INTERFACE STUDY OF SPIRO-OMETAD ON PASSIVATED P-, N-, AND N⁺-Si(111) FOR USE IN TANDEM PEROVSKITE/SILICON SOLAR CELL DEVICES

by

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ABSTRACT

LI CHAN NGUYEN. Interface Study of Spiro-OMeTAD on passivated n-, n⁺-, p-Si(111) for use in tandem perovskite/silicon solar cell devices. (Under the direction of DR. MICHAEL GEORGE WALTER)

The organic semiconductor 2,2',7,7'-tetrakis-(N,N-di-p-

methoxyphenylamine)9,9'-spirobifluorene (Spiro-OMeTAD) contact properties are studied on p-, n-, and n^+ -type silicon. Spiro-OMeTAD is a solid state hole conductor that has notably been used in perovskite solar cells achieving 20.1% efficiency.²⁰ In this work spiro-OMeTAD doped with 20 mol% bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI) is investigated as a spin and drop cast film on p, n, and n^+ -Si(111) surfaces terminated with H and CH₃. An ohmic like tunnel junction has been observed on CH₃terminated p-, n-, and n^+ -Si(111) and also H-terminated p and n^+ -Si(111). Rectifying contacts have been found on n type H-terminated silicon. Low contact resistances have been found when the doped hole transport material contacts n^+ -Si(CH₃) which has been found to be as low as $0.622 \ \Omega \cdot \text{cm}^2 \pm 0.439 \ \Omega \cdot \text{cm}^2$. Other types of methyl-terminated silicon have been found to have contact resistances of 22.92 k Ω ·cm² -54.34 k Ω ·cm² for n-Si and 0.51 k Ω ·cm² - 3.12 k Ω ·cm² on p-Si (111) surfaces. H-terminated data for n⁺-Si(111) has been found to be as low as $1.34 \pm 0.54 \text{ k}\Omega \cdot \text{cm}^2$ and $1.3 \pm 0.28 \text{ k}\Omega \cdot \text{cm}^2$ for p-Si(111). A photo-responsive CH₃NH₃PbI_xCl_{3-x} perovskite solar cell was fabricated utilizing n⁺-Si(CH₃) as an anode and a 20 mol% Li-TFSI doped spiro-OMeTAD which resulted in <1% photoconversion efficiency. The 'pre-doped' spiro(TFSI)₂ dicationic salt was used as an alternative to the uncontrollable air doping method from a spin cast film resulting in a contact resistance of 12 - 201 $\Omega \cdot cm^2$.

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CHAPTER 1: INTRODUCTION

1.1 Overcoming Limitations to Photovoltaic Adoption

Earth's climate is changing, with most of the observed warming attributed to human made greenhouse gas emissions. The Intergovernmental Panel and Climate Change has warned in 2014 that continued use of fossil fuels must be reduced drastically and eliminated by 2100 to prevent "severe, pervasive and irreversible" damage.³⁸ Solar power is an ideal source because the amount of energy that strikes the earth in just one hour exceeds the yearly needs of the entire human population.³³ This invaluable resource can be harvested using photovoltaic technology which converts solar radiation into electricity by use of solar cells as a renewable source of electricity. Photovoltaic devices harvest photons from sunlight and convert them to electricity using materials that generate electrical current under illumination. Currently the most widely used material in solar cell devices is silicon. Silicon solar cells have been heavily investigated since Bell Laboratories publically demonstrated the first device in 1954.

Improving efficiencies of single junction silicon devices have proven difficult as performance has leveled off at 25% photoconversion efficiency.²¹ A frequently mentioned barrier to solar energy adoption is their high cost per power output as compared to conventional fossil fuels with established systems in place .²² It has been suggested that improvement of existing silicon solar technology is advantageous due to

economies of scale allowing them to invest in new technology without incurring large risks.²⁰

Devices employing a single absorbing material, such as silicon, are limited in light harvesting efficiency due to inherent band gap limitations as demonstrated by the Shockley-Queisser limit.¹² It has been shown that energy in excess of the band gap is lost through recombination pathways as the excited state relaxes to the conduction band edge and energy below this gap is unable to generate charge carriers and does not contribute to photocurrent.¹²



Figure 1.1: Graph detailing the maximum efficiency obtainable by a single light absorbing material at various band gap energies.¹²

Devices using a silicon material (1.1eV band gap) results in a maximum of 29% light harvesting efficiency as shown in figure 1.1.¹² This limit presents a best case scenario for a silicon solar cell, in most cases approaching it becomes impractical due to lack of techniques for advanced material purification and surface treatments to optimize efficiency.

Enhancement of silicon or CIGS with a higher band gap top cell by using a tunnel junction to electrically connect them has been proposed as a route to achieving higher efficiencies.^{20, 23} A combined tandem device would require an ohmic, low absorption recombination layer in order to maximize the combined photovoltage. Currently there are few reports in the literature studying organic semiconductor contacts to silicon, although there have been studies forming hetero-junction solar cell devices.^{37,39} Exploration of hole transport materials (HTM) as recombination layers may provide a route to monolithic thin film silicon tandem devices.²⁰

1.2 Silicon P-N Junction

Silicon is the eighth most common element in the universe by mass and the lowest acceptable purity for electronic grade silicon is 99.9999999%.³² This pure crystal of silicon can be doped by diffusing an impurity into the lattice to disrupt covalent bonds. Phosphorus is used and has one extra valence electron available for bonding compared to silicon, which is weakly bound (0.045 eV) and is delocalized at ambient temperatures.³¹ Doping with atoms that increase delocalized electrons in silicon are referred to as n-type. Conversely silicon can also be doped with boron which has one less valence electron resulting in vacant sites in the lattice reducing covalent bonds in the structure to create an excess of vacant sites referred to as holes resulting in p-type silicon.³¹ At operational temperatures this positively charged site can shift within the material by attracting electrons to it allowing the positively charged hole to circulate within the lattice.³¹

When these two types of doped silicon come together a p-n junction is formed. The majority charge carriers of n-Si are electrons and holes for p-Si which differ significantly in energy. To minimize the energy difference when connected, majority charge carriers from one type diffuse into the other due to random thermal motion.³¹ This creates a built-in electric field at the junction due to a lack of majority charge carriers in each material. A depletion region is created where fixed charges come to rest in a minimal energy state which equilibrates their Fermi levels.³⁴ This action results in the band edges bending to form a barrier height and a width of depleted charges as shown in figure 1.2.1. In this equilibrium the barrier created directs the flow of electrons from p-Si to n⁺-Si as it would require energy to push electrons back up the barrier.



Figure 1.2.1: Formation of a p-n silicon junction showing barrier height $(q\Phi_b)$ and depletion width (w).

Study of junctions formed between the conductive polymer poly(3,4ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and certain Si(111) surfaces have reported ohmic, low resistance contacts with small barrier widths.¹ Ohmic contact has been demonstrated between PEDOT:PSS and n⁺-Si(111) H- or CH₃terminated. This polymer may not be the best choice due to its water solubility and absorption at longer wavelengths, studies with other p-type organic conductors are not yet known to be done.¹ Spiro-OMeTAD is a hole conductor which absorbs in the UV region at 385nm and when oxidized absorbs weakly around 500 nm which is negligible at applicable thicknesses.¹³ It is a solid state HTM for dye sensitized solar cells including but not limited to perovskite solar cells which have achieved upwards of 20% light conversion efficiency.²¹ With an ideal band gap and low cost material, perovskites are attractive components for use in inexpensive tandem systems if a suitable tunnel junction can be found to a silicon device.^{20, 23}

1.3 Silicon Contact Implications

Interfaces established between silicon and organic semiconductors could be the key to monolithic tandem devices. If a low resistance electrical contact can be made with an organic conductor, a thin film device could potentially be added in a stacked cell configuration. Study of the electrical junction behavior is accomplished by examining current-voltage (*J-V*) characteristics to determine contact resistance between the organic materials cast on p-, n-, and n⁺-Si (H, CH₃ terminated) surfaces. In previous studies PEDOT:PSS has been reported to make low resistance, ohmic contacts to p- and n⁺-type Si(111) while rectifying behavior was found with n-type silicon.¹ Due to an increase in dopant density the junction behavior between n⁺-Si(111) and PEDOT:PSS transitions from rectifying to ohmic-like and acts as a tunnel junction on H- and CH₃-terminated silicon surfaces.¹

Ohmic contact between PEDOT:PSS suggests the possibility that n⁺-Si(111), Hor CH₃-terminated, could potentially produce similar results with other p-type organic hole conductors. Spiro-OMeTAD is the HTM used for perovskite solar cells with a HOMO level at 5.22 eV achieving over 19% light conversion efficiency.⁶ Within a small timeframe, research in perovskite solar cells have increased in popularity due to the low cost of lead halides and small molecule organic salts used. Perovskites are air and moisture sensitive, however their extraordinary photophysical properties combined with a low cost make them an attractive solar energy conversion material.

If the hole conductor Spiro-OMeTAD can form an ohmic contact to silicon, a tandem device may can be made using the junction as a series connection to a thin film top perovskite cell as shown in figure 1.3.



Figure 1.3: Scheme of tandem solar device in which case the top cell could be any thin film cell using spiro-OMeTAD as a hole transporter.

Finding a material with a complementary absorption shifted toward lower wavelengths can minimize spectrum losses from silicon cells to maintain a high combined photovoltage. Ideally the top cell will be targeted to absorb high-energy photons that are in excess of the silicon 1.1 eV band gap and allow lower energy photons to pass through to the bottom silicon device.

1.4 Spiro-OMeTAD

Spiro-OMeTAD is a HTM that was originally designed to replace liquid electrolytes in dye sensitized solar cells which are disadvantaged by solvent instability.⁹ The nearly transparent solid state hole conductor is a solution processable replacement which allows for greater morphological control and reproducibility by spin coating deposition and melt infiltration techniques.⁵ The organic semiconductor shown in figure 1.4 was designed to reduce intermolecular interactions by arranging biphenyl cores into a perpendicular arrangement resulting in a lower glass transition temperature of $125^{\circ}C$ (T_g) at which it enters an amorphous glassy state.⁵



Figure 1.4: 2,2',7,7'-tetrakis-(N,N-di-*p*-methoxyphenylamine)9,9'-spirobifluorene (Spiro-OMeTAD).

An amorphous state can improve reproducibility by decreasing bifringence and scattering from inconsistent variations in crystal structure. Fusion of biphenyl cores with a spiro center inhibits crystallization at elevated temperatures allowing the film to conform to the morphology.⁹ The stability of this amorphous state was defined by three parameters from Naito and Miura which are symmetric globular structure, large molecular weight (1225.24 g mol⁻¹), and small intermolecular cohesion due to sterics.^{9,10,11} The compound enters this state as it is heated above 125 °C making the solid crystal fluid enough to conform to adjacent layers and maximize the contact between them.



Figure 1.5.1: Structure of lithium bis(trifluorosulfonylimide).

Lithium bis(trifluoromethylsulfonyl)-imide (Li-TFSI) is used as a p-type dopant and enhances the conductivity in sprio-OMeTAD by increasing the density of holes in the valance band. Doping effectively lowers the Fermi level of the material and changes the conductivity from a low 3×10^{-8} to 3×10^{-5} (S cm⁻¹) by increasing the concentration of Li-TFSI as shown in figure 1.2.^{7,13} The conductivity of the doped material is significantly less than CleviosTM PEDOT:PSS which reports up to 1000 (S cm⁻¹).¹



Figure 1.5.2: Effective Spiro-OMeTAD conductivity with UV-Vis absorption spectra at varying levels of Li-TFSI.⁷

Li-TFSI is necessary for the higher conductance but the increase only occurs when exposed to air and it has been reported that oxygen plays a central role as a codopant.⁷ It is believed that a donor acceptor-complex is created from the low ionization potential of spiro-OMeTAD and high electron affinity of oxygen which produce an oxidized spiro-OMeTAD (Spiro-OMeTAD⁺O₂⁻) which does not occur in the absence of Li-TFSI.^{7.} The addition of Li⁺ is reported to change the equilibrium in equation (1) by utilization of the lithium salt in equation (2).⁷

(1)⁷ Spiro-OMeTAD + $O_2 \iff$ Spiro-OMeTAD⁺ O_2^{-}

 $(2)^7$ Spiro-OMeTAD⁺ O₂⁻ + Li-TFSI \longrightarrow Spiro-OMeTAD⁺LiTFSI⁻ + Li_xO_y

 Li_xO_y represents lithium oxide complexes formed which have been found to be Li_2O or Li_2O_2 from ATR-FTIR and ⁷Li NMR data.⁷ Films of spiro-OMeTAD must be doped in air for them to form the singly oxidized spiro-OMeTAD. Due to this method some films have displayed rectifying and ohmic-like behavior, which can be attributed to incomplete doping. This method of doping also introduces a source of uncertainty in which results can vary because air is composed of multiple gasses. Some films are reported in a range to reflect the deviation in results found.

1.6 Spiro(TFSI)₂ 'Pre-doped'

The need for air as a co-dopant in the system has been reported requiring that exposure to air and light for 9-16 h is necessary to form an oxidized and thus conducting spiro-OMeTAD.¹⁵ Air doping introduces an uncontrollable method of oxidation which is shown to increase the variability in perovskite solar cell device efficiencies. Devices nonfunctioning.¹⁵



Figure 1.6.1: Histogram of devices made with conventional air doping as compared to a dicationic salt demonstrating variations in efficiencies from different methods of spiro-OMeTAD oxidation.¹⁵

A self-doped method of doping spiro-OMeTAD has been introduced by researchers who have synthesized a dicationic salt of spiro-OMeTAD by reaction with silver bis(trifluorosulfonylimide). The 'pre-oxidized' spiro(TFSI)₂ is effective because air is not necessary to form a conductive spiro-OMeTAD, only the reaction of the salt to produce a singly oxidized species.¹⁵ This method has been shown to result in higher efficiency devices which are shown in figure 1.6.1 demonstrating reduced variability. It can be expected that the use of spiro(TFSI)₂ may also lower the contact resistance as the conductivities measured reach 10⁻³ (S cm²).¹⁵ In this work Spiro(TFSI)₂ was synthesized according to the literature to compare reproducibility and total contact resistance to traditionally doped lithium salt films. A scheme of spiro(TFSI)₂ synthesis is shown in figure 1.6.2.



Figure 1.6.2: Reaction scheme for the formation of a dicationic spiro-OMeTAD salt with trifluorosulfonylamine counter ions.¹⁵

1.7 Spiro-OMeTAD as a Melt Pressed Contact

Due to the polycrystalline nature of perovskite films, an amorphous state is advantageous as melt coverage will ensure optimal contact for hole transfer from perovskite crystallites to spiro-OMeTAD. Melt-infiltration is a method used to increase the pore filling capacity by heating the film above 280° C to reach a liquid state that can flow through a mesoporous TiO₂ film increasing contact.⁵

The same strategy is applied here by heating the doped semiconductor on a silicon wafer until it becomes a viscous liquid and pressing it together with a perovskite film grown on a compact layer of TiO₂ with a fluorine doped tin oxide contact (FTO) (Pilkington-TEC15). The melted spiro-OMeTAD is expected to spread and conform to the polycrystalline perovskite surface while binding the two half cells as it crystallizes.

Methyl terminated surfaces have been reported to remain stable when annealed in a vacuum up to 720 K.³⁶ Silicon with H-terminated groups have been reported to be quickly oxidized over time resulting in different behavior compared to freshly terminated samples.³⁰ Barrier heights of Si/metal Schottky contacts on H-terminated samples varied over time and have been found to exhibit rectifying behavior when exposed to ambient air for 24 h.³⁰ Barrier heights on CH₃-terminated Si-(111) surfaces were more stable and are reported to have the same barrier heights whether or not they had been prepared freshly or exposed to air for extended amounts of time.³⁰

1.8 Tunnel Junction

Tunnel junctions were first discovered in highly doped germanium p-n junctions by L. Esaki.¹⁶ It was demonstrated that by utilizing high dopant levels, a tunneling effect was noticed in the *J-V* curves where in forward and reverse bias electrons are able to tunnel through the potential barrier width.¹⁶ By using highly doped n⁺-Si(111) and spiro-OMeTAD doped with lithium salts the depletion width is expected to become thinner which reduces the potential energy barrier electrons need to tunnel.¹⁶ During forward bias electrons may tunnel across materials if complementary (occupied/unoccupied) states exist at the same energy in both materials.¹⁶



Figure 1.8.1: Energy level of n^+ -Si and spiro-OMeTAD before and after equilibration of the Fermi level, giving rise to the barrier $q\Phi_b$. The small depletion width (W) allowing for tunneling.¹

Termination of silicon (111) surfaces has been reported to change surface energy by -0.4 eV by inducing a small interfacial dipole.^{24,30} The dipole effect on the surface shifts the energy at the band edges toward the vacuum level.²⁴ The effect on equilibrium would be expected to decrease the barrier width at the depletion region when compared to H-terminated samples increasing the probability of tunneling.^{1,27}

The interfaces studied here are of silicon to organic conducting molecules. The junction behavior is a result of the both materials minimizing energy at the interface resulting in equilibration between the Fermi energy (E_F) levels of two materials in a theory known as band bending.²⁵ The Fermi level energy changes based on the use of chemical dopants which change a materials' electrical properties through ionization by use of impurities. Use of p-type dopants such as Li-TFSI & spiro(TFSI)₂ shifts E_F closer to the valance band of the HTM.¹³ In the case of n-Si, E_F shifts toward the conduction band as n-type dopant levels increase and the bands bend as shown in figure 1.8.1.²⁶

The experimental data showing linear *J-V* curves about the origin gives insight into the barrier created in the junction. In the case of a p-n hetero-junction, the current comes from movement of holes as the spiro-OMeTAD is p-doped and thus the barrier for hole conduction must be smaller than that of electrons.²⁷ Thus the current would be a function of the barrier height, which increases sharply with a greater separation of Fermi levels.²⁷ The effect of tunneling has been demonstrated to strongly depend on the Schottky barrier thickness which is shown to result in increased tunneling current.^{28, 29}

This thesis focuses on studying the contact made between spiro-OMeTAD and p-, n-, and n⁺-Si and how the contact resistances will affect the possibility of using spiro-OMeTAD as a tunnel junction for a tandem perovskite/silicon solar cell device. The properties of the junction formed have been studied as a recombination layer for a tandem device as proposed in the literature.¹⁹ Connected in series, the open circuit voltages of each cell should be additive potentially boosting the efficiency of silicon. By targeting different parts of the solar spectrum, low cost and readily available perovskite precursors can enhance a silicon solar cell if the combined photovoltage outweighs the added series resistance. If sufficiently low electrical contact can be made with a semiconductor material, a thin film device could potentially be added in a stacked configuration. Study of the electrical junction behavior is done by examining current-voltage curves across the semiconductor cast on p-, n-, and n⁺-Si (H, CH₃ terminated) to find the contact resistance between the materials. Currently, the only reported tandem perovskite-silicon solar cell is made by mechanically stacking two separate modules together.¹⁹ A monolithic cell is advantageous over a mechanically stacked cell because it does not require 'transparent' electrodes which absorb low amounts of light, resulting in parasitic losses of efficiency.¹⁹

CHAPTER 2: EXPERIMENTAL

2.1 Silicon Preparation

Single side polished n⁺-Si wafers with 0.005 Ω ·cm (Addison Engineering) were cleaved into approximately 1 cm² pieces and sonicated for 10 min in acetone, Milli-Q water, and methanol with a final rinse of Milli-Q water. The pieces were then dipped in piranha solution heated to 100 °C for 20 min to remove residual organic matter. The cleaned pieces were then rinsed multiple times with Milli-Q water and dried under a stream of N₂. Substrates were then etched with buffered HF (Transene Co.) for 1 min to remove silicon oxides and create an H-terminated silicon surface.

For methyl termination, H-terminated silicon samples were brought into a N_2 filled glovebox for surface chlorination. A saturated solution of PCl₅ (95% Sigma-Aldrich) containing a grain of benzoyl peroxide (Aldrich) as a radical initiator in anhydrous chlorobenzene was used to chlorinate the surface.¹ The solution was heated at 90°C for approximately 1 hr and rinsed with chlorobenene followed by anhydrous tetrahydrofurann (THF) (Aldrich).¹ The Cl-terminated silicon is then placed in a solution of 1.0M CH₃MgBr (Aldrich) in THF and heated to 60°C for 3 hr with agitation by swirling the reaction vessel.¹ Wafers are then rinsed with THF, acetone, milli-Q water, and methanol before drying under N₂.

2.2 Drop Cast Films

The contact between Spiro-OMeTAD and a highly doped n^+ -Si(111) is investigated to ensure that the electrical contact can be established by running a currentvoltage curve (J-V curve). The film is made by drop casting a solution of Spiro-OMeTAD (90 mg/mL) with (Li-TFSI) (8 mg/mL) in anhydrous chlorobenzene stirred overnight and filtered through a 0.45µm pore diameter PTFE filter. The filtered solution is drop cast onto a clean n⁺-Si (H, CH₃) surface in an N₂ glovebox. The film is gently heated in air at 40°C for a minimum of 1 hr and slowly cooled to room temperature before testing with the source meter. The J-V setup is as shown in figure 2.1 where a Keithley 236 source measurement unit contacts the silicon substrate and the spiro-OMeTAD hole conductor. The first contact is established by using a platinum foil attached to an alligator clip that contacts a mercury droplet. A small washer with an area of 0.053 cm² is used to contain the mercury drop and define the working area of the contact to the spiro-OMeTAD. The back of the silicon wafer is mechanically scratched and contacted to a eutectic indium-gallium alloy on a polished copper plate attached to an alligator clip. The current is measured as the potential is scanned from -1V to +1V with a 20 mV step size.



Figure 2.2: A Keithley 236 source measure unit set up to measure the contact with n^+ -Si(111) using mercury as the Spiro-OMeTAD contact and eutectic gallium-indium on a copper plate as a silicon contact.

2.3 Spin Cast Films

A solution of 15% v/v spiro-OMeTAD was dissolved in anhydrous chlorobenzene assuming the density of spiro-OMeTAD to be 1 g/mL.⁷ This solution was mixed with 20 mol% Li-TFSI relative to spiro-OMeTAD from a pre-dissolved solution of 170 mg/mL in acetonitrile in the glovebox. Tert-butyl pyridine was added at 0.33 mol% of spiro-OMeTAD.⁷ Solutions made from this method dissolved well, contained no visible solids, and were left to mix for a minimum of 30 min before filtering through a 0.45µm Whatman filter. A piece of prepared silicon was partially covered with the solution and spun cast using a G3P spin coater at 800 RPM to create a thin film. The coated silicon is removed from the glovebox and heated on a hot plate in air at 70 °C for 30 min and immediately tested.

2.4 Melt Pressed Perovskite Cell Contact

A perovskite solar cell was fabricated using n⁺-Si(CH₃) as the anode connected by a melt pressed spiro-OMeTAD contact. FTO glass is cleaved into approximately 1"x.25" segments and sonicated for 10 min in alconox, Milli-Q, acetone, and isopropanol. After drying with N₂ they are placed into a BIOFORCE Procleaner[™] UV ozone cleaner for 20 min. Scotch[™] tape is used to cover a section of FTO from being coated with TiO₂. A solution of equal parts 40 mM HCl and 15 mM titanium (IV) isopropoxide (97% Aldrich) in isopropanol are mixed prior to spin coating the solution at 2000 rpm for 1 min onto FTO glass.¹⁷ The tape is removed and the film annealed at 100°C for 15 min and sintered at 500°C for 30 min. In the glovebox, a solution of 3:1 methylammomium iodide in 40% wt. anhydrous dimethylformamide (DMF) is stirred overnight and prepared by filtering through a 0.45µm PTFE media. The coated slide is spun at 2000 rpm and annealed at 90°C to prevent thermal decomposition of the perovskite crystals. The perovskite cells are recrystallized by placing them on a hot plate heated to 80 °C, covered with a 1000 mL beaker, and injected with 100 μ L of anhydrous DMF. The cells were observed to revert back to their exhibited color in solution and slowly transitioned to a dark reddish brown color after the solvent slowly left the beaker through the lip. Cells had an observable change in surface morphology and seemed to have an increase in perovskite 'islands' with larger crystallites. The perovskite cell is then placed over a hot silicon wafer with liquid doped spiro-OMeTAD heated to 185-190 °C in which observable melting was seen as shown in figure 2.40. Finally, the completed cell was clamped together with a binder clip and left to cool.



Figure 2.4.1: Tandem cell fabrication at $T > T_g$ (125°C) at an amorphous glassy state where the cells are pressed together and cooled to create a fused cell.

To obtain *J-V* curves detailing the added resistance of a spiro-OMeTAD melt pressed contact, the junction properties of spiro-OMeTAD melted in-between two conductive materials was studied. FTO and CH₃-terminated n^+ -Si(111) were used as the two contacts. A clip as used to hold the two together for a scan without spiro-OMeTAD, the HTM was then melted in-between to demonstrate a change in resistance. Instead of mercury, an alligator clip is clamped directly onto the FTO glass with the n^+ -Si wafer contacted to a copper plate using eutectic indium gallium alloy and wired to the source measurement unit.



Figure 2.4.2: Junction resistance test by testing a device with spiro-OMeTAD melted inbetween FTO and n^+ -Si(CH₃) and a device made from a pressed contact without spiro-OMeTAD.

2.5 Synthesis of Spiro(TFSI)₂

A round bottom flask, 2 dram vial with a rice sized stir bar are heated in an 80 °C oven for a minimum of 2 hr. The round bottom is then filled with anhydrous dichloromethane (\geq 99.8%) and degassed by 'freeze-pump-thaw' method four times before bringing the solvent into the glovebox. A molar ratio of 1:2.2 of spiro-OMeTAD to silver bis(trifluorosulfonylimide) was weighed and placed into the vial with the stir bar. 4 mL of degassed dichloromethane was added to the 2 dram vial containing the reagents and stirred at ambient temperature in a glovebox with < 0.5 ppm O₂/H₂O overnight. The crude mixture is mixed with excess DCM and filtered through a fritted funnel to obtain a dark maroon red solution. The solvent is evaporated using a rotary evaporator and the solid is dissolved in a minimal amount of DCM, when noticeably dissolved diethylether is added until the supernatant contains little to no color. The solid is filtered through a fritted funnel and the process is repeated for a total of four times to obtain a dark, hunter green solid.

2.6 Spiro(TFSI)₂ Doped Spiro-OMeTAD

A solution of spiro(TFSI)₂ to spiro-OMeTAD was made in the glovebox using 9.374 mg spiro(TFSI)₂ and 39.109 mg spiro-OMeTAD amount dissolved in 250 μ L chlorobenzene. The solution is stirred for 3 h and gently heated at 35 °C, when 5 μ L of 4-tert-butylpyridine is added. The solution is then spin cast at 800 RPM to create a uniform thin film with the appearance of a spray-coated substrate. A drop cast film was also made and heated at 50 °C for 1 hr before testing. The drop cast film had two distinct film regions. Some areas were smooth and reflective, while others were rough and diffracted light. No cracking of the resulting spiro-OMeTAD film was observed.

CHAPTER 3: RESULTS & DISCUSSION





Figure 3.1.1: *J-V* curves of spiro-OMeTAD on CH₃-terminated n-Si(111) spin cast samples (a) and drop cast samples (b) with inset semilog plots.



Figure 3.2.1: J-V curves of H-terminated n-Si(111) spin cast samples (a) and drop cast samples (b) with inset semilog plots.

Dopant levels (phosphorus) in n-Si were measured to be 7.2×10^{15} cm⁻³ using a Jandel 4-point probe. This is expected to yield a large barrier width due to Fermi level being closer to that of doped spiro-OMeTAD compared to n⁺-Si. Junction behavior is expected to be similar to PEDOT:PSS which shows rectifying contact on both CH₃- and H-terminated n-Si surfaces.¹ It is reported that the barrier heights of PEDOT:PSS (PH-1000 treated with 5% DMSO) on a n-Si surface increased from 0.889V (H-terminated) to 1.01 (CH₃ terminated) groups.¹ This can be explained from the interfacial dipole change from positive to negative on the surface which shifts the band edge toward the vacuum level decreasing the depletion width.^{24,30}

Interestingly, the effect observed with spiro-OMeTAD differs from PEDOT:PSS which remained rectifying regardless of the dipole on n-Si. Spiro-OMeTAD in contact to n-Si show *J-V* curves that transition from rectifying on H-terminated n-Si(H) to ohmic-like on CH₃-terminated n-Si on both spin and drop cast samples. The dipole shift toward the vacuum is expected to increase energy shifts for equilibration, decreasing the depletion width when compared to an H-terminated surface. The results show that this energy change is sufficient to minimize the Schottky barrier between the two materials allowing electrons to tunnel from spiro-OMeTAD to n-Si with a higher probability.



Figure 3.2.2: Relative energy levels of n-Si and spiro-OMeTAD a) before equilibration and b) after equilibration with depletion width (Φ_W) and barrier ($q\Phi_b$).

It is expected from figure 3.2.2 that even with a small dipole shifting the energy toward the vacuum, the barrier width would still remain fairly large. However the CH₃-terminated n-Si show linear *J-V* curves with currents in the k Ω ·cm² range as compared to rectifying curves that appears to pass very little current at low positive applied voltages. This change in electrical contact properties cannot be attributed only to the dipole change and may be a result of another process.

Mercury contact to n-Si CH₃-terminated have been reported to have a rectifying *J*-*V* curve with a mean barrier height value of 0.85 ± 0.02 eV.³⁰ This diode behavior has been demonstrated in this work as the control experiment in figure 3.2.3. This provides evidence that spin cast spiro-OMeTAD films made at 800 RPM are thick enough to prevent shorting. The data obtained showing ohmic junction behavior with spiro-OMeTAD on CH₃-terminated n-Si is not a result of mercury somehow contacting the underlying silicon.



Figure 3.2.3 Control experiment *J-V* curve of mercury contact to methyl terminated n-Si (111).



Figure 3.3.1: *J*-*V* curves of spiro-OMeTAD on CH₃-terminated n^+ -Si(111) spin cast samples (a) and drop cast samples (b) with inset semilog plots.



Figure 3.4.1: (a) *J*-*V* curves of spiro-OMeTAD on H-terminated n^+ -Si(111) spin cast samples (a) and drop cast samples (b) with inset semilog plots.

The highly doped n⁺-Si wafers used are doped with arsenic at a concentration of 1×10^{19} cm⁻³. This high dopant level shifts the Fermi level closer to the n-Si conduction band, which when in contact with a high work function material, results in a decreased depletion width. On CH₃-terminated surfaces, contact resistances on drop cast films resulted in overall contact resistances of 11.38 k Ω ·cm² (n-Si) to 9.81 k Ω ·cm² (n⁺-Si). Spin cast films displayed a 97% decrease in total contact resistance from 22.92 k Ω ·cm² to 0.622 Ω ·cm². This can be expected, as the largest resistance from contacts in figure 2.2 would come from the bulk resistance of spiro-OMeTAD and the contact that it forms with the silicon surface. Because this drop in resistance occurred by using a thinner film of spiro-OMeTAD, it can be expected that the actual contact resistance at the junction is lower than the overall measured resistance values.



Figure 3.4.2: Energy diagram demonstrating a narrow depletion width (w) as compared to figure 3.2.2

The decreased resistance of the junction compared to the junction formed with n-Si is directly correlated to the higher concentration of dopants in the silicon wafer used. This effect results in a more narrow depletion width, which allows higher currents to pass through the junction. The total contact resistance of $0.622 \ \Omega \cdot cm^2$ is four orders of magnitude less than other spiro-OMeTAD and silicon junctions. Because n^+ -Si is often used as a top layer in silicon p-n junction, the results are the most relevant for development of a high performing tandem device.

3.5 Junction Behavior of Spiro-OMeTAD on CH₃-Terminated p-Si(111)



Figure 3.5.1: J-V curves of spiro-OMeTAD on CH₃-terminated p-Si(111) spin cast samples (a) and drop cast samples (b) with inset semilog plots.



3.6.1: J-V curves of spiro-OMeTAD on H-Terminated p-Si(111) spin cast samples (a) and drop cast samples (b) with inset semilog plots.

Spiro-OMeTAD on p-Si reveals ohmic-like *J-V* curves on H- and CH₃-terminated samples. The reported conduction and valence band edge of silicon is 4.0 and 5.1 eV from the vacuum level.³⁵ Doped p-type silicon will have a Fermi level closer to the valence band which comes close to the work function of spiro-OMeTAD. The reported valence band edge of spiro-OMeTAD is reported to be 5.22 eV.⁶ After doping with Li-TFSI the Fermi energy of spiro-OMeTAD should drop close to the valence band edge and thus can be expected to result in ohmic-like contacts. Data from drop and spin cast films are conflicting on the effect the dipole may have on the junction. Spin cast films show higher total contact resistance for p-Si(H) and drop cast films have reversed data characteristics. It should be expected that a shift in the silicon band edge would create a larger barrier between the materials increasing the total resistance.



Figure 3.6.2: Band energy diagram for junction formation between p-Si and spiro-OMeTAD with a negligible depletion width and barrier height.

Table 1 Contact Resistance Data.

Spin Cast Films	$r_c (\mathrm{k}\Omega \cdot \mathrm{cm}^2)$ -H	$r_c (\mathrm{k}\Omega \cdot \mathrm{cm}^2) - \mathrm{CH}_3$	$N_{\rm D}-4$ pt. probe/cm ⁻³
n-Si		22.92 - 54.34	7.2×10^{15}
n ⁺ -Si	15.28 ± 9.51	$0.622 \pm 0.439 \times 10^{-3}$	1×10 ¹⁹
p-Si	4.77 - 13.63	0.51 - 3.12	4.8×10^{15}

Drop Cast Films	$r_c (\mathrm{k}\Omega \cdot \mathrm{cm}^2) - \mathrm{H}$	$r_c (\mathrm{k}\Omega \cdot \mathrm{cm}^2) - \mathrm{CH}_3$	$N_{\rm D}-4$ pt. probe/cm ⁻³
n-Si		11.38±1.51	7.2×10^{15}
n ⁺ -Si	1.34 ± 0.54	9.81 ± 1.58	1×10 ¹⁹
p-Si	1.3 ± 0.28	10.93 ± 3.67	4.8×10^{15}

3.7 Spiro-OMeTAD Thin Films

Difficulties obtaining uniform drop cast films complicated reproducible data collection. If left alone to evaporate at room temperature, the doped spiro-OMeTAD in chlorobenzene resulted in varying film morphologies most of which contained cracked surfaces. This may be due to the charged ionic species from the Li-TFSI dopant slowly rising to the surface as chlorobenzene evaporates in air forming pinholes along the way.²³ The solution has no natural affinity for to the methyl terminated silicon. Therefore, rather than spreading evenly across the surface, the solution aggregates into a large mass with varying thickness.

To obtain a more uniform film, annealing at low temperatures was tested in an effort to remove the solvent at a faster rate. Films that were annealed at 40°C were found to be uniform in the center and raised at the edges. The films made through this process resulted in extensive film cracking. This effect was observed during abrupt temperature changes, which occurred under normal laboratory conditions. It may be possible to reduce the heat slowly to reduce the occurrence of this issue, however, it seems unlikely that mercury with a high surface tension would fill in these pinhole fissures.

Drop cast films had less instances of electrical shorting over spin cast data due to usage of mercury as the film contact. Thick films made from drop cast spiro-OMeTAD were measured to average 16 µm when cast from solutions made at the concentration used. Although these films contain a larger resistance from bulk spiro-OMeTAD, thick films prevent shorting that may occur due to mercury contained in a small washer being pushed into the film with the platinum foil used to make contact. Some of the data obtained demonstrated a non-conducting junction or shorted devices and were thus removed from the data set presented here. The omitted data is attributed to poor or incomplete spiro-OMeTAD doping and/or film coverage.

Total resistances from drop cast films had large standard deviations. Film thicknesses were measured with a Tencor Alpha-Step 200 profilometer and averaged $16.60 \pm 0.22 \ \mu\text{m}$. The thicknesses of the films were consistent and varied only slightly in fractions of 1 μ m. This does not adequately explain the orders of magnitude difference in observed contact resistances from sample to sample. Variation occurred in almost all of samples and may possibly be attributed to non-uniform air doping the samples. With thicker films, it is likely that O₂ doping may not occur evenly throughout which would result in the observed differences.

Using pre-dissolved Li-TFSI in ACN and spiro-OMeTAD in chlorobenzene, uniform films could be spin cast on the silicon wafer pieces. By spinning the substrate just fast enough for the solution to cover it (700-800 RPM) and allowing the excess run off the surface, a solid, transparent, and uniform layer of spiro-OMeTAD was obtained with no observed cracking. Contact resistances are lower as would be expected with spin cast films that are 0.45 µm in height. Although *J-V* data was obtained many samples still had significant variations in contact resistance. Spin cast films were estimated using a color generated vs film thickness chart to be $\sim 500 \text{ nm.}^{40}$

3.8 Spiro-OMeTAD Oxidation UV-Vis



Figure 3.8.1: Absorption data from 400 to 900 nm of Li-TFSI doped spiro-OMeTAD detailing absorbance changes on spin cast film before and after annealing in air. Increased peak at 500 nm is representative of oxidized spiro-OMeTAD.

Spin cast data was also obtained as a film casting alternative to compare effects of film thickness on contact resistance. Absorption data shown in figure 3.8.1 was used to characterize changes in the film that occurs after annealing in air. An increase in the absorption peak at 530 nm is indicative of oxidized spiro-OMeTAD, which has a higher hole conductivity as shown in figure 1.5.2. The spiro-OMeTAD film was cast on a 6.45 cm^2 FTO substrate instead of a microscope slide. The solution deposited evenly on FTO

and a background spectrum was obtained to cancel out the small added absorption of the FTO layer. The film was a transparent clear to light yellow tinted film. After heating at 70°C for 30 min in air, the color changed to a transparent light red color and the absorption changed as shown in figure 3.8.1.

3.9 Perovskite Cell With n⁺-Si(CH₃) Anode

Spiro-OMeTAD tunnel junctions were used to fabricate a perovskite solar cell with an n^+ -Si anode. A piece of FTO glass with a compact layer of TiO₂ covered by a perovskite film was melt pressed onto a n^+ -Si(CH₃) substrate.



Figure 3.9.1: Perovskite solar cell made by melt-pressed contact using a n^+ -Si(CH₃) photoanode showing photoresponse under AM1.5 illumination.

Cell behavior (figure 3.9.1) is rectifying and shows the limits the obtainable photocurrent. Under AM1.5 illumination, the perovskite/spiro-OMeTAD cell exhibits a photo response with low photocurrent with short circuit current density (J_{sc}) found to be

0.00242 (mA·cm⁻²) and an open circuit voltage (V_{oc}) of 0.54 V. The photovoltaic properties of the cell shown in figure 3.9.1 utilizes the traditional Li-TFSI doping of the HTM and has a very low open circuit voltage for this type of perovskite material. A low fill factor (*ff*) of .27 was found and is due to the large series resistance found within the device, limiting its performance. However devices made as a pressed contact without spiro-OMeTAD were inoperable. The results indicate that the junction is operating as expected with proper movement of holes moving through the spiro-OMeTAD material to the n⁺-Si anode. Because of the low device performance one or more of the layers used likely require further optimization.

An ohmic-like tunnel junction is observed at the interface containing H- and CH₃terminated n⁺-Si(111) and doped spiro-OMeTAD. The junction shows signs of high resistivity despite using 20 mol% of Li-TFSI in the film. If high series resistances continue to dominate in thin melt-pressed films, it will likely be that the performance of silicon device will be hindered instead of enhanced. Use of a hole conductor with a lower melting point may reduce decomposition during the melting process.¹⁵ The need for a codoping agent also introduces an uncontrollable component as the process of lithium salts attracting molecular oxygen into the film has been shown difficult to reproduce.¹⁵ 3.10 Preliminary Spiro(TFSI)₂ Results

As an alternative doping method to Li-TFSI, a "pre-doped" spiro(TFSI)₂ is synthesized readily and is used as the sole doping agent for spiro-OMeTAD.¹⁵ This method of doping relies on the reaction between spiro-OMeTAD and the dicationic salt spiro(TFSI)₂ to react to create a singly oxidized conductive species. This alternative doping method reduces the possible variability that O₂ doping may introduce. Figure 3.10.2 and 3.10.3 are *J*-*V* curves from spin and drop cast samples of spiro-OMeTAD doped with spiro(TFSI)₂. Due to the small amount of solution available, it was not filtered through a 0.45 μ m filter, possibly affecting the electrical properties of the films made. Optimization of the solution processing and film casting is necessary to produce more consistent results.



Figure 3.10.1: Reaction of spiro-OMeTAD with silver bis(trifluoromethanesulfonyl)imide to generate the dicationic salt of spiro-OMeTAD.

As Nguyen et. al. reported with the traditional spiro-OMeTAD perovskite devices, made there is a much larger performance variability from the air doped HTM. Thus spiro(TFSI)₂ was synthesized and used to create a solution of pre doped spiro-OMeTAD which does not require air in order to increase conductivity. Instead the dicationic spiro-OMeTAD salt (figure 3.10.1) reacts with spiro-OMeTAD in solution to form singly oxidized spiro-OMeTAD, which allows the films to be made in a glovebox and tested immediately.¹⁵

The films are dried on a hot plate in a glovebox at 40 °C and tested immediately after removal from the glovebox. Preliminary results indicate higher conductivity on both spin and drop cast samples. Spin cast samples had small deviation from sample to sample supporting literature observations. Drop cast samples were visually different and contained areas with 'islands' that have thicker amounts of the HTM. Methods of drop cast film formation must be studied in order to obtain more uniform films, which may result in higher reproducibility. Spin cast films show even lower resistances due to the nature of the self-doping mechanism. Usage of spiro(TFSI)₂ doped spiro-OMeTAD is expected to result in higher performing devices as they can be melted in the glovebox directly after casting.



Figure 3.10.2: J-V curve of 14 mol% spiro(TFSI)₂ solution spin cast at 800 RPM.



Figure 3.10.3: *J-V* curve of 14% spiro(TFSI)₂ of a drop cast film.

3.11 Melt-pressed Contact Resistance Test Using Li-TFSI/O₂ Doping

To gain information on how the junction will act as a thin film melt-pressed contact, spiro-OMeTAD was melted in-between FTO and n^+ -Si(CH₃) using the traditional Li-TFSI/O₂ doping. The film thickness is assumed to be less than previous methods used and can be expected to have lower overall resistance with less spiro-OMeTAD. A *J-V* curve was obtained with n^+ -Si(CH₃) melt-pressed onto a piece of FTO glass using a binder clip as the control. A second *J-V* curve was obtained with spiro-OMeTAD melted in-between to see the added resistance. The small decrease in contact resistance in figure 3.11.1 supports the idea that spiro-OMeTAD may serve as a tunnel junction for a perovskite solar cell.

Due to the perpendicular arrangement of the spiro-OMeTAD molecule, intermolecular bonding is decreased and the material enters an amorphous state when heated from the glass transition temperature 125 °C to the melting point temperature 248 °C.⁵ Resistances of a melted spiro-OMeTAD film is expected to be less than both spin and drop cast films as a result of the decreased thickness. A control was also run with FTO and n^+ -Si(CH₃) as a pressed contact.



Figure 3.11.1: *J*-*V* curve for a melt-pressed contact (black) with spiro-OMeTAD in between n^+ -Si(CH₃) and FTO (red).

The resistance gain is shown (figure 3.11.1) as a decrease in the slope of the device containing spiro-OMeTAD. The resistance increases from 5.44 Ω ·cm² to 45.64 Ω ·cm² that is in agreement with prior results. The curves remain linear possibly from pin contacts from the peaks in the amorphous surface of FTO glass onto the n⁺-Si wafers. The resistances shown are much less than the kilo ohms found in drop and spin cast films.

CHAPTER 4: CONCLUSION

An ohmic-like tunnel junction has been observed with Li-TFSI and spiro(TFSI)₂ doped spiro-OMeTAD on p and n⁺-Si(111) H- and CH₃-terminated surfaces. On n-Si(111), changing the surface dipole from positive to negative (H- to CH₃-terminated) altered the junction properties from rectifying to ohmic-like. High dopant densities in silicon and spiro-OMeTAD have been found to be necessary for low resistance ohmic-like contact. It is has been shown in this work that n⁺-Si can be used as an anode for a perovskite solar cell by melting the spiro-OMeTAD to create a junction. Although the device was photoactive, it is still uncertain if melting the film negatively impacts device performance. The efficiency of the cell is poor, but demonstrates that electrons are tunneling from n⁺-Si to the perovskite and holes are traveling in reverse to n⁺-Si, which has not been shown in the literature. With observed contact resistances, spiro-OMeTAD may not be an ideal tunnel junction for a silicon-perovskite tandem solar cell, however the results demonstrate that Li-TFSI doped spiro-OMeTAD forms a conducting tunnel junction. Furthur studies with spiro(TFSI)₂ may yield better results.

The low performances of the perovskite cell using a n^+ -Si anode can also be attributed to the lack of technique required optimize each layer of the cell. The high performance of published perovskite cells are reported to depend on the method used to grow the crystals.⁶ Devices shown in figure 1.6.1 also contain low performing devices from the traditional doping method and do not approach the high efficiencies demonstrated and certified by NREL.²⁰

A compact TiO₂ layer may not be the best electron accepting layer for perovskites as the contact formed with the absorbing layer is smaller when compared to mesoporous titania. A melt pressed contact should provide good contact between perovskite crystals and the uniform silicon surface however the high temperature needed to melt spiro-OMeTAD may deteriorate perovskite performance. In the amorphous state the HTM can adapt to the perovskite surface so that contact is maximized.

Further studies with 'pre-doped' spiro(TFSI)₂ will provide more data on its effectiveness as a tunnel junction. The pre-doped spiro-OMeTAD absorbs high energy visible light, which should already be captured by the higher band, gap top cell and should not significantly impact lower energy absorption by a silicon bottom cell at meltpressed thicknesses. The effect that mercury has on the doping agents and how this can change the junction property is still unknown. Ideally, a spacer with a known thickness could be used to ensure that shorting does not occur as long as it is non-conductive and able to withstand high temperatures needed for melting the spiro-OMeTAD.

This study gives insight into conducting organics and the contact properties they have on silicon surfaces. Although high resistances were observed for most samples there is still an interesting effect on CH₃-terminated n-Si, which has yet to be fully explained. Experimentation with other hole conductors with similar energy levels may shed more insight on the tunneling effects observed. Design of other conducting molecules with lower glass transition temperature will make a melt-pressed contact more suitable for a tandem solar device as high temperatures attack the perovskite layer. Although tunneling

is a probability effect, further understanding of how current travels through organic conductors will provide more information on what may be a suitable junction for a perovskite/silicon tandem solar cell device.

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