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Work Function Modification of Metal Electrodes via Printing of PEDOT:PSS and Carbon Nanotubes

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WORK FUNCTION MODIFICATION OF METAL ELECTRODES VIA PRINTING
OF PEDOT:PSS AND CARBON NANOTUBES

A thesis submitted in partial fulfillment of the
requirements for the degree of
Master of Science

By

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B.S., Wright State University, 2013

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ABSTRACT


Work function tunability of metal electrodes provides a route to improving performance of organic electronic devices. Using an electrode with a different work function changes the potential barrier at the polymer/electrode interface, leading to altered device characteristics, such as turn-on voltage in light emitting diodes or series resistance photodiodes. In this work, we explore work function modification by employing solution-based conducting materials, poly(3,4-ethylenedioxythiophene) : poly(styrene sulfonate) (PEDOT:PSS) and carbon nanotubes (CNTs), printed as overcoatings on oxidized Ni. The capability of direct write technologies, namely inkjet and aerosol jet printing, to control thin film thickness is investigated. The correlation between film thickness and work function is evaluated from profilometer measurements and ambient Kelvin probe measurements of the work function of the modified electrode. We find that aerosol jet printing is an attractive tool for modifying printed film thickness of PEDOT:PSS and CNTs. The achieved variation in thickness of printed films allows for work function modification exhibiting values that vary from the bare oxidized Ni value to the bulk PEDOT:PSS or CNT value as the thickness of the printed film is increased.

Further, we fabricate infrared Schottky photodetectors, with poly(3-hexylthiophene):C61-butyric acid methyl ester (P3HT:PCBM) composite as the active organic layer, to demonstrate the change in device performance with the implementation of the PEDOT:PSS- and CNT-modified electrodes. The test devices exhibited improvement in photodetection with implementation of the modified electrodes.
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Chapter 1

Introduction

1.1 Objectives and Significance of the Study

The history of the photoelectric effect began in 1887 when Henrich Hertz observed the phenomenon through experiments by exposing a negative electrode to ultraviolet radiation.\(^1\) It was not until 1905 when Albert Einstein provided a daring extension on Max Planck’s quantum hypothesis illustrating the photoelectric effect in great detail entitled “On a Heuristic Viewpoint Concerning the Production and Transformation of Light”.\(^2\) Einstein proposed that light behaves not only as a wave, but like particle; a photon. He explained that the photoelectric effect occurs when light incident on a metal surface has at least the minimum energy to allow an electron to escape from the surface. When the electron on the metal surface absorbs the photon, it gains all the energy from the photon and expends some energy to escape from the metal. This minimum energy to escape from the metal is called the work function of the metal. The electron will then have a kinetic energy equal to the photon energy minus the work function of the metal. Einstein earned the Nobel Prize for this remarkable discovery in 1921.

The detection of light of low intensity became possible in 1913 when Elster and Geiter invented the photoelectric tube only eight years after Einstein proposed the theory of work function.\(^3\) Expanding upon the basic working principle of the photoelectric tube, RCA laboratories released the photomultiplier tube (PMT) in 1936 and it has been the
work horse for the detection of photons since it came out commercially. Today PMTs have changed remarkably by shape and reduced in price. The structure of PMTs have transformed into flat displays with a very good effective area and the dynode structure within the vacuum container dramatically decreased in the number of parts needed for operation with the addition of automated processes. PMTs today exhibit a high gain and the output signal can be obtained with standard electronics. However, the main disadvantage of PMTs is that they are sensitive to Earth’s magnetic field and must be shielded. The quantum efficiency of PMTs are low (~ 25%) and PMTs fabricated with gallium arsenic phosphide (GaAsP) have a higher efficiency (~ 45%) but are very costly. These drawbacks led to the research and development of photodetectors.

The marriage between the theory of work function and the operation of PMTs gave rise to solid state photodetectors (PDs). Modern PDs are classified as optoelectronic devices that absorb optical energy, which is then converted to electrical energy manifesting a photocurrent. PDs are an attractive technology because of their capabilities of fast response speed, high quantum efficiency, and long wavelength detection. More recently, PDs have emerged from having inorganic to organic electronic components.

In the arena of organic electronics, governing the working function (Φ/eV) of metal electrodes has been one of the most important objectives to optimize device performance. The work function of a metal (Φ_m) and semiconductor (Φ_s) are defined as the difference between the Fermi level (E_F) and vacuum level (E_Vac). For a metal, E_F can be found on top of the valence band (E_V) (Figure 1a).
Figure [1]. Energy diagram describing the work function of (a) a metal and (b) a semiconductor.

In addition to $E_V$, a conduction band ($E_C$) is seen in a semiconductor separated by an energy band gap ($E_g$) whereby within the $E_F$ can be found (Figure 1b). In both metal and semiconductor energy diagrams, $E_{Vac}$ is defined as the point where the electron is completely removed from $E_F$.

The primary goal of this thesis is to demonstrate the viability and the added benefit of work function tunability using printed semiconducting materials at controlled thicknesses via inkjet and aerosol jet printing. Work function modification will be achieved by employing solution-based conducting materials, PEDOT:PSS and CNTs, printed over oxidized Ni. We hypothesize that tuning can be achieved by varying the thickness of the printed materials. The specific objectives are as follows:

i) Investigate the capability to control thin film thickness via inkjet and aerosol jet printing.

ii) Evaluate the correlation between the thickness of the printed film and the degree of work function modification.
iii) Demonstrate the change in device performance with the implementation of modified electrodes to fabricate a Schottky photodetector.

The metal electrode chosen in this study is Ni, which is then oxygen-plasma treated to oxidize the surface. This is based on a previous study showing that NiO has favorable energy alignment with several relevant semiconducting polymers.\(^9\) Thus, it can be an Ohmic contact electrode for polymer-based devices and serve as a less expensive alternative to the commonly used Au and Pt.

PEDOT:PSS is a solution-based transparent conducting material that is widely used as a coating for ITO to improve the performance of organic devices.\(^{10}\) The improvement is generally attributed to the ability to control the work function of the ITO by polymeric coatings.\(^{11,12}\) Aside from modifying the work function of ITO, PEDOT:PSS is also known to have the appropriate surface energy for most polymer-based semiconductors to adhere.

Carbon nanotubes constitute another attractive coating material for work function modification of metal electrodes. A continuous film of CNT can be fabricated by solution-based deposition techniques such as spin coating and printing. It has been reported that multiwalled carbon nanotube thin films on flexible substrates can serve as transparent conducting electrode for polymer-based diodes.\(^{13}\) This report suggests that a CNT film may have the suitable work function and surface energy for polymer-based semiconductors.
1.2 Role of Work Function of Electrodes in Devices

Thin films of semiconducting materials deposited on various metal substrates constitute a new class of systems with tunable properties to potentially provide many applications. An important consequence upon the deposition of a thin film on a metal is the change in work function of the metal support which can be increased or decreased depending on the nature of the interface.\(^\text{14}\) When a metal and semiconductor come into direct contact, the semiconductor lowers its energy by transferring electrons into the metal and as a result a Schottky barrier (\(\Phi_B\)) is erected at the metal/semiconductor interface (Figure 2).

\textbf{Figure [2].} Erection of a Schottky potential barrier at the metal/semiconductor interface.

The misalignment of the electron affinity (\(\chi_s\)) of the semiconductor and \(\Phi_m\) results in \(\Phi_B\), therefore the capability to modify \(\Phi_m\) provides a route to controlling the barrier height, \(\Phi_B\). The possibility of tailoring \(\Phi_m\) the to match the \(\chi_s\) of the active organic layer is of great interest in the fabrication of organic devices to create barrier-free Ohmic contacts, where \(\Phi_B\) no longer governs device performance.

The choice of the metal electrode plays a critical role in the performance of devices, because adjustments of \(\Phi_m\) enables changes of the interfacial energy alignment.
with the active organic layer and allows for changes in carrier tunneling probability.\textsuperscript{15,16} Consider, for example, an organic light emitting diode (OLED) and an organic photovoltaic (OPV) device, with representative energy levels shown in Figures 3 and 4, respectively. In an OLED, the work function of the anode must be within 0.1 eV of the highest occupied molecular orbital (HOMO) of the hole transport layer (HTL) to transport holes efficiently.\textsuperscript{17} The cathode must consist of a low work function material to extract electrons into the LUMO (lowest occupied molecular orbital) contained in the electron transport layer (ETL).\textsuperscript{18} The holes and electrons will recombine and a photon of a specific wavelength will emit (Figure 3).

![Diagram](image)

**Figure [3].** Basic architecture of an OLED showing the work functions of the anode and cathode relative to the HOMO-LUMO energy levels of the organic active layer components.

Organic photovoltaics operate in the opposite way, where light is being used to generate photocurrent. Incident light is shined on the transparent indium tin oxide (ITO) anode and reaches the active material sandwiched between the anode and cathode (Figure 4a).
**Figure [4].** (a) Basic architecture of an OPV and (b) its corresponding energy level diagram.

An exciton (electron/hole pair) is generated within the active material and the holes and electrons are transported to their respective electrodes generating photocurrent (Figure 4b). Again, it is critical to have electrodes with work function energies that match the HOMO or LUMO energy level so that the device works efficiently.
1.3 Direct Write Technologies

Over the past few years, rapid progress has been seen in the fabrication of electronic devices by printing. Electronic devices fabricated from a “Direct Write” (DW) technology offers promising alternatives to conventional deposition techniques. The general definition of “Direct Write” can mean any technology which can create two- or three-dimensional architectures directly onto flat or conformal surfaces in complex shapes without the need for masks.\textsuperscript{19} The development of DW technologies accelerated in the 1990s by funding from the U.S. Defense Advanced Research Projects Agency (DARPA) and its Mesoscopic Integrated Conformal Electronics (MICE) program.\textsuperscript{20} DARPA provided funding to companies such as Matrix-Assisted Pulsed Laser Evaporation (MAPLE), nScrypt 3De, Maskless Mesoscale Material Deposition (M\textsuperscript{3}D, now known as Aerosol Jet), and Direct Write Thermal Spraying to enable the capability to manufacture complex electronic circuitry and devices onto flexible\textsuperscript{21} and 3-dimensional substrates.\textsuperscript{20,22} As a result, researchers have utilized the DW technology to write or print a wide range of electronic components such as thin films transistors,\textsuperscript{23,24} radio–frequency identification (RFID) tags,\textsuperscript{25,26} sensors,\textsuperscript{27,28} organic light emitting diodes,\textsuperscript{29} solar cells,\textsuperscript{30,31} and photodetectors.\textsuperscript{32,33} The capability to utilize DW technologies offers high efficiency fabrication, good quality patterns, take flexible substrates and are environmentally friendly compared to conventional deposition.

Shown in Figure 5 are two conventional device fabrication techniques, spin coating and photolithography. Spin coating is a very common fabrication technique to form homogeneous films (Figure 5a). Once the film is deposited onto the substrate, it is subject to morphological changes upon evaporation of the solvent. Although thin films
are formed, spin casting has its disadvantages. Much of the material is ejected during processing and the thickness of the films are very difficult to control.\(^{34}\)

**Figure [5].** (a) Film formation technique spin coating and (b) photolithographic device processing.

Photolithography is another popular technique to pattern substrates requiring many processing steps (Figure 5b). A typical patterned layer would be fabricated as follows: 1) a thin film of photoresist is deposited onto the oxide layer, 2) exposure to a lithographic technique (masked radiation, such as UV light), 3) development, 4) etching of the oxide layer to expose the silicon, and 5) finally stripping of the photoresist.\(^{35}\) This fabrication technique is very expensive, time consuming and most often performed in a clean room. Both of these techniques cannot be performed on curved, flexible, or polymeric substrates so they are limited. There is a growing need to develop alternative fabrication techniques for electronic devices and components.
Figure [6]. Flow chart of specific direct write methods, in particular, inkjet and aerosol jet printing.

Presented in this thesis is the use of DW ink-based processes, specifically inkjet and aerosol jet printing methods shown in Figure 6. The inkjet printer employed is a drop-on-demand printer equipped with a piezoelectric print head that enables deposition of inks for accurate placement. The aerosol jet printer (Optomec) employed has capabilities to produce printable features ranging from 10 μm to 1 cm. Direct write technology, such as inkjet and aerosol jet printing, offers distinct advantages: i) enables application such as personalized printing, variable data printing and print-on-demand for small runs, ii) consumes only the amount of ink to complete the pattern, iii) requires no screens; consequently eliminating all related costs, and iv) is noncontact. These advantages make inkjet and aerosol jet printing attractive fabrication tools to create electronic devices and components.
Chapter 2

Literature Review: Work Function Modification

2.1 PEDOT:PSS

Since Shirakawa et al. discovered that polyacetylene can reach high electrical conductivities, the field of conductive polymers has attracted the interest of researchers. Conductive polymers have found their way in electronic device applications due to their lightweight, flexibility, and simple processing requirements, in addition to their optoelectronic properties.

![PEDOT polymer backbone](image)

Figure [7]. PEDOT polymer backbone.

During the late 1980s, researchers at the Bayer AG research laboratories in Germany developed a new polythiophene derivative poly(3,4-ethylenedioxythiophene) or PEDOT, having the backbone shown in Figure 7. PEDOT is an electro-chemically stable conjugated polymer that when oxidized (doped) becomes a highly conductive polymer. The preparation of PEDOT is conducted by standard oxidative or electrochemical polymerization methods and is found to be highly conductive (400-600 S
(PEDOT), transparent, electrochemically stable, and thermally stable (up to 230 °C) in thin oxidized films.\textsuperscript{37}

![PEDOT: PSS diagram](image)

**Figure [8].** PSS chain ionically bonded to oligomeric units of PEDOT.

The major drawback of PEDOT is that it is insoluble in most solvents, directly affecting its processability. To overcome this drawback, PEDOT is polymerized with the water-soluble polyelectrolyte solution, poly(styrene sulfonate) or PSS, using Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} as the oxidizing agent (BAYTRON P). PSS is the charge-balancing dopant to PEDOT resulting in the commercially available PEDOT:PSS (Figure 8).\textsuperscript{40} In its pure form, PEDOT:PSS is dark blue in color and electrochemically stable in this p-doped form. It is moderately transparent, possesses high electrical conductivity (1-10 S cm\textsuperscript{-1}), and has excellent film-forming capabilities.\textsuperscript{41}

Studies have shown that the conductivity of PEDOT:PSS is increased among adding high boiling point liquid additives during solution processing\textsuperscript{37,42} to form a more homogenous morphology by relaxing the polymer chains. The morphology of the film, chemical and physical properties can also be modified by a variety of post-deposition treatments, such as exposing the film to heat.\textsuperscript{43} Not only will additives and heating
treatments improve conductivity, but polar solvents were also shown to display such effects. The addition of polar solvents allows the PEDOT to become partially dissolved in the PSS matrix, enhancing a morphological rearrangement and clustering for easier charge transportation.\textsuperscript{44,45}

Due to the variety of properties of the PEDOT:PSS complex, it has been used in many areas of industrial and laboratory fields from biology\textsuperscript{46} to engineering. It has been used in polymer capacitors, organic thin film transistors, polymer solar cells,\textsuperscript{44} infrared detectors, and as hole injection layers on ITO substrates for electroluminescent devices.\textsuperscript{40} PEDOT:PSS is most commonly used as an interlayer in organic electronic devices. This water soluble polymer composite can be formulated into inks and be deposited onto various substrates via direct writing techniques. Printed PEDOT:PSS found its way to be useful in devices such as transistor circuits\textsuperscript{47} and polymer solar cells.\textsuperscript{48} Over the past decade, it has been one of the most successful conducting polymers to be designed and studied. The rise in popularity is evident from the trend in Figure 9, which shows the number of publications related to the PEDOT:PSS complex over the past ten years.

\textbf{Figure [9].} Development of the number of publications on PEDOT:PSS over the past decade (2004-2014): SciFinder Scholar keyword “PEDOT:PSS”.

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2.2 Carbon Nanotubes

Findings of carbon nanotubes date back to 1952 and perhaps earlier.49 Early transmission electron microscopy (TEM) images of carbon filaments that are tubular in nature were published in the Journal of Physical Chemistry of Russia.50 However, during the Cold War western scientists were restricted from accessing Russian scientific journals.49 It was not until 1991 that the “re-discovery” of carbon nanotubes by Iijima was announced, referring to the structures as “helical microtubules of graphitic carbon” prepared by the arc discharge method.51 Since then, there have been a plethora of publications especially in the past decade (Figure 10).

![Graph showing the development of the number of publications on carbon nanotubes over the past decade (2004-2014): SciFinder Scholar keyword “carbon nanotube”.](image)

**Figure [10].** Development of the number of publications on carbon nanotubes over the past decade (2004-2014): SciFinder Scholar keyword “carbon nanotube”.

Carbon nanotubes are cylindrical shaped macromolecules with a radius as small as a few nanometers that can be grown to 20 cm in length.52 The walls of these tubes are composed of a hexagonal lattice of sp² hybridized carbon atoms analogous to graphene.
Single-walled carbon nanotubes (SWCNTs) can be visualized through the rolling of a graphene sheet (Figure 11a). Multiwalled carbon nanotubes (MWCNTs), as shown in Figure 11b, consist of two or more concentric arrangements with an interlayer distance around 3.4 Å.

The unique properties of CNTs offer a vast majority of potential applications in multidisciplinary fields of science. CNTs were shown to have unusually high thermal conductivity, $\lambda \approx 6600 \text{ W/m K}$, for an isolated $(10, 10)$ nanotube at room temperature. They also have a high mechanical strength showing a Young's modulus of $0.2 - 0.7 \text{ TPa}$ and tensile strength of $60 - 100 \text{ GPa}$. Semiconducting and metallic properties have been investigated as well. Marrying the mechanical and electrical properties of CNTs give rise to applications from membranes for water purification, bioimaging, OLEDs, transistors, flexible electrodes, and chemical sensors, just to name a few.
2.3 Previous Studies on Work Function Modification

The ability to tailoring the work function of metal electrodes has been shown to result to devices with improved overall performance. Materials that incorporate self-assembled monolayers (SAMS) were shown to increase or decrease work function depending on whether the monolayers have electron-withdrawing or electron-donating groups, respectively. Introduction of fluorides, such as LiF and CsF, by thermal evaporation, and the introduction metal oxides have also been shown to tune the work function of electrodes.

2.3.1 Self-assembled Monolayers

Campbell et al. first demonstrates that the Schottky barrier at the metal/semiconductor interface can be manipulated by the insertion of self-assembled monolayers (SAMs). Wang et al. investigates the interfacial electronic properties of SAMs-modified gold (Au). Depending on the dipole direction of the SAMs, the work function of the SAMs-modified Au electrode was tuned. For example, if the direction of the dipole starts from at a negative dipole (-δ) to a positive dipole (+δ) there was a decrease in work function with respect to the unmodified Au electrode. On the other hand if the dipole is +δ to –δ the work function is increased with respect to the unmodified Au.

Not only has the development of SAMs lead to work function modification by inducing a dipole on electrodes, it also influenced performance in organic devices. Boudinet at. el. employed SAMs in both p- and n-channel organic thin film transistors (OTFTs) to study the correlation of contact resistance and work function. The resulting contact resistance exhibits dependence on the work function of the metal channels. The
capability to tune the work function controls the contact resistance thus demonstrating the effect of the SAMs on the Schottky barrier height at the interface.

Knesting et al. used various phosphoric acid SAMs (PA SAMs) and PEDOT:PSS to modify the work function of ITO to improve the open-circuit voltage \( (V_{OC}) \) and carrier lifetime in bulk heterojunction organic photovoltaic (BHJ-OPV) devices.\(^6\) The resulting work function of the modified-ITO approaches the ionization energy of the polymer thus slowing the recombination of electrons at the interface and improving device performance.

### 2.3.2 Metal Oxides

Transition metal oxides typically serve as an interlayer to modify the work function of an electrode. Significant progress in power conversion efficiency (PCE) and stabilities of polymer solar cells has been accomplished utilizing semiconducting metal oxides as charge extraction layers [Sugiyama, 2000].\(^6\) Cheun et al. deposited various thicknesses of zinc oxide (ZnO) to modify the work function of ITO. At any thickness of ZnO the work function of ITO was lowered from 4.7 to 4.3 eV. As a result, the electrical performance such as fill factor (FF) and PCE was significantly improved with ZnO layers exceeding 10 nm.\(^6\) Amorphous indium zinc oxide \( (a-IZO) \) can be used as a replacement of ITO for an inverted solar cell to improve device performance.\(^6\) It was shown that modifying the work function of \( a-IZO \) by exposure to low O\(_2\) atmosphere lowered the work function from 5.2 eV to 4.46 eV. Cheun at. el. utilized these modified films for electron-collecting electrodes in inverted solar cells and their electrical performances was comparable to ZnO modified ITO solar cells.
Among the metal oxides previously discussed, nickel oxide (NiO) is the only p-type semiconducting oxide. The work function of NiO strongly depends on its surface chemistry, crystal orientation and how the film is deposited.\textsuperscript{69} Although NiO is sensitive to ambient air which induces a work function change, the work function of NiO is sufficient for the energy alignment with several relevant semiconducting polymers. \textit{Irwin et al.} demonstrated NiO hole extraction/electron blocking layers in conventional P3HT:PCBM cells by deposition of 10 - nm NiO on top of ITO. Inserting the NiO layer yields a PCE of 5.2\%, a FF of 69\%, $V_{OC}$ of 0.638 V and a $J_{SC}$ of 11.3 mA/cm$^2$\textsuperscript{70}.

### 2.3.3 Fluorides

The introduction of various fluoride containing compounds has shown to modify the work function of metal electrodes. Whitcher \textit{et. al.} studies the effects of various concentrations of caesium fluoride (CsF) solutions in efforts to modify the work function of ITO. They show that diluted solutions have a higher work function and concentrated samples have a lower work function.\textsuperscript{71} The use of LiF is another attractive technology to modify the work function of ITO. It was shown that thermo-evaporated or sol-LiF has different work functions due to the deposition technique.\textsuperscript{72} \textit{Brabec et al.} showed that white light efficiency of conjugated polymer/fullerence bulk heterojunction solar cells can be enhanced up to 3.3\% white light efficiency when using LiF/Al electrodes instead of Al alone.\textsuperscript{73} They suggest that the formation of a dipole moment across a junction, due to either orientation of the LiF or chemical reactions occurring lead to charge transfer across the interface is responsible for the enhancement.
Chapter 3

Experimental

3.1 Preparation of Metal Electrodes and Printed Films

In this work, oxidized Ni is used as the metal electrode, and its work function is modified by printing of PEDOT:PSS and CNTs. A glass slide with a dimension of 1 in\(^2\) was used as underlying substrate. First, the glass substrate was cleaned by ultrasonic washing in methanol, acetone and isopropyl alcohol for ten minutes each and dried with nitrogen before exposure to the next solvent. High purity Ni (99.995 \%) was electron beam (e – beam) evaporated onto the glass substrate via shadow mask to define two strips. The dimension (width x length x thickness) of each strip was 4 mm x 23 mm x 100 nm. Immediately after, the nickel electrodes were subject to oxygen plasma treatment at 200 W for 2 min (Figure 12).

![Oxygen plasma treatment of the nickel electrode resulting in an oxygen terminated surface.](image)

**Figure [12].** Oxygen plasma treatment of the nickel electrode resulting in an oxygen terminated surface.

Figure 13a shows a schematic of the oxidized Ni strips on glass. Four electrodes can be obtained from this set-up as depicted in Figure 13b. One of the four electrodes is
left as a bare oxidized Ni. The other three are printed with either PEDOT:PSS or CNT films, with thicknesses varied by varying the number of print passes. Measurements of film thickness were carried out using a surface profilometer.

**Figure [13].** Schematic diagram of (a) oxidized Ni strips e-beam evaporated on glass and (b) printed PEDOT:PSS or CNT film.

The PEDOT:PSS ink was purchased from Heraeus (Clevios™ P Jet N), whose formulation includes ethanol (15–20%) and 2,2’-oxydiethanol (4–8%). For aerosol jet printing, the original formulation was diluted with DI water at a 2:1 ratio by volume. For inkjet printing, it was used without further modification and in a formulation prepared by mixing 0.5 mL of PEDOT:PSS to 0.1 mL ethylene glycol (EG) anhydrous, 99.8% (Sigma-Aldrich) in 0.25 mL DI H2O. Ethylene glycol is added in attempts to improve the morphology of the printed film. Pure PEDOT:PSS and PEDOT:PSS containing ethylene glycol will be referred to as PEDOT:PSS and EG-PEDOT:PSS, respectively.

Two different CNT inks were employed in this study, CNTRENE (Brewer Science) and Nink 1100 (NanoLab), both of which were used with no further modifications.
3.2 Printing Techniques

3.2.1 Inkjet Printing

Inkjet printing was carried out using a Dimatix DMP-2800 (Fujifilm Dimatix, Inc., Santa Clara, CA, USA). This model utilizes a drop-on-demand technology, and it is equipped with a piezoelectric inkjet cartridge and a fiducial camera to view the printed patterns. To ensure stable jetting, the model allows capability to view how the droplets are formed and if any of the nozzles are clogged. The jetting of the droplet is controlled by the firing voltage and the waveform, which can be optimized to ensure the most stable jetting and to produce high quality printed lines. The ink is ejected from a 10 pL cartridge print head. The ink is evenly broken down into closely spaced droplets from 16 linearly spaced nozzles at 254 μm with orifice dimensions of 21.5 μm. The inkjet printing parameters used will be discussed in Section 4.1.2.

3.2.2 Aerosol Jet Printing

The instrument used for aerosol jet printing is the OPTOMEC Aerosol Jet Printer 300 Series. The OPTOMEC 300 Series is a stand-alone printer featuring an ultrasonic atomizer which allows for 1 to 5 cP ink viscosity in a temperature stabilized water bath. The inks were transferred to the source vial (1 mL) contained in the ultrasonic bath at room temperature (Figure 14a). Applied voltage to the ultrasonic bath creates high frequency vibrations that produce a dense aerosol composed of droplets with diameters 1 – 5 μm. As shown in Figure 14b, the aerosolized beam is focused using a sheath gas, nitrogen or argon, to printed onto the substrate. A summary of the printing parameters used for PEDOT:PSS and CNT inks are given in Table [1].
Figure [14]. Working principle of the aerosol jet where (a) ink is contained in source vial and (b) deposited onto the substrate via deposition head.

Table [1]. The aerosol jet printing parameters employed to print thin continuous films of PEDOT:PSS and CNTs.

<table>
<thead>
<tr>
<th>Aerosol Jet Print Parameters</th>
<th>PEDOT:PSS</th>
<th>Carbon Nanotubes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sheath gas (SCCM)</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Carrier gas (SCCM)</td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>Working Distance (mm)</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Stage Speed (mm/s)</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Stage Temperature (°C)</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Nozzle Size (μm)</td>
<td>3</td>
<td>3</td>
</tr>
</tbody>
</table>
3.3 Kelvin Probe Measurements

Work function measurements were taken with ambient Kelvin Probe (KP Technology). The work function is derived from the formula:

$$\Phi_{TIP} = \Phi_S - V_{CPD}$$

Figure 15 is an energy level schematic of how the Kelvin Probe operates. When two or more materials come into contact, their Fermi levels equilibrate by the flow of electrons from the lower work function to the higher. In Figure 15a, the energy diagram of two conducting materials, where $\Phi_{TIP}$ and $\Phi_S$ are the work functions of the tip and sample and $E_{F,T}$ and $E_{F,S}$ represent their Fermi levels. A potential gradient, or termed contact potential difference (CPD), is formed when an external electrical contact is made between the tip and the sample and $E_{F,T}$ and $E_{F,S}$ equalize. These two surfaces become equally and oppositely charged (Figure 15b). Applying the variable “backing potential” $V_b$ in the external circuit allows biasing of the tip or sample (Figure 15c). At this unique point when $V_b = -V_{CPD}$, a null output signal is obtained. Therefore, if CPD and $\Phi_{TIP}$ are known, $\Phi_S$ of the sample can be determined. Since PEDOT:PSS and CNTs are highly conductive materials, the CPD measured by the Kelvin probe is dominated by the sample $\Phi_S$ and not by its surface potential.
Figure [15]. (a) Energy diagram of two conducting materials, (b) the two surfaces become equally and oppositely charged (c) by applying the backing potential a null output signal is obtained, where $V_b = -V_{CPD}$.

The experimental setup for KP measurements is shown in Figure 16. The area to be measured is placed directly under 2 mm Au tip. The sample is grounded so that any static is removed. Also, the system is enclosed in a Faraday cage. An Au standard is measured prior to sample measurements to ensure that the instrument is calibrated correctly. A sample output for a measurement at a particular point in the sample is shown in Figure 17. Reported work function values are an average of five different points in the sample.
3.4 Surface Profilometer

To measure the thickness of the printed films a surface profilometer (Bruker Dektak XT) was employed. The following parameters were used: scan type: standard
scan; range: 65.5 μm; profile: hills and valleys; stylus type: radius 12.5 μm, stylus force: 10 mg; length: 500 μm, duration: 50 seconds; and resolution: 0.033 μm/pt. A sample profilometer scan of printed CNTs is shown in Figure 18. The first light region (0 – 140 μm) is for the glass only. The next region, shaded in green, is the glass with printed CNTs, while the next light region represents the glass, with Ni and printed CNTs. The thickness of the printed CNT is measured from the scan region shaded in green, which represents the average step height of printed CNT with the glass substrate as reference. Five scans are taken for each sample and averaging is done for the reported thickness.

Figure [18]. Profilometer scan of CNTs on a nickel electrode. The red vertical line is the reference point on glass and the green shaded area is the region where the average height of printed CNTs is calculated from.
3.5 Test Device Fabrication

To determine if modifying an electrode would consequently affect the properties of a completed device, Schottky photodetectors were fabricated utilizing PEDOT:PSS – and CNT – modified electrodes. A schematic showing the deposition of various layers to fabricate a device with the printed PEDOT:PSS is shown in Figure 19a. In Figure 19b, the device architecture showing various layers of a completed device are shown.

![Figure 19](image.png)

**Figure 19.** (a) A schematic showing the deposition of various layers to fabricate a device with the printed PEDOT:PSS is and (b) the device architecture showing various layers.

The active layer of the photodetector consists of poly(3-hexylthiophene) (Sigma-Aldrich) and C61- butyric methyl ester (Sigma Aldrich). A solution of 15 mg of each and 2mL o-dichlorobenzene (DCB) (Sigma-Aldrich) was prepared to achieve a 1:1 ratio by weight of P3HT:PCBM. The solution is stirred in a water bath at 40 °C for 24 hours
and the temperature is brought down to room temperature before use. This solution will be referred to as P3HT:PCBM throughout this thesis.

The P3HT:PCBM solution is deposited on the modified electrodes via airbrushing. The airbrush is shown in Figure 20. The solution was loaded into the cup of the gun via pipette (1 mL). The trigger and adjuster are used simultaneously to eject the material out of the nozzle over the 4 active areas depicted in Figure 20. The final thickness of the active area was ~1.5 μm. Aluminum was electron beam evaporated perpendicular to the bottom electrodes reaching a thickness of 30 nm to complete four PDs on one substrate (Fig. 19).

![Image of airbrush](image)

**Figure [20].** Airbrush utilized to deposit P3HT:PCBM solution onto the modified metal electrodes.

The completed photodetectors are tested inside an enclosure purged with N₂. The excitation source, a 1070 nm IR LED, is positioned approximately 2 cm above the top electrode of the photodetector under test. The LED is pulsed at 0.05 Hz, 50% duty cycle.
Chapter 4

Results and Discussion

4.1 Exploring Control of Film Thickness by Inkjet Printing

4.1.2 Optimization of the Inkjet Printing Parameters

Control over droplet ejection and formation is very important in printing. By optimizing the inkjet parameters and ink formulation, good morphology of films may be realized. We adopt an incremental optimization procedure previously demonstrated by Denneulin et al. for the inkjet printing of carbon nanotubes in conductive suspensions.74

For the succeeding incremental optimization, the frequency was set a 23 kHz, the cartridge height remained 1.00 mm above the substrate, and the cartridge temperature remained at room temperature. The frequency, which is the droplets ejected per second, allows for better control of the droplet trajectory. For example, a lower frequency results to overlapping of droplets causing them to splatter outside the printed pattern.

For the incremental optimization, a common parameter to start with is the firing voltage, which is the minimum bias applied to eject a droplet with a velocity of 7 - 9 m/s. That is the accepted velocity range for inkjet printed materials and is also recognized in the FUJIFILM Dimatix Series 2800 user manual. We find that the optimal firing voltage is 23 ± 1 V for the EG-PEDOT:PSS. Higher voltages exceeded the recommended velocity resulting in splattered lines while lower voltages did not eject the droplets.

Drop spacing controls the spacing between each posited droplet, allowing the ink to flow into one another forming a uniform line or area. A spacing of 25 ± 1μm was found to leave clean, uniform lines on the substrate (Figure 21a). A wide drop spacing
resulted in individual droplets (Figure 21b). A scalloped topology (Figure 21c) was observed with a drop spacing intermediate between those in Figures 21a and 21b. Below the 23 ± 1 µm drop spacing leads to discrete bulging, alternating with regions of a uniform narrow lines as shown in Figure 21d. The droplets are too close to the existing uniform bead forcing an outflow of fluid, which form the bulging.

**Figure [21]**. Inkjet printed line formations containing (a) ideal, (b) individual, (c) scalloped and (d) bulging.

For the platen temperature, the first layer of the EG-PEDOT:PSS ink was printed at room temperature and dried for 40 min under ambient conditions. Allowing one layer to dry provides a seed therefore reinforcing the next layer to stay within the printed pattern. Subsequent layers are printed at a platen temperature of 60°C with a 60 second interlayer delay. This allows for a more rapid evaporation of the ink and an optimal morphology.
Table [2]. Incremental optimization of the EG-PEDOT:PSS inkjet printing parameters.

<table>
<thead>
<tr>
<th>Trial</th>
<th>Voltage [V]</th>
<th>Drop Spacing [μm]</th>
<th>Platen Temp [°C]</th>
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<tbody>
<tr>
<td>1</td>
<td>24</td>
<td>20</td>
<td>23</td>
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<tr>
<td></td>
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<td>3</td>
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<td>50</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>Final Set</td>
<td>23 ± 1</td>
<td>25 ± 1</td>
<td>23, 60</td>
</tr>
</tbody>
</table>

A summary of the results for this incremental optimization of inkjet printing parameters for EG-PEDOT:PSS are presented in Table 2. The morphology of the printed EG-PEDOT:PSS and pure PEDOT:PSS are discussed in the next section.

4.1.2 Morphology of Printed Films

Sound morphology of printed films used in electronic devices is probably one of the most important features to control in order to obtain optimal device performance and avoid shorting. The coffee ring effect is a well-studied and understood phenomenon that occurs when a substrate does not absorb the solvent. This phenomenon is commonly observed in inkjet printing. Evaporation of the solvent at the edges around the perimeter of the printed line causes a diffusive migration of the solute towards the edges. This
results in the printed lines having a significant concentration of solute around the perimeter and few material in the center post evaporation of the solvent.

![Diagram of substrate drying with evaporation of solvent, Marangoni flow, and convective flow.](image)

**Figure** [22]. Coffee-ring effect.

The morphology in Figure 22 is due to the competing effect of the convective and inward Marangoni flows. There is no known way to solve the coffee ring effect, however there are ways to reduce it.

Previously it has been shown that the addition of a co-solvents, such as dimethyl sulfoxide (DMSO) and ethylene glycol (EG), improves the morphology of the film because they act as plasticizers, pushing out the insulating PSS units and organizing the PEDOT units.\(^{75}\) According to Wei *et al.* PEDOT:PSS with the addition of EG allows the PSS chains to relax and the PEDOT units to pack together to form a layered structure with higher order. EG was also shown to improve crystal ordering of the PEDOT:PSS when cast into thin films.\(^{42}\)

To test the effect of the addition of EG to PEDOT:PSS ink, on the printed lines are compared. Figure 23 displays a surface profile measurement of the cross section of one printed line of PEDOT:PSS (a) and EG-PEDOT:PSS (b).
Figure [23]. Profilometer measurements of cross section of one line of (a) PEDOT:PSS and (b) EG-PEDOT:PSS.

Clearly, PEDOT:PSS without any additive shows a distinct coffee-ring effect with a crater-like shape. The edges of the line are higher by about 20 nm then the middle of the line. In the case of the EG treated PEDOT:PSS line, by contrast, a hump rather than a crater-like shape is observed (Figure 23b). This result may be due to a decrease of the evaporation rate caused by EG, which as a high boiling point (197 °C). Such a reduction in of the evaporation rate would be expected to decrease the net flow rate in the droplet. The addition of EG eliminated the coffee-ring effect.

Expanding the PEDOT:PSS and EG-PEDOT:PSS inks into a printed film had some interesting effects. Figure 24 are fiducial camera images of the printed films using PEDOT:PSS and EG-PEDOT:PSS. Note that a maximum of four nozzles was used to print thin films to obtain both a reasonable morphology and better control over print placement.
A striated morphology with various regions of agglomerations exists with one print layer of PEDOT:PSS (Figure 24a). The PEDOT:PSS ink flows outside of the print pattern indicated by the red vertical line shown in Figure 24b. Ink flowing outside the desired pattern could result in shorting. The addition of EG helps stabilize the ink leading to an improved morphology as shown in Figure 24c, which is one print pass of EG-PEDOT:PSS. Also, EG keeps the ink within the print pattern indicated by the horizontal and vertical red lines (Fig. 24d). This can be explained by understanding the role of EG when used as a solvent additive. PEDOT can be found within a matrix of anionic PSS. During the polymerization process, the two polymers exhibit strong ionic interactions and coordinate to one another. The role of EG may involve reorganizing the matrix by coordinating with anionic PSS allowing the PEDOT units to stack, thus creating an enhanced morphology.
Figure [24]. Fiducial camera images of one print layer of PEDOT:PSS (a) without EG and (c) with EG. Edge of printed pattern 1 layer of PEDOT:PSS (b) without EG and (d) with EG.

Images in Figures 24b and 24d shows comparison of morphology for several print passes. The film is allowed to dry between print passes. From Figure 24d, we see that even with several print passes, the EG-PEDOT:PSS film has maintained its uniform morphology, allowing the thickness to be increased with subsequent print passes. The difference in morphology of the two films can also be seen from the surface profilometer scans shown in Figures 25a and 25b for PEDOT:PSS and EG-PEDOT:PSS, respectively.
Figure [25]. Surface profilometer scans of (a) PEDOT:PSS and (b) EG-PEDOT:PSS films.

Overall the defects in the pure PEDOT:PSS films exceed those of the EG-PEDOT:PSS films. The addition of EG helps to stabilize the morphology of the inkjet printed films and allows for various thicknesses to be achieved.

4.1.3 Work Function of EG-PEDOT:PSS-modified Electrodes

Figure 26 displays the work function of the nickel with various thickness of inkjet printed PEDOT:PSS. The dashed red line is the bulk work function of PEDOT:PSS, ~ 5.00 eV, which agrees with the literature value. For the thinnest film, corresponding to one print pass, the thickness is 200 nm, and is already giving a work function value close to the bulk value. The average droplet volume for the inkjet printer is about 10 p. This may be too large to provide finer control of the film thickness, and thus work function modification was not achieved by inkjet printing of PEDOT:PSS.
**Figure [26].** Work function dependence on thickness of printed EG-PEDOT:PSS films.  

The red dashed line indicates bulk work function of PEDOT:PSS ~ 5.00 eV.

There are several factors that can affect measured work function values. Adsorbents can alter the work function of the thin films because of the change in composition of the surface. PEDOT:PSS is very sensitive to adsorbents and contaminants found in ambient conditions. Also, the PSS/PEDOT ratio at the film surface was previously found to be a determinative factor for the work function of as-prepared films. A thin PSS-rich layer (3.5 nm in thickness) always appears at the surface of the PEDOT:PSS due to vertical separation during film formation or due to thermally annealing the two units may phase separate resulting in various work function values.
4.2 Work Function Modification via Aerosol Jet Printing

4.2.1 PEDOT:PSS

Aerosol jet printing allows for better control of film thickness than inkjet printing. Using the settings presented in Section 3.2.2, we achieved 25 nm increments in thickness per print pass of PEDOT:PSS. The work function of the oxidized Ni electrode without any coating was measured as $5.37 \pm 0.01$ eV. This value is consistent with the oxygen-plasma treated of Ni, reported to have a work function value in the between 5.0 – 5.6 eV.\textsuperscript{79} When the electrode was coated with 25 nm PEDOT:PSS, the work function dropped to $5.31 \pm 0.01$ eV. The work function continued to decrease to $5.27 \pm 0.01$ eV and $5.14 \pm 0.01$ eV when the PEDOT:PSS coating reached 50 nm and 75 nm thicknesses, respectively. A summary of the work function and thickness correlation is shown in Table 3. When modified with PEDOT:PSS, the work function decreases with increasing printed film thickness. This trend can be explained by the higher work function of PEDOT:PSS as compared to oxidized Ni. We found that for a 500 nm thick PEDOT:PSS film, the work function is 4.9 to 5.0 eV. The results suggest that the work function of oxidized Ni can be tuned to vary from its work function value to that of bulk PEDOT:PSS if the thickness of the printed film can be controlled.
Table [3]. Work function and thickness measurements of aerosol jet printed PEODT:PSS.

<table>
<thead>
<tr>
<th>Thickness (± 10 nm)</th>
<th>Work Function (± 0.01 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.37</td>
</tr>
<tr>
<td>25</td>
<td>5.31</td>
</tr>
<tr>
<td>50</td>
<td>5.27</td>
</tr>
<tr>
<td>75</td>
<td>5.14</td>
</tr>
</tbody>
</table>

4.2.2 Carbon Nanotubes

This section discusses our initial investigations to explore thickness control of CNT films via aerosol jet printing, along with corresponding work function modification due to CNT overcoatings. The CNT film bonds to the nickel electrode because of the hybridization of the side contact which consists of the $p_z$ orbitals of carbon (normal to the surface of CNTs) and the few unfilled d-orbitals of nickel. Fiducial camera images of the edges and printed area of CNT are shown in Figures 27a and 27b, respectively.
Figure [27]. Fiducial camera images of aerosol jet printed CNT showing minimal defects by its (a) edges and (b) over an area.

In Figure 28, the dependence of work function on the thickness of printed CNTs, (a) Brewer and (b) Nink 1100, are shown. The dashed lines represent the bulk work function of Brewer and Nink 1100 CNTs, which are 5.33 eV at 160 nm and 5.56 eV at 180 nm, respectively. Despite the large error bars, the general trend showing an increasing work function to approach the bulk value of CNT can be concluded from the graphs. These initial investigations suggest the potential of aerosol jet printing for tuning CNT film thickness. However, further investigations are necessary to improve thickness control, and consequently, the degree of work function modification.
It is well known that the work function of metal oxides strongly depends on its surface chemistry, crystal orientation among other factors so it is subject to change.\textsuperscript{69} It is well documented that the NiO surface adsorbs surface contaminants such as nitric oxide and hydroxyl species within minutes of air exposure and results in a reduction of work function. Any contaminates can effect the work function of the metal electrodes dramatically. Ratcliff \textit{et al} concluded that NiO post oxygen plasma deposition increased the work function of NiO from 4.7 to 5.3 eV. However, \textit{Ratcliff et al}'s previous study concluded that the work function of NiO decreased post O\textsubscript{2} treatment even when it was stored in a nitrogen environment.\textsuperscript{81} Therefore, the work function of NiO can vary supporting the error bars of the pure metal. The CNT films are exposed to ambient conditions, therefore contaminants are may be adsorbed onto the surface of the thin films. It is also a possible that water is trapped between each layer.

\textbf{Figure [28].} Work function dependence on thickness of the aerosol jet printed (a) Brewer and (b) Nink 1100. The red dashed line indicates the bulk work function of the CNT ink.
4.3 Test Devices Utilizing PEDOT:PSS- and CNT-modified Electrodes

To determine if modifying an electrode would consequently affect the properties of a completed device, Schottky photodetectors were fabricated utilizing PEDOT:PSS – and CNT – modified electrodes. The organic active layer of the photodetector consists of P3HT and PCBM. P3HT (Figure 29a) is a polythiophene derivative which is a semiconductive polymer. PCBM (Figure 29b) is a fullerene derivative with high hole mobility. Together P3HT:PCBM is a very popular blend used in a variety of organic electronic devices because of its easy preparation and processability.

![Photoactive materials](image)

**Figure [29].** Photoactive materials (a) P3HT and (b) PCBM.

In a Schottky photodetector, internal photoemission is responsible for the optical excitement of electrons of the metal to overcome the Schottky barrier.\textsuperscript{82} The electrons are then transported in the conduction band of the semiconductor producing current. Photoresponse cannot stem from exciton generation in the P3HT:PCBM active layer because P3HT is transparent at 1070 nm, which is the excitation energy used for the fabricated IR photodetector. The excitation source does not have enough energy to
promote an electron from the HOMO level of P3HT, therefore the photoresponse must arise from internal photoemission at the Al/polymer Schottky junction, which is the mechanism behind Schottky photodetectors. The figure below shows a comparison of P3HT band gap and IR excitation energy (Fig. 30).

**Figure [30].** Band gap of P3HT along with its respective HOMO-LUMO levels. The IR LED has an excitation energy of 1.16 eV.

To test differences in photoresponse of electrodes with different PEDOT:PSS thicknesses, a 7.5 mW IR LED for excitation at 1070 nm was used. Figure 31 shows the short circuit photocurrent during pulsed IR photoexcitation. The short circuit current is increased significantly with 50 nm and 75 nm PEDOT:PSS overcoatings with the highest $I_{sc}$ observed at 75 nm thickness of PEDOT:PSS.
Figure [31]. Photoresponse of the Schottky photodetectors using PEDOT:PSS-modified electrodes. Test devices were pulsed under an IR LED excitation source (1070 nm).

A comparison of the photoresponse of devices with CNT-modified electrodes was also done. The fabrication of the device differed from that of the PEDOT:PSS-PDs because there was a significant shorting problem. Spin casting of P3HT:PCBM at 50 mg/mL and 100 mg/mL both resulted to shorted devices. The shorting could be due to the rough morphology of the CNT film. With the rough morphology of printed CNT, spin coating of P3HT:PCBM is not ideal because spin coating causes most of deposited solution to go sideways, potentially increasing the probability of having voids or defects that do not have P3HT:PCBM coating. Upon e-beam evaporation of the Al top electrode, these voids could be filled with Al, which then causes the device to short. The problem of shorting with the use of CNT has been reported previously in the literature, where the reported investigation made use of PEDOT:PSS deposited on the CNTs to planarize the CNT network and avoids shorts.83

With airbrushing technique, we were able to significantly reduce the occurrence of electrical shorting. Airbrushing polymer layers has been previously used in device fabrication, and it has been shown that spray-on thin films allows for a change in film porosity and density.84 As compared to sideways solution flow in spin casting, spray
coating provides an increased probability for voids and defects to be covered with P3HT:PCBM by forcing the P3HT:PCBM to coalesce within rough regions in the printed CNTs.

Figure 32a shows the completed device with P3HT:PCBM spray coated multiple times, resulting to ~ 1.5 μm thickness. Figure 32b shows the device architecture.

**Figure [32]**. (a) Completed device and (b) device architecture for photodetectors utilizing the CNT-modified electrodes.

For this device the work function values of the CNT-modified electrodes are summarized in Table 4. The instrument uncertainty is 0.01 eV. Notice that the variation in the work function with CNT thickness is very small. Further investigations are necessary to follow up this initial work and arrive at more conclusive results regarding thickness dependence of the work function of CNT-modified electrodes.
Table [4]. Work function and thickness variations of the CNT – modified electrodes used to fabricate Schottky photodetectors.

<table>
<thead>
<tr>
<th>Thickness (± 10 nm)</th>
<th>Work Function (± 0.01 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.28</td>
</tr>
<tr>
<td>10</td>
<td>5.31</td>
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<tr>
<td>50</td>
<td>5.32</td>
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<tr>
<td>90</td>
<td>5.34</td>
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Despite the further need to study CNT thickness dependence of work function modification, we demonstrate, however, that CNT addition improves IR photodetection. In Figure 33, we show the change in IR photodetection capability of the devices with varying thicknesses of printed CNTs. A pulsed 1070 nm IR LED was used to generate the short circuit currents, measured using a Keithley 2400 sourcemeter. Comparing the bare oxidized Ni (PD - 0 nm) with the other three electrodes (PD – 10 nm, PD – 50 nm, PD – 90 nm), it is evident that the other three with CNT coatings improved photodetection. The short circuit current exhibited an increasing trend with increasing thickness of the printed CNT for the 0 nm, 10 nm, and 50 nm CNT films. However, for the 90 nm CNT thickness, the short circuit current dropped. The potential cause for this deviation from the trend can be explained by the dark I-V curves and leakage currents shown in Figure 34.
Figure [33]. Photoresponse of the Schottky photodetectors using CNT-modified electrodes. Test devices were pulsed under an IR LED excitation source (1070 nm).

Figure [34]. (a) Dark I-V curve and (b) leakage current for the CNT-modified Schottky diodes.
The dark I-V curves shown in Figure 34a qualitatively show that over the bias range -1 V to +1 V, the photoresponse of PD – 90 nm is significantly greater than the other three with no CNT or thinner CNT overcoatings. Examination of the leakage current also shows that it is greatest for PD – 90 nm. Both forward and reverse bias display a higher current flow. This implies that current flow is improved in both directions, indicating the presence of a partial electrical short (parasitic resistance), which is not desirable in diodes. The overall effect is a weaker photodetection capability of PD – 90 nm. However, device performance is still better for PD -90 nm, which has a 90 nm overcoating than for PD – 0 nm, which utilized an electrode with bare oxidized Ni.
Summary and Conclusions

Organic electronics can benefit from electrodes with tunable work functions. By depositing transparent, conducting materials, PEDOT:PSS and CNTs, on oxidized Ni electrode, we showed that the effective work function of the electrode can be modified. We explored the capability of two direct write techniques, inkjet and aerosol jet printing, to control the thickness of the printed films. The purpose was to test our hypothesis that the degree of work function modification should depend on the thickness of the printed PEDOT:PSS or CNT film.

We find that with inkjet printing, a single print pass produces a layer thickness that gives a work function value that is already the bulk value for the printed conducting material. Although, optimization of the inkjet printing parameters and modification of the ink formulation resulted to better morphology of printed PEDOT:PSS, they did not result to a capability to tune film thickness that would display incremental changes in work function.

Aerosol jet printing proved to be an attractive method for fine tuning printed layer thickness and is, in general, a promising tool for surface property modification. We demonstrated in this work that incremental changes in thickness of PEDOT:PSS layers can be achieved via aerosol jet printing. The different thicknesses resulted to varying degrees of work function modification, ranging from 5.37 eV for the bare oxidized electrode down to 5.14 eV for a 75 nm coating of PEDOT:PSS. Note that the work function of PEDOT:PSS is expected to be around 5.0 to 5.1 eV. With CNTs, we were able to aerosol jet print layers thin enough to not yet exhibit bulk work function values.
However, further work is needed to achieve the same level of control as was exhibited for the PEDOT:PSS.

To demonstrate the effect on device performance, Schottky photodetectors were fabricated utilizing the modified electrodes. The active layer used in the photodetectors is P3HT:PCBM. We find that IR photodetection is improved for both PEDOT:PSS– and CNT– modified electrodes. The work demonstrates that exploration of various metal-material coating combinations, along with thickness control of the coating, can serve as a route to optimizing device performance.
References


