and Equation (5).\textsuperscript{12}

**Table 2:** S(2p) and Ti(2p) RSF-corrected peak areas for PEDOT:PSS and PEDOT:PSS/TiO$_2$ samples measured sequentially.

<table>
<thead>
<tr>
<th></th>
<th>S(2p)</th>
<th>Ti(2p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>9.06</td>
<td>-</td>
</tr>
<tr>
<td>PEDOT:PSS/TiO$_2$</td>
<td>6.93</td>
<td>4.94</td>
</tr>
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</table>
**TiO$_2$ Growth on H-terminated Si**

During the course of growing TiO$_2$ on PEDOT:PSS it was observed that exposing the sample to the alkoxide precursor for increasing lengths of time did not give rise to greater thicknesses of the TiO$_2$ as measured by XPS. Instead, TiO$_2$ growth exhibited asymptotic behavior at thicknesses of approximately 1.5 nm. Goniometry measurements for freshly-prepared samples showed a hydrophobic surface ($70^\circ \pm 5^\circ$) when water was used as the liquid; a lower contact-angle would be expected for metal oxides free of hydrocarbons. Because these measurements were performed immediately after film deposition, it was assumed that the surfaces were free of adventitious carbon, which would increase the observed contact-angle. Based on these relatively high contact-angles compared to clean metal oxides, it was hypothesized that an alkoxide-terminated surface was still present. Pore, *et al.*, have used titanium $t$-butoxide alkoxides for atomic layer deposition, in which an alkoxide-terminated intermediate is generated after exposing the surface to alkoxide.$^{13}$ Exposure to water displaces the residual alkoxide and allows the growth of subsequent layers. Unfortunately, background carbon and oxygen signals from PEDOT:PSS make characterization of the C(1s) and O(1s) regions difficult for PEDOT:PSS/TiO$_2$ samples.

In order to ascertain whether any alkoxide species were present, hydrogen-terminated silicon (H-Si) was used as a surrogate substrate, as it would not contain species that would complicate analysis of the C(1s) and O(1s) XPS regions. The use of H-Si as a surrogate relies on the assumption that the mechanism of oxide growth is not governed by the substrate beyond the first layers, and thus if alkoxide were present on the Si/TiO$_2$ sample, it would be present on the PEDOT:PSS/TiO$_2$ sample as well. As with PEDOT:PSS substrates, H-Si substrates were cooled to -10 °C under vacuum ($1\cdot10^{-3}$ torr), then exposed to the precursor for various times. After
exposure, the precursor bulb was closed, and the substrates were annealed at 100 °C for five minutes.

The thickness of the film and index of refraction were determined simultaneously using ellipsometry with a model of a single thin film on silicon, with initial estimates of 3.0 nm for the thickness, 2.85 for the index of refraction, an absorption coefficient of zero for the TiO$_2$ film, and software values for the corresponding absorption coefficients of the silicon substrate. It is important that the initial estimate for the thickness be near the actual thickness because for a given index of refraction and absorption coefficient: The data collected from ellipsometry repeats with periodicity shown in Equation (7). This is not an issue for the TiO$_2$ films as they are very thin (<5 nm), and thus the period always is much greater than the thickness of the films as long as the index of refraction for these films is the same order of magnitude of the bulk films. While deviations from bulk values have been measured in very thin films on silicon, the deviations were not significant enough to complicate this analysis. Thus, bulk values should be an appropriate initial guess. The absorption coefficient of zero is reasonable because the wavelength of the HeNe laser (633 nm) is much smaller than the bandgap of bulk TiO$_2$.

$$T = \frac{\lambda}{2 \sqrt{n^2 - \sin^2 \Phi}}$$

(7)

TiO$_2$ growth also exhibited asymptotic behavior on Si substrates, as determined by ellipsometry and XPS, reaching a maximum thickness after approximately five minutes of Ti(Ot-Bu)$_4$ exposure. In order to ensure asymptotic thicknesses for the subsequent analyses, samples were prepared with an exposure time of 10 minutes.

AFM was used to measure the height and phase morphology of the deposited TiO$_2$ film. Like PEDOT:PSS samples, the height profiles of H-Si and Si/TiO$_2$ were similar, with RMS
roughness of 0.2 nm before and 0.3 nm after deposition. The AFM phase images of H-Si and TiO$_2$ were both smooth, with RMS phases of $1^\circ$. The RMS phase of the Si/TiO$_2$ sample is similar to the PEDOT:PSS/TiO$_2$ sample, with an RMS phase of $1^\circ$. These data suggest that TiO$_2$ grown on H-Si is both conformal and covers the surface fully with no evidence of islanding.

![Figure 13: H-Si AFM Height (Left) and Phase (Right) Images](image)

![Figure 14: Si/TiO$_2$ AFM Height (Left) and Phase (Right) Images](image)

XPS spectra show the unambiguous presence of silicon, titanium, oxygen, and carbon. The presence of carbon is not surprising, as samples usually exhibit some adventitious carbon contamination after exposure to ambient conditions. For example, scans of the C(1s) region in untreated H-Si contain a single peak at 284.5 eV that is attributed to adventitious carbon. However, detailed scans of the C(1s) region of Si/TiO$_2$ samples showed three distinct carbon peaks: a low binding energy peak at 284.5 eV characteristic of C-C bonds, a peak at 285.7 eV characteristic of C-O bonds, and a high binding energy peak at 288.3 eV characteristic of C=O
and O-C-O bonds. The C-O and C-C peaks care attributed to unreacted $t$-butoxide at the surface. While a peak area ratio of 3:1 C-C:C-O is expected for these peaks, the observed ratio is 2.5:1. The difference between the expected and observed ratio could be due to additional types of C-O species present in the sample (e.g. at 288.3 eV) of unknown nature or origin, and may be an artifact, as this peak is not observed in other spectra of this material.

Figure 15: XPS Survey (Left) and C(1s) Region (Right) of Si/TiO$_2$. The survey shows the unambiguous presence of Ti, O, Si, and C. The C(1s) region shows three distinct peaks, attributed to C from C-C, C-O, and C=O/O-C-O.

As with the PEDOT samples, Ti(2p) peaks were observed at binding energies of 458.1 eV and 463.8 eV (Figure 16, left); the binding energies and spin-orbit splitting confirm the presence of Ti in the +4 oxidation state. A prominent Si(2p) doublet was present with peaks at 99.3 and 100.0 eV (Figure 16, right). The binding energies and spin-orbit splitting (0.6 eV) are characteristic of elemental Si. A doublet with peaks at binding energies of 102.6 and 103.4 eV was also present. The binding energies and spin-orbit splitting (0.8 eV) agree with literature values for Si$^{+4}$, so this peak was attributed to SiO$_2$. Because silicon is oxidized, it would be expected that titanium is reduced; however, it is plausible that H-Si underwent oxidation due to
exposure to ambient atmosphere or trace oxygen in the vacuum system, or that titanium was reduced but quickly re-oxidized under ambient conditions. There is support for the former, as samples prepared and analyzed by XPS without exposure to ambient conditions did not show evidence of oxidized Si.\textsuperscript{20}

![Figure 16: XPS Ti(2p) (Left) and Si(2p) (Right) Regions of Si/TiO\textsubscript{2}. The Ti(2p) binding energy and spin-orbit splitting indicate Ti is present in the +4 oxidation state. The Si(2p) peaks and spin-orbit splitting indicate Si is present in the 0 and +4 oxidation peaks.](image)

**TiO\textsubscript{2} Thickness Quantification on Si**

Variable-angle XPS was used to try to determine the thicknesses of the SiO\textsubscript{2} and TiO\textsubscript{2} layers as well as more accurately determine the thin film structure. For this technique, the intensities of the peaks of interest are recorded as a function of the angle $\theta$ between the detector and a vector normal to the sample surface. The data can then be compared to a various models (e.g. flat films, films with roughness, films that exhibit islanding) in order to understand the thin film structure. The collected AFM and XPS data suggest a flat, thin film of TiO\textsubscript{2} on the substrate. The signal intensity of a flat film of thickness $t$ as a function of the angle $\theta$, is shown in Equation (8), where $I_\infty$ is the intensity from an infinitely thick sample of a given material, $G(\theta)$ is a
material-independent normalization function that corrects for photoelectron yield as a function of angle, and \( \lambda \) is the mean free path of electrons from the given core level through the thin film. For each overlayer of material above the material of interest, the intensity is attenuated by the factor \( \alpha \) shown in Equation (9), where \( t_o \) is the thickness of the overlayer and \( \lambda_{cl,o} \) is the mean free path of electrons from the core level of interest through the overlayer, which is a function of the electron kinetic energy.

\[
I(\theta) = I_\infty G(\theta) \left[ 1 - \exp\left(\frac{t}{\lambda \cos \theta}\right) \right]
\]

\[
\alpha(\theta) = \exp\left(-\frac{t_o}{\lambda_{cl,o} \cos \theta}\right)
\]

Variable-angle XPS is most often used to determine the thickness of an overlayer on an infinitely thick layer of substrate material. As stated earlier, in cases where electrons from the overlayer and underlayer (substrate) are of similar kinetic energies and have similar \( \lambda \)'s, the intensity ratio simplifies to the Equation (6). Metals and their corresponding metal oxides have similar core electron binding energies; this results in photoelectrons with similar kinetic energies. Thus the relative ratio analysis is typically used for determining the thickness of oxide layers of a given material on said material. For example, the kinetic energies of the Si\textsuperscript{0} (2p) and Si\textsuperscript{+4} (2p) electrons are 1153-1154 eV and 1150-1151 eV, respectively. These values are 0.35% different from each other, which means the mean free path of Si\textsuperscript{0} (2p) electrons in SiO\textsubscript{2} should be approximately equal to the mean free path of Si\textsuperscript{+4} (2p) in SiO\textsubscript{2}. Moreover, the mean free path of both types of electrons through TiO\textsubscript{2} should also be equal, so attenuation due to the TiO\textsubscript{2} overlayer should not affect this analysis.
\[
\frac{I_0}{I_{u}}(\theta) = \frac{I_{0,\infty}}{I_{u,\infty}} \left[ \exp \left( \frac{t}{\lambda \cos \theta} \right) - 1 \right]
\]  

(10)

While angle-resolved XPS should be able to determine \( \frac{I_{0,\infty}}{I_{u,\infty}} \) and \( t \) simultaneously by fitting the measured intensity ratio as a function of angles and performing regression analysis, it is not necessarily the best option because large changes in both \( \frac{I_{0,\infty}}{I_{u,\infty}} \) and \( t \) can still result in good fits: There exists dependency between the two fitting parameters. This dependency is shown below in Figure 17. Instead, many literature analyses rely on an experimental \( \frac{I_{0,\infty}}{I_{u,\infty}} \) ratio using sample standards (e.g. thick SiO\(_2\) and H-Si) so that only \( t \) is calculated, and dependency is eliminated. In practice, using a known value for \( \frac{I_{0,\infty}}{I_{u,\infty}} \), it is possible to calculate \( t \) from measurements taken at single angle, but this relies on knowing the surface model beforehand; variable-angle XPS can provide information about the validity of these assumptions.

![Figure 17: Variable Angle XPS results and fits to flat, uniform film models with different \( \frac{I_{0,\infty}}{I_{u,\infty}} \) ratios parameters, illustrating dependency between this variable and the calculated thickness.](image-url)
Because determining the thickness of SiO$_2$ on Si is important for microelectronics, there are many examples using angle-resolved XPS for this purpose.$^{18,19,21,22}$ For the Si/SiO$_2$/TiO$_2$ calculations, a value for $\frac{I_{Si(4),SiO_2,\infty}}{I_{Si(0),H-Si,\infty}}$ of 0.8 was used based on experimentally-determined values by Lu, et al., yielding a calculated value for $\frac{t}{\lambda}$ of 0.208 ± 0.007, which, when combined with their values for the mean free path of Si(2p) core electrons in SiO$_2$ (2.7 ± 0.1 nm), resulted in a calculated SiO$_2$ thickness of 0.56 ± 0.02 nm.$^{18,19}$ The above values are for thermally-grown SiO$_2$ on Si, so it is possible that the actual values of $\frac{I_{Si(4),SiO_2,\infty}}{I_{Si(0),H-Si,\infty}}$ and $\lambda$ are different for the surface in question due to differences in density or physical structure. Overall, the fit of the angle-resolved data is in good agreement with a model of a thin, flat film of SiO$_2$ on Si, although the quantitative information may not be accurate because of the aforementioned assumptions.

Unfortunately, angle-resolved XPS does not provide a simple solution for the determination of TiO$_2$ thickness using the relative ratio method. The Si(2p) core level electrons and Ti(2p) core level electrons have kinetic energies of ca. 1150 eV and 790-796 eV, respectively, so the mean free paths of the Si(2p) and Ti(2p) electrons are not similar. To reduce this to a one variable problem as above, it is essential to know the mean free paths of Si(2p) and Ti(2p) electrons in TiO$_2$ as well as the intensity of infinitely thick TiO$_2$ layer and an infinitely thick Si or SiO$_2$ layer. Since the thickness asymptotes in the temperature range used, it is difficult to get values for an infinitely thick layer (in practice, hundreds of nanometers will suffice) without substantially changing the procedure, which could induce structural changes in the material; thus the values would not accurately reflect what is observed for the thin films.

An alternative calculation involves using the absolute ratio method with the Si(2p) peak areas from samples of H-Si and Si/TiO$_2$, and calculating the thickness of the TiO$_2$ overlayer.
while correcting for the attenuation effect of the SiO$_2$ overlayer, as shown in Equation (11). The assumption is made that any adventitious carbon attenuates both signals equally, which cancels out in the final analysis, and that factors changing the electron yield (pressure, etc.) do not change between subsequent analyses during the hour in which the XPS spectra were taken. The samples used for this analysis were not of asymptotic thickness as determined by ellipsometry. From the Si$^{4+}$/Si$^0$ peak areas (Table 3), the calculated oxide thickness for this sample is $0.13 \pm 0.01$ nm. Using Equation (11), with $0.64 \pm 0.01$ for $\frac{I_{Si}}{I_{Si,\infty}}$ and a literature value of $\lambda_{TiO_2}$ of $1.7 \pm 0.1$ eV for electrons with a kinetic energy of $\sim 1150$ eV yields a calculated TiO$_2$ thickness of $0.68 \pm 0.04$ nm. As with the SiO$_2$ data, differences in the TiO$_2$ structure and density will have drastic effects on the value of $\lambda_{TiO2}$.

$$I = I_{\infty} \exp\left(-\frac{t_{SiO_2}}{\lambda_{SiO_2}}\right) \exp\left(-\frac{t_{TiO_2}}{\lambda_{TiO_2}}\right)$$  \hspace{1cm} (11)

**Figure 18:** H-Si survey (left) and Si(2p) region (right)
Figure 19: Si/TiO$_2$ survey (left) and Si(2p) region (right)

Table 3: RSF-corrected peak areas used for TiO$_2$ thickness determination

<table>
<thead>
<tr>
<th></th>
<th>Si$^0$ (2p)</th>
<th>Si$^{+4}$ (2p)</th>
<th>Ti(2p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Si</td>
<td>57.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Si/TiO$_2$</td>
<td>36.2</td>
<td>1.40</td>
<td>4.30</td>
</tr>
</tbody>
</table>

Using the observed $\frac{I_{Ti}}{I_{Si}}$ value and calculated thickness calculated TiO$_2$ thickness from this sample it is possible to calculate the TiO$_2$ thickness of other samples numerically using Equation (5), as was done with the PEDOT:PSS/TiO$_2$ samples. For the Si/TiO$_2$ sample used in variable-angle XPS with asymptotic ellipsometric thickness and $\frac{I_{Ti}}{I_{Si(0)}}$ of 0.792 (corrected for SiO$_2$ attenuation), the calculated thickness is 2.7 ± 0.1 nm, which is in good agreement with the ellipsometric values. This asymptotic thickness for Si/TiO$_2$ is twice the asymptotic thickness calculated for PEDOT:PSS/TiO$_2$ samples.
Experimental

Cleaning of ITO substrates

ITO-coated glass substrates (Colorado Concepts, 15-30 $\Omega/\square$) were cut into 16 mm x 16 mm pieces. The conducting side was cleaned with a soft-bristled toothbrush using a 1% w:w Alconox solution in deionized (18.2 M$\Omega$-cm) water, then thoroughly rinsed with deionized water. Samples were immersed in a 1% w:w Alconox solution and sonicated for 60 min at 50°C, thoroughly rinsed using deionized water, rinsed with absolute ethanol, and then dried with filtered nitrogen. This procedure gave a hydrophilic surface (water-wetting contact-angle <10° as determined by goniometry) and minimal surface carbon as determined by X-Ray photoelectron spectroscopy.

Spin-coating of PEDOT:PSS

Cleaned ITO substrates were placed on a vacuum chuck in a spin coater and covered with PEDOT:PSS (Clevios P1000) that had been filtered through a 0.45 μm PVDF syringe filter. Substrates were spun at 2000 rpm for 60s, then annealed on a hot plate at 130°C for 5 minutes in air. Thickness of the spin-coated layers was determined by AFM.

Preparation of hydrogen-terminated silicon

Silicon samples were first cleaned using the RCA organic clean with a 1:1:5 v:v:v ratio of H$_2$O$_2$:30% NH$_4$OH:H$_2$O. The chemical oxide was then stripped using 1:200 v:v HF:H$_2$O. This yielded hydrogen-terminated silicon with no oxide peak and minimal surface carbon as determined by X-Ray photoelectron spectroscopy.
**TiO₂ growth on PEDOT:PSS and Si**

PEDOT:PSS-coated ITO substrates were placed on a copper sample holder and pumped down to a base pressure of 1·10⁻³ torr. Substrates were cooled to -10°C using dry ice, then exposed to a vapor of titanium(IV) t-butoxide (Strem®, 99.95% Ti) under active vacuum. After exposure, the samples were annealed under active vacuum for ten minutes at 80°C.

**X-Ray photoelectron spectroscopy**

X-Ray photoelectron spectra were collected using a VG Scientific ESCALAB Mk. II in UHV (10⁻⁹ torr) using Al Kα (1486.7 eV) or Mg Kα (1253.6 eV) radiation from an Al or Mg anode at 15kV and 20 mA. Spectra were analyzed using CasaXPS and calibrated to the adventitious C(1s) peak at 284.5 eV. Atomic sensitivity factors were used from the literature for an X-Ray source/detector angle of 54.7°.

**Variable-angle X-Ray photoelectron spectroscopy**

Variable-angle X-Ray photoelectron spectra were collected in UHV (10⁻⁹ torr) using an X-ray source (SPECS XR50M) equipped with an aluminum anode (1486.74 eV, 400 W) and a monochromator (SPECS Focus 500). The kinetic energies of the ejected photoelectrons were measured using a hemispherical analyzer (SPECS PHOIBOS 150) equipped with a nine-channel electron multiplier array.

**Atomic force microscopy**

AFM height and phase spectra were taken using a Veeco NanoMan® AFM using Bruker® RTESP cantilevers. Spectra were taken at a resolution of 512 samples/line and 512 lines at a frequency of 1.0 lines/second; all other parameters used were default values. Images were analyzed using the Gwyddion® software suite. Images were processed by matching the line
median height, correcting horizontal scars, and subtracting a planar or paraboloidal background when appropriate.

**Contact-angle goniometry**

Contact-angle goniometry measurements were performed using an Attension® Theta Lite goniometer and the included software. A 1 μL droplet of deionized water was gently placed onto the surface using a microliter syringe. The droplet shape was fitted to the Young-Laplace equation, yielding left and right contact-angles. Measurements were performed at at least three separate locations on each sample, and average contact-angles and standard deviation were recorded.

**Ellipsometry**

Ellipsometry measurements were taken using a Gaertner® Scientific Instruments LSE Ellipsometer with a HeNe laser and the included software. Samples were centered and leveled using the tilting sample holder. For each sample, measurements were taken in triplicate at each of nine locations in a 3x3 grid. The thickness and index of refraction were calculated for each measurement using the software with the chosen thin film model. The thin-film model used was for a thin film on silicon with an absorption coefficient of zero, an initial guess for the thickness of 3.0 nm, and an initial guess for the index of refraction of 2.85.
References Cited


Chapter 4

Formation of SAMPs on PEDOT:PSS/TiO₂ Substrates:

Comparison to SAMPs on ITO
Rationale for Choice of Phosphonic Acids

Fundamental device research on phosphonate SAMs on ITO has revealed that charge carriers undergo quantum-mechanical tunneling through the SAM, which depends on the HOMO and LUMO energy levels of the phosphonates relative to the electrode work function, as well as the SAM thickness.\textsuperscript{1,2} In order to obviate tunneling through the self-assembled monolayer from becoming the limiting factor in device performance, it is important to minimize these $E_F$-HOMO/LUMO energy offsets and molecular thickness, while still maintaining a scaffold that allows synthetic diversity. Empirically, short SAMs do not limit the current density in devices regardless of the relative positions of their energy levels: They have been used in devices without contributing any significant degradation of performance.\textsuperscript{3,4} Using this empirical observation, phenylphosphonate SAMs were chosen to demonstrate improved carrier injection in electronic devices, as they are thin, conjugated, and provide synthetic diversity.

Previous research in this group determined that for aromatic SAMPs, the P-C bond is essentially perpendicular to the surface. This was demonstrated by AFM of the SAMP edge of an $\alpha$-quarterthiophene-2-phosphonate-modified SiO$_2$ surface, which showed that SAMP thickness was essentially equal to the molecular thickness.\textsuperscript{5} This observation is corroborated by DFT-optimized models that suggest that the P-C bond is essentially perpendicular to the surface in self-assembled monolayers of benzylphosphonates on ITO.\textsuperscript{6} This suggests that the $\zeta$-component of the molecular dipole for phenylphosphonic acids can be easily modified by placing functional groups in the ortho, meta, or para positions without having to worry about the effects of conformational changes (mainly, rotation of the P-C bond) on the component of the dipole that is normal to the surface. To that end, the molecules shown in Table 4 were chosen as synthetic targets. These molecules have the added benefit of having a wide-range of acidities, as
protonation of the surface could also alter the work function of the electrode.⁷ OMePA and F2PA, which have similar molecular dipoles but different acidities, can distinguish changes in the electrode work function result from the aggregate dipole or surface protonation.

Table 4: Phosphonic Acids Used in This Work

<table>
<thead>
<tr>
<th></th>
<th>CF3PA</th>
<th>FPA</th>
<th>HPA</th>
<th>OMePA</th>
<th>F2PA</th>
</tr>
</thead>
<tbody>
<tr>
<td>μz (Debye)</td>
<td>-2.37</td>
<td>-0.852</td>
<td>0.664</td>
<td>1.85</td>
<td>2.03</td>
</tr>
<tr>
<td>pKa</td>
<td>1.40</td>
<td>1.61</td>
<td>1.85</td>
<td>2.02</td>
<td>1.09</td>
</tr>
</tbody>
</table>

Previous work in this group resulted in the reduction of the work function of ITO using α-quarterthiophene-2-phosphonate SAMPs, which can be doped with the electron acceptor F4-TCNQ to yield a charge transfer complex that increases the work function of ITO.⁴ Recently, Marder, et al., have demonstrated modification of the work function of ITO using benzylphosphonic acids.⁶ Changes in work function showed good correlation with the z-component of the molecular dipole of the benzylphosphonic acid, although the effect of acidity was not considered. While the phenylphosphonic and benzylphosphonic acids molecules used for SAMP formation were successful in increasing the ITO work function, they were unable to obtain an appreciable decrease of the ITO work function. Benzylphosphonic acids have a disadvantage compared with aryl phosphonic acids, as substituent groups in the ortho- and meta-positions in benzylphosphonic acids can have different contributions to the z-component of the molecular dipole depending on rotation of the C-C bond, as shown in Figure 20. However, a
comparison of analogous phenylphosphonic and benzylphosphonic acids strangely showed that the analogs showed essentially the same changes in work function, despite the difference in structure. The authors hypothesized this was due to a change in binding mode or tilt angle between the benzyl- and phenylphosphonic acids, although no characterization was attempted.

\[ \text{Figure 20: Conformational changes with ortho-substituted benzyl phosphonate SAMPs, which can lead to unexpected changes in work function.} \]

Initial attempts to produce diethyl (2,6-difluorophenylphosphonate) using palladium-catalyzed cross-coupling reactions with 2,6-difluorobromobenzene and 2,6-difluoriodobenzene failed. However, the protons ortho- to fluorine atoms in aromatic systems are acidic, which allows facile deprotonation by organolithium reagents. For 1,3-difluorobenzene, this results in almost full selectivity for deprotonation of the 2- position. This has previously been exploited in the synthesis of 2,6-difluorobenzoic acid from 1,3-difluorobenzene using CO$_2$ as an electrophile. By using diethyl chlorophosphonate in place of CO$_2$, it was possible to synthesize diethyl (2,6-difluorophenylphosphonate) according to Scheme 8. The phosphonic ester could be hydrolyzed to the corresponding acid under reflux in acidic conditions.

\[ \text{Scheme 8: Synthesis of Diethyl (2,6-difluorophenylphosphonate)} \]
SAMP Formation on ITO

Previous research in this group showed that the T-BAG procedure and a simple dipping procedure both resulted in good SAMP coverage on ITO, as measured by QCM, changes in work function, and goniometry. The dipping procedure involved soaking the phosphonic acid in a millimolar solution of the phosphonic acid in ethanol for one hour. A critical step in both of those procedures is annealing in a tube furnace at 120 °C; compared to samples made without this step, samples made with annealing showed large changes in work function and more hydrophobic surfaces, suggesting higher phosphonic acid coverage on the ITO surface. This is most likely due to a change from hydrogen bonding of the phosphonic acid to covalent bonding, resulting in a surface-phosphonate bond.\textsuperscript{5,10} In a recent paper, Marder, et al., demonstrate that the annealing step can be eliminated using a dip procedure at elevated temperatures (75 °C).\textsuperscript{11} Samples dipped at room temperature and rinsed without annealing showed smaller changes in work function, which corroborates observations in this group. Both dipping at an elevated temperature and using a post-dip anneal gave identical changes in work function for the same phosphonic acid, suggesting that the dip/anneal procedure is sufficient. It was rationalized that a dip procedure was sufficient for the formation of SAMPs on the ITO surface due to the relative ease of breaking In-O and Sn-O bonds at the oxide surface under mildly acidic conditions. Due to its simplicity, the dip procedure was selected to demonstrate bonding of the aforementioned phosphonic acids on ITO in order to ascertain the effects of molecular dipole on changes in work function.

No significant differences were noted between untreated and phosphonic acid-treated ITO in the height image (Figure 21, Figure 22, RMS height roughness of 0.8 nm and 0.7 nm, respectively), suggesting that the phosphonic acids did not appreciably etch the surface or any
etching occurred uniformly. Phosphonic acid-treated samples showed a decrease in the RMS phase roughness relative to the untreated samples (4° vs. 11°), suggesting the ITO surface is rather heterogenous. While as-cleaned samples examined by contact-angle goniometry are wetting (θ < 20°), the water-wetting angle increases to approximately 40° after approximately one hour, suggesting the presence of hydrophobic species on the surface. This may be responsible for the increased RMS phase roughness in the ITO sample.

Figure 21: AFM height (left) and phase (right) images of ITO. The surface shows good height uniformity (RMS 0.8 nm).

Figure 22: AFM height (left) and phase (right) images of ITO/CF3PA. The surface shows height uniformity (RMS 0.7 nm) similar to ITO surfaces, and good phase uniformity (RMS 4°)
Table 5: Goniometry data for SAMP-modified ITO samples

<table>
<thead>
<tr>
<th>Material</th>
<th>θ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO (control)</td>
<td>&lt; 20</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS</td>
<td>&lt; 20*</td>
</tr>
<tr>
<td>ITO/CF3PA</td>
<td>91.6 ± 0.5</td>
</tr>
<tr>
<td>ITO/FPA</td>
<td>75 ± 4</td>
</tr>
<tr>
<td>ITO/HPA</td>
<td>72 ± 2</td>
</tr>
<tr>
<td>ITO/OMePA</td>
<td>69 ± 4</td>
</tr>
<tr>
<td>ITO/F2PA</td>
<td>73 ± 2</td>
</tr>
</tbody>
</table>

*dewets polymer from surface

Vibrating Kelvin Probe Measurements of ITO/SAMP Samples

There is a good correlation between the molecular dipole of the phosphonic acid and the change in ITO work function (R² = 0.98), and no correlation between the pKa of the phosphonic acid and the change in work function, suggesting that the change in work function is due to an aggregate surface dipole rather than surface protonation (Figure 23). The y-intercept, corresponding to a phosphonic acid with zero molecular dipole, shows an increase of the work function of 0.12 ± 0.03, which is attributed to an induced dipole resulting from P-O-In and/or P-O-Sn bond formation, and similar to values measured by Marder, et al.⁶
Figure 23: $\Delta \Phi$ as a function of calculated molecular dipole (left) and $pK_a$ (right) for ITO/SAMP samples. The change in work function shows good correlation with the molecular dipole, and no correlation with the $pK_a$.

**SAMP Formation on PEDOT:PSS/TiO$_2$ Substrates**

The T-BAG method demonstrated by previous group members did not prove amenable to SAMP formation on PEDOT:PSS/TiO$_2$ substrates: Shear forces pulled the polymer from the ITO substrate.$^5$ Instead, phosphonic acids were attached to the PEDOT:PSS/TiO$_2$ ensemble by dipping them in a 0.5 mMol solution in ethanol for 24 hours, annealing under argon, and rinsing with ethanol to remove excess phosphonic acid. XPS analysis of these samples revealed the presence of phosphorous, confirming the presence of the phosphonate. A representative XPS for PEDOT:PSS/TiO$_2$/CF3PA is shown below, clearly showing the F(1s) peak (survey, $\sim$687 eV) and P(2p) peak (not resolved to show (2p$_{1/2}$) and (2p$_{3/2}$) peaks). The Ti(2p) and S(2p) peaks are also preserved.
Figure 24: XPS Survey and P(2p) for PEDOT:PSS/TiO2/CF3PA. The survey shows the unambiguous presence of Ti, O, S, F, P, and C. The P(2p) region shows a single peak, attributed to CF3PA.

Contact-angle goniometry was also used to qualify the surface coverage in comparison to ITO. Since phosphonic acids are known to form compact, well-ordered SAMPs on ITO, and there is not a drastic difference in roughness between the two samples, the difference in contact-angles between the ITO substrates and the PEDOT:PSS/TiO2 substrates gives qualitative information about the surface coverage. For pristine PEDOT:PSS, water wetting contact-angles could not be obtained because water would wash the polymer from the ITO-coated glass substrates. Water-wetting contact-angles are similar to phosphonates deposited on ITO, suggesting good phosphonate coverage on the PEDOT:PSS/TiO2 surface.
Table 6: Goniometry data for SAMP-modified ITO and PEDOT:PSS/TiO$_2$ samples

<table>
<thead>
<tr>
<th>Phosphonic Acid</th>
<th>$\theta_{\text{ITO}}$ (°)</th>
<th>$\theta_{\text{PEDOT:PSS/TiO}_2}$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>&lt;20</td>
<td>70 ± 5</td>
</tr>
<tr>
<td>CF$_3$PA</td>
<td>91.6 ± 0.5</td>
<td>86.7 ± 0.8</td>
</tr>
<tr>
<td>FPA</td>
<td>75 ± 4</td>
<td>69 ± 1</td>
</tr>
<tr>
<td>HPA</td>
<td>72 ± 2</td>
<td>66 ± 1</td>
</tr>
<tr>
<td>OMePA</td>
<td>69 ± 4</td>
<td>57.2 ± 0.7</td>
</tr>
<tr>
<td>F$_2$PA</td>
<td>73 ± 2</td>
<td>63 ± 2</td>
</tr>
</tbody>
</table>

Vibrating Kelvin Probe Measurements of PEDOT:PSS/TiO$_2$ Samples

Changes in work function were measured by vibrating Kelvin probe using samples with a Ti(2p)/S(2p) ratio of 0.5 ± 0.2, corresponding to a TiO$_2$ thickness of approximately 0.5 nm. Prior to taking vibrating Kelvin probe measurements, SAMP-derivatized samples were rinsed with ethanol and dried under a stream of nitrogen in order to remove any residual phosphonic acids. Kelvin probe measurements showed that the absolute work function could be changed by ±0.4 eV compared to pristine PEDOT:PSS. There is a good correlation ($R^2 = 0.91$) between the z-component of the molecular dipole of the phosphonic acid and the observed changes in work function for the phosphonate-derivatized samples. Conversely, there is no correlation between the $pK_a$ and the observed changes in work function, showing that surface protonation is not responsible for these changes.
**Figure 25:** $\Delta \Phi$ as a function of calculated molecular dipole (left) and pKa (right) for PEDOT:PSS/TiO$_2$/SAMP samples. The change in work function shows good correlation with the molecular dipole, and no correlation with the pKa.

PEDOT:PSS/TiO$_2$ samples showed a work function that was lower than pristine PEDOT:PSS by 0.4 eV. The magnitude of this reduction in work function could be reduced to 0.2 eV by soaking PEDOT:PSS/TiO$_2$ samples in ethanol overnight. Because the as-deposited PEDOT:PSS/TiO$_2$ electrodes exhibit slight hydrophobicity, and XPS of model H-Si/TiO$_2$ samples showed evidence of $t$-butoxide groups, it seems plausible that the as-grown PEDOT:PSS/TiO$_2$ samples may contain some amount of $t$-butoxide termination, which would be expected to decrease the work function due to the C-O bond dipole. These butoxide groups are replaced by the SAMP upon exposure to phosphonic acids or removed through exposure to residual water in ethanol, which could lead to ligand substitution to form hydroxide groups and elimination to yield a more oxide-like surface. Interpolation to zero molecular dipole yields a decrease in work function of $0.06 \pm 0.05$ eV relative to PEDOT:PSS. However, the P-O-Ti induced dipole is the difference from the $\mu_z=0$ interpolation and the work function of the oxide.
Assuming that the ethanol-soaked PEDOT:PSS/TiO$_2$ results in an oxide surface yields an induced bond dipole of 0.1 eV, and suggests that the remaining 0.2 eV reduction in work function results from either a dipole at the PEDOT:PSS/TiO$_2$ interface, effects of the solvent on the work function of PEDOT:PSS, or some combination of the two. It is also possible that residual $t$-butoxide groups are still present even after soaking in ethanol, in which case the induced bond dipole cannot be accurately determined.

**Figure 26**: Comparison of changes in work function on ITO and PEDOT:PSS/TiO$_2$. After correcting for the change in y-intercept, which is attributed to the induced dipole of bond formation, the observed changes in work function are similar.

**UPS Measurements of PEDOT:PSS/TiO$_2$ Samples**

Vibrating Kelvin probe data were corroborated by Ultraviolet Photoelectron Spectroscopy (UPS). In UPS, the secondary electron onset (Figure 8, left, shown with dashed lines) corresponds to electrons with infinitesimal kinetic energy reaching the detector. Since the potential energy is calibrated with respect to the work function of the detector, the measured energy of the onset added to the work function of the sample should be equal to the energy of the
He (I) radiation (hv = 21.2 eV). The data for the modified PEDOT:PSS samples are shown in Figure 27.

![Graph](image)

**Figure 27**: He (I) UPS onset for PEDOT:PSS (black), PEDOT:PSS/TiO₂ (red), PEDOT:PSS/TiO₂/F₂PA (green), and PEDOT:PSS/TiO₂/CF₃PA (blue). An example quantification of the onset energy by curve-fitting is also shown (right).

**Table 7: Collected UPS Data**

<table>
<thead>
<tr>
<th></th>
<th>PEDOT:PSS</th>
<th>PEDOT:PSS/TiO₂</th>
<th>PEDOT:PSS/TiO₂/F₂PA</th>
<th>PEDOT:PSS/TiO₂/CF₃PA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4.75</td>
<td>4.33</td>
<td>4.18</td>
<td>4.90</td>
</tr>
<tr>
<td></td>
<td>4.53*</td>
<td>4.36</td>
<td>4.21</td>
<td>4.77</td>
</tr>
<tr>
<td></td>
<td>4.63</td>
<td>4.23</td>
<td>4.40</td>
<td>4.44</td>
</tr>
<tr>
<td>TiO₂ Ti(2p)/PEDOT S(2p) ratio</td>
<td>2.06 ± 0.28</td>
<td>0.513 ± 0.06</td>
<td>2.10 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>Calculated TiO₂ thickness</td>
<td>1.5 nm</td>
<td>0.5 nm</td>
<td>1.5 nm</td>
<td></td>
</tr>
<tr>
<td>PA Soak time (hours)</td>
<td>24</td>
<td>24</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

*soaked in ethanol

The data show that the modified electrodes have larger changes in work function with increased soak times. For short soak times, there were no changes in work function, even though
the He (II) UP spectra showed the presence of peaks characteristic to the phosphonic acids. This seems to suggest that either the phosphonic acid is weakly coordinated, perhaps by hydrogen bonding, or coordinated in such a way that the z-component of the molecular dipole is parallel to the surface. Changes in work function are similar between samples with a thicker oxide layer and a thinner oxide layer, suggesting similar phosphonate loadings. The above data corroborate the vibrating Kelvin probe data qualitatively, although the observed values differ slightly. For example, UPS data for F2PA samples show a much larger change in the work function of the material compared to vibrating Kelvin probe, while the changes in work function measured by UPS of CF3PA samples are not as large as observed by vibrating Kelvin probe. This may be due to a less than complete surface coverage, in which case a lower work function would be observed.12

Data near the Fermi edge were also collected with He(II) irradiation (hν = 40.8 eV) to limit the secondary electron background and give more detail at the Fermi edge (Figure 27). While PEDOT:PSS exhibits a broad tail that trails from -5 eV to 0 eV with respect to the detector work function, samples containing the TiO₂ layer show a much steeper falloff at -3.75 eV. This is most likely the observation of the deep-lying valence band of TiO₂ (~7 eV with respect to vacuum energy). The phosphonic-acid treated samples display characteristic peaks from ionization of their occupied molecular orbitals. These features are observed for both short and long soak times. Samples with both 1h and 24h phosphonic acid exposure times possess these characteristic peaks, suggesting that the phosphonatic acids/phosphonates are present. Thus, it is not the absence of the phosphonic acid that is responsible for the lack of work function changes in samples with a 1h exposure time may be due to hydrogen bonding to the surface instead of covalent bonding, or a difference in the binding mode.
**Figure 28:** He (II) UPS Valence Region for PEDOT:PSS (black), PEDOT:PSS/TiO$_2$ (red), PEDOT:PSS/TiO$_2$/F2PA (green), and PEDOT:PSS/TiO$_2$/CF3PA (blue). The PEDOT:PSS/TiO$_2$ samples show evidence of the TiO$_2$ valence band at -4.0 eV, and the SAMP species have unique peaks attributed to their frontier orbitals, which are observed for both short and long soak times.

**Energy level alignment at conductor/organic interfaces**

Unlike many inorganic semiconductors, which can be heavily doped ($\sim 10^{14}$-$10^{17}$ cm$^{-3}$), many organic semiconductors have a low intrinsic density of donors or acceptors. If the Fermi energy of the conductor is between the HOMO and LUMO of the organic, the lack of donors or acceptors in polymers results in little charge transfer, so materials often align with a common vacuum level (Figure 29).$^{13-17}$ If the work function of the electrode is lower than the HOMO or higher than the LUMO, there will be charge transfer or holes or electrons from the metal to the HOMO or LUMO, respectively, pinning the Fermi level.$^{13-17}$
Figure 29: Energy level alignment mechanism of electrodes and organic semiconductors. Samples share a common vacuum level.

**Choice of an n-type Organic Molecule for Devices**

PCBM ([6,6]-Phenyl-C61-butyric acid methyl ester) was chosen as a small molecule to demonstrate improved electron injection from modified polymer electrodes as it has a high electron mobility (2.7×10^{-3} \text{ cm}^2/\text{V} \cdot \text{s}), low-lying LUMO (-3.8 eV vs. vacuum), is easily processed by spin-coating, and is stable under ambient conditions, eliminating the need for either fabricating and measuring devices in a glovebox.\textsuperscript{18,19} Based on the difference in energies between the LUMO of PCBM and the measured work function of PEDOT:PSS (4.75 eV), we would expect a Fermi-level/LUMO barrier height of approximately 1.5 eV for these devices. This large barrier height allows much room for tuning of the E_F-LUMO barrier. Moreover, assuming that the thin TiO\textsubscript{2} film has the electronic structure of bulk TiO\textsubscript{2}, which has a LUMO energy level at -4.0 eV vs. vacuum, TiO\textsubscript{2} would not be expected to block the tunneling of electrons into PCBM. Based on the literature values of the LUMO energies results in the following calculated energy level alignments for PCBM with PEDOT:PSS, PEDOT:PSS/TiO\textsubscript{2}, and PEDOT:PSS/TiO\textsubscript{2}/F2PA.
Figure 30: Expected PEDOT:PSS (left), PEDOT:PSS/TiO$_2$ (center), and PEDOT:PSS/TiO$_2$/F2PA (right) energy level alignments with PCBM, based on work function measurements and literature values for the LUMO energy with respect to $E_{\text{vac}}$.

Energy Level Alignment of Modified PEDOT:PSS Electrodes with PCBM

Energy level alignments between modified PEDOT:PSS electrodes and PCBM was determined by UPS in order to ascertain the effective barrier to electron injection. F2PA and PEDOT:PSS/TiO$_2$ were compared to PEDOT:PSS as they gave the largest reductions in effective work function, which should translate to lower $E_F$-LUMO energy barriers. For these measurements, a very thin film of PCBM was used in order to minimize the effects of charging on the conducting polymer. The films had a thickness of 11.7 ± 0.4 nm and showed good uniformity (RMS roughness 0.4 nm) with no signs of pinholes. Based on the thinness of the polymer layer, UPS would not be expected to result in charging of the polymer surface, which would shift the observed binding energies to higher values.
Figure 31: Determination of PCBM thickness for UPS energy level alignment studies. The “high” region is due to buildup of material after scratching the polymer. The PCBM thickness is 11.7 ± 0.4 nm.

UPS Spectra yielded the work functions by He (I) UPS (Figure 33) and $E_F$-HOMO energies by He (II) UPS (not shown), which were determined by fitting the photoelectron onset and peak onset to their respective baselines (Table 8). From these values, it is possible to determine the $E_F$-LUMO energy by adding the HOMO-LUMO energy difference to the observed $E_F$-HOMO; for these calculations a HOMO-LUMO energy of 2.0 eV was used, which was based on combined UPS and inverse photoelectron spectroscopy measurements.\(^\text{19}\) PEDOT:PSS/PCBM samples showed an increase of the work function by 0.30 eV compared to pristine PEDOT:PSS, which is assigned to a PEDOT:PSS/PCBM interfacial dipole, yielding a $E_F$-LUMO energy difference of 0.92 eV. PEDOT:PSS/TiO$_2$/PCBM showed a shift of the Fermi energy by 0.1 eV, which is also attributed to an interface dipole between PCBM and PEDOT:PSS. The lower work function and smaller interface dipole of the PEDOT:PSS/TiO$_2$ resulted in a net decrease in the $E_F$-LUMO energy to 0.25 eV. PEDOT:PSS/TiO$_2$/F2PA showed a decrease in the work function by 0.36 eV compared to PEDOT:PSS, and a PCBM/electrode dipole of 0.23 eV, resulting in a
barrier to electron injection of 0.37 eV. PEDOT:PSS/TiO$_2$ samples that were soaked in ethanol were also used. The ethanol-soaked samples show a work function that is lower than pristine PEDOT:PSS by 0.18 eV. For this sample, there was a shift of the work function of 0.05 eV after spin-coating of PCBM, again attributed to a PCBM/electrode interface dipole, which yielded an $E_F$-LUMO energy difference of 0.37 eV. These data yield the band alignments shown in Figure 32.

**Figure 32:** Observed PEDOT:PSS (top left), PEDOT:PSS/TiO$_2$ (top right), PEDOT:PSS/TiO$_2$ (ethanol rinse, bottom left) and PEDOT:PSS/TiO$_2$/F2PA (bottom right) energy level alignments with PCBM, based on He (I) UPS data, showing the PCBM/electrode interface dipole.
Figure 33: Electrode (black) and electrode/PCBM (red) He (I) UPS Spectra of PEDOT:PSS (top right), PEDOT:PSS/TiO$_2$ (top right), PEDOT:PSS/TiO$_2$ (ethanol rinse, bottom left) and PEDOT:PSS/TiO$_2$/F2PA (bottom right)
Table 8: Values Extracted from PCBM Measurements

<table>
<thead>
<tr>
<th>Electrode</th>
<th>PCBM Work Function (eV)</th>
<th>(E_F)-HOMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>4.96</td>
<td>1.08</td>
</tr>
<tr>
<td>PEDOT:PSS/TiO(_2)</td>
<td>4.38</td>
<td>1.75</td>
</tr>
<tr>
<td>PEDOT:PSS/TiO(_2)*</td>
<td>4.53</td>
<td>1.63</td>
</tr>
<tr>
<td>PEDOT:PSS/TiO(_2)/F2PA</td>
<td>4.53</td>
<td>1.63</td>
</tr>
</tbody>
</table>

*ethanol rinse

The collected data show that TiO\(_2\) acts as an adhesion layer allowing SAMP formation. The SAMPs allow the tuning of the work functions, which correspond well with the molecular dipole and not the acidity, suggesting that well-ordered monolayer formation, as opposed to surface protonation, is responsible for the changes in work function. PCBM aligns with an interfacial dipole, and changes in work function correspond to changes in the \(E_F\)-HOMO and \(E_F\)-LUMO energy differences. The latter can be reduced using both TiO\(_2\) and TiO\(_2\)/F2PA, which should translate to increased current injection in PCBM electron-only diodes.

**Experimental**

**General**

Phenylphosphonic acid was purchased from Sigma Aldrich and recrystallized from acetonitrile.

**Diethyl 4-fluorophenylphosphonate\(^{20}\)**

Tetrakis(triphenylphosphine) palladium(0) (2.65g, 2.3 mmol), 4-fluoro-bromobenzene (5.0 mL, 46 mmol), diethyl phosphite (6.4 mL, 50 mmol), and triethylamine (7.0 mL, 50 mmol) were added sequentially to dry toluene (20 mL) under argon. The yellow solution was heated to reflux for two hours, during which a white powder, triethylamine hydrobromide, precipitated. Diethyl
ether (50 mL) was added to the reaction mixture, which was then filtered through Celite. The crude, brown solution containing the desired product and residual catalyst was purified by vacuum distillation to yield the desired product as a clear, colorless oil (5.0 g, 22 mmol, 48%).

\[ ^1H \text{ NMR (300 MHz, CDCl}_3 \text{)} \delta 7.82 (dddd, J = 12.7, 6.6, 5.5, 2.0 \text{ Hz, 2H}), 7.22 - 7.07 (m, 2H), 4.28 - 3.96 (m, 4H), 1.32 (td, J = 7.1, 0.6 \text{ Hz, 6H}). \]

4-Fluorophenylphosphonic acid\(^{20}\)

The corresponding acid was obtained by adding diethyl 4-fluorophenylphosphonate (3.0 g, 15 mmol) to a 1:1 v:v hydrochloric acid:water solution (40 mL, excess) and heating to reflux for 72 h. Solvent was removed by rotary evaporation to yield a white powder, which was rinsed with chloroform and collected by suction filtration, yielding the desired product (1.0 g, 5.7 mmol, 38%).

\[ ^1H \text{ NMR (501 MHz, CD}_3\text{OD)} \delta 7.83 (ddd, J = 13.1, 8.6, 5.7 \text{ Hz, 1H}), 7.22 (td, J = 8.9, 2.7 \text{ Hz, 1H}). \]

Diethyl 4-(trifluoromethyl)phenylphosphonate\(^{20}\)

Tetrakis(triphenylphosphate) palladium(0) (2.65g, 2.3 mmol), 4-trifluoromethylbromobenzene (6.4 mL, 46 mmol), diethyl phosphite (6.4 mL, 50 mmol), and triethylamine (7.0 mL, 50 mmol) were added sequentially to dry toluene (20 mL) under argon. The yellow solution was heated to reflux for two hours, during which a white powder, triethylamine hydrobromide, precipitated. After cooling to room temperature, diethyl ether (50 mL) was added and the reaction was filtered through Celite. The crude, yellow solution containing the desired product and residual catalyst was further purified by vacuum distillation to yield the desired product as clear, colorless oil (5.3 g, 21 mmol, 46%).

\[ ^1H \text{ NMR (300 MHz, CDCl}_3 \text{)} \delta 7.94 (dd, J = 13.0, 7.8 \text{ Hz, 2H}). \]
Hz, 2H), 7.73 (dd, J = 7.9, 3.6 Hz, 2H), 4.54 – 3.50 (m, 4H), 1.33 (td, J = 7.1, 0.6 Hz, 6H). $^{31}$P NMR (121 MHz, CDCl$_3$) $\delta$ 16.28 (m).

4-(Trifluoromethyl)phenylphosphonic acid$^{20}$

The corresponding acid was obtained by adding diethyl 4-(trifluoromethyl)phenylphosphonate in 1:1 v:v hydrochloric acid:water solution (40 mL, excess) and heating to reflux for 72 h. Upon cooling, a white crystalline solid precipitated at the bottom of the flask. This was collected by suction filtration and rinsed with deionized water and chloroform to yield 2.5 g of the desired product. $^1$H NMR (300 MHz, CD$_3$OD) $\delta$ 7.98 (dd, J = 13.0, 7.9 Hz, 2H), 7.80 (dd, J = 8.2, 3.2 Hz, 2H). $^{31}$P NMR (121 MHz, CD$_3$OD) $\delta$ 11.72 (m).

4-Methoxyphenylphosphonic acid

4-Bromoanisole (2.0 mL, 16 mmol) was dissolved in dry tetrahydrofuran (40 mL) under argon. After cooling to -78 °C, n-butyllithium (2.5 M in hexanes, 16.8 mmol, 6.7 mL) was added dropwise, resulting in a white, cloudy suspension that was stirred for 30 minutes. Dropwise addition of diethyl chlorophosphonate (2.5 mL, 17.6 mmol) immediately resulted in the formation of a clear, yellow solution that, upon warming to room temperature and being stirred overnight, turned colorless. The organic phase was rinsed three times with brine, once with water, and then dried with sodium sulfate. Solvent was removed via rotary evaporation, yielding a clear yellow liquid containing diethyl 4-methoxyphenylphosphonate and residual 4-bromoanisole. The crude product was purged with argon, and an excess of bromotrimethylsilane (ca. 50 mmol) was added. After being stirred overnight, the reaction was quenched with methanol. Solvent and 4-bromoanisole were then removed via rotary evaporation. Upon addition diethyl ether, 4-methoxyphenylphosphonic acid precipitated as a white, sticky solid, which was
collected via suction filtration and rinsed with dichloromethane, yielding a fine, white powder. The powder was recrystallized from acetonitrile to yield 4-methoxyphenylphosphonic acid as white crystals. $^1$H NMR (501 MHz, CD$_3$OD) δ 7.73 (dd, J = 12.9, 8.8 Hz, 2H), 7.01 (dd, J = 8.8, 3.1 Hz, 2H), 3.84 (s, 2H). $^{31}$P NMR (203 MHz, CD$_3$OD) δ 17.15 (s).

**Diethyl 2,6-difluorophenylphosphonate**

1,3-Difluorobenzene (0.99 mL, 10.0 mmol) was dissolved in dry tetrahydrofuran (40 mL) under nitrogen atmosphere. After cooling to -78 °C, n-butyllithium (2.5 M in hexanes, 11.0 mmol, 4.4 mL) was added dropwise and the clear, colorless solution was stirred for 30 minutes. Next, diethyl chlorophosphonate (1.66 mL, 11.0 mmol) was added dropwise. The clear, yellow solution was warmed to room temperature and allowed to stir overnight. 2 mL of distilled water was added to quench the clear, amber-colored reaction. The organic phase was rinsed three times with brine, once with water, and dried with sodium sulfate. Solvent was removed via rotary evaporation, yielding diethyl-2,6-difluoro-phenylphosphonate as an amber liquid. The amber liquid was used without purification for the subsequent hydrolysis to the phosphonic acid. $^1$H NMR (501 MHz, CDCl$_3$): δ 7.54 – 7.45 (m, 1H), 6.95 (td, J = 8.4, 5.1 Hz, 2H), 4.32 – 4.15 (m, 4H), 1.37 (t, J = 7.1 Hz, 6H). $^{31}$P NMR (203 MHz, CDCl$_3$) δ 8.16 (t, J = 2.5 Hz).

**2,6-Difluorophenylphosphonic acid**

The acid was obtained by refluxing diethyl 2,6-difluorophenylphosphonate in 1:1 v:v hydrochloric acid:water solution (20 mL, excess) overnight. Solvent was removed from the clear, yellow solution via rotary evaporation to yield a yellow powder (1.89g) that was rinsed with dichloromethane to remove any residual organics. The powder was purified by recrystallization in ethanol to yield 1,3-difluorophenylphosphonic acid as white crystals. $^1$H NMR (501 MHz,
CD$_3$OD) $\delta$ 7.58 (tt, $J$ = 8.4, 6.3 Hz, 1H), 7.04 (td, $J$ = 8.4, 4.8 Hz, 2H). $^{31}$P NMR (203 MHz, CD$_3$OD) $\delta$ 4.61 (t, $J$ = 4.8 Hz).

**SAMP formation on ITO**

Clean ITO substrates were immersed in 1mL of 1 mM phosphonic acid for 24 hours. Next, samples were removed from the solution and blown dry with filtered nitrogen. Samples were then annealed in a tube furnace under a flow of argon overnight at 120°C. After removal from the tube furnace, samples were cooled to room temperature, rinsed with absolute ethanol, and dried with filtered nitrogen.

**SAMP formation on PEDOT:PSS/TiO$_2$**

Clean ITO substrates were immersed in 1mL of 1 mM phosphonic acid for 24 hours. Next, samples were removed from the solution and blown dry with filtered nitrogen. Samples were then annealed in a tube furnace under a flow of argon overnight at 120°C. After removal from the tube furnace, samples were cooled to room temperature, rinsed with absolute ethanol, and dried with filtered nitrogen.

**Measurement of work functions using a vibrating Kelvin probe**

The conducting sample was used as the input for the lock-in analyzer using a preamplifier with a gain of $10^9$ V/A, and an audio oscillator (30V peak-peak) served as the piezo voltage source and the reference signal for the lock in analyzer (stepped down to 5V peak-peak to meet the voltage requirements of the analyzer). To tune the resonant frequency, phase, and working distance, a 30V tip-sample bias was applied to a gold tip (1 mm$^2$ sphere) suspended from a piezoelectric, and the tip was brought to approximately 1 cm from the sample. The phase of the lock-in amplifier was adjusted so that the current from the conducting sample and reference
signal were in phase. The frequency of the audio oscillator was adjusted (ca. 220 Hz) to result in maximum amplitude from the lock in amplifier (ca. 5 mV). The tip-sample distance was then adjusted to provide maximum signal (ca. 50 mV) without touching the sample. The tip-sample bias was then manually adjusted until the portion of the current in phase with the oscillation was zero. At zero current, the tip-sample bias is equal to the difference in work function between the sample and the tip, which was calibrated to a highly-oriented pyrolytic graphene standard to give absolute work functions.

**Ultraviolet photoelectron spectroscopy**

Ultraviolet photoelectron spectra were collected using a VG Scientific ESCALAB Mk. II in UHV (10^{-9} torr) using a differentially pumped discharge lamp with a helium pressure of 20 mtorr operating at 1.5 kV and 20 mA to produce He I (21.2 eV) radiation. The work function of the detector was calibrated using the Fermi edge Ar-sputtered silver, which was set to a binding energy of 0.0 eV. For determination of the photoelectron onset energy, the photoelectron onset and baseline were fit to linear equations, and the intercept of these two lines was reported as the photoelectron onset energy. The E_F–HOMO energy difference was determined analogously.

**PCBM spin-coating for energy level alignment studies**

PCBM thin films were spin-coated on the PEDOT:PSS, PEDOT:PSS/TiO₂, and PEDOT:PSS/TiO₂/SAMP substrates. PCBM was dissolved in chloroform (3 mg/mL) and filtered through a 0.45 micron PTFE syringe filter onto the substrate, covering it fully, then spin-coated at 4000 rpm. Thickness was determined by scratching the polymer with carbon fiber-tip tweezers and taking an AFM height image across the scratched area. The image was processed using Gwyddion AFM Suite as mentioned previously. The thickness was determined by averaging the
height data from a 32 line wide sample across the scratch, fitting constant functions to the substrate and polymer films, and taking the difference of these functions, which yields the height.

**Calculation of dipole moments**

Geometries of the substituted phenylphosphonic acids were optimized in the Gaussian® software package using density functional theory with a B3LYP hybrid functional and a 3-21G basis set. The z-component of the dipole was extracted using basic trigonometry.

**Calculation of Acid Constants**

pKₐs for the substituted phenylphosphonic acids were calculated using ACD/Percepta®.
References Cited


Chapter 5:

Performance of Devices using Modified Electrodes
Charge Transport in Organic Semiconductors

As discussed in the Introduction and the previous chapter, organic molecules and polymers can exhibit vacuum level alignment with metal electrodes, with shifts in the relative energetics due to interfacial dipoles. When two electrodes are connected, the electrodes will align with a common Fermi level. Because organic semiconductors are mostly undoped, they are assumed to be fully depleted under equilibrium conditions. Charge transfer between the two electrodes is responsible for Fermi level alignment. The transfer of charge between the two electrodes results in a built-in voltage \((V_{BI})\) that is approximately equal to the difference in the electrode work functions, which results in a corresponding electric field at zero bias. This electric field, as a function of voltage, is shown in Equation (12). For high doping levels of organic semiconductors \((10^{14}-10^{15} \text{ cm}^{-3})\) depletion of carriers and resulting band-bending is observed over thicknesses of 1 μm, and for high doping (0.02%), band-bending is observed over tens of nanometers, and depletion of carriers will influence the energy level alignment in the device.

\[
F = \frac{V - V_{BI}}{t} \tag{12}
\]

**Figure 34:** Left: Band diagram showing the built-in voltage of an organic semiconductor (green) between two electrodes (grey). Right: At zero bias, there is a corresponding built-in electric field associated with the built-in voltage.
In organic electronic devices, carriers are injected from either one or both electrodes into the active device layer. Barriers to carrier injection can impede charge transfer if $E_F$ of the electrode and the LUMO (for electron injection) or HOMO (for hole injection) of the organic semiconductor are at different energies. In this case, the contact is not ohmic, and carrier injection can be observed via three processes: direct tunneling, Fowler-Nordheim (F-N) tunneling, and thermionic emission.

*Direct tunneling*

Direct tunneling occurs when charge carriers tunnel through a potential barrier, as shown in Figure 35. Direct tunneling is typically observed in metal-insulator-metal (MIM) devices and metal-insulator-semiconductor (MIS) devices, such as diodes or MOSFETs. For thick films (>10 nm), the magnitude of the current from direct tunneling is generally negligible compared to F-N tunneling and thermionic emission.

![Figure 35: Examples of direct tunneling between two electrodes (grey) in through an insulator (blue). Left: electrons can tunnel into vacant states through a potential barrier due to the insulator LUMO. Right: holes can tunnel into occupied states through a potential barrier associated with the insulator HOMO.](image)

In the low-bias regime, current densities due to direct tunneling are approximated by Equation (13), where $t$ is the device thickness, $m_{\text{eff}}$ is the charge carrier effective mass in the
insulator, and $\varphi$ is the barrier height. For the device shown in Figure 35, $\varphi$ is the $E_F$-LUMO energy difference for electrons and the $E_F$-HOMO difference for holes. At high fields ($10^8$ V/m), devices typically transition from direct tunneling to F-N tunneling:\(^3,4\)

$$J_{d,low} \approx \frac{q}{4\pi^2\hbar} F^2 \exp\left(\frac{2t\sqrt{2\varphi m_{eff}}}{\hbar}\right)$$ (13)

Fowler-Nordheim Tunneling

F-N tunneling occurs at high biases, and describes the process by which charge carriers tunnel through a triangular potential barrier into vacant states (Figure 36).\(^3\) After injection of the carrier into the semiconductor, the electric field will result in transport to the other electrode. MIM and MIS devices can transition from direct to F-N tunneling when the voltage dropped over the semiconductor is larger than the barrier to carrier injection; this occurs when the applied bias is greater than the built-in potential plus the barrier to carrier injection ($V > V_{BI} + \varphi$).

![Figure 36: Example of F-N tunneling from electrodes (grey) into a semiconductor (green). Left: F-N tunneling of electrons through the LUMO into vacant states. Right: F-N tunneling of holes through the HOMO into occupied states.](image)

For devices in which carrier injection is limited by F-N tunneling, the current density, $J$, is given by Equation (14), in which $A$ and $B$ are constants; $\beta$ is the field enhancement factor, which corrects for local field-enhancement at the interface ($\beta$ often scales with surface roughness.
and can have values of up to 1000 for rough electrode surfaces); \(v(y)\) and \(t(y)\) are functions that correct for the change in barrier height due to image charge, \(F\) is the electric field; and \(\varphi\) is the barrier to carrier injection. For electron injection, this is the \(E_F\)-LUMO energy difference; for hole injection, this is the \(E_F\)-HOMO energy difference. The correction functions \(v(y)\) and \(t(y)\) can be approximated using Equations (17) and (18), where \(y(F)\) is the Nordheim parameter.\(^5\) A straight line in a plot \(\ln(J/F^2)\) vs. \(1/F\) typically indicates that F-N tunneling is the dominant current injection mechanism.

\[
J_{FN} = A \frac{(\beta F)^2}{t^2(y) \varphi} \exp \left( -v(y) B \frac{\varphi^{3/2}}{\beta F} \right)
\]

\[
A = \frac{q^3}{16\pi^2 \hbar} \approx 1.54 \times 10^{-6} \frac{A\ eV}{V^2}
\]

\[
B = 4 \frac{\sqrt{2m_{\text{eff}}}}{3\hbar q} \approx 6.83 \times 10^9 \frac{V}{m\ eV^{3/2}}
\]

\[
v(y) \approx 1 - y^2 - \frac{y^2 \ln(y)}{3}
\]

\[
t(y) \approx 1 + \frac{y^2 - y^2 \ln(y)}{9}
\]

\[
y(F) = \frac{c \sqrt{\beta F}}{\varphi}
\]

\[
c = \sqrt{\frac{q^3}{4\pi \varepsilon_0}} \approx 1.20 \frac{eV\ nm^{1/2}}{V^{1/2}}
\]

**Thermionic Emission**

Thermionic emission is the injection of thermally excited carries that have enough energy to overcome the potential barrier (Figure 37). Experimentally, thermionic emission can be distinguished from tunneling by examining the temperature dependence of the \(J-V\) characteristics: thermionic emission exhibits temperature dependence, whereas F-N and direct
tunneling do not. Thermionic emission is typically observed at low fields; at high fields, devices often transition to F-N tunneling.

![Thermionic emission](image)

**Figure 37:** Thermionic emission, in which thermally excited electrons (left) or holes (red) can be injected into the semiconductor active layer.

For organic semiconductor devices without extrinsic dopants, depletion of carriers is not observed, and the barrier height would be expected to remain unchanged under an applied bias. However, the barrier height *does* change due to the Schottky effect (Figure 38), which results in a decrease in the barrier height due to image charge; this decrease is proportional to $\sqrt{F}$. Taking this reduction of the barrier height into account results in Equation (22) for the thermionic emission current, where $\lambda$ is a correction factor that typically has a value near 0.5, $k$ is the Boltzmann constant, $T$ is temperature, and $A_R$ is the Richardson constant.

![Schottky effect](image)

**Figure 38:** The Schottky effect reduces the barrier to charge carrier injection by an amount proportional to $\sqrt{F}$. 

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Since many organic semiconductors have low carrier mobilities, space-charge limited current (SCLC) is common; in this regime, injection of new carriers is limited by removal of charged carriers from the active layer. SCL transport typically occurs at high current densities. The current density is given by Equation (23), where $\epsilon$ is the dielectric constant of the material, $\epsilon_0$ is the electric constant, $\mu$ is the mobility of the charge carriers of interest, and $L$ is the device thickness. Charge carriers in many organic devices often move between localized states (as opposed to delocalized states present in inorganic semiconductors), in which case a field dependent mobility is observed. This field dependent mobility is equal to $\mu_0 \exp(\sqrt{F/E_0})$, where $\mu_0$ is the measured value at a particular field $E_0$; this results in the current density shown in Equation (24). Experimentally, SCLC is often tested for by repeating device measurements with different thicknesses of the active layer.

$$J_{SCLC} = \frac{9}{8} \epsilon \epsilon_0 \mu \frac{F^2}{L^3}$$  \hspace{1cm} (23)$$

$$J_{SCL} = \frac{9}{8} \epsilon \epsilon_0 \frac{F^2}{L^3} \mu_0 \exp \left( \frac{F}{\sqrt{E_0}} \right)$$  \hspace{1cm} (24)$$

In general, organic electronic devices show either injection-limited or space-charge limited charge transport. In the case of injection-limited charge transport, the injection of carriers can take place by direct tunneling, F-N tunneling, or thermionic emission. The different charge
transport mechanisms have distinct current-voltage characteristics; this allows determination of the mechanism of charge transport through analysis of the device characteristics.

**Prior Work on MEH-PPV Diodes and Light-Emitting Diodes**

MEH-PPV is a well-studied polymer material often used as the emissive layer in OLEDs. Much work has gone into characterizing hole injection into this material and determining methods to increase such hole injection from ITO using conducting polymers, including PEDOT:PSS. MEH-PPV devices can be treated as a MIM device, with a built-in voltage that is essentially equal to the difference in cathode and anode work functions and a corresponding built-in electric field.\(^1\) In a comparison between ITO and ITO/PANI:PSS electrodes, Yang, *et al.*, determined that device ITO/MEH-PPV devices were hole-injection limited, and increasing the effective work function using a conducting polymer afforded increased current densities in devices by decreasing the E\(_F\)-HOMO energy difference.\(^7\) The authors attributed the current to F-N tunneling, although device analysis was not thorough: it was not ascertained whether PANI:PSS yielded devices that showed injection-limited or SCL currents. Malliaras, *et al.*, fabricated MEH-PPV diodes with Au anodes and different cathodes; after correcting for the built-in voltage, devices showed the same current densities for a given V-V\(_{BI}\), except in the cases where a Ca cathode was used; the low work function of Ca results in electron injection contributing to a substantial portion of the total device current.\(^8\) Because of the small E\(_F\)-HOMO energy difference between gold and MEH-PPV, the contact was essentially Ohmic, and after exceeding the built-in voltage, devices showed SCLC with a field-dependent mobility attributed to a conduction mechanism with localized charge carriers. Interestingly, the authors did not observe the “pillow effect” that is common with Au/organic interfaces and that leads to a reduction in the effective Au work function. In a subsequent paper, Malliaras, *et al.*, fabricated
symmetric devices using the same metal for the anode and cathode. It was determined that, for
$E_f$-HOMO $< 0.3$ eV, devices showed SCL current densities at all applied biases. At higher $E_f$-
HOMO energy differences (0.3-0.5 eV), devices showed injection limited current at low fields
($<10^8$ V/m). In injection-limited devices, thermionic emission of carriers was implicated as the
mechanism of carrier injection, as a plot of $\ln(J/F^2)$ vs. $\sqrt{F}$ yielded a straight line; for F-N
tunneling, $\ln(J/F^2)$ is proportional to $1/F$. As thermionic emission and SCLC display similar
voltage dependences, it can be difficult to distinguish between the two phenomena. At higher
electric fields ($>1.5 \times 10^8$ V/m), devices that are injection-limited can undergo a transition to the
SCL regime. This was experimentally demonstrated by plotting $\ln(J/F^2)$ vs. $\sqrt{F}$ for a variety of
metal electrodes, yielding plots that contained two linear regions: one at low fields ($<10^8$ V/nm),
which was a function of the $E_f$-HOMO barrier ($\phi$), and attributed to the Schottky effect, and one
high fields ($>1.6 \times 10^8$ V/m), which was independent of the choice of electrode, and attributed to
SCLC.

A summary of published MEH-PPV device data is as follows: For small barrier heights
(0.3-0.5 eV) and low fields, hole-only MEH-PPV devices have been shown to be injection
limited, with thermionic emission (barrier derived) as the mechanism of carrier injection. For
larger barrier heights, devices are injection limited, with F-N tunneling as the dominant carrier
injection mechanism. At large enough fields ($\sim 1.6 \times 10^8$ V/m), devices with small barrier
heights (0.3-0.5 eV) can undergo a transition from injection-limited to space-charge limited
current.
Fabrication and Measurement of MEH-PPV Diodes

MEH-PPV was spin-coated onto freshly-cleaned ITO or ITO/SAMP substrates from a 12.0 mg/mL chloroform solution at 1500 rpm, yielding a polymer thickness of $78.8 \pm 0.8$ nm (Figure 39). Films showed good uniformity (RMS height of 0.8 nm, RMS phase of 0.3°) with no noticeable pinholes (Figure 40).

**Figure 39:** AFM Height Image of scratched MEH-PPV and accompanying height profile across line “1”. The red line is the polymer edge; the thickness is $78.8 \pm 0.8$ nm.

**Figure 40:** AFM height and phase images of MEH-PPV on ITO, showing good height (RMS 0.8 nm) and phase (RMS 0.3°) uniformity across the whole sample, and no observable pinholes.
An Al cathode was evaporated on the ITO, ITO/SAMP, and ITO/PEDOT:PSS samples. An Al cathode has previously been shown to suppress electron injection due to the large $E_F$-LUMO barrier of 0.9 eV, ensuring that hole injection from the modified electrodes is responsible for the observed current. Devices were run from zero bias to $+10V (V_{ITO} - V_{Al})$ until the current density saturated, then recorded. Samples that exhibited shorts were not included in the device analysis. For the data shown in Figure 41, the current-voltage data were averaged over at least four separate devices on the same chip; ITO/CF3PA and ITO devices showed currents that were equal within error across chips, suggesting good reproducibility. Devices with larger work functions showed higher current densities, consistent with an expected reduction of the $E_F$-HOMO barrier.

Figure 41: J-V plot for MEH-PPV with ITO, ITO/SAMP, and ITO/PEDOT:PSS electrodes: ITO/CF3PA (red), ITO/4FPA (purple), ITO/PEDOT:PSS (green), ITO (black), and ITO/F2PA (blue).
Plots of the J-V data on lin-log and log-log scales are shown in Figure 42. The log-log plots of the ITO and ITO/SAMP devices appear linear at intermediate biases, but not at high biases, which suggests F-N tunneling may not be the dominant current mechanism at high biases. Instead, a logarithmic plot of the ITO and ITO/SAMP J-V data is linear at high biases. Linearity in the lin-log plot could be explained by SCLC or thermionic emission. However, the high fields (~10^8 V/m) suggest that if the devices were injection-limited, F-N tunneling would be the expected injection mechanism. Furthermore, the current densities for the ITO and ITO/F2PA devices are much lower than for ITO/FPA and ITO/CF3PA; the lower observed work functions of the ITO and ITO/F2PA electrodes would yield injection-limited device, and thus SCLC cannot adequately explain the increased current density at higher voltages for all samples.

**Figure 42:** Log-log (left) and lin-log (right) J-V plots of MEH-PPV devices. The log-log plot shows a slope that increases with increasing voltage, suggesting that tunneling is not the dominant carrier injection mechanism. The lin-log plot shows a constant slope at high biases for the untreated ITO and ITO/SAMP samples.
An ITO/CF3PA device is shown in Figure 43. For this device, the current is proportional to the voltage at low biases, indicative of Ohmic behavior; at intermediate biases (2-7 V), the voltage is proportional to \((V-V_{\text{BI}})^2\), where \(V_{\text{BI}} = 1.33 \pm 0.03\) V. The built-in voltage is similar to the difference in the work functions between Al (\(\Phi = 4.1\) eV) and ITO CF3PA (\(\Phi = 5.3\) eV); the difference could be due to the presence of an interfacial dipole between the SAMP and MEH-PPV. This current-voltage relation at intermediate biases is indicative of SCLC or F-N tunneling. At higher biases (>7 V), the slope increases with increasing voltage, which suggests SCLC with a field-dependent hole mobility. Overall, the high work function of ITO/CF3PA (\(\Phi = 5.3\) eV) and the ionization potential of MEH-PPV (5.1 eV) suggests a low barrier to hole injection. Since the work function of the electrode is on the order of the ionization potential of MEH-PPV (5.1 eV), it is likely that the Fermi level of the electrode is pinned to the HOMO of MEH-PPV. Based on previous work that demonstrates SCLC of holes with a field-dependent mobility in MEH-PPV diodes with high work function metals,\(^8,9\) attributing the observed current-voltage characteristics of the ITO/CF3PA/MEH-PPV diodes to SCLC seems well-justified.
Figure 43: Log-log J-V plot of a representative MEH-PPV diode with ITO/CF3PA as the hole-injecting electrode. The device exhibits Ohmic conduction at low biases (dotted line), and SCLC at intermediate biases (dashed line), with a field-dependent hole mobility at high biases (>7 V). This curve shape is typical for MEH-PPV devices made with ITO and ITO/SAMP electrodes.\(^7\)

The relative current densities were compared in order to ascertain the mechanism of carrier injection (Table 9); this has been demonstrated by other authors with other systems, and has also been used by Malliaras, et al., with MEH-PPV.\(^9\) For the analysis of this work, the current densities at +10V were used, as the large bias should lessen the effects of the differences in the built-in voltage due to the different work functions of the hole-injecting electrode, and \(V-V_{BI}\) could not be accurately determined by curve fitting for some devices. If thermionic emission were responsible for the observed device behavior, a plot of the log of the current density vs. the change in work function (which should correlate linearly with the change in \(\phi\)) would give a straight line with a slope of \(1/kT\). For this fit (Figure 44, left) the slope is much less than \(1/kT\) (observed: 3, expected: 39), which means that the decreases in barrier height gives a much smaller increase in current density than expected. This suggests that thermionic emission is not
the dominant carrier injection mechanism. Alternatively, if current injection takes place primarily by F-N tunneling in the high-field regime, where the exponential portion of Equation (14) the equation evaluates to unity, the current density should be inversely proportional to \( \phi \). If the ITO/CF3PA sample is excluded from this analysis, under the assumption that the Fermi level is pinned to the HOMO of MEH-PPV and the change in work function is not equal to the change in barrier height for this sample, the remaining data show a good fit (Figure 44, right). This fit yields a calculated \( E_F - \text{HOMO} \) energy difference of 0.31 eV for the ITO sample, which seems low based on the difference between the work function of ITO (\( \Phi = 4.5 \) eV) and the ionization potential of MEH-PPV (5.1 eV), although a reduction of the barrier by an electrode/MEH-PPV interfacial dipoles could explain this discrepancy. It should be noted, however, that this number is in good agreement with Heeger, et al., based on measurements of ITO/MEH-PPV devices.\(^\text{10}\)

Unfortunately, there is not much literature to which to compare this analysis. Heeger, et al., have compared the effect of work function to electron injection into MEH-PPV using quantum yield as a metric for electron injection, as the rate of recombination should scale linearly with electron concentration.\(^\text{10}\) The authors noted that the change in metal work function correlates with quantum yield as predicted by Equation (14), with the exponential portion being most important the quantum yield. However, the authors provide no information about the fields at which this data was accumulated, so this could be due to the data being collected at low fields. Moreover, hole-injection still makes up the majority of the measured current density in these devices. For the large fields (1.3 x 10^8 V/m) employed in this work, the exponential could be expected to evaluate to unity (depending on the field-enhancement factor and evaluation of the correction function \( v(y) \)). This assumption fits the measured current-voltage dependences, as
they are nearly proportional to \( V^2 \). Thus, the pre-exponential inverse barrier height dependence would determine device current among the ITO and ITO/SAMP devices.

### Table 9: Relative Current Densities for Different Electrodes

<table>
<thead>
<tr>
<th>Electrode</th>
<th>( \Delta \Phi )</th>
<th>Relative Current Density at +10V</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO (control)</td>
<td>0</td>
<td>1.00 ± 0.07</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS</td>
<td>-</td>
<td>7 ± 3</td>
</tr>
<tr>
<td>ITO/CF3PA</td>
<td>0.73</td>
<td>15 ± 5</td>
</tr>
<tr>
<td>ITO/4FPA</td>
<td>0.28</td>
<td>7 ± 3</td>
</tr>
<tr>
<td>ITO/F2PA</td>
<td>-0.36</td>
<td>0.4 ± 0.2</td>
</tr>
</tbody>
</table>

### Figure 44: Log (left) and linear (right) plots of the relative current density at +10V vs. \( \Delta \Phi \) for MEH-PPV devices made with ITO and ITO/SAMP electrodes. Left: An exponential fit yields a slope much less than \( 1/kT \) (observed: 3 eV\(^{-1}\), expected: 39 eV\(^{-1}\)), suggesting thermionic emission is not responsible for the observed device behavior. Right: An inverse function \( (J(\Delta \Phi) = 1/(\Phi_0-\Delta \Phi)) \) shows a good fit for the ITO, ITO/F2PA, and ITO/FPA data, with a derived \( E_F-HOMO \) difference of 0.31 eV for ITO/MEH-PPV; this value is in agreement with literature values.\(^{10}\)
Prior Work on PCBM Diodes

Prior work on PCBM diodes showed that low work function metals (Ca, LiF:Al) are needed to achieve SCLC transport. LiF:Al cathodes gave a thousand-fold increase in current density compared to Al cathodes, due to the lower work function of the LiF:Al electrode.\(^{11}\) The authors attributed this increase in current density to a change from F-N tunneling (with Al) to SCLC (with LiF:Al). Chiguarve, et al., have also fabricated and tested PCBM diodes with Al contacts. For these devices, current densities were proportional to the square of the \((V-V_{\text{bi}})^2\), which suggested that F-N tunneling was the dominant current mechanism. The authors suggested that local field enhancement at the rough electrode interface decreased the effects of the \(E_{\text{F}}\)-LUMO offset, which they calculated to be 0.89 eV.\(^{12}\) This value is similar to the PEDOT:PSS/PCBM \(E_{\text{F}}\)-LUMO offset extracted from UPS measurements, which was measured to be 0.92 eV.

Fabrication and Measurement of PCBM Devices

Fabricated devices had films of PCBM that were 80-nm thick as determined by AFM (not shown). The film showed a smooth morphology with rms roughnesses of 0.7 nm over a 5 \(\mu\)m x 5 \(\mu\)m sample (Figure 45), and 1.3 nm over a 20 \(\mu\)m x 20 \(\mu\)m sample (not shown), and exhibited no obvious change in thickness by optical microscopy except at the substrate edges. These low rms roughnesses, combined with the low rms roughnesses of PEDOT:PSS suggest devices with a flat PCBM film on a flat PEDOT:PSS substrate.
Figure 45: AFM height (left) and phase (right) images of PCBM on ITO.

Devices were measured using hanging mercury drop electrode in order to rapidly screen multiple samples. The mercury drop had a radius of approximately 0.48 mm, leading to a device area of 0.72 mm$^2$. Devices were forward biased to test electron injection from PEDOT:PSS from zero bias to +4V ($V_{\text{Hg}} - V_{\text{PEDOT:PSS}}$) until the current density saturated, then recorded; devices were not tested in reverse bias.

PEDOT:PSS Electrodes

PEDOT:PSS/PCBM devices behaved similarly to devices reported by Chiguarve, et al., exhibiting Ohmic conduction at low biases (Fig. 1, dashed line) and current densities proportional to $(V-V_{\text{BI}})^2$ at high biases (Fig. 2, dotted line). This suggests the device current is due to a field-dependent mechanism such as F-N tunneling or SCLC. The devices in this work with PEDOT:PSS electrodes show current densities two orders of magnitude lower than devices with Li:F/Al electrodes; this and the large measured $E_F$-LUMO difference suggest that devices in this work are not SCL, but injection-limited, with injection taking place via F-N tunneling.
Typically, metal/organic/metal devices have a positive built-in voltage: the lower work function electrode is used for electron injection, and the higher work function electrode for hole injection. The PEDOT:PSS/PCBM devices have a negative built-in voltage of \(-0.248 \pm 0.001\) V, which would be expected because PEDOT:PSS has a higher work function than the mercury electrode (4.66 vs. 4.5 eV, respectively). This value is larger than the difference between the two work functions (-0.16 eV), although this simple calculation neglects the presence of any interfacial dipole between the electrodes and the PCBM. UPS data implies an interfacial dipole between PEDOT:PSS and PCBM, which effectively increases the PEDOT:PSS work function by 0.30 eV (to 4.96 eV), which suggests a Hg/PCBM dipole of 0.21 eV. The field-squared dependence at high biases suggests the device could be injection limited, with F-N tunneling being the dominant injection mechanism, or space-charge limited. A plot of the \(\ln(J/V^2)\) vs. \(1/(V-V_{BI})\) yields a straight line at high biases, suggesting that F-N tunneling is responsible for the observed device behavior. This makes sense, given that the barrier height (0.92 eV) is very large and the relative value of the current density compared to devices with Li:F/Al electrodes. Fitting
to a simplified F-N equation of the form $J/V^2 = A_0 \exp[-V_0/(V-V_{B1})]$ using the previously determined $V_{B1}$ yields a pre-exponential constant, $A_0 = 309 \pm 1 \text{ A/m}^2\text{V}^2$, and an exponential decay constant, $V_0 = 0.286 \pm 0.006 \text{ V}$. The values of these constants are shown in Equations (25) and (26), where $L$ is the device thickness, and $v(y)$ and $t(y)$ are the functions previously described in Equations (17) and (18).

$$A_0 = A \frac{\beta^2}{t^2(y) \varphi L^2} \quad (25)$$

$$V_0 = v(y) B \frac{L \varphi^{3/2}}{\beta} \quad (26)$$

**PEDOT:PSS/TiO₂ Electrodes**

An interesting behavior was noted in PEDOT:PSS/TiO₂/PCBM diodes, in which the current rose sharply after a threshold voltage ($V_t, \sim 1.5 \text{ V}$) was applied (Figure 47, black). Subsequent measurements (Figure 47, blue) showed an order of magnitude increase in the current density compared to the current densities measured before exceeding the threshold voltage. In an effort to understand the cause and effect of this transformation, the initial sweep and a sweep of the device after exceeding the threshold voltage were compared.
**Figure 47:** J-V before (black) and after (blue) exceeding the threshold voltage.

In the first sweep, the device shows Ohmic conduction at low biases, and current proportional to \((V-V_{BI})^2\) at high biases (Figure 48, left) with \(V_{BI} = 0.280 \pm 0.008\) V. The change in the built-in voltage from negative to positive is consistent with a decrease of the effective PEDOT:PSS work function by \(0.548 \pm 0.009\) V. UPS measurements show a decrease in work function of \(0.40 \pm 0.05\) eV and a reduction in the electrode/PCBM interfacial dipole by \(0.18 \pm 0.05\) eV. *In toto*, this results in a change in the effective work function of \(0.6 \pm 0.1\) eV. The changes in work function determined by UPS and fitting of the J-V data are equal within error, suggesting that the observed shift in the built-in voltage is explained by the change in the effective electrode work function.

The F-N plot (Figure 48, right) yields a pre-exponential factor, \(A_0 = 3500 \pm 200\) A/m\(^2\)V\(^2\), and a decay constant, \(V_0 = 4.76 \pm 0.007\) V. The increases in both \(A_0\) and \(V_0\) cannot be explained alone by a change in the barrier height: if this were the case, an increase of one of these parameters would lead to a decrease in the other.
Figure 48: Log-log J-V (left) and F-N (right) plots before exceeding $V_t$.

After exceeding the threshold voltage (Figure 49), the current density is similar to unmodified PEDOT:PSS. There is Ohmic conduction at low biases, and a current proportional to $(V-V_{Bi})^2$ at higher biases, although the built-in voltage has changed ~0.7 V after exceeding $V_t$: from $+0.280 \pm 0.008$ V to $-0.419 \pm 0.007$ V. A F-N plot suggests F-N tunneling to be the dominant current mechanism, with a pre-exponential factor $A_0$ $1893 \pm 8 \text{ A/m}^2\text{V}^2$, and an exponential decay term $V_0$ of $0.880 \pm 0.008$ V.
The changes of $A_0$ and $V_0$ between samples suggest that changes in barrier height alone are not responsible for the observed device behavior as an increase in one value would be expected to lead to a decrease of the other value. It is possible that a combination of changes in the barrier height and the field-enhancement factor, $\beta$, are responsible, although this complicates the analysis. Changes in the field-enhancement factor are not surprising, however, as the field-enhancement factor depends on the local electric field at the surface, and deposition of the TiO$_2$ adhesion layer could substantially change this local electric field. Overall, the values of $A_0$ and $V_0$ are similar for the PEDOT:PSS electrode and for the PEDOT:PSS/TiO$_2$ electrode after exceeding $V_t$, while vastly different for the PEDOT:PSS/TiO$_2$ electrode before exceeding $V_t$, which suggests the barrier height and field enhancement factor are similar between the former, and much different for the latter.

Overall, the change in the effective work function did not lead to an increase in the current density, although an interesting turn-on behavior was noted, in which after exceeding a threshold voltage, $V_t$, the device behavior changes dramatically. F-N plots suggest that the
devices are injection-limited. Before exceeding $V_t$, PEDOT:PSS/TiO2 devices show decreased current densities when compared to PEDOT:PSS devices. After exceeding $V_t$, the device characteristics and F-N fitting parameters are similar between the PEDOT:PSS and PEDOT:PSS/TiO2 devices.

**IPES Studies of TiO2 on H-Si**

One of the assumptions in this work is that the TiO2 would not serve as an electron-blocking layer based on the conduction band energies of bulk TiO2. However, IPES measurements of Si/TiO2 reveal that the TiO2 layer has an ionization electron affinity of 3.0 eV and a bandgap of 4.5 eV, both of which are stable under air and with annealing at 400 °C. The ionization potential and bandgap here are much higher in energy and larger, respectively, than those of nano-crystalline TiO2 used as an electron transport layer in dye-sensitized solar cells, which have a bandgap of 3.0 eV for ~10 nm crystalline particles, equal to the bulk bandgap. Thus, the original hypothesis that TiO2 would not act as an electron blocking layer was somewhat flawed, as the thin films used in this work show a massive deviation from the bulk properties of TiO2, with a corresponding negative impact on device performance. The deviation between the electronic properties is likely a due to differences in crystallinity of the material. Amorphous material or material with very small grain sizes would be expected to result in a larger bandgap due to a lack of long-range order.

The fact that these TiO2 layers are electron-blocking may seem counter-intuitive as TiO2 grown using this method has been employed as a hole-blocking/electron transport layer in Si/TiO2 photovoltaics. The difference between these two devices is as follows: In Al/TiO2/Si devices, electrons in the conduction band of Si can tunnel into vacant states in the Al electrode;
in PEDOT:PSS/PCBM devices, vacant states in PCBM are higher in energy than the work function of the electrode, so carriers must tunnel through TiO₂ and PCBM. The measured value of the electron affinity of this TiO₂ layer leads to energy level alignments shown in Figure 50.

![Energy level diagram](image)

**Figure 50:** Expected energy level alignments in PCBM devices, including the TiO₂ conduction and valence band energies from IPES measurements of H-Si/TiO₂ samples.

Thus, the decrease in the current density of devices with a PEDOT:PSS/TiO₂ electrode compared to the unmodified PEDOT:PSS electrode might be attributed to the barrier to electron injection resulting from the presence of TiO₂ (Figure 51). This potential barrier does not limit device performance after exceeding V_t, where the change in built-in voltage attributed to the residual t-butoxide groups vanishes, and the total device current and F-N fitting parameters are similar to unmodified PEDOT:PSS electrodes. The same behavior is observed in PEDOT:PSS/TiO₂/F2PA electrodes: compared to PEDOT:PSS electrodes, there is a shift in the built-in voltage arising from the presence of F2PA before exceeding V_t. After exceeding V_t, the
device currents are comparable to pristine PEDOT:PSS, and the shift in the built-in voltage reverses. Based on this information, it is proposed that electrochemical reduction of the TiO$_2$ (to conductive Ti$^{3+}$) and the phosphonate to a non-bound phosphinate$^{15}$ are responsible for the change in device properties. The data are presented vs. $V_{\text{Hg-ITO}}$; as $V_{\text{Hg-ITO}}$ increases, the PEDOT:PSS cathode is more reducing. This electrochemical reduction would be facilitated by the acidic protons in PEDOT:PSS.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure51.png}
\caption{Comparison of PEDOT:PSS (red) and PEDOT:PSS/TiO$_2$ (black) devices after correcting for built-in voltage. For PEDOT:PSS/TiO$_2$ devices, only the data below the threshold voltage is shown, as analysis suggests the built-in voltage changes after exceeding $V_t$.}
\end{figure}

Overall, this device behavior suggests that while the TiO$_2$ adhesion layer allows subsequent attachment of phosphonic acids and modification of the effective PEDOT:PSS work function, it hinders electron injection into PCBM. As noted in Chapter 4, both thin (~0.5 nm) and thick (1.5 nm) TiO$_2$ adhesion layers allowed attachment of phosphonic acids and provided similar changes of the effective work function of PEDOT:PSS. Thus, it may be possible to use a thinner adhesion layer, which could allow attachment of phosphonic acids but not appreciably
block the electron current, in order to improve electron injection into PCBM, although if the change in device behavior is indeed due to electrochemical reduction, this may only help at sub-reduction potentials.

**Experimental**

**MEH-PPV Spin-coating for device fabrication**

MEH-PPV thin films were spin-coated on clean ITO and SAMP-treated ITO substrates. MEH-PPV (Aldrich) was dissolved in chlorobenzene (12.0 mg/mL) using ultrasonication. The solution was filtered through a 5 μm PTFE syringe filter onto the substrate, covering it fully, then spin-coated at 1500 rpm. Thickness was determined by AFM. Devices were fabricated by evaporation of aluminum contact pads onto the MEH-PPV-coated samples through a shadow mask. The shadow mask featured a 4x4 grid of circles with 0.03 cm² total area per device. Samples in the corners were not used due to the polymer accumulation at the sample edge. The base pressure of the evaporation chamber was 2-3·10⁻⁶ torr, the evaporation pressure was 4-5·10⁻⁶ torr, the evaporation rate 1-2 nm/s, and the aluminum thickness was 200 nm. I-V measurements were taken using an HP Semiconductor Parameter Analyzer. VITO-VAl was swept from 0-10V and back in 50mV increments and a medium integration time. This was repeated until the devices showed stable I-V characteristics, at which point the data was recorded.

**PCBM spin-coating and device Fabrication**

PCBM (Nano C) was dissolved in chloroform (20 mg·mL⁻¹) using ultrasonication. The solution was filtered through a 0.45 μm PTFE syringe filter onto the substrate covering it fully then spin-coated at 1500 rpm. Thickness was determined by AFM. I-V measurements were taken using an HP Semiconductor Parameter Analyzer and a hanging mercury drop electrode. The contact
radius of the mercury drop was 0.48 mm. $V_{\text{Hg}}-V_{\text{PEDOT:PSS}}$ was swept from 0-4V in 50mV increments and a medium integration time. Data from the first measurement were recorded. The bias was then swept until the devices showed stable I-V characteristics, at which point the data were recorded.
References Cited


Chapter 6

Conclusions and Proposals for Future Work
Major Conclusions of this Work

The growth of TiO$_2$ thin films on PEDOT:PSS was accomplished using chemical vapor deposition with titanium(IV) $t$-butoxide as the precursor. Cooling of the substrate was found to be critical for thin film growth, and film thicknesses were found to increase with exposure time up to a thickness of approximately 1.5 nm as determined by XPS. Residual $t$-butoxide groups were hypothesized to be responsible for slowing the growth rates at this critical thickness, as they could prevent coordination of additional Ti(IV) $t$-butoxide to TiO$_2$. TiO$_2$ thin films were also grown on hydrogen-terminated silicon in order to characterize any residual carbon-containing species that may be present. XPS spectra showed high binding energy C(1s) peaks, which were attributed to residual $t$-butoxide groups.

The TiO$_2$ serves as an adhesion layer that can react with phosphonic acids to form bound phosphonates using a simple dip procedure. The use of phosphonic acids with permanent molecular dipoles allows facile tuning of the PEDOT:PSS work function by ±0.4 eV, with a good correlation between the gas phase molecular dipole and the total change in work function, which indicates well-oriented films of phosphonates that are nearly perpendicular to the TiO$_2$ surface. The changes in work function with the PEDOT:PSS/TiO$_2$ electrode were similar to those observed on ITO. Since phosphonates are known to form good, well-ordered monolayers on ITO, this suggests good molecular coverage of the phosphonate on PEDOT:PSS/TiO$_2$. For as-grown PEDOT:PSS/TiO$_2$ samples, a decrease of the work function of 0.4 eV relative to PEDOT:PSS samples was observed. This decrease was attributed to a surface dipole resulting from residual $t$-butoxide groups; the magnitude of this reduction in work function change could be decreased by soaking in ethanol, which results in ligand exchange with trace water.
The modified PEDOT:PSS electrodes were used to fabricate PCBM diodes. UP spectra showed that changing the work function using TiO$_2$- and TiO$_2$/phosphonate-modified electrodes allowed tuning of the $E_F$-LUMO energy difference at the electrode/PCBM interface. PEDOT:PSS/PCBM devices exhibit a large $E_F$-LUMO energy difference of 0.92 eV, which can be reduced to 0.37 eV with PEDOT:PSS/TiO$_2$/F2PA, and as low as 0.25 eV with as-grown PEDOT:PSS/TiO$_2$ containing residual $t$-butoxide groups. PEDOT:PSS/PCBM, PEDOT:PSS/TiO$_2$ and PEDOT:PSS/TiO$_2$/F2PA diodes all showed injection limited current, with F-N tunneling as the mechanism for charge carrier injection. The built-in voltage could be extracted from device data: good agreement between $V_{BI}$ and $\Delta \Phi$ of the modified electrodes indicates that this change in built-in voltage is due to a change in the effective work function of the PEDOT:PSS electrodes.

As PCBM is an n-type electron organic semiconductor and PEDOT:PSS/PCBM diodes show injection-limited current, reduction of the $E_F$-LUMO energy difference should have resulted in increased electron injection with modified PEDOT:PSS electrodes. However, the TiO$_2$ devices show decreased device currents; IPES measurements of Si/TiO$_2$ show that the band gap of TiO$_2$ grown using this procedure (4.5 eV) is much larger than the band gap of nanocrystalline or bulk TiO$_2$ (3.1-3.2 eV).$^1$ This suggests that the TiO$_2$ adhesion layer adds a barrier to electron injection. This may seem counter-intuitive, as TiO$_2$ grown using this method has been employed as a hole-blocking/electron transport layer in Si/TiO$_2$ photovoltaics.$^2$ The difference between these two devices is that electrons in the conduction band of Si can tunnel into vacant states in the Al electrode; in PEDOT:PSS/PCBM devices, vacant states in PCBM are higher in energy than the work function of the electrode, so carriers must tunnel through TiO$_2$ and PCBM.
PEDOT:PSS/TiO$_2$ and PEDOT:PSS/TiO$_2$/F2PA devices showed a substantial change in the behavior at ~1.5 V, with the current density increasing dramatically along with a change in the built-in voltage; this change leaves the built-in voltage close to the built-in voltage of unmodified PEDOT:PSS. These changes are attributed to a reduction of Ti$^{4+}$ in TiO$_2$ to Ti$^{3+}$, resulting in conducting TiO$_{2-x}$ and reduction of the phosphonate to a non-coordinating phosphinate.$^3$ This reduction is likely facilitated by the acidic protons in PEDOT:PSS.

The purpose of this project was to develop a method to control energy level alignment at organic/organic interfaces that could be usable for devices. While control of energy level alignment was demonstrated, this system proved to be unusable for use in devices. It has been hypothesized that reduction of the adhesion layer and the phosphonate are responsible for the change in device behavior; it could be possible to replace TiO$_2$ with another metal oxide that is not easily reduced, such as SiO$_2$, although reduction of phosphonates could prohibit the use of a SAMP to lower the work function. Presumably different functional groups could be employed that are not susceptible to reduction. It has been hypothesized that this reduction is facilitated by acidic protons in the conducting polymer; since conductive polymers typically employ an acid-containing polymer, it may not be possible to use the TiO$_2$ adhesion layer/SAMP system with these conducting polymers. On the other hand, this system could prove to be usable with semiconducting polymers or small molecules that lack acid functionality.

It may be tempting to use suggest these for improving hole-injection from conducting polymers, as the opposite potential would not result in reduction of TiO$_2$ or the phosphonate. However, conducting polymers are already high work function electrodes. Moreover, the deep valence band of TiO$_2$ would block holes more strongly than electrons; indeed, the TiO$_2$ grown
using this method has been employed as a hole-blocking layer for silicon/TiO₂ heterojunction photovoltaics.²

**Proposals for Future Work**

Future work should include a test of the hypothesis that reduction of TiO₂ is responsible for the change in device behavior. This could be confirmed by applying a voltage greater than the threshold voltage to the sample, removing the PCBM from the modified PEDOT:PSS electrode under inert atmosphere, then determining the oxidation state of Ti by XPS (Figure 52). Furthermore, it should be possible to determine whether the acidic environment provided by PEDOT:PSS is necessary for the reduction of TiO₂. This could be accomplished through the use of ITO/TiO₂ electrodes, and the measurement of ITO/TiO₂/PCBM diodes: a lack of switching behavior should support this hypothesis.

![Figure 52: Proposed experiment for testing TiO₂ reduction hypothesis](image)

If TiO₂ can indeed be electrochemically reduced with PEDOT:PSS electrodes, it may be possible to reoxidize TiO₂ at the PEDOT:PSS/TiO₂ interface. Changes in the oxidation state of the TiO₂ could be probed by XPS as illustrated above. Before reduction, devices exhibited low current density, while after reduction, current density increases. If it is indeed possible to switch TiO₂ between conductive (reduced) and resistive (oxidized) states, the PEDOT:PSS/TiO₂ system could be used for non-volatile memory. In this device, a large positive or negative “write” voltage is applied to oxidize or reduce the TiO₂, yielding it highly resistive or conductive, respectively; next, a smaller voltage is applied to “read” whether the device is in a low- or high-
resistance state. This phenomenon has been utilized by many researchers for non-volatile memory devices based on the TiO$_2$/TiO$_{2-x}$ system. The PEDOT:PSS/TiO$_2$ system could be advantageous for low-cost, flexible devices, and because it does not require elevated fabrication temperatures, could be compatible with a wide variety of organic electronic devices.

It was hypothesized that the acid functionality of conducting polymers is responsible for the “switching” behavior. It may be that the TiO$_2$ adhesion layer/SAMP is unsuitable for acid-containing conducting polymers. However, there are still a wide range of semiconducting polymers and small molecules for which this treatment may be applicable. This treatment has been explored with the semiconducting polymer poly(3-hexylthiophene-2,5-diyl) (P3HT) and the small molecule PCBM. P3HT/TiO$_2$/SAMP/P3HT$^5$ and PCBM/TiO$_2$/SAMP/α-NPD$^6$ interfaces were fabricated, and it was shown that the adhesion layer/SAMP allowed control of the energy level alignment between the material and itself or the two materials, respectively. However, the effect of this treatment on device performance remains to be seen.
References Cited


