

**OPTIMIZING PERFORMANCE OF CHEMICALLY PASSIVATED
CARRIER SELECTIVE PEDOT: PSS BASED
HETEROJUNCTION SOLAR CELLS**

by

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A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Master of Science in Electrical and Computer Engineering

Spring 2017

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ACKNOWLEDGEMENTS

There is a long list of people whom I would like to acknowledge in helping me accomplish my thesis. I hope I do justice in acknowledging them all. There are countless number of people, whom you meet regularly or accidentally and everyone ends up teaching you some life lesson or I have at least learned something from every person I have met. Their wise words to spending time in lab to involving in extra and co-curricular activities to playing FIFA to taking care of me to travelling with me, all have helped me enjoy this process. I would like to thank them all.

People remember movies by actors but I have always done it by the directors, for its their vision that made the movie. Similarly, in this movie, the first person I would like to thank is none other than my director, my adviser- Dr. Robert Opila. Without his guidance, encouragement and enthusiasm this work would not have been possible. I still remember the day when I approached you and you readily accepted me. You asked me to start from the next day and get my hands wet. It has been a wonderful journey and if there is something I have learned from graduate school it would be the never-ending process of “learning by doing with enthusiasm” from you. Life has been easier because I had right adviser in every form. Your encouragement, support and wise advices are responsible for what I am today.

I would also like to thank the faculty, staff, and students who were so generous with their time and expertise throughout my time at the University of Delaware. Thank you to Kjeld Krag-Jensen, Lulian Codreanu, Kevin Shreve and Charles Garbini for always being there to help in and around lab. To Gwendolyn Looby, Kathy Forwood and Christine Williamson, thank you for helping me with academic and office related work. To Dr. Steven Hegedus and his graduate students, thank you so much for taking

the time and effort to help with characterization at the Institute of Energy Conversion. To Kevin Dobson at IEC for introducing New Zealand and the UV-VIS spectroscopy tool. Thanks to every staff member at IEC who have always welcomed us and hosted us for the seminars and conferences. To Dr. Joshua Zide and Bo Tew, thanks for helping with Van Der Paw measurements. Special mention to Dr. Willett Kempton under whom I took the Electric vehicles course. You have been a wonderful support and have influenced me in the way I do research. Dr. Sushoban Avasthi, professor at IISC, India and former graduate student with Princeton University, big thanks for sharing your expertise in the field and providing direction to my research. Rarely have I encountered personalities like you. Dr. Ken Nagamatsu, you have done incredible work in this field of solar and have your research was the source of answers to all my questions. Special mention to the entire team at Quantum Energy and Sustainable Solar Technologies (QESST) and special mention to Dr. Stuart Bowden and his team at Arizona State University for taking interest in my work and providing valuable suggestions. To Dr. Som Dahal, you are an excellent mentor. Thanks, a lot for Solar Cell 101. This work would not have been possible without the solar wafers fabricated at the ASU Solar Power Lab which was supported by the Nanotechnology Collaborative Infrastructure Southwest (NCI-SW) with funding from the National Science Foundation, contract number ECCS-1542160. To every other professor under whom I took classes, thanks a lot for sharing your wisdom and knowledge. My heartfelt thanks to the entire team at Venture Development Cell and HORN program in entrepreneurship. Professor Vince Defelice, Professor Dan Freeman, John Currie and Professor Keith Modzelewski- thanks a ton for fostering the entrepreneurship passion in me and helping me reach heights. You all made me realize the true potential

of my research by helping me discover and understand the world outside lab. This journey would be incomplete without you all.

Research is not fun or interesting without lab mate to work with. To being my first and best friend in the USA to being hydrofluoric acid buddy to introducing me to national politics to driving me all over places during NSF I-Corps to spending sleepless nights preparing me for the big presentations to ‘hacky’ jokes to being my mentor and the best lab mate, life would not have been the same without you, Jimmy Hack. You have been and shall remain the person I shall look forward to every time in my research. “Jimmy” Hack is above Jimmy Fallon and Jimmy Kimmel to me. Kevin Jones, you are the perfect definition of a “true gentleman and caring friend”. Thanks for hanging out with me in lab and outside lab for table tennis and bowling. Meixi Chen and Nicole Kotulak, thanks a lot for training me to Opila lab. Your work in this field has been indispensable to this project. Xi Lin, John Church, Colin Davis, Bo Yuan, Paul Parsons- You all have been wonderful group mates. Big thanks to my fellow graduate students with whom I had the great pleasure of collaborating and learning new techniques and tools. Roddel Remy, thanks a lot for introducing me to spin coating and x-ray diffraction. Gowri Manasa, you have been a wonderful friend and researcher. Thanks for helping me out in classes and at IEC. Ugo, you are one of a kind. Big thanks for guiding me whenever I needed any help. Ryan Hickey and Kevin Shreve, I have always looked up to you guys. Your expertise with tools in Dupont hall 247, professional and upbeat approach to research has always fascinated me. Bo Tew, thanks for helping us with resistivity measurements.

To my wonderful family in the USA- my cousins. Anand Mahalingham, Anuradha, Priya, Siddharth, tubby, Kala Gopalkrishnan, Hari and Keshav- thanks a lot

for making me feel at home during those holidays and taking us places around.

Houston and Boston are our new homes. Many thanks to introducing me to the “Fake” football- NFL, although I enjoy watching the games. I am confused whom to support- Houston Texans or New England patriots- maybe the Patriots because of Tom Brady and the effort Anand took on selling Tom Brady to me.

As Hubert Humphrey once truly said, “The greatest gift of life is friendship, and I have received it”, I agree completely and am proud to say that. To my family away from home- Vivek Subramanian, Chinmay Powar, Rohit Kakodkar, Sourabh Dwivedi, Ramachandran Balasubramanian, Karthik Sainathan, Saravanan Ramesh, Akirt Sridharan, Suhas Prasad, Pranjal, Ajith Nangare, Yasha Patel, Sucharitha Parthsarathy, Sai Durga, Pravallika Santhil and Arun Prabhu- Thanks a lot for taking good care of me- the late night cooking, the boring movies made funny, the countless sleepless nights playing cards, frisbee, baking, hiking and long drives are the highlights of my grad life. Thanks, a lot for making my life colorful outside lab. No matter where we all go from here, we shall always remain in touch. Rohit, Vivek, Chinmay, Arun, Suhas and Karthik- thanks for those countless nights spent playing FIFA on PS4. Not only we did we play together but we also bonded well over time- friends for life, FIFA for life. Big shout out to the entire Indian graduate student association at UD- for the Diwali events to intramural tournament together to cricket to the ‘real’ football- Home dint seem far away. To Arun Prabhu, thanks for teaching me the importance of simplicity and persistence in life. I found a brother in you. Ramachandran Balasubramanian, thanks for introducing me to cooking and god bless your sense of humor. Karthik Sainathan, watching and playing soccer will always be cherished. Akirt and Saravanan, thanks for keeping the home buzzing and cheerful

with your sense of humor. Sucharitha, partner in crime, hope to doing more in future. Sai Durga- you have been constant source of motivation. Your attitude in life has always amazed me. Vivek Subramanian- brother from another mother. Big thanks to my friends from undergrad who instilled the passion for solar in me- Ajith Venkateshwaran, Vivek Narayanan, Akрати Gupta, Atmaj Bhushan, Shilpa, Bhargav, Ayushi Agarwal, Sirish, Surya, Prudhvi Mouli, Pawan, Bhavna Damani, Brinda Roy, Divya Jena and Fathima Hussein. Lastly, Yasha Patel and Pravallika Santhil- thanks for being there, always and taking care of me. I shall, forever, remain indebted to you both.

Last but not the least, my parents, my twin brother and my family. This thesis is dedicated to both my grandfathers. You both have taught me the importance of positive attitude, helping others and simplicity by living your lives. Half the battle is won if your mind believes it and you both have taught me that lesson in every phase of my life. To my grandmothers for their incomparable love and the tasty food they prepared during my trips back home. To my uncle, aunt and cousins who have been wonderful role models.

No thesis is complete without parents. At first place, USA happened because of their love, support, prayers, sacrifices and the unwavering faith. To my mom, from the beginning you have always stressed on being a good, helping and caring person with values than anything else. I shall forever keep that in my mind. Staying away from you was tough but you always kept me motivated and focused on my work. Dad; One man army-your attitude, work ethics and dedication to family has always been an inspiration to me. This is not the end of journey; this is the beginning. I shall continue to work hard and make you all proud. In the very end, my reflection- my twin brother,

Abhijeet Iyer. I am what I am because of you. Best wishes to you on your thesis and future endeavors.

This material is based upon work primarily supported by the National Science Foundation (NSF) and the Department of Energy (DOE) under NSF CA No. EEC 1041895. Any opinions, findings and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect those of NSF or DOE.

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ABSTRACT

With today's photovoltaic technology we would require about 10,000 square miles of solar panels—an area the size of New Hampshire and Rhode Island combined to completely meet the country's energy demand [1]. Solar must be financially competitive to compete with other renewable energies and replace the conventional finite resources. There is constant effort to establish a solar technology which can achieve high power efficiencies with lower manufacturing costs. The most dominant solar technology is crystalline silicon which constitutes more than 90% of the solar market [2]. It has high proven efficiencies and the potential to rise to higher efficiencies with lower processing costs. Commercial scale crystalline silicon solar cells are based on aluminum back surface (AL-BSF) or passivated rear emitter contact (PERC) cell technologies that rely on high temperature processing. High temperature processing despite the most adopted process has few challenges like high capital expenditure (CAPEX) and operating costs (OPEX) of the tools, inability to process thin wafers easily and silicon impurities getting activated during the high-temperature steps leading to reduced minority carrier lifetimes and higher losses.

This thesis focusses on an alternative approach to forming silicon based solar cells using heterojunctions with materials that can be deposited at low temperatures. These carrier selective induced junction solar cells demonstrate a heterojunction like solar architecture with an organic polymer, poly(3,4-ethylenedioxythiophene) poly styrene sulfonate (PEDOT PSS), a chemical passivant- benzoquinone (BQ) and crystalline silicon as absorber with aluminum back surface field. These cells are also called hybrid solar cells because they involve the marriage of organics and inorganics. Device optimization of the hybrid solar cells is of interest in this thesis and is largely

based off the work previously done at the University of Delaware. Work is aimed at improving the solar cell performances by better cell design and processing techniques. These hybrid cells have demonstrated 10% power efficiencies at lab scale and are comparable to record efficiency hybrid solar cells (~14%). The potential commercial impact of this cell technology has also been discussed in this thesis.

Chapter 1

INTRODUCTION

1.1 Motivation

21st September, 2014 is a date I would never forget. I was with at least 300,000 other demonstrators in the streets of midtown Manhattan with demands for global leaders to act to avert catastrophic climate change. People from various parts of the world to all age groups flooded the streets of New York City vaulted environmental threat as the top most concern for the country. Such a huge gathering reflected the need for strict actions. We have inherited this place from our ancestors and we must ensure that we return it in the same way to our future generations. We must start acting on climate change. In "Climate 101: Introduction to Climate Change," a 2015 paper from the Center for Strategic and International Studies, the authors explain two main approaches to the problems posed by climate change: mitigation and adaptation. Mitigation refers to efforts to limit further global warming, while adaptation refers to implementing policies and innovations to respond to the warming conditions [3]. We know, climate change is largely driven by greenhouse gas emissions. Electricity production accounts for more than one-third of U.S. global warming emissions, with the majority generated by coal-fired power plants, which produce approximately 25 percent of total U.S. global warming emissions; natural gas-fired power plants produce 6 percent of total emissions. Compared with natural gas, which emits between 0.6 and 2 pounds of carbon dioxide equivalent per kilowatt-hour (CO₂ E/kWh), and coal, which emits between 1.4 and 3.6 pounds of CO₂ E/kWh, wind emits only 0.02 to 0.04 pounds of CO₂ E/kWh, solar 0.07 to 0.2, geothermal 0.1 to 0.2, and hydroelectric between 0.1 and 0.5 pounds. [4,5].

Today, renewable energy provides only a tiny fraction of its potential electricity output in the United States and worldwide. Estimates of the technical potential of each

renewable energy source are based on their overall availability given certain technological and environmental constraints [6]. In 2012, NREL found that together, renewable energy sources have the technical potential to supply 482,247 billion kilowatt-hours of electricity annually (Fig 1.1). This amount was 118 times the amount of electricity the nation consumed [7]. However, it is important to note that not all this technical potential can be tapped due to conflicting land use needs, the higher short-term costs of those resources, constraints on ramping up their use such as limits on transmission capacity, barriers to public acceptance, and other hurdles.

Table 1:			
Renewable Resource	Electricity Generation Capacity Potential (gigawatts)	Electricity Generation Potential (billion kilowatt-hours)	Renewable Electricity Generation as Percent of 2012 Electricity Use
Wind			
Land-Based	10,955	32,784	809%
Offshore	4,223	16,976	419%
Subtotal	15,178	49,760	1,227%
Solar			
Photovoltaics	154,856	283,664	6,997%
Concentrating Solar Power	38,066	116,146	2,865%
Subtotal	192,922	399,810	9,862%
Bioenergy			
Subtotal	62	488	12%
Geothermal			
Hydrothermal	38	308	8%
Enhanced Geothermal Systems	3,976	31,345	773%
Subtotal	4,014	31,653	781%
Hydropower			
Existing Conventional	78	277	7%
New Conventional	60	259	6%
Subtotal	138	536	13%
Total	212,314	482,247	11,896%

Figure 1.1 Technical potential of renewables

It is pretty much clear that shifting energy base from fossil fuels to renewable energy is the path forward for a safer planet. This would not happen today but it is vital that we have strong policies and leaders who encourage this movement. Within the various mix of renewables like wind, solar, ocean energy, hydroelectric, geothermal the adoption of any source is largely determined by topographical limitations, land/water use, climatic conditions, cost of technology and infrastructure to name a few.

Solar on other hand has slightly better technical potential. The sun is unlimited source of energy. The total solar energy absorbed by Earth's atmosphere, oceans and land masses is approximately 3,850,000 exajoules (EJ) per year. In 2002, this was more energy in one hour than the world used in one year [8]. The amount of solar energy reaching the surface of the planet is so vast that in one year it is about twice as much as will ever be obtained from all the Earth's non-renewable resources of coal, oil, natural gas, and mined uranium combined [9]. Solar energy from the sky can be trapped in form of solar thermal and solar photovoltaic energy. Solar thermal involves the heat properties of sunlight whereas solar PV utilizes the solar spectrum which when falls on certain materials convert it to useful electricity. The potential solar energy that could be used by humans differs from the amount of solar energy present near the surface of the planet because factors such as geography, time variation, cloud cover, and the land available to humans limit the amount of solar energy that we can acquire. The biggest challenge that lies for solar or any other mentioned renewables on the chart is renewable energy integration. Intermittency and lack of cheap storage techniques are two reasons renewables are criticized. The famous duck curve phenomenon with California is an instance of the

challenges to renewable integration challenge. The peak output from a solar plant is usually during noon times when the net load on the grid is relatively less. This results in more production than consumption per solar installed home. An interesting thing happens in the evening when the sun goes to sleep and people get back from job. There is a sudden shoot in electricity demand. People turn on the air conditioners, watch television, cook etc. and the demand goes up exponentially and there are not any renewables to support the grid unless stored. Hence renewables are not often preferred by utilities because they are intermittent and integrating them at the right time in day is challenging. The utilities have to depend on complex prediction models to understand solar and wind influx. Batteries with higher power density and lowered cost can make this transition smooth.

1.2 Thesis Outline

In chapter 2, a background to p-n junction and solar cell operation is provided. The performance factors of a solar cell are discussed and way to improve device performances are also discussed. In chapter 3, introduction to carrier selective induced junction hybrid solar cells is presented and reason behind choice of PEDOT: PSS is discussed. Chapter 4 discusses the hybrid solar cell device fabrication and characterization. J-V curve, Quantum efficiency, UV-VIS spectroscopy, Van Der Paw measurements and spin coating are discussed in this chapter. Chapter 5 talks about the entrepreneurship aspect associated with this research. The National Science Foundation Innovation Corps program is discussed in it. Chapter 6 will summarize the work and the path forward is discussed.

Chapter 2

SOLAR CELL BASICS

2.1 Background

A solar cell is a p-n junction under illumination. A p-n junction as the name explains is formed by placing a p-type semiconductor next to a n-type semiconductor. Before we discuss the process, we need to understand how these are formed. A n-type semiconductor is formed when silicon is doped with a group 5 element like phosphorous or arsenic. This results in formation of an excess electron which is not bonded to silicon atom. So, the majority charge carriers in a n-type semiconductor is an electron and the minority being holes. On contrary a p-type semiconductor is formed when silicon is doped with group 3 element like boron or aluminum and this results in formation of a hole. So, the majority charge carriers in a p-type material would be holes and minority being electrons. The band diagram for both the materials is shown in fig.1.1

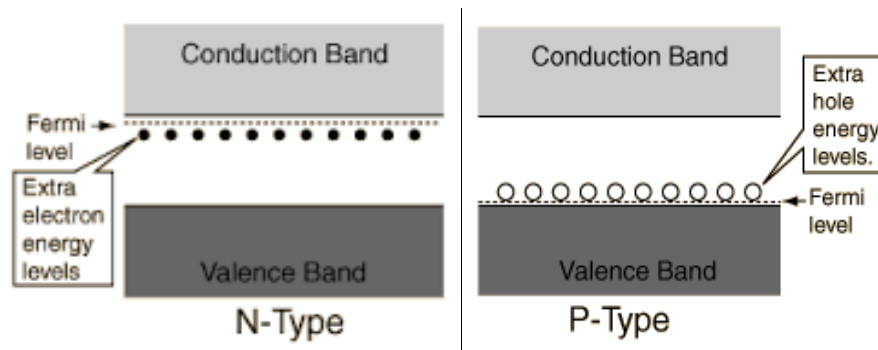


Figure 2.1 Diagram representing a p and n type semiconductor band structure.

Now a n-type semiconductor will have the Fermi level close to the conduction band whereas the p-type would have it closer to the valence band because of the structure

of the semiconductor. Fermi level is the energy level where there exists a 50% probability that the energy level will be occupied. At thermal equilibrium, the Fermi energy level would be constant. Now when a p-n junction is formed by bringing a p type material in contact with a n-type material the process of diffusion is initiated. Since electrons are majority carriers in n-type, they diffuse towards the p-type and similarly holes being majority charge carriers in the p-type start diffusing towards the n-type. This happens due to difference in concentration on both sides. Now this diffusion of charges leaves the p-type negatively charged and the n-type positively charged. The region with depleted charges is called the depletion region or space charge region. This region is the region with uncompensated immobile charges and it creates an electric field that restricts the flow of charges on either side of the junction. Also, once the majority charges carriers leave to other side they end up being minority charge carriers on the other side. They exist for a small time before which they recombine. This lifetime is called minority carrier lifetime. Figure 2.2 explains the p-n junction in short.

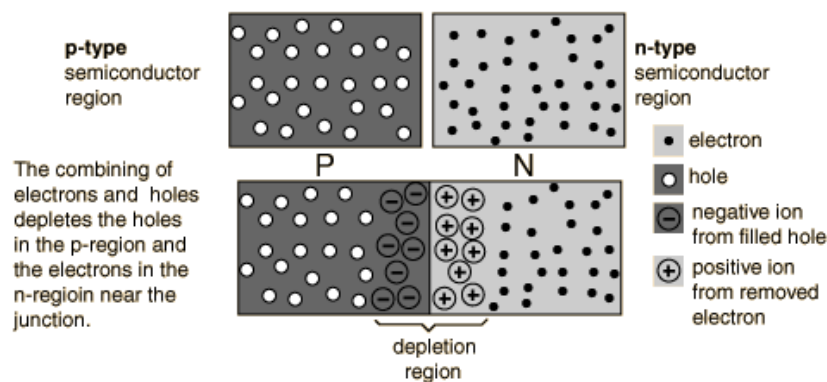


Figure 2.2 A p-n junction explained [10].

2.2 Solar Cell

A solar cell converts sunlight into electricity. It is a special type of p-n junction. The absorption of photon results in excitation of an electron from valence band to the conduction band. This also results in vacant energy level in the valence band which is termed as a hole. These electrons and holes stay in the new states only for some small time before they are lost by recombination: when electron falls into the hole (empty state in the valence band). This affects the minority charge carriers in the solar cell i.e. the density of electrons in p region and the density of holes in n region of the device. Subsequently many electrons drift from p to n region and holes from n to p region i.e. the electrons move to the lower energy and holes move towards higher energy. When the p side is connected to the n side by a wire or a resistor, current starts flowing through the external circuit (least resistance). The current density for an ideal solar cell can be given as,

$$J = J_0(e^{qv/nkT} - 1) - J_L \quad (2.1)$$

where J is the current density, J_0 is the dark saturation current, q is charge on electron, k is the Boltzmann constant, T is the temperature, n is the ideality factor and J_L is the illuminated current density. J_0 is a measure of recombination in the device and it is calculated from the below formula,

$$J_0 = q \left(\frac{D_n n_i^2}{L_n N_A} + \frac{D_p n_i^2}{L_p N_D} \right) \quad (2.2)$$

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. We can infer that J_0 term is highly dependent upon material quality.

A good way to understand parameters that affect the performance of solar cell is the J-V curve. The J-V curve is a plot of voltage with current density and is a good way to determine the operating parameters of the solar cell.

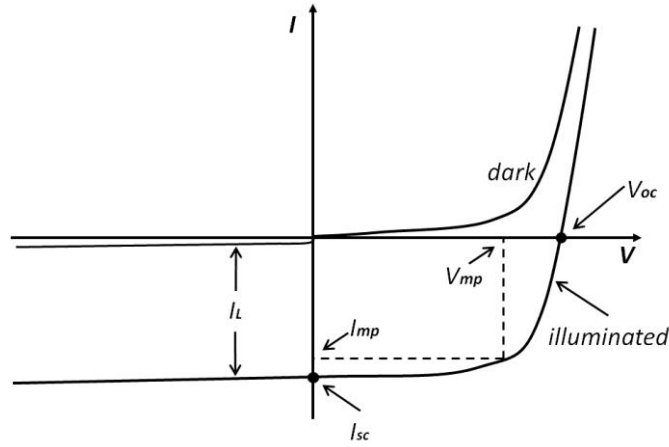


Figure 2.3 A J-V curve with performance parameters.

The two most important parameters for any solar cell are the open circuit voltage (V_{oc}) and the short circuit current density (J_{sc}). The open circuit voltage is the voltage when there is no current flowing through the circuit and the cell solely produces voltage. From the J-V curve, V_{oc} is the point of intersection of the J-V curve with zero current density. From equation 2.1 we have,

$$V_{oc} = \frac{nk_bT}{q} \ln \left(\frac{J + J_L}{J_0} \right) \quad (2.3)$$

The open circuit voltage depends on band gap of the absorber material, amount of doping, quality of the material, light generated current density and temperature. The open circuit voltage also depends on the dark saturation current which reflects recombination in the

solar cell. As recombination is reduced, the lifetime increases and the open circuit voltage also increases. Recombination is defined as the phenomenon by which generated carriers get back to their normal states. The time for this process is called lifetime and is defined as the average time for which the generated carriers exist before being lost by heat or radiation or any other form. Recombination at the surface of the cell is commonly referred to as surface recombination and in the bulk of the solar cell is called bulk recombination.

There are different types of recombination processes. They are:

- Radiative recombination
- Auger recombination
- Shockley Read Hall recombination

Lifetime at bulk level is referred to as bulk lifetime and is denoted by τ_{bulk} . It can also be expressed in the form of the above three recombination processes. The equation that relates them to bulk lifetime is given in Equation 1.4.

$$\frac{1}{\tau_b} = \frac{1}{\tau_{radiative}} + \frac{1}{\tau_{auger}} + \frac{1}{\tau_{SRH}} \quad (2.4)$$

Radiative recombination is the average time an electron and hole exist before they recombine to give energy by photon. It is more important to direct bandgap materials like GaAs than indirect bandgap materials. It is often neglected for indirect bandgap materials because it is very slow.

The second term is Auger recombination is a process in which the minority carrier recombines by transferring energy to another charge carrier. It usually involves three carriers- the electron and hole recombine but unlike radiative recombination they pass on the energy to a third carrier often an electron in the conduction band. Highly doped materials are at higher risk of recombination by Auger mechanism and this affects the material largely if the thickness is less. For example, Kerr et al. showed for n-type samples

with $N_D = 3.2 \times 10^{15} \text{ cm}^3$, Auger recombination was not observed to begin reducing τ_{eff} until the excess carrier density was near $1 \times 10^{15} \text{ cm}^3$ (close to high-level-injection) [11]. At this point, the Auger-limited lifetime was $\sim 50 \text{ ms}$, which is a very high lifetime. The highest quality wafers used in this work had bulk lifetimes of $\sim 1 \text{ ms}$ at an excess carrier density of $1 \times 10^{15} \text{ cm}^3$, suggesting that other types of recombination were dominant.

The third and final mode of recombination is the Shockley-Read-Hall (SRH) and it is a special case because it happens only in imperfect and contaminated substrates. The energy of carriers recombining via trap states is given off by low energy photons. It is a two-step process:

1. The charge carrier is trapped by an energy state in the forbidden region which is because of the defects or contaminants. These defects can either be unintentionally introduced or deliberately added to the material during doping of the substrate.
2. If a hole (or an electron) moves up to the same energy state before the electron is thermally re-emitted into the conduction band, then it recombines.

In addition to the above-mentioned bulk recombination there also exists surface recombination. It largely results from the nature of the material because at the surface, the crystal structure ends and this disruption can result in dangling bonds at the surface. These dangling bonds break the symmetry of the lattice and this results in formation of surface states in the forbidden region of the material. These surface states end up serving as recombination centers by creating a trap state. This just initiates the SRH recombination and the rate of it is given by Equation 1.5 where N_{it} , σ_{it} and E_{it} , are the concentration, capture cross-section, and energy level of traps at the interface respectively.

$$U_{surface,SRH} = v_{th} N_{it} \sigma_{it} \frac{np - n_i^2}{p + n + 2n_i \cosh(\frac{E_i - E_{it}}{kT})} \quad (2.5)$$

The other parameter is the short circuit current density. If we short circuit both terminals of the solar cell the illuminated solar cell would produce no voltage but current only. This current density is J_{sc} . From the curve, it is the intersection between the vertical line corresponding to zero voltage and the J-V curve. The short circuit current is given by:

$$J_{sc} = qG(L_p + L_n) \quad (2.6)$$

where, G is the generation rate due to illumination and L_p & L_n are the hole and electron diffusion lengths, respectively. The relation assumes that the depletion width in both n and p regions is much less than the diffusion lengths, L_p & L_n and it also neglects the effect of surface recombination. The short-circuit current depends on several factors which are described below:

- **Incident photons and collection probability-** The short circuit current depends largely on the power of the incident source. An ideal state is denoted by 1 sun where 1 sun corresponds to standard illumination at AM1.5, or 1 kW/m² (i.e., the power of the incident light source). One way of increasing the light capturing ability of the solar cell surface is by texturing or anti-reflecting coatings. Surface texturing increases the collection probability by reducing the energy lost by reflections. While many methods of texturing silicon surfaces can be employed, one of the most common in solar cell processing is anisotropic etching in wet-chemical solutions [12]. Alkaline solutions such as potassium hydroxide or sodium hydroxide have been shown to etch preferentially along silicon $\langle 111 \rangle$ crystal planes [13]. Tetramethylammonium hydroxide (TMAH) has also shown to be an effective, metal-ion free anisotropic etching solution [14]. These wet

chemical etches provide a simple process that will transform a < 100 > silicon surface into a randomly pyramidal-textured surface (with no patterning) or an ordered pyramidal textured surface (with lithographic patterns). While both KOH and TMAH seem to do the job, there exists some little differences between the two which can be understood by the SEM images. KOH is a metal hydroxide whereas TMAH is an organic hydroxide. The presence of metal in KOH can be detrimental to some applications like in MEMS but several studies suggest that KOH etches the nicest and continues to be used by most. Studies of the SEM images suggests that there are differences in the etching mechanisms of the two etchants in terms of crystallographic orientation. The etching rates depend on the concentration of KOH and TMAH solutions. Silicon solar cells also implement anti reflection coating(ARC) on the front and silicon nitride is the material of choice. The dark color of solar cells is due to the silicon nitride deposited on the front. The collection probability of the solar cell is dependent on passivation and minority lifetime which will be discussed later in the thesis.

- **Spectrum of the incident light-** Solar cell measurement is always done at AM 1.5 G. AM refers to air mass which is the path length sunlight takes to strike earth in comparison to when the sun is right above during noon and G refers to global radiation which includes both direct and diffused radiation. The efficiency of a solar cell is sensitive to variations in both the power and the spectrum of the incident light and hence AM 1.5G is the spectrum we are interested in.
- **Optical properties-** Optical losses can be summed up as the potential electron-hole pair which could have been generated but did not due to reflection at surface or not being absorbed appropriately. From solar spectrum for most crystalline

solar cells, the entire visible spectrum (350 - 780 nm) has enough energy to create electron-hole pairs and therefore all visible light can yield electricity under ideal state. Two major ways of decreasing optical losses is by surface texturing and by growing anti-reflective coatings. Surface texturing has already been discussed in the above section. Anti-reflective coatings for silicon solar cells involve the deposition of silicon nitride by plasma enhanced CVD process. ARC coating decreases the optical loss by minimizing reflection by maximizing the transmission (light trapping). The thickness of this layer will determine the color of the solar cell. Reflection can further have minimized if the refractive index of the anti-reflection coating is the geometric mean of that of the materials on either side. The graph below from PVEDucation suggests the advantage of ARC.

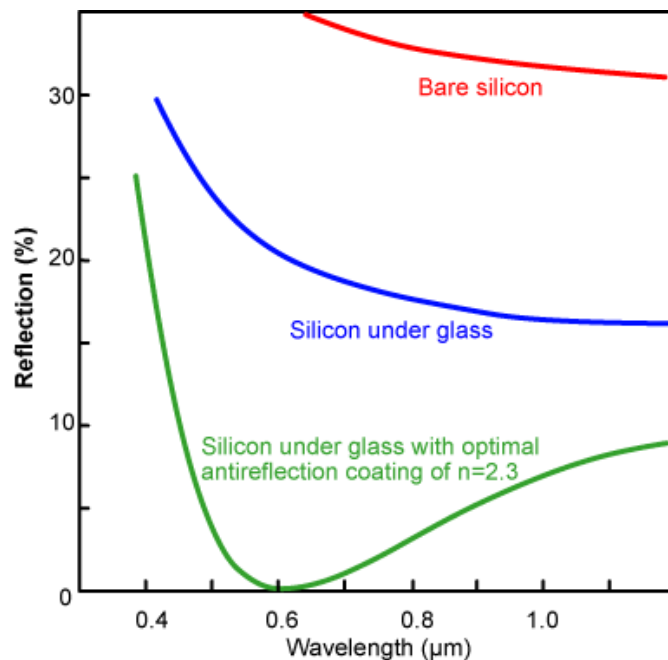


Figure 2.4 Comparison of surface reflection from a silicon solar cell, with and without a typical anti-reflection coating (Source- PVEDucation.org).

The power density is obtained by multiplying the voltage and current at every instance. At short circuit, current and open circuit voltage conditions the power density is zero. It is maximum at certain voltage and current density. This voltage is called V_{mp} and the corresponding current density is called J_{mp} and the power under this condition is called maximum power density. The solar cell will perform best at this state. The factor that relates maximum power to the open circuit voltage and short circuit current is the fill factor. The diagram is a good explanation of the fill factor. It is impossible for a solar cell to have fill factor of 1. The fill factor is basically a measure of the quality of a solar cell or also the squareness of the J-V curve.

$$FF = \frac{V_{mp} * J_{mp}}{V_{sc} * J_{sc}} \quad (2.7)$$

Fill factor has high dependence on the shunt and series resistance. These are mentioned in the Fig. 2.4 below. Series resistance is denoted by R_s and shunt resistance by R_{sh} as shown below.

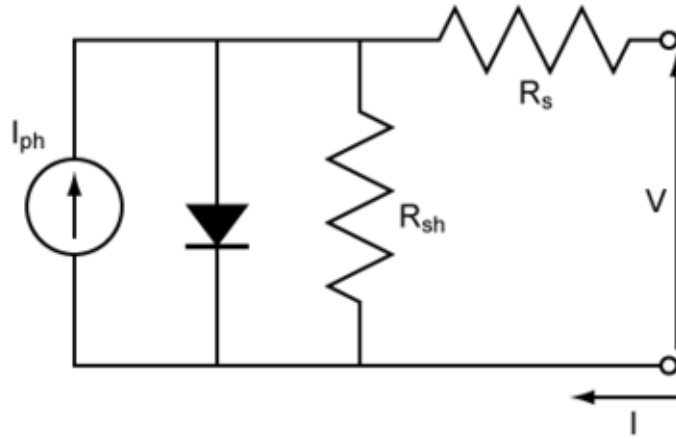


Figure 2.5 Equivalent circuit for a solar cell.

A solar cell behaves like a diode in absence of light and under light, it generates electricity by photovoltaic effect. A solar cell can be explained by the equivalent circuit as shown in figure 2.5. I_{ph} showed in the figure is a current source connected in parallel to the diode. It reflects the current generated by light. An ideal solar cell is a current source in parallel with a diode; but no solar cell is ideal. A shunt resistance and a series resistance component are added to the non-ideal solar cell. So, being connected in series, as current flows through the series resistance, there will be losses due to heat. Series resistance arises because of the contact resistance between the metal contacts and the silicon substrate, resistance of front and back contacts and the conventional current flow between emitter and base. The loss due to series resistance largely affects the fill factor and the area under the J-V plot. It does not affect the open circuit voltage. The slope at this voltage will give us the series resistance and ideally we would want it to be zero. The impact of series resistance on fill factor can be understood better by Equation 2.8,

$$I(V) = I_L - I_0 \exp\left(\frac{q(V+IR_s)}{nkT}\right) \quad (2.8)$$

where: I is the cell output current, I_L is the light generated current, V is the voltage across the cell terminals, T is the temperature, q and k are constants, n is the ideality factor, and R_s is the cell series resistance.

The shunt resistance provides additional dark current path in parallel with the diode shown in the Fig 2.4. It is a macroscopic defect which provides an alternative path to the generated photocurrent. It could be a defect in the substrate layer or a current path at the edges. This results in drop of voltage from the solar cell. Solar cell in presence of shunt resistance can be denoted by the below equation.

$$I = I_L - I_0 \exp\left[\frac{qV}{nkT}\right] - \frac{V}{R_{sh}} \quad (2.9)$$

where: I is the cell output current, I_L is the light generated current, V is the voltage across the cell terminals, T is the temperature, q and k are constants, n is the ideality factor, and R_{sh} is the cell shunt resistance.

The efficiency of a solar cell is the ratio of output power to input power. The output power can also be referred to as the maximum power from the solar cell which from the above formula can be written as

$$\eta = \frac{P_{out}}{P_{in}} = \frac{P_{max}}{P_{in}} = \frac{I_{mp}V_{mp}}{P_{in}} = \frac{I_{sc}V_{oc}FF}{P_{in}} \quad (2.10)$$

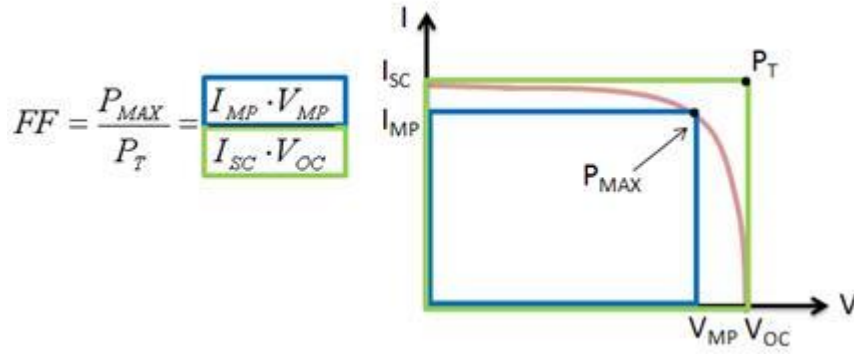


Figure 2.6 J-V curve parameters [15].

2.3 Solar Technologies

While there exist many recipes for making a solar cell, the widely manufactured solar cell is based out of the aluminum back surface field technology (AL-BSF). These cells dominate the market today because they have mature manufacturing processes, lower costs (since they involve diffusion, screen printing and contact firing techniques), high proven efficiencies (~20%) and less losses. Another technology which is catching up is the PERC and PERL cell which stand for passivated emitter rear contact solar cell

and passivated emitter locally diffused solar cell. From the NSF I-Corps experiences, we learned that the solar industry was making shift from the aluminum back surface field to the PERC/PERL cells because the shift was a mere upgrade in terms of manufacturing and the PERC architecture essentially enabled to improve light capture near the rear surface and to optimize electrons capture. The holy grail in the solar industry is to increase efficiencies with minimal increase in manufacturing costs and technology. The best crystalline silicon p-n junction based solar cells have reached 25% efficiency under AM1.5 illumination [16]. The passivated emitter rear locally-diffused (PERL) cell developed at the University of New South Wales has reached efficiencies of (25.0 ± 0.5) % [17], and the all back-contact cell made by SunPower Corporation has achieved an efficiency of (25.0 ± 0.7) % [18].

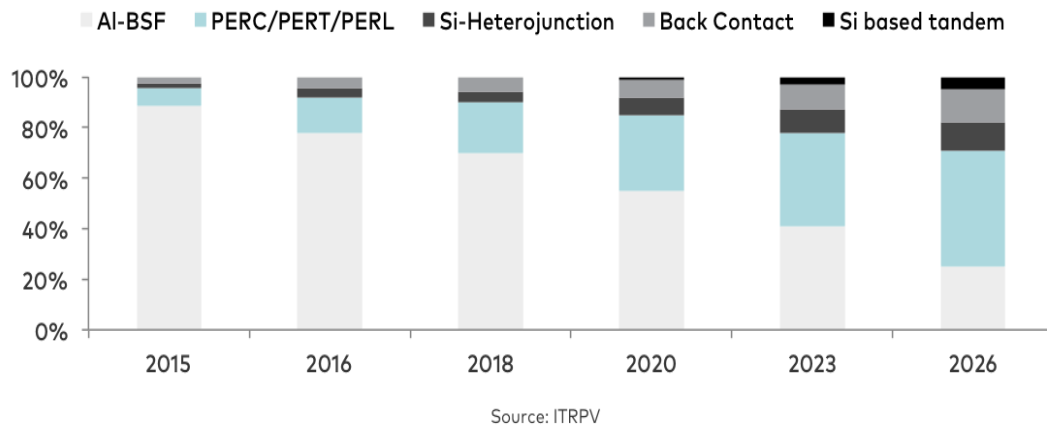


Figure 2.7 Solar manufacturing technologies and their share.

In conclusion, a major limitation for the above discussed solar cells is that each implement a different structure and thereby the process involved in fabrication vary

significantly. An AL-BSF cell is different from IBC or HIT cell. Although, studies suggest that heterojunction solar cells, if engineered properly, do not require doping of the substrate, and therefore theoretically can achieve higher open-circuit voltage and efficiency than p-n junction solar cells [19]. Furthermore, devices that involve organics can be deposited using solution based techniques which are amenable to large-scale, roll-to-roll manufacturing. Due to the higher processing temperature in above mentioned solar technologies, the existing defects in c-Si wafers may exhibit further deteriorative effect. Thus, a combination of both the crystalline and amorphous Si technology in the form of the heterojunction with intrinsic thin layer (HIT) was considered a potential solution to these issues.

With 25.6% record efficiency, the HIT cells are state of the art in the solar industry [19]. These cells have attracted attention of photovoltaic research community due to its low process temperature, as compared to crystalline silicon (c-Si) solar cell and relatively high efficiency (η). 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 the n type c-Si substrate. The next layer in the heterojunction is the intrinsic Amorphous-Si (α -Si(i)). This layer provides high quality passivation of the defects on the c-Si surface to reduce recombination losses. Finally, the α -Si(p+) and α -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-pair.

The principle of operation of the HIT solar cell can be described in equation by:

$$J(V) = J_{01} \left(e^{\frac{q(V-JR_s)}{nkT}} - 1 \right) + J_{02} \left(e^{A_1(V-JR_s)} - 1 \right) + \left(\frac{V-JR_s}{R_p} \right) - J_{ph} \quad (2.11)$$

where q is electron charge, J_{ph} is photo current density, J_{01}, J_{02} are reverse saturation current densities, n diode ideality factor, k Boltzmann constant, T temperature, R_s series resistance, R_p parallel resistance, A_1 is a temperature independent constant. Because of different energy band structure of the layers, the unwanted reverse flow of charge carriers can be reduced. The conduction and valence band discontinuities prevent electrons and holes to travel towards p-type and n-type layers respectively, whereas the valence and conduction band continuities help a smooth diffusion and tunneling of the holes and electrons towards the p-type and n-type layers respectively.

Chapter 3

CHEMICAL PASSIVATION

3.1 Introduction

An excellent electrical interface quality is essential for solar cells [20]. The surface of silicon is susceptible to higher recombination losses due to presence of dangling bonds. Dangling bond defects could correspond to either surface recombination or Auger recombination or Shockley-Read-Hall recombination. These recombination losses can be mitigated through two basic types of passivation- chemical and electrical. Chemical passivation aims at reducing the surface trap states by linking either hydrogen atoms or semiconductor film or some dielectric materials. For example, the midgap interface defect density of c-Si can be as low as $10^9 \text{ eV}^{-1}\text{cm}^{-2}$ after growth of a high quality thermal SiO_2 film and a subsequent anneal in a H_2 atmosphere[21]. Electrical passivation on other hand reduces the electron or hole concentration by creating an electric field.

3.2 Passivation

Let us assume we have an unpassivated solar surface and we shine light on it to generate excess electrons and holes. Considering the excess electrons in the system, we tend to have diffusion from the site of excess electrons to the site with deficiency of electrons due to a concentration gradient. These excess electrons tend to decrease as they approach the surface. The above explanation can be represented with a formula that relates diffusion with surface recombination.

We have,

$$-(D_p \frac{\partial n}{\partial x}) = -SRV * \Delta n \quad (3.1)$$

where, D_p is the diffusion constant, SRV is the surface recombination velocity measured in cm/sec and Δn being the excess charge carriers generated. From the above relation, surface recombination is zero when we have a very good passivation and there are not any surface states present as such and it is maximum(infinite) when Δn is zero which indicates no excess carriers being generated. A good solar cell has surface recombination velocity ranging between 1-10 cm/sec though most cells have SRV ranging from 100-1000 cm/sec with metal passivation. Surface recombination velocity is found to be high when the number of holes are equal to the number of electrons and the presence of surface states provides these carriers a recombination center and they end up recombining before they are extracted to generate electricity. There are several methods like back surface field, fixed charge present in the oxide that help reduce this velocity which would be discussed later in the thesis.

Conventional solar cells are passivated with silicon dioxide or silicon nitride. While they are effective passivants, they involve high temperature deposition and processing techniques. They are costly too because of the setup and apparatus required. Amorphous silicon is the low-temperature alternate although this process is challenging. On other hand, chemical passivation is less intensive and involve low processing costs. Most of the chemical passivation can be achieved under lab environment. Also, since it is quick, they have become standard for lifetime measurements which determine wafer quality or help in ingot characterization.

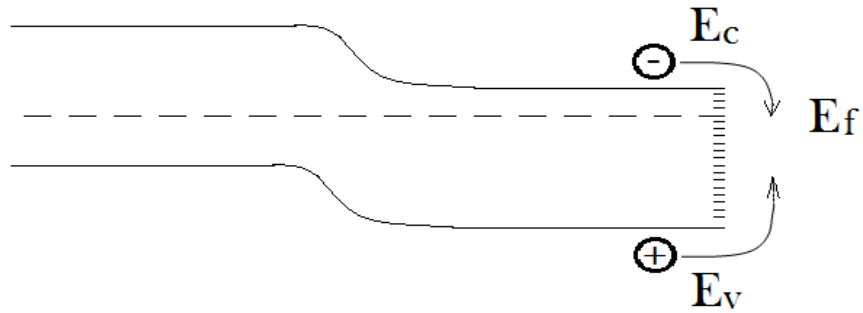


Figure 3.1 High concentration of surface states/recombination centers.

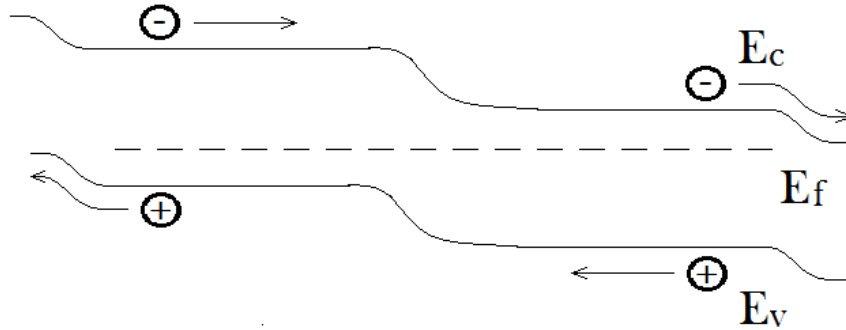


Figure 3.2 Passivation effect.

There exist various cost-effective and efficient chemical passivants like iodine-methanol, hydrofluoric acid, methanol, bromine-methanol, quinone family compounds. From a lot of studies that have been performed on these chemical passivants, quinhydrone and methanol solution were found to be simple, easy, less-hazardous and a relatively stable chemical passivation techniques. Besides they can come useful to measure the effective lifetime and testing the ingot/wafer quality by measuring its bulk lifetime at

initial stages in contrast to high temperature passivation techniques. Amongst the chemical passivants, there remains a special interest towards quinhydrone. They are comparatively more stable than other chemical passivants but degradation in presence of air remains the biggest challenge to it. This conclusion comes out largely from the experiments that suggested that lifetime of samples was higher when immersed in solution than when removed out of the solution. Previous studies in the group have focused on the use of quinhydrone derivatives, such as benzoquinone, for passivation of silicon <100> surfaces. Quinhydrone is a solid charge-transfer complex consisting of an equimolar mixture of benzoquinone (BQ) and hydroquinone. When dissolved in a solvent these two constituents form a two-electron redox couple. Quinhydrone was first shown as a passivant by Takato et al.[22] Studies by Chhabra et al.[23] showed the ability to achieve high minority carrier lifetimes in both p-type and n-type silicon by treating hydrogen-terminated silicon surfaces with solutions of quinhydrone in methanol. Subsequent studies provided evidence that benzoquinone was the more active constituent in the quinhydrone complex[24].

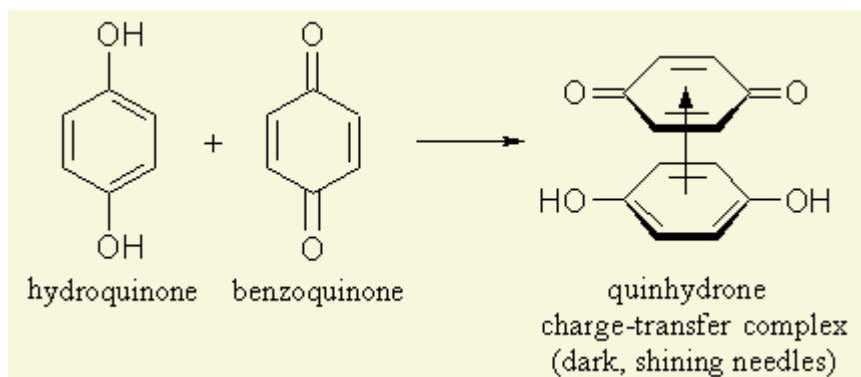


Figure 3.3 Quinhydrone constituents.

3.3 Quasi-Steady-State Photoconductance Decay measurement

When light falls on a silicon substrate, photons with energy greater than the bandwidth of silicon would be absorbed and would generate excess charge carriers. These charge carriers get excited and jump to higher energy level but fall back soon to their original levels. The phenomenon of falling back to their original state is called recombination. And photo conductance decay is reflection of the change in conductivity of the silicon substrate due to these excess charge carriers generated. The quasi-steady-state photoconductance decay(QSSPCD) method is an extremely useful technique that allows the measurement of the effective minority carrier lifetime as a function of carrier density [25].

By measuring the time, it takes for the crystal conductivity to return to equilibrium after the excitation is called the lifetime of the minority carriers. If the lifetime of charge carriers is more than the time it takes to travel the thickness of the substrate, then these carriers are collected as current. Contactless methods for measuring PCD have been achieved through the Sinton WC-120 tool [25]. The number of excess charge carriers generated by the Xenon flash are estimated by measuring the change in conductivity of the sample through an inductive coil. The tool used is shown in figure below.



Figure 3.4 Sinton WC-120 lifetime tester.

N.A. Kotulak et al. [26], examined the passivation properties of quinhydrone (QH) by understanding the contributions of hydroquinone(HQ) and benzoquinone(BQ) that make quinhydrone. For these tests, two types of wafers were tested- 1. N-type, P-doped, <100>, double-side polished(DSP), 500 microns thick, 20-30 ohm-cm resistivity, 2 inch by 2-inch size, and 2. P-type, B-doped, <100>, DSP, 525 microns thick, 10 kilohm-cm resistivity and 2 inch by 2 inch sized. The wafers were initially cleaned using a three-step process- 5-minute dip in solution of 4:1 piranha (sulphuric acid and hydrogen peroxide) at 100°C followed by 5 min de-ionized(DI) water dip and a 2 min in dilute hydrofluoric acid. After cleaning the water wafer was given a DI water dip and dried using nitrogen gun. Wafers were then put in two different zip lock bags containing 0.1M solution of BQ in methanol (ME) and HQ in ME. Lifetime measurements were taken

from $t=0$ indicating the immersion of wafer inside the solution and was recorded every 15 minutes. The lifetime measurements are shown in the figure below.

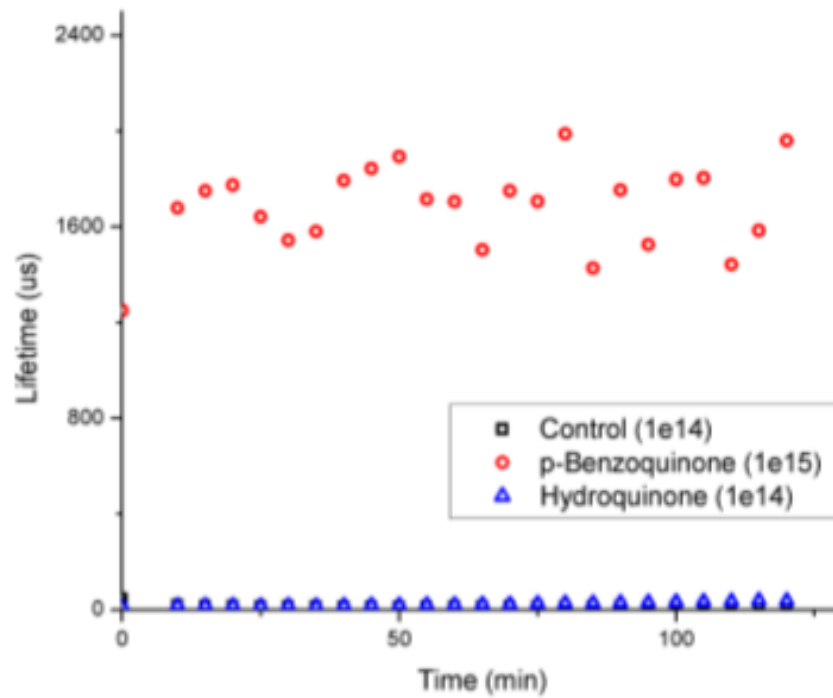


Figure 3.5 Change in lifetime over 2 hours for a p-type wafer in BQ/ME, HQ/ME and ME.

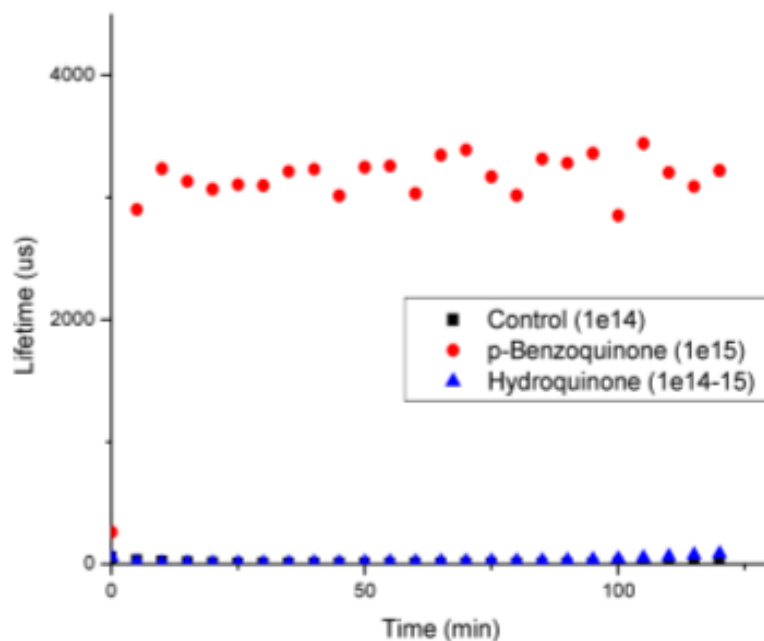


Figure 3.6 Change in lifetime over 2 hours for a p-type wafer in BQ/ME, HQ/ME and ME.

We know that quinhydrone passivates but from the lifetime values that we obtained we can say that benzoquinone is the active passivant than hydroquinone in given period. As can be seen from both figures, BQ/ME solution provides immediate, high lifetime passivation whereas the HQ/ME solution does not have the same immediate effect. X-ray photoelectron spectroscopy (XPS) was carried out on these wafers to understand the bonding mechanism which won't be discussed here. The passivation effects of QHY/ME were investigated on c-Si surface and after a series of lifetime and XPS tests, it can be said that BQ is the active component of QHY/ME. HQ/ME tends to show contribution after longer exposure in light. The free radical $QH^\cdot$ is likely the passivating specie which was demonstrated by a systematic study showing the effect of

protons and light exposure on the passivation reaction. XPS studies also confirmed the presence of methoxy and QH[•] on the c-Si samples in rough 1:1 ratio [26]. The precise mechanism by which the silicon <100> surface is passivated in benzoquinone and methanol solution is still under active study. N.A. Kotulak suggested a free radical bonding mechanism by which both quinone radicals and methanol radicals bond to the silicon surface[26]. XPS studies[27] have shown evidence of both quinones and methanol bonded to the surface. They appear to form essentially a monolayer at the surface.

3.4 Device Architecture

Organic semiconductors have been an area of interest since a long time. As far as their structure is concerned, they also possess valence and conduction bands although they are called by different names. The valence and conduction bands for these materials are translated to highest occupied molecular level(HOMO) and lowest un-occupied molecular levels(LUMO). The HOMO is equivalent to valence band whereas LUMO is conduction band equivalent. The Fermi level lies between these levels. Excitation from HUMO to LUMO does not result in free carriers but excitons. Excitons are electrons and holes tightly bound, with binding energies varying from 0.1ev to 0.5ev [28]. These binding energies are high because of the lower dielectric constant for these molecules. These organic semiconductors are usually deposited on any substrate through spin coating, doctor blading, dip coating, screen printing and hence the operational expenses associated with these tools/techniques are very low. Also, they require less maintenance than traditional vacuum based deposition tools. These unique properties make organics an attractive choice to traditional high temperature based solar cells.

Solar cells based out of crystalline silicon are often called “homojunction” devices because they involve forming a p-n junction (same material with different doping). In contrast, heterojunction solar cells, as the name suggests, involve different bandgaps, materials, crystalline properties, phases etc. Devices discussed in this thesis are also called hybrid solar cells because it is marriage between organic conducting polymers, chemical passivants and silicon substrate. The induced junction is formed between the organic conductive polymer- PEDOT: PSS and silicon substrate and the chemical passivant- benzoquinone is believed to bend the bands. In this section, we shall discuss on why PEDOT: PSS was chosen as the material. Band alignment is the first and biggest challenge while designing carrier selective solar cells. Depending on the band alignment these can be hole-selective and electron blocking or hole-blocking and electron-selective. Hole-selective, electro-blocking junctions will block electrons from recombining at the anode and this would result in net dark current getting generated. Conversely, an electron-selective, hole blocking junction would block hole recombining at cathode and let the electrons to pass through freely. This results in two types of heterojunction like structures as shown below.

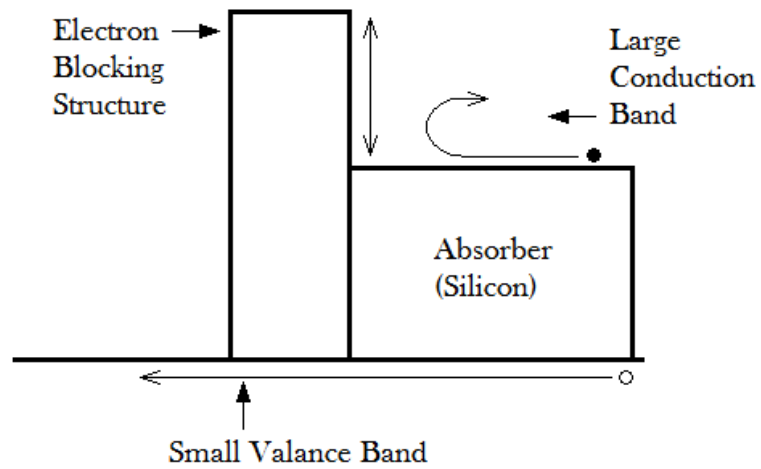


Figure 3.7 Band diagram of an electron blocking- hole selective induced junction cell.

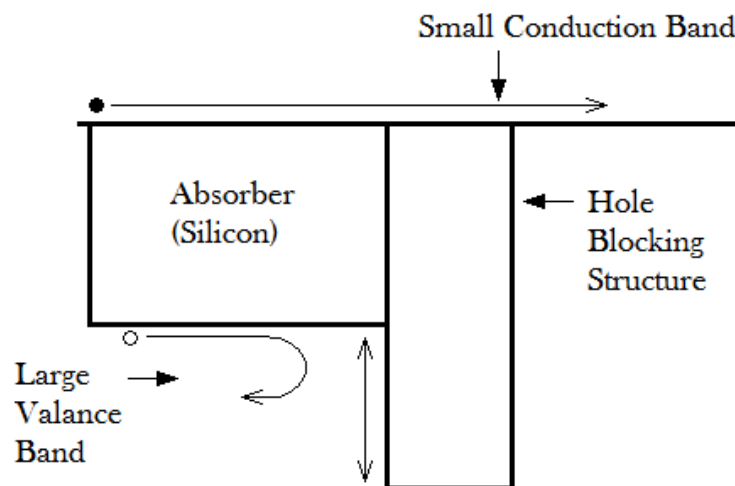


Figure 3.8 Band diagram a hole blocking- electron selective induced junction solar cells.

We observe that electron blocking devices have a large offset to the conduction band of the absorber whereas the hole-blocker has opposite band alignments. The larger

offset results in the electrons repelling from crossing the barrier and getting collected on cathode end whereas holes have an easier path to get collected at anode due to small valence band. It can be implied for the hole-blocking devices as well where due to large valence band, the holes are blocked off from going to the cathode and small conduction band yield way for electrons to get abstracted at cathode. Thereby the structure of this cell facilitates the movement of electrons and holes. Additionally, work functions of the anode and cathode must be high and low respectively, such that they are aligned with the valence and conduction bands [29].

This is necessary for because it provides pathways for electrons or/and holes. Assuming a n-type substrate, we shall have an electric field built up near the electron-blocking junction due to the presence of high work-function anode. There might exist built-in electric field at the hole-blocking side but it is not strong due to n-type substrate.

The reason why PEDOT: PSS was chosen as the carrier selective contact for hybrid solar cells can be understood by analyzing its band structure. Location of energy levels of this organic molecule is essential to realizing the device architecture. This was studied through photoelectron spectroscopy techniques, namely ultraviolet photoelectron spectroscopy(UPS) and inverse photoelectron spectroscopy(IPES). These photoelectron spectroscopy methods use photoelectric effect to measure the kinetic energy and number of electrons emitted to understand the binding energies of the material. The UPS gives a picture of the filled states(HOMO) and measurement of work function of the material while IPES yields energy levels of the empty states or the unoccupied states(LUMO). From the UPS and IPES studies conducted, the determined LUMO and HUMO for PEDOT: PSS are around 3.46eV and 4.94eV respectively [29]. The position of LUMO at 3.46eV below vacuum level is about half an eV above the conduction band of silicon and

the HUMO of PEDOT: PSS at 4.94eV indicates its closeness to the silicon valence band of 5.16eV [29]. It can be inferred from the LUMO positioning that PEDOT: PSS forms a barrier to electrons in the conduction band. Thus, PEDOT: PSS based device tends to behave more like a hole-transport/hole-selective device.

In recent years many groups have produced research on a hybrid organic-inorganic device structure using PEDOT:PSS deposited on silicon[30-32]. Solar cells fabricated in the lab have a structure that uses silicon as the primary light absorber, utilizing PEDOT: PSS as a carrier selective contact. Such a device structure enables the creation of a silicon-based junction through solution-based processing. In this device structure, the PEDOT: PSS layer can induce an inversion layer within the silicon. However further improvement to the passivation of the silicon at this interface should be able to improve the open circuit voltage and achieve stronger inversion.[33]

Based on this desire, we propose a device structure that uses a thin passivating layer to promote carrier inversion and achieve high open circuit voltages, while using the organic semiconductor to serve as a carrier-selective transparent conductive layer. This device follows the basic band structure used in the high-efficiency HIT solar cell architecture. For the sake of simplicity, we will focus primarily on developing the front surface initially. Here, a thin benzoquinone layer can serve to passivate the silicon, while a thicker PEDOT: PSS layer facilitates transfer of holes. The figure below is an assumption of how the bands are aligned and how the device functions in this case. Future work is aimed at understanding the exact band alignments by identifying the band gap for each material.

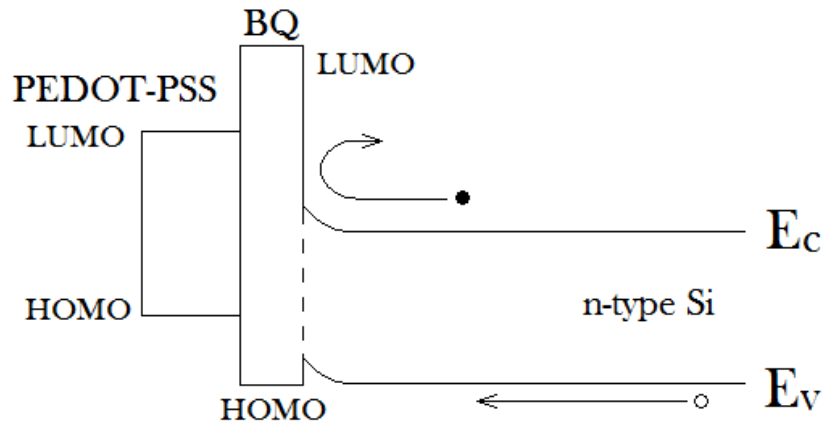


Figure 3.9 Expected band diagram and energy level alignment of device interface.

For solar cells fabricated in the lab, n-type substrates are preferred over p-type substrates because of superior performances. In n-type wafers due to absence of boron, there is no light induced degradation (LID) which is a major concern for p-type substrates [34]. LID is a serious threat to reliability of solar panels. Besides that, n-type silicon has higher minority carrier diffusion lengths which improves the light conversion ability of the solar cell. Owing to the two reasons discussed above, most high efficiency solar cells are based out of n-type base.

Heterojunction solar cells like the ones commercialized by Sanyo, now Panasonic offer several advantages:

- They can achieve higher open circuit voltages than homojunction cells [35]. Panasonic HIT cells have record open circuit voltages which was achieved with amorphous silicon.
- These cells can be fabricated at low cost and under room environment in contrast to high temperature vacuum based processing.

- Properties of organics can be tuned easily to meet the requirements of the solar cell.
- Conventionally HIT cells are bifacial in nature and thereby can produce more energy than any other type of solar cell on a longer run. With higher efficiency and superior temperature characteristics, HIT generates 43.4% more energy than conventional cells in 25 years [35].
- Amorphous silicon is better performing than crystalline silicon at higher temperatures because of the material's resiliency to heat. HIT cells produce 13% more energy than conventional cells at given high temperature [35].

Chapter 4

HYBRID DEVICE FABRICATION AND CHARACTERIZATION

4.1 Introduction

In the previous sections, we have realized PEDOT: PSS as a potential layer for carrier selective induced junction solar cell with benzoquinone as the chemical passivant. The next step is on realizing actual solar cells which incorporate PEDOT: PSS as the carrier selective layer and BQ which passivates the front surface of silicon. Solar cells work on three basic steps- charge excitation, charge collection and charge separation. Unlike organic solar cells, the active light absorbing material in hybrid solar cells is the silicon. PEDOT: PSS is a transparent organic polymer and BQ is a monolayer thick. Typical approach to device fabrication involve starting with a silicon substrate which post cleaning would be passivated with BQ. This is followed up with PEDOT: PSS spin coating and now the device is ready for metal deposition. Metals are deposited through electron beam deposition technique on the front and back to collect the carriers and generate current. Recently, efficiencies as high as 10% have been achieved for these devices.

4.2 Background

N.A. Kotulak et al. [36] and Nagamatsu et. al [31] fabricated PEDOT: PSS based solar cell with a the planar PEDOT: PSS/Si devices which would be combined with the BQ/Si device, and the BQ will have similar functionality to SiO_x layer from Thomas, et al. [30]. This device will result in a PEDOT: PSS/BQ/Si stacked on top of each other before the metal contacts. In the literature, there are multiple configurations for device design, and this work will follow the method found in Nagamatsu, et al. [31]. Aluminum will be used as the back contact to silicon, and silver will be used for the front contact to

PEDOT: PSS and BQ. Based on the literature, the PEDOT: PSS films will be prepared with the co-solvents Dimethyl sulfoxide(DMSO) or ethylene glycol(EG) and Triton(surfactant) for increased conductivity and wetting of PEDOT: PSS. Average thickness of PEDOT: PSS would be around 70 nanometers. The resulting device will be a standalone solar cell structure [36], designed to implement a BQ passivation layer and PEDOT: PSS carrier selective layer, and demonstrate the functionality of BQ in a device.

4.3 Devices Summary

The purpose of this work is to demonstrate the potential of hybrid organic/inorganic solar cells and as an enabling technology for materials that could be manufactured and processed under lab environment. A continuation of the work done in the Opila lab, the work is mostly focused on enhancing the performances of the hybrid solar cell by improved cell design and processes. These devices have doubled up efficiencies, from 5% to 10% in 2 years.

The hybrid solar cells fabricated earlier implemented a n-type silicon substrate and a PEDOT: PSS and Benzoquinone on top of that. These cells were solution-based processed under lab environment. The maximum temperature they underwent was during the electron beam deposition step but besides that everything else was achieved under lab conditions and this eliminates the requirement for vacuum based high temperatures based processing. These devices implemented a single sided polished n-type 500-micron thick silicon as the substrate. The wafers underwent the usual clean followed by 2-hour dip in benzoquinone solution. After BQ passivation, aluminum was evaporated by electron beam deposition technique. Back metal deposition was carried first because the organic front contact might degrade if left for long time. After the back metal is deposited, the wafer is given a clean. To induce a p-n junction, PEDOT: PSS with 10% dimethyl

sulphoxide (DMSO) is spin coated on the front side. The device was placed in nitrogen atmosphere to dry and post it, front metal was deposited. With the front and back metal deposited, the solar cell is ready and it was further tested for various parameters. Devices fabricated have been described in the table below.

Device	Short circuit current ($\frac{mA}{cm^2}$)	Open circuit voltage(mV)	Fill Factor	Efficiency (%)
Base 32.33 ohm-cm	21.11	321	0.42	2.83
23.03 ohm-cm	22.73	386	0.44	3.84
16.91 ohm-cm	23.32	404	0.42	3.97
1.22 ohm-cm	22.29	437	0.42	4.08

Figure 4.1 Comparison of the devices fabricated previously in the lab.

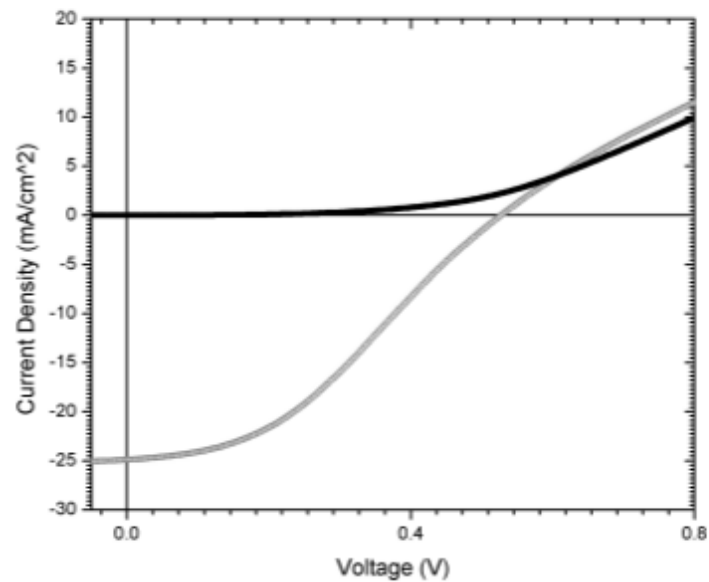


Figure 4.2 J-V curve of the best device previously fabricated in lab.

It can be observed from the J-V curve that the cells suffered from very low open circuit voltage and short circuit current. The light curve resembles a S- shape which reflects high parasitic resistance losses. The series resistance especially seems very high and its reflected in the fill factor value. The open circuit voltage is about 150mV lower than the champion hybrid solar cell back then. Upon analyzing the device processing and characteristics, few changes are recommended below which would improve device performances.

1. Back metal deposition before passivation would make the passivation the ineffective. This may be because of aluminum contamination.
2. Quantum efficiency is a good technique to analyze the solar cell characteristics. The short circuit current of the device can be improved by implementing texturing. Texturing would improve the light capturing ability of the solar cell and thereby improve the short circuit current. The wafers can be either KOH textured or TMAH textured. KOH is inorganic whereas TMAH is organic texturing and TMAH eliminates the possibility of metal contamination. Although, KOH is the standard mixture used in solar cell fabrication.
3. Surface recombination at the rear side can be reduced by implementing a back-surface field structure. More about the back-surface field will be discussed in the upcoming section.
4. Clean Si is hydrophobic and PEDOT: PSS is water soluble. Clearly the two do not like each other. To make PEDOT: PSS stick to silicon surface, triton or zonyl can be used as surfactants. This would reduce the surface energies and help wet the surface better. Besides the PEDOT: PSS-silicon interface, the lateral conductivity of PEDOT: PSS is also crucial to device performances. It can be

enhanced by adding co-solvents. Varying percentages of co-solvent would change the conductivity of PEDOT: PSS. DMSO and ethylene glycol(EG) are the widely-used co-solvents. UV-VIS spectroscopy and Van-Der paw are good techniques to analyses the PEDOT: PSS performances.

5. Series resistance in the above devices is very high. Few places to consider are the Si-PEDOT: PSS interface, grid pattern on front, metal- PEDOT interface and amount of metal deposited. Front metal grid pattern for the current pattern is way too small. These masks enabled a solar cell only 3.25mmx3.25 mm in size. This design was way too small and preparing wafers on that scale is difficult. Newer grid design can also reduce the losses due to shadowing.
6. A thinner silicon is also known to provide a higher open circuit voltage due to the lower bulk recombination and more efficient carrier extraction [37]. Shift from 500 micron thick wafers to lesser thickness would enhance the open circuit voltage for these cells. Although, with proposed incorporation of back surface, it must be ensured that the diffusion length after BSF should be greater than thickness of the substrate.

After analyzing the device characteristics, this thesis was aimed on the understanding device performances by implementing the above-mentioned techniques. The device architecture for the new hybrid cells is shown in the figure below. First, a 145 micron, KOH textured, 1.5 cm by 1.5 cm sized n-type silicon wafer is chosen and cleaned in 5 minutes' piranha followed by 5 minute DI water rinse and 2 minute 10% HF acid. The wafer is given a water dip and dried with nitrogen. This results in a hydrogen terminated surface. Then the wafer is immersed in a 0.1M solution of benzoquinone in methanol. After this surface passivation is complete, a layer of PEDOT: PSS is spin-

coated onto the substrate. The PEDOT: PSS solution includes 7% dimethyl sulfoxide (DMSO) to increase the conductivity and 0.25% w/w Triton X-100 to act as a surfactant. Metal contacts are deposited via electron beam physical vapor deposition. For the front contact, a silver pattern is deposited through a shadow mask. The rear contact consists of aluminum covering the entire back surface. The J-V curve is obtained using the J-V setup shown in figure below.

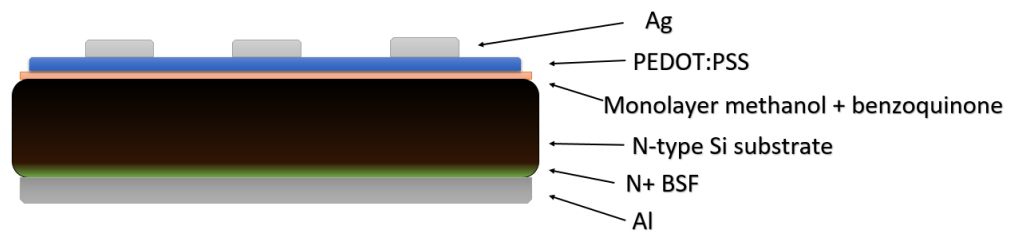


Figure 4.3 Hybrid solar cells.

Table 4.1 Device characteristics of hero cell fabricated in lab

J_{sc} (mA/cm ²)	V_{oc} (V)	η (%)	FF (%)	R_s (Ohm cm ²)	R_{sh} (Ohm cm ²)	Area (cm ²)
28.6	.545	9.6	61.6	1.769	425.336	1

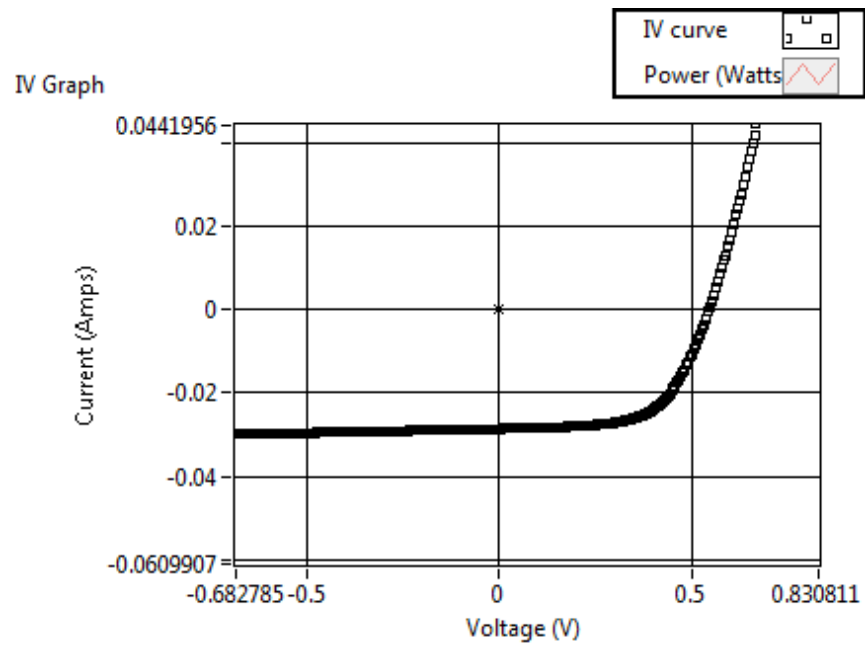


Figure 4.4 Light curve for hero cell.

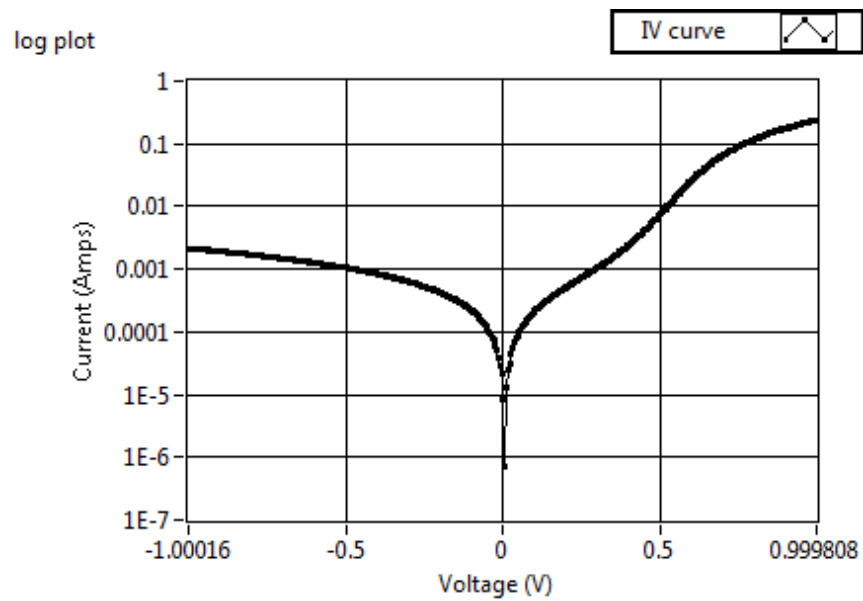


Figure 4.5 Dark curve for hero cell.

From the device light and dark curves of the hero cell fabricated with the device structure mentioned in figure 4.3, we observe that the limiting factor to high efficiency is fill factor. Fill factor is largely a reflection of parasitic resistance losses. Higher series resistance or lower shunt resistance values infer a low fill factor. In a good solar cell, series resistance is usually in order of milli ohms whereas for shunt resistance it is in order of thousands. Reduced shunt resistance (increased shunt conductance) results in a steeper slope in the I-V curve near short circuit current and a reduced fill factor. The series and shunt resistance values for the above mentioned solar cell are 1.765 and 425 ohms respectively. Lowered series resistance would improve current in the light curve and in the dark curve it would make the left side of the curve less exponentially saturating. Greater shunt resistance would improve the open circuit voltage in the light curve and in the dark curve it would make the right-hand side of the curve go exponentially up after the second slope (it linearly increases in this curve). These parasitic resistance losses can be further analyzed by the method described by Hegedus and Shafarman [38].

By plotting the Plotting dJ/dV as a function of voltage would produce a curve which should be linear within the reverse bias region of the voltage. This would give us value for the shunt conductance which is inverse of shunt resistance.

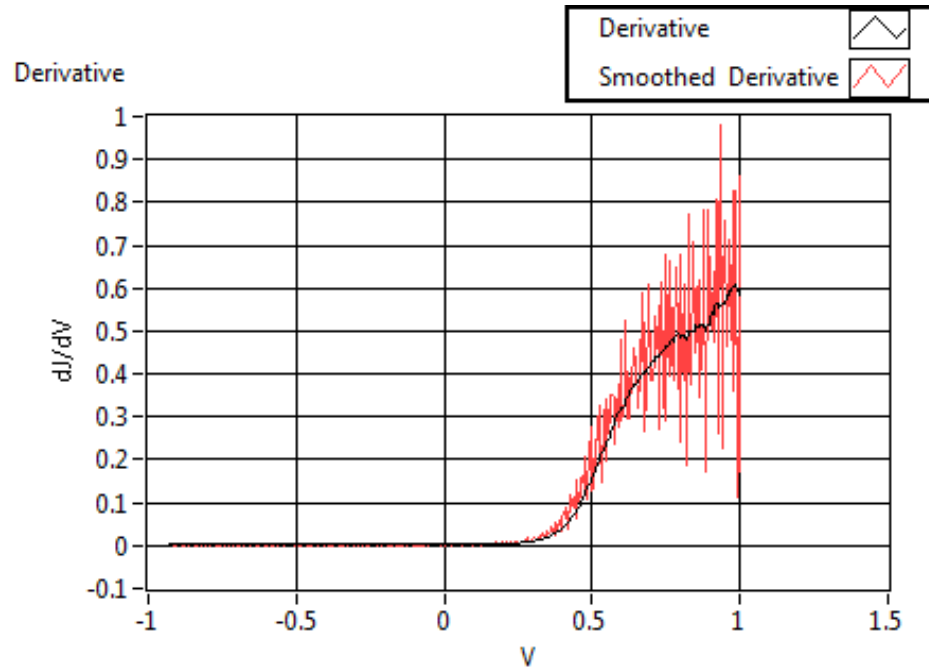


Figure 4.6 Plot for estimation of shunt resistance of hybrid solar cell under light.

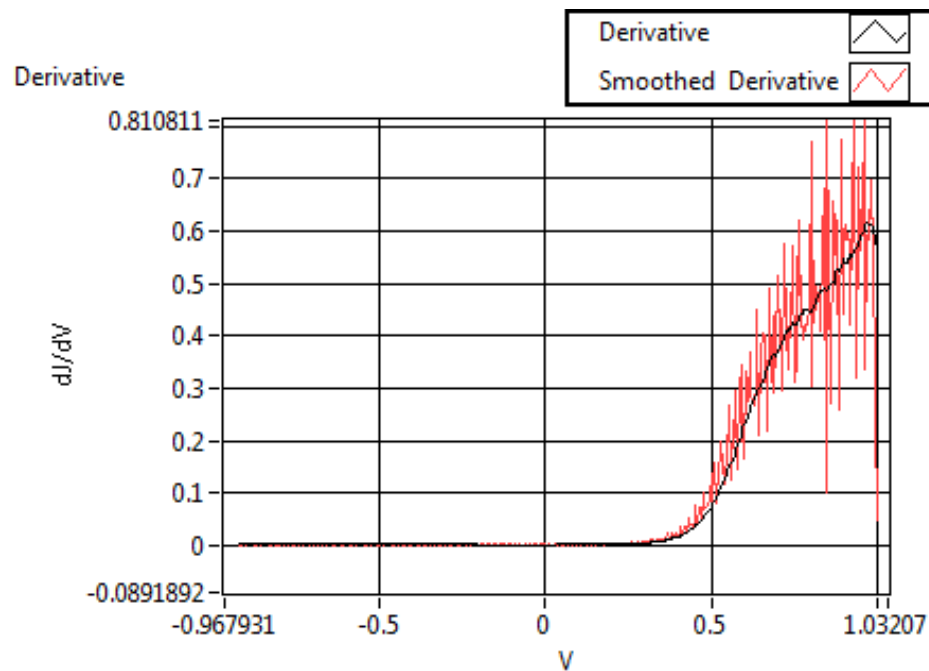


Figure 4.7 Plot for estimation of shunt resistance of hybrid solar cell under dark.

We observe from the curve above that the values for shunt resistance in the reverse bias region is almost constant although the value is noisy in the forward bias region. Hence, the shunt conductance value is calculated from the reverse bias region which is slightly above zero and shunt resistance can be reciprocated. The value obtained ($R_{sh}=425$ ohms) is obtained through a labview program which incorporates this principle. Clearly, R_{sh} value is a one of the blocking element to higher efficiencies in these cells. An ideal solar cell has infinite shunt resistance.

Series resistance is the primary concern for these devices. The series resistance losses have been reduced by implementing a new grid pattern, metallization scheme and optimizing PEDOT/Si interface but it remains a concern for these devices. The series resistance can be extrapolated by plotting dV/dJ is plotted against $(J + J_{sc})^{-1}$. The curves obtained under light and dark conditions are the same because derivative remains the same. From the curve below, we can estimate the series resistance by calculating the y-intercept from linear fit of the curves. The calculated series resistance value under light is 1.765 ohms which was calculated from the labview program. As discussed earlier, series resistance losses have been optimized but there remains more work to be done on optimizing the Si/PEDOT interface. Future work is aimed series resistance optimization.

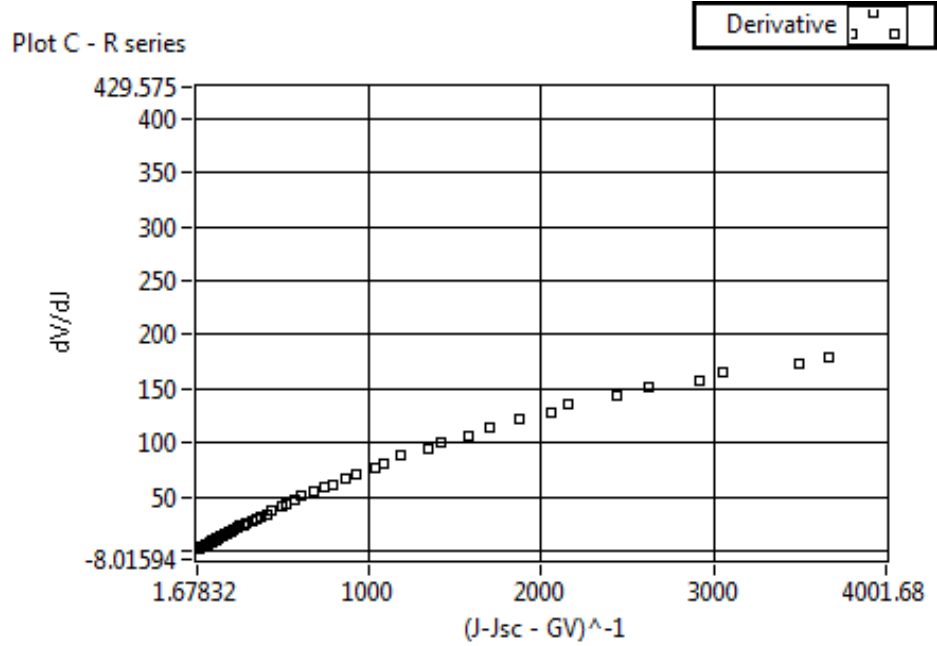


Figure 4.8 Plot for estimation for series resistance.

4.4 Wafer Preparation

The heart to any silicon based solar cell is the silicon substrate. There are various parameters like doping, resistivity, silicon grade, lifetime, crystallinity etc. that affect the final device performances. 500micron thick, low resistivity, n-type Czochralski(CZ) wafers were initially used for device fabrication. Later, a shift to thinner textured substrates about 145 micron thick, n-type CZ with 1-3ohm-cm resistivities with back surface field was made. The following sections would discuss the reason behind the shift. The thinner substrates were fabricated in the solar power labs at the Arizona State University. A 156 mm×156 mm silicon wafer was taken and saw damage removal was done on the wafers for 6minutes in 30% KOH at 80°C. This etched about 10micron from each side. After DI water rinse, the wafer was textured in 2% KOH (with an additive added to reduce the surface tension of KOH and improve the coverage on silicon) for

about 25 minutes and this results in pyramidal surface on front and back with 3-5micron base sizes. This was followed by cleaning before diffusion was done. Since its n-type, POCl_3 was bubbled at 820°C for 15 minutes (phosphorous diffusion) and this was followed up with phosphate glass removal. Back surface field was achieved after this and the wafers were shipped to UD after processing.

Wafer cleaning before solar cell fabrication is crucial. The cleaning procedure implemented was:

- 1) Piranha (4 parts sulphuric acid to 1 part of hydrogen peroxide) – Addition of hydrogen peroxide to sulphuric acid is an exothermic reaction. This clean removes organic matter from the wafer surface. The wafer is first immersed in this solution for 5 minutes. It is essential for the solution to remain hot for effective clean($\sim 80\text{-}100^\circ\text{C}$).
- 2) Deionized Water (DI H_2O) - Following removal of organic material, the wafer is rinsed in DI water for 5 minutes. It is highly recommended to have DI water flow constantly throughout this time.
- 3) Hydrofluoric acid (10% HF) – The final and shortest step in cleaning is the HF dip. Hydrofluoric acid is a dangerous chemical and proper safety steps should be incorporated while doing this clean. HF is not just oxide removing agent but it also provides short-term surface passivation by bonding the hydrogen atom to dangling bonds of silicon. This step lasts 2 minutes.

After the HF dip, the wafer is given a dip in DI water (to ensure hydrophobicity) and dried with nitrogen. The wafer is then put in a zip lock bag containing 0.01M solution of benzoquinone in methanol for 2 hours (passivation step). Post passivation, the wafer is removed and rinsed with methanol. After drying with nitrogen, the wafer is spin coated with PEDOT: PSS (with 7% DMSO and 0.25% w/w triton). Once the p-n junction is

created, metal contacts are deposited through electron beam deposition which would be discussed in more detail. Silver is chosen as the front contact and aluminum as the back contact. With metals, the solar cell is ready for characterization.

4.5 Back Surface Field

In the previous chapter, we discussed about various types of recombination and various methods to limit this effect in a solar cell. Creating surface fields on the front or back limit the recombination tendencies. The structure used to create these surface fields, broadly classified as chemical and electrical passivation is achieved either through combination of dielectric layers (silicon oxide and silicon nitride), floating p-n junctions, or doped high-low junctions (p/p⁺ or n/n⁺) [39]. One technique to reduce the surface recombination at the back of solar cell is by creation of back surface field. Assuming a p-type semiconductor with n⁺ emitter, we have a p-n junction structure where we collect electrons on the emitter end and holes on the opposite end. This can be illustrated in the diagram below. The minority charge carriers on each end, electrons in p-side and holes on n-side usually recombine due to presence of trap states. These trap states behave as recombination centers and ideally, front side passivation as we discussed in previous section is aimed at reducing these trap states on front side of the solar cell. On the back side of the solar cell by creating a field to repel the electrons and holes from recombining, the surface recombination can be reduced. For a p-type semiconductor, this can be realized by having an additional p⁺ layer on the back and this would create a downhill for electrons and uphill for holes and it would prevent them from recombining. The electrons get repelled from the p side whereas holes would get pulled towards p side due to presence of the field.

Hence by creating a highly doped region in the rear end of the solar cell, the electric field created helps us reduce the minority carrier recombination. The minority carrier concentration is thus higher in the bulk of the solar cell resulting in necessary generation and thereby passivating the surface [40]. There has been performance enhancement with the implementation of back surface field which would be discussed in more depth under the devices summary. Wafers with a 100 Ohm/square sheet resistance BSF were created by POCl_3 diffusion at the Solar power labs in Arizona State University.

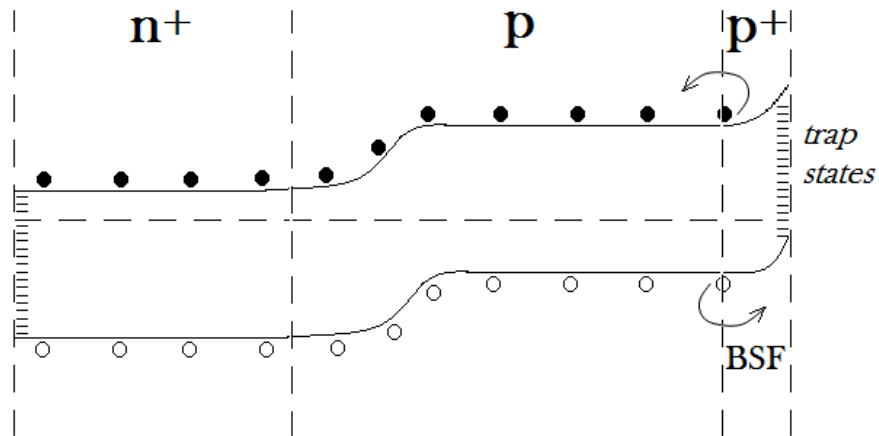


Figure 4.9 Back surface field on p-type substrate.

4.6 Metallization

Once a solar cell is fabricated, we need contacts to extract the electrons and holes and generate electricity. Metals used for front contact in these solar cells are silver as front contact and aluminum as the back contact. These metals are deposited on silicon

using electron beam deposition technique (e-beam). The e-beam tool used is attached in the figure below.



Figure 4.10 Diagram representing a p and n type semiconductor band structure.

Electron beam physical vapor deposition (or E-beam Evaporation) is a technique that allows for relatively rapid material deposition. The metal to be deposited is placed in a crucible (filled a little more than half with metal chunks) and is bombarded with a focused electron beam. This focused beam instantly heats up the metal and it starts to evaporate onto the silicon substrate via line of sight. The e-beam tool can run deposition

on multiple substrates simultaneously. Since this is a line of sight deposition process, the use of a shadow mask can also allow for patterning of the desired deposition. The front metal deposition is usually done with a grid pattern which would be discussed in more detail in the next section.

The electron beam is provided by running an emission current through a filament. The ejected electrons are focused using a magnetic lens system to evaporate the target material. The evaporated material deposits onto the substrate as well as the surrounding chamber walls and a crystal sensor. The rate of deposition can be monitored by measuring the shift in vibrational frequency of the calibrated crystal sensor. The system relies on two vacuum pumps- mechanical and cryo.

Metallization scheme for a solar cell can incorporate different types of metals like aluminum or silver or titanium/palladium/silver. Presence of metal on top brings up contact resistance between the metal and silicon and it is necessary to keep the contact losses low. Often the emitter is highly doped to reduce this impact but besides that a good design is equally important. To evaluate a good front and back metallization scheme, transmission line measurements were performed. For each metal type, transmission line measurements (TLM) were carried out using four-point probe tool and then contact spacing vs resistance was plotted from it, which would give us a better understanding on metallization scheme. A 500-micron double side polished n-type wafer was chosen for TLM measurements. These wafers were cleaned using standard clean method involving 5-minute dip in piranha followed by 5 minute DI water rinse and then 2 minute of 2% HF dip. Post the clean, the wafers were passivated in benzoquinone for 2 hours. The wafers were dried and are ready for deposition. A micron of aluminum and nickel were deposited for back side measurements whereas 200 angstroms titanium, 200 angstroms of palladium

and a micron of silver were deposited for third metallization scheme. Due to the nonstandard geometries of the contacts used, it is difficult to convert the contact resistance measured to a scalable contact resistivity.



Figure 4.11 Four-point probe tool at Dupont 247.

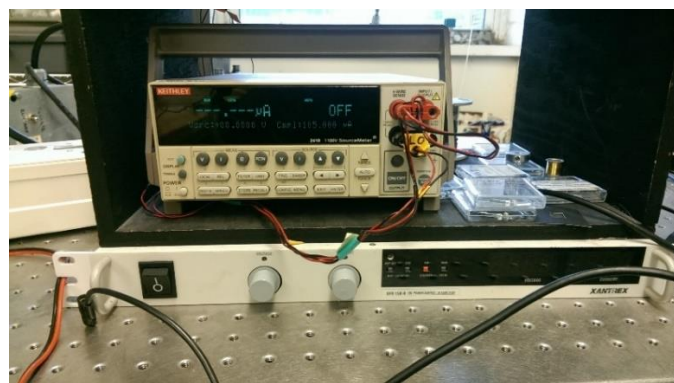


Figure 4.12 Keithley 2400 sourcemeter (single channel I-V sourcing).

We cannot simply assume that the current is distributed evenly across the contact area. Using TLM, we are evaluating a good metallization scheme for back contact and for front contact. For the back contact, aluminum(Al) was compared with titanium, palladium, silver(Ti/Pd/Ag) and nickel whereas for the front contacts silver was compared with titanium, palladium, silver. The curves below represent the I-V measurements for various values of current.

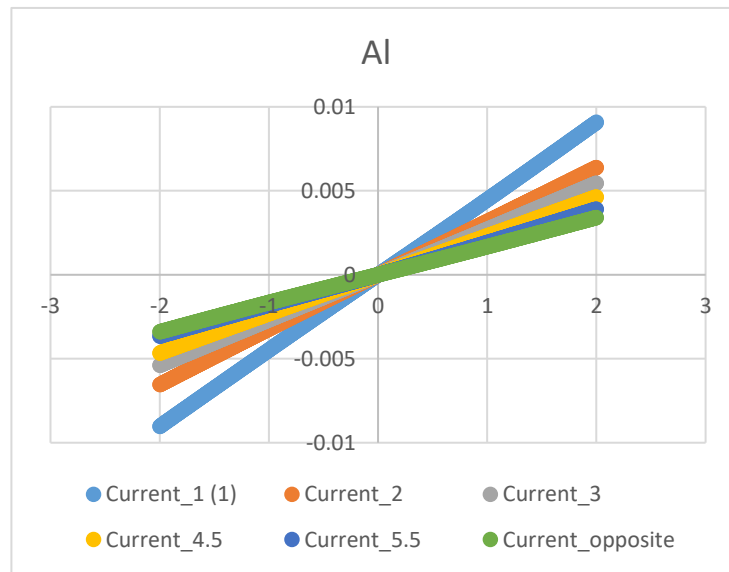


Figure 4.13 I-V dependence for various currents using TLM for aluminum (back contact).

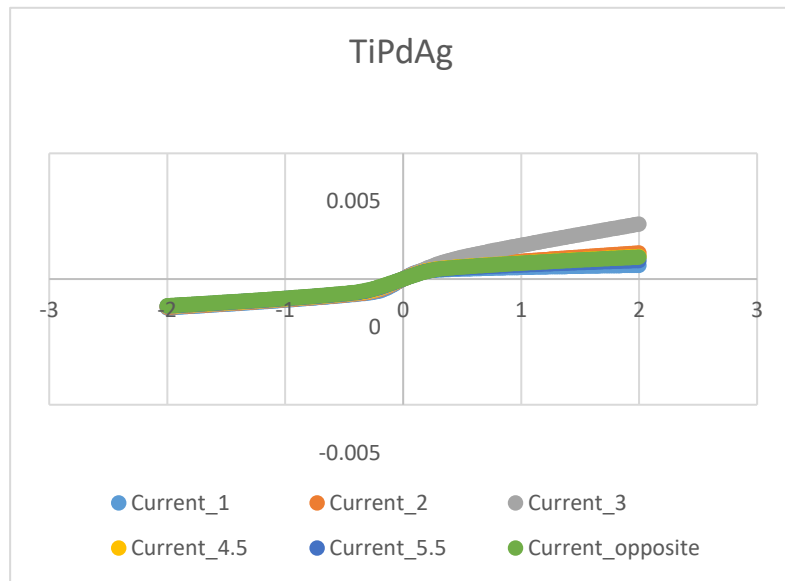


Figure 4.14 I-V dependence for various currents using TLM for titanium/palladium/silver (back contact).

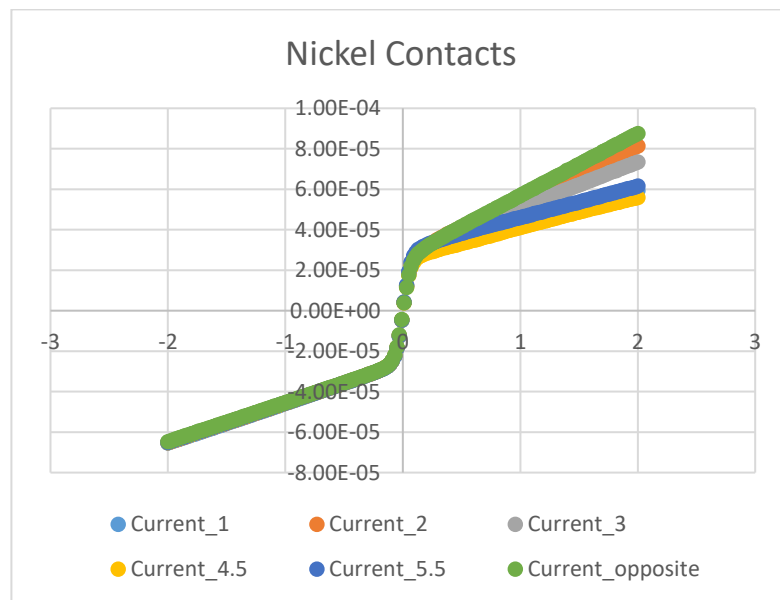


Figure 4.15 I-V dependence for various currents using TLM for Nickel (back contact).

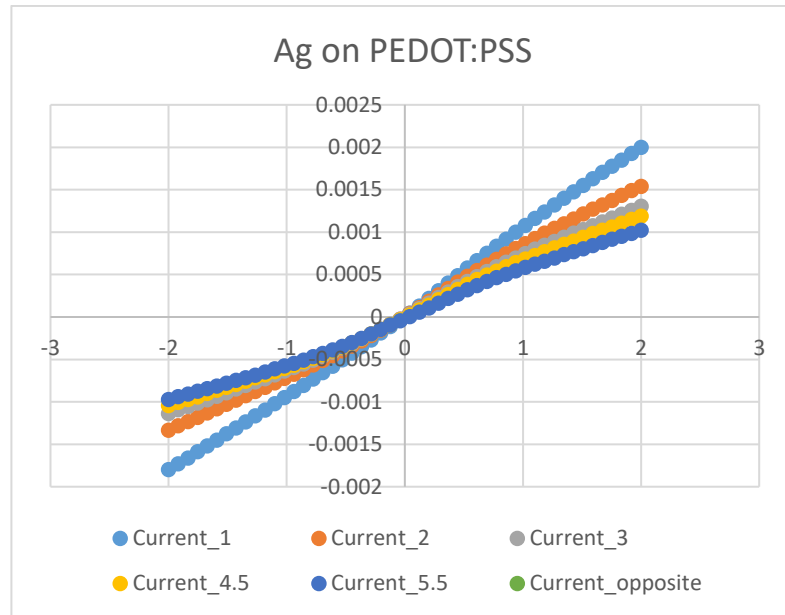


Figure 4.16 I-V dependence for various currents using TLM for silver on PEDOT: PSS (front).

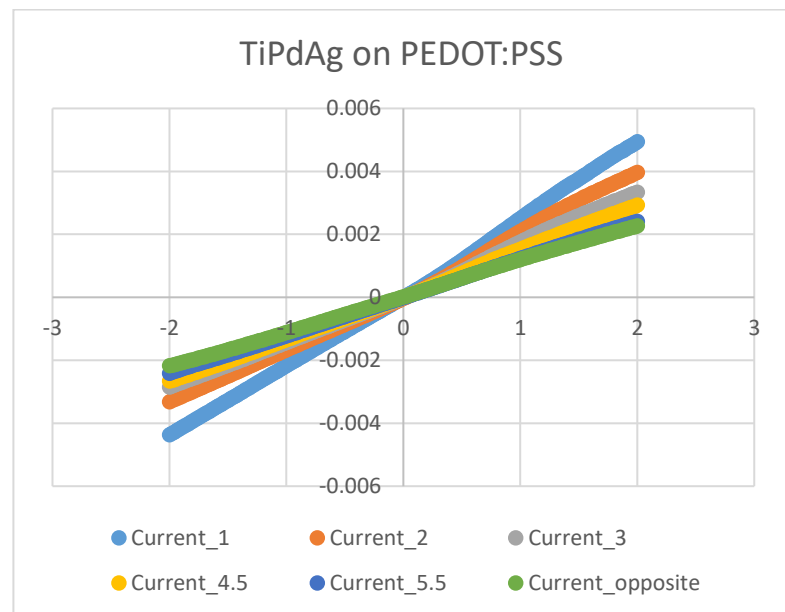


Figure 4.17 I-V dependence for various currents using TLM for titanium/palladium/silver on PEDOT: PSS(front).

It is most desirable to create an ohmic contact to reduce resistive losses and avoid the creation of an additional junction at the contacts. It can be observed from back contact analysis that the nickel and Ti/Pd/Ag schemes have a non-linearity in the I-V curves which indicates that they are not a good match(non-ohmic). On other hand aluminum is a very good fit for or solar cells because they have obeyed ohm's law and measured contact resistance is relatively lower than any other metal. Aluminum is also the metallization scheme used for commercial solar cells with the distinction that it is screen printed and not deposited by E-beam technique. As far as the front contact is concerned, bot schemes seem alike a good fit for us. The Ti/Pd/Ag looks slightly better but just silver will be used for front metallization in these devices. This is largely because of economic reasons. The table below shows the initial measurements of contact resistance. For each metal type, contact spacing vs resistance can be plotted, as shown below for Al.

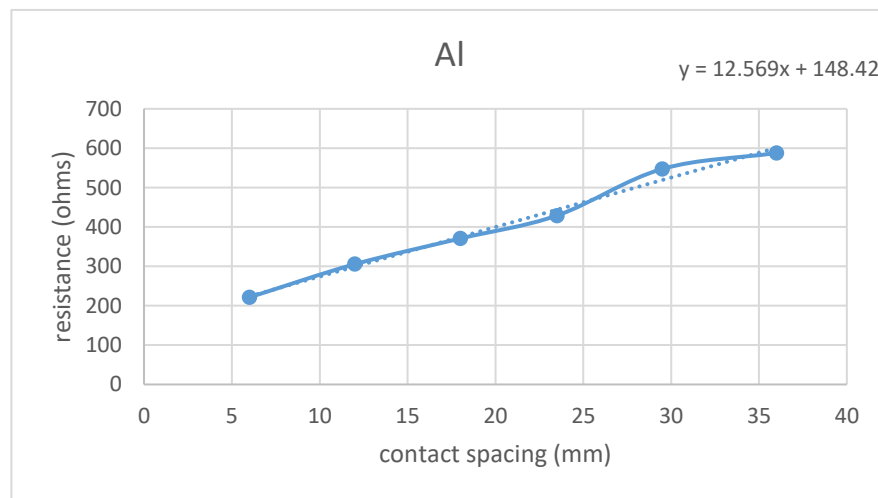


Figure 4.18 Resistance change with increasing contact spacing (each finger is 6 mm apart from other).

Table 4.2 Comparing metallization schemes.

Material	Voltage Measured At	Contact Resistance
Al (back)	2V	74.21 ohms
TiPdAg (back)	2V	862.2 ohms
Ni (back)	2V	15259.5 ohms
Ag on PEDOT: PSS (front)	0.1V	306.37 ohms
TiPdAg on PEDOT: PSS (front)	2V	202.765 ohms

4.7 Front Grid Design

The original solar cell masks enabled a solar cell only 3.25 mmx3.25 mm in size. This design was way too small and preparing wafers on that scale was difficult. Also, device performances were affected because of dominance of edge effects. The calculate diffusion length of carriers in these wafers is about half a millimeter. However, since the devices are so small, about half of the total area of the solar cell is within one diffusion length of an edge, where the cell will perform as a dark diode. Boosting the total area of the solar cell allows to greatly improve this ratio. A size of 1 cm x 1 cm seemed a reasonably achievable size which would begin to minimize this effect, and in decent agreement with other groups in literature. Increasing the device dimensions to 1 cmx1 cm greatly decreased the energy losses due to recombination at the device edges.

Redesigning new grid pattern for front side was largely aimed at reducing the losses due to shadowing. Devices in literature had reported shading ratios of between 8-15% of the front area. Most of the high efficiency devices fell in the 10-12% shading range. The older devices had a 26.7% shading ratio but the new mask dimensions gave 10.4% shading ratio. These devices implemented silver as front contact which was deposited on PEDOT: PSS and the contact resistance between these layers was way too

high. Power losses at this interface are directly proportional to the total area of metal, so there is an unavoidable tradeoff between power losses due to shading and contact resistance. Direct measurement received an unreasonably high number of 15 Ohm-cm^2 so a literature value of $.79 \text{ Ohm-cm}^2$ was used instead. Even this value indicated losses of nearly 50% from contact resistance alone, and did not seem to match well with experiment. A much lower alternative value of $.064 \text{ Ohm-cm}^2$ was used for comparison calculations that seemed to yield more realistic results. Further optimization of mask dimensions would require a more reliable measurement of contact resistance. If this contact resistance number was accurate, an alternative design was made using wider 200 um fingers with a 22.4% shading ratio.

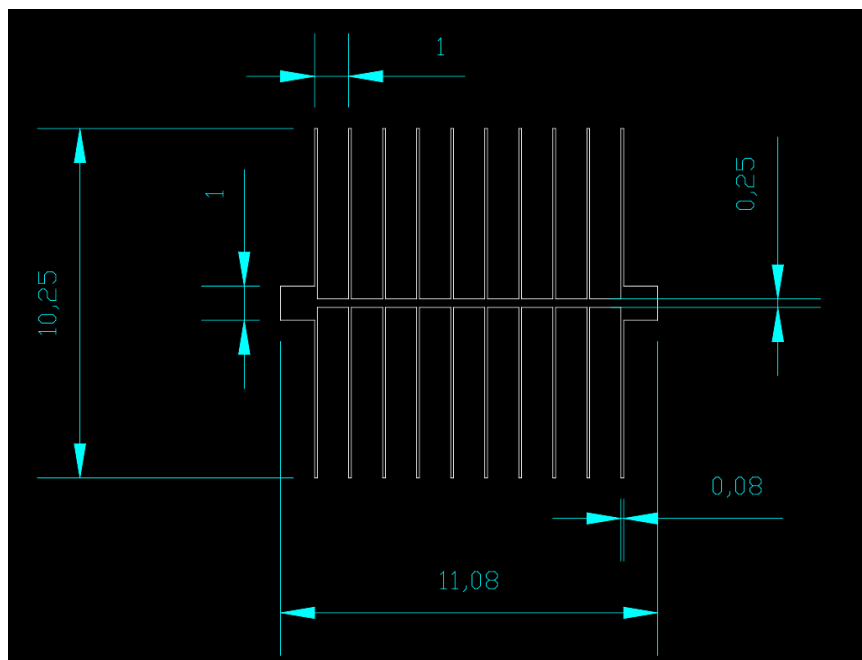


Figure 4.19 Front grid design.

Once the shadowing ratio was determined, the next parameter was designing the finger width. Here 80 μm was selected as a minimum manufactural finger width, based primarily off other similar designs.

So now that the two key parameters of shading ratio and minimum finger width have been determined the rest of design can be figured easily. The finger spacing can be determined largely from these values, and then a bus bar width can be selected to minimize resistive losses within the metal to an acceptable amount. Metal pads were chosen to be of a size reasonable for contacting a probe. Calculations of losses from the design were made in Excel using the formulations from the Martin Greene Solar Cell book. Additional calculations on design shadow ratio and losses were determined using pvlighthouse calculator. Using these approaches, power losses due to finger resistance, buss-bar resistance, finger shading, bus-bar shading, contact resistance and PEDOT: PSS resistance can be evaluated.

Table 4.3 Comparison of new grid design with the previous design.

INPUTS	A (busbar length) (cm)	B (finger length + busbar width) (cm)	S (finger spacing) (cm)	W_b (busbar width) (cm)	W_f (finger width) (cm)
New design	0.5	0.525	0.1	0.0125	0.008
Old design	0.3175	0.3	0.08	0.05	0.008

The final design yielded loss of about 13% of which 10.4% were due to shading (contact resistance was excluded). Even using the lowest estimate of contact resistance

still yielded 6% power loss due to contact resistance, the highest losses in the device except for shading. Adequately determining and minimizing the contact resistance between PEDOT: PSS and the metal contacts could enable significant improvements to front metal contact design.

4.8 Spin Coating

4.8.1 Introduction

Conventional solar cells based of aluminum back contact technology have dependence on high temperature processing. The aim of this thesis is to understand and improve the performances of hybrid solar cells which are based of room temperature processing. Besides having high open circuit voltages these solar cells have lower processing costs attached to them. Conducting polymers have always been field of interest in solar because of the flexibility involved in altering their electrical, optical and processing properties. Several polymers like Poly (3- hexylthiophene-2,5-diyl), pentacene have been tried in the past but poly (3,4- ethylenedioxythiophene): poly(styrenesulfonate)- PEDOT: PSS was the chosen polymer for study here because of its superior conductivity and transparency. To reduce the thermal budget, solar cells based of this technique are formed with an organic passivation layer and an organic conductive polymer- PEDOT: PSS. The active p-n junction in these cells is formed between the n-type silicon and PEDOT: PSS- hole transport layer with crystalline silicon absorbing light. These cells are alternatively called solution-processed solar cells.

4.8.2 Background

PEDOT: PSS is a polymer that can be formulated to be highly conductive and transparent, making it useful for a variety of applications [41]. Some examples include use as a static dissipative coating, for flexible transparent electrodes, and for hole contacts in organic photovoltaic devices [42-44]. PEDOT: PSS on a n-type wafer ends up behaving as a rectifier. Below shown are PEDOT and PSS molecules respectively.

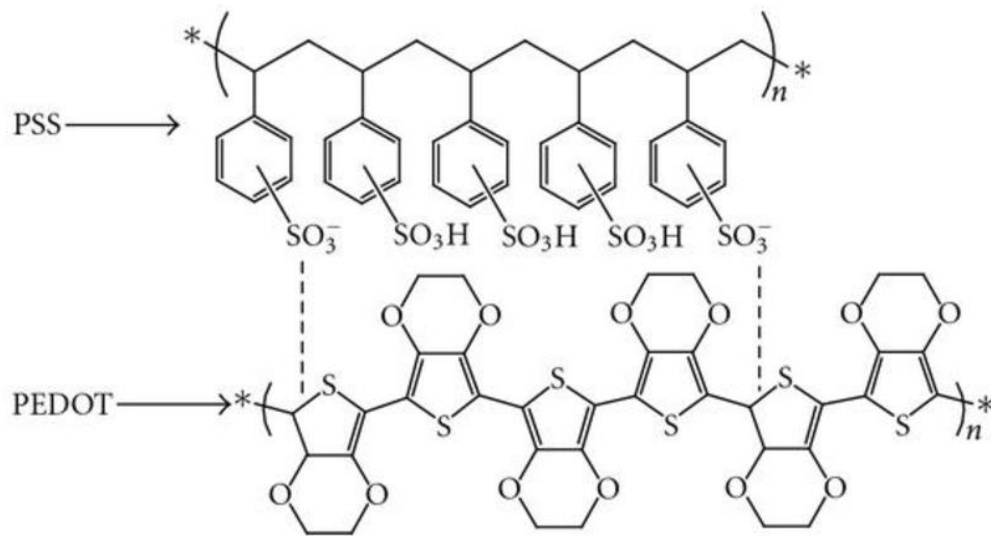


Figure 4.20 Structure of PEDOT: PSS films.

Together they form a macromolecular salt in which the oxidized PEDOT is the cation and PSS is deprotonated as the anion [44,45]. Due to this charge transfer, the PSS ends up behaving as a dopant and eventually the PEDOT ends up behaving as a degenerately doped p-type organic semiconductor [46, 47]. This high charge density thereby makes PEDOT: PSS highly conductive [45].

PEDOT: PSS is usually available as an aqueous solution and is obtained from Baytron P process which involves polymerizing EDOT monomers using PSS as the electrolyte and $\text{Na}_2\text{S}_2\text{O}_8$ as the oxidizing agent. In the following sections, the fabrication of PEDOT: PSS, spin coating technique and the conductivity measurements and enhancement with additives are discussed.

4.8.3 Fabrication of PEDOT: PSS

The Clevios PH1000 PEDOT: PSS used for the hybrid solar cells discussed here were obtained from Heraeus. Clevios™ PEDOT: PSS is a substituted polythiophene ionomer complex with a polyanion that offers the highest conductivity of about 1000S/cm. The product is offered as the monomer for in-situ polymerization, as neat water based dispersions or as ready-to-use formulations mixed with solvents and additives [48].

For devices, PEDOT: PSS purchased from Heraeus was 1.4% dispersion by weight in water and 7% w/w dimethyl sulfoxide (DMSO) was added to enhance the conductivity of the film which would be discussed in the next section. There were studies carried out with 7% w/w ethylene glycol as well to understand the conductivity enhancements to PEDOT: PSS and how that translated when making a complete solar cell. Although in these devices, a passivation step is involved after clean, the passivate often makes the surface a little hydrophilic. Nevertheless, 0.25% triton(surfactant) was added to improve the wettability of PEDOT: PSS on the wafer [49, 50].

For the devices, post the benzoquinone passivation step for ~2 hours, the wafer was given a methanol rinse and dried using nitrogen gun. The wafer was placed in the spin coating holder(chuck) and PEDOT: PSS with 7% DMSO and triton was spun on the wafer for 300 seconds at 4000rpm. Post the PEDOT: PSS spin coating, the wafer was

annealed for 15 minutes at 130°C. This was followed up with metal deposition in the electron beam evaporator.

PWM32-PS-R790 Spinner System from Headway research Inc. was used for spin coating purposes. This spin coater consists of a PS motor and a R790 bowl. The motor has spin speeds up to 10000 rpm and the bowl 7.9- inch, reduced by a removable splash deflector to a maximum recommended substrate dimension of 5 inches [51].



Figure 4.21 Spin coater used for spin coating for these devices.

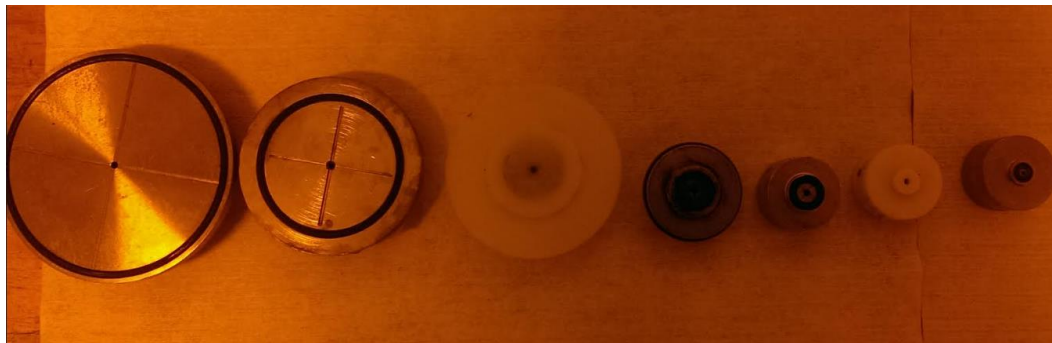


Figure 4.22 Various chucks used for spin coating depending on size of sample.

Larger samples can be handled by the coater but it'll result in removing the splash deflector which is not recommended. Before spin coating, it is always recommended to do a test run to ensure the wafer sits well on the chuck. There are various sized chucks available depending on the size of the wafers. Chuck size should either match substrate size or be slightly smaller to have a good spin.

4.8.4 Effect of Co-solvents

Additives, such as dimethyl sulfoxide (DMSO) or ethylene glycol (EG) are often added to PEDOT: PSS to improve its conductivity. Addition of PSS to PEDOT enhances the process ability but it comes at the sacrifice of electrical conductivity. Since PEDOT: PSS structure implements a shell structure of PSS around PEDOT, with the given structure, Pietsch, et al. [52] suggested 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 the open circuit voltage and the short circuit current. To test the effect of co-solvents and find the right co-solvent for the devices, conductivity measurements were carried out by Van Der Pauw Hall effect technique.

Van Der Paw technique is based off hall effect and resistivity measurements. The hall effect is based of Lorentz force which considers electric and the magnetic force experienced by a charge that moves in an electric field which is perpendicular to the applied magnetic field. The Van Der Paw Method employs a four-point probe placed around the edges of the sample (usually soldered contacts) [53]. It measures resistivity of the substrate twice (bi-directional by switching the four contacts between voltage and current probes) and averages it in contrast to linear four-point probe technique where resistivity is obtained in one direction only. This technique can measure the sheet resistance, resistivity, mobility, type of doping and sheet carrier density of the substrate. There are five conditions that must be satisfied to use this technique [54]:

- The substrate should have uniform layer on top.
- The substrate must be square in shape (square is highly preferred for accuracy during resistivity measurements)
- The sample must be homogeneous
- The sample must have ohmic contacts, usually soldered. For conductivity measurements, indium was soldered as contacts
- Contacts must be small and only on the edges.

Conductivity measurements were aimed at comparing the effect of co-solvents- DMSO and EG on PEDOT: PSS conductivities. 1.5 cm×1.5 cm sized double sided polished intrinsic silicon samples were chosen as the base. Intrinsic silicon was used as substrate instead of glass because of improved uniformity and wettability of PEDOT: PSS on silicon. These samples were cleaned by standard cleaning procedure mentioned in section 4.4. Post cleaning, the samples were introduced in BQ solution in a zip lock bag for 2 hours. In the meanwhile, three solutions were prepared- 7% DMSO and 7% EG

were prepared w/w with PEDOT: PSS(PH1000) and 0.25% w/w of triton(surfactant) and the third was PEDOT: PSS(PH1000) straight from container with 0.25%w/w triton. Triton was added to improve the wettability of PEDOT: PSS on silicon. Each of the recipe was spin-coated on the i-silicon sample for two spin speeds- 4000 rpm and 2250 rpm for 300 seconds each. The six samples were then annealed at 120°C for 20 minutes so that the spin solution dried completely.

The samples were soldered with Indium ohmic contacts on the edges for Van Der Paw measurements. After the contacts were checked, the Van Der Paw resistivity measurement was performed.

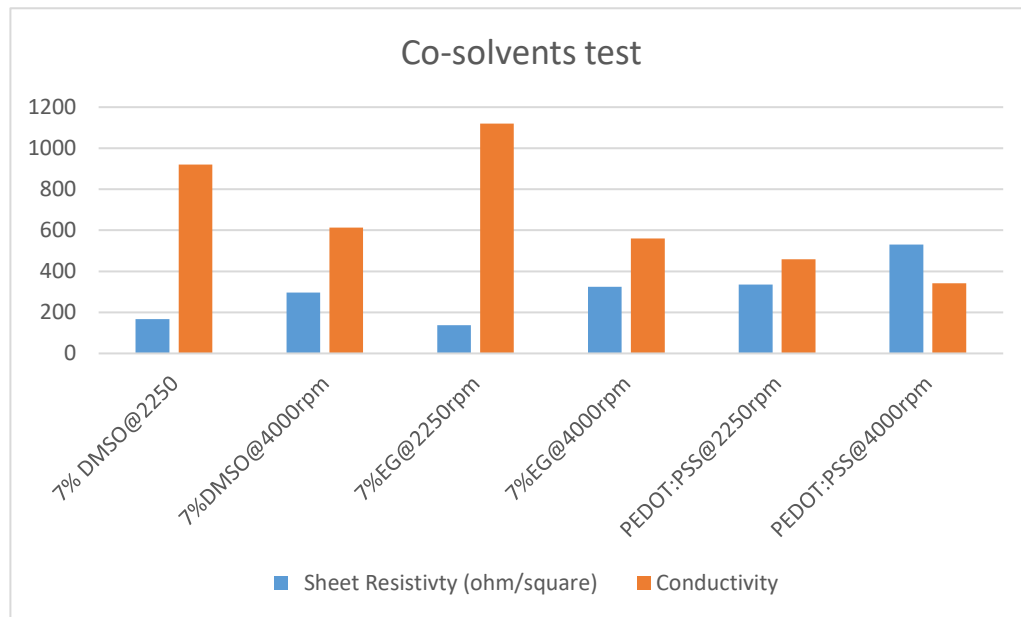


Figure 4.23 Comparison of sheet resistivity and conductivity for various co-solvent.

Table 4.4 PEDOT: PSS conductivity tests with co-solvents

Recipe	Mobility (m²/V. s)	Sheet resistivity(o hm/square)	Resistivity(o hm-cm)	Conductivity(S /cm)
7%DM SO@2250rpm	1.40	167.17	0.00108	920.2
7%DM SO@4000rpm	1.61	296.44	0.00163	613.3
7%EG @2250rpm	1.37	137.33	0.00080	1120.19
7%EG @4000rpm	1.92	324.12	0.0017	560.95
PEDOT: PSS@2250rpm	13.33	335.28	0.0021	458.85
PEDOT: PSS@4000rpm	29.95	530.72	0.0029	342.58

From figure 4.23 and table 4.4, it can be observed that the co-solvents DMSO and EG have enhanced conductivity and reduced sheet conductivity impact on PEDOT: PSS. The 7% EG has the highest conductivity (1120 Siemens/cm) and the least sheet resistivity as well whereas pristine PEDOT: PSS with triton has the least conductivity of 342.58S/cm. It is also observed that lower spinner speeds have better performances than higher spinner speeds which can be inferred as greater thickness is a good fit for conductivity. 4000rpm gives a thickness of about 55nm whereas 2250 yields around 65nm on the silicon surface. PEDOT: PSS PH100 straight from the container with 0.25% w/w triton does not have a good conductivity because of higher PSS content. PEDOT: PSS has a structure which consists of randomized PEDOT molecules covered by PSS shells. Addition of co-solvents tends to decrease the thickness of PSS shell and is also known to induce a rearrangement of the PEDOT chains, from the coil-like benzoid

structure that may be present along the grain boundaries to a more linear or extended quinoid structure [55-58]. This structural modification increases the PEDOT size and promotes closer packing of the PEDOT grains [57]. As PSS by itself is insulating in nature, a thinner PSS shell could enhance bulk conductivity and lowered sheet resistance. Morphological studies on these samples would give us a better idea on change of PSS content with addition of co-solvents. For devices, 7% DMSO with 0.25% w/w triton was chosen as the spin recipe for fabricating devices because of the uniformity obtained and higher conductivities over a range of spin speeds.

4.9 UV-VIS Spectroscopy

4.9.1 Introduction

The Ultraviolet visible spectrophotometry (UV-VIS) is a technique to study absorption, transmission and reflection spectroscopy from surfaces. The Perkin-Elmer Lambda 750 UV/Vis/NIR spectrophotometer at Institute of energy conversion (IEC) was used for understanding the optical properties of the devices. The spectrophotometer utilizes a light source, optical mirrors, monochromators, chopper and an integrating sphere. The theory of integrating spheres is based on two general assumptions:

1. Light hitting the sides of the sphere is diffused.
2. Light that is received by the detector is considered for further calculations.

This technique provides an average of all the reflections from the surface. Light is produced at the source which travels through a filter wheel, before it travels to the monochromators [59]. The monochromators then split the light before traveling to the chopper, which separates the light into two different beam paths, for the cuvette holders

[60]. For background collection, a scan is run with no sample present at the Sample (T) location as in figure below. The software takes this into account for every other calculation. Firstly, depending on what measurements need to be carried position of the sample is altered. For transmission measurements, sample, with film facing away from integrating sphere, is placed in beam path in front of the integrating sphere. Light that passes through sample reflects inside integrating sphere and is detected by adjacent detector. For reflection measurements, sample, with film facing integrating sphere, is placed in beam path behind integrating sphere at Sample (R) location. Integrating sphere allows for measurement of total reflection of diffuse or “rough” samples [61]. Index of refraction (n), extinction coefficient (k), absorption coefficient (α), sample thickness (d), bandgap (Eg), and other parameters can be determined from Transmission (T) or Reflection (R) data [62]. Absorption coefficient is related to Transmission and Reflection by the equation 4.1 [62]:

$$T = \frac{(1-R)^2 \exp(-\alpha d)}{1-R^2 \exp(-2\alpha d)} \quad (4.1)$$

where T and R are Transmission and Reflection, respectively, α is absorption coefficient, and d is thickness of the substrate. For highly absorbing samples, $\alpha d \gg 1$, denominator goes to one and Equation 4.1 can be approximated as [18]:

$$T \approx (1 - R)^2 \exp(-\alpha d) \quad (4.2)$$

For these devices, only reflection measurements were necessary. The motivation behind UV-VIS for these samples is to understand the effect of varying thickness of PEDOT: PSS. As mentioned earlier, PEDOT: PSS, the organic polymer has anti-reflection (ARC) properties and eliminates the need for additional ARC coating for the solar cell. The ability to reflect is dependent on the thickness of the ARC coating and

thereby UV-VIS measurements were carried out to understand the reflection from surface for varied thicknesses of the PEDOT: PSS.

4.9.2 Texturing

Initial devices made on two types of substrates- potassium hydroxide(KOH) textured 145-micron thick n-type silicon samples and on a n-type single side polished 145-micron thick silicon substrates. These devices were received from Solar power labs at the Arizona State University. The samples were cleaned by the cleaning procedure mentioned in section 4.4. Post cleaning, they were immersed in a zip lock bag containing solution of 0.01M benzoquinone and methanol. In the meanwhile, PEDOT: PSS recipe was prepared with 7% Dimethyl sulphoxide and a drop of triton. Finer details about the recipe will be discussed in the next section. After letting it stay in the bag for 2 hours in room with ambient light conditions, they were given a methanol rinse followed by blow drying with nitrogen. The samples were placed on the spin coater. Spin coating was performed for three different speeds- 600, 1000, 2250 rpm which give approximately 150nm, 85nm and 60nm thick layers of the organic polymer on the polished substrate. Samples were spun coated for 300 seconds. Post spin coating the samples were annealed at 135°C for 20 minutes. Samples were introduced in the UV-VIS spectrophotometer after calibrating the tool and the curves obtained are shown in the figures below. The textured samples are labelled as ASU KOH N02's and the un-textured ones are named ASU SAW N01's.

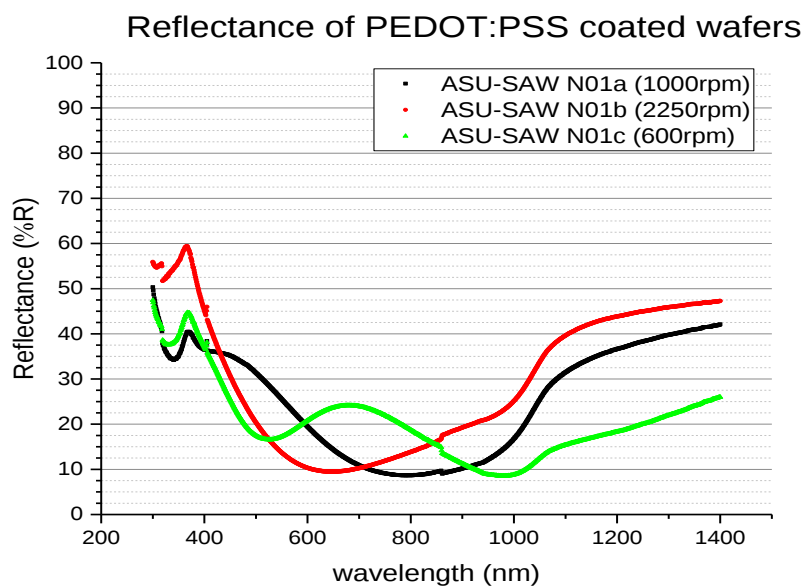


Figure 4.24 Reflectance from singles sided polished wafers for various spin speeds.

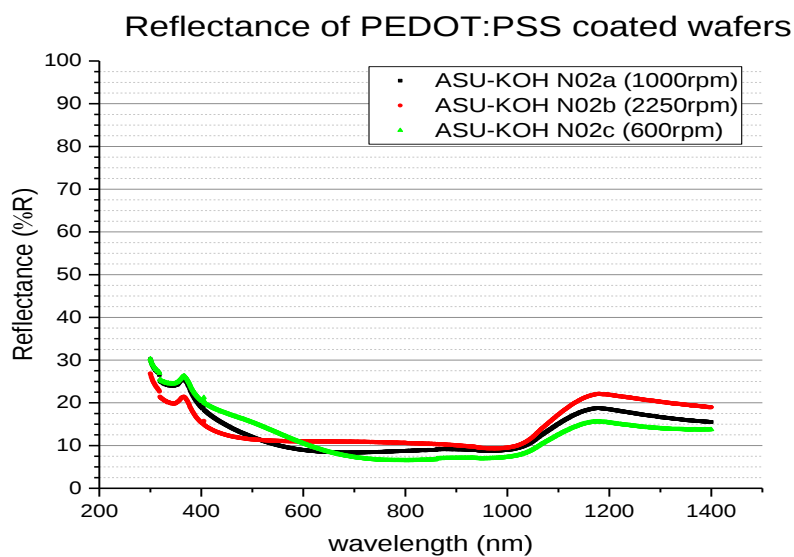


Figure 4.25 Reflectance from textured wafers for various spin speeds.

From the two figures above, the reflectance from the textured wafers are significantly lower than the un-textured ones at all wavelengths. Also, amongst the three different spin speeds, the thickest sample performs the best for the textured wafer whereas for the un-textured one the thickest wafer performs best at all wavelengths except for 500-900nm range. The irregular shape of the ASU SAW N01c sample could also be attributed to noise. The textured ones perform better than the un-textured ones because of improved light trapping by the PEDOT: PSS on the pyramidal front surface. Not only is the textured surface helping but the PEDOT: PSS coverage also adds to the anti- reflection properties which result in reduced reflection from the surface and improved trapping. Further analysis on these samples suggest that the short circuit current improved many folds with texturing than without texturing.

4.9.3 Spin Recipe

As discussed in the previous sections that PEDOT: PSS demonstrates anti reflection properties and the properties like stability and lateral conductivity vary with the co-solvents presence. Tests were carried to understand how reflection properties change with different co-solvents. Three samples, cut into quarters, each 500-micron thick double sided polished n-type silicon were used for the test. Samples aJa 6a, 6b and 6d were cleaned using the process mentioned in section 4.4 with 2% hydrofluoric acid. Post the clean these samples were subjected to 2hr passivation inside the zip lock bag containing BQ and methanol. In the meanwhile, two spin recipes were prepared. One being 7% solution of Dimethyl sulphoxide(DMSO) and PEDOT: PSS and the second being 7% Ethylene glycol(EG) and PEDOT: PSS. A drop of surfactant triton was added to both recipes to reduce the surface tension of the solution with the treated silicon surface. The spin speeds on samples aJa 6b and 6d was 2250rpm whereas sample 6d was spun coated

at 1000rpm. The DMSO recipe was spun for 240 seconds whereas the EG recipe was spun coated for 480 seconds because it seemed wet after 240 seconds. Post the spin coating, the samples were rushed for metal deposition. 200 nm of silver was first deposited on the front side using a mask by dual electron beam deposition tool followed by 2 microns of aluminum on the back side. Post devices were made; they were introduced in the UV-VIS spectrophotometry to study the reflection from the surface. It was ensured that the area under exposure of the beam had no metal.

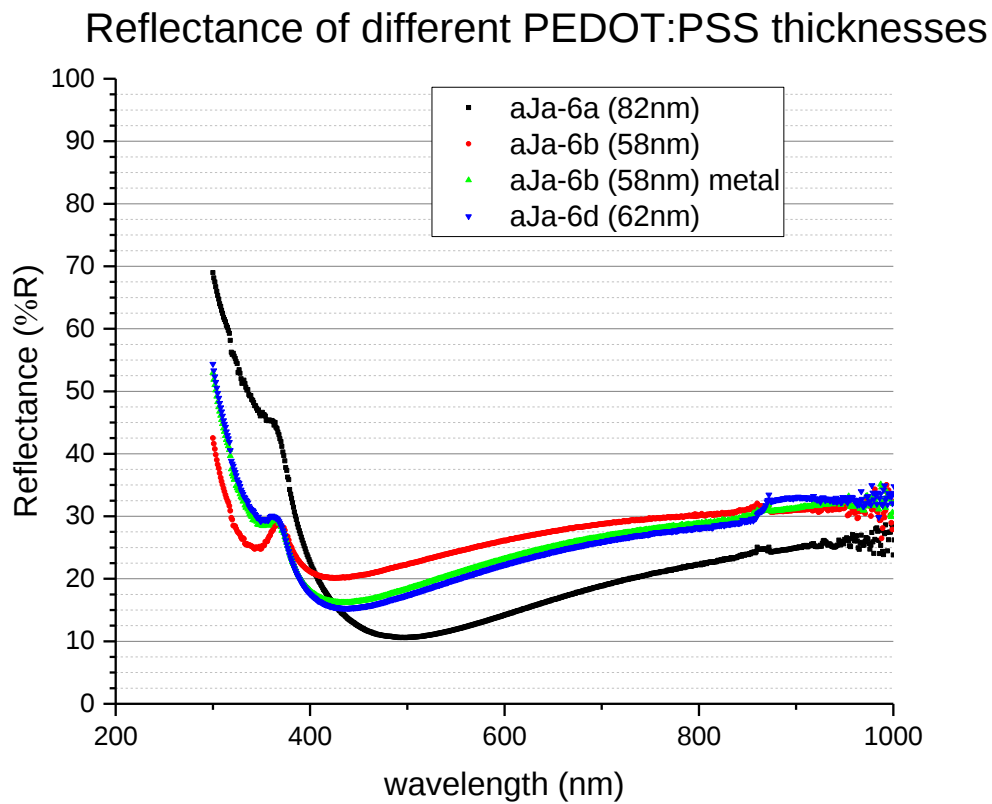


Figure 4.26 Reflectance for varied PEDOT: PSS recipes.

In the diagram, above, the blue curve represents the aJa 6d sample which was spun with 7% DMSO, sample aJa 6b in red and green represent the 7% EG solution with and without metal and sample aJa 6d represents 7% EG as well. It is interesting to compare the blue and the red curves which are approximately the same thickness of coating but different recipes. It is observed that the blue curve reflects lesser than the red curve in most wavelengths. Although below 400nm, the red reflects more than blue. It can be inferred that the 7% DMSO recipe spun coated on these samples demonstrates better results than EG samples. Further various other device analysis confirm that DMSO is a better co-solvent than EG. This has also been discussed in the previous section.

4.10 QUANTUM EFFICIENCY

4.10.1 Introduction

A technique to understand the photocurrent of a solar cell is achieved by measuring the quantum efficiency (QE). The QE is the ratio of number of carriers that are collected by the solar cell in contrast to the number of photons which are incident on the solar cell. A QE value of 1 or 100% indicates that all photons are absorbed and collected by the solar cell at that given wavelength. A QE value of 0 basically indicates that the light is not absorbed because the wavelength of light is greater than the bandgap of the material. A high QE value indicates good absorption-collection ability of the solar cell or also demonstrates low loss mechanisms active in that region. Assuming light incident on the solar cell, the blue region of the light usually gets absorbed early in the substrate because of lower wavelength whereas longer wavelengths like the red region are absorbed/collected in the other end of the device. So, lower QE response in blue region is a virtue of high front surface recombination or poor passivation or inefficient

light trapping whereas poor response in the red region is indicative of high recombination in the back end of the solar cell, reduced absorption or low diffusion lengths. There are two types of QE:

1. External Quantum efficiency (EQE)- The "external" quantum efficiency of a silicon solar cell when measured includes the effect of optical losses such as transmission and reflection. EQE tells the fraction of incident photons getting converted to electrons in the device.
2. Internal Quantum efficiency (IQE)- "Internal" quantum efficiency considers the ability of solar cell to convert the photons that are not reflected or transmitted into useful collectable carriers. By measuring the reflection and transmission of a device through UV-Vis spectroscopy, the external quantum efficiency curve can be corrected to obtain the internal quantum efficiency curve. IQE tells you about the fraction of absorbed photons that are being converted to electrons in the device. Basically, if R is the reflection then,

$$IQE = \frac{EQE}{1-R} \quad (4.3)$$

4.10.2 Basic Setup and Operations

The quantum efficiency measurements for the hybrid solar cells fabricated were performed at the Institute for Energy Conversion(IEC) and the Arizona State University. Although both the QE setups are slightly different, the setup at IEC would be discussed because it was used more frequently.

The QE setup at IEC runs measurement using a halogen bulb light source, a monochromator that produces a chopped light beam with wavelength λ (full width half

max=10-15 nm) and frequency f (~71 Hz) which flashes light on the cell placed which is held by holder. The cell is connected at a bias voltage V , producing an AC photocurrent. The AC photocurrent is then converted to an AC voltage using trans-impedance and further amplified using a lock in amplifier which is referenced to the light chopper frequency. Then the amplified signal is read by a computer. The above procedure is repeated N types over a wavelength range from λ_{min} to a maximum wavelength λ_{max} where,

$$\lambda_{max} > \frac{hc}{E_g} \quad (4.4)$$

with E_g as the absorber bandgap so that at λ_{max} , a negligible amount of light is absorbed by the cell and QE (λ_{max})=0.

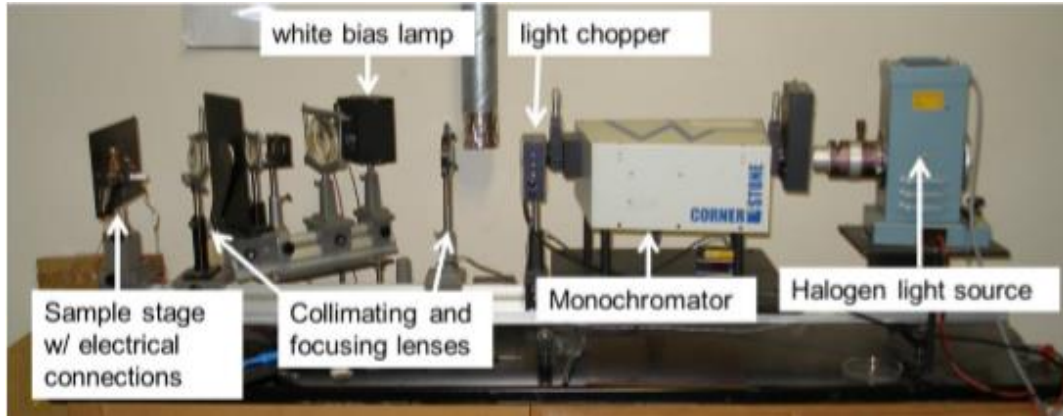


Figure 4.27 QE setup at IEC.

Prior to QE measurements on these cells, calibration is essential. Calibration is done with a standard silicon cell with its standard J_{sc} value (obtained under AM 1.5G

conditions) and is performed for varied wavelengths (350-1200nm). It is necessary to have the IQE measured within 1% of the reference value (AM 1.5G conditions). However, spectral variations do occur over time due to aging of the halogen bulb or other systematic factors, which result in spectral variations greater than 1% of the reference IQE.

4.10.3 Quantum Efficiency Comparative Studies

Initial quantum efficiency tests were conducted on devices with 500-micron thick n-type polished wafers, the sample name being Virginia N01H. Upon analysis of these devices, it can be said that the QE for wavelengths from 450nm- 1000nm was low and primarily was an indication of high recombination in the device. The QE is slightly better at lower wavelengths but way lower than conventional silicon based devices. The front surface of these cells has anti-reflection properties due to the presence of PEDOT: PSS. This will be discussed in the UV-VIS spectroscopy results. Although in comparison, the QE for these devices is way lower than the conventional devices at these wavelengths and this can be attributed to the lack of good light trapping techniques. Thus, excellent light trapping is necessary for good low wavelength performances and high short-circuit current. In the mid wavelength region, the biggest contributing factor is low diffusion lengths. The thickness of solar cells should be less than the diffusion length of the induced carriers.

The relationship of cell performance to bulk and surface recombination effects can be described by the effective lifetime τ_{eff} , defined by

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{bulk}} + \frac{2S_{eff}}{d} \quad (4.5)$$

where, τ_{bulk} is the bulk lifetime, S_{eff} is the effective recombination velocities at the cell surfaces, and d is the cell thickness.

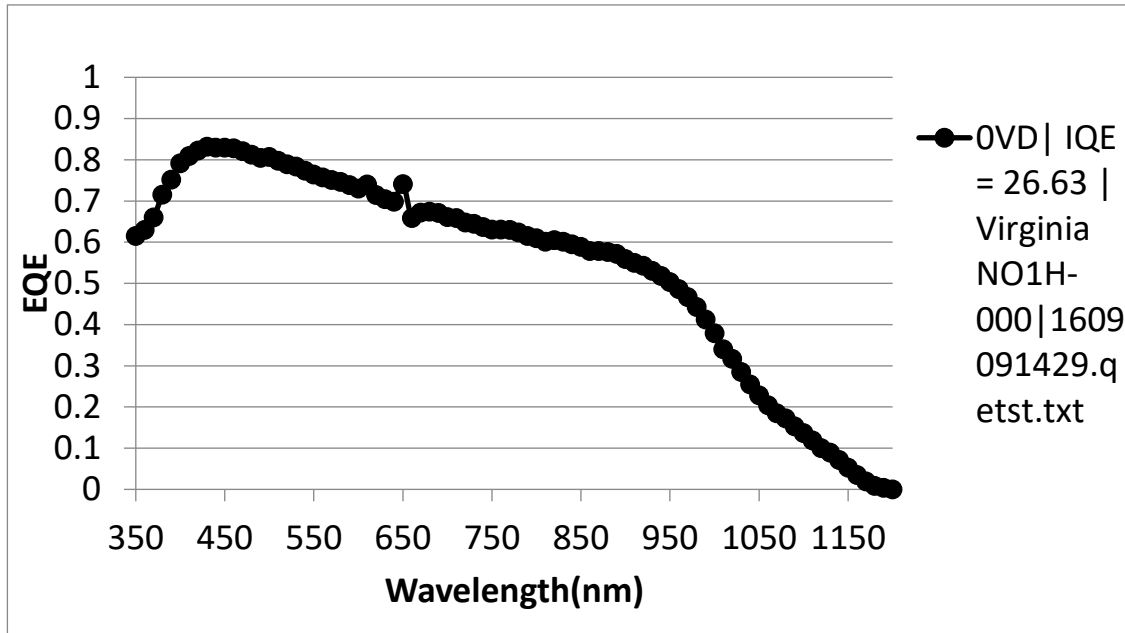


Figure 4.28 QE for thick wafer.

From the device analysis, it can be interpreted that:

- Low QE at lower wavelengths is because of poor light trapping ability.
- At mid and higher wavelengths, recombination dominates and is responsible for low QE.

Owing to the above mentioned, QE was carried for different architecture cells which were not just thinner but also had front texturing and back surface field to improve the short circuit current and reduce recombination at the back side respectively. In addition, thin

devices with no texturing but back surface field were also tested. Below are the QE curves for these devices in comparison to the previous device.

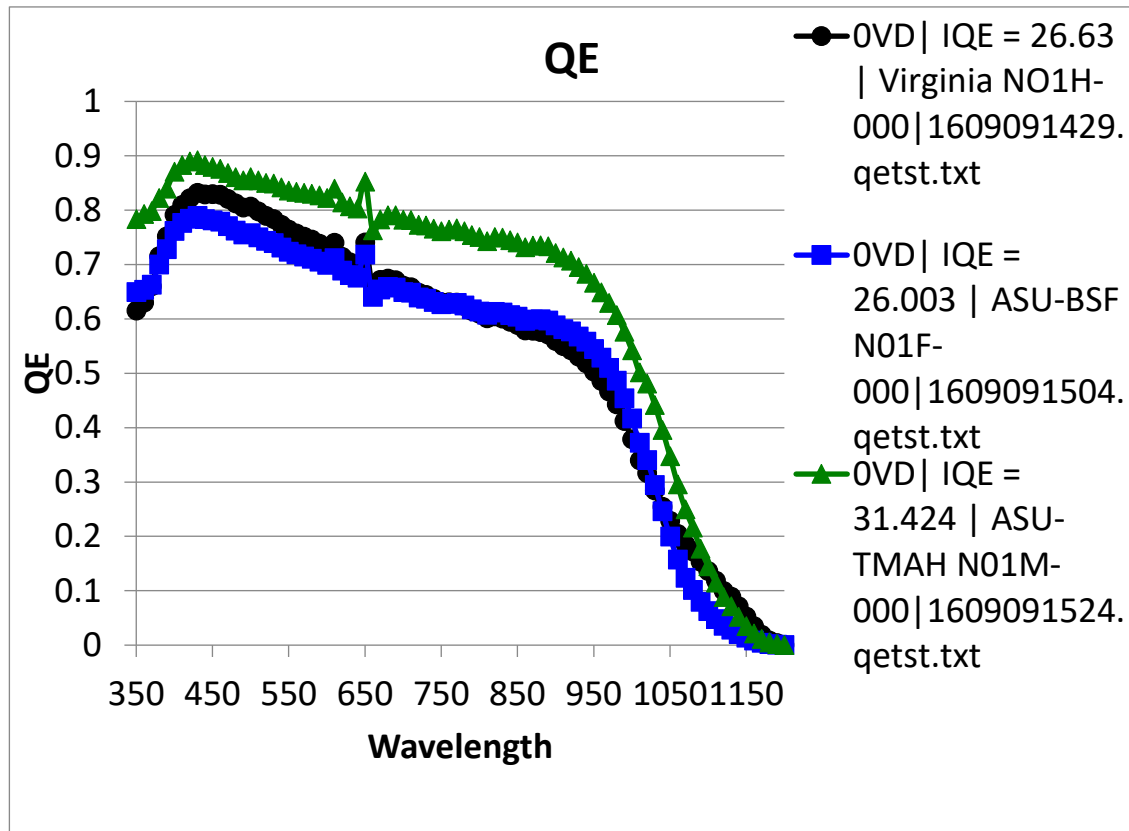


Figure 4.29 QE comparison for different cell architectures.

From figure 4.29, it is observed that the green plot is above the black plot for all wavelengths except for above 1050nm wavelengths. This is indicative of a better performing solar cell. Major changes made in the new solar cell architecture are:

1. Reduced thickness- The new device architecture is on a 145-micron thick n-type silicon substrate in contrast to 500-micron thick substrate. Reducing the device

thickness helps in lowering the recombination as the volume for recombination (thickness) is reduced (Green, 1999; and Tiedje et al., 1984). With reduced device thickness, the shunt resistance losses can also be minimized since it is a parameter dependent upon the manufacturing and processing of the wafer. But as the thickness of the substrate goes down more challenges will be encountered. Reduced thickness implies lot of photo-generated charge carriers generated at the surface and good passivation is necessary to extract current from the carriers.

2. Improved front surface- The new device has textured front surface. The texturing is achieved as follows- Saw damage removal in 30% potassium hydroxide (KOH) at 80 °C for 6 minutes (this etches about 10 μm from each side) and then rinse in de-ionized water (DI) water for 10 minutes and after this the wafers were textured in 2% KOH (with an additive that lowers the surface tension of KOH so that it spreads well on silicon surface) for about 25 minutes. This gives us the pyramid sizes of about 3-5 μm base size. Achieving such a frontal surface will result in improved light trapping because of increased probability of light getting captured. Besides, the textured front surface there is improved PEDOT: PSS coverage on the front which adds to the anti-reflection properties.
3. Back surface field- The new devices have implemented a back-surface field to reduce the recombination losses at the rear end of the device. This has been discussed already in this chapter.

Besides QE measurements, a comparison was made with traditional back surface field solar cells. The plot below explains the difference in QE behavior for a hybrid solar cell (in red) and AL-BSF based crystalline solar cell fabricated in Arizona State University solar power labs (in blue).

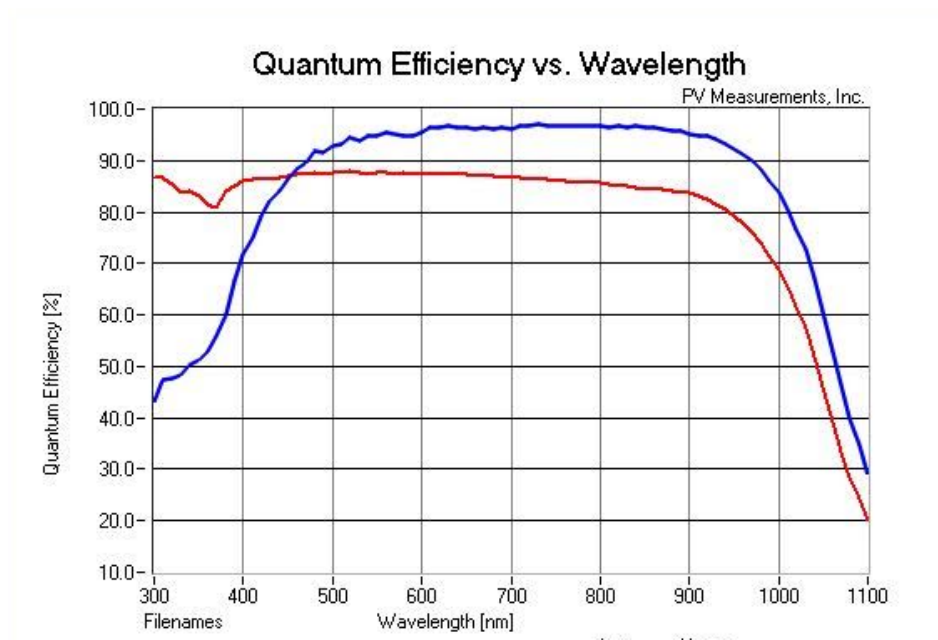


Figure 4.30 QE comparison of a p-type AL-BSF cell (in blue) vs n-type hybrid solar cell (in red).

The blue curve dominates the red curve in all wavelengths but the lower ones. At mid-range and higher wavelengths, the collection efficiency of the hybrid solar cell is low and it is reflected on the QE curve. But the most interesting phenomenon is at lower wavelengths. The hybrid solar cells have amazing response for lower wavelengths and this phenomenon differentiates the architectural difference between the two cells. In a conventional solar cell, the emitter is usually highly doped and often this results in

formation of a “dead region” which is a region with no electric field. In this region, the collection efficiency of the solar cell is very low. Many commercial cells have a poor "blue" response due to this "dead layer". Therefore, the region under the contacts should be heavily doped, while the doping of the emitter is controlled by the trade-offs between achieving a low saturation current in the emitter and maintaining a high emitter diffusion length [50]. Heavy doping in this region reduces the contact resistance and recombination losses at the top of the cell. But in an induced junction hybrid solar cell, there exists an electric field at the top (Si/PEDOT interface) and this is responsible for the peak at lower wavelengths. This electric field prevents minority carrier recombination at the front interface and reduces the negative impact of front surface recombination.

Chapter 5

ENTREPRENEURIAL JOURNEY: NSF I-CORPS

5.1 Introduction

Anything we do in our life must have a purpose. I have always wanted my research to progress to real world applications and give something back to community. Research has relevance when it is aimed at solving real life or industrial scale challenges. It could be in any form, like making things work faster to run them efficiently to reducing the cost to build them to make it more reliable. One reason I chose solar as my field of research was because I have seen people back in my country who despite having sun for about 300 days in a year could not taste the benefits of this wonderful resource. Growing up in India, I saw small scale industries suffer due to power cuts. With a meager income, power cuts added to the misery. I was largely moved by listening to the state of farmers in my country. Their lives totally revolved around power cuts. I believe solar is the solution to this crisis and one day I want my country to make the best out of the available resources.

5.2 Journey

It is always elating to see researches have potential commercial impacts and identify opportunities to apply their research. Our path towards commercializing our research started through the 2016 Hen-Hatch, University of Delaware's premier startup funding competition. Usually, any solar research at lab scale is focused on achieving higher efficiency or lower costs, or finding alternate materials, and that continues to be the easiest way to enter the market. We wanted to address the same issues, but with a twist. Our initial discussions and analyses with people who have or have not pursued solar for their homes gave us an idea that there was substantial sector with an "inability" to buy solar for their home because of aesthetics of solar panels. A million-dollar homeowner

would expect a premium product on the roof, and would be willing to pay the premium for it. In a few states in the USA, people staying in condominiums must get prior approval from the homeowners' association (HOA) in their neighborhood to get solar for their roofs. Some HOA's do not like the look of solar panels for aesthetic reasons, and the fact that they are big, bulky, and flashy is something that concerns them. Solar on few roofs in a community looks like chicken pox suffering community. But things are changing slowly. States like Maryland, have "solar access rights" laws that limit homeowner associations from banning solar panels. The law overrides the homeowners' association contract that restricts one from installing the panels. Unfortunately, HOA's can still dictate where to put panels and how to install them. These laws usually say that some restrictions are still possible. But if HOA denies an individual's request to have solar panels installed, the individual can go to the extreme of suing the HOA [63].

We understood that we wanted to target the aesthetics market, and we ventured into the Hen Hatch competition with the concept of solar shingles using our hybrid solar cells research work. These solar shingles not only protect the roof like normal shingles, but also power the home like solar panels. From the outside, they look like normal asphalt shingles but behind each shingle lies the solar component that powers the home. This would not classify as a roofing product or a solar product exclusively. It is a mix of both and would require expertise from both departments. Residential homeowners interested in buying this would have to replace their entire roof with the product, and thus it makes the most sense to have them installed for homes which are looking for roof replacement. The average lifetime of an asphalt roof in the east coast is about 15-20 years, and this relates well with the solar warranty which also ranges from 20-25 years. Being the lead on this project, I pitched for the novelty and utility of these solar shingles which caught

the attention of the judges. The biggest selling point was the fact that with such a multipurpose roof one can become his own generator in just a few years. The idea was well appreciated. While the idea did not win, it caught the attention of a couple of professors who teach at the Venture Development Cell. They took interest in learning about solar shingles, our underlying technology, and suggested customer discovery and consider the National Science Foundation I-Sites program.

A year back, there were hardly a few people who knew what solar shingles were or what they did. However, today, they are making headlines because of two major developments. The first development was DOW stepping out of the solar shingles race after being about half a decade in the business. Most analysts believed that the technology on which DOW solar shingles worked on was expensive, and the market for the product was dead. Others stated the cost of having DOW products was 4-6 times the cost of conventional panels. This raised eyebrow of many because a big company like DOW exiting from business did reflect something about the state of industry. On other hand, the bigger news was the acquisition of the largest solar installer in the country, SolarCity, by Tesla, and the attempt to change the business model and product altogether. Elon Musk, the founder of Tesla, said he wants to build a solar roof and not solar on roof. This solar roof comes in 4 variants and thereby customers have options to choose from. During the launch of the product he said “Would you like a roof that looks better than a normal roof, lasts twice as long, costs less, and by the way generates electricity? It is like, why would you get anything else?” The launch of this product blew everyone’s mind because it was revolutionary and was launched by none other than Elon Musk who changed the automobile industry. Many claimed these solar roofs to be the “Tesla of Solar”. Below is how the Tesla’ solar roof would look like:



Figure 5.1 Tesla solar roof.

We went on to apply for the I-Sites program upon the recommendation of our mentors. The I-Sites program nurtures students and/or faculty who are engaged in projects that have the potential to be transitioned into the marketplace. We got accepted and not only received a funding of \$3000 to carry out customer discovery, but also got the ability to use the Venture Development Cell's lab space, resources, mentoring, and networking opportunities. Under the guidance of Dan Freeman, Vincent DeFelice, and John Currie at the Venture Development Center(VDC), we underwent an enthralling four-week long journey. Our team, which consisted of Dr. Opila, Akirt Sridharan, Jimmy Hack, and I, was introduced to basics of lean start-up techniques. We also engaged in customer discovery to understand the problem in our respective markets. The motivation behind this program was to understand the problems in the market and see if we had value propositions to address the problem. We chose residential homeowners as our primary customers. We ended up speaking to 19 homeowners on their perception of solar over the 4 weeks, and learned the following:

- 20% of the people already had solar, and they love their decision to go solar.

- 58% of the people felt they were “Okay” with looks of solar, but if they were offered a product with same utility and better looks, they would want to change their decision.
- 20% of the people wanted to go solar but could not because of shading issues in their community.
- 63% of the people wanted hassle and maintenance free roofs.
- 16% of the people wanted to go solar but could not because their roof had to be replaced.
- 50% of the people felt Solar was costly and would rather lease them than buy them.

Solar installers, roofing contractors, developers, and wholesales must also be considered as potential customers.

At the end of the program we realized that aesthetics did drive solar adoption to certain extent and that 19 interviews was not enough to generalize it. We also discovered other potential customer segments. We decided on “persist and pivot” and wanted to apply for a larger grant so that we could take part in a more effective and engaging customer discovery process and more precisely understand the problem in the market. We also started working with the mechanical engineering senior design students who loved our idea and decided on building a model of solar shingles with the resources they had. Meanwhile, my team also participated in the Department of Energy’s Launch R held at Rutgers University. The U.S. Department of Energy had selected Rutgers as one of eight institutions in the country to host one of its regional Cleanest University Prize Competitions. The competitions are designed to help fund and develop viable, innovative clean energy business ideas at universities across the country [64]. Our team made it to the top 6 in the mid-Atlantic area and won recognition for “best customer segment” model.

5.3 NSF I-Corps

NSF I-Sites, Hen Hatch and LaunchR ignited the passion for entrepreneurship in me. Our ideas were well received, but we wanted more validation to commercialize the idea. With the NSF I-Sites background and the recommendation from our program instructors and peers, we applied for the NSF I-Corps grant. This was a \$50,000 grant from the National Science Foundation that was spread over 6 months. Teams were to involve in intense customer discovery, at least 100 customer interviews with the potential customer segment in 45 days. This program teaches NSF grantees to identify valuable product opportunities that can emerge from academic research, and offers entrepreneurship training to participants by combining experience and guidance from established entrepreneurs through a targeted curriculum (lean startup model). The important part during the application phase was to find a mentor who has had entrepreneurial experience in the past and could guide the team in the business aspect during the program. It was difficult to find a mentor because every team member, including the mentor, had to devote 15 hours a week for customer discovery and had to involve in a 3 hour WebEx session every Wednesday. Given that the mentor is already engaged with his own start-up, it sounded demanding. We found our mentor in Modzelewski who was recommended by DeFelice at VDC. Modzelewski was working with SolarCity and was an adjunct professor in the business school at UD. He had a startup of his own in the past, and this felt like the perfect match for our team because of his versatile solar experience and business acumen. With his addition, I felt the team was complete. I was the entrepreneurial lead for the team with Jimmy Hack as the co-entrepreneurial lead, Dr. Robert Opila, the principal investigator, and Keith Modzelewski as the mentor. After several interviews with the NSF team, we were accepted into the fall cohort, 2016 based in Detroit under University of Michigan, Ann Arbor.

Upon being accepted into the program, we were excited to venture out and gain a sound understanding of the market. We went to Detroit and presented our unique value propositions and our potential customer segment. We addressed our research work, the aesthetics issue with existing solar panels, and our background work in the university on these value propositions. But the teaching team was not interested in our story. They felt that addressing the aesthetics concern should not be our primary concern and that it had to be manufacturing because we had a recipe for making a solar cell and not a good looking solar cell. Aesthetics was more of an add-on feature than a direct result from our research work. So, we focused our value propositions on solar manufacturing companies and began testing our hypothesis by talking to process engineers, production line experts, and the chief technology officer at manufacturing facilities. The two big hypotheses we were testing were:

- High temperature is a bottleneck to production at cell level.
- High temperature is the biggest cost-driver at cell level.

We realized that there are four major technologies or recipes for making commercial solar cells. They are Aluminum Back Surface Field (AL-BSF), Passivated Rear Emitter Contact/Locally diffused (PERC/PERL), Interdigitated Back Contact(IBC) and Heterojunction with Thin Intrinsic layer (HIT). The AL-BSF cells, also called screen printed solar cells were developed in early 1970's. They are the most mature and widely used technology because of the simplicity in fabrication. The screen-printed cells employ simple techniques like diffusion, screen printing, firing, chemical vapor deposition that are high-temperature based processes. The PERC/PERL cells are evolution to the AL-BSF cells because they implement micro-electronic techniques to attain higher efficiencies. The IBC cells eliminate the losses due to shadowing in the front by placing

both contacts on the rear of the cell. Mostly n-type silicon based, these cells also have high short-circuit current which boosts the performance of the solar cell. Sunpower is the largest manufacturer of the high efficiency IBC cells. The high efficiency HIT cells by Sanyo (now Panasonic) were motivated by low-temperature processing. They implement an amorphous silicon layer on the front which is deposited at low temperatures using PECVD and it also serves a very good passivation layer. These high efficiency cells have promising open circuit voltages due to lowered recombination losses.

Since we had just 6 weeks to work on this project, we had to devote time scheduling interviews, at least 15 every week. This was especially challenging because there were just two solar manufacturing plants in the USA. There were many manufacturing plants in the about a decade back but today most of the manufacturing happens in Asia because of renewable energy policies, federal incentives, cheap land acquisition cost and cheap labor. The people to whom we spoke with had extensive experience working in this field, and we tried understanding from them why the shift happened. It became difficult to schedule at least 15 interviews every week, and at certain point we even decided to go to China to attend a conference where the tier one manufacturers would put up stalls. Unfortunately, it did not work out in our favor because of visa issues. Trade shows and conferences were useful to us because we could capture a larger crowd under the same roof and we could conduct more customer discovery.

Since I belong to India, I tried understanding the Indian solar manufacturing market as well. Through my contacts, I got the opportunity to talk to the process engineers at the big solar manufacturing firms back in my country. Personally, I felt India is more a “follower” of the tier 1 manufacturers and is expanding its capacities conservatively. It is still doing the AL-BSF based solar cells, because it is more mature and prevalent

elsewhere in the world. They do not wish to invest in risk and play it safely especially because the solar market is catching up in India and is not as matured as in China or the USA. Manufacturing capacity in India is around 1GW in total and module capacity is about 2GW with almost half the cell capacity being imported. There are about 10 players in the market who merely follow the tier one manufacturers of China. As far as solar installation is concerned, the world's largest solar plant at one site became operational 2 months back in South India. Commercial solar is a big thing in India and residential solar is yet to kick start in a grand fashion. State based and federal policies have a big role to play in solar adoption in any country. Making solar affordable to masses is the key behind widespread adoption. Most companies did turnkey lines as their first lines because they were not much aware of the processing that goes behind solar. The turnkey companies are mostly European based like Schmidt or Meyer Burger or Centrotherm. These companies also trained the engineers, and this has ended up being very useful to the solar manufacturing business in India.

From our initial customer discovery with people involved in manufacturing, we realized that high temperature was not a shark-bite to these companies. Not only did the tools run at peak efficiencies and not only were the processes optimized, but despite having high temperature processing involved they also achieved a yield which was higher, 98%- 99.3%. This reflected the robustness and maturity of the processing techniques and technology. Though these facts were enough to invalidate our hypotheses, we did learn a few things. We realized that the industry was not keen on shifting to thin wafers because the cost of raw silicon has fallen drastically. Being priced at 20-40\$/kg in early 2000s, they went as high as 400\$/kg during peak demand (2004-2008) until the Chinese mastered the art of Siemens process and ran the business to over-supply. Today

they are fairly priced at 15-30\$/kg. So, there does not exist the motivation to go thin crystalline silicon. We also understood that the industry was conservative and believed in evolution than revolution. The industry was slowly shifting towards PERC cells from the AL-BSF cells and the shift in technology is happening because it is cost-efficient and does not require any major upgrade. It was sheer upgrade at processing level rather than at industry or technology level. As far as numbers are concerned, it costs about 8-10 cents/W to make an AL-BSF solar cell whereas the PERC cell was about 12-14c/W and this translated to at least a 2-4% increase in efficiency. It made more sense than doing the IBC cell by SunPower which costs four times the cost of conventional AL-BSF cells and is 4-6% higher in efficiency. We learned that the premium a company could pay for 1% increase in efficiency was about two cents. We also got the opportunity to visit both the manufacturing facilities in the USA, SolarWorld in Portland and Suniva in Atlanta. Seeing large scale manufacturing in such a sophisticated environment left me awestruck. It was surprising to see complete automation and hardly 15-20 people working in a 500MW factory. The SolarWorld factory tour was indeed the best experience during this journey, because it is a vertically integrated company. Everything from wafer to module is done under the same roof and to get to see all of it was a wonderful experience. They are also the largest manufacturers in the western hemisphere and the first ones to commercialize the PERC cell technology. We got a chance to interact with the people who worked with tools and they told us what they loved about their work and what kept them work overtime. This experience was unique is because not everybody gets a chance to visit such a sophisticated manufacturing environment without working in them. And personally, since I see myself working in a solar industry after I graduate, I have also learned what work feels like.

We also learned that the state of industry today is tricky. The Chinese had not only mastered the art of making solar cells, but also do it in the cheapest possible way. It is just not possible for American companies to compete with Chinese in the cost game. An interesting quote was made in one of our interviews where the interviewee said that the “Chinese are selling the solar panels like rotten vegetables, and buyers in the market availed it in the price they wanted”. This over supply state has largely affected the pricing in the market. Most solar companies have increased sales over every year but their profit margins have decreased because it has become a tough race to compete in. Suniva, the second largest manufacturer in the USA, expanded their manufacturing from 150MW to 400MW just to meet economies of scale and remain alive in the market. As far as entry to the market is concerned, a few licensed their technology and have made revenue through that, whereas others have built their own manufacturing facilities, demonstrated the impact and advantages of their technology, and then scaled up manufacturing. We learned that recipe licensing is also challenging because it is difficult to do reverse engineering on that.

By the time we had invalidated the high temperature hypothesis, we were already half way through our journey. We quickly understood the industry requirements and the numbers game. We started focusing our value propositions on high efficiency high cost solar cells and how and what could be done to drive their prices down. These were the heterojunction with thin intrinsic layer of amorphous silicon solar cells (also called as HIT cells popularly) by Panasonic and Interdigitated all back contact solar cells (IBC cells) by SunPower. Both these cells are considered premium solar cells. They have high proven efficiencies, and high manufacturing costs as well, mostly because of the cell architecture. They also used n-type wafers which were slightly costlier than p-type

substrates. These n-type wafers have better resilience to light induced degradation, an issue which is critical, and they have higher diffusion lengths. However, just about 5% of the solar cells today are n-type based and this is largely because it is challenging and not cost effective to grow n-type silicon especially because of the doping process. Compared to standard p-type (boron-doped) Si, n-type (phosphorus-doped) Si crystals show a larger distribution of specific electrical resistance. While for boron doping, a range between one and three ohm centimeters (Ω cm) can be easily maintained, in the case of phosphorus doping, this range increases to three to 12 Ω cm or more. As standard cell concepts require quite a narrow resistivity distribution to allow stable efficiencies for all the wafers coming from one crystal, the large variation of the resistivity of n-type Si crystals decreases their yield for cell production thus increasing overall production costs [65]. From our customer discovery, we realized that we had value propositions for the HIT cell rather than the IBC cell. After talking to people involved in the HIT cell processing industry, we realized that the two biggest challenges to HIT cell processing were the deposition of amorphous silicon using monstrous sized tools and silver consumption. This was usually done by chemical vapor deposition. The bigger concern for HIT cells is amorphous silicon uniformity (yield) and sensitivity to moisture, which requires hermetic encapsulation (cost and weight). In addition, the Sanyo-like HIT process (used by Panasonic) requires low-temperature firing silver. The low temperature means that the metal retains considerable porosity and is therefore not as conductive as would be conventional, high temperature firing silver inks. consequently, the amount of silver used must be increased, which is a big cost issue. In contrast, SolarCity acquired the Silevo process where the silver printed metal was replaced with plated copper, but in that case, there are significant costs added back due to the need for definition of the contact area, waste disposal issues,

and the overall sensitivity of plating processes to surface and chemical cleanliness (leads to occasional dramatic loss of yield). Unfortunately, we were almost towards the end of the program when we found our potential customer. We still have money left on our grant and even after finishing the program, we wish to be involved in customer discovery process to understand HIT cell processing.

Though the NSF I-Corps journey ended and we were a NO-GO, we have a path forward. Our biggest learnings after 45 days, visiting 7 states, and 107 customer interviews were:

- Our research has value propositions for a technology which would be the next big shift in solar manufacturing (4-5 years from now). We wish to be ready by then.
- The solar manufacturing industry is conservative today. Innovation at process level is more accepted than revolution in terms of technology.
- A new technology should be disruptive in terms of both high efficiency and low cost. They must co-exist.
- There is an oversupply in the market today largely because the Chinese have mastered the art of making solar cells in the cheapest possible way. Because of the federal incentive in China which was expiring in June 2016, there was massive oversupply and costs were very low.
- We have a direction for our research and a commercialization path forward.

The reason why this complete journey constitutes a chapter in my thesis is because it has helped me focus and direct my research in the direction which the industry needs. It has opened a new world of opportunities in front of me and to see how much impact

my research can make is indeed overwhelming. We started out with solar shingles and today we are working on building value propositions for HIT cell manufacturing and make them more prominent. All this has happened in course of 1.5 years. Going back to lab after this project has helped me focus on the specific parameters like efficiency, throughput and type of tools, bankability, durability etc. I have understood the shortcomings of the technology I work on and challenges in commercializing it. It feels good to have an industrial approach to lab scale research work and having direction to step out of lab.

Going forward, along with my professor we are planning on building an enterprise with all that we learned through these ventures. We wish to apply for a patent for our invention right away and with larger grants like NSF Small Business Innovative Research(SBIR) or Proof of Concept funding, we plan on building a small-scale manufacturing base. This is an ongoing work and we must keep track of the developments happening in the world around us. In the end, I would like to thank my Dr. Opila from the depth of my heart for igniting the passion for entrepreneurship and the team at Venture Development Cell HORN program for introducing me to the new world of entrepreneurship and keeping me motivated always.

Chapter 6

CONCLUSION

6.1 Summary of Results

In this thesis, induced junction carrier selective induced junction solar cells based on PEDOT: PSS were studied in detail. Effective passivation is key to enabling high-efficiency silicon based devices. Solution processed techniques provide a potential means to achieve high-quality passivation. With low equipment costs (CAPEX) and simple deposition (OPEX), this could enable a lower cost alternative to current high-efficiency solar cells. Devices fabricated with this architecture implemented chemical passivation technique using benzoquinone. The hybrid solar cells fabricated were about 10% efficient which brings them in relevance to other research happening on hybrid cells. Hybrid solar cell optimization was discussed and the impact of thinner wafers, texturing, improved grid design, improved metallization scheme and PEDOT: PSS conductivity was studied thorough J-V measurement, quantum efficiency and UV-VIS spectroscopy. Post device optimization, the hybrid solar cells exhibit a 9.6% efficiency with open circuit voltage of 0.545 volts and a short circuit current of 28.6 mA/ cm². The fill factor though on weaker side was 61.6%. Device shortcomings were analyzed and future work is aimed at attending these concerns. These solar cells have showcased promising results with a rise from 4% in 2015 to about 10% in 2016. The entrepreneurial journey associated with this research is discussed in the very end. The NSF I-Corps journey gave direction to this research and serves as motivation to higher performance and reliability. Induced junction solar cells have reduced capital expenditure and operation expenditure costs because of lab-scale processing. If efficiencies tend to increase in this manner, they could be a

competition to the Panasonic based HIT cells- the commercial opportunity to step outside lab.

6.2 Future Work

The focus on this thesis was on device optimization but the final device is not the champion cell. There still lies scope for improvement. Simulations of double-sided silicon/organic heterojunction show that hybrid cells can achieve power efficiencies of over 20%, as good as the AL-BSF cells and heterojunction solar cells [29].

The first and immediate plan of action would be discovering surface passivation mechanism for compounds belonging to quinone family. Understanding benzoquinone passivation is essential to device performance. BQ does show lifetime improvement but in terms of devices, cells with and without BQ have not shown big difference in performance. A lot of studies like XPS, Density functional theory, Sentaurus modelling have been conducted in the past within the group to understand the way BQ interacts with silicon but there is nothing conclusive yet. It will also be necessary to measure the strength of band bending induced by BQ. Surface photovoltage (SPV) measurements provide a method to quantify band bending near the surface of a semiconductor. In a SPV experiment the sample is measured both with and without light. Saturating the sample with illumination results in the generation of free carriers in the material. These will adjust the Fermi level in the depletion region, building up charge near the surface, resulting in a flattening of the previously bent bands. If the energy levels of the bands are measured both before and after illumination, this energy shift can be determined. SPV can be measured using XPS, which measures the energy shift in each XPS peak.

PEDOT: PSS looks like a good fit for a hole transport/electron blocking layer but an alternate hole transport layer could be better performing. Metal oxides have started

gaining popularity recently because they also can behave as hole transport layer. Few metal oxides which have demonstrated results are Nickel oxide, Molybdenum trioxide, Vanadium oxide and Tungsten trioxide [66]. Molybdenum trioxide (MoO_3). They have received significant interest as a high-work-function contact for silicon photovoltaics [67]. MoO_3 contacts with amorphous silicon passivation layers and heterojunction contacts have been demonstrated to achieve very high conversion efficiencies [68], most recently reaching 22.5% [69].

While current work was aimed at improving PEDOT: PSS performance, the future work would be on getting improved coverage on textured samples. Insufficient interface conformity is a challenge faced in achieving high efficiency hybrid solar cells because using conventional pyramid antireflection texturing provokes the porosity of the interface [70]. This porosity in the organic-silicon interface ends up forming local shunt that affect the fill factor of the solar cell. The contact resistance and lateral resistance are affected due to this phenomenon. Scanning electron microscope (SEM) could be a good technique to understand surface coverage of PEDOT: PSS on textured silicon. In addition, calculating the bandgap of PEDOT: PSS (LUMO and HOMO) will give us a better idea on band alignment of these solar cells. The best way to characterize transport bandgaps and band-alignment is using UPS/IPES/XPS. UV-VIS can also be performed but it gives what is often called the "optical gap", which is not the same thing as transport bandgap but can be used to characterize the bandgap and absorption depth of PEDOT: PSS. Additionally, PEDOT: PSS also behaves as an anti-reflection coating and understanding the change in ARC properties with varying in thickness and co-solvents would be interesting.

The obtainable open circuit voltage of a device is limited by the amount of recombination occurring, and so this parameter can give a measure of the effectiveness of passivation at the interfaces. The photoconductance decay is a useful means of obtaining minority carrier lifetimes for a sample. It can also be used to obtain a measure of the obtainable open circuit voltage for a given recombination velocity measured. This implied Voc can be treated as an upper bound for the open circuit voltage. Implied Voc measurements taken before subsequent processing can help to identify initial wafer passivation quality. Sinton's Suns-Voc method is a method of measuring a curve of open circuit voltage versus illumination intensity. This gives a curve analogous to an IV curve, while eliminating the effect of series resistance. The Suns-Voc curve can then be used to determine the performance of the junction itself before deposition of metal contacts. This technique will be quite useful in reducing the number of variables in device performance and will allow measurements of junction performance of unfinished devices.

Future work would incorporate device optimization, understand passivation mechanism, material engineering and improved theoretical understanding of band bending which would make these devices the next generation of PV technology.

As far as the entrepreneurial journey is concerned, the foremost work to be done is on establishing intellectual property and forming a company (legal entity). Proof of concept on a larger scale would help us understand the challenges to scalability. Also, during the NSF I-Corps journey there were questions raised on the reliability of organics in the solar cell. At this stage, we have not focused much on reliability but an area we wish to work on. There do exist solutions like encapsulation barriers or protective layer which have not been implemented/tried for these cells. The issue of stability is a more general problem that plagues all organic-based devices and there is growing body of

research that deals with precisely this issue. Some of the possible encapsulations that can be considered are “Hybrid-permeation barrier”, ALD deposited AlO_x , parylene/ AlO_x , parylene/ SiN_x , etc. [71, 72, 73].

REFERENCES

- [1] Institute for Energy Research-
<http://instituteeforenergyresearch.org/topics/encyclopedia/solar/>
- [2] Allied Market Research- <https://www.alliedmarketresearch.com/crystalline-silicon-photovoltaic-pv-market>
- [3] CBS News- <http://www.cbsnews.com/news/technology-that-could-change-the-course-of-climate-change/>
- [4] Environmental Protection Agency- Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2010.
- [5] Energy Information Agency (EIA)- How much of the U.S. carbon dioxide emissions are associated with electricity generation?
- [6] NREL- U.S. Renewable Energy Technical Potentials: A GIS-Based Analysis.
- [7] Nature-
<http://www.nature.com/nature/journal/v443/n7107/full/443019a.html>
- [8] Global Climate and Energy Project, Stanford University-
<http://gcep.stanford.edu/research/exergycharts.html>
- [9] De Anza College-
<http://www.deanza.edu/faculty/hamidiridha/esci61/pdf/esci61-solar-radiation-slides.pdf>
- [10] HyperPhysics Condensed matter- <http://hyperphysics.phy-astr.gsu.edu/hbase/solids/pnjun.html>
- [11] Beech, J. P., Holm, S. H., Adolfsson, K., & Tegenfeldt, J. O. (2012). Sorting cells by size, shape and deformability. *Lab on a Chip*, 12(6), 1048-1051.
- [12] Bean, K. E. (1978). Anisotropic etching of silicon. *IEEE Transactions on Electron Devices*, 25(10), 1185-1193.
- [13] Seidel, H., Csepregi, L., Heuberger, A., & Baumgärtel, H. (1990). Anisotropic etching of crystalline silicon in alkaline solutions I. Orientation dependence and behavior of passivation layers. *Journal of the electrochemical society*, 137(11), 3612-3626.

- [14] Green, M. A., Emery, K., Hishikawa, Y., Warta, W., & Dunlop, E. D. (2015). Solar cell efficiency tables (Version 45). *Progress in photovoltaics: research and applications*, 23(1), 1-9.
- [15] National Instruments- <http://www.ni.com/white-paper/7230/en/>
- [16] Manea, E., Budianu, E., Purica, M., Cristea, D., Cernica, I., Muller, R., & Poladian, V. M. (2005). Optimization of front surface texturing processes for high-efficiency silicon solar cells. *Solar energy materials and solar cells*, 87(1), 423-431.
- [17] Cousins, P. J., Smith, D. D., Luan, H. C., Manning, J., Dennis, T. D., Waldhauer, A., ... & Mulligan, W. P. (2010, June). Generation 3: Improved performance at lower cost. In *Photovoltaic Specialists Conference (PVSC), 2010 35th IEEE* (pp. 000275-000278). IEEE.
- [18] Swanson, R. M. (2005, January). Approaching the 29% limit efficiency of silicon solar cells. In *Photovoltaic Specialists Conference, 2005. Conference Record of the Thirty-first IEEE* (pp. 889-894). IEEE.
- [19] Masuko, K., Shigematsu, M., Hashiguchi, T., Fujishima, D., Kai, M., Yoshimura, N., ... & Yamanishi, T. (2014). Achievement of more than 25% conversion efficiency with crystalline silicon heterojunction solar cell. *IEEE Journal of Photovoltaics*, 4(6), 1433-1435.
- [20] Queisser, H. J., & Haller, E. E. (1998). Defects in semiconductors: some fatal, some vital. *Science*, 281(5379), 945-950.
- [21] Yoo, W. S., Kim, B. G., Jin, S. W., Ishigaki, T., & Kang, K. (2014). Ultra-Thin SiO₂/Si Interface Quality In-Line Monitoring Using Multiwavelength Room Temperature Photoluminescence and Raman Spectroscopy. *ECS Journal of Solid State Science and Technology*, 3(11), N142-N150.
- [22] Takato, H., Sakata, I., & Shimokawa, R. (2003, May). Surface passivation of silicon substrates using quinhydrone/methanol treatment. In *Photovoltaic Energy Conversion, 2003. Proceedings of 3rd World Conference on* (Vol. 2, pp. 1108-1111). IEEE.
- [23] Chhabra, B., Bowden, S., Opila, R. L., & Honsberg, C. B. (2010). High effective minority carrier lifetime on silicon substrates using quinhydrone-methanol passivation. *Applied Physics Letters*, 96(6), 063502.

- [24] Kotulak, N., Chen, M., Schreiber, N., & Opila, R. L. (2014, June). Time and light-dependence of electrical passivation of c-Si surfaces with quinhydrone constituent solutions. In *Photovoltaic Specialist Conference (PVSC), 2014 IEEE 40th* (pp. 1529-1533). IEEE.
- [25] Sinton, R. A., Cuevas, A., & Stuckings, M. (1996, May). Quasi-steady-state photoconductance, a new method for solar cell material and device characterization. In *Photovoltaic Specialists Conference, 1996., Conference Record of the Twenty Fifth IEEE* (pp. 457-460). IEEE.
- [26] Kotulak, N. A., Chen, M., Schreiber, N., Jones, K., & Opila, R. L. (2015). Examining the free radical bonding mechanism of benzoquinone–and hydroquinone–methanol passivation of silicon surfaces. *Applied Surface Science*, 354, 469-474.
- [27] Chhabra, B., Weiland, C., Opila, R. L., & Honsberg, C. B. (2011). Surface characterization of quinhydrone–methanol and iodine–methanol passivated silicon substrates using X-ray photoelectron spectroscopy. *physica status solidi (a)*, 208(1), 86-90.
- [28] Clarke, T. M., & Durrant, J. R. (2010). Charge photogeneration in organic solar cells. *Chemical reviews*, 110(11), 6736-6767.
- [29] Nagamatsu, K. A. (2016). *Crystalline silicon photovoltaics via low-temperature TiO₂/Si and PEDOT/Si heterojunctions* (Doctoral dissertation, Princeton University).
- [30] Thomas, J. P., & Leung, K. T. (2014). Defect-minimized PEDOT: PSS/planar-Si solar cell with very high efficiency. *Advanced Functional Materials*, 24(31), 4978-4985.
- [31] Nagamatsu, K. A., Avasthi, S., Jhaveri, J., & Sturm, J. C. (2014). A 12% efficient silicon/PEDOT: PSS heterojunction solar cell fabricated at < 100 C. *IEEE Journal of Photovoltaics*, 4(1), 260-264.
- [32] Mahato, S., Gerling, L. G., Voz, C., Alcubilla, R., & Puigdollers, J. (2016). PEDOT: PSS as an Alternative Hole Selective Contact for ITO-Free Hybrid Crystalline Silicon Solar Cell. *IEEE Journal of Photovoltaics*, 6(4), 934-939.
- [33] Liu, R., Lee, S. T., & Sun, B. (2014). 13.8% Efficiency hybrid Si/organic heterojunction solar cells with MoO₃ film as antireflection and inversion induced layer. *Advanced Materials*, 26(34), 6007-6012.

- [34] PVTECH- https://www.pv-tech.org/guest-blog/n_type_silicon_solar_cell_technology_ready_for_take_off
- [35] Panasonic- <https://panasonic.net/ecosolutions/solar/why/index.html>
- [36] Kotulak, N. A. (2014). *Developing novel hybrid heterojunctions for high efficiency photovoltaics* (Doctoral dissertation, University of Delaware).
- [37] Brendel, R., & Queisser, H. J. (1993). On the thickness dependence of open circuit voltages of pn junction solar cells. *Solar Energy Materials and Solar Cells*, 29(4), 397-401.
- [38] Hegedus, S. S., & Shafarman, W. N. (2004). Thin-film solar cells: device measurements and analysis. *Progress in Photovoltaics: Research and Applications*, 12(2-3), 155-176.
- [39] Fossum, J. G. (1977). Physical operation of back-surface-field silicon solar cells. *IEEE Transactions on Electron Devices*, 24(4), 322-325.
- [40] Aberle, A. G. (2000). Surface passivation of crystalline silicon solar cells: a review. *Progress in Photovoltaics: Research and Applications*, 8(5), 473-487.
- [41] Elschner, A., Kirchmeyer, S., Lövenich, W., Merker, U., & Reuter, K. (2011). PEDOT. *Principles and Applications of an Intrinsically Conductive Polymer*.
- [42] Alemu, D., Wei, H. Y., Ho, K. C., & Chu, C. W. (2012). Highly conductive PEDOT: PSS electrode by simple film treatment with methanol for ITO-free polymer solar cells. *Energy & environmental science*, 5(11), 9662-9671.
- [43] Do, H., Reinhard, M., Vogeler, H., Puetz, A., Klein, M. F., Schabel, W., ... & Lemmer, U. (2009). Polymeric anodes from poly (3, 4-ethylenedioxythiophene): poly (styrenesulfonate) for 3.5% efficient organic solar cells. *Thin Solid Films*, 517(20), 5900-5902.
- [44] Na, S. I., Kim, S. S., Jo, J., & Kim, D. Y. (2008). Efficient and Flexible ITO-Free Organic Solar Cells Using Highly Conductive Polymer Anodes. *Advanced Materials*, 20(21), 4061-4067.
- [45] Hwang, J., Amy, F., & Kahn, A. (2006). Spectroscopic study on sputtered PEDOT· PSS: role of surface PSS layer. *Organic electronics*, 7(5), 387-396

- [46] Steirer, K. X., Ndione, P. F., Widjonarko, N. E., Lloyd, M. T., Meyer, J., Ratcliff, E. L., ... & Berry, J. J. (2011). Enhanced efficiency in plastic solar cells via energy matched solution processed NiOx interlayers. *Advanced Energy Materials*, 1(5), 813-820.
- [47] Heraeus-
https://www.heraeus.com/en/group/products_and_solutions_group/conductive_polymers/cpolymers/conductive-polymers.aspx
- [48] Liu, Q., Ono, M., Tang, Z., Ishikawa, R., Ueno, K., & Shirai, H. (2012). Highly efficient crystalline silicon/Zonyl fluorosurfactant-treated organic heterojunction solar cells. *Applied Physics Letters*, 100(18), 183901.
- [49] Erickson, A. S., Zohar, A., & Cahen, D. (2014). n-Si–organic inversion layer interfaces: a Low temperature deposition method for forming ap–n homojunction in n-Si. *Advanced Energy Materials*, 4(9).
- [50] Jeong, S., Garnett, E. C., Wang, S., Yu, Z., Fan, S., Brongersma, M. L., ... & Cui, Y. (2012). Hybrid silicon nanocone–polymer solar cells. *Nano letters*.
- [51] Headway Research, Inc.-
<http://headwayresearch.com/products/pwm32psr790.html>
- [52] Pietsch, M., Bashouti, M. Y., & Christiansen, S. (2013). The role of hole transport in hybrid inorganic/organic silicon/poly (3, 4-ethylenedioxy-thiophene): poly (styrenesulfonate) heterojunction solar cells. *The Journal of Physical Chemistry C*, 117(18), 9049-9055.
- [53] Koon, D. W., & Knickerbocker, C. J. (1992). What do you measure when you measure resistivity?. *Review of scientific instruments*, 63(1), 207-210.
- [54] Webster, J. G., & Eren, H. (Eds.). (2014). *Measurement, instrumentation, and sensors handbook: electromagnetic, optical, radiation, chemical, and biomedical measurement*. CRC press.
- [55] Palumbiny, C. M., Heller, C., Schaffer, C. J., Körstgens, V., Santoro, G., Roth, S. V., & Müller-Buschbaum, P. (2014). Molecular reorientation and structural changes in cosolvent-treated highly conductive PEDOT: PSS electrodes for flexible indium tin oxide-free organic electronics. *The Journal of Physical Chemistry C*, 118(25), 13598-13606.

- [56] Thomas, J. P., Zhao, L., McGillivray, D., & Leung, K. T. (2014). High-efficiency hybrid solar cells by nanostructural modification in PEDOT: PSS with co-solvent addition. *Journal of Materials Chemistry A*, 2(7), 2383-2389.
- [57] Łapkowski, M., & Proń, A. (2000). Electrochemical oxidation of poly (3, 4-ethylenedioxythiophene)—“in situ” conductivity and spectroscopic investigations. *Synthetic Metals*, 110(1), 79-83.
- [58] Thomas, J. P., Srivastava, S., Zhao, L., Abd-Ellah, M., McGillivray, D., Kang, J. S., ... & Leung, K. T. (2015). Reversible structural transformation and enhanced performance of PEDOT: PSS-based hybrid solar cells driven by light intensity. *ACS applied materials & interfaces*, 7(14), 7466-7470.
- [59] Perkin Elmer Lambda 650/850/950 Hardware Guide (Accessed June 2013), Available- <http://www.nyu.edu/fas/dept/chemistry/mdi/pdfs/UV.pdf>
- [60] Perkin Elmer Lambda 750 UV/Vis/NIR Spectrophotometer Brochure (Accessed June 2013). Available: http://www.perkinelmer.com/CMSResources/Images/4474449BRO_LAMBDA-750-UV-Brochure.pdf
- [61] Perkin Elmer Lambda 650/750/850/950/1050 Accessories Guide (Accessed June 2013). Available: http://www.perkinelmer.com/CMSResources/Images/44135972BRO_009201B_0LambdaAccessories.pdf
- [62] Pankove, J. I. (2012). *Optical processes in semiconductors*. Courier Corporation.
- [63] Solargaines- <http://blog.solargaines.com/solar-panels-hoa-rules>
- [64] Rutgers University- <http://www.business.rutgers.edu/news/ctec-class-project-takes-top-prize-rutgers-universitys-first-launchr-pitch-competition>
- [65] PVmagazine- <http://www.pvmagazine.com/archive/articles/beitrag/switch-from-p-to-n-100007072/501/#ixzz4RX3RJUn>
- [66] Gerling, L. G., Mahato, S., Morales-Vilches, A., Masmitja, G., Ortega, P., Voz, C., ... & Puigdollers, J. (2016). Transition metal oxides as hole-selective contacts in silicon heterojunctions solar cells. *Solar Energy Materials and Solar Cells*, 145, 109-115.

- [67] Battaglia, C., Yin, X., Zheng, M., Sharp, I. D., Chen, T., McDonnell, S., ... & Wallace, R. M. (2014). Hole selective MoO_x contact for silicon solar cells. *Nano letters*, 14(2), 967-971.
- [68] Battaglia, C., De Nicolas, S. M., De Wolf, S., Yin, X., Zheng, M., Ballif, C., & Javey, A. (2014). Silicon heterojunction solar cell with passivated hole selective MoO_x contact. *Applied Physics Letters*, 104(11), 113902..
- [69] Geissbühler, J., Werner, J., Martin de Nicolas, S., Barraud, L., Hessler-Wyser, A., Despeisse, M., ... & Ballif, C. (2015). 22.5% efficient silicon heterojunction solar cell with molybdenum oxide hole collector. *Applied Physics Letters*, 107(8), 081601.
- [70] Yang, L., Liu, Y., Chen, W., Wang, Y., Liang, H., Mei, Z., ... & Du, X. (2015). Interface Engineering of High Efficiency Organic-Silicon Heterojunction Solar Cells. *ACS applied materials & interfaces*, 8(1), 26-30.
- [71] Mandlik, Prashant, Jonathan Gartside, Lin Han, I-Chun Cheng, Sigurd Wagner, Jeff A. Silvernail, Rui-Qing Ma, Michael Hack, and Julie J. Brown. "A single-layer permeation barrier for organic light-emitting displays." *applied physics letters* 92, no. 10 (2008): 89.
- [72] Madakasira, P., Inoue, K., Ulbricht, R., Lee, S. B., Zhou, M., Ferraris, J. P., & Zakhidov, A. A. (2005). Multilayer encapsulation of plastic photovoltaic devices. *Synthetic Metals*, 155(2), 332-335.
- [73] Park, S. H. K., Oh, J., Hwang, C. S., Lee, J. I., Yang, Y. S., & Chu, H. Y. (2005). Ultrathin film encapsulation of an OLED by ALD. *Electrochemical and solid-state letters*, 8(2), H21-H23.