

**DEVELOPING NOVEL HYBRID HETEROJUNCTIONS FOR HIGH
EFFICIENCY PHOTOVOLTAICS**

by

Nicole Antonette Kotulak

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Electrical and Computer Engineering

Winter 2014

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by

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ABSTRACT

Photovoltaic (PV) devices hold great promise for the future of renewable energy - especially with an ever increasing societal demand for electricity. In order for PV to be able to compete with incumbent energy sources it must be financially competitive. With today's state-of-the-art technology, high efficiency devices reduce balance of system costs, but this also comes with a higher initial cost. In order to make PV competitive, then, the trend between high efficiency and high cost must be broken to introduce high efficiency devices that are also low cost. In order to address this issue, work on hybrid organic/inorganic PV devices will be presented here.

This work begins with the concept of the induced junction - or heterojunction - device. A layer of amorphous material is deposited on a crystalline substrate. This amorphous material performs two functions: passivating the substrate and causing band bending at the crystal surface. Traditionally, this device has used amorphous silicon (α -Si) deposited on crystalline silicon (c-Si), with impressive results. In this work, the α -Si is replaced with an organic layer to perform the same device functionality.

The organic compound quinhydrone (QHY) is a high-quality c-Si passivant, and, for this work, was broken into its constituent components - p-benzoquinone (BQ) and hydroquinone (HQ) - for the study of its bonding mechanisms. After examining the effects of time and light on the passivation by BQ and HQ of c-Si, a bonding mechanism is proposed and BQ is shown to be the active passivant. Density functional theory confirms the role of light in the surface reaction and its effective passivity, and surface analysis through XPS experimentally shows the types of bonds being formed.

Hybrid devices were also fabricated, using BQ as both passivant and band-bending layer in an organic/inorganic hybrid device. A Poly(3,4ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS) layer is the contact layer. Experimental analysis of methods for the improvement of open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF) is performed, and pathways for device improvement presented.

Theoretical modeling of these devices is also included, using the finite element method software Sentaurus TCAD. The expected characteristics and performance of the proposed device structure based upon the devices fabricated are calculated, and shown to corroborate the experimental results. This analysis will assist in the direction of future work on these hybrid organic/inorganic structures.

Chapter 1

INTRODUCTION

1.1 Purpose

The purpose of this work is to demonstrate the value of hybrid organic/inorganic device structures as an enabling technology for materials and systems that require gentle processing and cost effective production. The development of high efficiency, low cost photovoltaics using new materials begins with an understanding of the qualities required of each material, and follows through with fabrication, characterization, and first principles analysis of the structures. The importance of this work is the use of p-benzoquinone in a fully fabricated photovoltaic device, which has not been previously demonstrated.

1.2 Background

1.2.1 Fundamentals of Photovoltaics

The overarching definition of a solar cell is a semiconductor device that converts photons into charge carriers. The engineering of different materials and structures is intended to enhance the conversion efficiency of the devices and to tailor them to specific environments or applications. The most basic structure for an inorganic solar cell is a p-n junction. For hybrid organic/inorganic devices, however, we will use another device structure – the heterojunction.

1.2.1.1 P-N Junction Devices

A p-n junction diode is formed when an electron-rich material (n-type) is brought into contact with a hole-rich material (p-type). When the materials are the same (e.g. Si), the band gap (E_g) is the same, but the Fermi levels (E_f) are different. The E_f

is the energy level at which there is a 50% probability that the level will be occupied. The more electron-rich materials will have E_f closer to the conduction band (E_c), while the more hole-rich materials will have E_f closer to valence band (E_v). At thermal equilibrium, however, E_f must be constant.

When a p-type and n-type material are brought into contact, diffusion of charge carriers begins to occur. Due to diffusion principles, electrons will move into the p-type material and holes will move into the n-type material. This diffusion of charges leaves the surface of the p-type material in a negatively-charged state, and the surface of the n-type material in a positively charged state. This region of uncompensated immobile charges is called the depletion region, and it has an electric field formed by the opposing charges on either side of the junction. Once the structure reaches equilibrium, when E_f is continuous, there is a balance between diffusion forces and drift forces (from the electric field), resulting in the band structure shown in Fig. 1.1.

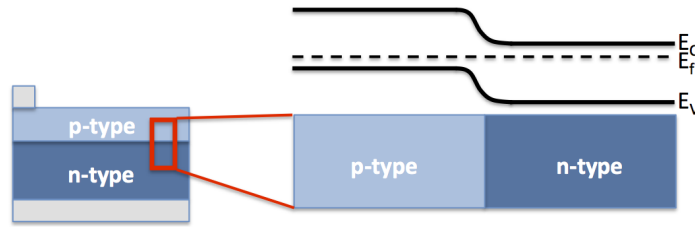


Figure 1.1: Diagram representing a p-n junction band structure. Left: A simple device. Upper right: Band diagram of junction. Lower Right: Physical junction of materials.

By using the natural electrical characteristics of p- and n-type materials, a method for directed carrier movement is enabled. When an incoming photon excites an electron from E_v to E_c , the electron moves to the lower energy level E_c (i.e. toward the n-type material), while the hole moves toward the higher energy E_v (i.e. toward the p-type material). If the moving carriers have no way of leaving the device, there is a buildup of charge that generates a voltage across the device. At open circuit conditions ($J = 0$), this value is the open-circuit voltage (V_{oc}). When carriers are allowed to freely

move through and out of the device, this buildup of charge does not occur. At short circuit conditions ($V = 0$), the current density is the short-circuit current density (J_{sc}). Both of these values are important metrics used to analyze device performance as part of the ideal diode equation.

The change in current density of an ideal solar cell as a function of voltage is explained by

$$J = J_0(e^{\frac{qV}{nkT}} - 1) - J_L \quad (1.1)$$

where J is current density, J_0 is dark saturation current, q is the elementary charge, n is the ideality factor, k is Boltzmann's constant, T is temperature, and J_L is the light generated current density. Often, J_{sc} is assumed to be equivalent to J_L . The J_0 term is an important parameter that indicates levels of recombination within the device, and it can be calculated using

$$J_0 = q\left(\frac{D_n n_i^2}{L_n N_A} + \frac{D_p n_i^2}{L_p N_D}\right) \quad (1.2)$$

where $D_{n/p}$ is the diffusivity of electrons/holes, n_i^2 is the intrinsic carrier density, $L_{n/p}$ is the diffusion length of electrons/holes, and $N_{A/D}$ is the acceptor/donor density. As can be seen from Eq. 1.2, the J_0 term is highly dependent upon material quality.

When analyzing device performance, a JV sweep is performed by illuminating the solar cell and measuring the change in current density as the voltage bias is changed. This sweep produces a curve that can be fit by Eq. 1.1. A representative JV curve is shown in Fig. 1.2. The JV curve is used to determine the performance metrics of the solar cell, including the J_{sc} , V_{oc} , Fill Factor (FF), and efficiency (η). The shape of the curve can also be used to help determine the sources of parasitic loss that may be detrimentally affecting device performance.

The J_{sc} and V_{oc} have already been defined as the current when $V = 0$ and the voltage when $J = 0$, respectively, making these two values the y- and x-intercepts of

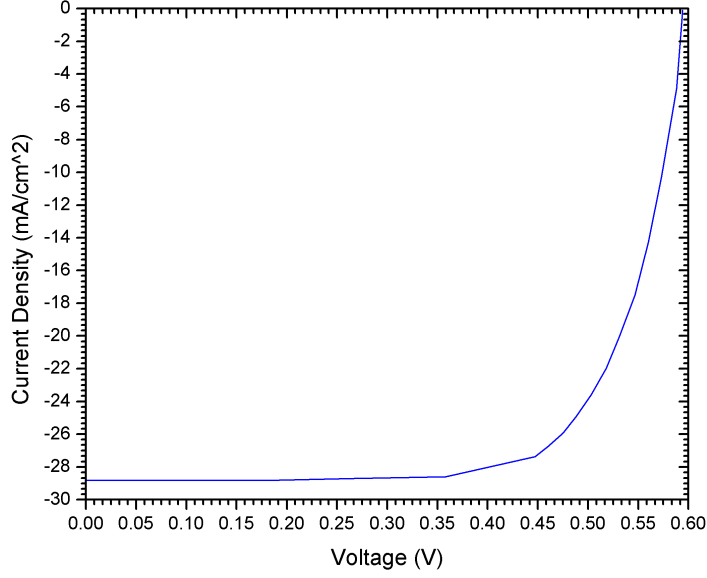


Figure 1.2: An example of a JV curve.

the JV curve, respectively. FF is a measure of the “squareness” of the JV curve, and the higher the FF , the better. FF is calculated using the following equation

$$FF = \frac{J_{mp}V_{mp}}{J_{sc}V_{oc}} \quad (1.3)$$

where J_{mp} and V_{mp} are the current density and voltage, respectively, at the maximum power point of the curve. FF can then be used to calculate the η of the device,

$$\eta = \frac{J_{sc}V_{oc}FF}{P_{in}} \quad (1.4)$$

where P_{in} is the input power, usually calibrated to one-sun conditions ($100 \frac{mW}{cm^2}$).

While this is a simplified review of the p-n junction, and its functionality, these equations are still applicable to the performance of other solar cells (i.e. diodes). Although the structures fabricated for this work will be using the concept of the heterojunction, the goal of the structure is the same – separation of photo-generated electron-hole-pairs, and guided flow of the charge carriers.

1.2.1.2 Heterojunction Devices

In a heterojunction solar cell, there are multiple layers that perform specific tasks within the structure that go beyond the basic p-n junction. An example of one of these devices is shown in Fig. 1.3, and the resulting band structure is shown in Fig. 1.4.

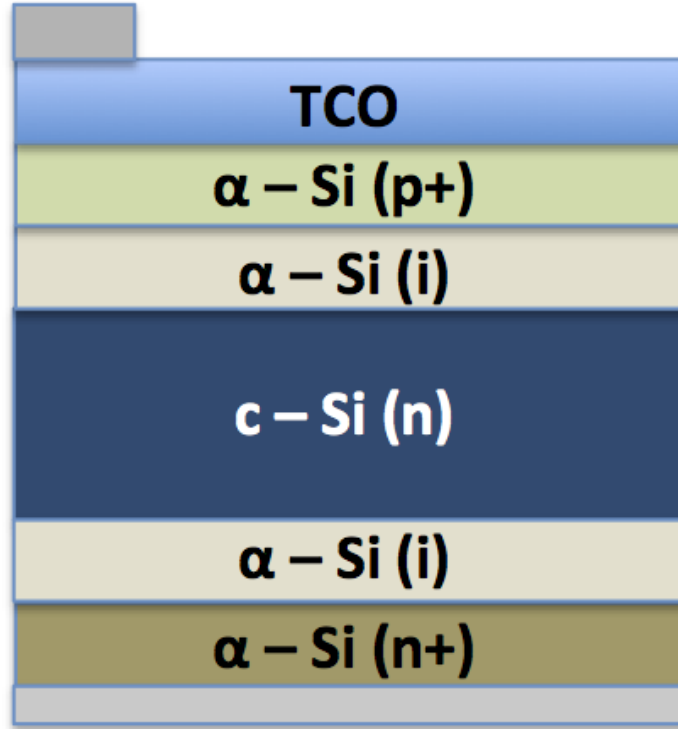


Figure 1.3: An example schematic of a heterojunction solar cell. *Not to scale.*

The first main difference between the p-n junction and the heterojunction is the functionality of the c-Si substrate. While both the p- and n-type layers are active within the p-n junction device, the active region of the heterojunction is, in this case, the n-type c-Si substrate. The next layer in the heterojunction is the intrinsic amorphous-Si ($\alpha\text{-Si(i)}$). This layer provides high quality passivation of the defects on the c-Si surface so as to reduce recombination losses. Finally, the $\alpha\text{-Si(p+)}$ and $\alpha\text{-Si(n+)}$ layers on either end of the structure induce band-bending at the surface of the c-Si that assists in the separation of electron-hole-pairs.

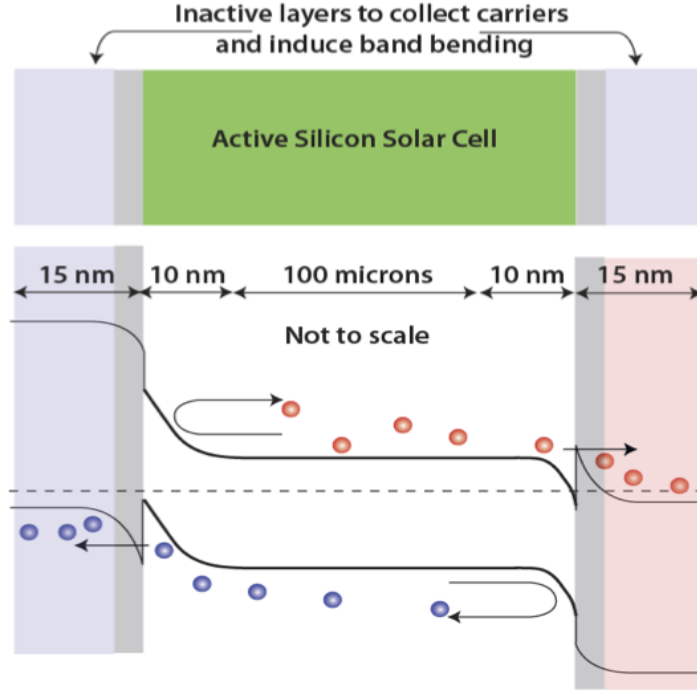


Figure 1.4: An example band diagram of a heterojunction solar cell.

The fabrication of heterojunction devices uses the deposition of the α -Si layers rather than growth or diffusion at high temperatures. It is possible, then, to implement other types of amorphous materials in this device architecture, and take advantage of the method of fabrication to expand beyond traditional inorganic semiconductors. High efficiencies are able to be achieved with α -Si/c-Si devices, and substituting the α -Si with other types of materials should allow these structures to maintain the high efficiency and reliability from the c-Si substrate, while reducing cost and introducing room temperature, gentle processing techniques.

1.2.2 High Efficiency – Low Cost

In order for the photovoltaic industry to continue to grow, the technology must first be able to meet growing energy demand, and second be financially competitive with other, more prevalent energy sources. Energy demand in the US and the world is

shown in Fig. 1.5.

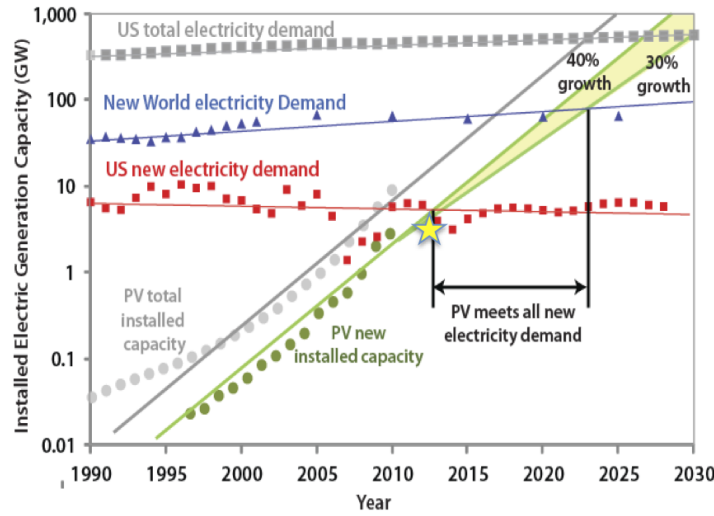


Figure 1.5: Installed electrical generation capacity by year, with forward predictions, and an indication of new electricity demand and PV installed capacity. The star indicates the approximate new installed PV capacity in the year 2013. [24]

The important point on this graph is where new electricity demand intersects with PV new installed capacity. At this intersection, the amount of installed PV generation capacity is equal to the new demand for electricity created in that year. At all points where installed capacity is above the new demand, PV generation starts to compensate for already-existing electricity demand. Based on the location of the star (approximate installed PV capacity in 2013), PV installation is very close to breaking even with new demand. The key to this graph, however, is that PV must be installed in order to generate electricity, and installation requires that PV technology be financially competitive.

There are two methods by which PV technology become financially competitive that will be addressed here – maintain high efficiency and reduce material costs. As demonstrated in Fig. 1.6, the \$/Watt cost of electricity decreases by simply increasing the efficiency of a module. The important point to note is that, for this analysis, the module cost is fixed. At efficiencies greater than 20%, however, the cost reduction

benefits of increasing efficiency start to level off. The first step to reduce \$/Watt is to increase efficiency, but there must be another change to the technology in order to bump the cost curve even lower at high efficiencies. To this end, reduction in the module cost can help provide a solution.

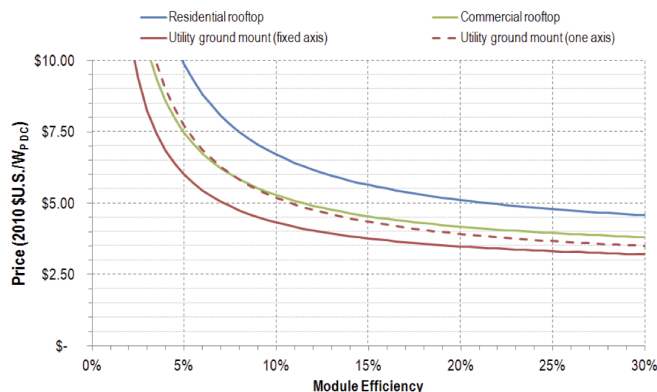


Figure 1.6: Graph of \$/Watt for electricity as a function of module efficiency (fixed module cost). [15]

One of the easiest methods to reduce module cost is to lower the material cost. The effects of reduction in material cost are shown in Fig. 1.7. As can be seen in the figure, lowering the cost of the component pieces of a module leads to a lower \$/Watt. One area of potential improvement is the thickness of the Si substrates. Reduction in substrate thickness (this work targets 50-100 μ m as its long-term goal) will eliminate some material costs. Additionally, the use of organic molecules that allow for room-temperature deposition are not only low cost for materials, but also for processing requirements. It is this goal for high-efficiency, low cost technology that motivates the hybrid organic/inorganic device platform.

1.2.3 Hybrid Organic/Inorganic

The concept of the hybrid organic/inorganic device structure lends itself well to a heterojunction device design. The non-crystalline organic molecules replace the

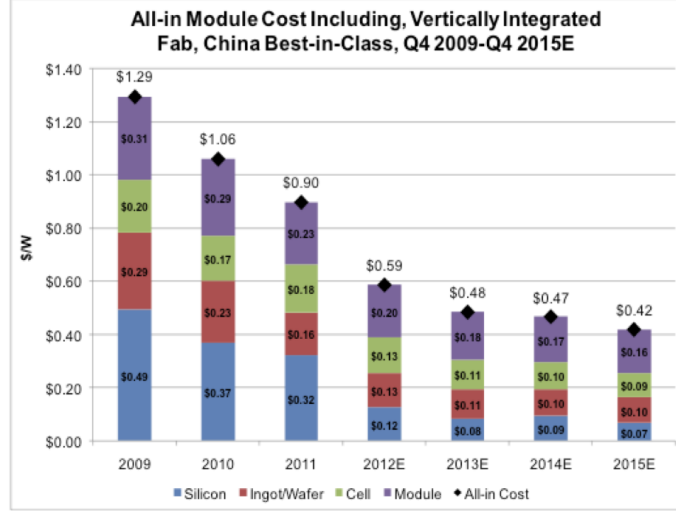


Figure 1.7: Graph of \$/Watt for electricity as a function of module cost, broken down by module component cost. [16]

α -Si in functionality. The easy, room-temperature deposition method for the organics allows for the formation of a diode structure within minutes at low temperatures. Keeping c-Si as the inorganic substrate reduces cost in comparison to other inorganic semiconductor material options, and has the ability to maintain the high efficiency and reliability that has already been demonstrated by Si-based structures. Once the hybrid organic/inorganic structure is better understood, the ability to find or engineer molecules that perform the necessary functions for the device allow for in-depth optimization of the structure. Finally, the organic films at the surface of the structure also provide a platform for a tandem organic PV (OPV) on c-Si device, with the top junction being formed from an OPV device.

The first step for transferring the standard α -Si/c-Si heterojunction device architecture to an organic/inorganic hybrid is determining the function of each deposited layer in the device. Referring to Fig. 1.3, there are three layers on the front surface to consider. The first is the α -Si(i), which functions as a passivant for the c-Si substrate surface. The second layer is the α -Si(p+), which induces band bending at the surface of

the c-Si to facilitate in carrier movement and electron-hole pair separation. The third and final layer on the front of the device is the transparent conductive oxide (TCO), which functions as a transparent contact layer to facilitate the collection of carriers at the front contact. In order to fully emulate this device structure, organic materials that perform each of these functions must be determined.

For this work, the first layer to be addressed is the replacement for the α -Si(i) passivant. As will be discussed in Section 3.2, there has already been work demonstrating replacement layers for the α -Si(p+) and TCO. PEDOT:PSS has been used as a single film that performs the functions of both layers. There has not been, however, much work to find a replacement for the α -Si(i). Finding a high-quality passivant is especially important for this work, as the long-term goal is the use of very thin substrates. As qualitatively shown in Fig. 1.8, the surface area to bulk ratio of a substrate increases as the wafer thickness decreases. This means that, while the bulk properties of a substrate may be high quality, a thinner wafer with the same bulk properties will begin to be dominated by surface effects – such as recombination from surface defects and dangling bonds. It is, therefore, imperative that a high-quality organic surface passivant be found to manage the c-Si surface of the proposed hybrid organic/inorganic structures. To this end, a solution of the molecular mixture Quinhydrone (QHY) dissolved in methanol (ME) – which has been demonstrated to provide high-quality Si surface passivation – will be studied as the passivation layer.



Figure 1.8: A sketch demonstrating the increase of the surface area to bulk ratio of substrates as thickness of the wafer is decreased.

1.3 Thesis Objectives

The focus of this work will be the study of an organic passivant for c-Si, and the implementation of the passivant in a fully fabricated solar cell device in order to demonstrate the functionality of a hybrid organic/inorganic photovoltaic device. This goal will be investigated through the following objectives:

1) Identify the bonding mechanism for QHY/ME solutions on c-Si: This objective will result in an improved understanding of how the molecules react in solution and eventually bond to the c-Si surface, identifying the process requirements for device implementation.

2) Fabricate a hybrid organic/inorganic photovoltaic device using QHY/ME: This objective will demonstrate the initial performance capabilities of the organic passivant in an active device role.

3) Analyze the device: This objective will aid in understanding the present performance characteristics of the hybrid organic/inorganic device, as well as identify areas of improvement.

4) Model the device: This objective will produce a model of the theoretical device performance of the fabricated hybrid structures once they are optimized, utilizing finite element method to evaluate the system.

1.4 Thesis Outline

To address the objectives of this work, the following chapters will cover the experimental methods, resulting data, analysis, and modeling for the development of the hybrid organic/inorganic devices:

Chapter 2: This chapter will cover the identification of the bonding mechanism for QHY/ME on c-Si.

Chapter 3: This chapter will discuss the fabrication methods, device results, and analysis of the hybrid device performance.

Chapter 4: This chapter will detail a theoretical analysis of the hybrid device structure, identifying its potential performance capability and available areas of improvement for device fabrication.

Chapter 5: This final chapter will present the conclusions of this body of work, and propose future work for the advancement of this topic of study.

Chapter 2

PASSIVATION OF SILICON SURFACES WITH QUINHYDRONE/METHANOL SOLUTIONS

2.1 Introduction

To realize high-efficiency hybrid induced junction devices using thin c-Si wafers, the replacement of the passivating intrinsic α -Si is an important step. As discussed in Section 1.2.3, the surfaces of c-Si wafers have an increasing affect on device performance as the thickness of the substrate is reduced. This large surface area can be very detrimental to device performance if the surface recombination centers are not controlled. In order to manage these surfaces, proper electrical passivation methods must be developed, which will both passivate the defects to eliminate recombination sites through the elimination of dangling bonds and induce a field effect that drives specific carriers away from the defect-rich surface. The molecular mixture Quinhydrone (QHY) has been demonstrated to act as a c-Si surface passivant, and it is a solution of QHY in methanol (ME) that has been examined in order to more fully understand the bonding mechanisms involved and its potential efficacy as the organic counterpart to α -Si(i) for hybrid induced junction devices.

2.2 Background & Literature Review

Solution-based passivation of c-Si wafers has a long history, and many varied solutions have been studied for this purpose, including bromine/ME [12, 32, 51] and iodine(I_2)/ME [26, 32, 33, 54]. More recently, QHY in an alcohol solution has been studied for its improved passivation capabilities over I_2 /ME.

QHY is a 1:1 mixture of p-benzoquinone (BQ) and hydroquinone (HQ), as shown in Fig. 2.1 [29]. To date, much work has been done to evaluate the characteristics of QHY solutions when used for the passivation of c-Si surfaces.

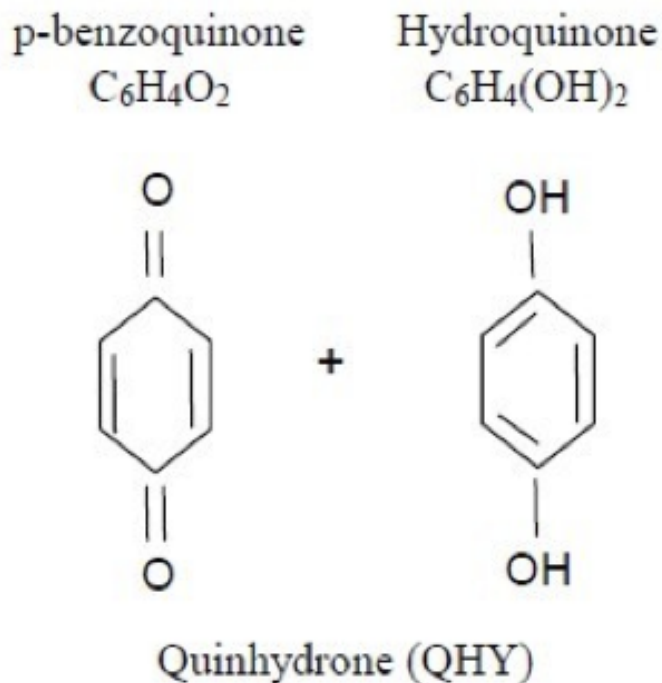


Figure 2.1: Constituent molecules of the Quinhydrone compound.

Nagai, et al., used QHY/ME as a passivant for spherical Si surfaces, however, the QHY/ME solution was not studied directly [34]. Other studies have examined the optimum conditions for using QHY as a passivant. Beginning with QHY in ethanol, Takato, et al., demonstrate that the lifetimes resulting from passivation by 0.01-0.05 M solutions of QHY/ethanol are higher, and the effect is longer lasting, than those from 0.09 M solutions of I_2 /ethanol [54]. Then, Takato, et al., show that the performance of the QHY passivant improves when using ME as the solvent instead of ethanol [55]. Additionally, the lifetimes from QHY/ME passivated samples remain higher than those from I_2 /ME passivated surfaces as shown by Takato, et al., Chhabra, et al., and Opila,

et al. [8, 9, 37, 55]. QHY/ME was also demonstrated by Takato et al., Page, et al., and Chhabra, et al., to be an effective passivant on different substrate orientations and resistivity values [8, 38, 56], and additional work by Takato, et al., shows that a bias light improves the QHY/ME passivation effect on wafers that have been removed from the solution and dried [57]. One final observation by Chhabra, et al., and Opila, et al., has been that the passivation effect of QHY/ME degrades over time once the c-Si substrate has been removed from the QHY/ME solution and allowed to dry [8, 9, 37]. Further study into the nature of the bonding mechanism of QHY to the c-Si surface is required to understand why this high quality passivation degrades over time.

As part of this effort, some studies have separated QHY into its constituent parts and evaluated the characteristics of these molecules separately, as well as other molecules with similar structural features. In studies by Opila, et al., and Har-Lavan, et al., BQ/ME is slightly less effective than QHY/ME, but outperforms HQ/ME [18, 37]. Additionally, Opila, et al., demonstrate that no other molecular structures have a comparable performance to that of QHY/ME or BQ/ME [37]. It was observed by Har-Lavan, et al., that, while HQ/ME is a less effective passivant than BQ/ME, lifetimes from HQ/ME passivated substrates improve when the substrate remains in contact with the solution for an extended period of time (longer than 3 hours) [18]. All of these studies evaluate the different molecules through effective lifetime measurements.

Another method for evaluating this passivation mechanism has been surface analysis after the passivation treatment in order to determine the species which have bonded to the c-Si surface. In earlier work by Chhabra, et al., XPS and FTIR surface studies have indicated that organic molecules have bonded to the surface of the Si and that the QHY/ME treated surfaces have less oxidation than I₂/ME treated surfaces [9]. More recent studies by Har-Lavan, et al., that use ATR-FTIR have shown more detail, identifying that surfaces treated with QHY/ME, BQ/ME, and HQ/ME all display Si-methoxy and Si-HQ bond vibrations, with little if any noticeable Si-O bonds present [18]. It was further shown that QHY/ME and BQ/ME produce the same FTIR data with Si-HQ peaks being stronger for the QHY/ME-passivated surface, and that

HQ/ME treated surfaces have a larger ratio of Si-methoxy bonds to Si-HQ bonds. This information, combined with effective lifetime data, has led to different hypotheses about the chemistry of the reaction between the quinones and the c-Si surface.

Surface passivation with the QHY/ME solution results in a Si surface terminated with HQ-like molecules, as proposed and demonstrated by Chhabra, et al., Har-Lavan, et al., and Harper, et al. [8, 18, 20]. Har-Lavan, et al., and Harper, et al., suggest that BQ becomes a free radical ($\text{QH}^\bullet$) through the abstraction of a H, and that $\text{QH}^\bullet$ subsequently bonds to a dangling Si bond [18, 20]. For HQ solutions, Har-Lavan, et al., suggest that HQ must first convert to BQ, a process which has been demonstrated by Akai, et al., through the conversion of HQ-(water)₂ to BQ, in order for the surface passivation to occur [4, 18]. The existence of $\text{QH}^\bullet$ has been demonstrated by Beck and Brus through the photolysis of both aqueous HQ and BQ in ME to yield predominantly $\text{QH}^\bullet$ [5]. It has also been shown by Rosetti and Brus that the H abstraction by BQ to form $\text{QH}^\bullet$ will not occur in pure H₂O, but will occur in the presence of 10% alcohol [42]. Another study by Cicero, et al., has demonstrated the possibility for H-terminated Si to facilitate chain-reaction surface bonding – a Si dangling bond is bound by an organic molecule to form C-Si, which facilitates abstraction of a neighboring H, thereby creating another dangling bond site for the reaction to continue [10].

All of these solution-based studies are self-consistent and support the conclusion that the c-Si after QHY/ME treatment has HQ-like molecules bound to the surface, and further support a bonding mechanism that includes an intermediary species (the free radical $\text{QH}^\bullet$) and indicates the importance of available H to the reaction. There is a disconnect, however, between the various studies. Studies of the solution alone have demonstrated the existence of $\text{QH}^\bullet$ and the solvent requirements for the system. Studies of the surface after passivation have shown HQ-like molecules on the surface. It has been hypothesized that $\text{QH}^\bullet$ is the link between the solution reactions and the surface bonding. Thus far, however, there has been no experimental demonstration that $\text{QH}^\bullet$ exists within the system considered here (QHY/ME and c-Si), or if it played a role in the surface passivation of the c-Si. It is this link that this work seeks to

provide.

There is one more study that was performed in an Ultra High Vacuum (UHV) system by Ning, et al., that shows BQ bound to the Si(111) surface in a “cycloaddition” or “laying down” configuration [36]. This process was not solution-based, and did not clearly indicate the use of H-terminated Si. This procedural difference, combined with the inability to locate other studies in the literature to support the cycloaddition bonding of BQ to c-Si, suggests that this study is an outlier.

High quality passivation of the c-Si surfaces is the first goal of the QHY/ME work, therefore, the surface preparation for this treatment is another important factor to review. There are many ways in which the substrate can be cleaned and prepared for passivation, the most common for Si using an RCA clean, HF treatment, or a combination of the two. A review of the studies cited within Section 2.2, concludes that many different substrate cleaning procedures have been used for this same passivation method. It is, therefore, important to note whether any single substrate preparation provides the best results. As shown by Tian, et al., there is a clear difference between the surface characteristics of a Si substrate treated with RCA versus one treated with HF [59]. The RCA clean leaves a surface with atomic step features and a well-defined chemical behavior. The HF treatment utilized here does not exhibit the same clear step features or chemical behavior, however, the electronic properties are superior to those of the RCA-cleaned surface. This finding will influence the development of the substrate preparation protocols developed for this work.

2.3 Experimental Methods

2.3.1 Photoconductance Decay

Photoconductance decay (PCD) is a measure of the change in conductivity of a material due to photogenerated carriers resulting from exposure to electromagnetic waves. It is a useful technique for determining minority carrier lifetimes in a semiconductor crystal. A crystal in an equilibrium state will have a conductivity determined by the equilibrium carrier concentration. When the crystal is exposed to a light source,

excess carriers are generated, and the presence of these photogenerated carriers alters the conductivity of the crystal. By measuring the time it takes for the crystal conductivity to return to equilibrium after the excitation event - i.e. the time it takes for the photogenerated carriers to recombine and return the crystal to its equilibrium carrier concentration - minority carrier lifetime can be estimated. Contactless methods for measuring PCD have been used for this work [49, 50].

2.3.1.1 Equipment

Effective lifetime (τ_{eff}) was measured using a WCT-120 from Sinton Consulting, Inc., shown in Fig. 2.2. The base of the tool contains an RF coil and a reference cell, and a flash bulb is suspended above the base. The flash bulb provides light to create photogenerated carriers, and the duration of the flash can be varied to change the type of measurement taken, which will be discussed in Section 2.3.1.2. The reference cell is used to monitor the flash duration and intensity for each measurement. The tool is connected to a computer, which collects the data and performs the calculations to determine τ_{eff} .

In order to take an τ_{eff} measurement, a Si wafer is placed on the base, where the RF coil inductively couples to the wafer to monitor the wafer conductivity. Wafer specifications such as thickness, resistivity, and doping type are input into the Sinton software. Other measurement parameters, including specified minority carrier density (MCD) and measurement type, are also entered. For the measurement, the flash bulb illuminates the wafer for a specified duration. The reference cell collects data regarding the duration and decay of the flash, while the coil in the base monitors the change in photoconductivity of the wafer with light exposure and how long it takes for wafer conductivity to decay to its equilibrium level. This information is used along with the user input values to calculate τ_{eff} as a function of MCD, inverse lifetime with auger correction as a function of MCD, and implied V_{oc} as a function of light intensity.



Figure 2.2: Sinton WCT-120 Lifetime Tester

2.3.1.2 Measurement Types

The PCD method has three different measurement types available, which are dependent upon the magnitude of the expected τ_{eff} of the sample: Quasi-Steady-State (QSS), Transient, and Generalized [27].

The QSS measurement technique is based upon keeping the wafer in a state where carrier generation and recombination are equal and opposite - i.e. the wafer is in steady state. In order to have the wafer in steady state, generation must be occurring during the measurement. To accomplish this, the PCD data is collected for the duration of the flash from the bulb. Using this method, τ_{eff} can be calculated using

$$\tau_{QSS} = \frac{\Delta n}{G} \quad (2.1)$$

where Δn is the excess carrier density and G is the generation rate. The QSS measurement is recommended for lifetimes less than 200 μs .

The transient technique is best for higher lifetime samples (greater than 200 μs). This uses a shorter flash to generate carriers, and the measurement begins after the flash has terminated. Because there is no active generation during the measurement, the sample is not in steady-state, and the measurement focuses on the change in Δn to determine lifetime, as per

$$\tau_{trans} = \frac{-\Delta n}{\frac{d\Delta n}{dt}} \quad (2.2)$$

where τ_{trans} is equivalent to the characteristic decay time. For both the transient and QSS measurements, it is important to know the expected τ_{eff} range beforehand to determine which method is best for a particular sample. If this information is not known, or to have more flexibility in measurement analysis, the final option available is a generalized approach.

The generalized measurement case is an overarching scenario that takes into account both generation and change in Δn as per

Table 2.1: c-Si Wafer Specifications

Type	Dopant	Orientation	Surface	Thickness	Resistivity	Dimensions
n	P	<100>	Double-side polished	500 μm	20-30 $\Omega\text{-cm}$	2" x 2"
p	B	<100>	Double-side polished	525 μm	10k $\Omega\text{-cm}$	2" x 2"

$$\tau_{eff} = \frac{\Delta n}{G - \frac{d\Delta n}{dt}} \quad (2.3)$$

where the equation simplifies to the QSS or transient case when the appropriate component of the denominator goes to zero. The generalized case is, therefore, applicable to any light conditions and lifetime ranges. Without prior knowledge of expected sample performance, it is often useful to measure τ_{eff} using Eq. 2.3 first. Once more is known about the sample performance, QSS or transient measurements can be used for further analysis.

In order to form an overall view of the changes in passivation effects, with lifetimes that cross from the QSS-appropriate range into the transient lifetime range over time, the generalized measurement type was used for all samples. All lifetime values reported here are able to be directly compared because of this consistency in measurement type.

2.3.2 Wafer Preparation

For this work, n- and p-type c-Si wafers are examined. The wafer specifications can be found in Table 2.1. Wafer preparation includes cleaning and hydrogen termination of the surface, followed by solution-based surface passivation. The specifics for these procedures are presented in the following sections.

2.3.2.1 Wafer Cleaning

Wafer cleaning was performed using chemical solutions that are standard for Si processing. Three solutions were used in the following process:

- 1) Piranha (4:1 $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2$) - This clean removes organic matter from the wafer surface. The wafer is first immersed in this solution for 5 minutes.
- 2) Deionized Water (DI H_2O) - Following removal of organic material, the wafer is rinsed in DI H_2O for 5 minutes.
- 3) Dilute Hydrofluoric Acid (1:50 $\text{HF:DI H}_2\text{O}$) - HF is an oxide removal agent that also provides short-term surface passivation of the c-Si by bonding a H atom to the dangling Si bonds exposed by native oxide removal. The wafer is immersed into the HF solution for 2 minutes.

Following HF cleaning and passivation, the wafer is dipped briefly into DI H_2O to remove residual HF solution, then dried using N_2 . The wafer is then immersed in the passivation solution prepared according to the procedure presented in Section [2.3.2.2](#).

2.3.2.2 Surface Passivation

The surface passivation process is solution-based. Using the following molecules, 0.01M solutions are prepared with methanol (ME) (J.T. Baker CMOS grade, as-is) as the solvent, unless otherwise noted:

- 1) p-Benzoquinone (BQ) (98+% Alfa Aesar, as-is)
- 2) Hydroquinone (HQ) (99% Acros Organics, as-is)

The solution is mixed in an acid-proof clear plastic bag with a zip closure. The wafer is immersed into the solution immediately after cleaning, the bag is sealed, and lifetime measurements begin immediately following wafer immersion.

2.3.3 Lifetime Measurements

Lifetime measurements followed the standard operating procedure for the Sinton WCT-120. First, the wafer specifications were input into the appropriate sections of the operating software. The wafer, immediately after immersion in the passivation solution,

was placed onto the base and centered over the sensor area. The wafer remained in solution for the duration of the experiment, which was made possible by the fact that this PCD test method is contactless.

A lifetime measurement was taken every 15 minutes, unless otherwise noted, for a specified duration ranging from 2 to 24 hours for each sample. Minority carrier lifetimes were recorded as a function of time since initial wafer immersion, with $t = 0$ signifying the first measurement immediately after wafer immersion.

Lighting conditions were varied to probe the effects of light on the passivation reaction. In order to vary light conditions, a light-proof enclosure was built around the PCD tool. In this way, ambient light could be eliminated from some experiments, exposing the wafer to light only when the flash briefly illuminates the sample for data collection. The following lighting conditions were examined:

- 1) *Full Light* – The entire measurement preparation process was performed in full ambient laboratory light conditions.
- 2) *Partial Light* – The passivation solution was prepared in full ambient laboratory light conditions. After cleaning and H-termination of the surfaces, the c-Si wafer was immersed into the passivation solution in an environment absent of light. The PCD measurements were taken in a light-proof enclosure, and the sample remained in said enclosure for the full duration of the experiment (2-24 hours). The solution and immersed wafer were exposed to light only during the illuminating flash for each measurement.
- 3) *No Light* – The passivation solution was mixed in the absence of light, followed by wafer immersion, also in the absence of light. The PCD measurements were taken in a light-proof enclosure, and the sample remained in said enclosure for the full duration of the experiment (2-24 hours). Again, the solution and immersed wafer were exposed to light only during the illuminating flash for each measurement.

2.4 Results & Discussion

2.4.1 Confirming the Active Bonding Constituent in QHY/ME Solutions

In order to begin to decipher the bonding mechanism behind the QHY/ME passivation, it was first necessary to confirm which of the constituent components of QHY is the active component. Preliminary work and studies from literature suggested that BQ is the active passivant, however, further analysis was required [18, 37].

To accomplish this, BQ/ME and HQ/ME solutions were used to passivate the wafers described in Table 2.1 under Full Light conditions. Additionally, a wafer immersed in pure ME was used as a control sample. Measurements were taken every 5 minutes for a 2-hour duration. The results are shown in Figs. 2.3 through 2.7.

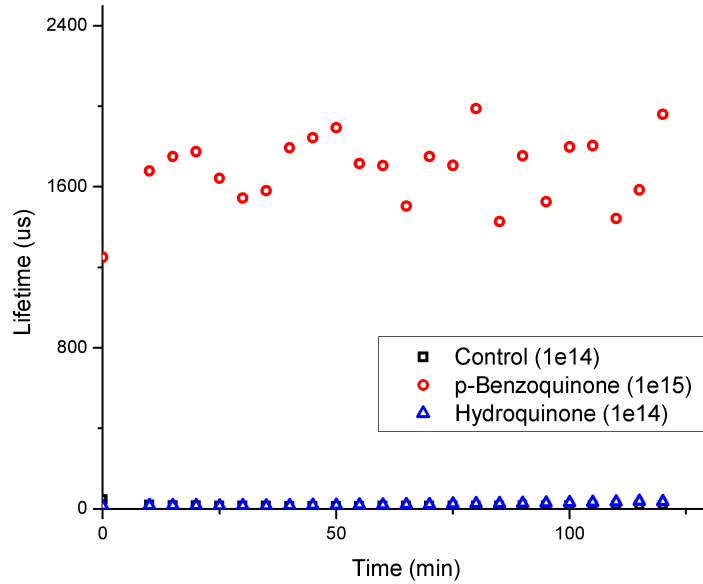


Figure 2.3: A comparison of change in lifetime over 2 hours for a p-type wafer in BQ/ME, HQ/ME, and ME.

Evaluation of the p-type samples (Figs. 2.3-2.4) supported the previous data that BQ is the active constituent. While providing minimal passivation effects over the span of two hours, HQ/ME does passivate the c-Si surface more effectively than the control, as seen in Fig. 2.4.

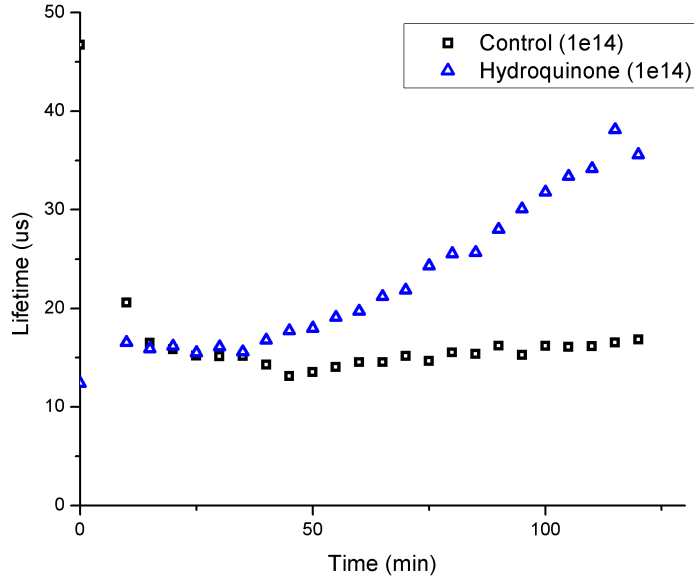


Figure 2.4: A comparison of change in lifetime over 2 hours for a p-type wafer in HQ/ME and ME.

Initially, the n-type samples (Figs. 2.5-2.6) showed similar characteristics to the p-type results. Upon closer examination of the change in lifetime of the HQ/ME passivated sample, as seen in Fig. 2.6, there appeared to be an increased rate of lifetime improvement toward the end of the 2 hour timespan. This observation was made in comparison to the rate of lifetime increase for the p-type sample as shown in Fig. 2.4. In order to determine if this increased rate of lifetime improvement would continue, the sample was left in solution, and lifetime measurements were taken at approximately 24 and 48 hours after wafer immersion. The results of this experiment, shown in Fig. 2.7, display improved lifetimes for the HQ/ME sample that are comparable with those for BQ/ME. This indicates a more complicated passivation mechanism than originally expected. Thus, the long term effects of HQ/ME on both p-type and n-type samples were studied.

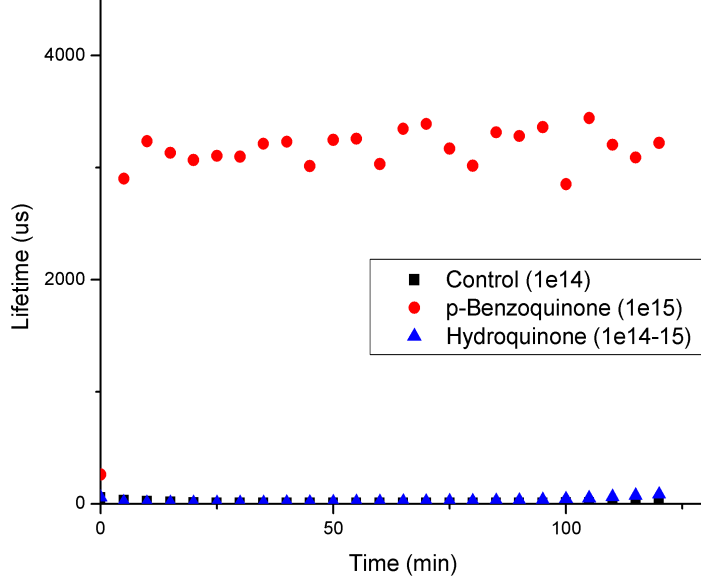


Figure 2.5: A comparison of change in lifetime over 2 hours for an n-type wafer in BQ/ME, HQ/ME, and ME.

2.4.2 Effect of Time on the HQ/ME Passivation Mechanism

In order to determine how the passivation of the c-Si surface varied over time with exposure to a HQ/ME solution, both p- and n-type samples were prepared as per Sections 2.3.2 and 2.3.3.

Both sets of measurements were taken under Full Light conditions. The durations varied for p- and n-type wafers for each sample to reach its maximum achievable passivation level. For p-type wafers, 20 hours was required for the lifetime to settle to an asymptote, as seen in Fig. 2.8. The n-type sample reached its maximum at a faster rate, requiring a 14 hour exposure to solution, as seen in Fig. 2.9.

For both p- and n-type samples, the lifetimes of wafers immersed in HQ/ME do improve with time as suggested by the data from Fig. 2.7, and the change in carrier lifetime over time follows a comparable trend to that seen in the literature [18]. The initial 2 hours display negligible lifetimes, while at around 70-120 minutes of exposure time, the lifetimes begin to increase rapidly. The p-type samples show a lower rate of lifetime increase than the n-type samples, which explains why the phenomenon was

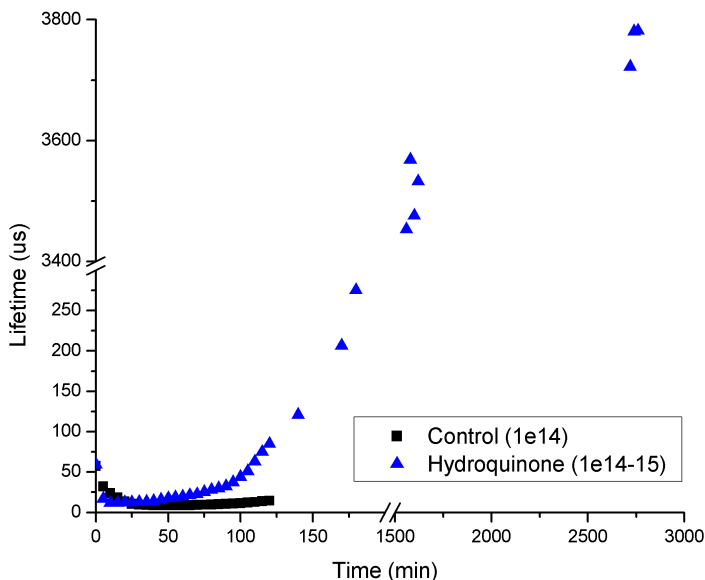


Figure 2.6: A comparison of change in lifetime over 48 hours for an n-type wafer in HQ/ME and ME.

not readily apparent for p-type wafers in the initial studies.

While HQ/ME passivated substrates never reach the same lifetimes as BQ/ME passivated samples, this increase in performance is enough to suggest a time-dependent reaction within the HQ/ME solution that converts the HQ into a more effective passivating species. The initial hypothesis was that the HQ was converting directly to BQ through the loss of the H atoms to form the carbonyl groups. A noticeable increase in passivation quality would require a large number of BQ molecules, which is immediately available in the BQ/ME solution, but would need time to develop from the conversion of HQ to BQ in the HQ/ME solution.

2.4.3 Free Radical Bonding Species

As demonstrated in the literature, BQ and HQ will convert back and forth in solution through an intermediary third species – $\text{QH}^\bullet$ [4, 5, 42]. The suggested conversion pathway is shown in Fig. 2.10. In addition to providing a pathway for HQ to convert to BQ, this opens up the possibility that BQ is not the only active

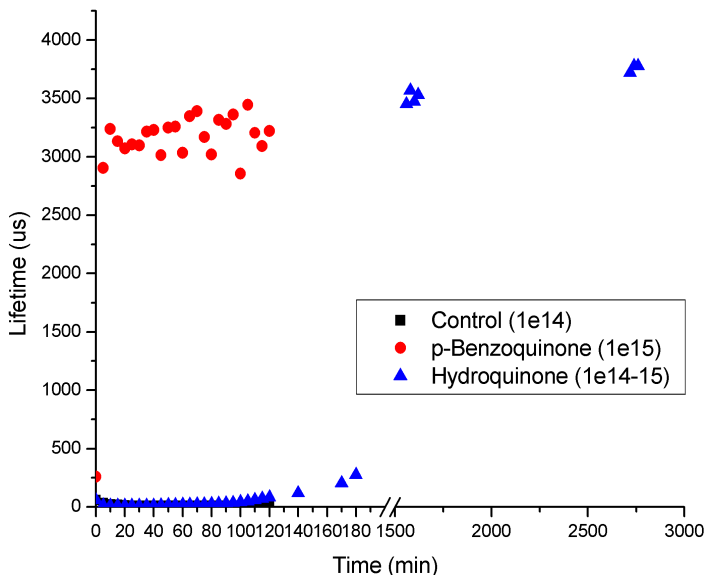


Figure 2.7: A comparison of change in lifetime over 2 hours for an n-type wafer in BQ/ME, HQ/ME, and ME, where the HQ/ME sample also has data points at 24 and 48 hours

constituent now that there may be a third molecular species, albeit with a short lifetime, in solution. This free radical would be consistent with our findings thus far, as well as those in the literature. As noted in Section 2.2, examination of the c-Si surface after passivation with QHY/ME constituent solutions shows HQ-like molecules. We have already demonstrated, however, that BQ (which does not have an OH) is the active bonding species. It is necessary, then, for BQ to convert into a species that does have an OH bond in order for the lifetime results to agree with the surface analysis. Additionally, while HQ has OH bonds on either side of the molecule, it does not passivate as readily as BQ, as demonstrated by the lifetime experiments. HQ, therefore, must also undergo a conversion in order to become a more active passivant. $\text{QH}^\bullet$ is an intermediary between these two configurations, and it is for this reason the focus will now turn to demonstrating that $\text{QH}^\bullet$ is present in this work, and that it is the most likely passivating species.

While this intermediary species has been observed in solution for other systems,

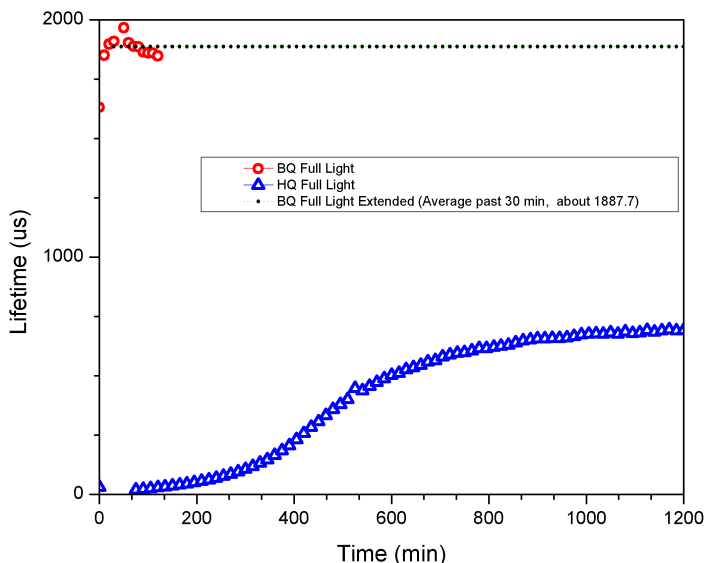


Figure 2.8: Change in lifetime during exposure of p-type wafer to HQ/ME for 20 hours.

there must be evidence of the existence of this molecular conversion pathway in this particular system (BQ/ME with c-Si and HQ/ME with c-Si) before either confirming that HQ is converting to BQ or considering $\text{QH}^\bullet$ to be the passivating species. Additionally, a solution of purely $\text{QH}^\bullet$ is not stable, so indirect methods of testing for the existence of $\text{QH}^\bullet$ must be employed. As seen in Fig. 2.10, the conversion pathway requires either the addition or subtraction of a proton in the form of H (depending on the direction along the pathway), as well as a photon. By examining the effects of protons and photons on the lifetimes of wafers passivated with BQ/ME and HQ/ME, the possibility of $\text{QH}^\bullet$ and its actions within the system can be indirectly probed.

2.4.3.1 Importance of Protons to the Passivation Mechanism

For all of the experiments to this point, ME (CH_3OH) was used as the solvent, and it is known to have a labile proton on the alcohol oxygen. If the $\text{QH}^\bullet$ was being formed, it was likely that the extra protons from the solvent were facilitating the conversion. Additionally, removal of the excess protons by replacing ME with an aprotic

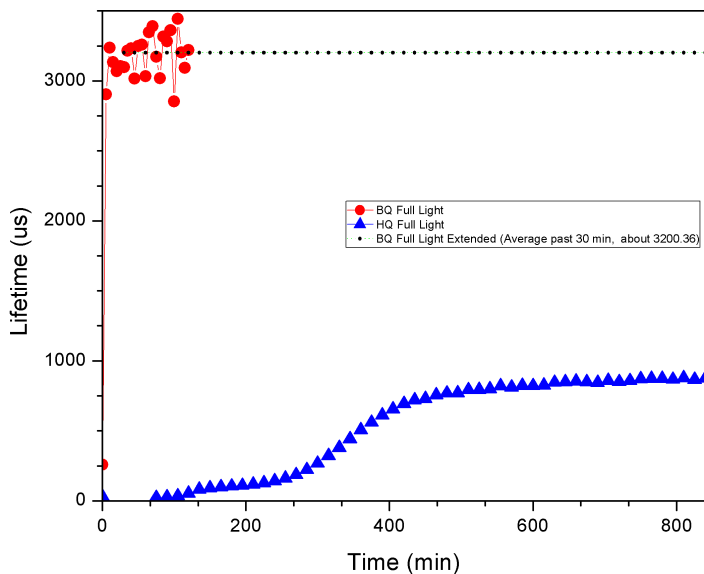


Figure 2.9: Change in lifetime during exposure of n-type wafer to HQ/ME for 14 hours.

solvent should display a decrease in the passivation capability of the solution. In order to compare these two scenarios, the effective lifetimes of wafers immersed in BQ/ME were compared with wafers in BQ dissolved in diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$), an aprotic solvent. The changes in lifetimes were recorded over a period of two hours, and are shown in Figs. 2.11 and 2.12.

As can be seen from the comparison of lifetimes for the two solvents, those wafers which were immersed in BQ/Ether were not as effectively passivated as those wafers which were immersed in BQ/ME. This difference in performance for an aprotic solvent suggests that the availability of excess protons is beneficial to the bonding mechanism, and ME was used for all remaining experiments.

It was also noted for Figs. 2.11 and 2.12 that the lifetimes in ether were improving over time. The possibility that the solvents – both ME and ether – were being contaminated with H_2O over the duration of the experiment was proposed. H_2O has more excess protons than either solvent, which could have provided a source of additional protons that was improving the performance of the solution over time. To test

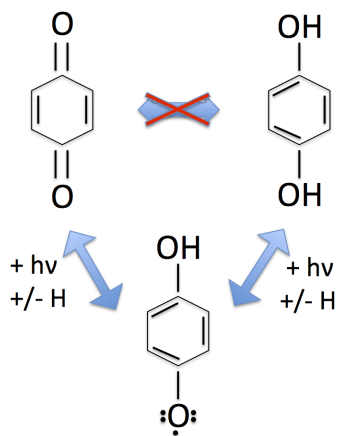


Figure 2.10: Suggested conversion pathway between BQ and HQ through the intermediary free radical $\text{QH}^\bullet$.

this possibility, anhydrous ME was used as the solvent for lifetime measurements with a BQ/ME solution. These results were compared with those from solutions where the anhydrous ME was purposefully contaminated with 2% by volume H_2O . No significant difference was observed between the two results, indicating that contamination of the solution by H_2O was not affecting the passivation mechanism. This result also coincides with the findings by Rosetti, et al., where solutions of BQ in H_2O with 10% alcohol will still form $\text{QH}^\bullet$, allowing for a much higher level of H_2O “contamination” than observed in this work [42].

The formation of the $\text{QH}^\bullet$ species was supported through these results comparing solvents with different excess proton availability. In addition, its role as the bonding species which passivates the c-Si surface was supported. In order to further examine this hypothesis, however, the effect of light on the passivation mechanism must also be considered.

2.4.3.2 Effect of Light on the Passivation Mechanism

For the formation of $\text{QH}^\bullet$, Brus, et al. and Rosetti, et al., demonstrated there must be both available protons and photons to facilitate the reaction [5, 42]. As

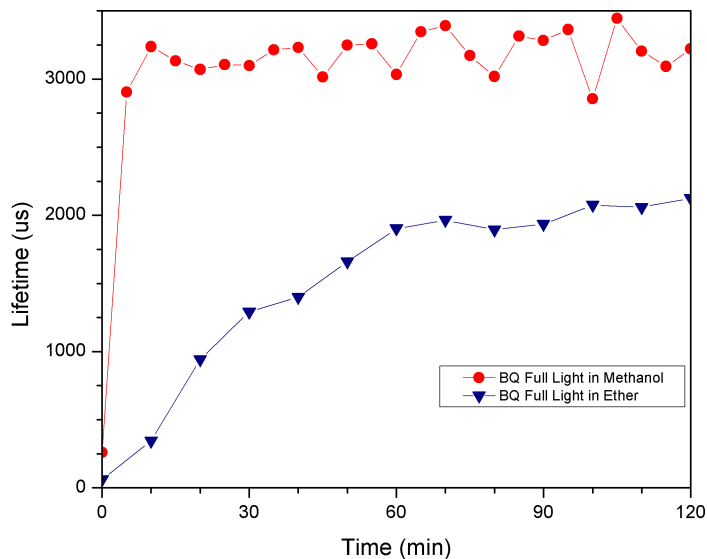


Figure 2.11: Comparison of lifetimes of n-type wafers in BQ/ME versus BQ/Ether.

demonstrated in Section 2.4.3.1, protons do, in fact, play a role in the effectiveness of the passivation reaction. In order to determine if light plays a role in the reaction, the passivation characteristics of BQ and HQ demonstrated thus far must be considered. Passivation by BQ/ME is an almost immediate reaction, indicating that the conversion from BQ to $\text{QH}^\bullet$ – if occurring – is a very fast reaction. Conversely, passivation by HQ/ME requires a much longer period of time, indicating that the conversion from HQ to $\text{QH}^\bullet$ is a much slower reaction, in comparison. This differing time scale for conversion should become more apparent when the exposure of the system to ambient light is reduced or eliminated.

For this set of experiments, the three light conditions as described in Section 2.3.3 were used. Both n-type and p-type wafers were passivated in BQ/ME and HQ/ME solutions, and the change in lifetime for each sample was recorded for the following durations: 2 hours for all BQ/ME solutions, 14 hours for n-type wafers in HQ/ME, and 20 hours for p-type wafers in HQ/ME. The results are presented in Figs. 2.13 through 2.16.

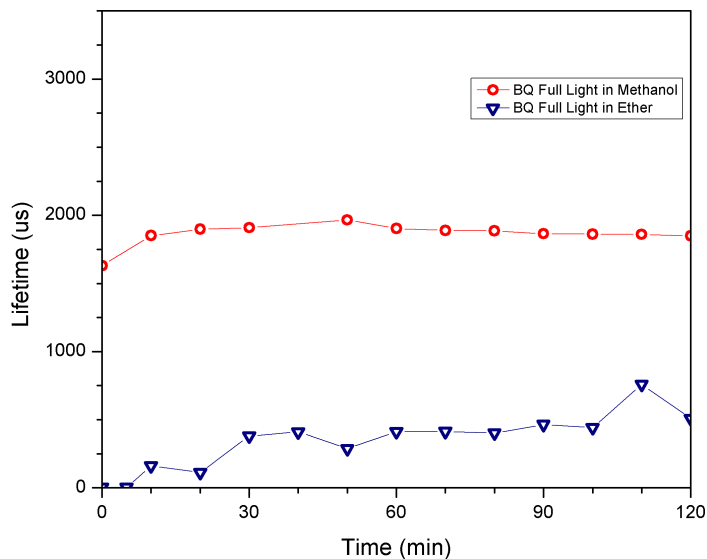


Figure 2.12: Comparison of lifetimes of p-type wafers in BQ/ME versus BQ/Ether.

In all cases, the Full Light samples had higher lifetimes due to better passivation. At its most fundamental level, this data shows that, in order initiate the bonding mechanism for high quality passivation, continual exposure to light must occur when the wafer is in contact with the solution. This discovery introduces nuances to the hypothesis of $\text{QH}^\bullet$ as the active bonding species that must be discussed.

First, for the BQ/ME solution as shown in Figs. 2.13 and 2.14, the Partial Light samples have comparable lifetimes to the No Light samples, and both have significantly lower lifetimes than the Full Light samples. For the Partial Light condition, the solution by itself was the only part of the system exposed to light. If the active bonding species were $\text{QH}^\bullet$, and this species was formed with the presence of light, we would expect the Partial Light samples to have comparable lifetimes to Full Light. Additionally, due to this same logic, because the No Light samples had no light exposure at all, we might expect to see little to no passivation effect from the solution under the No Light condition. As neither of these results are the the case, there are several factors to consider when attempting to explain this phenomenon, beginning with the time for

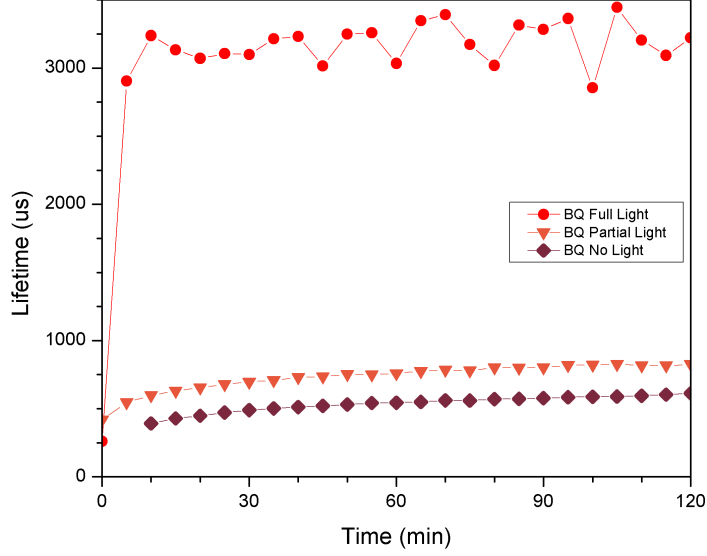


Figure 2.13: Comparison of different lighting conditions on the lifetimes of n-type wafers in BQ/ME.

the conversion from BQ to $\text{QH}^\bullet$.

The conversion from BQ to $\text{QH}^\bullet$ is on the order of nanoseconds [42], and the free radical will presumably rapidly convert back into BQ without the presence of a site to which it can bond. For the Partial Light case, then, the $\text{QH}^\bullet$ was formed while the solution was sitting in the light, but it quickly converted back into BQ when the solution was placed in the dark for wafer immersion. During data collection, the flash required for initializing the PCD measurement is on the order of milliseconds. This is a long enough exposure to convert some BQ into $\text{QH}^\bullet$, but only those free radical species which are close enough to the c-Si surface survive to form a passivating bond. All the remaining $\text{QH}^\bullet$ converts back into BQ, and the process repeats at the next measurement. This also accounts for the slight improvement in lifetime over time.

The hypothesis, then, is that no $\text{QH}^\bullet$ exists in solution once the solution no longer has light exposure. This means that the Partial Light case is equivalent to the No Light case, which has never had light exposure outside of the PCD measurement flash. As the No Light samples do, in fact, have comparable lifetimes to the Partial

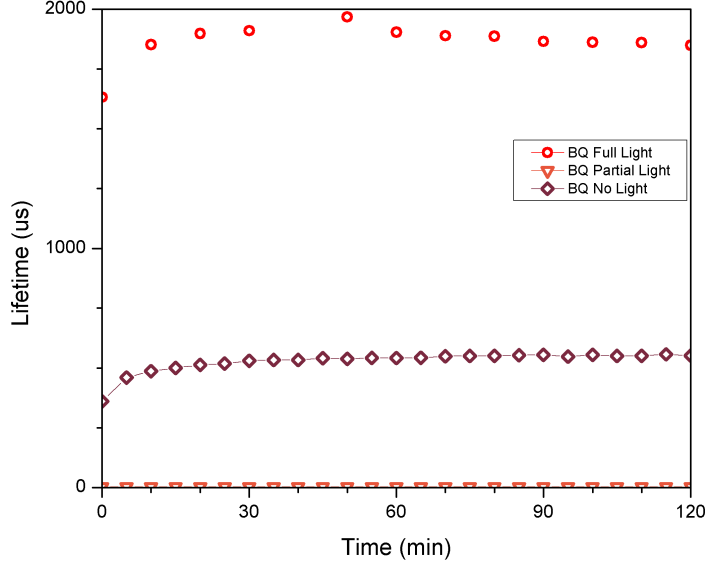


Figure 2.14: Comparison of different lighting conditions on the lifetimes of p-type wafers in BQ/ME.

Light samples, it is likely that this mechanism of conversion from BQ to $\text{QH}^\bullet$ holds.

The outlier for this set of data is the Partial Light condition for a p-type wafer in BQ/ME, which can be seen in Fig. 2.14. This sample condition repeatedly provides little to no passivation effect, and there is, at this point, no indication of a reason for this discrepancy in performance.

Next, for the HQ/ME solution as shown in Figs. 2.15 and 2.16, there is a clear difference in relationship between the data from these three lighting conditions when compared to the data from the BQ/ME solution. For the BQ/ME solution, Partial and No Light lifetimes were comparable. For HQ/ME, Full, Partial, and No Light lifetimes are relatively evenly distributed, with lifetimes decreasing from Full to Partial to No Light. This can also be explained using the conversion time of BQ to $\text{QH}^\bullet$, with the additional consideration of the longer conversion time of HQ to $\text{QH}^\bullet$.

Referring to Fig. 2.10, there are two pathways to form $\text{QH}^\bullet$: either from BQ or from HQ. Based on the results from the time experiment in Section 2.4.2, we hypothesize that HQ does convert to $\text{QH}^\bullet$, but that the conversion time is much longer when

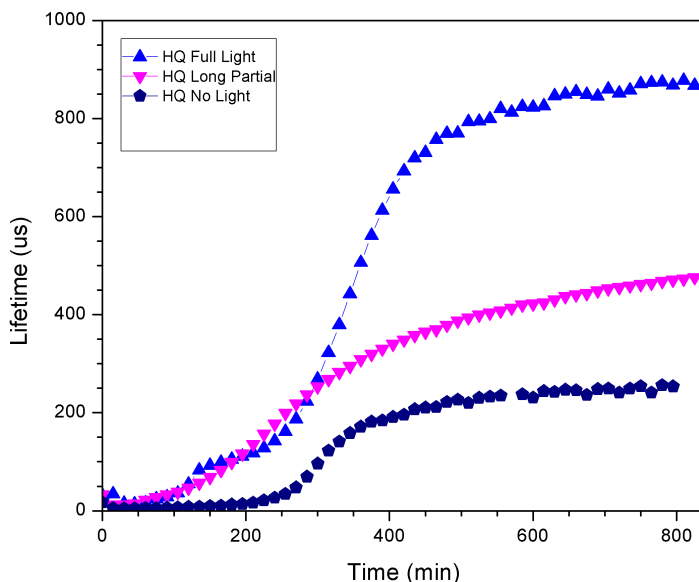


Figure 2.15: Comparison of different lighting conditions on the lifetimes of n-type wafers in HQ/ME.

compared to the time required for BQ to convert to $\text{QH}^\bullet$. This accounts for the length of time required for the wafer to be immersed in solution for lifetime improvements to be witnessed.

This time component can also be used to explain the difference between the Partial and No Light samples. For Partial Light, the solution is exposed to light for a length of time before being placed in the dark. During this light exposure, HQ is converting to $\text{QH}^\bullet$. When the solution no longer has light to maintain the conversion process, however, the $\text{QH}^\bullet$ rapidly converts into BQ – the faster leg of the molecular pathway. When the wafer is immersed in the solution and the measurements begin, the solution has some BQ, which forms $\text{QH}^\bullet$ and begins to react with the c-Si immediately, and some HQ, which takes a longer time to convert into $\text{QH}^\bullet$ before reacting with the c-Si surface. The No Light case has a solution of only HQ, as there has been no light exposure to begin converting the HQ into $\text{QH}^\bullet$. The decrease in lifetime, then, is due to the time required for the solution to build up enough $\text{QH}^\bullet$ or BQ, which then converts to $\text{QH}^\bullet$, to passivate the c-Si surface.

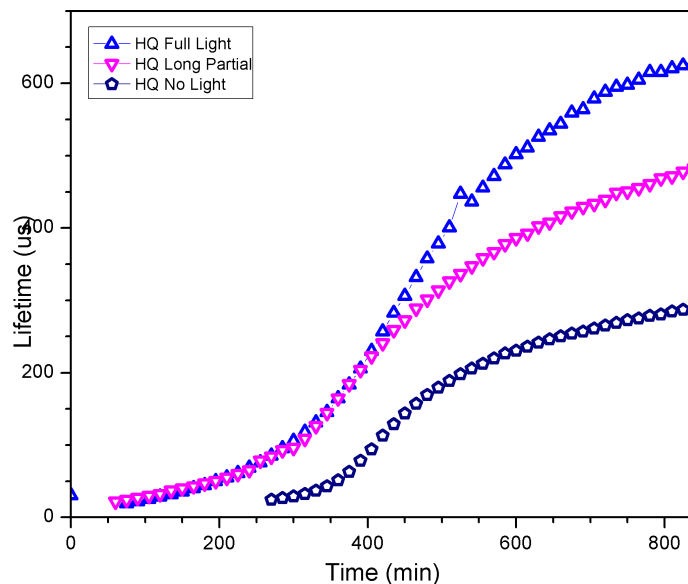


Figure 2.16: Comparison of different lighting conditions on the lifetimes of p-type wafers in HQ/ME.

Based upon the lifetime data for the different solvent and light exposure conditions, there is support for the existence of the free radical $\text{QH}^\bullet$ in the solution, and its role as the passivating molecule. It must be noted, however, that the solution is not the only photoreactive component of this system. The c-Si itself responds to light, resulting in the generation of charge carriers. These carriers may cause charge centers at the surface of the c-Si, which facilitate the surface bonding of the passivant. It is also possible that the excitation of the c-Si may result in Si dangling bonds at the crystal surface, which facilitate the passivation bonding mechanism. Another method for the creation of free radicals on the c-Si surface is the removal of the H-terminating atom, which can be facilitated by the molecules in solution [10]. While these scenarios remain possible components in the passivation effect observed, a study of these particular mechanisms is outside the scope of the work presented here.

Once the molecule $\text{QH}^\bullet$ was isolated as the most likely passivation-inducing bonding agent through experimental data, the next step was analysis by theory. To

this end, density functional theory (DFT) was used to calculate the energetically favorable configurations of our system, and the results were compared with the hypotheses generated thus far.

2.4.4 Density Functional Theory Calculations

In order to theoretically evaluate the hypotheses developed surrounding BQ, $\text{QH}^\bullet$, and their potential bonding mechanisms for passivation of c-Si surfaces, density functional theory (DFT) was used. DFT is a quantum mechanical modeling method used to calculate the properties of many-electron systems. Through the study of atoms, molecules, crystals, surfaces, and the interactions of these structures, properties such as molecular structures, vibrational frequencies, and atomization energies can be predicted. It is through this technique that the likely bonding formations for the passivation mechanism are predicted.

Three different scenarios have been calculated using DFT. The first is the thermodynamic probability of BQ bonding to an H-terminated c-Si surface. The second, provided that it is possible for BQ to bond, is the comparison of energy of the BQ and $\text{QH}^\bullet$ bonds, respectively, to a c-Si surface with a dangling bond. This scenario is calculated in order to determine which of the two bonds with c-Si is energetically favorable. The third and final scenario is an evaluation of the orientation of the BQ molecule on the c-Si surface.

2.4.4.1 Thermodynamic Evaluation of a BQ Bond

The first scenario is to evaluate whether it is thermodynamically possible for BQ to bond to an H-terminated c-Si surface. If this is not a possibility, the entire passivation mechanism hypothesis must be re-evaluated. A visualization of the bonding is shown in Fig. 2.17.

The result of the calculation confirms that it is thermodynamically possible for BQ to bond to H-terminated c-Si through a system energy reduction of 188.8 KJ/mol. The final configuration involves the removal of the H atom from the c-Si surface, and

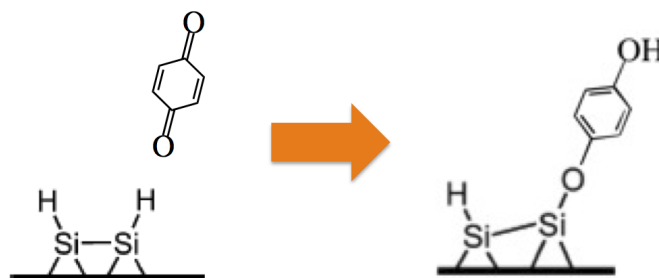


Figure 2.17: A visual representation of the BQ bonding scenario evaluated through DFT.

the addition of a H to the “free” side of the molecule for the formation of OH, which is a configuration experimentally confirmed in the literature [18, 20]. While it is possible to postulate the mechanism by which the system reaches this final state, DFT does not provide the steps by which this reaction occurs. As an example, a BQ molecule could remove an H atom from the c-Si surface, form $\text{QH}^\bullet$, and this free radical bonds to the newly-formed dangling bond [18, 20]. This is, again, only a hypothesis, as these intermediate details are not part of the DFT calculation. Once the possibility of BQ to bond to the c-Si surface is confirmed, the next theoretical evaluation is of the favorability of BQ versus $\text{QH}^\bullet$ as the bonded species.

2.4.4.2 Energetic Favorability of BQ vs. $\text{QH}^\bullet$

Based on the experimental results discussed in Sections 2.4.3.1 and 2.4.3.2, it is strongly suggested that the free radical $\text{QH}^\bullet$ is an important component of the passivation mechanism. It is also possible that $\text{QH}^\bullet$ is, in fact, the bonding species, as suggested by the previous DFT results. In order to further evaluate this possibility, DFT was used to compare BQ and $\text{QH}^\bullet$ and the resulting energy of each molecular system when bonded to a c-Si dangling bond, as shown in Fig. 2.18.

The results indicate that $\text{QH}^\bullet$ bonded to the c-Si surface is the energetically favorable configuration with an energy 1675.7 KJ/mol lower than that of BQ/c-Si. Combined with the experimental results thus far, it is most likely that $\text{QH}^\bullet$ is the

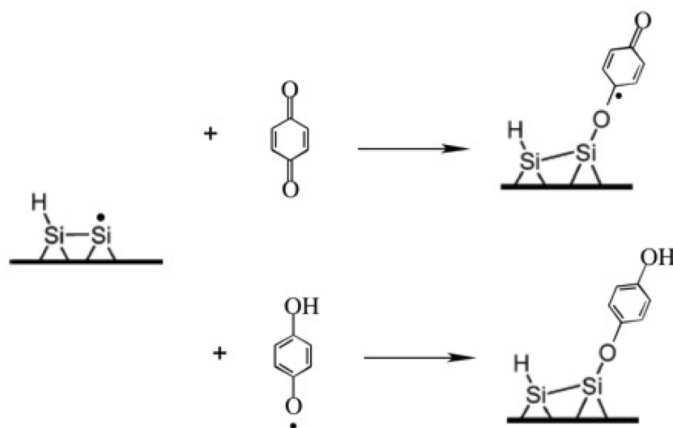


Figure 2.18: A visual representation of the bonding scenarios for BQ and QH• evaluated through DFT.

active bonding constituent. Further study is required to confirm this hypothesis, but this combination of experimental and theoretical analysis provides a clear indication of what must be looked for in order to do so.

2.4.4.3 Molecular Orientation on the c-Si Surface

The final scenario evaluated using DFT is the orientation of the molecules on the surface once bonded, specifically the standing up and “cycloaddition buckle” orientations, which are illustrated in Fig. 2.19. This information has implications for several aspects of this work. The first is the affect on the bonding mechanism, as the bonding mechanisms for molecules standing up versus laying down could be different. The second aspect affected is the modeling of the film for devices, more specifically the film thickness. The third aspect is further device development, especially as relates to the addition of further layers of molecules and to which part of the passivating molecule the additional films will be in contact.

The conclusion of this analysis is that, for BQ bonding to a c-Si surface with two dangling bond sites located next to each other, a standing up configuration is energetically favorable to a cycloaddition buckle by an energy 127 KJ/mol lower. It

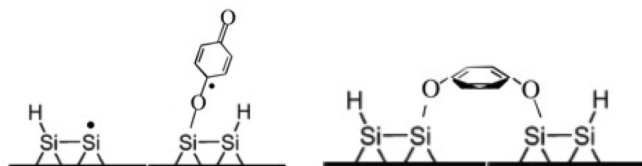


Figure 2.19: A visual representation of the bonding scenarios for BQ molecular orientation on the c-Si surface as evaluated by DFT. Left: “Standing Up”, Right: “Cycloaddition Buckle”

should be noted that contradictory results of this calculation through DFT are available in literature, which proposes that the cycloaddition buckle is the favorable configuration [36]. It has already been determined that this contradictory work is an outlier because the Si surface is allowed to relax, and further examination of this result is beyond the scope of the work presented here.

2.4.5 XPS Surface Analysis

All of the efforts to this point were studies of the bonding mechanism through changes in effective lifetime of the c-Si wafers. Through these experiments, we were able to define the molecular structures that should be observed if the c-Si surface were to be directly analyzed after passivation with BQ/ME. For this surface analysis, x-ray photoelectron spectroscopy (XPS) was used. During XPS measurements, a sample is bombarded with x-rays that photo excite electrons out of the material. The kinetic energy of these electrons is measured and the number of electrons at each energy counted, generating XPS spectra. The energy of each peak in the spectra correlates to a certain type of atom, and the amplitude indicates the number of electrons counted at that particular energy level. Using this information, the surface chemistry of a sample is determined.

The XPS spectra were obtained from c-Si wafers that had been passivated with BQ/ME and left in solution under full ambient lighting conditions for 36 hours. The resulting spectra are shown in Figs. 2.20–2.22, and a representation of Si-methoxy and

Si-QH• bonds is shown in Fig. 2.23.

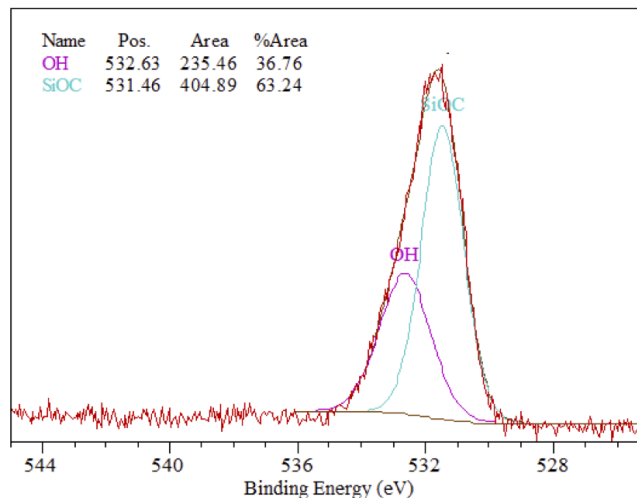


Figure 2.20: O 1s spectrum the SiOC and OH bond peaks for BQ/ME on H-terminated c-Si.

In Fig. 2.20, the O 1s spectrum shows two bonds - SiOC and OH. There is a ratio of approximately 2:1 SiOC:OH bonds on the surface of the c-Si. If we consider the molecules that could be bonded to the surface, using Fig. 2.23 as a guide, we have the methoxy radical from the methanol (an SiOC bond), and the QH• radical, which has one SiOC bond to the surface of the c-Si, and one OH bond at the opposite side of the structure. For the QH•, therefore, the SiOC:OH ratio is 1:1. For the methoxy radical, the ratio is 1:0. Using this spectrum, then, we can conclude that both methoxy groups and QH• are bound to the surface in an approximate ratio of 1:1.

While we observe SiOC and OH bonds at the surface of the c-Si, it is also important to keep in mind the ease with which c-Si develops a native oxide. For evidence of this material, Fig. 2.21 shows a very small SiO_x peak, indicating that there is little bonding between only Si and O at the c-Si surface.

The final consideration for surface analysis is a more in-depth look at the ratio of methoxy to QH• groups bound to the surface of the c-Si through the number of C bonds observed. For a methoxy group, there is one CO bond. For QH•, there are two

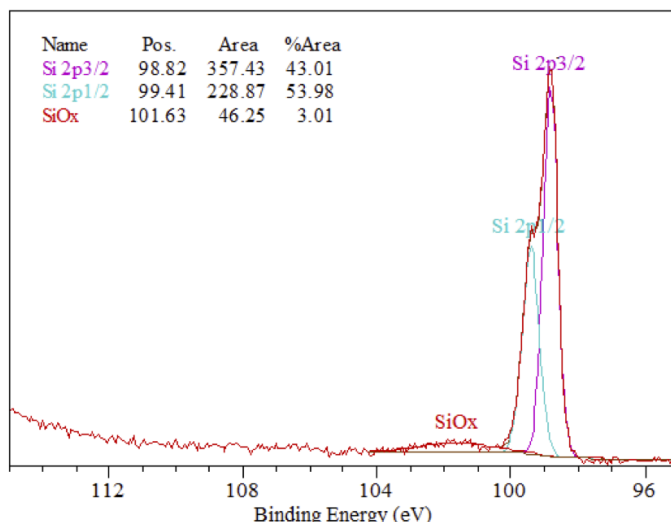


Figure 2.21: Si 2p spectrum showing the Si and SiOx bond peaks for BQ/ME on H-terminated c-Si.

CO bonds and four CH bonds. If we have the same ratio of methoxy to $\text{QH}^\bullet$ observed in Fig. 2.20, we should see three CO bonds for every four CH bonds. In Fig. 2.22, we observe the CO and CH bonds in the approximate ratio of 3:4, corroborating the evidence from the SiOC and OH data that indicates a 1:1 ratio of methoxy groups to $\text{QH}^\bullet$ bonded to the c-Si surface.

With this information, then, the hypothesis that there are $\text{QH}^\bullet$ species bonded to the surface is supported. Additionally, we observe the presence of methoxy groups also bonded to the surface. Further investigation is required to confirm the ratio of these molecules on the surface, which can only serve to shed more light on the bonding of BQ to c-Si and the mechanism by which the c-Si is electrically passivated.

2.5 Conclusions

Throughout this chapter, the passivation characteristics of QHY/ME solutions on c-Si surfaces have been examined experimentally and theoretically. It has been demonstrated, utilizing effective lifetime measurements, that BQ is the active component of the QHY/ME solution. Additionally, HQ will improve in its efficacy given a

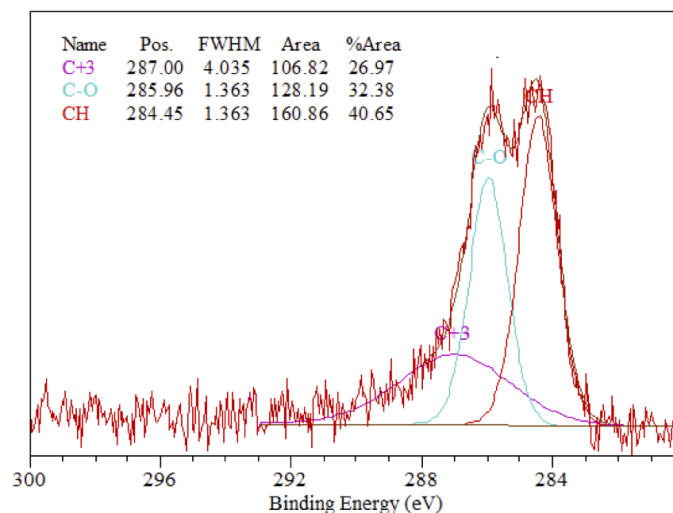


Figure 2.22: C 1s spectrum showing the CH, CO, and -COOH bond peaks for BQ/ME on H-terminated c-Si.

long exposure time of the wafer to the solution, most likely due to a conversion from HQ into BQ and/or $\text{QH}^\bullet$. The hypothesis of an intermediary species – the free radical $\text{QH}^\bullet$ – has been tested and supported through a systematic study of the effects of protons and light exposure on the passivation reaction, as well as theoretical evaluation through the use of DFT. DFT has shown that it is energetically favorable for the molecules to be in a standing up orientation on the c-Si surface. Finally, surface analysis through XPS has shown that there are both methoxy groups and $\text{QH}^\bullet$ bound to the c-Si surface in an approximate 1:1 ratio. The next step is to use the information gathered throughout this experimentation to fabricate a hybrid organic/c-Si device using BQ as a device film.

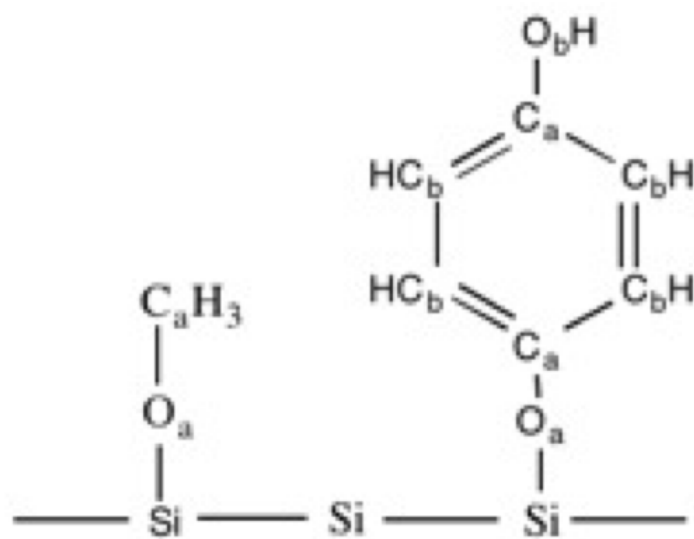


Figure 2.23: A representation of the molecules bonded to the Si surface after passivation. Left: Si-methoxy, Right: Si-QH•

Chapter 3

ORGANIC/INORGANIC DEVICE FABRICATION & CHARACTERIZATION

3.1 Introduction

The implementation of BQ in a hybrid organic/inorganic device requires a full device architecture design. As a monolayer, BQ by itself is not sufficient for the front surface of a device. Contacting the material would prove difficult, and the degradation of the passivation effects observed for BQ/Si out of solution might not survive the full device fabrication and testing process. To protect the BQ monolayer and provide a surface to which front contacts can be applied, Poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) will be employed. This transparent, conductive polymer is a well-known material for use in organic semiconductors. Recently, it has also demonstrated high performance as the organic film for hybrid organic/inorganic devices, which is an important characteristic upon which to build the structures for this work.

3.2 Background & Literature Review

Within the last few years, the idea to develop and fabricate hybrid devices through organic/inorganic material interfaces has become increasingly important [7, 19, 35, 39, 40, 45, 58]. While the organic materials may change, a vast majority of the devices utilize c-Si as the inorganic substrate. Additionally, there is a BQ-based structure from Har-Lavan, et al. [19], but PEDOT:PSS directly contacted with c-Si is the most widely used organic material for this type of device [7, 35, 40, 58].

PEDOT:PSS is a well-known transparent conductive polymer. These features make PEDOT:PSS an ideal material for consideration as the top layer for hybrid PV

devices. The transparency of the film allows light to pass through for absorption in the c-Si, but the conductivity of the film allows for the collection of carriers at the front contacts. The specific transparency and conductivity values of the PEDOT:PSS considered in this work can be found in Chapter 4. Additionally, the band alignments of PEDOT:PSS and c-Si are well-suited for the heterojunction structure. For organic semiconductors, the band structure is composed of the highest occupied molecular orbital (HOMO) level, which is the equivalent of the valence band maximum for inorganic semiconductors, and the lowest unoccupied molecular orbital (LUMO) level, which is the equivalent of the conduction band minimum. When applied to the surface of an n-type c-Si substrate, the PEDOT:PSS layer acts as a p-type material and an electron-blocking film. The HOMO level of the PEDOT:PSS (-4.9eV) is higher than the valence band of the c-Si (-5.17eV), while the LUMO level (-3.3eV) is higher than the conduction band of the c-Si (-4.05eV) [35], as shown in Fig. 3.1. This encourages movement of holes into the PEDOT:PSS film, while reducing any current from electrons passing into the PEDOT:PSS. This material has shown promise for hybrid devices of differing geometries, with the earliest using PEDOT:PSS deposited on nanostructured or non-planar c-Si.

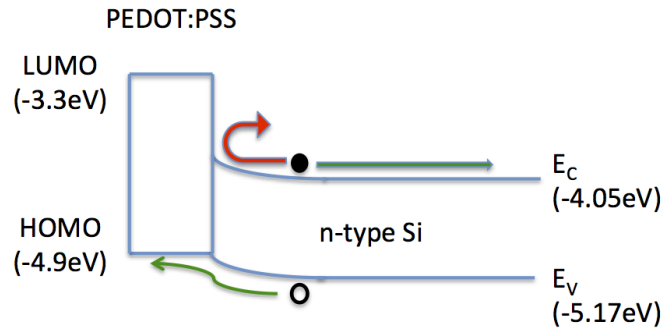


Figure 3.1: Band structure of PEDOT:PSS/c-Si heterojunction.

The use of PEDOT:PSS on nanostructured c-Si surfaces and Si nanowires are early iterations of the hybrid organic/inorganic device [7, 45]. Shiu, et al. deposited

PEDOT:PSS on Si nanowires grown on a bulk Si wafer, combining the nanowires with a planar structure [45]. The combination planar/nanowire structure resulted in a 5.09% efficiency under one-sun. In a similar vein, Chen, et al. deposited PEDOT:PSS on a nanostructured Si surface design to improve light trapping [7]. In addition to implementing surface nanostructures, the evaluation of various PEDOT:PSS thicknesses showed an optimum thickness of 70nm and that the film uniformity and coverage improves with increasing spin speed. Improved film adherence to the c-Si can be achieved by the use of a wetting agent, although the FF decreases due to the inclusion of the nonconductive material into the PEDOT:PSS film. Overall device performance for these structures reaches a 8.84% efficiency. While PEDOT:PSS is a useful material for these nanostructured devices, due to the ability to coat varying geometric surfaces, there are many more devices implementing PEDOT:PSS on planar Si surfaces.

Hybrid devices using PEDOT:PSS on c-Si evaluate different methods for increasing device performance, much of which focuses on improvements to the PEDOT:PSS film. Most use additives, such as dimethyl sulfoxide (DMSO) or ethylene glycol (EG), to improve PEDOT:PSS conductivity. Based upon the morphology of PEDOT:PSS films (i.e. PEDOT:PSS grains surrounded by PSS shells), Pietsch, et al. suggest from a combination of XPS, absorption spectra, and device results, that the addition of secondary additives reduces the thickness of the PSS shell, thereby improving both film conductivity and device V_{oc} and J_{sc} [39]. Pietsch, et al. also discuss the effect of substrate doping level on the V_{oc} of these hybrid devices, namely, that increased dopant density in the n-type Si leads to an increase in V_{oc} [40]. It is also important to note whether the PEDOT:PSS layer does, in fact, block electrons. Nagamatsu, et al. demonstrate that, for the $n=1$ region, where recombination is dominated by the surfaces and bulk of the device, the dark current is due to hole current, not any electron current [35]. This indicates that PEDOT:PSS is an effective electron-blocking layer. Finally, beyond the demonstration of device performance for PEDOT:PSS directly on planar c-Si, others have evaluated the need for an additional layer to help passivate the surface of the c-Si. To this end, Thomas, et al. have added a thin layer of native SiO_x

to passivate the Si surface prior to the deposition of PEDOT:PSS [58]. This film, at 1.5–1.8nm thick, has not only demonstrated an improvement in device performance, but improves the ability for PEDOT:PSS to wet the surface and create a uniform film. While all of the devices mentioned thus far use PEDOT:PSS as the organic layer, there is another material that has been used to fabricate devices – HQ/ME.

For the BQ device, a full standalone structure has not been fabricated. Rather, Har-Lavan, et al. passivated the c-Si with a HQ/ME solution, leaving a monolayer of HQ and methoxy molecules bonded to the surface [19]. These devices are contacted with a Hg drop, and standard I-V measurements are performed. The resulting devices are diodes with up to 585 mV of V_{oc} , and FF in the 75-80% range. An important observation is the same as seen for the PEDOT:PSS/Si devices – increasing substrate dopant density increases V_{oc} . From this point, we look to implement a combination of the work found in literature to develop a standalone PEDOT:PSS/BQ/Si solar cell.

In order to fabricate this structure, the planar PEDOT:PSS/Si devices will be combined with the BQ/Si device, and the BQ will be used in a similar fashion to the SiO_x layer from Thomas, et al. [58]. This device will result in a PEDOT:PSS/BQ/Si stack. In the literature, there are multiple configurations for device design, and this work will follow the method found in Nagamatsu, et al. [35]. Al will be used as the back contact to Si, and Ag will be used for the front contact to PEDOT:PSS. Based on the literature, the PEDOT:PSS films will be prepared with the solvent DMSO for increased conductivity, and will initially deposit a 70nm thick film. Additionally, because the BQ/ME passivation makes the surface of the Si hydrophilic, no surfactants will be used to enhance surface adhesion. The resulting device will be a standalone solar cell structure, designed to implement a BQ passivation layer, and demonstrate the functionality of BQ in a device.

3.3 Experimental Methods

The devices fabricated here will follow the general structure of the previously demonstrated PEDOT:PSS/c-Si device from Nagamatsu, et al. discussed in Section 3.2

Table 3.1: c-Si Fabrication Wafer General Specifications

Type	Dopant	Orientation	Surface	Thickness	Dimensions
n	Phos.	<100>	SSP	500 μm	100mm

[35]. Rather than having PEDOT:PSS directly in contact with the c-Si substrate, a monolayer of the passivant BQ will be applied to the c-Si first, followed by a layer of PEDOT:PSS. The generalized method used to fabricate the devices proceeds as follows, with details of adjustments to device structure specifics noted as necessary in Section 3.4.

3.3.1 Wafer Characterization

Prior to fabricating wafers into devices, two important characteristics were measured – resistivity and effective lifetime. The resistivity of each wafer was measured using four-point probe and confirmed using the Sinton lifetime tester, which will return a measured resistivity as part of each test. Additionally, the effective lifetime of each wafer was determined using the Sinton lifetime tester. No wafers were cleaned or altered in any way prior to these measurements, and the specifications are reflective of the wafer characteristics straight from the cassette. The wafer characteristics common to all of the wafers are shown in Table 3.1, and the characteristics unique to each wafer (i.e. resistivity and lifetime) are noted where applicable.

3.3.2 Back Contact Ebeam Evaporation

Once deposited, the organic films for these devices will begin to degrade. Additionally, the PEDOT:PSS film is easy to scratch and damage. Due to these considerations, it was determined that the back contact of the device should be evaporated as the first step in device fabrication. The time spent in the chamber for pumpdown and evaporation, then, would not also be time during which the organics are degrading. Damage to the front surface films will also be reduced, as the PEDOT:PSS will

only come into contact with one potentially-damaging item during fabrication – the shadow mask for front contact evaporation – rather than two surfaces – the shadow mask during front contact evaporation and the magnetic holder during back contact evaporation.

Prior to evaporation of the contacts, the wafers were cleaned in Piranha (5 minutes), DI H₂O (5 minutes), and dilute HF (2 minutes). At the completion of this cleaning step, the samples were loaded into the ebeam for full back surface wafer coverage with the chosen metallization scheme. The wafers were not annealed further after deposition.

3.3.3 Surface Passivation

After deposition of the back contacts, the p-n junction structure could begin to be formed. The first step for this was passivation of the c-Si sample with BQ/ME as described in Chapter 2.

First, the substrates with back contacts were cleaned to prepare the surface for passivation. An important change, however, was made to the cleaning procedure. The Piranha solution used previously for BQ/ME passivation was at the newly-prepared temperature (which can reach up to 120°C), which is too aggressive for the back contact to survive the cleaning procedure. In order to protect the integrity of the back contact, the Piranha was allowed to cool to slightly higher than room temperature before sample immersion and cleaning for 5 minutes. The sample was then immersed in DI H₂O for 5 minutes, just as before. The final step - dilute HF immersion - only took place long enough for the wafer to become hydrophobic (indicating full surface hydrogen termination), no more than 30 seconds [17, 30]. Again, the duration of this step was reduced in order to protect the integrity of the contact.

Once the wafer surfaces were cleaned and prepared for passivation, the samples were immersed in 0.01M solutions of BQ/ME and held in solution under full ambient laboratory light conditions for a minimum of two hours.

3.3.4 PEDOT:PSS Deposition

The final device layer is a PEDOT:PSS film deposited on top of the BQ monolayer on the surface of the c-Si. The PEDOT:PSS was prepared as a new batch for each individual sample, then spin-coated onto the surface of the passivated wafer.

For this work, a 1.0-1.3% solid content aqueous dispersion with a PEDOT:PSS ratio by weight of 1:2.5 was employed (Clevios PH1000). This particular PEDOT:PSS is a high conductivity material, however, the addition of a solvent is required in order to reach the conductivity values specified by the manufacturer. In order to increase the conductivity of the films, a mixture of 10% w/w DMSO PEDOT:PSS was prepared.

After preparation of the PEDOT:PSS mixture, the wafer sample was removed from the BQ/ME solution, quickly rinsed in a beaker of DI H₂O to remove any large surface contaminants, and dried with N₂. The PEDOT:PSS material was then applied over the surface of the wafer while stopped on the spinner. Once the coating was applied, the wafer was spun to the desired film thickness. For this work, 2250rpm resulted in a film thickness of 65-70nm, and 4000rpm resulted in a film thickness of approximately 50nm. The film thicknesses were measured using X-ray reflectivity (XRR) [11, 41]. After PEDOT:PSS deposition, the sample was removed from the spinner and placed in a N₂ atmosphere to dry prior to front contact metallization.

3.3.5 Front Contact Evaporation

The PEDOT:PSS films were allowed to dry in a N₂ atmosphere for a half hour. Then, the samples were mounted onto a magnetic holder for front contact metallization. In order to create the front contact grid pattern, a shadow mask was used. The vacuum required for evaporation facilitates the drying process, so the PEDOT:PSS film is believed to dry more fully during the 2-hour pumpdown duration used for the ebeam evaporator to reach the proper vacuum [3]. For all devices in this work, 100nm of Ag was evaporated as the front contact metallization. Immediately after unloading from the evaporator, device characterization was performed.

3.4 Results & Discussion

The presentation of device results begins with the fabrication and characterization of the first generation base device. This discussion includes the structure of the device, film thicknesses, and a comparison with device results from the literature. Then, new devices were fabricated to evaluate methods for improving V_{oc} , J_{sc} , and FF. The effectiveness of each method is addressed. Finally, using the results from these experiments, a hero device was fabricated and characterized so as to identify areas for further improvement.

3.4.1 Base Device

The structure of the base device is designed to combine the PEDOT:PSS/c-Si device found in literature with the lifetime experiments performed using BQ/ME. The substrate used was comparable to the wafer used for passivation testing on n-type substrates, and the device was fabricated according to the methods described in Section 3.3. The specifics of the device structure are shown in Fig. 3.2.

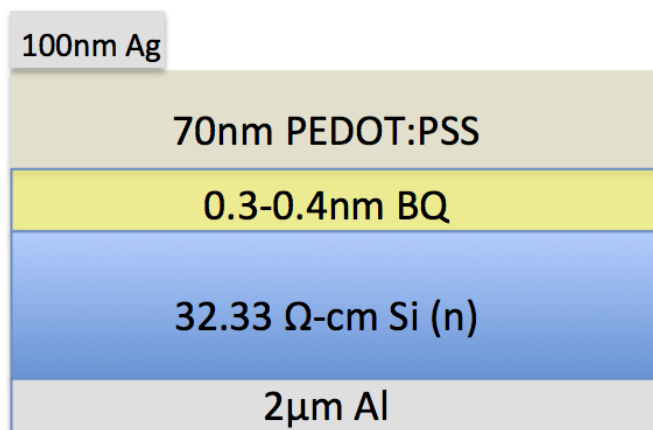


Figure 3.2: Structure of Base PEDOT:PSS/BQ/c-Si device.

For this device, the resistivity of the substrate was $32.33 \Omega\text{-cm}$, which is at the higher end of the resistivity used for BQ/ME passivation testing. The device results

Table 3.2: Non-isolated device results of base PEDOT:PSS/BQ/c-Si device.

Device	$J_{sc} \left(\frac{mA}{cm^2} \right)$	$V_{oc} (mV)$	FF	η
Lit. [35] 2-4 $\Omega - cm$ No BQ	27.8	570	0.73	11.7%
Base 32.33 $\Omega - cm$ BQ	21.11	321	0.42	2.83%

are reported for the non-isolated here device from this sample using an aperture to illuminate only the device area in question. This was done in order to establish baseline device characteristics without the interference of edge effects, and the performance results are shown in Table 3.2 under 1 sun illumination, and the Light JV curve is shown in Fig. 3.3.

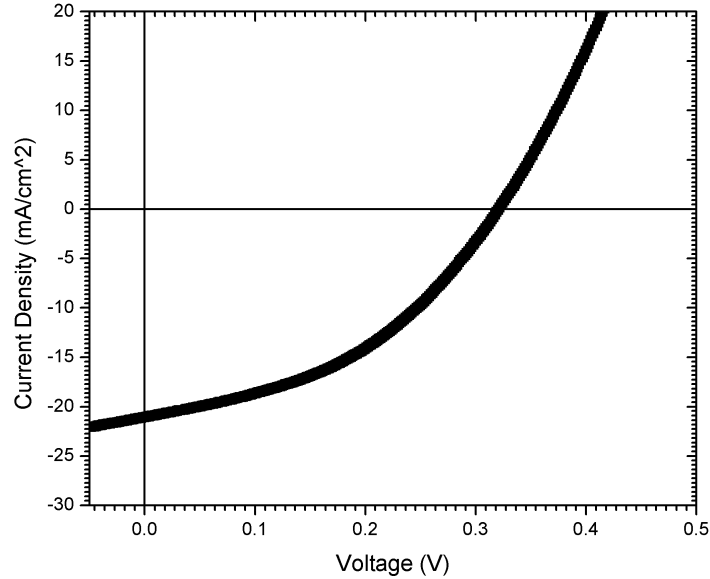


Figure 3.3: Light JV curve of Base PEDOT:PSS/BQ/c-Si device.

As we can see from the base device results, the structure does not perform as

well as the device from literature in all categories. The most important thing to note at this stage, however, is that there is rectification. Inserting a layer of BQ in between the c-Si and PEDOT:PSS in place of a 1.5-1.8nm SiO₂ layer does allow the structure to continue to function as a diode [58].

Initial observations of the JV curve, and the low FF , indicates that the device is suffering from both low shunt (R_{sh}) and high series (R_s) resistance. It is difficult, however, to draw any conclusions from exact R_{sh} ($\sim 37 \Omega - cm^2$, measured) and R_s ($\sim 0 \Omega - cm^2$, measured) data from the non-isolated device results [21]. This particular structure did not survive the isolation process (being cleaved from the substrate using a diamond scribe), so no isolated performance evaluation is possible. Future devices discussed within this chapter are isolated so that a full characterization may be performed.

3.4.1.1 Base Device Conclusions

For this initial device, the most important performance factor is the proof of concept. This device is the first implementation of BQ as a device layer, and there remained the possibility that the PEDOT:PSS/BQ/c-Si device would not function as a diode due to the BQ layer. As demonstrated with this device, however, BQ is able to be used as a device layer with carriers able to pass through the BQ from the c-Si to the PEDOT:PSS for collection. From this point, methods to improve the device performance will be evaluated, beginning with V_{oc} .

3.4.2 Method for Increasing Open-circuit Voltage

The first device performance parameter evaluated for improvement is V_{oc} . The V_{oc} of the base device is approximately 150mV lower than the literature device, indicating room for much improvement. In the literature, it has been demonstrated that substrate resistivity has a large impact on the V_{oc} of hybrid device structures. Diodes made from HQ on c-Si display an increase of approximately 70mV in V_{oc} for every order of magnitude decrease in substrate resistivity [19], relating to the ability to increase the

Table 3.3: Non-isolated device results of PEDOT:PSS/BQ/c-Si device on substrates with different resistivity.

Device	$J_{sc} \left(\frac{mA}{cm^2} \right)$	$V_{oc} (mV)$	FF	η
Lit. 2–4 $\Omega - cm$ [35]	27.8	570	0.73	11.7%
Base 32.33 $\Omega - cm$	21.11	321	0.42	2.83
23.03 $\Omega - cm$	22.73	386	0.44	3.84%
16.91 $\Omega - cm$	23.32	404	0.42	3.97%
1.22 $\Omega - cm$	22.29	437	0.42	4.08%

distance between the quasi-Fermi levels for devices under illumination. For this next set of devices, then, we evaluate the change in V_{oc} with changes in substrate resistivity.

In order to examine only the effect of substrate resistivity, the device structure and metallization remains the same as that of the base device. The PEDOT:PSS film is 65-70nm thick and back contact metallization is 2um of Al. The substrate resistivity values used for this set of experiments were 23.03, 16.91, and 1.22 $\Omega - cm$. The non-isolated device results are shown in Table 3.3.

Based on these initial results, it appears that the V_{oc} does, in fact, improve with reduced substrate resistivity. The increase in V_{oc} is comparable to the results found in literature, increasing by approximately 100mV for a decrease in resistivity from 32 to 1.22 $\Omega - cm$ [14, 19]. The J_{sc} and FF do not appear to change to follow any trend, so the increase in efficiency can be attributed to the increase in V_{oc} . As mentioned previously, however, these non-isolated results are shown only to display a trend. The isolated device results for two of the samples are shown in Table 3.4, including a comparison with the pre-isolation results in order to see the changes in device performance characteristics.

As shown in Table 3.4, there is little change in J_{sc} between the pre- and post-isolation devices, an increase in V_{oc} , and a decrease in FF . For the device using the 23.03 $\Omega - cm$ wafer, the decrease in J_{sc} and FF was enough to reduce the overall device efficiency, despite a 75mV increase in V_{oc} after isolation. For the 1.22 $\Omega - cm$ device,

Table 3.4: Isolated device results of PEDOT:PSS/BQ/c-Si device on substrates with different resistivity, and a comparison with pre-isolation results.

Device	Area (mm^2)	J_{sc} ($\frac{mA}{cm^2}$)	V_{oc} (mV)	FF	η
Lit. [35] 2-4 $\Omega - cm$		27.8	570	0.73	11.7%
Base 32.33 $\Omega - cm$ Pre-Iso		21.11	321	0.42	2.83
23.03 $\Omega - cm$ Pre-Iso		22.73	386	0.44	3.84%
23.03 $\Omega - cm$ Isolated	18.89	21.43	461	0.30	2.96%
16.91 $\Omega - cm$ Pre-Iso		23.32	404	0.42	3.97%
1.22 $\Omega - cm$ Pre-Iso		22.29	437	0.42	4.08%
1.22 $\Omega - cm$ Isolated	17.3429	24.90	527	0.37	4.86%

however, an increase in both J_{sc} and V_{oc} was enough to counteract the decrease in FF to result in an efficiency increase. The one thing these devices have in common is a decrease in FF , which is clearly hurting device performance. In order to more fully understand the factors affecting FF , JV curve analysis is required.

3.4.2.1 JV Analysis for V_{oc} -Focused Device

For this analysis, both Light and Dark JV curves were examined using the method detailed by Hegedus and Shafarman [21]. The isolated 1.22 $\Omega - cm$ device was the focus, and the resulting analysis is as follows, beginning with Fig. 3.4.

As can already be seen in the Light and Dark JV curves of the 1.22 $\Omega - cm$ device, there is a problem with both R_{sh} and R_s . Both curves have a poor shape, however, the important feature to note is the slight S-shape characteristic around the V_{oc} of the Light JV curve. This particular feature was also observed in the 23.03 $\Omega - cm$ device, and is indicative of majority carrier blocking. Further analysis and

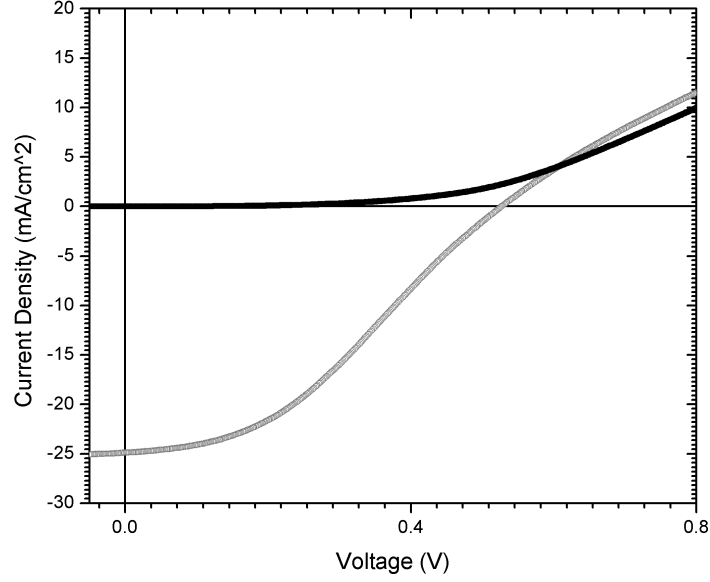


Figure 3.4: Light and Dark JV curves of $1.22 \Omega - cm$ device.

comparisons between device structures will be necessary in order to determine the nature and potential cause of this trend.

In order to first determine the R_{sh} characteristics of the device under illumination and in the dark, the curves shown in Fig. 3.5 are plotted. Plotting dJ/dV as a function of voltage produces a curve that should become linear within the reverse bias region of the voltage. The value of this curve in the reverse bias region is the shunt conductance ($G = \frac{mS}{cm^2}$), the inverse of which will give the R_{sh} for the device. As can be seen in this set of curves, the data does become linear within the reverse bias region. Additionally, one can see that the illuminated data is noisy, although it still follows the proper trend. For this reason, the R_{sh} value was taken to be the average of the values in the reverse bias region. The results show that $G_{dark} = 0.04 \frac{mS}{cm^2}$ and $G_{light} = 6.3 \frac{mS}{cm^2}$, with $R_{shdark} = >24000 \Omega - cm^2$ and $R_{shlight} = 159 \Omega - cm^2$. Solar cell device performance improves as $R_{sh} \rightarrow \infty$, so R_{sh} of the device when illuminated is one hindrance to device performance. Again, this trend is also observed in the $23.03 \Omega - cm$ device. It is possible that changes in the PEDOT:PSS film upon illumination

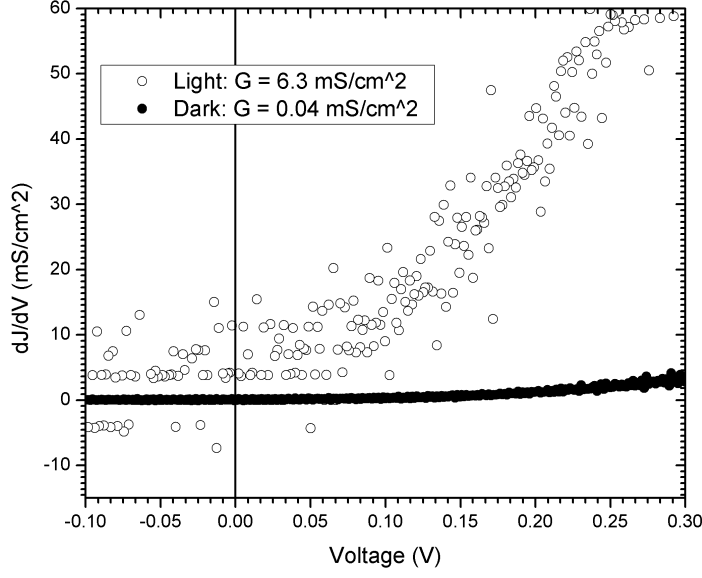


Figure 3.5: Plot for the characterization of shunt resistance for the $1.22 \, \Omega - cm$ device.

are activating shunt pathways not observed in the dark curve analysis.

After finding the R_{sh} values, the next step in the analysis is the determination of the R_s for the light and dark performance of the device. In order to do this, the dV/dJ is plotted against $(J + J_{sc})^{-1}$. The resulting curves can be seen in Fig. 3.6. For this set of curves, the R_s information is found by producing a linear fit of each data set. The y-intercept of the fit line is the R_s for the respective illumination situation. For this device $R_{s\text{dark}} = 25.87 \, \Omega - cm^2$, and $R_{s\text{light}} = 9.52 \, \Omega - cm^2$. The higher series resistance is not surprising when looking back at the JV curves in Fig. 3.4, as it can be qualitatively seen that the dark JV curve shows a higher R_s trend. It is important to note, however, that the dark data is more noisy than the light data for this curve, which may be inflating the dark R_s value. There is also an interesting characteristic in the light curve for this particular analysis, toward the origin. Rather than continuing linearly, the light dV/dJ curve jumps upward (a feature observed in both devices). A similar phenomenon is presented by Hegedus and Shafarman, and is attributed to blocking behavior [21]. This curve feature corroborates the S-shape seen in the light

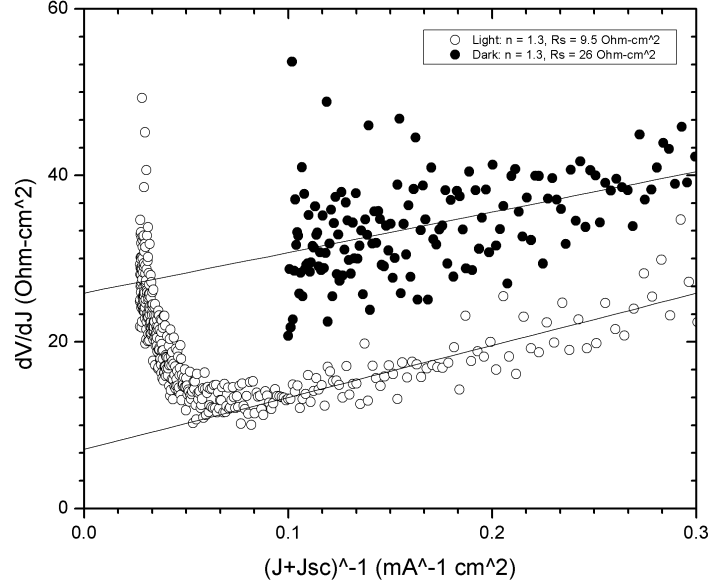


Figure 3.6: Plot for the characterization of series resistance for the $1.22 \Omega\text{-cm}$ device.

JV curve, and further suggests some part of the device is causing blocking. As before, it is unclear at this point as to what such behavior can be attributed, but the second manifestation of blocking characteristics requires that serious consideration be given to possible causes.

An additional feature of this particular curve set is the determination of ideality factor (n), using the slope of the linear fit to the curve to calculate the values for both light and dark. For this device, both n_{light} and n_{dark} are equal to 1.3.

The final device characteristics to be determined are the dark saturation current (J_0) and the ideality factor. A logarithmic plot of $J + J_{sc} - GV$ on the vertical axis with a linear horizontal axis of $V - RJ$ results in the curves shown in Fig. 3.7. The curves are fit in the linear region of each condition, respectively. The slope of the fit is equal to $\frac{q}{nkT}$, with k as Boltzmann's constant, T as temperature (300K), and q as the electronic charge. The y-intercept is equal to J_0 . For this plot, the device is not well behaved under either lighting condition. Due to this, it is difficult to say with certainty either the ideality factor or the J_0 of the device. If a linear fit is done of specific regions of the

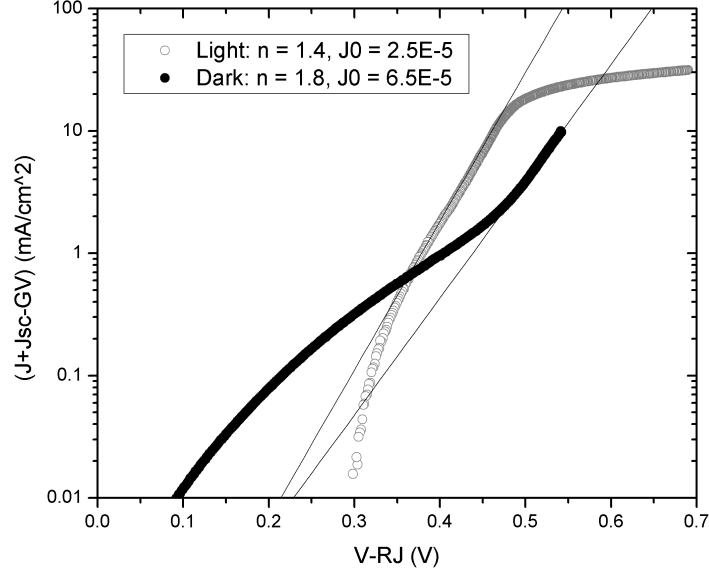


Figure 3.7: Plot for the determination of J_0 and ideality factor for the $1.22 \Omega - cm$ device.

plot, as shown in Fig. 3.7, we can determine ideality factors and J_0 terms. For the dark case, the ideality factor is 1.76 and $J_0 = 6.5 \times 10^{-5} \frac{mA}{cm^2}$. For the illuminated case, the ideality factor is 1.38 and $J_0 = 2.5 \times 10^{-5} \frac{mA}{cm^2}$. If we compare the ideality factors found using these curves with those from Fig. 3.6, the values are close, lending support to the ideality factor evaluation. The dark and light values for J_0 are also similar, however, it is necessary to point out that the deviations of the $J + J_{sc} - GV$ curves lessen the reliability of the exact values. The J_0 terms determined here will, therefore, be used largely for comparison with other devices rather than as strict device characteristics.

Through this analysis, we have found that decreasing the resistivity of the substrate does increase the V_{oc} of the devices. We have also found, after improving the device performance enough to distinguish important JV characteristics, there is a blocking behavior shown in both the JV and $\frac{dV}{dJ}$ vs $(J + J_{sc})^{-1}$ curves. The next set of devices will evaluate the effect a thinner PEDOT:PSS film has on J_{sc} .

3.4.3 Short-circuit Current Analysis

The current produced in a device is directly related to the number of photons absorbed within the structure. Often, basic models will assume each photon absorbed by the device is converted into a single carrier, and the sum of all carriers becomes device current. In order to increase current, then, one approach is to increase the number of photons absorbed in the device.

There are two layers on the front surface of this structure through which photons must pass in order to be absorbed in the c-Si – the PEDOT:PSS and the BQ. Both of these materials have a respective absorption coefficient for each wavelength, which indicates how far into a material a photon will travel before being absorbed. If the absorption coefficient indicates that a photon will be absorbed at a depth that falls within the thickness of either the PEDOT:PSS or the BQ layer, it is probable that the photon will be absorbed in one of these materials before being able to pass through for absorption in the c-Si. In order to maximize the number of photons that pass through these first two layers, then, a reduction in thickness of PEDOT:PSS should theoretically reduce the number of photons able to be absorbed in these unwanted regions.

In this device, it is only possible to reduce the thickness of the PEDOT:PSS layer. The BQ film is one monolayer, therefore, its thickness cannot be reduced. For the reduction of the PEDOT:PSS thickness, however, we used a spin speed of 4000 rpm to produce a 50nm film. The isolated device results are shown in Table 3.5, which displays a comparison of 70nm and 50nm thick PEDOT:PSS devices.

Based on these device results, the reduction of the PEDOT:PSS thickness did not, in fact, increase the J_{sc} of the devices. To determine the cause of this reduction in performance, we first consider the factors that affect J_{sc} . Chief among these is the optical properties of the device. As mentioned before, reducing the thickness of the PEDOT:PSS was intended to increase J_{sc} by allowing more photons to pass through the film into the c-Si. There is another, unintended consequence to altering the PEDOT:PSS thickness, however. When returning to the literature, PEDOT:PSS

Table 3.5: Isolated device results of PEDOT:PSS/BQ/c-Si device on substrates with different resistivity and a 50nm PEDOT:PSS layer, compared with 70nm devices.

Device	Area (mm^2)	J_{sc} ($\frac{mA}{cm^2}$)	V_{oc} (mV)	FF	η
Lit. [35] 2-4 $\Omega - cm$		27.8	570	0.73	11.7%
Base 32.33 $\Omega - cm$ Pre-Iso		21.11	321	0.42	2.83
23.03 $\Omega - cm$ 70nm	18.89	21.43	461	0.30	2.96%
23.03 $\Omega - cm$ 50nm	16.38	9.85	148	0.39	0.56%
16.91 $\Omega - cm$ 50nm	12.06	21.26	452	0.33	3.18%
1.22 $\Omega - cm$ 70nm	17.3429	24.90	527	0.37	4.86%
1.22 $\Omega - cm$ 50nm Isolated	17.09	19.95	482	0.39	3.70%

in structures such as this one is discussed as having anti-reflection coating (ARC) properties [58]. If this is the case, altering the thickness of the PEDOT:PSS would have an affect on the reflection at the front surface, in addition to the transmission of photons. The optical losses that are caused by increased reflection at the front surface of the device could account for the decrease observed in J_{sc} .

In order to determine the effects of PEDOT:PSS as an ARC for the front surface of the device, the Opal 2 simulator managed by PV Lighthouse was utilized. The complex index of refraction data for PEDOT:PSS was uploaded to the software, and the thickness of the film above a c-Si substrate was changed between 70nm and 50nm. The results are shown in Figs. 3.8 and 3.9.

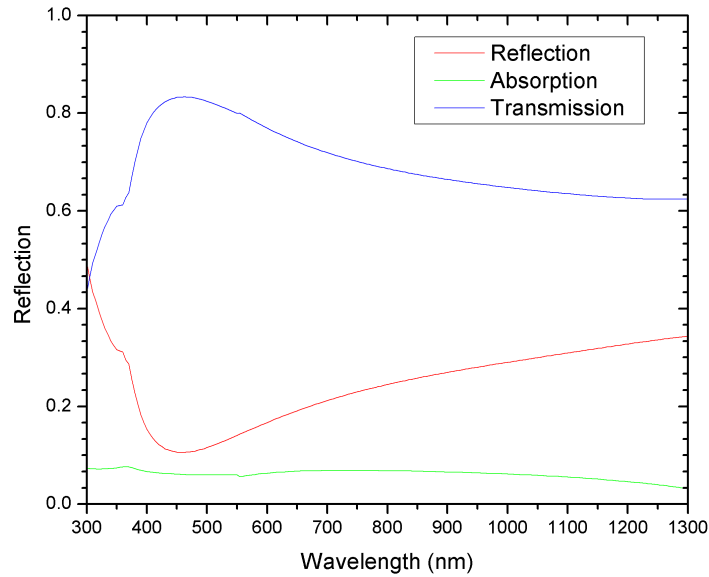


Figure 3.8: Reflection, Transmission, and Absorption Graph of 70nm PEDOT:PSS on c-Si.

What can be observed from this analysis, is that the reflection of the structure does increase when the thickness of the PEDOT:PSS film decreases. For a 70nm film, enough photons are absorbed in the substrate to generate $31.65 \frac{mA}{cm^2}$ of current. For a 50nm film, however, a current of $30.56 \frac{mA}{cm^2}$ is possible, accounting for an approximate $1.1 \frac{mA}{cm^2}$ reduction. The magnitude of the theoretical reduction in current is comparable

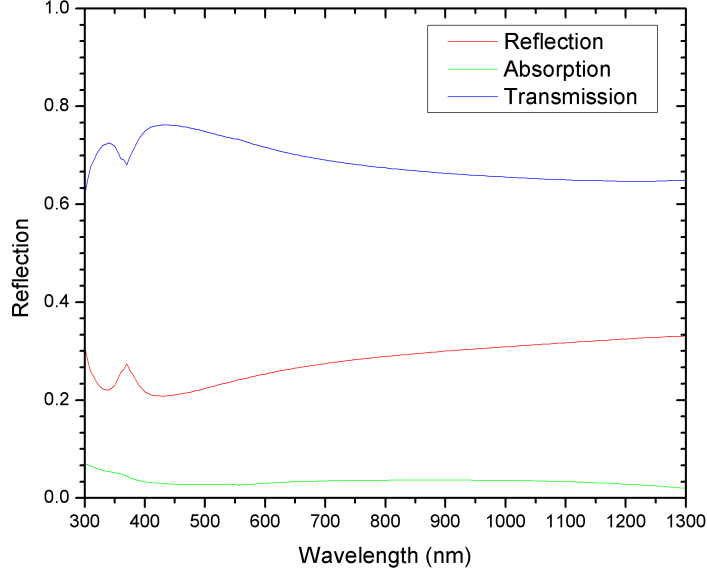


Figure 3.9: Reflection, Transmission, and Absorption Graph of 50nm PEDOT:PSS on c-Si.

to the J_{sc} reductions observed in the experimental devices, indicating that the increased reflection of the thinner PEDOT:PSS film is likely the root cause.

Once a trend for the effect of PEDOT:PSS thickness on J_{sc} was determined, a new back contact metallization scheme was tested to see if improvements in series resistance could be accomplished.

3.4.4 Metallization Analysis

In order to examine the effectiveness of using Al as the back contact for the devices, a Ti/Pd/Ag back contact was used. The latter is a more common metallization scheme for contacting n-type Si, which is the substrate for these devices. In order to perform the metallization analysis, devices were fabricated using a 70nm thick PEDOT:PSS layer on the front surface and 20nm/20nm/1um Ti/Pd/Ag was evaporated for the back contact. The performance results for these devices are shown in Table 3.6.

As can be seen from these results, there is no clear trend of either improvement in performance or reduction in performance due to the change in back contact

Table 3.6: Isolated device results of PEDOT:PSS/BQ/c-Si device on substrates with different resistivity and Ti/Pd/Ag back contacts, compared with Al back contacts .

Device	Area (mm^2)	J_{sc} ($\frac{mA}{cm^2}$)	V_{oc} (mV)	FF	η
Lit. [35] 2-4 $\Omega - cm$		27.8	570	0.73	11.7%
Base 32.33 $\Omega - cm$ Pre-Iso		21.11	321	0.42	2.83
23.03 $\Omega - cm$ Al	18.89	21.43	461	0.30	2.96%
23.03 $\Omega - cm$ Ti/Pd/Ag	13.89	20.58	482	0.34	3.35%
16.91 $\Omega - cm$ Ti/Pd/Ag	16.15	22.51	473	0.27	2.91%
1.22 $\Omega - cm$ Al	17.3429	24.90	527	0.37	4.86%
1.22 $\Omega - cm$ Ti/Pd/Ag	22.49	15.66	381	0.23	1.35%

metallization. Other than the $1.22\ \Omega - cm$ device, which appears to be an outlier in its significant reduction in performance, there is a mix of performance parameter increases and decreases. Curve analysis of the devices using the method described in Section 3.4.2 does not provide any further indication of a trend in device performance. The R_{sh} , R_s , and J_0 values are all comparable between devices of either metallization.

The ultimate effect of changing the metallization from Al to Ti/Pd/Ag is not apparent at this point. Thorough device analysis does not provide any key performance parameter changes. While not fully successful, it appears that some performance increase is possible through a change in metallization scheme for the back contact. Further study is required in order to evaluate possible configurations for improved performance.

3.4.5 Final Device Design

For the final device design, all of the results from the previous three analyses were evaluated to determine the optimum combination, at this stage, of structural parameters to result in the highest performance. A low resistivity wafer was used as the substrate, the PEDOT:PSS film was deposited at a thickness of 70nm, and Al was used as the back contact for the device. The structure is shown in Fig. 3.10, and performance results are shown in Table 3.7.

From these results, we observe an overall increase in device performance. While there is a slight decrease in J_{sc} , there are increases in V_{oc} and FF resulting in a final device performance of 5.02%. This device has reached the same V_{oc} as the literature device, with improvements that can still be made to improve J_{sc} and FF . In order to determine sources of performance degradation, curve analysis is performed, and the results are shown in Figs. 3.11 through 3.14.

The curve analysis shows that there are still parasitic issues with series and shunt resistance. Additionally, there is still the manifestation of the blocking behavior seen in earlier devices, however, the level of blocking is not as strong in the final device. This blocking behavior is negatively affecting both R_s and FF , which, in turn, is reducing

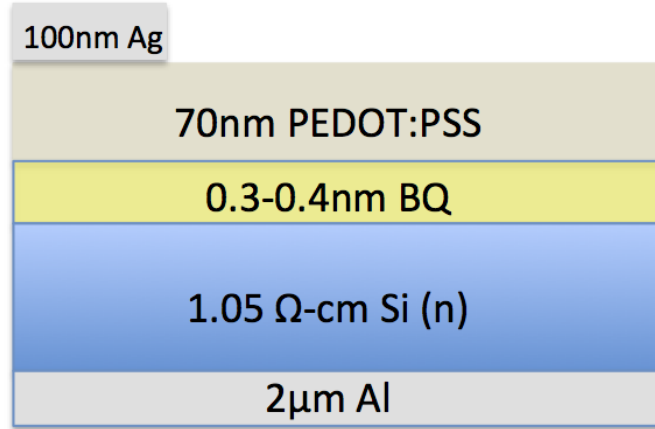


Figure 3.10: Final PEDOT:PSS/BQ/Si Device Design.

the possible device performance. In order to address the issue of blocking, we must first determine the cause. In the following section, we will examine all of the devices in order to determine how varying device elements affect the strength of the blocking behavior. This will help lead to solutions for how to eliminate blocking and improve overall device performance.

3.4.6 Blocking Behavior

The largest impediment to device performance at this stage is the blocking behavior observed in all of the devices fabricated thus far. Blocking issues have been discussed in the literature, and occurs where band alignment issues (as can often be found at heterointerfaces) hinder movement of carriers through the device [23]. For this structure, the presumed band alignment is shown in Fig. 3.15.

The structure of this device relies on the ability to extract holes through the BQ and PEDOT:PSS layers while blocking the movement of electrons through those same layers. The band misalignment between the Si conduction band and BQ LUMO level is, therefore, not an issue. Theoretically, this difference in bands should ensure that electrons do not move toward the front of the device. The misalignment of the

Table 3.7: Final performance results of optimized PEDOT:PSS/BQ/c-Si device, compared with devices of other resistivities.

Device	Area (mm^2)	J_{sc} ($\frac{mA}{cm^2}$)	V_{oc} (mV)	FF	η
Lit. [35] 2–4 $\Omega - cm$		27.8	570	0.73	11.7%
Base 32.33 $\Omega - cm$ Pre-Iso		21.11	321	0.42	2.83
23.03 $\Omega - cm$ Iso	18.89	21.43	461	0.30	2.96%
16.91 $\Omega - cm$ Pre-Iso		23.32	404	0.42	3.97%
1.22 $\Omega - cm$ Iso	17.3429	24.90	527	0.37	4.86%
<i>Final - 1.05 $\Omega - cm$ Iso</i>	<i>20.27</i>	<i>18.57</i>	<i>572</i>	<i>0.47</i>	<i>5.02%</i>

Si valence band and BQ HOMO level are a different matter. Because the holes have to move down in energy to go from the Si to the BQ, this misalignment is an energy barrier for the movement of holes. Unlike the misalignment preventing the movement of electrons into the BQ, however, this hindrance of hole movement is not beneficial to device performance and is the most likely cause of the observed phenomenon.

Now that we have identified the likely source of the blocking behavior, we can begin to evaluate methods to aid in hole movement from the Si to the BQ. One way to improve the alignment of the Si valence band and BQ HOMO level is to reduce the barrier height by altering substrate doping density. For an n-type Si substrate, increasing the dopant density raises the Fermi level. When the “new” Fermi levels align, the barrier height between the c-Si valence band and the BQ HOMO level is reduced. A higher dopant density should, therefore, result in a reduction in the magnitude of blocking.

In order to show this relationship, the peaks observed in the $\frac{dV}{dJ}$ curve can be used to compare blocking behavior for the device. Using the maximum value for the

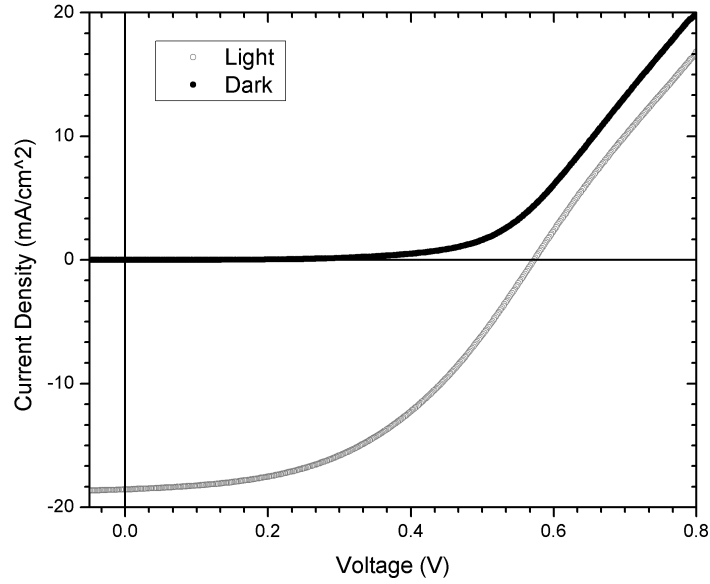


Figure 3.11: Light and Dark JV curves of final device.

peak, and plotting it against wafer resistivity, we obtain Fig. 3.16. The trend for blocking behavior does follow that increased dopant density of the substrate reduces the magnitude of the “blocking peak”, which implies a decrease in the effect of blocking. Another trend is observed, however, indicating that PEDOT:PSS thickness also plays a role in the degree of blocking observed. In Fig. 3.16, we observe that, aside from the devices on $23.03 \, \Omega - cm$ substrates, a reduction in PEDOT:PSS thickness strengthens the blocking behavior.

3.4.7 Device Degradation

One final consideration for these devices is the time over which the organic materials - and, therefore, the devices themselves - degrade. When not being tested, the devices are maintained in a N_2 atmosphere, which is intended to slow the degradation of the organic films. Due to constraints of the fabrication and testing timeframe of the devices, there is no data displaying one single device’s degradation over a 14-day timespan. Additionally, the devices degraded at different rates. In order to assess the

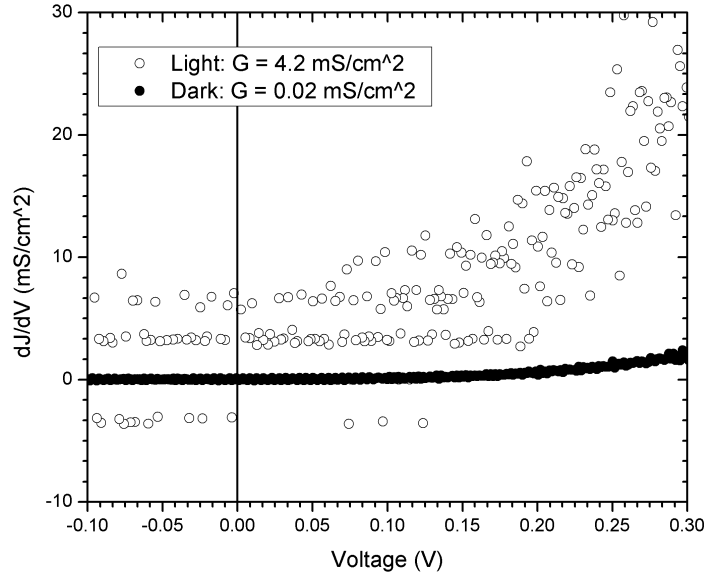


Figure 3.12: Plot for the characterization of shunt resistance for the final device.

generalized degradation of these devices, the following procedure was used: A batch of devices was tested, making note of the V_{oc} , J_{sc} , FF , and η of each device, as well as the date of testing. The decrease in performance is recorded as the difference between the new test value and the value measured immediately after fabrication for each device. These performance decrease values are then averaged for all devices tested at the same number of days since fabrication (i.e. all devices tested 10 days post-fabrication are averaged together, all devices for 11 days, etc.), and plotted accordingly. The results are shown in Fig. 3.17.

Based on these findings, it appears that the V_{oc} is the performance factor that degrades to the largest degree, followed by J_{sc} , FF , and η , in that order. It is also apparent that, despite significant decreases in performance for some parameters, the devices still function for a much longer period of time than expected post-fabrication.

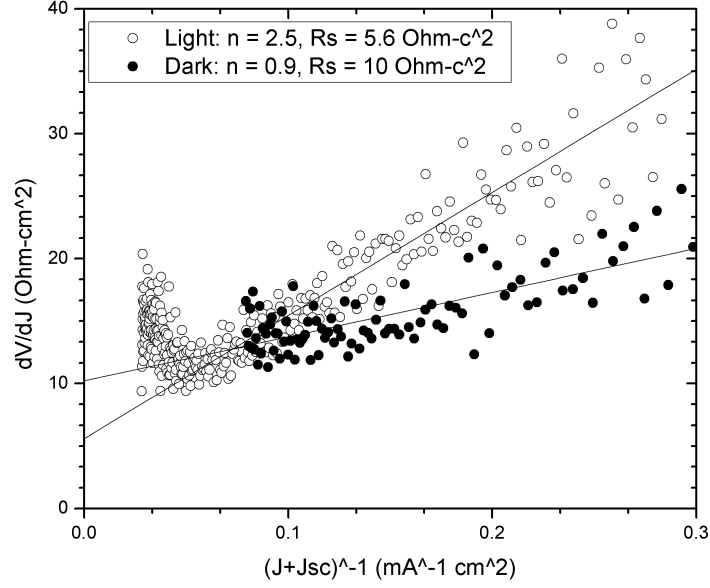


Figure 3.13: Plot for the characterization of series resistance for the final device.

3.5 Conclusions

Hybrid PEDOT:PSS/BQ/c-Si devices have been fabricated and analyzed. First, BQ has been demonstrated to act as a functional device layer, producing active solar cells. The effects of substrate resistivity, PEDOT:PSS thickness, and back contact metallization are evaluated. In order to increase V_{oc} of the devices, it is necessary to reduce the resistivity of the substrates. It is also demonstrated that the PEDOT:PSS film acts as an ARC, and the thickness of the layer directly affects the reflection from the front surface of the device. A 70nm PEDOT:PSS film is shown to have a lower surface reflection than a 50nm thickness, which corroborates the higher J_{sc} of the devices with 70nm films. Two different back metallization schemes were evaluated - Al and Ti/Pd/Ag. There is no clear indication of any improvements to device performance from the Ti/Pd/Ag devices, however, improved metallization is a subject of interest for future device work. The blocking behavior of the devices is also discussed, including the effects of substrate resistivity and PEDOT:PSS film thickness. An increase in both substrate dopant density and PEDOT:PSS film thickness reduce the magnitude of the

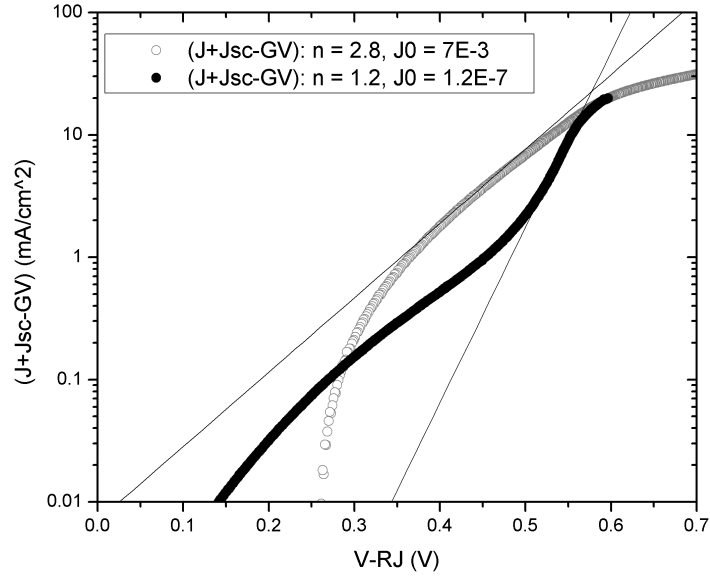


Figure 3.14: Plot for the determination of J_0 and ideality factor for the final device.

blocking behavior. The change in substrate resistivity addresses blocking through the decrease(increase) in barrier height from an increase(decrease) in dopant density. The cause for change in blocking behavior due to PEDOT:PSS thickness, however, requires further study. Finally, a study of the degradation in device performance over time is presented, showing that V_{oc} is the parameter affected most over time. The devices, while suffering a decrease in performance, will still function as a solar cell after two weeks when stored in a nitrogen atmosphere. In the next chapter, these experimental results will be replicated using theoretical modeling in order to further analyze the device results.

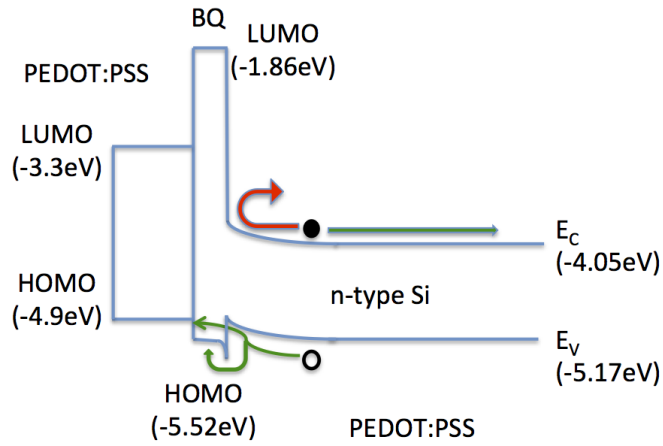


Figure 3.15: Band diagram for PEDOT:PSS/BQ/Si device.

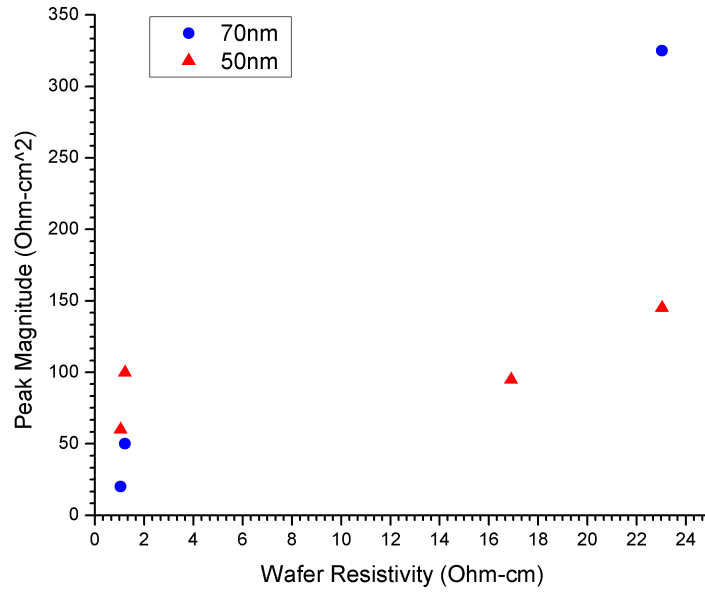


Figure 3.16: Strength of blocking behavior as a function of wafer resistivity and PEDOT:PSS thickness. Peak magnitude refers to the highest value of the peaks seen in the $\frac{dV}{dJ}$ vs. $(J + J_{sc})^{-1}$ curves used for the characterization of sheet resistance.

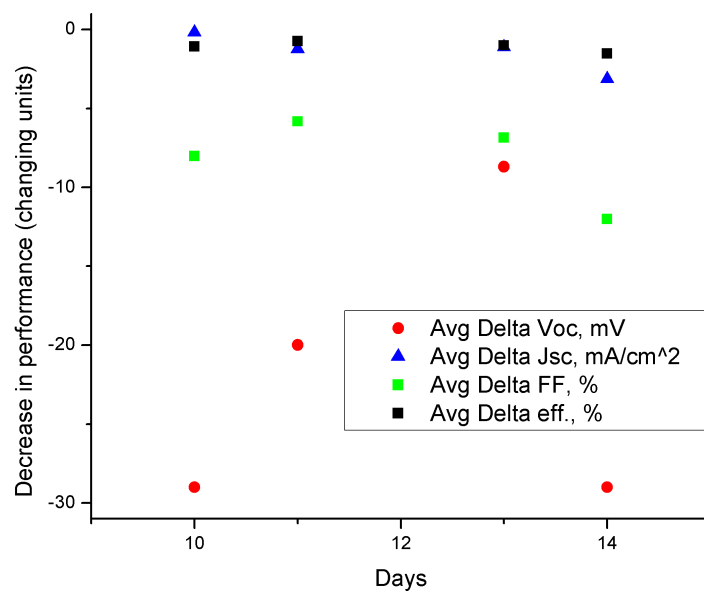


Figure 3.17: Average decrease in performance metric (V_{oc} , J_{sc} , FF , and η) as a function of number of days since fabrication.

Chapter 4

MODELING AND SIMULATION OF ORGANIC/INORGANIC HETEROJUNCTION SOLAR CELLS

4.1 Introduction

In order to more fully understand the performance capabilities for new device materials and structures, theoretical modeling provides a platform for comparison between real and theoretical device performance. In order to consider the varied material properties of the organic materials PEDOT:PSS and BQ, a robust modeling system is required. Sentaurus TCAD is capable of running a 2D simulation that takes into account many different material parameters and allows for full customization by the user. The Dark JV, Light JV, and Quantum Efficiency (QE) are all able to be simulated using this software – providing the ability to evaluate multiple performance metrics for the devices. Additionally, as more is understood about these materials and the functionality of the devices, the software allows the model to be increased in complexity to account for these new discoveries. This is a powerful tool with which to evaluate device performance, and to corroborate experimental data.

4.2 Background & Literature Review

Due to the recent developments for hybrid organic/inorganic devices, there is little literature regarding the theoretical evaluation of the devices presented in this work. There is even less information regarding the use of Sentaurus TCAD for the modeling of such devices. There has been work using Sentaurus TCAD to theoretically model α -Si/c-Si heterojunction devices, however, which is the conceptual foundation structure to these devices. For the theoretical modeling, then, the background work

on α -Si/c-Si heterojunction modeling will be used as a guideline for the development of a model for these new, organic materials using a heterojunction architecture.

For the development of a model for these structures, the first consideration is the geometry of the device. Using Sentaurus TCAD, defining the device geometry can ultimately affect the remaining model design. Ghosh considered planar structures in the simulation of α -Si/c-Si devices [13]. Herasimenka, et al. evaluated heterojunctions with interdigitated back contacts [22]. Shu, et al., combined the interdigitated back contact with a textured front surface, but also investigated planar front surfaces [46, 47]. It is also possible to perform the simulations in a one-dimensional geometry, as demonstrated by Bivour, et al. [6]. For the models in this work, it is not necessary to introduce texturing, as the devices fabricated do not have a textured front surface. Using a 2D model, however, allows for easier inclusion of texturing or other 2D structural considerations in the future, if device development leads to such configurations. The geometry of the simulations developed here will, therefore, be 2D planar structures.

Once the geometry is decided, it is necessary to input the proper material parameters. These include, but are not limited to, band gap (E_g), electron affinity (χ), mobility (μ), relative permittivity (ϵ_r), surface recombination velocity (SRV), and the real and imaginary components of the complex index of refraction ($n(\lambda)$ and $k(\lambda)$, respectively). These parameters account for some of the most basic values required for such a simulation, however, further understanding of the material properties and interfaces can lead to the implementation of other more complex material considerations. Ghosh, Herasimenka, et al., and Shu all consider trap states both within the band gap of the α -Si and at the interfaces [13, 22, 48]. There are also considerations made for the movement of charges through the device, with Shu implementing thermionic emission and Ghosh implementing both thermionic emission and tunneling [13, 48]. A thorough understanding of these trap states and carrier transport mechanisms requires in-depth study of the materials and interfaces involved, and is a factor to consider for future work with these devices.

Using these sources provides a pathway toward building a hybrid organic/inorganic

device model. The first step is determining the appropriate geometric structure to consider. The second is the implementation of the fundamental material properties required to accurately portray the organic films.

In order to begin the simulation development, it is ideal to use a well-performing device as a template. For this initial model, the PEDOT:PSS/c-Si device from Nagamatsu, et al. was used [35]. The device parameters were well-documented, including layer thicknesses, metallization parameters, substrate resistivity, and ultimate device results. This allows for the introduction of material properties from literature for the PEDOT:PSS film – parameters that were not detailed in the literature – in such a way as to compare the literature device performance with a simulation combining specified and non-specified material properties. Once these values are verified to produce a sound base model, the BQ film can be added and the device results evaluated.

4.3 Experimental Methods

4.3.1 TCAD Sentaurus Software

The modeling software package used for this work is TCAD Sentaurus, a finite element modeling system for the design and performance evaluation of semiconductor devices. TCAD Sentaurus is capable of performing analysis for 2D and 3D models, and covers the full range of performance situations for many device types – including optoelectronic devices. The software package consists of a suite of modules, each of which performs a separate step in the device design and modeling process. A brief overview of the modules used for this work and their individual functions are presented here, as well as the specifics used in the development of the model for this work.

4.3.1.1 Sentaurus Workbench

Sentaurus Workbench (SWB) is the main hub for complete model analysis. Projects can be sorted and accessed, individual modules controlled, full projects and experiments run, and results viewed from this one GUI. An image of the interface is shown in Fig. 4.1

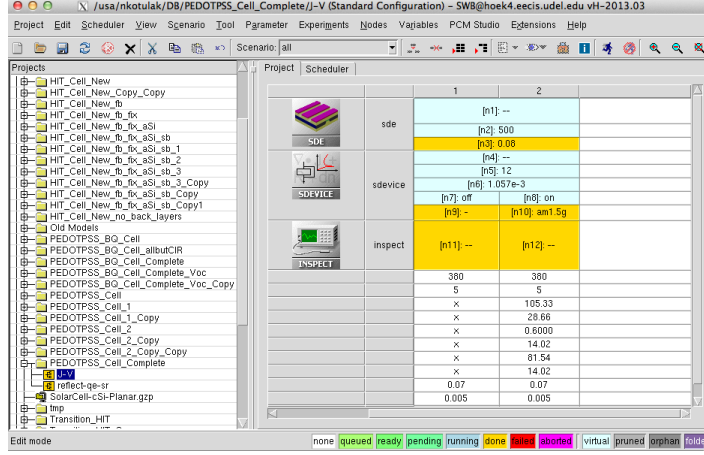


Figure 4.1: GUI of Sentaurus Workbench, the main hub of TCAD Sentaurus.

The GUI for SWB is divided into different sections. To the left is the project directory, which includes a list of all accessible projects. From this point, projects may be opened, moved, copied, renamed, or deleted. To the right, the open/active project is shown. The modules and variables for the project are visible. Each module and its command and parameter files can be accessed from this pane. Additionally, individual nodes can be chosen to be run, or have their output viewed. Actions available to the user may be accessed in the toolbar, which is located at the top of the GUI window.

4.3.1.2 Sentaurus Structure Editor

Sentaurus Structure Editor (SSE) is the first module used in this work. This module allows the user to create a geometric representation of the device to be analyzed, input materials, and create the mesh used for the finite element method calculations. SSE can be run through two methods – a GUI and a command file. The GUI is shown in Fig. 4.2.

The large window of the SSE GUI allows for the visualization of the device architecture as it is created. The user can directly build and manipulate the structure within this window using the available processes from the toolbars across the top, left,

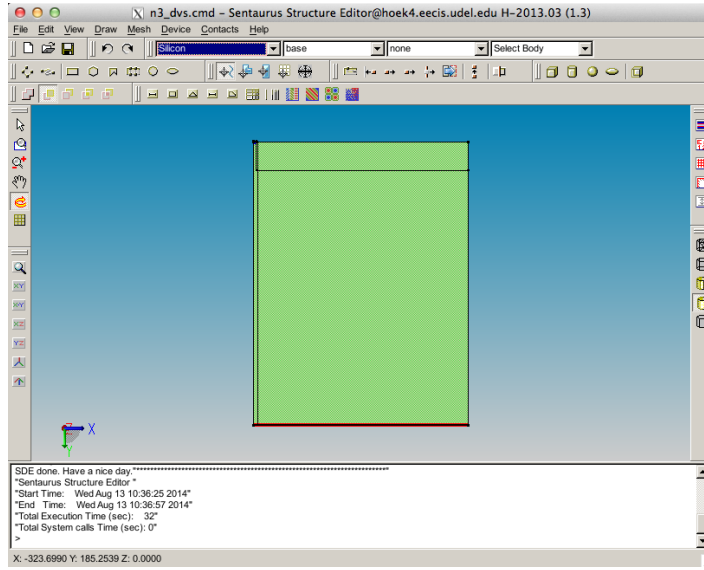


Figure 4.2: GUI of Sentaurus Structure Editor, the module for device architecture and mesh generation.

and right sides of the interface. Additionally, the bottom pane is a command box, where the user can type commands that will generate the device geometry. These same lines of code can be input into the SSE command file in SWB, and the device can be built and meshed from the SWB interface. Once built and meshed, SSE produces output files with the relevant information. These output files are used by the next module in the process flow in order to calculate the electronic properties of the device.

4.3.1.3 Sentaurus Device

Sentaurus Device (SD) is the main computational module of the system, calculating the device performance using device physics, optical input properties, and material parameters for each device component. It does not have a GUI, and, therefore, runs its computations from commands. There are two main input files required for SD – command and parameter – both of which may be altered by the user.

The command file contains all of the device physics to be considered, as well as other necessary considerations such as specifying input and output files. The command

file is separated into the following sections: File, Electrode, Physics, Plot, Math, and Solve:

- 1) *File* – Specifies input and output files. Input files include the device geometry, material parameters, and any required spectra for optical devices.
- 2) *Electrode* – Any electrodes are named and defined.
- 3) *Physics* – Separate “Physics” sections are defined for each device area of interest. “Physics” for the overall device (e.g optical generation) is coded separately from each material, region, or region interface. Material/region-specific considerations such as trap distributions, band tails, and interface recombination and emission are addressed within these sections.
- 4) *Plot* – The user specifies which characteristics can be plotted, including doping profiles and band structures.
- 5) *Math* – The user specifies details pertaining to how the solver will manage the device performance calculations. An example is the maximum number of iterations allowed for each calculation, after which the run will exit with an indication of failure.
- 6) *Solve* – Instructions are given for how to ramp voltages at the electrodes in order to calculate the electrical performance of the device.

4.3.1.4 Inspect

Sentaurus Inspect (SI) is a calculation and data display tool. This module uses the data generated from SD to calculate standard device characteristics (J_{sc} , V_{oc} , FF , η), as well as J-V and QE curves. Run through a command file, SI will output graphs, as shown in Fig. 4.3, and numerical values, as can be seen in the lines below the modules in Fig. 4.1.

4.3.1.5 Sentaurus Visual

Sentaurus Visual (SV) allows for further analysis of device performance and electrical properties through a GUI, as shown in Fig. 4.4. Device characteristics, such as doping concentration throughout the device, band diagrams, and current flow, can

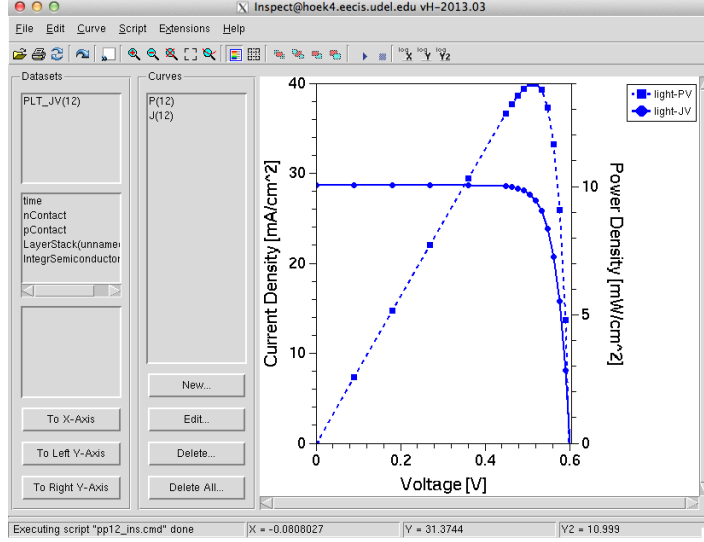


Figure 4.3: Example of visual output from Sentaurus Inspect.

be visually represented. The user may also define cross-sections of the device over which SV will create graphs and diagrams of the chosen characteristics.

The GUI is divided into several sections. Along the top, left, and right sides are toolbars for the available actions that may be used to examine and alter the active plots. Along the bottom is a command window, into which actions may be directly coded (or copied from, in order to create a command file to run through SWB). In the left center of the GUI are options for characteristics to plot and display. The right center shows the created plots that are ready for further analysis.

4.3.2 Developing the Organic/Inorganic Heterojunction Model

For this work, two different devices will be simulated: PEDOT:PSS/c-Si and PEDOT:PSS/BQ/c-Si. The first device has already been demonstrated in literature, and will be used as the base scenario [35]. The second device includes a layer of BQ to enhance the c-Si surface passivation and band-bending.

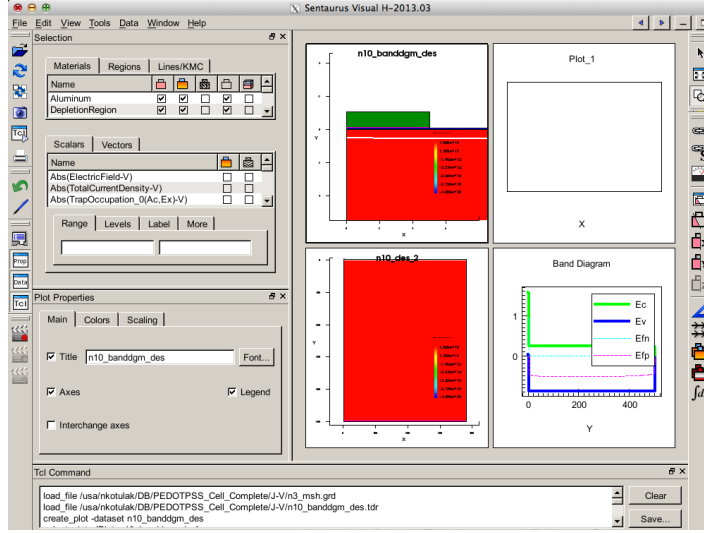


Figure 4.4: GUI of Sentauros Visual, the module for electronic property visualization.

4.3.2.1 Device Geometry

To create a simulation of the organic/inorganic heterojunction solar cell, its architecture must first be determined. When defining the 2D device geometry, the thickness and width of each layer are the first input components. In SSE, additional material parameters must be defined, such as the material for each device region and the dopant density, as well as the location for each contact. The final steps are defining refinement areas to generate the mesh that will be used by SD to simulate device performance. The specific geometries used for each device will be covered in this section.

The first choice in device geometry was the number of dimensions to be used. These devices were simulated using a 2D model as texturing and other 3D design elements were not to be included in the simulation. The 2D cross-section of the device shows each layer, and, due to the symmetric nature of solar cell functionality, the final geometric unit was defined as the 2D cross-section from the middle of a grid finger to the middle of the space between two fingers. This configuration has a vertical symmetry where repeatedly mirroring the defined unit will create a full device cross-section. A

Table 4.1: PEDOT:PSS/c-Si Base Device Geometry Parameters

	Width μm	Thickness μm	Material	Dopant	Dopant Density cm^{-3}
Front Contact	5	0.1	Silver	N/A	N/A
PEDOT:PSS	380	0.07 [35]	PolySi	Boron	3e20 [3]
Substrate	380	500	Silicon	Phosphorus	1.5e15 [35]
Back Contact	380	2	Aluminum	N/A	N/A

representation of the geometric unit is shown in Fig. 4.5.

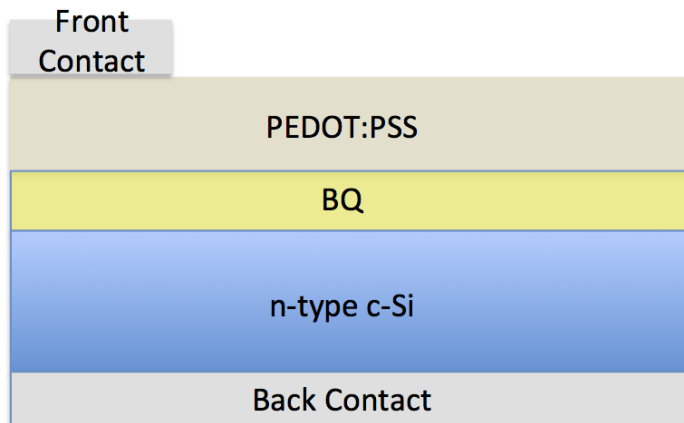


Figure 4.5: A visual representation of the smallest unit used for defining the device geometry. The half of a grid finger is visible at the top left of the device, while the middle of the area between two grid fingers is to the right. *Not to scale.*

Using information from literature, the appropriate thickness, material, and dopant density for each region was determined. The base values used for each device can be seen in Tables 4.1 and 4.2. Any change in these values will be noted as necessary.

It is at this point that the material choice for the organic molecules should be discussed. As can be seen in Tables 4.1 and 4.2, both PEDOT:PSS and BQ are modeled as “PolySi,” rather than as organic materials. In order to maintain convergence within

Table 4.2: PEDOT:PSS/BQ/c-Si Base Device Geometry Parameters

	Width μm	Thickness μm	Material	Dopant	Dopant Density cm^{-3}
Front Contact	5	0.1	Silver	N/A	N/A
PEDOT:PSS	380	0.07 [35]	PolySi	Boron	3e20 [3]
BQ	380	0.00035 [18]	PolySi	Boron	2e19
Substrate	380	500	Silicon	Phosphorus	varies
Back Contact	380	2	Aluminum	N/A	N/A

Sentaurus, it was necessary to have the program view the organic films as inorganic layers. This reasoning also explains the dopant and dopant density choice for the organic films. Both PEDOT:PSS and BQ are electron-blocking materials, and, as such, mimic a p-type inorganic semiconductor. Having been modeled as PolySi, Boron was chosen as the p-type dopant, and the dopant densities were chosen to approximate the strength of the “p-type nature” of the organic films. All of the other material parameters, which are discussed in Section 4.3.2.2, are those of the organic molecules, not PolySi. In this way, Sentaurus handles the organic films as it would inorganic materials, but the parameter values are those of the organics – an “inorganic” film with “organic” properties.

The final step to creating the device geometry is mesh generation. Refinement areas are defined with maximum and minimum height and width values for each mesh component. The mesh is set to be more dense at the interfaces between materials so as to improve continuity and model convergence. Additionally, minimum mesh values are set to be smaller than the region dimensions. For example, if the BQ film is 0.35 nm thick, the minimum height for the mesh components in that region would be set to $<0.35\text{nm}$. The dimensions of the mesh are critical for achieving convergence of the model in SD, as the device only exists at the mesh vertices. Often, initial convergence problems in new models may be solved by refining the mesh dimensions. Once the mesh is generated, the file is ready for use by SD in order to simulate device performance.

4.3.2.2 Material Parameters

Material parameters are input in two locations for SD. The first of these is the parameter file (.par), where material parameters may be either directly input in a section of the .par file unique to each material or assigned by calling a separate material-specific parameter file. The material parameters found in the .par file include bandgap (E_g), electron affinity (χ), carrier mobility (μ), relative permittivity (ϵ_r), refractive index ($n(\lambda)$), and extinction coefficient ($k(\lambda)$). Additionally, interface-specific properties, such as surface recombination velocity, may be specified in the .par file in a “RegionInterface” command section. There are many other material parameters that may be adjusted in the .par file, however, the parameters mentioned here are the only ones necessary to adjust for this model. The second input location is the “Physics” section of the command file. Each region or interface has its own “Physics” section, in which properties such as recombination type and trap type, density, location, cross-section, and shape are defined. Between the two locations – .par file and command file – a complete material profile is produced.

TCAD Sentaurus has a large portfolio of supported materials for which there are already detailed parameter files. For this work, the Silicon, Aluminum, and Silver parameters developed by Synopsys were used to model the c-Si substrate, rear contact, and front contact, respectively [52]. If a material is not found in the database, as is the case for the PEDOT:PSS and BQ films, the user may input their own parameters to “create” the material of interest. In this work, the PolySi parameters are called as described in Section 4.3.2.1, but the material parameters of interest are overridden by user-input values in the SD .par and command files. The input parameters for PEDOT:PSS and BQ are detailed in Table 4.3.

As can be seen in Table 4.3, the parameters for these organic materials are found in many different sources, rather than as a full collection. Some parameters can change with material manufacturer and fabrication specifications, making it difficult to find a complete material profile like those that are available for inorganic semiconductors. Additionally, some parameters are not available for a specific material. In this case, μ ,

Table 4.3: PEDOT:PSS and Benzoquinone Base Material Parameters

	PEDOT:PSS	BQ
E_g (eV)	1.6 [35]	3.66 [44]
χ (eV)	3.3 [35]	1.86 [1]
μ ($cm^2V^{-1}s^{-1}$)	20 [3]	0.1 (Benzene) [28]
ϵ_r	2.2 [43]	2.2825 (Benzene) [2]
Avg. τ_{eff} (ms)	4e-4	3.2
SRV (cm/s)	62.5	7.32
$n(\lambda)$	See Fig. 4.6	See Fig. 4.7 (Benzene)
$k(\lambda)$	See Fig. 4.6	See Fig. 4.7 (Benzene)

ϵ_r , $n(\lambda)$, and $k(\lambda)$ were not readily available for BQ. The information was available for Benzene, which is a comparable molecule for our purposes, and the parameter values which are actually those of Benzene data are noted.

While most of these parameters could be found in the literature, some values were extrapolated or calculated in order to fulfill the needs of the simulation. The first of these, the $n(\lambda)$ and $k(\lambda)$ values, were determined using extrapolated data. Curves depicting the $n(\lambda)$ and $k(\lambda)$ values as a function of wavelength (λ) were obtained from the literature and digitized [25, 31]. From this digitized data, trendlines were generated for each curve. Lastly, these trendlines were used to populate tab-delimited tables of values over a wavelength range of 190-1430nm that were input into the .par file in the respective PEDOT:PSS and BQ sections. Graphs of the data ultimately used for this work are shown in Figs. 4.6 and 4.7.

After completing the collection of the CIR components, the SRV for each organic material when forming an interface with c-Si was calculated. The SRV can be calculated using

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{S_{front}}{W} + \frac{S_{back}}{W} \quad (4.1)$$

where τ_{eff} is the effective lifetime, τ_{bulk} is the bulk lifetime, S_{front} and S_{back} are the front and back SRV, respectively, and W is the thickness of the wafer [27]. In an

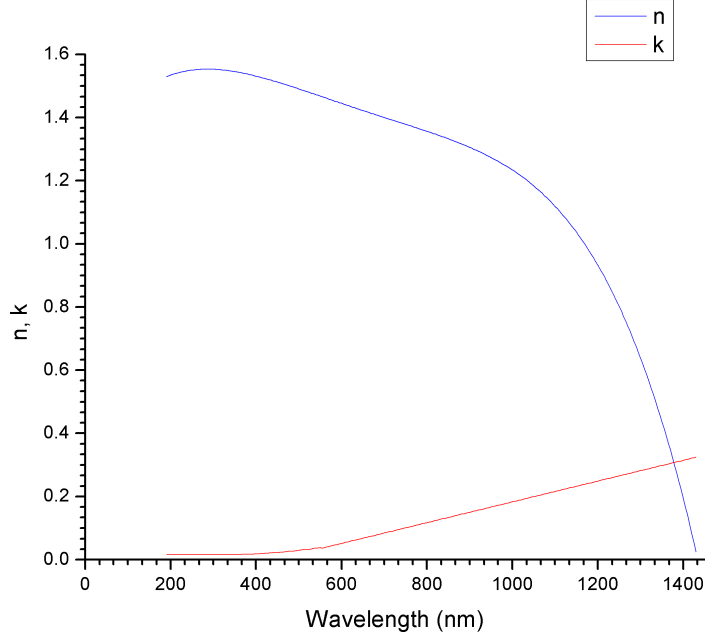


Figure 4.6: PEDOT:PSS $n(\lambda)$ and $k(\lambda)$ values. [25]

undiffused wafer where both the front and back surfaces are identical, Eq. 4.1 reduces to

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{2S}{W} \quad (4.2)$$

and the SRV for both surfaces may be calculated. If the assumption is made that $\tau_{bulk} \rightarrow \infty$, the term $\frac{1}{\tau_{bulk}} \rightarrow 0$, and the resulting SRV is the worst case scenario. Otherwise, τ_{bulk} may be calculated based upon the dopant density of the substrate, which will result in a smaller SRV than in the first scenario. This SRV data was input into the respective “RegionInterface” sections of the .par file. The PEDOT:PSS SRV would be used under the “SurfaceRecombination” heading for the interface of PEDOT:PSS/c-Si, and the same would be done for BQ in the device where the interface is BQ/c-Si.

For all of the aforementioned parameters, the values are input in the .par file. There are other parameters, however, which are identified in the command file. Within

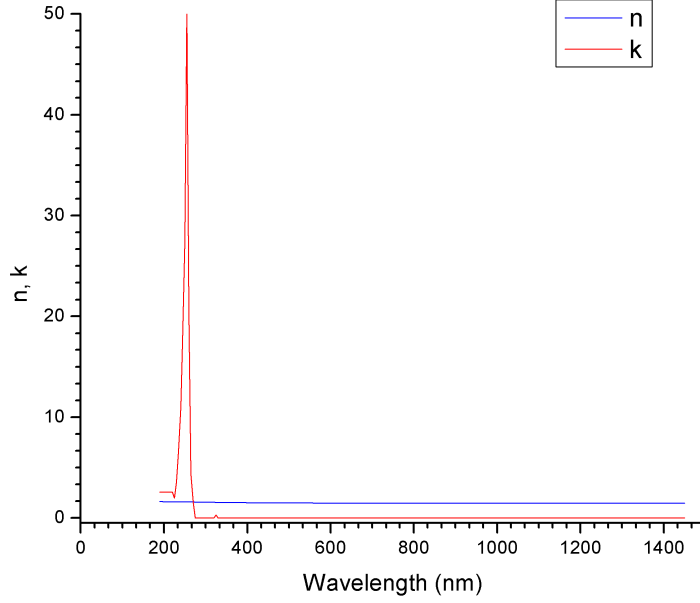


Figure 4.7: BQ $n(\lambda)$ and $k(\lambda)$ values from Benzene data. [31]

the command file both region-specific and interface-specific parameters may be identified by the user. These include types of recombination to consider, traps that may be present, and heterojunction considerations. For this work, each region or interface includes SRH as the recombination or surface recombination type, respectively. Because no band tails or defect states exist within the band structure of the organic molecules, no traps were defined. For the interface between the organic film and c-Si, the keyword “HeteroInterface” was used in conjunction with the keyword for thermionic emission [53]. At an abrupt heterojunction, large barrier errors caused by band offsets can occur with the mesh as is generated under normal circumstances. A much finer mesh at the interface is required in order to eliminate the error. The “HeteroInterface” keyword introduces double points at the mesh interface between the two regions, and continuous quasi-Fermi levels are maintained between the two points. This reduces the barrier error without having to further refine the mesh at the interface. It is recommended to have some form of emission or tunneling specified for the heterojunction

when “HeteroInterface” is employed. For this work, the keyword “Thermionic” is used to implement thermionic emission as the transport mechanism at the junction.

4.3.2.3 Input Spectrum

For PV cells, it is important to simulate device performance under both dark and light conditions, as each set of data can help diagnose performance-reducing issues with the device. The choice of spectrum for the light simulation is important, and dependent upon the device application. PV cells that will be in space (i.e. outside of Earth’s atmosphere) should be simulated using AM0, while terrestrial devices should use AM1.5. The options for AM1.5 include direct (only direct irradiation) and global (both direct and diffuse light). The former is best for concentrator devices, while the latter is best for flat-panel systems that will capture both direct and diffuse light. Due to the application for this work – terrestrial, flat-panel devices – AM1.5g was used.

Another facet of identifying the appropriate spectrum is understanding the wavelengths of interest for the device in question. The main absorber of this structure is c-Si, therefore, wavelengths much longer than 1400nm are not necessary to include in the input spectrum, despite the fact that the available AM1.5g data goes out as far as wavelengths of 3 μm . It is also critically important to consider the available complex index of refraction (CIR) values and the way in which SD handles the generation of optical data for the device. When generating the optical files, SD matches each wavelength from the input spectrum to its corresponding wavelength in the CIR data for each material through which the photons will pass. If there is no exact match in the CIR data, SD will use the data available to extrapolate the $n(\lambda)$ and $k(\lambda)$ values for the wavelength in question. It is, therefore, important to ensure that the wavelength range for the input spectrum and the CIR data have significant enough overlap to ensure accurate extrapolation by SD.

Taking these factors into consideration, the wavelengths used for the AM1.5g input spectrum ranged from 300nm (the first available data for AM1.5g) to 1420nm. The CIR wavelengths covered the range from 190-1450nm, so as to provide enough data

for SD to perform an accurate extrapolation. The spectrum is saved as a tab-delimited .txt file where the first column is wavelength in μm and the second column is intensity in $\frac{W}{\text{cm}^2}$. This file is called in the “File” section of the SD command file for generation of the optical characteristics for device simulation.

4.3.2.4 Optical Generation

Optical generation can take many forms in SD, and varies based on the level of detail required and the geometry in question. For example, 3D textured devices may require a raytracing method to account for the specific movement of photons, whereas a 2D cell with a flat surface does not require such a level of precision. As mentioned in Section 4.3.2.3, optical generation begins with the input spectrum file, then requires the specification of the optical solver within the “OpticalGeneration” section of the SD command file. For this work, the Transfer Matrix Method (TMM) is the designated optical solver, which uses “transfer matrices” to calculate the propagation of incident waves through and between each layer of the device [53]. This method is the simplest method of optical generation within SD, and is perfectly suited to the structure examined here.

Keywords of interest for the optical generation section include “QuantumYield,” “Theta,” “Polarization,” and “IntensityPattern.” The keyword “QuantumYield” describes the number of carriers generated per photon, and this value defaults to 1. For this work, additional keywords of “Stepfunction(EffectiveBandgap)” were used as the arguments of “QuantumYield” to declare that only photons of energy higher than the bandgap would generate carriers in each material. “Theta” and “Polarization” were set to 0 and 0.5, respectively, to indicate that the photons had normal incidence to the surface of the device and were unpolarized, also respectively. The final keyword of interest, “IntensityPattern,” was set to “Envelope,” to assist with convergence of the optical file. These keywords are important components of the optical generation section, and ensure that each photon is properly accounted for. Once the optical generation file is complete, the results are used to calculate the electrical properties of the

device.

4.3.2.5 Electrical Computations

In order to determine the performance of the device, the movement of carriers throughout the structure must be calculated. As discussed in Section 4.3.2.1, as far as SD is concerned, the device only exists at the mesh vertices. The solid state equations used to calculate the movement of carriers must be consistent from vertex to vertex, otherwise, the resulting model will not converge. It is for this reason that, if the model converges in the optical generation section, but fails to converge during the electrical computations, a finer mesh is often required (although, sometimes, more complex device issues are to blame).

The definition of which combination of equations to solve is up to the user, and each will bring a new level of complexity and accuracy to the resulting simulation. For this work, the Poisson equation and the electron and hole continuity equations were solved. The keyword “Coupled” was used in order to implement an iterative algorithm to solve a linear system for each step of the simulation. Within the “Coupled” command, boundary conditions may be placed in order to control error and either make more stringent or relaxed requirements for a simulation step to be considered converged.

These three equations (Poisson, electron continuity, and hole continuity) were solved using different methods depending upon which resulting data was desired. The required output was defined within the “Quasistationary” command. For the determination of J-V curves, the voltage of the device was ramped from 0.0 V to 0.8 V in order to determine the current characteristics at each voltage point. The same ramping procedure was performed for both the dark J-V simulation, which did not use an optical generation file, and the light J-V simulation in order to map the curves. The QE simulations ramped the wavelength from a user designated start and end point in order to determine the QE of the device at each indicated wavelength in the set. The resulting data was input into the SI tool, and J-V and QE curves were calculated and graphed. The SV tool was used to generate band diagrams of the devices both

at equilibrium and under forward bias, which also required the input of the electrical simulation results. The resulting output will be presented and discussed in Section 4.4.

4.4 Results & Discussion

Device performance simulations are developed to inform, and to be informed by, the performance results of tangible devices. For this reason, multiple iterations of the simulation are performed in order to better represent the real-world counterpart. The simulations presented here begin with a “base” cell design, which is comprised of material properties and device characteristics found in literature. As devices were fabricated and tested, as described in Chapter 3, the model parameters were altered to reflect the changes in fabrication and device results. The changes from base cell to final device simulation are presented here.

4.4.1 PEDOT:PSS/c-Si Device Simulation

The PEDOT:PSS/c-Si structure was demonstrated in the literature, as described in Section 4.2 [35]. This device structure was well-defined, including most material parameters, therefore, the device from literature was used as the base cell. Further iterations took into account the differences in structure and material parameters from the device described in literature and the device fabricated for this work.

It is important to note that the information presented in Sections 4.3.2.1-4.3.2.5 applies in its entirety to the base cell scenarios. Only the device geometry and material parameters are changed for the new iterations of devices. The information contained in Sections 4.3.2.3- 4.3.2.5 are not “device specific” for this work and, therefore, remain unchanged throughout the work. Any change in simulation parameters from a previous iteration of the device will be noted as necessary.

4.4.1.1 Literature Cell Design

The literature cell design utilized the device geometry from Table 4.1, material parameters found in Table 4.3, and optical data from Fig. 4.6.

Table 4.4: PEDOT:PSS/c-Si Literature Device Simulation Performance

Device	$J_{sc} \left(\frac{mA}{cm^2} \right)$	$V_{oc} (V)$	FF	η
Literature Device [35]	27.8	0.57	0.73	0.12
Literature Device Sim.	28.66	0.600	0.82	0.14

Table 4.5: PEDOT:PSS/c-Si Literature Device Simulation Performance using different PEDOT:PSS dopant densities.

Device	$J_{sc} \left(\frac{mA}{cm^2} \right)$	$V_{oc} (V)$	FF	η
Literature Device [35]	27.8	0.57	0.73	0.12
Literature Device Sim. $3 \times 10^{20} cm^{-3}$	28.66	0.600	0.82	0.14
Literature Device Sim. $9 \times 10^{19} cm^{-3}$	28.67	0.600	0.72	0.12

Using these values, the device results are shown in Table 4.4. As can be seen from these results, there is a good agreement between the simulation and actual device performance. These results use the PEDOT:PSS dopant density of $3 \times 10^{20} cm^{-3}$ [3]. This dopant density is a function of the number of PEDOT molecules within the PEDOT:PSS film. It is, therefore, a calculated estimate, which can be adjusted to more closely portray the device performances.

For the next set of simulations, the dopant density is adjusted to $9 \times 10^{19} cm^{-3}$, and the largest change in simulation performance is a drop in FF , as shown in Table 4.5. The importance of accurate material property values for the PEDOT:PSS film becomes apparent, as seen here. The Dark JV, Light JV, and QE curves for this simulation are shown in Figs. 4.8, 4.9, and 4.10.

Because these simulations closely portray the performance of a PEDOT:PSS/c-Si device, they can be used as a basis for simulating a PEDOT:PSS/BQ/c-Si device. The analysis of these new device structures will cover changes in V_{oc} and J_{sc} , as well as a simulation using the final device parameters.

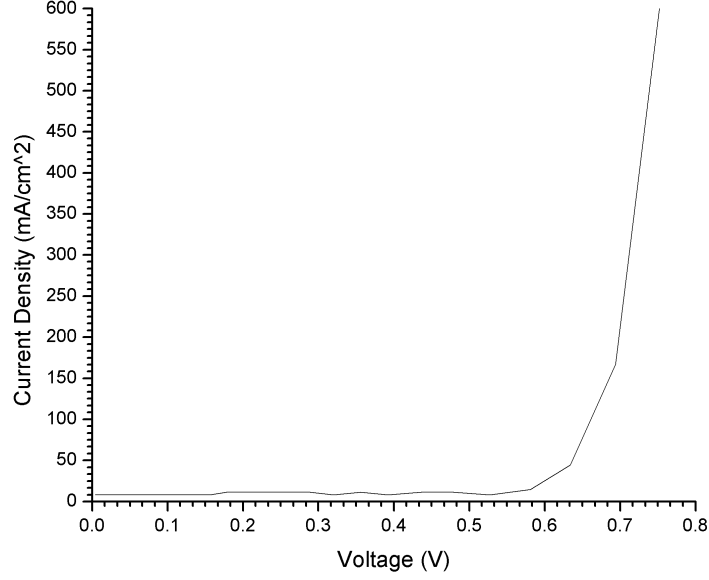


Figure 4.8: Simulated Dark JV curve for PEDOT:PSS/c-Si Literature Device

4.4.2 PEDOT:PSS/BQ/c-Si Device Simulation

4.4.2.1 V_{oc} Trend Simulation

In order to simulate the PEDOT:PSS/BQ/c-Si device, modification of the PEDOT:PSS/c-Si simulation begins with the addition of the BQ layer to the device geometry using the parameters shown in Table 4.2. Next, the material properties of the layer are adjusted to reflect the BQ characteristics, as shown in Table 4.3. Although the second simulated device for PEDOT:PSS/c-Si used a PEDOT:PSS dopant density of $9 \times 10^{19} \text{cm}^{-3}$ to most accurately model the device, the initial PEDOT:PSS/BQ/c-Si simulation uses the original value for dopant density – $3 \times 10^{20} \text{cm}^{-3}$ – in order to simulate a theoretical maximum performance.

The first set of simulations performed with the PEDOT:PSS/BQ/c-Si device is a test of different wafer resistivities to evaluate the effect of V_{oc} . This is a replication of the devices fabricated in Section 3.4.2. The device simulation results are shown in Table 4.6.

While these values for V_{oc} are about 100mV higher than those achieved in the

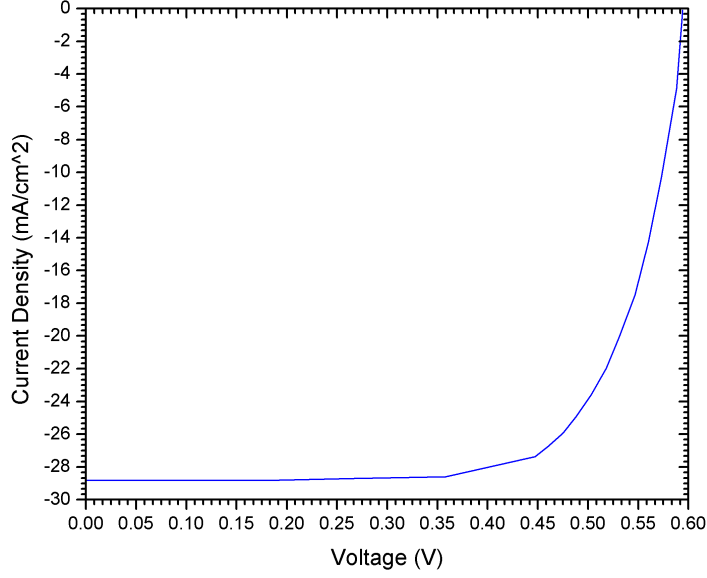


Figure 4.9: Simulated Light JV curve for PEDOT:PSS/c-Si Literature Device

Table 4.6: PEDOT:PSS/BQ/c-Si V_{oc} -Focused Device Simulation Performance

Device	$J_{sc} \left(\frac{mA}{cm^2} \right)$	$V_{oc} (V)$	FF	η
$23.03 \Omega - cm$	29.09	0.559	0.77	0.13
$16.91 \Omega - cm$	28.93	0.566	0.78	0.13
$1.22 \Omega - cm$	28.53	0.625	0.83	0.15

fabricated devices, this model accurately predicts the increase in V_{oc} as a function of substrate resistivity. The V_{oc} increase from $23.03 \Omega - cm$ to $1.22 \Omega - cm$ is 66mV according to the simulation. The V_{oc} increase of the fabricated devices was 66mV over the same resistivity change. It is likely that the discrepancy in values between the simulation and the fabricated devices stems from both a non-ideal PEDOT:PSS film and edge recombination. Preparation and deposition of the PEDOT:PSS film is critical to device performance, as any processing changes ultimately change the electrical properties of the films. This concept is evaluated by Pietsch, et al., demonstrating that the final morphology of the PEDOT:PSS film, as affected by additives such as DMSO

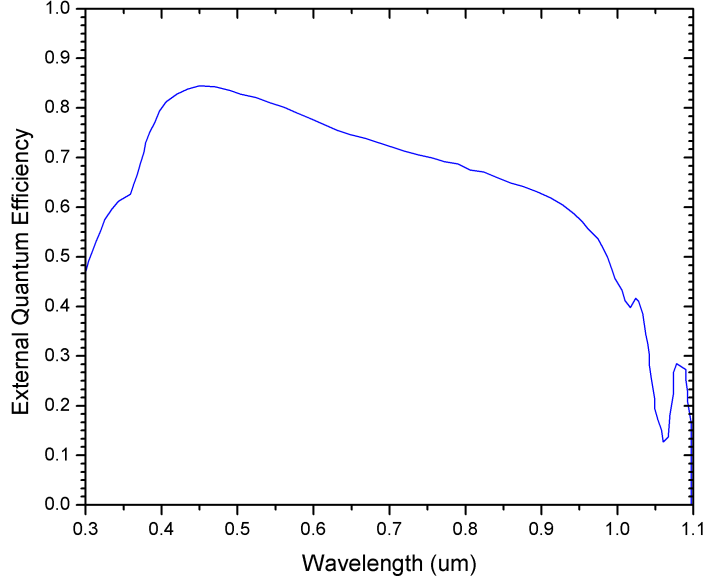


Figure 4.10: Simulated EQE curve for PEDOT:PSS/c-Si Literature Device

and EG, will affect film conductivity and device V_{oc} and J_{sc} [39]. The V_{oc} is also largely affected by recombination in the device through the J_0 term. As observed in the device analysis for the devices in Chapter 3, the J_0 is high in these structures. It is, therefore, likely that a combination of PEDOT:PSS film quality and high recombination in the device that accounts for the discrepancy between the simulated and actual device V_{oc} values. Ultimately, the results of this simulation indicate that the models can accurately predict changes in V_{oc} , and the next performance metric to simulate is changes in J_{sc} .

4.4.2.2 J_{sc} Trend Simulation

The next set of simulations reduces the thickness of the PEDOT:PSS film to 50nm, as fabricated in Section 3.4.3. The device simulation results are shown in Table 4.7.

Again, we see the simulation following the trend of a just under $1 \frac{mA}{cm^2}$ reduction in current. This simulation result also ties in with the predictions of current loss (1.1

Table 4.7: PEDOT:PSS/BQ/c-Si J_{sc} -Focused Device Simulation Performance

Device	$J_{sc} \left(\frac{mA}{cm^2} \right)$	$V_{oc} \text{ (V)}$	FF	η
23.03 $\Omega - cm$ 70nm	29.09	0.559	0.77	0.13
23.03 $\Omega - cm$ 50nm	28.01	0.557	0.77	0.12
16.91 $\Omega - cm$ 70nm	28.93	0.566	0.78	0.13
16.91 $\Omega - cm$ 50nm	27.85	0.565	0.78	0.12
1.22 $\Omega - cm$ 70nm	28.53	0.625	0.83	0.15
1.22 $\Omega - cm$ 50nm	27.47	0.624	0.83	0.14

$\frac{mA}{cm^2}$) due to increased reflection discussed in Section 3.4.3. Additional support for this loss of current due to reflection is shown in a comparison of the External Quantum Efficiency (EQE) curves shown in Fig 4.11. The loss in current shown by decreases in the EQE curve track well with the increases in reflectivity shown in Figs. 3.8 and 3.9. The loss in simulated current, therefore, can be attributed to the optical properties of the PEDOT:PSS film.

The overall J_{sc} values for this simulation are higher than those achieved by the fabricated devices. This lower J_{sc} can most likely be attributed to imperfections within the fabricated devices, which could include non-optimal PEDOT:PSS films and differences between the optical properties of the real versus simulated films.

The final simulation is that of the best performing PEDOT:PSS/BQ/c-Si device (using a 70nm PEDOT:PSS film and 1.05 $\Omega - cm$ substrate). The results are shown in Table 4.8 and Figs. 4.12, 4.13, and 4.14.

As with all of the simulated devices, the final structure follows the appropriate trends, and this structure outperforms the other simulated devices. The fabricated counterpart, however, underperforms in comparison with its theoretical simulation.

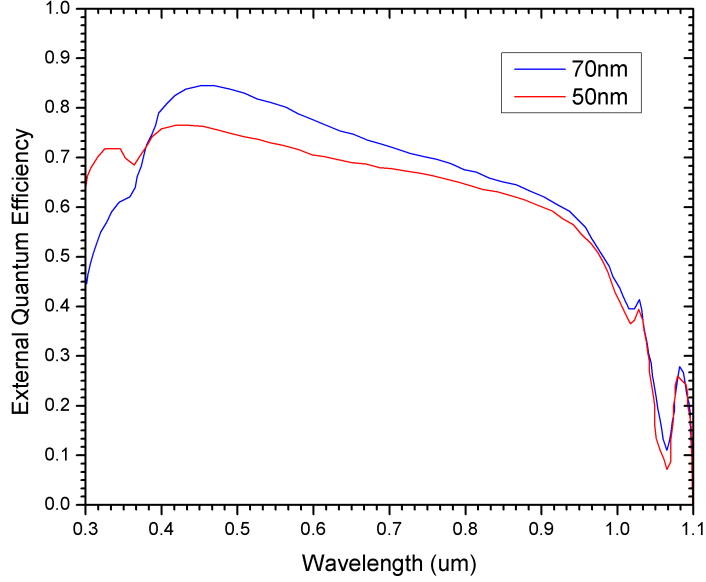


Figure 4.11: Simulated EQE curves for PEDOT:PSS/BQ/c-Si Devices on a $1.22 \Omega - cm$ substrate: one with 70nm PEDOT:PSS versus one with 50nm PEDOT:PSS.

This can be attributed to parasitic factors in the real devices that are not considered within the model, as these simulations are designed to portray the performance trends and theoretically attainable performance for a material that has previously never been implemented in this kind of device structure.

4.5 Conclusions

Theoretical simulations for the PEDOT:PSS/c-Si and PEDOT:PSS/BQ/c-Si devices have been presented. These models show good agreement with the trend for changes in V_{oc} and J_{sc} with these devices based on changes in substrate resistivity and PEDOT:PSS film thickness. From these simulations, we confirm that an increase in substrate dopant density increases the V_{oc} of the devices, and that the theoretical magnitude of increase tracks well with the increase values found in literature and device performance. The affect of PEDOT:PSS thickness on J_{sc} is also corroborated, indicating that the PEDOT:PSS film produces ARC effects in addition to being a film

Table 4.8: PEDOT:PSS/BQ/c-Si Final Device Simulation Performance

Device	$J_{sc} \left(\frac{mA}{cm^2} \right)$	$V_{oc} (V)$	FF	η
Literature Device [35]	27.8	0.57	0.73	0.12
Base Device Sim.	28.66	0.600	0.82	0.14
23.03 $\Omega - cm$	29.09	0.559	0.77	0.13
16.91 $\Omega - cm$	28.93	0.566	0.78	0.13
1.22 $\Omega - cm$	28.53	0.625	0.83	0.15
1.05 $\Omega - cm$ Real	18.57	0.572	0.47	0.05
1.05 $\Omega - cm$ Sim	28.53	0.628	0.83	0.15

for the transport of holes through the device. The simulation results show this through both a decrease in J_{sc} comparable with that of the device performance and a decrease in EQE that tracks with changes in reflection from the reflection, absorption, and transmission calculations in Section 3.4.3. The final observation from these simulations is that this structure is capable of higher performance than is presently being achieved in the fabricated structures, therefore, there is room for improvement in these devices, as discussed in the final chapter.

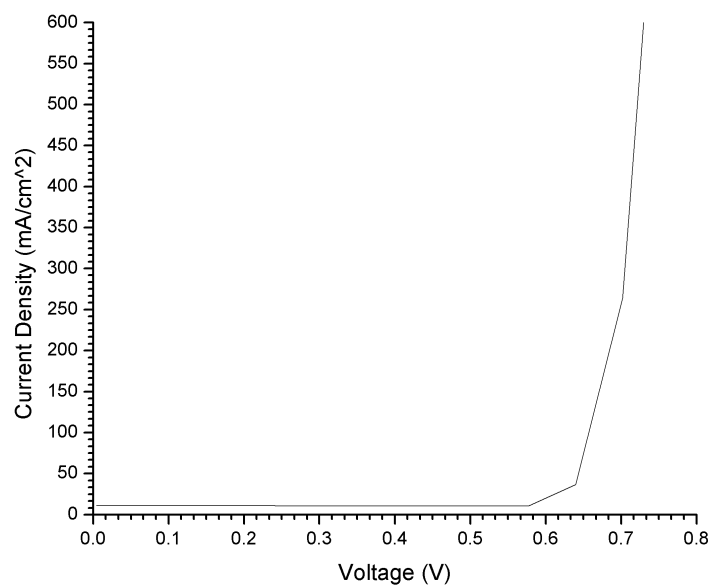


Figure 4.12: Simulated Dark J-V curve for PEDOT:PSS/BQ/c-Si Device

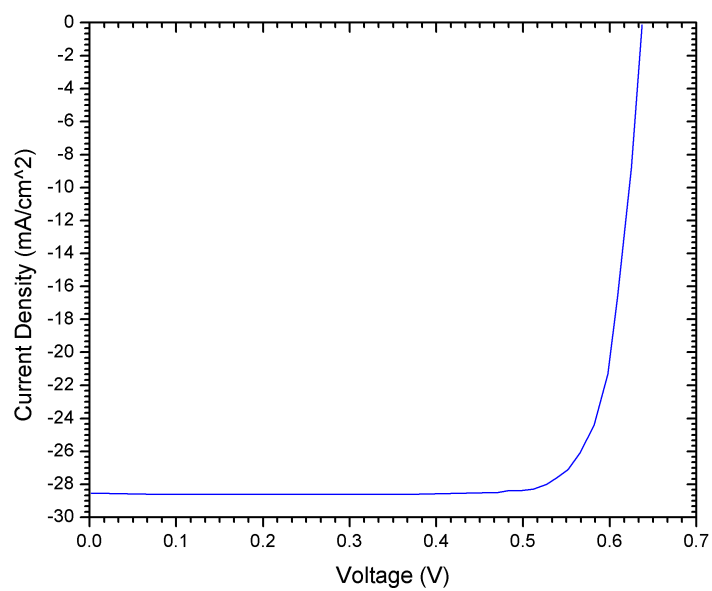


Figure 4.13: Simulated Light J-V curve for PEDOT:PSS/BQ/c-Si Device

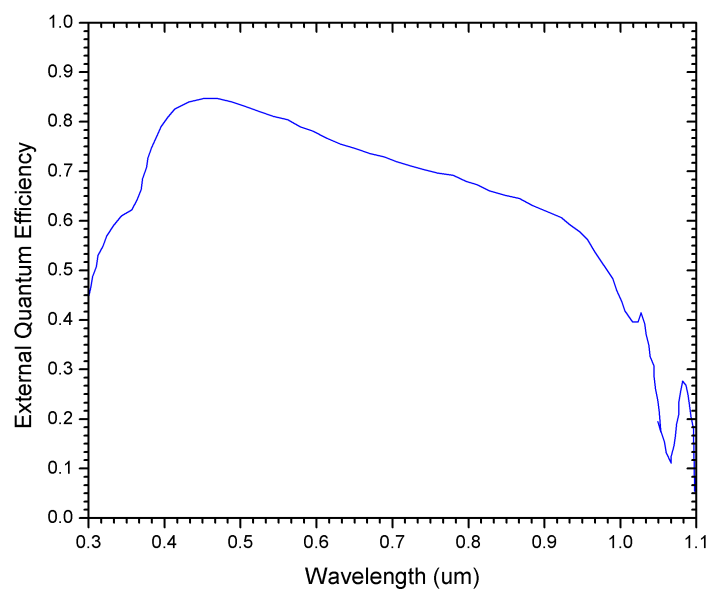


Figure 4.14: Simulated QE curve for PEDOT:PSS/BQ/c-Si Device

Chapter 5

CONCLUSIONS AND FUTURE WORK

Throughout this work, experimental and theoretical findings have been presented for the passivation of c-Si surfaces with organic molecules and, ultimately, the implementation of those molecules in a photovoltaic device structure. While these findings have led to some conclusions, they have also presented paths forward for future work. These conclusions and improvement opportunities are presented in the following sections.

5.1 Conclusions

There are three main components to this work: surface passivation studies, device fabrication, and theoretical modeling.

Beginning with a study of QHY and its constituent components – BQ and HQ – the passivation capabilities of these molecules under varying conditions were evaluated. BQ was determined to be the active passivant, however, it is possible for HQ to improve the passivation the c-Si surface if the substrate is allowed enough time to interface with the HQ solution. After this determination, a bonding mechanism was proposed. The free radical $\text{QH}^\bullet$ proposed in literature, with a conversion pathway between BQ and HQ, was experimentally evaluated. The conversion pathway requires extra protons in solution and exposure to photons in order for either BQ or HQ to convert to $\text{QH}^\bullet$. The importance of both of these factors – protons and photons – was experimentally demonstrated, indicating that $\text{QH}^\bullet$ is present in the system and is acting as the passivant. DFT calculations support this bonding mechanism, and XPS surface analysis details the appearance of methoxy and $\text{QH}^\bullet$ molecules on the Si surface after solution-based passivation.

After the determination of a bonding mechanism and the optimal passivation conditions, the BQ solution was used to passivate the c-Si surface in a hybrid organic/inorganic device structure. This device used PEDOT:PSS as the transparent conductive top layer. The first device shows that BQ can act as a functioning layer in a diode. V_{oc} was shown to improve by reducing substrate resistivity, and the change in J_{sc} with PEDOT:PSS thickness demonstrates that the film also acts as an ARC for the device. Using the results from the fabrication of a series of structures, a final device was designed and fabricated, with a V_{oc} of 572 mV, a J_{sc} of $18.57 \frac{mA}{cm^2}$, FF of 47%, and an efficiency of 5.02%. This fully isolated device is $20.27 mm^2$. These devices display blocking behavior, as well as degradation that reduces V_{oc} by approximately 30mV in 14 days.

Finally, theoretical modeling was used to determine the performance capability of the device structure designed here. The changes in design for the fabricated devices were copied in the device simulations. For the V_{oc} analysis, the performance of the simulated devices were higher than the fabricated devices, however, the trend for change in V_{oc} matched with that of the fabricated structures. The change in J_{sc} also followed the same trend between the simulated and fabricated devices, with the change in PEDOT:PSS thickness demonstrating an ARC effect from the film within the simulation. These results indicate that a higher performance threshold is possible from these structures, and future work will be able to greatly improve the efficiency of these organic/inorganic hybrid cells.

5.2 Future Work

Future work for the hybrid organic/inorganic photovoltaic devices will focus on optimizing the materials chosen for the structure, processing procedures, better understanding of the interface between materials, and improved modeling of the devices.

The first piece to improve for the structure is the manifestation of blocking behavior. This could include improvements in organic film quality, as well as the use of other organic molecules at the surface of the c-Si. Examining other molecules which

may have a similar passivating effect for c-Si as BQ, but a reduced barrier height between the HOMO level and valence band, could provide a first step. An example of a molecule to consider is 9,10-anthraquinone, which has a very similar structure to BQ. Additionally, other conductive polymers, such as P3HT, may prove an appropriate substitute for PEDOT:PSS.

In addition to examining the prospective uses of other molecules in this structure, an optimization of processing for the materials chosen is required. This optimization will be material-specific, and will improve device performance and fabrication repeatability. A thorough evaluation of processing used throughout the literature – including solvent use and film deposition techniques – will prove useful for this task. In addition to processing optimization for the organic materials, improvements to inorganic processing – cleaning methods, metallization structures for better contact to the n-type Si, grid optimization, and edge isolation – are also necessary.

Along with the improvement of device quality, the ability to more fully analyze the effects of each film and the interfaces of the different materials should be possible. This analysis will lead to a better understanding of which materials are best suited for the structure, as well as the parameters required to improve theoretical modeling. A theoretical model that more closely describes the real structure will aid in driving farther-reaching device improvements for these structures.

Ultimately, device optimization, material engineering, and improved theoretical understanding of these devices will allow these structures to enable the next generation of PV technology.

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