Processes and Materials for Organic Photovoltaics

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The field of organic photovoltaics is driven by the desire for better and cheaper solar cells. While showing much promise, current generations of organic photovoltaic (OPV) devices do not exhibit properties that are suited for wide scale commercialization. While much research has been dedicated towards this goal, more yet needs to be done before it can be clear whether this is an achievable goal.

This thesis describes new materials investigations for higher efficiency better stability organic photovoltaics, as well as new processes that broaden the application and fabrication space for these devices. The application of electro-polymerization, a deposition process, towards organic thin-film fabrication is discussed. This novel process for OPVs is followed by an analysis of new and interesting materials for OPV devices, including a higher efficiency hole-transporting material, and two hole-transporting molecules that exhibit self-assembly during OPV fabrication. The results of these investigations indicate the possibility for increased fabrication freedom and control, molecular species design that could allow higher efficiency devices, as well as indications of the role that molecular interactions in OPV heterojunctions play.

In addition, the possibilities of integrating graphene, the two-dimensional form of carbon, into OPV architectures is discussed. A new process for graphene transfer that allows the integration of graphene into chemically and physically more fragile systems including those composed of small molecule semiconductors is described and experimentally verified.
Graphene is then integrated as a cathode in OPVs, and a modeling and experimental investigation is performed to evaluate the potential for integrating graphene as a recombination layer in tandem OPVs. Based on this investigation, the integration of graphene into tandem OPVs could enable higher efficiency devices and significantly broadened architectural freedom for tandem fabrication.
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Chapter 1

Organic Solar Cells

1.1 Motivation

The desire to produce energy directly from the sun, particularly in light of the potential externalized costs of oil and coal energy, has driven interest in the development of affordable solar energy. Silicon solar cells, which currently make up a majority of the commercially available technology, have become steadily less expensive as economies of scale have driven prices of production and raw materials down. Prices to date have not, however, been able to rival those of competing energy sources. As such, solar energy currently produces only a small fraction of the total energy consumed today.

The field of organic photovoltaics (OPVs), in which semiconducting materials are primarily composed of carbon, is driven by the desire to produce less-expensive solar cells. Inorganic solar cells typically require fabrication in high-energy processes such as the high temperatures required to process silicon. The thermal budget and purities required for these processes increase the costs of production significantly. Furthermore, the high temperatures
required are not compatible with many substrates, such as plastic, and are not compatible with most flexible materials. Organic semiconductor materials, in contrast, are easily processed at temperatures of 100°C and can be deposited amorphously on virtually any relatively low temperature surface. Despite the advantages that OPVs exhibit in fabrication parameters, they suffer from a range of issues including low stability and limited efficiency. Since the first demonstration of a heterojunction OPV by Tang et al.\cite{11} in 1986 the efficiency and stability of OPVs has steadily improved, but has not yet approached a level where their price advantage has offset their disadvantages enough to be competitive with inorganic cells, a comparison usually made in terms of dollars per watt produced.

1.2 Inorganic Solar Cells

The basic phenomenon by which solar cells produce electricity is the photovoltaic effect. In this process an incident photon hits a material and, if that photon is energetic enough, this impact imparts sufficient energy to the system that an electron is kicked out of its rest state, and the photon is absorbed. In a semiconductor material this process transfers an electron from the valance band to the conduction band, leaving a hole (absence of an electron) behind. A solar cell is a combination of specially designed semiconductor materials that is able to take advantage of this process to produce usable power.

1.2.1 Physics of Operation

Inorganic solar cells are created by putting two different semiconducting materials, $n$-type and $p$-type, into intimate contact. $n$-type semiconductors are those that have been doped
to boost electron density, and $p$-type semiconductors are those that have been doped to boost their hole density. When an $n$ and $p$-type semiconductor are put into contact, excess electrons from the $n$-type material and excess holes from the $p$-type materials diffuse into the each other as dictated by their concentration gradients. These excess holes and electrons recombine near the interface, forming a depletion region, defined as the region where no excess charge carriers remain. As this depletion region forms charges build up on either side of the depletion region and create an electric field which eventual equals and opposes the diffusion current. The resulting structure is a diode that allows current flow in only one direction.

When light is incident on this $p-n$ diode, holes and electrons created in the depletion region will, based on the electric field present, separate and travel to the $p$ and $n$ side, respectively. Some of these charges then diffuse to the electrodes of the solar cell, contributing to power.

**Equivalent Circuit**

A solar cell can be modeled as an electrically equivalent circuit, shown in Figure 1.1.

In this figure, each discrete component combines to model the function of a solar cell. $I_L$ is the photogenerated current in the cell, which is counteracted by $I_D$, the diode current, and $I_{SH}$, the shunt current. These currents sum to equal the output current, or $I$, as shown in Figure 1.1 and represents the current that flows out of a cell at the electrodes.

$$I = I_L - I_D - I_{SH}$$ (1.1)
In addition to the parasitic diode current, there is a shunt current, $I_{SH}$, that is defined by a parasitic resistance across the device, or the shunt resistance, $R_{SH}$. The output voltage, $V$, is related to these currents by Equation 1.2, where $V_J$ is the voltage across both the diode and the resistor, $R_{SH}$.

$$V_J = V + IR_S$$  \hspace{1cm} (1.2)

### 1.2.2 Figures ofMerit

Solar cells are defined by figures of merit including short circuit current ($J_{SC}$), open circuit voltage ($V_{OC}$), maximum power point, and fill-factor. These figures of merit are illustrated in Figure 1.2[12], where the $J_{SC}$ is defined as the current output by a solar cell when short-circuited under illumination, $V_{OC}$ is the voltage present when no current is allowed to flow. The maximum power point, where the power generated by the cell (current times voltage) reaches a maximum, gives the current and voltage at this maximum, $I_m$ and $V_m$.

$I_m$ and $V_m$ also help to define the fill-factor (FF) as shown in Equation 1.3.

Figure 1.1: Solar cell equivalent circuit diagram
Figure 1.2: Current-voltage characteristics of an ideal solar cell.

\[ FF = \frac{J_m V_m}{J_{SC} V_{OC}} \]  

(1.3)

The external power conversion efficiency of a solar cell, denoted by \( \eta \), is defined in Equation 1.4, where \( P_S \) is the incident light power density.

\[ \eta = \frac{J_m V_m}{P_S} \]  

(1.4)
1.3 Organic Solar Cells

The field of OPVs is dominated by two material categories, dye sensitized solar cells and heterojunction solar cells. The materials used in heterojunction solar cells can be broken down into two materials sets: conjugated polymers and small molecules.

1.3.1 Physics of Operation

In contrast to the valence and conduction bands in an inorganic semiconductor, organic semiconductors exhibit a highest occupied molecular orbital (HOMO), and a lowest unoccupied molecular orbital (LUMO). Photogeneration and charge separation in an OPV also differ from inorganic solar cells in that they exhibit no depletion region. Instead, absorbed photons create a hole-electron pair, or exciton, that is uncharged and free to diffuse throughout the absorbing material. This exciton will statistically survive to travel one exciton diffusion length from the point of absorption, where it will either recombine to form light or, more likely, a phonon, or dissociate at a heterojunction. Dissociation results in lone electrons and holes which can then diffuse to an electrode where they will contribute to power.

1.3.2 Materials

Organic Semiconductors

Organic semiconductors are materials, primarily composed of carbon, that exhibit semiconducting properties as a result of conjugated $\pi$ orbitals. Intermolecular conduction is accomplished via overlapping $\pi$ orbital clouds, resulting in bulk semiconductor characteristics. In contrast to inorganic semiconductors, organic semiconductors exhibit lower mobility\cite{13} but
significantly higher optical absorption[14], making their application in thin-film devices a topic of great interest.

These materials can exhibit widely varying characteristics depending on their molecular structure, including color, conductivity, and chemical affinity. For photovoltaics, key metrics include absorption profile and optical density, charge-carrier mobility, band gap and fermi-level, and exciton diffusion length.

Figure 1.3: Energy level schematic of a donor and acceptor organic semiconductor material.[1]

Different categories of organic semiconducting materials exist, and this categorization is generally dictated by the energy levels of the materials HOMO and LUMO, as shown in Figure 1.3[1]. Here, the electron affinity, or LUMO, and ionization potential, or HOMO,
shown for a donor and acceptor material. Dotted lines denote the exciton binding energy ($E_B$) for the materials. A donor material, or hole transporting layer (HTL), has a low ionization potential and thus functions typically by transporting holes as its majority carrier. An acceptor material, or electron transporting layer (ETL), is characterized by a high electron affinity and transports charge primarily via electrons.

There are other classes of materials as well, notably exciton blocking layers (EBLs). These materials have similar HOMOs or LUMOs as ETLs and HTLs, respectively, but their band-gap is significantly larger, making the transport of bound hole-electron pairs (excitons) exponentially less likely.

Some common materials used in OPVs include:

- **HTLs**: copper phthalocyanine (CuPC), $N,N'$-bis(naphthalen-1-yl)-$N,N'$-bis(phenyl)-benzidine (NPB), $N,N'$-bis(3-methylphenyl)-$N,N'$-bis(phenyl)-9,9-spirobi fluororene (TPD)

- **ETLs**: fullerenes ($C_{60}$), Tris(8-hydroxy-quinolinato)aluminium ($AlQ_3$)

- **EBLs**: Poly(3,4-ethylenedioxythiophene (PEDOT), which is used as a buffer layer between the anode and HTL, and Bathocuproine (BCP)[1], which is used as a buffer between the ETL and the cathode.

Material research is resulting in an ever-expanding library of available photovoltaic materials. Some recent advances have yielded materials such as the HTL boron sub-phthalocyanine chloride (Sub-Pc), which has been shown to exhibit higher $V_{OC}$ than devices incorporating CuPC[15–17], and the EBL 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi), which has been been linked to higher stability than BCP.[18]
Electrodes

With the advent of the heterojunction solar cell any metal can be used as an electrode for OPVs. To maximize device efficiency, however, ohmic contact must be made at the metal-semiconductor interface. This requires that the electrode work-function match closely with the majority charge-carrying band of the semiconductor. Since there are a finite number of materials that exhibit metallic characteristics, a close match is sometimes the best that one is able to achieve.

To compensate for a poor energy match between the metal electrode and semiconductor, an injection layer is sometimes used between the two materials. Injection layers exhibit work functions or energy levels intermediate between the metal and semiconductor levels, and provide a stepping stone that lowers the energy cost of traversing the interface. For organic photovoltaics, these interlayers have been found to increase the $V_{OC}$[14].

1.3.3 Architectures

There are many different architectures that can be employed to fabricate solar cells. The first organic photovoltaics were single-layer cells, and were composed of an organic semiconductor with different metal electrodes on either side. To produce usable power these electrodes were required to have different work functions in order to provide the built-in electric field for exciton dissociation.
Planar Heterojunction Cells

Heterojunction solar cells provide the driving force for exciton dissociation via different electron affinity band gaps rather than via metals of different work-function, and are typically comprised of one donor and one acceptor material. A heterojunction is defined as a junction where two materials with differing band gaps come into contact, as opposed to a homojunction where similar semiconductor materials with different doping levels come into contact. The p-n silicon diode is an example of a homojunction.

A simple heterojunction OPV require 4 parts; an anode, an HTL, an ETL, and a cathode. The schematic of a prototypical OPV cell is shown in Figure 1.4.

![Figure 1.4: Schematic of a simple heterojunction OPV](image)

Here, HTL and ETL layers must remain thin enough that their resistance does not adversely impact their operation, but thick enough that there is enough interaction with light to produce power. A simple energy band diagram of this planar heterojunction cell is shown in Figure 1.5. The maximum $V_{OC}$ of a heterojunction cell is defined as the difference between the HOMO of the HTL and the LUMO of the ETL. Exciton binding energies, interfacial losses, and other parasitic losses generally yield $V_{OC}$s below this maximum value. The $I_{SC}$ of a heterojunction cell depends on the amount of absorption of the cell in conjunction with
the probability and energetics of charge extraction from the device. Only excitons formed
within an exciton diffusion length of the heterjunction may contribute to power, limiting the
amount of material in a cell that is photovoltaically active.

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**Figure 1.5: Energy band diagram of a simple heterojunction OPV**

**Bulk-Heterojunction Cells**

**Figure 1.6: Schematic of a simple bulk-heterojunction OPV**

Bulk heterojunctions can be fabricated which increase the volume of photovoltaically
active material in a cell by departing from a planar heterojunction architecture. This archi-
tecture, shown in Figure 1.6, typically results from the wet deposition of a donor and acceptor
material from the same solvent. By controlling the drying conditions of the deposition, the
size of donor and acceptor domains can be affected, resulting in vastly increased interfacial
area. While this can result in orphaned domains, which cannot contribute to power, this can yield photovoltaic devices with significantly higher efficiencies. The band diagram, shown in Figure 1.7, is represented by two super-imposed band gaps signifying that each point can generate and dissociate an exciton.

![Energy band diagram of a simple bulk heterojunction OPV](image1)

**Figure 1.7:** Energy band diagram of a simple bulk heterojunction OPV

**Tandem Cells**

![Schematic of a tandem OPV](image2)

**Figure 1.8:** Schematic of a tandem OPV

Tandem solar cells incorporate two or more heterojunction solar cells into the same architecture (Figure 1.8). Similar to a single-layer cell, a tandem still has only one anode
and one cathode. When excitons are generated at the heterojunctions of each tandem cell, dissociation generates holes on the ETL of one side of the tandem, and electrons on the other. Without a site for efficient charge recombination between these two cells, charges would build up and oppose the generation of more charge. To address this issue, very thin layers of metal are deposited in-between cells in a tandem device. This layer is called the recombination, or inter-layer. Common recombination layers are fabricated by the deposition of extremely thin layers of gold or silver.

In operation, the LUMO of the bottom cell’s ETL and the HOMO of the top cell’s HTL become aligned. If an ideal tandem cell is fabricated with the first cell exhibiting a $I_{SC}$ of ‘x’ and a $V_{OC}$ of ‘y’, with a second cell exhibiting a $I_{SC}$ of ‘x’ and a $V_{OC}$ of ‘y’, the resulting tandem would exhibit a $I_{SC}$ of ‘x’ and a $V_{OC}$ of ‘2y’, effectively doubling the efficiency of per unit area. Figure 1.9 illustrates the band diagram of a tandem cell.

![Energy band diagram of a tandem OPV](image_url)

Figure 1.9: Energy band diagram of a tandem OPV

The main advantage of the tandem architecture is the ability to combine two cells that have different absorptions together. This allows the fabrication of a PV cell that harnesses a greater fraction of the solar spectrum.
1.3.4 Efficiency

The efficiency of a solar cell is can be characterized in two ways. The external quantum efficiency (EQE), denoted by $\eta$ and defined in 1.4, is a measure of the percentage of incident photons that are absorbed and contribute to power. Internal quantum efficiency (IQE) is the percentage of absorbed photons that contribute to power.

There are many factors that dictate the efficiency of an OPV device. As stated above, only the material that is within one exciton diffusion length of a heterojunction can contribute to power and, thus, efficiency. If an exciton is created on an organic semiconductor molecule that is within one exciton diffusion length of an electrode, that exciton will recombine on the metal and be quenched. As such, using or designing a material with a very large exciton diffusion length would not in and of itself maximize efficiency. In order to try and design a high efficiency single cell, researchers must attempt to simultaneously optimize device thickness (optical field within a device), exciton diffusion length of the molecule, heterojunction architecture, and material absorbance and location, among many other factors.

In addition to optimizing the efficiency of a single cell, many researchers turn to tandem cells to increase the external quantum efficiency of OPVs. Here, one can integrate solar cells that absorb different parts of the solar spectrum to attempt to convert a greater percentage of solar radiation. Cells need not produce the same voltage, as most of these cells are fabricated in series, however care must be taken to balance generated current, as a series tandem cell will operate at the lowest cell $I_{SC}$.

To date, the highest efficiency cells are reported to be approximately 10% for a tandem cell, and 4.2% for a single cell.[19]
1.3.5 Stability

One of the most significant hurdles facing organic photovoltaics is the question of stability. In general, most organic semiconductor materials are air sensitive and undergo a photocatalyzed interaction with oxygen and/or water that irreversibly yields a non-semiconducting state.[14] There are two main approaches to increasing the stability of OPVs. The first is the development of materials with intrinsic stability in ambient. The second strategy is the development of encapsulation techniques to limit the exposure of OPV materials to reactive elements.

The stability of an OPV is often defined in terms of the time it takes for performance, typically EQE, to drop to 50% of its original value. Due to the differing decay paths and characteristics of OPVs on the whole, particular decay metrics can vary significantly.[20]

1.4 Graphene

Graphene is a two-dimensional crystalline form of carbon, made up of a hexagonal lattice of carbon atoms.

First isolated by Novoselov et al. in 2004 [21, 22], graphene has been the subject of intense research as a result of its excellent electrical [23–27], mechanical [28–30], and optical [31] properties.

Due to its high transparency (∼97.5%), graphene could be a good replacement for ITO which contains indium, an expensive and dwindling resource. In addition to transparency, graphene has been shown to exhibit very high conductivities and high flexibility, making it an ideal electrode material for photovoltaics.
1.5 Objectives and Approach

The work detailed in this thesis concentrates on furthering the field of organic photovoltaics (OPVs) via a combination new materials research and investigation and the development of processes to integrate new materials and interfacial properties.
Chapter 2

Organic Solar Cells

When an organic photovoltaic device is exposed to light, a number of processes take place that result in the generation of electrical power. To further the field of organic photovoltaics it is important to understand each of these processes individually. This section will elucidate on each one of these major processes.

2.1 Photon Absorption and Exciton Formation in Organic Semiconductor Photovoltaics

This section will concentrate on two-layer organic photovoltaics. Figure 2.1 [2] illustrates a prototypical organic semiconductor material set and their electronic band structure.

When these materials are put into contact, the Fermi levels of the materials align, and charges flow to equilibrate the built-in field generated by this contact, as shown in Figure 2.2 [2].

When a photon is incident on this photovoltaic, if the energy of the photon is greater
than or equal to the bandgap of the organic semiconductor, that photon may be absorbed. This absorption process excites an electron into the LUMO, as shown in Figure 2.3[3] This figure also points out two significant sources of energy loss in organic solar cells; sub-band photon transmission and thermalization losses, which will be discussed in more detail below. As electrons are excited into the LUMO, a hole is generated in the HOMO. In organic
semiconductors, this electron is highly bound to the hole by the exciton binding energy (∼0.5eV[32]), forming an exciton.

Figure 2.3: Absorption of a photon and energy loss processes [3]

2.2 Exciton Diffusion, Dissociation and Charge Transfer in Organic Semiconductors

Since a generated electron-hole pair, or exciton, is uncharged, the mode of transport is diffusion, typically via Förster transport, in which energy is transferred via dipole-dipole coupling between close molecules. An exciton will diffuse through a semiconductor material
until it either 1) recombines on the organic semiconductor or an electrode and dissipates as heat or 2) diffuses into an electric field where the opposite charges dissociate into free charge carriers.[32] This dissociation requires a sufficiently large electric field, large enough to overcome the exciton binding energy, leading to implications for organic solar cell design.

2.3 Recombination in Tandem Solar Cells

In order to address two significant sources of energy loss in single-heterojunction solar cells, sub-band photon transmission and thermalization losses described above, tandem solar cells were developed. These solar cells, which combine two or more heterojunctions into a single device, are able to absorb different photon energies by virtue of their differing photovoltaic components. For instance, an OPV that absorbs red light most efficiently can be paired with and behind an OPV that absorbs blue light, alleviating the sub-band loss of the lower energy light and minimizing the thermalization losses of the higher energy light. A prototypical tandem solar cell is shown in Figure 2.4. [3]

When two organic photovoltaics are combined to form a tandem solar cell, the electrical contact formed between these two devices is important to overall device performance. For the device to function, an electron from one heterojunction must be able to combine with a hole from the other heterojunction, else charge build-up occur which will reduce the charge generation in each heterojunction. In most cases the HOMO and LUMO of each heterojunction are dissimilar, and a photo-generated hole or electron at the junction between both cells would require energy to jump to the adjacent cell. Since proximity is required for an electron to combine with a hole, a simple tandem cell with two cells attached will lose,
from its power generation, the energy required to facilitate this jump. The integration of a recombination layer in between cells is a common solution to this problem, facilitating this recombination by creating a recombination site where both holes and electrons can reside via downward energetic transfer. A metallic recombination layer is generally used.

2.3.1 Metal - Semiconductor Interface

When a metallic and a semiconducting material are brought together there are two types of contact possible, as defined by the characteristics of the metal and semiconducting materials shown in Figure 2.5.

Here $\phi_M$ and $\phi_S$ are the Work Function of the metal and semiconductor respectively, $\chi_S$ is the Electron Affinity of the semiconductor, $E_F$ are the Fermi levels of the metal and
semiconductor, $E_C$, $E_V$, and $E_G$ are the Conduction Band, Valance Band, and Band-gap of the semiconductor respectively.

**Ohmic Contact**

Ohmic contact between a metal and organic occurs when the electrical characteristics of the contact allow the conduction in both directions with a potential barrier. This occurs for an $n$-type semiconductor when $\chi_S > \phi_M$ as shown in Figure 2.6, and for a $p$-type semiconductor when $\phi_M > E_G + \chi_S$ as shown in Figure 2.7.

**Schottky Barrier**

A Schottky barrier between a metal and organic occurs when the electrical characteristics of the contact allow the conduction in only one direction with a potential barrier $\phi_B$. This
Figure 2.6: Ohmic contact between a metal and an \( n \)-type semiconductor

occurs for an \( n \)-type semiconductor when \( \phi_M > \chi_S \) as shown in Figure 2.8, and for a \( p \)-type semiconductor when \( \phi_M < E_G + \chi_S \) as shown in Figure 2.9.

Figure 2.8: Schottky barrier between a metal and an \( n \)-type semiconductor
2.4 Graphene

Graphene is the 2-dimension form of carbon, defined by a hexagonal arrangement of atoms in a plane shown in Figure 2.10[4]. The unit cell is composed of 2 atoms, with carbon-carbon bonds of 1.41Å.
2.4.1 Band Structure

In graphene, carbon atoms, with four valance electrons, share a bond with three neighbors. These three bonds correspond to $sp^2$ hybridized orbitals, leaving the 4th orbital, perpendicular to the graphene plane, to form $\pi$ covalent bonds. In graphene, an energy band is formed by the one electron per carbon atom that is not involved in carbon-carbon bonding.[4, 33, 34]

The band structure of graphene near the Fermi level is shown in Figure 2.11.

![Graphene band structure](image)

Figure 2.11: Graphene band structure [4]

Here one can see that the conduction band and valence bands cross at the corners of the Brillouin zone, K and K’. Figure 2.12 shows this “Dirac Cone”, called so due to the massless relativistic particle behavior of electrons in this region as defined by the Dirac equation.
Additionally, the K and K’ points are often referred to as the Dirac points for the same reason.

![Figure 2.12: Dirac cone [4]](image)

The implication of this is that graphene is a zero-bandgap semiconductor, with a density of states of zero at the Dirac point and a linear variance around the Dirac point, as shown in Figure 2.13.

![Figure 2.13: Graphene density of states [4]](image)

As a consequence of being a semi-metal, any photons that are absorbed by graphene, forming an electron and hole, will quickly recombine on the picosecond timescale.[35]
Charge Transfer and Electrical Characteristics

One implication of the linear dispersion of the $\pi$ band around the Dirac points are that electrons in these regions behave as particles whose kinetic energy dwarfs their rest mass. As a result, electrons in graphene move with an energy independent velocity equal the Fermi velocity, approximately $10^6$ m/s\cite{34}. As a consequence of the Dirac equation for massless particles, electrons near the Dirac points take on an effective spin, referred to as “pseudospin”\cite{34, 36}. This pseudospin has implications for the mobility of electrons in graphene; since backscattering of charge carriers would involve the reversal of this pseudospin, backscattering is suppressed in these systems. The result is that graphene exhibits large mobilities at room temperature approaching 20,000 cm$^2$/Vs\cite{34}.

2.4.2 Graphene as a recombination layer

When graphene is used as a recombination layer in tandem solar cells its function is dependent on the energy levels of the organic semiconductor in contact. When contemplating the electronic characteristics of this interface, there are three general scenarios one must consider:

Graphene Fermi level close to the HOMO

When the HOMO of a hole-transporting organic semiconductor material is close to the graphene Fermi level, as shown in 2.14, an Ohmic contact is formed between the two materials. Many hole transporting materials exist with relatively low LUMO and HOMO levels, as the low electron affinity of the material makes it more likely to conduct holes and thus be
classified as a hole-transporter.

Figure 2.14: Graphene energy band diagram situated close to the HOMO of a hole-transporting layer (HTL)

Figure 2.14 illustrates the electronic coupling of these two materials which, due to the matching of Fermi levels on contact, bends the LUMO and HOMO bands to form an Ohmic contact, where holes are freely conducted between HTL and graphene.

Graphene Fermi level close to the LUMO

When the LUMO of an electron-transporting organic semiconductor material is close to the graphene Fermi level, as shown in 2.15, an Ohmic contact is formed between the two materials. Many electron transporting materials exist with relatively high LUMO and HOMO levels, as the high electron affinity of the material makes it more likely to conduct electrons and thus be classified as an electron-transporter.

Figure 2.15 illustrates the electronic coupling of these two materials which, due to the matching of Fermi levels on contact, bends the LUMO and HOMO bands to form an Ohmic contact, where electrons are freely conducted between ETL and graphene.
Graphene Fermi level in-between HOMO and LUMO

When the graphene Fermi level is located in between the HOMO and LUMO of a material, as shown in 2.16, often a Schottky barrier is formed between the two materials. In this figure, an electron transporting material comes into contact with graphene.

Here, due to the matching of Fermi levels on contact, a barrier is formed to the majority
electron charge carriers for the ETL, forming a Schottky barrier. This barrier impedes electron flow from graphene to the ETL. A similar scenario emerges when an HTL with a similar electron affinity is put into contact with graphene, where a Schottky barrier to holes would result.

Contact Doping

In order for graphene to be used with many materials sets it is important to be able to tune its Fermi level. To do this one must add or remove electrons from the material. The effect of adding and removing electrons to/from graphene is apparent from the density of states figure above, where a small number of added charges affects the work function of graphene greatly, with diminishing returns as the Fermi energy moves farther from the Dirac point. An additional consequence of doping on graphene, and the effective change in Fermi energy, is an increase in conductivity as shown in Figure 2.17.

Figure 2.17: The conductivity of graphene increases as the Fermi energy is moved away from the Dirac point [4]

There are currently three common paths towards changing the work function of graphene:
Chemical

There is much work on the chemical substitutional doping of graphene.[37, 38] One method elementally substitutes in the graphene lattice during graphene synthesis, donating or accepting electrons to/from the lattice.

Electric Field

The Fermi level of graphene can also be affected by the application of a strong electric field to the material.[39] In work by Kim et. al., detailed below, the Fermi Level can be changed by up to 0.2eV.

Contact Doping

A large amount of research has been performed on charge transfer between graphene and other materials[40, 41] showing the shift of graphene Fermi level by up to 0.5eV. In recent work[42] we showed that graphene’s Fermi level could be shifted, by contact with an organic semiconductor material, far enough to allow its use as a cathode in an organic photovoltaic device. Most work to date has been on the application of unmodified graphene as an anode in devices, as its intrinsic work function is similar to that of Indium Tin Oxide, a common anode material.

Graphene has been shown, in various examples, to accept holes as an anode as well as to accept electrons as a cathode. Further, the work function of graphene can be controlled via \( n \) or \( p \) doping to not only shift its Fermi level up or down to match a material set, but
to increase its conductivity as well. This allows researchers, in the context of electrodes, to dope graphene to form a highly conductive Ohmic contact to whatever material set is desired. In the context of tandem cells, it allows us to engineer an ideal recombination layer, and even affords the possibility of engineering rectifying behavior as well, if desired.
Chapter 3

Materials Development for Organic Photovoltaics

3.1 Electrochemical Photovoltaic Fabrication

Traditional organic photovoltaics are typically fabricated by one or a combination of two means: vacuum evaporation and solution processing. There are many commercial processes that deposit quantities of high-quality material via electrochemical deposition that have not been used extensively for OPV fabrication. The use of electropolymerization is one such technique. Electropolymerization has been used for the fabrication of doped hole-injection layers [43–45]. The development of electrochemical deposition for EBLs[6], planar heterojunctions,[7], and bulk heterojunctions[5] could further the field of organic photovoltaics by enabling new architectures and fabrication techniques.
3.1.1 Morphological and spectroscopic studies of electrochemically deposited hole extraction layer for organic photovoltaic device fabrication

This work concentrates on the analysis of electrodeposition of PEDOT films on ITO. The films were fabricated via potential cycling of electrodes in a 3,4-ethylenedioxythiophene (EDOT) solution followed by reduction to yield PEDOT. Figure 3.1 shows the absorbance of PEDOT films after 5, 15, 30, and 45 electrochemical deposition cycles, illustrating the dependance of cycle number on deposition thickness.

![Figure 3.1: UV-vis-NIR spectra of PEDOT layer following various potential cycles.[5]](image)

Figure 3.2 shows AFM images of films following various deposition cycle numbers. It is clear from these images that increasing the electrodeposition cycles yields a thicker film, but that these films become more rough, with a film roughness of approximately 100nm after 45 cycles.

To evaluate the electrochemical deposition process for OPV device integration, devices were fabricated that incorporated electrodeposited PEDOT films with between 0 and 60 cycles. The results, shown in Figure 3.3, show a maximum in device metrics at approximately
It is likely that the device efficiency and figures of merit reach a maximum at 15 cycles as a sufficient and uniform layer of PEDOT is deposited. Further deposition, as seen in Figure 3.2, results in long tendrils, which adversely affect device performance.

Finally, electrodeposited PEDOT film devices were compared with spin-coated PEDOT film devices. Figure 3.4 shows $I-V$ characteristics of these devices. It is clear from this comparison that electrodeposited PEDOT films perform competitively to spin-coated PEDOT films.

This work illustrates the viability of electrodeposition for organic thin-film layer fabrication. In addition, the fact that electrodeposition can be done at different biases, with
alternate reduction biases and processes, indicates the possibility that electrodeposition could be used to fabricate HIL layers with increased morphological and chemical control over traditional spin-coating techniques.
3.1.2 Electrochemically prepared polymer solar cell by three-layer deposition

This work evaluates the application of electrodeposition techniques for the fabrication of an entire OPV stack. Here, the electrodeposition of PEDOT[6] was combined with the electrodeposition of poly(2,20-bithiophene) (PBT) as a donor layer and fullerenes as an acceptor layer. Figure 3.5 shows the process flow for device fabrication.

First, PEDOT is electrochemically polymerization on ITO films, followed by the electrochemical polymerization of PBT. Subsequently, $C_{60}$ is electrodeposited on top of this PBT layer, and an aluminum cathode is thermal evaporated to finish the device.

Previous experimental results indicate that 15 cycles result in good layers of PEDOT, and thus 15 cycle deposition was used for both PEDOT and PBT electropolymerized layers.
Figure 3.5: Schematic process flow for OPV fabrication.[6]

Figure 3.6 shows the evolution of device absorbance with varying cycles of fullerene electrodeposition. It is apparent from this figure that subsequent deposition cycles of C$_{60}$ yield an increased absorption at higher photon energies, indicating increased C$_{60}$ layer thickness and successful electrodeposition.

To evaluate the morphological characteristics of each layer, Atomic Force Microscopy (AFM) was performed after each electrodeposition.

Figure 3.7 shows the surface characteristics of each film in the electrodeposited device. It is clear from these results that the device exhibits increasing roughness after each electrodeposition. To evaluate the effects of this process on electrical device characteristics, aluminum cathodes were evaporated and the devices were evaluated in a AM1.5 solar simulator. Figure 3.8 shows device performance.

Here, the layer thickness of PBT (donor) was varied by increasing cycle counts. It is interesting to note that increasing PBT thickness results in the tradeoff of $I_{SC}$ for increased $V_{OC}$. 
Figure 3.6: Absorbance evolution with increasing fullerene deposition cycles. [6]

Figure 3.7: AFM analysis of the electrodeposition of PEDOT (b), PEDOT/PBT (c), PEDOT/PBT/C_{60} (d). (a) ITO. [6]
This work shows that full heterojunction OPV devices can be fabricated via electropolymerization and electrodeposition. Furthermore, the control of deposition parameters via electrodeposition bias, cycle number, and film reduction can provide means to increase the uniformity of deposited layers and devices, as well as allow interesting and new architectures.
3.1.3 Electrochemical codeposition: An approach to a bulk heterojunction organic photovoltaic device

This work evaluated the possibility of combining the electrodeposition processes described above into simultaneous process for the codeposition of materials towards the electrodeposition of bulk-heterojunction OPVs.[7] Here, the codeposition of poly(thieno[3,2-b]thiophene) (PTT) and $C_{60}$ was performed on top of electropolymerized PEDOT.

It is possible to combine the electrodeposition processes of both HTL and ETL material into the same process step. To evaluate the results of this, films of electrodeposited $C_{60}$ and electropolymerized PTT, as well as co-deposited films, were fabricated and analyzed in an AFM. Figure 3.9 shows this analysis.

Figure 3.9: AFM images of (a) $C_{60}$, (b) PTT, (c) PTT-$C_{60}$, (d) PTT-$C_{60}$ in friction mode.[7]
These images indicate that films of high quality co-deposited materials are fabricated. To evaluate whether electrodeposition bias has an effect on species concentration in co-depositied films, UV–Vis–NIR spectra of films after varying deposition conditions were performed.

Figure 3.10 shows the affects of varous deposition potentail shifts. This data indicates that more positive ranges enrich the PTT content of the films, while more negative ranges enrich the \( C_{60} \) content. This provides a highly selective tool for dialing in material ratios.

To test the implication of this fabrication process for device fabrication, co-deposited layers were fabricated in OPV cells to yield bulk-heterojunction devices. Aluminum cathodes were thermally evaporated to complete devices, which were then measured in an AM1.5 solar simulator, the results of which are shown in Figure 3.11.

Exhibiting an efficiency of 0.30%, the bulk-heterojunction device fabricated via co-electrodeposited HTL and ETL shows significant potential. The potential control over component concentrations, and deposition conditions that are made available in electrodeposition could lead to higher efficiency devices and new possible architectures and design parameters.
3.2 Solar Cells from a Solution Processable Pentacene with Improved Air Stability

Pentacene is one of the most studied organic semiconductors to date. The stability of its photo excited state in ambient, however, is very low.

Figure 3.10: UV–Vis–NIR spectra of PTT–C$_{60}$ layers deposited via various potential ranges. (a) shifts to higher potential ranges (b) shifts to lower potential ranges.

[7]
This work[8] evaluates a modified pentacene molecule, 6,13-di-(2-thienyl)pentacene (BTP) as a HTL for higher stability photovoltaics following the previous report of a solution processable air-stable pentacene derivative.[46]

To evaluate the affect of increased molecular stability on photovoltaic stability, OPV devices were fabricated with BTP as the HTL.

PEDOT:PSS was spin-coated on ITO pre-patterned glass, followed by a spin-coated layer of BTP to approximately 15nm. C$_{60}$ was then thermally evaporated as an ETL to a thickness of 40nm, followed by that thermal evaporation of a 60nm aluminum cathode. Control devices were fabricated with unmodified pentacene in the place of BTP. Figure 3.12 illustrates the architecture of this device along with the energy band diagram and molecular structure of BTP.

Following fabrication devices were tested under an AM1.5 solar simulator. Figure 3.13
Figure 3.12: Schematic illustration of device architecture and energy band diagram. Shown below is the molecular structure of 6,13-di(2-thienyl)pentacene (BTP).[8]

shows the device performance of BTP devices versus pentacene devices. It is apparent that the modified pentacene devices illustrate a higher $V_{OC}$ and a slightly lower $I_{SC}$ than their unmodified counterparts, resulting in an efficiency of 1.4% compared to 0.4% for pentacene devices.

Figure 3.13: $I-V$ characteristics of devices fabricated with BTP compared to unmodified pentacene devices.[8]
Figure 3.14 shows the $I$–$V$ curves for BTP devices stressed in ambient atmosphere under constant 100mW/cm$^2$ (B), and without constant light exposure (A). It is apparent from these results that BTP devices, while undergoing a significant reduction in efficiency, still exhibit photovoltaic function even after 24 hours of constant solar illumination. For comparison, unmodified pentacene devices undergo complete degradation in minutes under similar conditions.

Figure 3.14: $I$–$V$ characteristics of BTP devices tested with (B) and without (A) constant illumination at 100 mW/cm$^2$ after 1 and 24 hours of exposure in air.[8]
To test BTP for longer term stability in less aggressive environments, devices were evaluated after storage in a nitrogen environment for two months. Figure 3.15 shows $I-V$ characteristics both before and after this storage.

![Graph showing $I-V$ characteristics of BTP devices tested immediately after fabrication and after 2 months of storage.](image)

Figure 3.15: $I-V$ characteristics of BTP devices tested immediately after fabrication and after 2 months of storage.[8]

This data indicates that BTP devices undergo a decay of less than 50% efficiency after two months of storage in an inert environment, indicating that decay is likely the result of interaction with air. The stability increase for BTP devices is thus a likely result of the molecular modifications affect on oxidation rate.

The demonstration of a significantly higher stability OPV device through a simple molecular modification indicates an interesting and potentially promising avenue of research towards higher stability organic photovoltaics.
3.3 Photovoltaic Universal Joints- Ball-and-Socket Interfaces in Molecular Photovoltaic Cells

In an attempt to analyze the implications of p-n junction molecular interaction on photovoltaic function, an analysis of two complimentary semiconducting small molecules was carried out[9].

To investigate the affect of shape complimentarity on device performance, we analyzed contorted hexabenzocoronene (HBC, shown in Figure 3.16b), which is a p-type semiconductor, as a paired material with C_{60}, a n-type semiconductor. The molecules exhibit a good match between their curvature and size. Figure 3.16 shows the expected interface between the two materials in a heterojunction and bulk-heterojunction cell, while Figure 3.16c illustrates the expected interaction of HBC with C_{60} and it’s correlation to Figure 3.16a.

Figure 3.16: Here we depict a possible schematic interaction of these molecules in a planar and bulk-heterojunction device (A). (B) shows the chemical structure of HBC. (C) shows a zoomed-in schematic of the interaction of HBC with C_{60}:[9]

These molecules were found to combine into two crystal phases. Shown in Figure 3.17, these crystal phases correlate to those synthesized from solution (Figure 3.17a) and gas phase (Figure 3.17b). The first crystal phase, that of the ABAABA configuration, was grown to
sufficient size for conductivity analysis. This analysis, shown in Figure 3.18, show a dramatic increase in conductivity when exposed to light.

Figure 3.17: Crystal phases of HBC and C\textsubscript{60} in co-crystals of C\textsubscript{60} and HBC A) from solution and B) from the gas phase.[9]

Figure 3.18: A large solution phase crystal (A) and affect of light (blue) versus no light (red) on crystal conductivity (B).[9]

To evaluate the implications of crystalline interactino in a device, OPVs were fabricated
using these materials, the architecture of which is shown in Figure 3.19a, and analyzed. Current-Voltage analysis under solar illumination, shown in Figure 3.19b, shows a surprisingly high $V_{OC}$. It is evident from this I-V curve that, under solar illumination, the device exhibits a poor fill-factor (FF). This could be the result of the poor overlap between the absorption spectrum of HBC and the simulated solar spectrum (Figure 3.19c). To analyze the device under more optimal lighting conditions $I-V$ characteristics of the device were measured under 422nm LED illumination. This result, shown in Figure 3.19d, shows a highly efficient device (5.7%). The $V_{OC}$ measured is within 10% of the theoretical maximum as defined by the energy mismatch between C$_{60}$ and HBC.

Figure 3.19: Device architecture (A) along with the optical absorption of the device in contrast to the solar spectrum and a UV LED emission spectra (C). Device $I-V$ characteristics of OPV under solar (B) and UV LED (D) illumination.[9]

The HBC/C$_{60}$ system was further analyzed via X-ray diffraction (GIXD), X-ray photoelectron spectroscopy (XPS) and near-edge Xray adsorption spectroscopy (NEXAFS) to
probe the molecular interactions between the two species. These results, shown in Figure 3.20, show that HBC and C$_{60}$ form a crystalline region at the heterojunction that affects charge transfer and is indicative of intimate electrical interaction between the two species that is likely the cause for the enhanced $V_{OC}$.

To confirm that shape complimentality is indeed the basis for improved device performance devices were built with a molecule similar to HBC but without the concavity. This molecule, hexa-peri-hexabenzocoronene (flat-HBC), is similar in electronic, physical, and chemical characteristics, and differ mainly only in that one is contorted and one is flat. Devices fabricated with flat-HBC exhibited $V_{OC}$s that were an order of magnitude smaller than devices fabricated with contorted-HBC.

In summary, it has been shown that the shape complimentality of contorted-HBC with C$_{60}$ has significant implications on device characteristics. Experimental data shows that devices incorporating contorted-HBC exhibit close-to-ideal $V_{OC}$s, while those incorporating similar but flat-HBC perform at significantly lower values. X-ray analysis indicates that highly ordered interactions take place due to shape-complimentality between contorted-HBC and C$_{60}$ and that electronic interactions are greatly increased by this interaction. These results indicate that the interaction between molecular species at the heterjunction of OPVs can have a significant affect on device performance.

### 3.4 Reticulated Heterojunctions for Photovoltaic Devices

Based on the excitement generated by the results obtained above with Hexabenzocoronenes, work was continued on this class of materials to determine if modifications to the small
Figure 3.20: A) GIXD measurements (2D images on the left and integrated intensity on the right) for films of C$_{60}$ (40 nm), bilayers of increasing thickness of C$_{60}$ on HBC, and pure HBC (25 nm). HBC, complex 2 and C$_{60}$ reflections obtained from powder samples are also shown. Integrated intensities of the diffraction pattern are normalized by the maximum peak height; 2D images for x=0-10 nm share the same intensity scale while x $\geq$ 20 nm has a larger upper limit due to the thickness of the film (see inset for peak intensity). Peak A corresponds to diffraction intensity which increases in intensity at the HBC/C$_{60}$ interface before disappearing under the C$_{60}$ signal. Note: the sharp peak appearing at Q=1.53Å$^{-1}$ in the 10 nm C$_{60}$ data corresponds to the (222) reflection of pure C$_{60}$.[9]

molecule size would result in interesting assembly.[10]

It was found in this work that dibenzotetrathienocoronene (6-DBTTTC, shown in Figure
3.21a), a modified hexabenzocoronoene molecule, formed supramolecular cables (schematic shown in Figure 3.21b) on the order of 25nm thick when dried from solvent and heat-treated. This interesting feature raised the possibility for fabricating thin films of 6-DBTTC with a built-in roughness on the order of the film thickness, giving a possible route towards a more ordered bulk-heterojunction cell.

Figure 3.21: a) Molecular structure of 6-DBTTC. b) Illustration of the assembly of 6-DBTTC into hole-transporting columns.[10]

Solar cells were fabricated using 6-DBTTC as the hole transporting layer. Patterned ITO was coated with PEDOT:PSS, followed by a spin-cast of 6-DBTTC which was then annealed at 150°C. The electron transporting layer, C₆₀, was then evaporated to a thickness of 40nm, followed by an aluminum cathode evaporation.

Figure 3.22: a) Illustration of the OPV device architecture with a nanostructured active layer. b) Typical current density-voltage (JV) curves for a 6-DBTTC device with (blue) and without illumination (red) at 100 mW/cm².[10]

Figure 3.22a shows the schematic of the ideal proposed bulk-heterojunction cell with projection of 6-DBTTC wires into the electron transporting layer. The increase in surface area
that this affords has been shown to benefit the performance of bulk-heterojunction cells.[47–51] Device I-V characteristics are shown in Figure 3.22b, which shows a $V_{OC}$ on par with similar devices, while exhibiting a significantly improved $I_{SC}$ over planar devices with similar materials. Control devices with as-spun 6-DBTTC hole-transporting layers exhibited a 3-fold drop in efficiency, indicating that the heterojunction interfacial area increase results in higher efficiency charge separation and collection.

To gather further information about the interfacial physical characteristics fluorescence microscopy was performed on 6-DBTTC films after initial spin (Figure 3.23a), after annealing at 100°C (Figure 3.23b) and after a 150°C anneal (Figure 3.23c). AFMs were also performed on similar samples as shown in Figure 3.23d, e, and f. Here we see that, as spun, the 6-DBTTC films show little surface roughness. After annealing, however, these films begin to coalesce into long fibers, ultimately forming the image shown in Figure 3.23f with 25nm wires side by side. This image, if made into a device, would very closely mimic the ideal schematic shown in Figure 3.22a.

Based on these results the chemical modification of hexabenzacorones remains an exciting avenue for organic photovoltaic research for ordered bulk-heterojunction OPV fabrication where an increase in heterojunction surface area can be achieved without the dead-ends typically found in solution-cast BHJs.
Figure 3.23: Fluorescence microscopy images of films from 6-DBTTC that were a) unannealed, b) annealed at 100°C, and c) annealed at 150°C. The corresponding non-contact AFM images and cross-sectional profiles (indicated in blue) of films from 6-DBTTC for conditions (a) and (c) are shown in (d) and (f), respectively. [10]
Chapter 4

Graphene Transfer Strategies

One of the most exciting new materials for the integration into organic photovoltaics is graphene, the two-dimensional form of carbon. This is, in particular, due to its high transparency in conjunction with its high conductivity, which allows graphene to function as a particularly good electrode in these devices where transparency typically comes at the cost of conductivity or, in the case of ITO, with the incorporation of a rare element such as Indium.

A significant barrier to the incorporation of graphene into OPV devices, apart from the synthesis of graphene itself (which is an area of much research), is the process of transfer. Since graphene is a single atom thick it is macroscopically fragile, and great care must be taken during any transfer process. To compound this process difficulty, for OPVs, any process parameter that itself is harmful to organic semiconducting materials cannot be tolerated, such as heat, most solvents, and mechanical strain. Small-molecule semiconducting thin-films are held together via Van Der Waals forces and as such are extremely fragile.
4.1 Current Transfer Strategies

To date, transfer process development has concentrated on the transfer of CVD graphene onto high surface energy materials, such as glass and silicon. This has been sufficient for the bulk of organic electronics graphene research where graphene has been used as bottom electrodes for OPVs[52–54], field effect transistors[27, 55–57], among other topics[26], where the initial transfer of graphene onto silicon or glass represented a first or early step in the fabrication process.

Since CVD graphene is grown on a metal film[58, 59], any integration process for single or few-layer graphene must first remove the growth substrate via chemical etching. To keep graphene intact during and following this step, a transfer substrate must be introduced, such as PDMS[54, 60] or polymethylmethacrylate[59, 61]. After the growth substrate is removed, this transfer substrate is used to apply graphene to the surface to which transfer is desired. Once in contact the method for transfer substrate removal varies. A typical process includes a period of applied pressure at elevated temperatures, after which the polymer is removed mechanically or chemically from the graphene. This process, while effective, has been shown to leave behind polymer residue[62, 63]. Many transfer processes are followed by an annealing step[63] where residual polymer materials is effectively burned off.

Recently the process of graphene transfer via PDMS was successfully used to integrate graphene onto a polymeric semiconductor thin-film for OPVs[64]. This device process allowed the use of moderately elevated temperatures, though likely suffered from residual polymeric residue.

To date there has not been a transfer process demonstrated that allows the integration
of graphene onto an organic thin-film material that retains the mechanical, electronic, and semiconducting properties of the graphene and OPV materials.

4.2 Fluorinated Transfer

The integration of graphene into small molecule OPVs could provide significant benefits to the field. In order to develop such a process, we investigated the use of an Orthogonal resist layer as a low-energy transfer substrate whose removal could be accomplished via one of the few solvent systems that do not interact with organic small molecules (the particular solvent in this case is proprietary to Orthoganol, Inc.). Below we describe a process that allows for the non-destructive high-quality transfer of single-layer graphene onto an organic semiconductor thin film enabling for the first time the use of graphene as a transparent electrode for all small-molecule organic transparent electronic devices.

4.2.1 Experimental

As a target small-molecule organic substrate, 2,2',2'"-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole (TPBi, LumTec) films, for Raman Spectroscopy and Scanning Electron Microscopy (SEM) transfer analysis, were evaporated on ITO-coated glass (LumTec) at 1 Angstrom per second to a thickness of 40nm via an Angstrom Engineering thermal evaporator mated to an MBraun glovebox.

To evaluate the electrical quality of fluorinated resist (FR) transferred graphene, organic LED (OLED) devices were evaporated on pre-patterned ITO substrates (LumTec) for graphene cathode lamination. PEDOT:PSS (HC Stark) was spin-coated on cleaned
substrates at 3000rpm at 1000rpm/s and baked at 120°C for 1 hour. Following PEDOT deposition the substrates were taken into the nitrogen environment of the glovebox. 40nm of N,N'-Bis(3-methylphenyl)-N,N'-diphenyl-9,9-spirobiﬂuorene-2,7-diamine (E105, LumTec) and followed by the evaporation of 40nm of Tris(8-hydroxyquinolinato)aluminium (AlQ₃, LumTec).

A 60nm Aluminum cathode was evaporated on Control devices. All OLED devices were kept in nitrogen for the duration of the experiment.

The transfer of graphene is accomplished via a treated PDMS (DuPont) stamp with a proprietary FL material manufactured by Orthoganol, Inc. PDMS was cured in a petri dish at 80°C for 1 hour. Small stamps of PDMS were cut from this mold, and coated with 0.4g (approximately 400nm) of Parylene-C via a Specialty Coating Systems Labcoter. These PDMS-Parylene stamps were then spin-coated with FR at 3000rpm and 1000rpm/s acceleration.

Large-area films of graphene were grown using previously reported CVD processes on copper foil. Small sections of graphene/copper was cut and placed, graphene-side down, on the PDMS-Parylene-Orthoganol stamp (referred hereafter as ”transfer stamp”). A schematic of this process is depicted in Figure 4.1. Copper is then etched in ammonium persulfate (Transene APS-100 copper etchant) until no copper is evident (periodic removal of bubbles via deionized water is typically required). It is important, after the application of Parylene and for the remainder of the experiment, to avoid flexing the stamp, as graphene/copper delamination will result. To effectively adhere the graphene/copper foil to the stamps without significant flexion the transfer stamp was placed on a non-adhesive side of scotch tape (3M),
while uniform pressure was applied to the top of the graphene/copper foil by a glass-backed PDMS stamp with an additional scotch tape layer. The non-adhesive side of scotch tape does not adhere to PDMS.

In order to transfer graphene onto organic thin-films the transfer stamp was placed, graphene-side down, onto the organic thin films in the desired location (Figure 4.1). Pressure was applied with a thumb for 5 seconds. The stamp was then removed from the substrate. What is left on the substrate is single-layer graphene along with a thin film of the Orthoganol resist. This resist was removed by two subsequent spin-coats of the Orthoganol resist stripper.

Figure 4.1: Schematic of the fabrication of a transfer stamp, above, and graphene lamination and transfer, below

Graphene transferred on TPBi was then analyzed via Raman Spectroscopy in a Renishaw
Invia Raman Microscope using a 532nm laser, followed by SEM in a Hitachi 5000. OLED devices were driven by a Kiethley 2400 sourcemeter and current-voltage data was collected.

4.2.2 Results

To evaluate the presence and quality of transferred graphene on organic films Raman spectroscopy was performed on graphene transferred using this method onto a TPBi thin-film. The Raman signature of the background thin-film without graphene was also measured, and the background corrected Raman signature is shown in Figure 4.2a.

The presence of a strong signal from the G and 2D peaks, located at 1590.54 cm\(^{-2}\) and 2683.0 cm\(^{-2}\) respectively, indicate that graphene is successfully transferred by the FR method onto organic small-molecule substrates. The small D-peak, located at 1352.5 cm\(^{-2}\), demonstrate that not only is CVD graphene grown with high quality, but that the transfer process does not induce significant defects in the transferred graphene film.

Graphene was also transferred onto Si substrates and Raman was measured for comparison (Figure 4.2b).

Peak position and full-width-half-maximum (FWHM) for G and 2D peaks of graphene transferred on both substrates are listed in Table 4.1. The close agreement demonstrates the effectiveness of the Fl transfer process of graphene onto both high and low energy substrates and that Raman Microscopy can be used as an effective tool for characterization of graphene cathodes on organic substrates.

Broadening of the peak FWHMs on organic vs Si can be attributed to increased substrate-induced disorder in graphene films on organic versus silicon. Slight deviations in the G and 2D peak positions between the two substrates is likely due to transfer-induced local dopent
In order to probe surface morphology and transfer cleanliness, we inspected the transferred films via SEM. Figure 4.3 shows SEM images taken at 10,000 times magnification at an energy of 2kV. Figure 4.3b shows Fl-transferred graphene on silicon, with expected morphology and a high level of cleanliness. Figure 4.3a shows graphene transferred on an organic thin-film of TPBi, illustrating the high fidelity transfer of graphene onto a low-energy surface concentrations and local strain.

<table>
<thead>
<tr>
<th>Sample</th>
<th>D Peak FWHM</th>
<th>G Peak FWHM</th>
<th>2D Peak FWHM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fl Transferred Graphene</td>
<td>28.0 cm⁻²</td>
<td>19.1 cm⁻²</td>
<td>54.5 cm⁻²</td>
</tr>
<tr>
<td><strong>Position</strong></td>
<td>1352.5 cm</td>
<td>1590.5 cm</td>
<td>2683 cm</td>
</tr>
<tr>
<td>Typical Graphene on Si</td>
<td>12.6 cm⁻²</td>
<td>32.4 cm⁻²</td>
<td>2685.2 cm⁻²</td>
</tr>
<tr>
<td><strong>Position</strong></td>
<td>1346.7 cm</td>
<td>1594.2 cm</td>
<td>2685.2 cm</td>
</tr>
</tbody>
</table>

Table 4.1: Transferred graphene peak characteristics compared with typical values

(a) Background corrected Raman spectrum of graphene on TPBi

(b) Typical Graphene Raman spectrum on Silicon Oxide

Figure 4.2: Raman spectra of graphene on various substrates
with a transfer quality similar to that expected on silicon with existing transfer techniques.

As a final demonstration of the quality, chemical orthogonality, and capabilities of this process, an organic LED was fabricated with fl-transferred graphene serving as the cathode. OLED devices are typically fabricated with an Aluminum cathode, which gives a good match to the Lowest Unoccupied Molecular Orbital (LUMO) of the electron transporting material (in this case, TPBi). An Aluminum cathode also reflects light with high efficiency, increasing the external quantum efficiency of the device when viewed through the anode, but resulting in an opaque device. Graphene has found use in organic devices as an anode, due to the ability to transfer graphene onto a high energy substrate prior to organic deposition[55, 61, 65], and as a cathode [42], but no process has yet enabled a direct and clean transfer of graphene onto organics. A viable process for a transferrable graphene onto organics allows for highly transparent electrodes and can enable new architectures and devices.[42]

Figure 4.4a shows the Current-Voltage characteristics of the graphene OLED device in comparison to a control device with an Aluminum cathode. The graphene device requires higher voltage to turn on as a result of what are likely shorts throughout the device. As a result, the device requires significant current density before voltage can drop over the diode. This can be ameliorated by process iteration and refinement to transfer graphene with a lower roughness. Figure 4.4b shows an image of the functioning graphene OLED. The transparency of the device is directly attributable to the presence of graphene in conjunction with an ITO anode. The transparency of graphene (∼97.5%[31]) is higher than any existing cathode material.
4.2.3 Conclusion

Graphene was successfully transferred via a modified PDMS fluorinated transfer stamp in a process that is compatible with low-energy, fragile, and chemically vulnerable surfaces. Raman spectroscopy indicates high-quality graphene transfer, while SEM shows good surface morphology and little contamination. An OLED was fabricated using this process to transfer a graphene cathode. This functioning OLED is evidence of long-range high-fidelity graphene transfer to vulnerable substrates. As graphene quality improves with further research this process may allow large-scale, patternable transfer to various substrates of choice enabling flexible and transparent OLEDs, OPVs, as well as provide a new and promising material integration process for tandem organic photovoltaics.
Figure 4.3: SEM images of graphene transferred on an organic thin-film and silicon
Figure 4.4: Functioning OLED with a directly-transferred graphene cathode
Chapter 5

Integration of Graphene into Organic Solar Cells

5.1 Graphene as a Cathode in Organic Photovoltaics

Graphene, a two-dimensional crystalline form of carbon, was first isolated by Novoselov et al. in 2004 [21, 22]. The high transparency [31], conductivity [23–27], flexibility [28–30] and elemental abundance of graphene indicate that it is an excellent replacement for transparent conducting oxide electrodes. Indeed, graphene [30] and graphene oxide [52, 66, 67] have been previously considered as anode materials in organic photovoltaic devices (OPVs). Here we describe OPV devices with single-layer chemical vapor deposition (CVD) grown graphene as a cathode.

While several studies have demonstrated that graphene can serve as an anode material, there is only a single study that has utilized graphene as a cathode material.[68] In this work, multi-layer graphene modified with a dipole layer served as the cathode in in P3HT/PCBM
OPVs; interestingly, a photo response was observed for devices from dipole layer treated graphene, but not for devices from bare graphene. To understand this effect, it is important to note that as a result of graphene’s small density of states around the Dirac point, single-layer graphene exhibits a highly tunable work function that shifts when it contacts other materials.[40, 69, 70] Furthermore, in PCBM:P3HT bulk heterojunctions, the P3HT segregates at electrode surfaces. [71] Therefore, when bare graphene comes into contact with an electron donor (P3HT) charge transfer will ”contact dope” the cathode or raise its work function. This effect would not be expected for graphene treated with a dipole layer.

To demonstrate the utility of contact doping, we fabricated OPVs with laminated graphene cathodes (the device architecture and corresponding band diagram are shown in Figure 5.1a and Figure 5.1b). Pre-patterned indium-tin-oxide (ITO) substrates (Luminescence Technology Corporation) were solvent cleaned, exposed to UV-ozone (Jelight UVO cleaner) for 10 minutes, and coated with PEDOT (HC Starck) at 3000rpm for 60 seconds. The samples were baked at 120°C for 45 minutes and then transferred into a nitrogen glove box-coupled vacuum deposition system (Angstrom Engineering) for device fabrication. 40nm of copper phthalocyanine (CuPC), 40nm of C60, and 10nm of 1,3,5-tri(phenyl-2-benzimidazole)-benzene (TPBi) [72, 73] were evaporated in succession to form the device stack.

To complete the devices, the electrodes were fabricated as follows. For the graphene devices, graphene was grown via CVD and transferred to a polydimethylsiloxane (PDMS, Sylgard 184) substrate as previously described.[29, 56, 59, 74, 75] This graphene/PDMS “stamp” was used to laminate the graphene cathode, yielding an active area of 0.4cm² (Figure 5.1c and Figure 5.1d). For the aluminum control devices, 60nm of Al was evaporated
as a cathode, yielding an active area of 0.16cm$^2$. $I - V$ measurements were performed under AM1.5 solar simulated illumination in a nitrogen environment and under various monochromatic (620nm) LED intensities (Phlat Light PT-120-R) in ambient.

![Graphene device schematic and energy level diagram](image)

Figure 5.1: (a) Schematic illustration of the device architecture. (b) The HOMO and LUMO energy level diagram of the device with values equal to the energy below the vacuum level. (c) Image of a graphene device which shows the vertical ITO anode strip and the graphene cathode (graphene edges are indicated by arrows). (d) Image of a graphene device illustrating its high transparency.

Figure 5.2 shows typical $I - V$ curves for graphene and Al devices (100 mW/cm$^2$), which clearly indicate that our graphene cathode devices function as solar cells in the absence of chemical doping or work-function matching. The graphene devices exhibit a power efficiency of 0.02%, and the aluminum controls exhibit a power conversion efficiency of 0.41%. The open
circuit voltage ($V_{OC}$) for both types of devices is approximately 0.45V. This large efficiency disparity in conjunction with similar $V_{OC}$’s indicates that parasitic series resistances dominate the characteristics of the graphene devices. To quantify the differences between aluminum and graphene cathode devices, both data sets were fit to the ideal diode equation. The fit yielded a series resistance of 700Ω and a shunt resistance of 10kΩ in the control devices versus a series resistance 10.5kΩ and shunt resistance of 3.5kΩ for the graphene cathode devices. The large parasitic resistances of the graphene devices directly induces lower efficiencies due to poor fill-factors under solar illumination. This observation is analogous to the series resistance/fill factor degradation found in few-layer graphene anode devices [54, 66, 67].

![I-V characteristics for graphene and aluminum cathode devices under 100mW/cm² solar simulated illumination](image)

**Figure 5.2:** I-V characteristics for graphene and aluminum cathode devices under 100mW/cm² solar simulated illumination

To minimize the influence of the parasitic series resistance we probed the devices under low-intensity monochromatic illumination (Figure 5.3). At an incident power of 4.6 mW/cm², the graphene device exhibits a power conversion efficiency of 0.22% and a $V_{OC}$ of 0.38V, while the aluminum device exhibits a power conversion efficiency of 1.19% and a $V_{OC}$ of 0.38V. At
Figure 5.3: Graphene and aluminum control devices were analyzed under different illumination intensities to investigate fill factor and $V_{OC}$ as a function of incident power.

An incident power of 6.6 mW/cm$^2$, the graphene device exhibits a power conversion efficiency of 0.24% and a $V_{OC}$ of 0.40V, while the aluminum device exhibits a power conversion efficiency of 1.84% and a $V_{OC}$ of 0.43V. Given the 0.3 eV difference between the work functions of graphene and aluminum, the nearly identical $V_{OC}$ values are particularly noteworthy. These values can only be the result of graphene undergoing contact doping and adjusting its work function upon contact with a strong electron acceptor (TPBi).

The optical transparency of graphene also enabled us to compare device performance with both anode and cathode side illumination (Figure 5.1d). The power conversion efficiency was 0.01% for anode-side solar illumination and 0.03% for cathode-side solar illumination. In addition, the power conversion efficiency was 0.24% for anode-side monochromatic illumination (6.57 mW/cm$^2$) and 0.41% for cathode-side monochromatic illumination (6.57 mW/cm$^2$). These differences in device performance were due to an increase in the short-circuit current density for cathode-side illumination. We attribute this difference to the strong absorbance of CuPC. Anode side illumination results in the majority of excitons being formed at the
PEDOT/CuPC junction, which is not within an exciton diffusion length of the power producing CuPC/C60 interface. Cathode side illumination results in the majority of excitons being produced at the energy producing CuPC/C60 heterojunction. This leads to an increase in efficiency for cathode side illumination relative to anode side illumination.

We have demonstrated that single-layer graphene undergoes contact doping and can serve as cathodes in OPVs. The power conversion efficiencies of graphene devices were limited by their series resistance, indicating that the preparation of graphene samples with lower sheet resistances could improve device performance. The $V_{OC}$’s of our devices indicated that the work functions of graphene sheets shift when placed in contact with electron-donating material. This type of contact doping is a potentially valuable characteristic not currently shared by any known cathode material. The transparency of graphene also enabled us to demonstrate a simple strategy for doubling the efficiency of OPVs. The demonstration of a functioning graphene cathode device allows for the fabrication of all-graphene electrode devices. Overall, our findings portend favorably for the fabrication of metal free, truly organic solar cells with graphene as a cathode and anode.
Chapter 6

Recombination in Tandem OPVs

The integration of single photovoltaic cells into tandem architectures is an exciting avenue of research. By this method, cells that absorb different portions of the solar spectrum can be combined to form a single, higher efficiency solar cell.

6.1 Current Strategies

Currently, tandem cells are almost exclusively series tandem cells, as each cell is intimately integrated with its adjacent cell. This is a consequence of the need to, first, aid hole and electron recombination at the interface of different cells and, second, to maintain the highest transparency so as not to absorb light traversing to subsequent cells. Since recombination requires only a very small amount of metallic material, most organic tandem solar cells employ a \( \sim 1 \text{nm} \) layer of metal as a recombination layer.[76–82] These thin metal layers, during deposition, coalesce into metal nanoparticles. The resulting structure provides the basis for charge recombination while remaining highly transparent (\( \sim 98\% \)[76]), but do not
have lateral conductivity, necessitating a series integration.

6.2 Graphene as a recombination layer

Graphene represents a significant opportunity as a recombination layer in tandem organic photovoltaics. Its high transparency (∼97.5%) coupled with its high conductivity could enable a recombination layer that is laterally conductive, enabling a non-series tandem cell.[83]

If one takes two identical cells and connects them in series, the first cell with absorb a greater amount of light than the second. The result of this is that more current is generated in the first cell than the second, a phenomenon well known in OPV device physics. Despite the higher current being generated by the first cell, the tandem cell will generate only as much current as the weakest cell, throwing away the additional power being generated by the first. If that tandem cell is fabricated as a non-series tandem, however, all of this power can in theory be harnessed.

A model was built to evaluate the implications of this possible architecture. A 5nm thick layer of SubPC, a popular HTL, and a 5nm thick layer of $C_{60}$ was measured for absorption in a UV-Vis spectrometer. The absorption data, is shown in Figure 6.1 along with the AM1.5 solar spectrum, an average representation of the power of the sun that is measured on the surface of the earth for mid-latitudes.

The model assumed a tandem solar cell made up of two identical single cells with 20nm of SubPC and 40nm of $C_{60}$ with light first entering the SubPC, as shown in Figure 6.2.

Also assumed is that every absorbed photon generates an exciton, only excitons generated
Figure 6.1: Absorption data for 5nm thick films of SubPC and C\textsubscript{60}, and the AM1.5 solar spectrum power versus wavelength.

within 10nm of the heterojunction can contribute to power, which they do with 100% extraction. The model includes incident light and one reflection off of a perfectly reflective cathode, and does not include reflection losses at the anode or absorption in non-semiconducting materials.

The power generation versus wavelength for this model is shown in Figure 6.3. Here we see the power generated by wavelength for the first and second cell, as well as the calculated power generated in a series versus a non-series tandem cell.

One can see from this model the dramatic absorption differences between the first and second cell. This result is in agreement with many laboratory measurements. A large amount of light is absorbed in the first cell, much of which cannot contribute to power, leaving a substantially reduced amount of light for absorption in the second cell. As a result, the
current generated by the first cell is significantly higher than that generated by an identical second cell. For series tandem cell architectures, only the lowest generated current dictates the current for the whole device, and this fact is the driving force for much research in tandem OPVs to balance the current generation in each tandem cell. One can see from the power generation of the non-series tandem cell the enabling possibilities of a laterally conductive recombination layer. Here, despite large imbalances between subsequent cell current generation, the entirety of the generated power can be harnessed. The efficiency of the devices, which is the integral of these curves divided by the total incident light power, yields an efficiency of 5.5% for cell 1, 1.79% for cell two, 3.58% for the series tandem cell (deleteriously affected by series connection), and 7.3% for the non-series tandem (the sum of efficiency from cell 1 and 2).
6.2.1 Quenching Experiment

In order to test graphene’s ability for recombination in a tandem solar cell a quenching experiment was performed. This experiment relies on the fact that the exciton diffusion length in organic semiconductors is approximately 12nm. As a result, if a fluorescent organic molecule is within ~12nm of a recombination site, such as a metal, any exciton that finds itself on that molecule will have a high probability of decaying non-radiatively on that metal. In order to probe graphene’s ability to provide a recombination site for tandem solar cells, 25nm of a fluorescent small molecule, Tris(8-hydroxyquinolinato)aluminium (Alq₃) was deposited on ITO-coated glass and graphene was transferred on top of this layer. Without graphene, a 25nm layer of Alq₃ on ITO, when bombarded with UV light, would result
in ∼12nm of quenched Alq₃ adjacent to the ITO, and ∼13nm of unquenched and, thus, fluorescing Alq₃ on top of this quenched layer. Figure 6.4 illustrates the schematic of this substrate.

![Figure 6.4: Schematic of 25nm Alq₃ on ITO glass.](image)

To test the efficacy of graphene as a recombination site and to attempt patterned graphene transfer this Alq₃/ITO substrate as well as a transfer stamp was fabricated. Figure 6.5a is a picture of this substrate under UV illumination. This stamp was processed as described above, with the caveat that the fluorinated resist spin was done while masking a stripe in the stamp with scotch tape. During the copper etch step of the stamp fabrication, since there is very little adhesion between parylene and graphene, this “patterned” region allow graphene to float away during the etch, resulting in the patterned stamp that you see in Figure 6.5b.

This stamp was used to transfer graphene onto the Alq₃/ITO substrate, and the substrate following this transfer step is shown in Figure 6.6a. By transferring a graphene monolayer onto the top of this substrate, assuming graphene is successfully transferred and performs as a recombination site, it should effectively quench the top ∼12nm of Alq₃. Figure 6.6b shows this transferred substrate under UV illumination, which clearly indicates that quenching is occurring where graphene has been transferred.

In Figure 6.6a one can see that a pattern larger than just the graphene was transferred
onto the target substrate. This transfer includes a thin film of the fluorinated resist, which itself is a critical portion of the transfer process. It was chosen, in addition to exhibiting a
near ideal surface energy for the adhesion of graphene and subsequent release from parylene, because it is soluble in a fluorinated solvent that does not have a detrimental affect on most organic semiconductors. Since its presence is not desired in a device fabrication stack, this layer was removed by two back–to–back spin-cleans of a proprietary resist stripper. Figure 6.7a shows the substrate after this cleaning, where it is difficult but possible to see the patterned graphene still on the substrate. Figure 6.7b shows this same substrate under UV illumination, where the patterned graphene that remains is clear from the quenching that its presence results in.

![Image](a) Patterned graphene on Alq3/ITO substrate after resist stripper clean (b) Patterned graphene on Alq3/ITO substrate after cleaning under UV illumination

Figure 6.7: Transfer of patterned graphene onto Alq3/ITO substrate after fluorinated resist cleaning

To test this fabrication with a slightly more complex pattern the process was repeated. Figure 6.8a shows the unmodified Alq3/ITO substrate under UV illumination, Figure 6.8b shows the patterned graphene stamp, Figure 6.8c shows the substrate after graphene transfer, Figure 6.8d shows this transferred graphene under UV illumination, and Figure 6.8e and
Figure 6.8f show the substrate under visible light and UV illumination, illustrating the successful transfer and patterned quenching of graphene onto a small-molecule organic thin film.

6.3 Conclusions

It is clear from modeling results that non-series tandem cells could enable new architectures and potentially higher-efficiency solar cells. Graphene has been successfully transferred on top of small molecule organic thin films where it provides sites for recombination, a critical step in the successful integration of graphene as a recombination layer in tandem OPVs.
Figure 6.8: Transfer of CU–patterned graphene onto Alq$_3$/ITO substrate
Chapter 7

Conclusion

The field of organic photovoltaics is driven by the desire to create low-cost photovoltaic devices. To be commercially viable these devices, however, must demonstrate efficiencies and stabilities that allow an economic argument to be made for them. This is currently not the case.

We first established that, in addition to thermal evaporation and spin coating, there are additional existing processes that can be used to build OPV devices, such as electropolymerization. With its wider range of process parameters, this process could be used, for instance, to more precisely control the concentration and morphological properties of bulk-heterojunction devices.

Next we show that by integrating new and promising materials OPV devices with improved characteristics could be fabricated. By integrating a small modification in the well-known pentacene molecule, a higher stability molecule could be synthesized which then imparts a higher stability to an OPV device. Further, molecular interactions within devices were shown to impart significant and novel affect on device function, where the “ball and
socket” interaction of HBC and C60 resulted in a near theoretical maximum $V_{OC}$ operating photovoltaic device. Then, by further modifying an HBC molecule we were able to control molecular self-assembly in a thin film, resulting in the fabrication of ordered thin films with implications for higher efficiency OPV devices.

OPVs electrode materials represent another area of potential advance, particularly with the promise of the recently discovered 2-D material graphene. Here, while process techniques exist for transfer onto various high-energy surfaces, the lack of a chemically and energetically delicate transfer process had hindered it’s integration into most OPV devices. To enable this type of integration we developed a novel transfer process that involves only a single orthogonal solvent step, showing the direct transfer of graphene onto an organic thin film while retaining the mechanical and electronic integrity of both materials. In addition to establishing a transfer process and demonstrating it’s faculty as a highly versatile top cathode in OPVs and OLEDs, we illustrated the potential for graphene as a recombination layer in tandem OPV devices. By first demonstrating that graphene effectively quenches recombination on an organic thin film, we showed that the process is viable. By developing a simple model we illustrate the utility that a conductive graphene interlayer could provide for a non-series tandem cell, significantly expanding the possible architectures for organic photovoltaics.

A significant advantage for OPVs is that their potential material set is literally infinite. The challenge for the industry is thus to develop rational frameworks with which to identify promising materials and to develop processes that allow the integration of a wider range of materials as well as additional architectures to expand the possible design space for their integration. The aim of this thesis to contribute to this cause.
Chapter 8

Bibliography


Appendix A

List of Publications


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Appendix B

LED-based Optical Device for In Vivo Perfusion Measurement

We demonstrate a reflectivity-based perfusion sensor comprised of surface mounted light emitting diodes on a flexible substrate with integrated photodetectors in a form factor suitable for direct brain contact and chronic implantation. This reflectivity monitor is able to measure blood flow through change of the surface reflectivity, and through this mechanism detect the perfusion changes associated with epileptic seizures with a signal to noise (SNR) response of 42dB. The device is tested in an in vivo model confirming its compatibility and sensitivity. The data taken demonstrates that placing the sensor into direct brain contact improves the signal/noise ratio more than four orders of magnitude over current non-contact technologies.
B.1 Introduction

Epilepsy is a neurological condition characterized by recurring seizures in which clusters of neurons fire synchronously with no external stimulus. Approximately 1% of the human population suffers from the condition, 20% of whose symptoms cannot be satisfactorily treated pharmaceutically.[84] This minority relies almost exclusively on invasive surgery,[85], an important part of which is the in vivo surface analysis of brain tissue using arrays of electrical probes to localize the focus of the seizures and direct surgical intervention.[86]

There are several established approaches for mapping activity in the brain. The most established, electrophysiological recording from electrodes, does not have the temporal or spatial sampling necessary for the acute study of neuronal activity generation and spread due to volume conduction effects.[87] Other techniques, including functional magnetic resonance imaging (fMRI), positron emission tomography (PET), and single-photon emission computed tomography (SPECT), do not have sufficient resolution to record brief paroxysmal events such as interictal spikes (the synchronous firing of neuron populations).[88]

Optical imaging using a charge-coupled device (CCD) camera has been successfully used to measure short-duration events such as interictal, ictal, and secondary homotopic foci in vivo [86] as well as normal brain function.[89] A direct correlation between interictal spikes and neocortex tissue reflectivity due to cerebral blood flow changes and the resulting change in hemoglobin oxygenation in response to increased neuronal activity has been demonstrated.[90] This method has high spatial and temporal resolution, and images can be generated at a high frame rate, making the process clinically valuable for tissue analysis prior to ictal onset zone and frequent interictal spike-zone removal.[86] The assembly used
APPENDIX B. LED-BASED OPTICAL DEVICE FOR IN VIVO PERFUSION MEASUREMENT

requires a significant amount of movement damping and can only be performed in a surgical environment, as the device must be externally mounted to the patient and the brain tissue must be exposed.\[91\] In optimal situations, the signal to noise ratio is less than 5.\[92\]

Chronically implanted optical sensors for unmolested long term epileptic study have not yet been demonstrated. This technology would constitute a significant advance; Suh et al. have shown a correlation between interictal spikes and subsequent epileptic seizure with a temporal offset of approximately 12 seconds.\[86\] The presence of a quantifiable warning signal exterior to the neocortex provides an opportunity for real-time in vivo monitoring and detection for seizure management. \[93\]

Here we demonstrate an integrated LED and photo-detector device applied to in vivo optical detection in a form factor suitable for chronic implantation and array development. This device is enabled by the miniaturization and high efficiency of LED technology, and allows the development of a clinically applicable measurement system.

B.2 Approach

A small and scalable probe was designed which measures reflected light with the precision necessary to distinguish between oxygenated and non-oxygenated brain tissue. Neural activity associated with seizures causes a 0.1 to 5.0% reflectance change, depending on the intensity of the neural activity.

Commercially available surface mount components were used to produce a thin form factor element compatible with implantation for chronic measurement (<1mm thick). The LEDs and photodetectors are operated using a synchronous detection approach to improve
Figure B.1: The process flow for device integration. A polyethylene naphthalate substrate is used, and the optical components are attached to the gold/chrome interconnect using a low melting point indium-based solder paste. The integrated unit is encapsulated with parylene-C.

The signal to noise ratio and heterodyne the detected signal away from the frequency composition of physiological noise. The emitter-sensor pair architecture can be scaled to multiple wavelengths and multiple sites using frequency domain or phase space encoding techniques.

B.2.1 Process flow

The device was assembled using a flexible circuit board fabricated on polyethylene naphthalate (PEN-Dupont/Teijin Q65A). This substrate material demonstrates excellent transparency, reagent compatibility, flexibility, and tolerance of high processing temperatures (in excess of 200°C in air) with minimal shrinkage or warpage. PEN can serve as an optically transparent replacement for polyimide in flexible circuit applications.

The process is summarized in Fig. B.1. The substrate is first solvent cleaned, and 10 nm of chrome and 80 nm of gold are thermally evaporated under vacuum. These metal films are patterned via contact photolithography, etched, and cleaned. Low melting point indium
solder paste is dispensed on the bonding attachment pads, and the LED and photodetector are positioned on the paste. The assembly is reflowed on a hot plate at 170°C for 15 seconds. The indium composite wets the chrome/gold intermetallic underlayer while alloying with the gold pads, preventing gold scavenging from the interconnect lines, and also drawing the components into position via surface tension. The completed device is electrically contacted via an anisotropic conducting adhesive through a ribbon cable to a custom circuit board where the individual component connections are made using shielded coaxial connections.

For increased structural robustness and environmental encapsulation, the devices are first CVD coated with 200nm of parylene-C, an optically transparent polymer used as a moisture barrier and electrical insulator. This is followed by a thin layer of a chemically activated epoxy adhesive. Once the adhesive is cured, the device is coated with a final 1 micrometer thick layer of parylene-C for biocompatibility and insulation against the saline environment of the brain. Fig. B.2 shows a completed and encapsulated device.

The high efficiency and miniaturization of commercial surface mount light emitting diodes enable this application. The light emitter used for this study (Kingbright, APHK1608VGC-Z) is a commercially available surface-mount light emitting diode, chosen for its small size (0.7mm thickness, 1.6x0.8mm length and width) and emission wavelength near an isosbestic point for hemoglobin and deoxyhemoglobin (535nm), yielding a measure of total hemoglobin (Hbt).[92] A surface mount broad spectrum phototransistor (Optek OP-500) was used. The use of a dual wavelength measurement would allow separate measurement of perfusion and oxygenation.[88]
Figure B.2: Microscope image of completed sensor device. The top device is the LED, the bottom device is the phototransistor. The finished package is 2mm x 2mm, and 0.8mm thick, suitable for use in a rat model and thin enough for chronic implantation.

**B.2.2 Measurement and signal analysis**

Reflected light from the target as well as a waveguided baseline is incident on the photodetector. To improve the SNR, a synchronous detection approach is applied. The LED is driven directly with a function generator (Agilent 33220A) synchronized to a lock-in amplifier (Signal Recovery 7265) at 497Hz, out of band and non-harmonic with traditional periodic noise sources (e.g. 60Hz line hum) and above the frequencies of broadband animal metabolic activity (<20Hz). The photoresponse is conditioned through a current preamplifier (Stanford Research Systems SR570) which is then detected by the lock-in. Using synchronous detection and discarding the DC baseline which is structurally waveguided through the system, it is possible to measure reflectivity changes yielding reflected power changes less than 4 nW/cm². Thanks to the high output flux of the LEDs (0.5cd), this can yield a measured reflectivity signal to noise ratio of 42dB for the brain surface measured during a seizure against the background noise of a surgical environment.
B.3 Results

Figs. B.3 and B.4 illustrate results obtained from two separate *in vivo* experiments performed at the Weil Medical College of Cornell University’s Neurological Surgery department.

The device was placed on the intact dura above the rat neocortex, where the local field potential (LFP) was monitored via a contact electrode. Seizures were chemically induced by introducing 4-aminopyridine (4AP) to the neocortex, yielding polyspikes and bicuculline methiodide (BMI) yielding interictal spikes. Synchronous data recording was performed, and the raw data is shown in Fig. B.3 (a). These neocortical surface tissue reflectance changes follow seizure events. This reflectance change conforms to the expected 1-2 second delay for metabolic demand to respond with an increase in Hbt.[86] In the absence of seizure, the reflectance approaches an asymptote corresponding to the equilibrium tissue blood volume.

Fig. B.3 illustrates the small-signal sensing capabilities of the device; (a) shows polyspikes induced by 4AP treatment to the brain tissue to induce seizures and (b) shows the interictal response induced by BMI exposure. Some of the power in the small perturbations in the optical signal correspond to the heartbeat and respiration of the animal.

Reflectivity deviation from the asymptote indicates a blood flow modulating event, and the strength of the deviation is correlated to the departure distance. In order to quantify the response, a 4AP induced polyspikes data set in Fig. B.4 (a) was notch filtered to remove the reflectivity change attributable to the bandlimited animal heartbeat (3-8Hz). The 3-8Hz response and the notch filtered response are shown in Fig. B.4 (b) and (c) respectively. The signal to noise ratio (SNR) for the device for seizure detection is 17,000:1 (42dB) as measured by comparing the RMS deviation of the unfiltered RMS out of band signal noise
Figure B.3: In vivo device results with both optical reflectivity and local field potential (LFP) electrode data. (a) shows polyspikes induced by 4AP treatment to the brain tissue and (b) shows the interictal response induced by BMI exposure. The figure shows interictal spikes caused by BMI; the optical reflectivity is scaled to eliminate the waveguided baseline.

to the total excursion seen during seizure, several orders of magnitude higher than external camera based in vivo imaging technologies.[92] Because the sensor moves with the subject and is in direct contact with the brain, artifacts which limit the SNR with remote camera sensing are significantly reduced, and the larger sensor area and effective sampling window leads to greater photon capture. Processing of the signal to remove the heartbeat and respiration oscillations can lead to even greater sensitivity to seizure events.
Figure B.4: *In vivo* device results: (a) shows the raw reflectivity data measured using the miniature reflectivity monitor. The data in all three graphs is linear in power and has been normalized and scaled together. The signal/noise ratio on this data as measured by comparing the RMS power of the in- and out-of signal band response is 42dB. (b) shows the 3-8Hz bandlimited signal, which is primarily the animal heartbeat, and (c) shows the data with the 3-8Hz components notch filtered.

### B.4 Conclusion

Miniature light emitting diodes can enable reflectivity monitoring in a form factor suitable for biological application in both acute and chronic measurement scenarios. When mounted on a flex circuit and used with synchronous illumination and detection strategies, it is possible to measure real-time blood volume *in vivo* with enough SNR to reliably detect and classify seizure events. This system detects the blood flow changes associated with epileptic seizures...
with performance exceeding that of other optical measurement strategies.

Further development of this sensor class will allow advance in detection technology and expansion into clinical applications. Use of dual wavelength sensing will allow separate measurement of perfusion and oxygenation, further improving the device utility. An arrayed device formatted into an implantable structure will allow localization of seizure activity in chronically monitored individuals. This implantable architecture can also be applied to other chronic reflectivity and fluorescence monitoring applications where blood volume, oxygenation, or a fluorescent analyte are monitored.
Appendix C

Photonic Crystal Spectrometer

During the investigation of photonic crystals for enhanced light extraction for organic light emitting devices, a potential application of photonic crystals for low-cost spectroscopy was identified. The work summarized below[94] describes the development of a spectrometer that uses photonic crystals to identify the spectral content of light.

C.1 Introduction

The development of lower cost spectrometer has enabled the application of spectroscopy to a significantly wider set of applications than were previously possible. This lower cost technology was enabled by reducing the size and versatility of existing systems, primarily through a fixed grating design. The requirement for a grating, however, has established a lower limit of price for traditional spectrometers, as this component requires significant precision and thus is expensive to produce. A particular tradeoff in traditional spectrometers is that of module size with resolution, as the spectral dispersion from a grating is directly
dependant on the distance travelled from the grating to the optical detector. The photonic crystal spectrometer departs from this requirement by patterning different photonic crystals on an optical waveguide, directing light of specific wavelengths out of the waveguide at spacially distributed point defined by the photonic crystals. A diagram showing how a photonic crystal spectrometer functions is shown in C.1.

![Diagram of photonic crystal spectrometer](image)

Figure C.1

In C.1 white light is directed into a planar waveguide. Four different photonic crystals with spectral responses in the red, blue, green, and yellow are patterned on the surface of this waveguide. Because of the spectral interaction of each photonic crystal, light of specific wavelengths will interact with each photonic crystal at different locations. By measuring the intensity of the light at each location, and knowing the spectral interaction defined by the photonic crystal pattern, a spectrum can be mathematically extracted. A proof of concept of this device is presented below by characterizing a white LED using an array of photonic crystal patterns.
C.2 Experimental

Photonic crystals were patterned in polymethylmethacrylate (PMMA) films on glass via electron beam lithography (EBL). Photonic crystal array measurements were performed using a USB camera (Matrix Vision mvBlueFox-120c) as light was waveguided into the optical waveguide via plastic optical fibers. RGB images of the photonic crystal arrays were taken through a 4x objective with a numerical aperture (NA) of 0.096 (Infinity Photo-Optical Infinistix). The photonic crystal pattern optical responses were characterized via a programmable light source (Newport Apex Xe Arc lamp and monochromator). The performance of the photonic crystal spectrometer was tested by measuring a while LED driven at 5mA. This LED was also measured with a commercial spectrometer for comparison (Ocean Optics USB4000). A 3x3 array of photonic crystals was used in the analysis.

C.3 Results and Discussion

C.2 shows the optical response of the photonic crystal array to four different light inputs. C.2a, b, and c show the response to narrow-band spectral inputs. Multiple fields are illuminated under this condition because the response functions of different photonic crystals overlap slightly. Since the photonic crystal spectrometer functions by mapping spectral intensity from wavelength space to pattern space, we can represent this transformation as a matrix operation as shown in C.1

\[ Ax = b \]  \hspace{1cm} (C.1)
Where $A$ is a $m \times n$ matrix containing the intensities of $m$ patterns at $n$ wavelengths, $x$ is the wavelength representation of the optical input, and $b$ is the pattern representation of the optical input. Since, when measuring a signal via our photonic crystal array spectrometer, $b$ can be measured via the optical responses shown in C.2 and $A$ is a full-rank matrix that can be found via optical characterization of the photonic crystal pattern array, the spectral response of the optical signal can be derived via multiplying both sides of C.1 by the inverse of $A$.

![Figure C.2](image)

To develop $A$ an analysis of the photonic crystal patterns was performed and is shown
in C.3. Here we can see the spectral response of each photonic crystal pattern.

![Spectral response of photonic crystal patterns](image)

**Figure C.3**

Using this data to build A and by measuring the spatial response of the photonic crystal array to a white LED input, the photonic crystal spectrometer can be used to derive a spectral response, shown in C.4 along with a mathematically derived performance limit based on the response functions of the photonic crystal array. Also shown is the measured spectrum via a commercially available spectrometer. C.4 shows a close match between the performance of the photonic crystal spectrometer and the actual spectrum as measured with an Ocean Optics spectrometer. In particular, we show that the performance is closely matched with the calculated performance limit.

While our photonic crystal spectrometer measurement is close to that of the commercial measurement, there is room for improvement. C.5 shows how this performance limit is affected by increasing photonic crystal pattern number.
C.5a represents that actual spectrum of a white LED. When using 9 photonic crystal elements, the spectral response of these elements (C.5b) does not provide a robust enough basis to build a high-performance photonic crystal spectrometer, and the performance limit includes a number of large deviations from this measured spectrum, as shown in C.5c. C.5d illustrates a response function that includes a larger number of response functions whose impact on performance limit, shown in C.5e, is indistinguishable from the actual LED spectrum.

C.4 Conclusion

This work shows that a photonic crystal spectrometer can successfully extract spectral information. Using only 9 photonic crystal patterns, a coarse spectrum of a white LED was measured and compared to the actual spectrum as measured on a commercial spectrometer.
Analysis shows that a photonic crystal spectrometer composed of additional photonic crystal patterns will result in a photonic crystal spectrometer of significantly better performance.