

**RADICAL-DRIVEN SILICON SURFACE PASSIVATION FOR ORGANIC-
INORGANIC HYBRID PHOTOVOLTAICS**

by

Meixi Chen

A dissertation submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry and Biochemistry

Winter 2018

© 2018 Meixi Chen
All Rights Reserved

**RADICAL-DRIVEN SILICON SURFACE PASSIVATION FOR ORGANIC-
INORGANIC HYBRID PHOTOVOLTAICS**

by

Meixi Chen

Approved: _____
Brian Bahnson, Ph.D.
Chair of the Department of Chemistry and Biochemistry

Approved: _____
George H. Watson, Ph.D.
Dean of the College of Arts and Sciences

Approved: _____
Ann L. Ardis, Ph.D.
Senior Vice Provost for Graduate and Professional Education

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed:

Robert L. Opila, Ph.D.
Professor in charge of dissertation

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed:

Andrew V. Teplyakov, Ph.D.
Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed:

David Martin, Ph.D.
Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed:

Karl S. Booksh, Ph.D.
Member of dissertation committee

ACKNOWLEDGMENTS

First and foremost, I want to thank my adviser Dr. Robert Opila for introducing me to the world of renewable energy, and for providing me with the opportunity to explore a field that I have since grown deeply connected to. Dr. Opila has supported me, not only by providing a research assistantship for over almost six years, but as well as academically and emotionally through my challenging journey leading to this thesis conclusion. Thanks to him, I have had the opportunity to develop new PV technology, participate in a variety of nationwide conferences, exchange programs and internships, as well develop my career passion. My time with Dr. Opila, with his remarkable knowledge and his ability to connect local and international politics, literature, arts and sciences, has broadened my mind immensely and has inspired my personal ambition of pursuing science and engineering innovation.

I would also like to thank my thesis committee for their guidance throughout the years. Dr. Andrew Teplyakov supported in-depth studies on silicon surface reaction and DFT calculations; Dr. Karl Booksh provided much assistance with data analysis and characterization, as well as with electrochemical analysis; Dr. David Martin guided me through the understanding of PEDOT:PSS and device fabrication. My committee members' contributions ensured that my research remained on track and their support has been invaluable to me.

My studies abroad have afforded me the privilege of meeting and forming industry partnerships that were instrumental to my growth and professional development. I would like to thank Dr. Dominik Lausch from Fraunhofer CSP for

being my advisor during the exchange program in 2015, with whom I worked on SiNx deposition and characterization. Some special thanks goes to the group I worked with at Air Liquide Laboratories. I praise the enormous amount of education and guidance provided by Dr. Christian Dussarrat, Dr. Kazutoshi Iida, Dr. Changhee Ko and Dr. Naoto Noda, and am especially grateful for their tremendous support with the SiOC passivation study project which I could not have completed without their help. I would also like to thank Dr. Raphael Rochat, Ikuo Suzuki, Ivan Oshchepkov, Mikiko Kimura, Rocio Arteaga and Yann Martelat for all of their training and assistance. Working alongside them has taught me things that no academic course could have.

There are dozens of friends and coworkers who have helped and inspired me immensely along the way, especially all of the members of the Opila group. I want to thank Jimmy Hack and Abhishek Iyer for the all the lively scientific discussion and for spending every day, shoulder-to-shoulder, with me in the lab playing with HF and “Sinton.” I also want to thank Kevin Jones, who has been an inspiration on how to conduct “perfect” XPS measurements. Additionally, I want to thank Xi Lin, Bo Yuan and Zijian Wang, as well as my other friends in the Material Sciences Department and the Chemistry Department, who have been inspirational and encouraging in every way. Everyone’s support and friendship has been invaluable.

And finally, I would like to warmly thank my loving parents for supporting me unconditionally all these years so that I could pursue my dreams and passion. My parents have always been there for me and they continue to provide me with invaluable advice for making the best life choices. I also want to give special thanks to my boyfriend Matthew Orr, who supported me through the highs and lows along the road. I could not have done this without his support, encouragement and inspiration.

TABLE OF CONTENTS

LIST OF TABLES	ix
LIST OF FIGURES	x
ABSTRACT	xiv

Chapter

1	INTRODUCTION	1
1.1	Summary.....	1
1.1.1	Thesis Motivation.....	1
1.1.2	Thesis Objectives.....	2
1.1.3	Thesis Outline.....	3
1.2	Photovoltaics Background.....	4
1.2.1	Fundamentals of Photovoltaics.....	4
1.2.2	Figures of Merit	6
1.3	Passivation Background	9
1.3.1	Inorganic Passivation.....	11
1.3.2	Methyl Termination Passivation.....	13
1.3.3	Solution-Based Organic Passivation	14
2	RADICAL-DRIVEN SI SURFACE PASSIVATION MECHANISM.....	17
2.1	Introduction	17
2.2	Background & Literature Review	18
2.3	Minority Carrier Lifetime Measurements	21
2.4	Experimental Methods.....	28
2.4.1	Wafer Cleaning.....	28
2.4.2	Wafer Thinning	28
2.4.3	Passivation Treatment	29
2.4.4	Lifetime Measurements	29
2.4.5	Photoinitiation Set-up.....	30

2.4.6	Electrochemical Cell Set-up	31
2.5	Results and Discussion	32
2.5.1	Passivation using BQ, HQ and Methanol.....	32
2.5.2	Impact of External Radicals	35
2.5.3	Passivation Using Quinone Derivatives	40
2.5.4	Passivation Using Radical Photoinitiators.....	41
2.5.5	BQ Reaction on Si in an Electrochemical Cell	47
2.6	Conclusions	50
3	SURFACE COMPOSITION STUDY	52
3.1	Introduction	52
3.2	Experiment	52
3.3	Results	53
3.3.1	Time Evolution of BQ/ME Bonding to Si.....	53
3.3.2	Quantification of Surface Coverage	54
3.4	Conclusions	58
4	BONDING THERMODYNAMIC STUDY BY DENSITY FUNCTIONAL THEORY	60
4.1	Introduction	60
4.2	Experiment	61
4.3	Results	63
4.3.1	Thermodynamic Possibility of QH* Bonding.....	63
4.3.2	Interface Bonding Structure	64
4.3.3	Competing Process Study.....	66
4.4	Conclusions	68
5	ELECTRONIC STRUCTURE CHATACTERIZATION.....	70
5.1	Introduction	70
5.1.1	Band Bending	70
5.1.2	Band Bending Measurements.....	72
5.1.3	Surface Dipole	76
5.2	Experiment	77

5.3	Results	78
5.3.1	SPV Measurements by XPS	78
5.3.2	SPV Measurements by SKPM.....	81
5.3.3	Surface Dipole and Work Function Calculation	85
5.4	Conclusions	87
6	ORGANIC-INORGANIC HYBRID DEVICE	89
6.1	Introduction	89
6.2	Experiment	91
6.3	Results	92
6.4	Conclusions	95
7	INORGANIC PASSIVANTS- SiOC by PLASMA-FREE ALD.....	96
7.1	Introduction	96
7.2	Experiment	97
7.3	Results	98
7.3.1	Influence of Surface Treatment Prior to ALD.....	98
7.3.2	Lifetime Performances	100
7.3.3	Stability – In-air Degradation.....	102
7.3.4	Stability – Heating Effect	103
7.4	Conclusions	104
8	CONCLUSIONS AND FUTURE WORK.....	106
8.1	Conclusions	106
8.2	Future Work.....	109
8.3	Disseminations	110
	REFERENCES	111
	Appendix	
A	COPYRIGHT	120

LIST OF TABLES

Table 2.1. Scan rate comparison of Fc/Fc ⁺ potential on Pt electrode in methanol.....	48
Table 3.1. XPS Data for BQ/ME-24hr Sample	55
Table 6.1. Results of the hero hybrid device. © 2017 IEEE	93

LIST OF FIGURES

Figure 1.1. A photovoltaic process (top) and the correlated energy band diagram (bottom).	5
Figure 1.2. Overview of best research-cell efficiencies. © 2017 NREL	7
Figure 1.3. Percentage of global annual PV production by technology. ² © 2017 Fraunhofer ISE	8
Figure 2.1. ECEC mechanism, and the structures of semiquinone radicals.....	18
Figure 2.2. Jablonski diagram.	20
Figure 2.3. Lifetimes measured for an n-type wafer in different sample-holding conditions. © 2015 IEEE.....	24
Figure 2.4. Measurements of a wafer with thermally grown oxide (N4) and native oxide (N3) (Note the logarithmic axis). © 2015 IEEE.....	26
Figure 2.5. Passivants used in this paper.	29
Figure 2.6. Photoinitiation set-up.	31
Figure 2.7. Electrode configuration for BQ/ME reaction on Si electrode.....	32
Figure 2.8. Passivation results of BQ/ME(0.01M), HQ/ME(0.01M) and the control sample, methanol.	33
Figure 2.9. Reversible redox reaction of BQ/QH [*] /HQ system. ⁶⁶	34
Figure 2.10. Inverse of the effective lifetime after BQ/ME treatment plotted vs. the inverse of thickness for extrapolation of SRV from the fit of data at each injection level.	35
Figure 2.11. External radical effects on HQ passivation.....	36
Figure 2.12. Reactions of HQ (a) and TEMPO (b) with hydrogen atoms.....	37
Figure 2.13. External radical effects on BQ passivation	38

Figure 2.14. BQ abstract H^* from ME becomes QH^*	39
Figure 2.15. Ethanol can be the hydrogen donor facilitating BQ passivation as well as methanol.	39
Figure 2.16. Lifetime performance of alternative passivants..	40
Figure 2.17. I819 radical formation, Norrish type I reaction.	41
Figure 2.18. BPO radical formation.	42
Figure 2.19. CQ radical formation, Norrish type II reaction.	42
Figure 2.20. Si lifetime performance in I819/ME and CQ/ME with irradiation treatment for up to seven hours.	43
Figure 2.21. Si lifetime performance in BQ/ME with irradiation treatment.	44
Figure 2.22. Passivation of CH_2Cl_2 in ambient room light versus time.	46
Figure 2.23. RE calibration with Fc/Fc^+ couple.	47
Figure 2.24. CV of Fc/Fc^+ couple on Pt electrodes in methanol using Ag/Ag^+ as reference electrode.....	48
Figure 2.25. LSN of BQ/ME and ME solutions using Si as WE, Pt as CE and Ag/Ag^+ as RE.....	49
Figure 2.26. CV of BQ/ME on Si electrode using Fc/Fc^+ as internal standard.	50
Figure 3.1. Carbon 1s peak evolution of the substrates after 1 hour (bottom), 7 hours (middle) and 24 hours (top) BQ/ME treatment.	53
Figure 3.2. Carbon 1s spectra of the substrate after 24 hours BQ/ME treatment.....	56
Figure 3.3. Silicon 2p spectra of the substrate after 24 hours BQ/ME treatment.....	57
Figure 3.4. Oxygen 1s spectra of the substrate after 24 hours BQ/ME treatment.....	58
Figure 4.1. 2x1(monohydride), 1x1(dihydride), and 3x1(mixture of mono and dihydride) silicon surface reconstruction.	60
Figure 4.2. A $Si_{35}H_{40}$ monohydride cluster with bulk atoms fixed (atoms in shadow).	62

Figure 4.3. A dihydride-passivated (a) and BQ-adsorbed (b) Si slab with bulk atoms fixed (atoms in shadow) modeled in VASP.	63
Figure 4.4. Proposed BQ reaction schematic on monohydride Si surfaces. QH* bonding can lower the system energy by 1.96 eV.	64
Figure 4.5. The "edge-on" mode (left) is 1.32 eV lower in energy than the "face-on" mode (right).	65
Figure 4.6. Competing processes in the BQ/ME passivation solution on Si monohydride and dihydride defect sites.	67
Figure 4.7. Electron distribution of bonded MEO* and QH* molecules. Larger numbers indicate greater electronegativity of each atom.	68
Figure 5.1. Plots showing the formation of semiconductor surface band bending when a semiconductor contacts a metal. Copyright 2002 Elsevier Science. ⁹⁹ ..	71
Figure 5.2. Upward band bending on n-type semiconductor surface.	72
Figure 5.3. The charge behavior on exposure to light.	73
Figure 5.4. The basic structure of the Kelvin probe for surface photovoltage by measuring the contact potential difference between two surfaces.	74
Figure 5.5. Surface photovoltage experiments with PES.	76
Figure 5.6. N type silicon peak shift with light on and off for H-Si (a) and BQ-Si (b).	79
Figure 5.7. Si 2p binding energy (left) and normalized binding energy shift (right) in repetitive dark and light conditions.	80
Figure 5.8. Downward band bending on n-Si treated by BQ and the SPV measurement.	80
Figure 5.9. CPD map of n-type silicon wafers under three surface treatments: H-Si, BQ-Si and ME-Si.	82
Figure 5.10. CPD values measured by Kelvin probe for n-type silicon wafers under three surface treatments, H-Si, BQ-Si and ME-Si, with respect to HOPG.	82
Figure 5.11. SPV values measured by Kelvin probe for n-type silicon wafers under three surface treatments, H-Si, BQ-Si and ME-Si.	83

Figure 5.12. Energy levels measured in a dark Kelvin probe measurement (a) and light Kelvin probe measurement in the flat-band condition (b).....	84
Figure 5.13. Cross-section of a unit cell and the corresponding laterally averaged electrostatic potential profile for the H-Si (a) and BQ-Si (b) slab.....	86
Figure 5.14. Electronic structure of BQ passivated n-Si surfaces.....	87
Figure 6.1. OPV device operating principle.....	90
Figure 6.2. PEDOT:PSS is a polymer mixture of two ionomers.....	91
Figure 6.3. Device structure of the PEDOT:PSS-BQ-Si solar cell. © 2017 IEEE.....	92
Figure 6.4. IV curve of hero device. (top) light IV curve, (bottom) dark IV curve	94
Figure 6.5. External quantum efficiency measurements with integrated short circuit current of devices. © 2017 IEEE	95
Figure 7.1. PREC structures © 2017 IEEE	97
Figure 7.2. The home-built ALD reaction system and gas delivery sequences. © 2017 IEEE	98
Figure 7.3. ALD mechanism. © 2017 IEEE.....	99
Figure 7.4. Lifetime performance of the films deposited by three PRECs as a function of film thickness (nm). © 2017 IEEE.....	100
Figure 7.5. XPS depth profiles of R#2_1. © 2017 IEEE.....	101
Figure 7.6. Lifetime as a function of time in air of R#2 samples. © 2017 IEEE	102
Figure 7.7. Lifetime performances of BTCSM samples in high temperature. © 2017 IEEE	103

ABSTRACT

Surface passivation has become increasingly crucial for thin silicon photovoltaic (PV) devices. Quinhydrone/ methanol (QH/ME) has been utilized in the past as a temporary passivant for hydrogen terminated silicon surfaces with an outstanding lifetime. The work described in this thesis investigates the passivation mechanism of quinone molecules on silicon. The passivation behaviors of free radicals in quinone molecules, and other radical sources like photoinitiators, are discovered for the first time.

This work confirms that radical intermediates are the reactive species in quinhydrone/ methanol (QH/ME) passivation on silicon surfaces. The two constituent parts, p-benzoquinone(BQ) and hydroquinone(HQ), have been studied separately. BQ abstracts the hydrogen atom from methanol to become semi-quinone radicals (QH^{*}). Both QH^{*} and the resulting methanol radical are responsible for the large, instantaneous increase in minority carrier lifetime in BQ/ME, obtaining the lowest surface recombination velocity of 1.6cm/s. HQ releases a hydrogen atom to become QH^{*}. This radical-driven passivation mechanism is also valid on other radical sources like photoinitiators and weak bonds like C-Cl.

The chemical passivation mechanism was further investigated by X-ray photoelectron spectroscopy (XPS), which confirmed the bonding of aromatic groups to the surface. Density functional theory (DFT) results support the possibility of QH^{*} bonding from a thermodynamic perspective. The methanol radical has the most favorable adsorption energy for bonding, followed by QH^{*} and then BQ molecule.

The electronic structure of BQ/ME passivated Si is determined by a combination of the surface band bending and electron affinity/dipole. Both the photoemission and Scanning Kelvin Probe Microscopy (SKPM) techniques indicate a downward band bending of H-Si and BQ and ME treated samples. DFT calculations show that a dipole is formed upon bonding of BQ radicals on the surface, decreasing the surface electron affinity and work function. Both the dipole and downward band bending contribute to the formation of electron accumulation on n-Si by BQ bonding resulting in the observed surface passivation.

Hybrid organic/silicon devices combining PEDOT:PSS on Si with BQ/ME as a surface passivant were fabricated. The introduction of the BQ passivating layer does not provide a barrier to charge transfer. A device efficiency of 9.6% was achieved. Quantum efficiency data shows a good light absorption near the front of the cell indicating a well-passivated front surface.

At last, another alternative passivation method -- SiOC passivation was studied, where the SiOC films were deposited with plasma-free ultra-low-temperature ALD. The surface passivation effect and stability of the SiOC films were compared with the quinone passivation.

Chapter 1

INTRODUCTION

1.1 Summary

The work described in this thesis investigated the radical passivation mechanism of organic molecules on silicon for photovoltaic (PV) applications. The passivation behaviors of free radicals in quinone molecules, and other radical sources like photoinitiators, were discovered for the first time. To advance the understanding of such mechanism, experimental and theoretical investigations were carried out. The importance of this work is the new insights into the passivation mechanism and the discovery of a group of effective organic silicon passivants, which had not been previously demonstrated. Utilizing these organic passivants for an enhanced photovoltaic efficiency of hybrid organic/silicon solar cells was also explored as a logical extension of this work.

1.1.1 Thesis Motivation

Solar photovoltaics energies have gained increasing attentions in the energy industry because of the substantial benefits for climate, health, and the economy. In order to thrive in today's energy market, PV technology must continue to push device efficiencies higher and drive the \$/W of devices lower. Traditionally, however, device efficiency and device \$/W have been proportional - higher efficiency devices are also higher cost. In order to overcome this challenge, an approach to device design has been proposed in this work that combines the strengths of both organic materials and

traditional inorganic semiconductor materials in a novel hybrid device. This involves passivation, which reduces the surface recombination velocity of minority charge carriers and eventually pushes device efficiencies higher. Organic materials are low cost, and they provide simple fabrication requirements. Traditional semiconductor materials - such as silicon – provide stability, high efficiency, and ease of integration into present methods of manufacturing. The combination of organic and inorganic materials allows for the maintenance of high efficiency while reducing cost - effectively breaking the proportional trend that dominates present PV technology.

1.1.2 Thesis Objectives

The focus of this work is the further understanding of the quinone passivation mechanism on c-Si, seeking alternative passivants, and the implementation of the passivation layer in a hybrid organic/silicon solar cell device. This goal will be investigated through the following objectives:

1) Identify the chemical passivation mechanism: This objective will improve the understanding of how radicals are formed in passivation solutions, and how the radicals bond on the c-Si surface.

2) Identify the electrical passivation mechanism: This objective will further explain how radicals affect the silicon energy band structures and improve surface quality for higher efficiency solar cells.

3) Mechanism study by density function theory (DFT) calculation: Both Gaussian and VASP calculation tools were used to compare with the experimental results in order to aid in understanding the chemical and electrical passivation mechanism.

4) Fabricate hybrid organic/silicon devices using quinones: This objective will confirm the functionality of the passivation layer in a solar cell, demonstrate the device performance, as well as identify areas for improvement.

1.1.3 Thesis Outline

In Chapter 2 I propose a radical-driven passivation mechanism, and discuss the passivation behaviors of free radicals in benzoquinone (BQ), hydroquinone (HQ), under the impact of external radicals, radiation and electronegative groups substituted in quinone molecules, and other radical sources like photoinitiators and chloromethane compounds.

In Chapter 3 I investigate the bonding of quinones on silicon via X-ray photoelectron spectroscopy (XPS). The time evolution of the bonding and the surface monolayer quinone coverage are reported.

In Chapter 4 density function theory (DFT) calculations are used to study the thermodynamics of quinone bonding on silicon surfaces, the bonding structure and electronic density of states. Two calculation tools, Gaussian and VASP, were used.

In Chapter 5 I examine the electrical passivation mechanism by exploring the quinone-induced silicon band bending and dipole with Scanning Kelvin Probe Microscopy (SKPM), XPS and VASP. The work function of BQ passivated n-Si surfaces is calculated.

Chapter 6 is dedicated to the hybrid solar cells with the implementation of the quinone passivation layer. Fabrication and characterization of the hybrid devices are covered to discuss the functionality of the quinone passivation layer.

SiOC passivation films deposited with plasma-free ultra-low-temperature ALD are presented in Chapter 7. This work was done in collaboration with K.K. Air Liquide

Laboratories, Japan. Composition and bonding of the SiOC films are studied using XPS and FTIR. The surface passivation effect and stability of the SiOC films are studied and compared with the quinone passivation.

To sum this thesis up, a general discussion and future directions for quinone passivation on silicon and hybrid organic/silicon solar cells are discussed in Chapter 8.

1.2 Photovoltaics Background

1.2.1 Fundamentals of Photovoltaics

A photovoltaic (PV) process is a process which directly converts sunlight into electricity, illustrated in Figure 1.1 (top): A photon of a suitable energy is absorbed by a semiconductor material, step 1. The energy of this photon promotes electrons to higher energy level, generating electron-hole pairs, step 2. The charge carriers then separated by the built-in electric field in the device and collected by the metal contacts on the front and back-side, step 3. The electron then dissipates its energy in the external circuit and returns to the solar cell, step 4. Therefore, the essential parts in a solar cell are a semiconducting material for photoelectric conversion, and a built-in electric field for charge separation.

A variety of materials and processes can potentially meet the requirements for photovoltaic conversion, but in practice semiconductor materials in the form of a p-n junction are widely used. A p-n junction diode is formed when an electron-rich material (n-type) is brought into contact with a hole-rich material (p-type). In an n-type semiconductor, the fermi level (E_f), at which there is a 50% probability that the level will be occupied, lies closer to the conduction band (CB). While in an p-type semiconductor, the fermi level (E_f), lies closer to the valence band (VB).

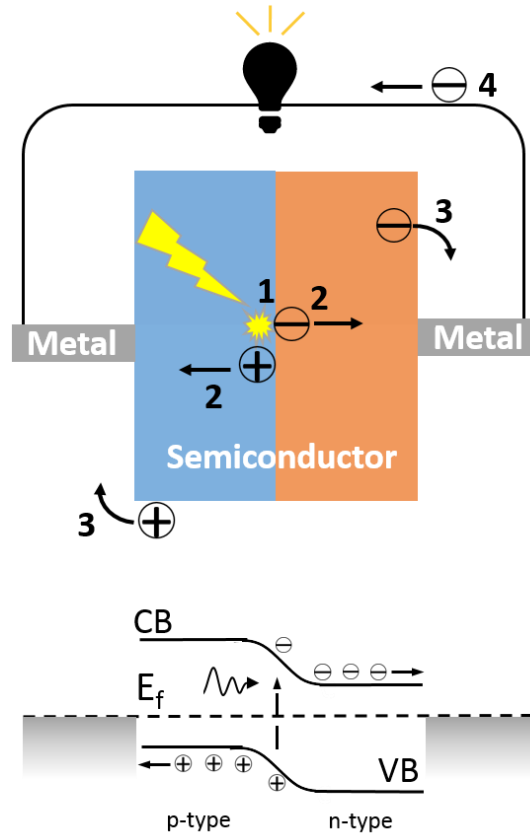


Figure 1.1. A photovoltaic process (top) and the correlated energy band diagram (bottom). Step 1, light absorption; step 2, charge separation; step 3, charge collection; step 4, current generation. CB: the bottom of conduction band; E_f : the fermi energy level; VB: the top of valence band.

Diffusion of charge carriers occurs when p and n-type materials contact and the E_f reaches equilibrium, where electrons move into the p-type material and holes move into the n-type material. This diffusion leaves the surface of the p-type material in a negatively-charged state, and the surface of the n-type material in a positively charged state forming an electric field. This built-in electric field separates the light-generated carriers described in step 2, illustrated in Figure 1.1 (bottom).

The term quantum efficiency (QE) describes the device's ability of converting incident photons to electricity. It's defined as is the ratio of the number of charge carriers collected by the solar cell to the number of incident photons, Equation 1.1.

$$QE = \frac{\text{collected electrons/sec}}{\text{incident photons/sec}} \quad \text{Equation 1.1}$$

QE therefore depends on both the absorption of light and the collection of charges. Once a photon has been absorbed and has generated an electron-hole pair, these charges must be separated and collected at the front and back contacts. However, sometime the charges recombined before they can be collected, and this is called recombination. Charge recombination causes a reduction in the efficiency, which a high performance solar cell avoids as much as possible. This thesis will give an in-depth discussion on how to lower the recombination lost and improve the solar cell's efficiency.

1.2.2 Figures of Merit

The 2017 April overview of the best research-cell efficiencies by the National Renewable Energy Laboratory (NREL), Figure 1.2, shows that solar cell efficiencies vary from 10% for organic-based solar cells to 46.0% for multi-junction cells. Those multi-junction devices consist of a stacking of several cells and absorb a broader range of the solar spectrum with less thermalization losses.¹ However, the highest efficiency cells have not always been the most economical because of the considerable high manufacturing costs, and the use of the multi-junction is limited to special roles, like in aerospace where their high power-to-weight ratio is desirable.

NATIONAL RENEWABLE ENERGY LABORATORY



7

Si-wafer based PV technology accounted for about 94% of the total production in 2016, Figure 1.3.² The lab-record silicon cell efficiency is 27.6% for mono-crystalline silicon with concentration and 21.9% for multi-crystalline silicon wafer-based technology. For the past decade, thin film photovoltaics like Cadmium Indium Gallium Selenide (CIGS) and cadmium telluride (CdTe) cells have been developed as the top candidates to replace silicon cells with efficiencies reaching around 23%.^{3,4} However, the higher costs associated with these materials and the growing momentum for a relatively new technology have kept them in the margins in the market. In 2016, the market share of all thin film technologies account to about 6% of the total annual production, Figure 1.3.² The relatively new area of emerging PV like perovskite and quantum dot cells has been growing rapidly with lab efficiencies doubled in the past few years.⁵⁻⁷ However, the efficiency is still low to make into the market in comparison with silicon cells.

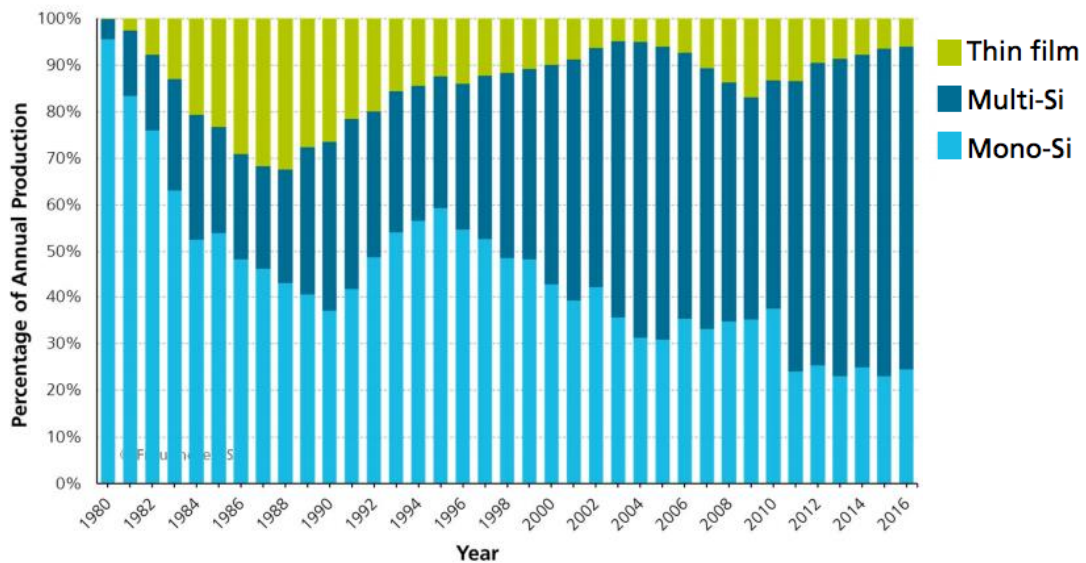


Figure 1.3. Percentage of global annual PV production by technology.² © 2017 Fraunhofer ISE

Overall, silicon solar cells remain dominant in the solar market because of a reliability record unmatched by any other materials and the industrial maturity inherited from the semiconductor world. Progress in silicon solar cells lies in pushing the efficiency even higher and reducing the cost. In this work, I will focus on silicon cells and discuss the efficiency improvement by the implementation of organic monolayer, which takes advantage of the stability of silicon and also the low cost of organics.

1.3 Passivation Background*

An excellent electrical interface quality is essential for many devices relying on the bulk electronic properties of semiconductors.⁸ For example the oxide/semiconductor interface in field effect transistors must be effectively defect-free to ensure high mobility through the channel. Similarly, in photovoltaics, charge carriers can recombine at defects at semiconductor/dielectric interfaces, leading to decreased power efficiencies. These semiconductor interfaces, with minimal interaction with charge carriers, are said to be electrically passivated. This differs from surfaces whose further chemical reaction is limited, which are called chemically passivated. Electrical defects, on the order of $10^9/\text{cm}^2$, may still be significant, but remain virtually undetectable by standard chemical surface analytical techniques.

Cleaved Si surfaces contain a large number of dangling bonds, and reconstruct to minimize the number of energetically unfavorable dangling bonds. Nevertheless,

* Reprinted with permission from Chen, M.; Hack, J.; Iyer, A.; Lin, X.; Opila., R. L. In *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*; Elsevier Inc., 2017. Copyright 2017 Elsevier Inc.

these surfaces are still very chemically reactive. One of the remarkable things about silicon is that the SiO_2 surface on Si essentially chemically passivates that surface. Moreover, because the SiO_2/Si interface is so defect free this surface can also be electrically passive. This remarkable property permitted the fabrication of metal oxide semiconductors and the growth of the microelectronics industry, even though the carrier mobilities in Si are not remarkable.

The discovery by Chabal et al. that freshly cleaved Si surfaces (or those whose oxide has been just etched) can react stoichiometrically with hydrogen in HF solutions to saturate the dangling bonds is very important.⁹ These surfaces are chemically passivated (although far from as stable as SiO_2 interfaces). However, their electrical passivation does not obviously follow the chemical passivity. Hydrogen-terminated Si(111) surfaces were compared.¹⁰ One surface was prepared atomically flat, as in the standard for chemical functionalization. Another surface was prepared with a recipe that resulted in a rough, perhaps not stoichiometric hydrogenation. The first surface would generally be judged to be the better chemical passivation. However, the electrical passivation of these two surfaces can be determined by measuring the lifetimes of photoexcited carriers; that is, how long did it take before photoexcited carriers recombine. The second surface was found to be much better electrically passivated.

In this section, we will explore the requirements for good electrical passivation. While passivation is important across the entire electronics industry, we will emphasize the effect that electrical passivation has on the performance of photovoltaics.

1.3.1 Inorganic Passivation

The surface of silicon has significant disturbances in symmetry due to the presence of dangling bonds. Dangling bond defects could cause increased surface recombination through Shockley-Read-Hall or defect 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 bonding to the surface atoms either hydrogen atoms, another semiconductor film, or some other 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, i.e., a forming gas anneal.¹¹ Electrical passivation on the other hand reduces the electron or hole recombination at the interface by creating an electric field.

There exist several passivation techniques but not all are commercially viable or economical. For example, growing silicon dioxide on the silicon surface is a very effective passivation technique but can be commercially challenging because it requires a high temperature (at least 1000°C), is a high electricity consuming process, and has throughput limitations. Other techniques, including deposition of SiN_x and Al_2O_3 have demonstrated promising results in the photovoltaics industry. There have been several attempts at finding the right match between excellent passivation ability and cost-effectiveness at industrial scale. Silicon nitride (SiN_x) front side passivation using plasma enhanced chemical vapor deposition (PECVD) has evolved as an alternative to high temperature oxidation of silicon and is a widely practiced passivation technique in industry.^{12–14}

Comparing passivation techniques is often a reflection of the fixed charge density created in the dielectric layer or at the semiconductor/passivant interface. The

photoexcited carrier lifetime is a good representation of the effectiveness of the passivation technique. The carrier lifetime can be related to the surface recombination velocity, SRV, where the effective lifetime τ is a function of bulk lifetime τ_b , and the wafer thickness W ,

$$\frac{1}{\tau} = \frac{1}{\tau_b} + \frac{2SRV}{W} \quad \text{Equation 1.2}$$

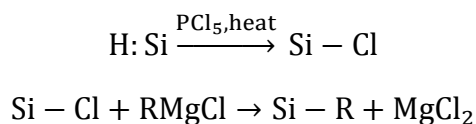
Interface charge density, represented by Q_f , has a positive value for SiN_x passivation whereas it is negative for Al_2O_3 passivation. Besides difference in charge densities, the silicon nitride and aluminum oxide passivation techniques have fundamental differently charged defects. For SiN_x , the charged defects are uniform throughout the bulk of the film. The positively charged defects are microscopically assigned to silicon dangling bonds which are back-bonded to three nitrogen atoms (instead of four), the so-called K^+ centers.^{15,16} Al_2O_3 on the other hand is complicated. An ultrathin, interfacial SiO_x layer (up to $\sim 1\text{nm}$) is expected, and has been detected in some studies, which has been conjectured to play a crucial role in the formation of negative Q_f .¹⁷ Agostinelli et al. reported that thermal atomic-layer-deposited (ALD) aluminum oxide layers provide effective surface recombination velocities S_{eff} below 100cm/sec on $2\ \Omega\text{-cm}$ p-type Cz-Si.¹⁸ Al_2O_3 is effective on p-type silicon, because the minority carriers are electrons, which are Coulombically repelled by the negative charge in the Al_2O_3 . In addition, Hoex et al. reported that plasma-assisted atomic-layer-deposited (PA-ALD) aluminum oxide can provide a $13\ \text{cm/sec}$ SRV on $2\ \Omega\text{-cm}$ p-type float zone Si and $S_{\text{eff}}=2\ \text{cm/s}$ on $2\ \Omega\text{-cm}$ n-type Cz-Si samples.¹⁹ A record low effective surface recombination velocity (SRV) of $4\ \text{cm/s}$ has been obtained on $1\ \Omega\text{-cm}$ p-Si wafers for SiN_x passivation using remote plasma enhanced chemical vapor deposition (PECVD) or high frequency ($13.56\ \text{MHz}$) direct PECVD.²⁰ SiN_x

passivation for the front surface of c-Si solar cells is deemed to be superior to other passivation techniques such as SiO₂ or TiO₂ for a number of reasons. One is due to its field effect passivation provided by positive interface charges. In addition, hydrogenated passivation of bulk defects also helps with surface recombination velocity. Its adjustable refractive index helps the material double as an antireflection coating (ARC).^{20–23}

1.3.2 Methyl Termination Passivation

Another alternative to the silicon-oxygen passivation is the silicon-carbon passivation layer, where the kinetically stable silicon-carbon covalent bond slows the oxidation of silicon and also retards the formation of charge-carrier recombination centers on the silicon surfaces. Many techniques have been developed to functionalize silicon with alkyl.^{24–27}

N. S. Lewis et al. have reported that the CH₃-Si(111) surface can be prepared by a two-step chlorination/alkylation process, where the H-terminated Si(111) surface is chlorinated in a benzene solution of PCl₅ and then reacts with an organic Grignard reagent.^{28,29}



This CH₃-Si(111) surface has shown a low surface recombination velocity smaller than 100 cm/s.²⁸ Bulky alkyl groups such as (CH₃)₂CH- (iso-propyl), (CH₃)₃C- (tert-butyl), and C₆H₅- (phenyl) moieties give a comparable passivation effect as methyl-Si, but the long alkyl chains are more reactive than CH₃-Si and provide a

potential easier secondary functionalization.²⁸ A well-defined, high-yield secondary functionalization can also be obtained by using the mixed methyl/allyl monolayer as the first base layer, permitting attachment of further organic moieties to the surface.³⁰

Silicon-carbon passivation on the Si (100) surface, on the other hand, is significantly different from Si(111) because of the atomic roughness of H-terminated Si(100). The two-step chlorination/alkylation method gives surfaces containing SiH(CH₃)-, SiH₂(CH₃)-, and Si(CH₃)₂-type species. A surface recombination velocity smaller than 30 cm/s for methylated surfaces, and 60 cm/s for Si surfaces functionalized with the other alkyl groups have been reported.³¹

1.3.3 Solution-Based Organic Passivation

Solution-based techniques can allow for a less capital-intensive surface passivation process that can be performed at low temperatures to avoid affecting the bulk properties of the silicon. There are two historically dominant classes of wet-chemical passivation for silicon: Oxidation-based and hydrogen-terminated passivations. Oxidation-based passivations allow for the formation of a thin oxide layer of varying thickness and surface charge.³² Hydrogen terminated passivations subsequently etch away this formed oxide layer using a solution of NH₄F or HF.⁹ Angermann et al. studied the defect density of a variety of these surface treatments using large-signal field-modulated surface photovoltage measurements. They found that obtaining low surface defect densities was heavily dependent on the microroughness of the surface formed during the oxidation step of silicon (111) and (100) samples. Oxides prepared via a hot-water treatment produced the lowest surface defect densities.³²

Hydrogen terminated silicon surfaces are only stable for on the order of 10 minutes, and so more air-stable alternatives for non-insulating passivation layers are desirable.³² Several groups have followed the hydrogen-termination step by subsequently substituting the hydrogen for a molecular monolayer of an alternative passivant. Treatment of wafers in an iodine-ethanol solution has historically been used by the photovoltaic industry for testing wafer bulk quality via photoconductive decay.^{33,34}

Quinhydrone-methanol was first demonstrated as an alternative to iodine-ethanol by Takato et al.^{33,35} Subsequent studies by Chhabra et al. demonstrated the ability to achieve high minority carrier lifetimes in both p-type and n-type silicon.³⁶ Quinhydrone is a charge-transfer complex consisting of equal parts benzoquinone and hydroquinone, which form a two electron redox couple in solution.³⁷ The capability of hydroquinone – alcohol solutions to produce Schottky-Mott limited junctions on silicon was demonstrated by Har-Lavan et al.³⁸ The treatment was shown to result in field-effect passivation and benzoquinone was suggested as the more active constituent in the quinhydrone complex.^{38,39} A free radical bonding mechanism by which both quinone radicals and methanol radicals bond to the silicon surface was suggested by Kotulak et al.⁴⁰ XPS studies have shown evidence of both quinone and methanol bonded to the surface, appearing to form essentially a monolayer.⁴¹ There may be some charge associated with this layer.

An alternative deposition method was performed by Avasthi et al. who used thermal evaporation to deposit a layer of 9,10-phenanthrenequinone, demonstrating an absence of Fermi-level pinning, with subsequent IPES and UPS studies of the resulting surface band structure.^{42,43}

Continued research into alternative passivation methods works to meet the goals of simple deposition, air stability, low recombination velocities, and compatibility with subsequent processing steps.

In this work, we will focus on the solution-based quinone passivation on silicon to better understand the chemical and electrical passivation mechanism, and further investigate the role of the quinone passivation layer in a solar device.

Chapter 2

RADICAL-DRIVEN SI SURFACE PASSIVATION MECHANISM*

2.1 Introduction

As discussed in the previous chapter, one of the fundamental limitations of the silicon devices comes from the abundant defect states introduced by the dangling bonds on the silicon surface. These defect states act as minority carrier recombination centers, and can change the surface band structures detrimentally. In developing silicon-based photovoltaics with thinner substrates and higher efficiencies, an effective surface passivation that reduces the density of defect states and surface recombination losses is increasingly important. High temperature passivation using a silicon dioxide or a silicon nitride layer has a long history and is still the standard method used in industry.^{13,44} In comparison, room temperature, solution-based electronic passivation by molecules like halides and quinones, especially quinhydrone (QHY) in alcohol (mostly methanol), is emerging, because of the easier and cheaper processing and superior electronic passivation effects.^{41,45–47} However, the QHY passivation mechanism is still not clear, and we will discuss about it in this chapter.

* Reprinted with permission from Chen, M.; Hack, J. H.; Iyer, A.; Jones, K. J.; Opila, R. L. *J. Phys. Chem. C*. **2017**, 121 (39), 21364. Copyright 2017 American Chemical Society.

2.2 Background & Literature Review

Quinhydrone (QHY) is a 1:1 mixture of p-benzoquinone (BQ) and hydroquinone (HQ). The electrochemical behavior of BQ/HQ couples associated with electron-proton transfer equilibrium has been studied for several decades. It is well known that in buffered aqueous media, BQ/HQ couples undergo the ECEC mechanism (electron transfer, chemical reaction, electron transfer, chemical reaction), which is comprised of two steps of electron-transfer coupled with proton acceptance (chemical reaction), summarized in Figure 2.1.⁴⁸ BQ/HQ couples in methanol solution, in which researchers show the direct formation of HQ from BQ without the appearances of any semiquinone radicals, observed via cyclic voltammetry (CV).⁴⁹

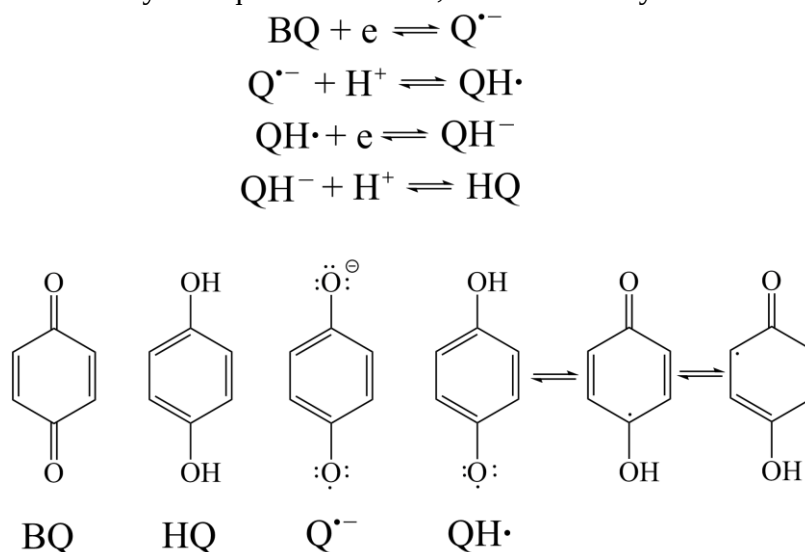


Figure 2.1. ECEC mechanism, and the structures of semiquinone radicals. The radical in QH[•] can either reside on the oxygen atom, or be partially delocalized over the π system.

However, it has been found under certain circumstances, such as when electronegative groups are introduced into the quinone structures, the quinone molecules form an equilibrium involving the semiquinone radicals. For example, in

the ubiquinone/methanol (Q_{10}/ME) solution, $Q_{10}^{\bullet-}$ radicals are found, as well as the protonation of $Q_{10}^{\bullet-}$ to $Q_{10}H^{\bullet}$, confirmed by UV/Vis and IR spectra.⁴⁹

Presumably, when introducing BQ/ME or HQ/ME onto silicon surfaces, the active defects on silicon surfaces affect the electrochemical behavior of BQ and HQ as well, and radicals are likely to exist in the reactions, which can be essential in forming the Si-quinone or Si- ME bonding that passivates silicon surfaces. Cahen et al. have observed Si-hydroquinone surface bonding via infrared spectroscopy by attenuated total reflection (ATR-IR) after quinhydrone/ methanol treatment of n-Si(100).⁵⁰ Previous work in our group has demonstrated that the level of silicon surface passivation achieved in BQ/ME solution is affected by the availability of hydrogen atoms in the solutions,³⁹ but it is still not clear if the semiquinone radicals are the responsible species for passivation.

On the other hand, photons can be another radical-initiation source. Photoinitiators are widely used in photopolymerization. A photoinitiator can be excited from ground state S_0 to the lowest singlet excited state S_1 via absorption of radiation. The excited singlet state, S_1 , can nonradiatively pass to the triplet state, T_1 , when the vibrational levels of the two excited states overlap. This process is known as intersystem crossing (ISC), illustrated in the Jablonski diagram in Figure 2.2.⁵¹ The parallel spin in the T_1 state is caused by the substantial spin and orbital interactions. Intersystem crossing can be enhanced in molecules containing halogen, ketone groups, or paramagnetic species.⁵²

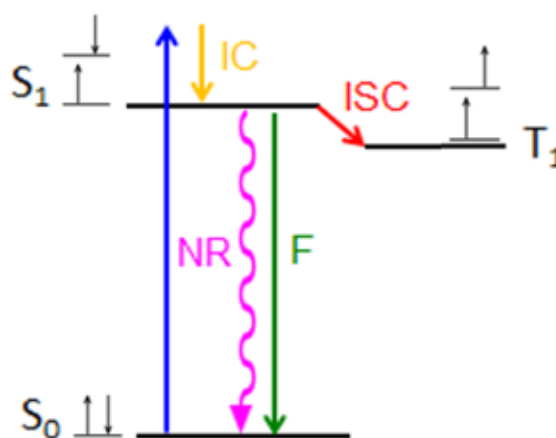


Figure 2.2. Jablonski diagram.

Two general mechanisms for photoinitiation are the ionic and free radical mechanisms, where either ionic photoinitiators or free radicals are generated from excited states S_1 or T_1 , to participate in polymer cross-linking when radiated with light.^{53,54} Highly efficient photoinitiators should have a quantum efficiency as close as possible to one, but a number of factors affect the efficiency for the creation of radicals, for instance, the photo absorption cross-section size, initiation velocity, side reactions, etc.⁵⁵ The photoinitiator quantum efficiency is usually in the range of 0.4 to 0.8.^{55,56} In this work, we focus on the radical mechanism, and two commercial radical photoinitiators, bis(2,4,6-trimethylbenzoyl)- phenylphosphineoxide (I819) and camphorquinone (CQ) were studied.

In this chapter, we will discuss the passivation behavior of free radicals in BQ, HQ, under the impact of external radicals, radiation and electronegative groups substitution in quinone molecules, and other radical sources like photoinitiators and chloromethane compounds.

2.3 Minority Carrier Lifetime Measurements*

The minority carrier lifetime, or lifetime for short, of a material is the average time which a carrier can spend in an excited state after electron-hole generation before it recombines, and it is widely used to evaluate the recombination rate, as show in Equation 1.2. Lifetime can be measured by Photoconductance Decay method with a Sinton WCT-120 Lifetime tester: The sample wafer is inductively coupled to an RF coil, which measures the conductivity of the wafer. A flash of light excites carriers within the wafer, and the photoconductance decay is measured. The intensity of the flash is monitored by a light sensor. The slope of the photoconductance decay curve provides the effective lifetime at a given minority carrier density (MCD).

In monitoring the effects of organic surface passivants such as benzoquinone on carrier lifetime, it is desirable to be able to perform lifetime measurements while the specimen is still immersed in solution. This allows for study of the time evolution of the reaction and avoids atmospheric exposure which may lead to further surface modification.³⁶ Carrier lifetime measurements are performed using a WCT-120 Sinton lifetime tester. Since the wafers are not being placed directly on the measurement surface of the lifetime tester, but are instead sealed within a liquid-containing bag, it is expected that this modified experimental setup will have some effect on the resulting lifetime measurements. The liquid filled bag may act to modify the amount of light reaching the wafer and also affect the coupling between the wafer and the inductive coil.

* Reprinted with permission from Chen, M.; Hack, J. H.; Iyer, A.; Opila, R. L.; In *IEEE Photovoltaic Specialists Conference.*; 2015; pp 1–6. Copyright 2015 IEEE.

The Sinton lifetime tester operating in the quasi-steady state mode calculates the effective minority carrier lifetime of a specimen based on Equation 2.1.⁵⁷

$$\tau_{eff} = \sigma_L / (J_{ph}(\mu_n + \mu_p)) \quad \text{Equation 2.1}$$

The value of the photoconductance, σ_L , is measured from the bridge circuit voltage while the electron and hole mobilities ($\mu_n + \mu_p$) are determined from tabulated values at known average minority carrier densities Δn_{av} to satisfy Equation 2.2. Here W is the thickness of the sample and q is the elementary charge.

$$\sigma_L = q\Delta n_{av}(\mu_n + \mu_p)W \quad \text{Equation 2.2}$$

The value for the photogeneration, J_{ph} , is related to the incident light intensity, which is measured relative to a reference photodiode. From this measured irradiance, the value of J_{ph} can be estimated by making assumptions about the absorption properties of the sample. For a bulk silicon sample of known thickness, the absorptivity is well documented and can be used to estimate J_{ph} . However, modifications to the reflectivity of the surface and other optical properties of the laboratory setup may affect the amount of the incident light which is transmitted to the bulk of the wafer. To account for these factors, an optical constant representing the percent of incident light absorbed is introduced. The Sinton lifetime tester assumes for silicon samples of sufficient thickness and low surface reflectivity an experimentally determined value of J_{ph} of 38mA/cm². The optical factor directly scales this value, for instance, a constant of 0.7 represents reduced photogeneration for a bare silicon wafer with high reflectivity, while higher photogeneration with optical constants exceeding 1 are possible for thick samples with exceptional anti-reflection coatings. The proper choice of optical constant will linearly affect the inverse of the resulting measured minority carrier lifetime.

A second potential source of error arises from the determination of the value of the photoconductance σ_L . This value is calculated from the voltage across an impedance bridge inductively coupled to the sample wafer. The relationship between the measured bridge voltage and the conductance of a wafer is determined in the calibration of the instrument. However, this relationship may be modified due to changes in the distance between the wafer and inductive coil, and the presence of a liquid solution.

The instrument calibration fits a quadratic relation between the bridge voltage, V_B , and wafer conductance, however this relation can generally be simplified to a linear relationship in the measurement range of interest with reasonable accuracy.⁵⁸

$$\sigma_L = K_B V_B \quad \text{Equation 2.3}$$

When using the quasi-steady state photoconductance (QSSPC) technique as described above, the measured lifetime is dependent on the optical constant and the bridge voltage scaling factor K_B . Mismatch in the value of the optical constant will lead to a linear change in the inverse of the measured lifetime, while mismatch in the bridge voltage scaling factor will have a nonlinear effect, due to a dependency on average minority carrier concentration. When instead using the transient photoconductance decay (PCD) analysis method, the dependence on the optical constant is removed, and our error depends only on the mismatch in K_B . A third technique, the generalized analysis method, is a combination of these two methods dependent on the value of the optical constant at low lifetimes while becoming largely independent of optical constant values at high lifetimes. In the generalized analysis mode, a change in the optical constant value from 0.78 to 0.58 is seen to yield about a

30% increase in measured lifetime for lifetimes around 20 μ s, a 20% increase for lifetimes around 200 μ s, and almost no increase at lifetimes of around 3000 μ s.

To examine the magnitude of these effects on the measured lifetime, repeat measurements were made on the same wafer in various candidate containers, Figure 2.3. Lifetimes were measured in the generalized analysis mode for a minority carrier density of $1 \times 10^{14} \text{ cm}^{-3}$. A clear decrease in measured lifetime was observed with increased thickness of the container. The 4 mil plastic bag, as the thinnest of the containers was seen to have the smallest effect on the measurement. For the wafer in a plastic bag, the decrease in lifetime is expected to be the result of both the increase in distance from the inductive coil and the decrease of light intensity reaching the sample. These measurements were repeated on two additional wafers, which showed similar nonlinear decreases in measured lifetime with container thickness.

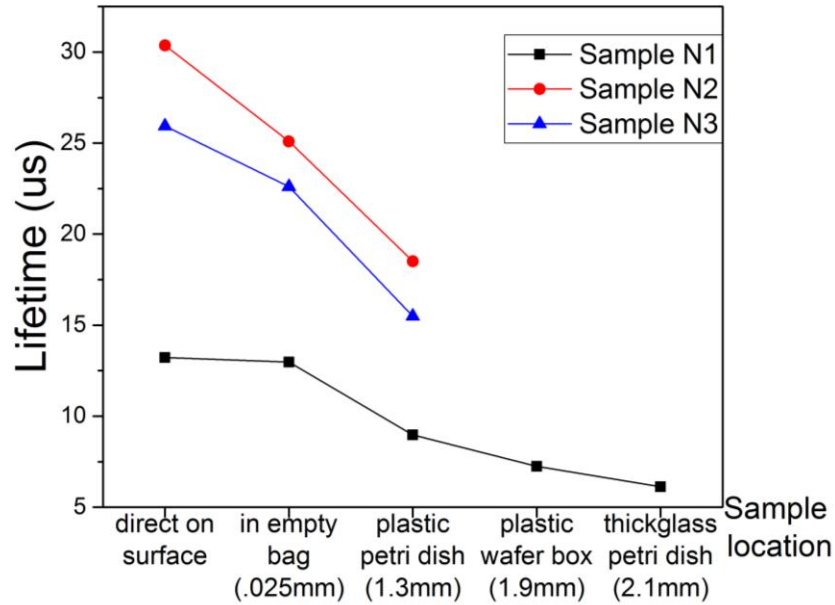


Figure 2.3. Lifetimes measured for an n-type wafer in different sample-holding conditions. Measured lifetime is seen to decrease with increased distance from the instrument surface. Data is acquired for samples placed directly on the surface (0mm), in an empty bag (0.1mm), on a glass slide (1.0mm), a plastic petri dish (1.3mm), a plastic wafer box (2.0mm) and a glass petri dish (3.0mm). © 2015 IEEE

A further change in measured lifetime is expected for the samples when placed in the liquid solution. An initial test shown compares the difference in lifetimes recorded for wafers when placed directly on the measurement surface and when placed in a plastic bag containing 50 ml of methanol (ME) solution. Changes of lifetime of -15%, -4%, -25%, -42% and were observed for lifetimes at a minority carrier density of $1 \times 10^{15} \text{ cm}^{-3}$ using an optical constant of 0.7. A simple trend is not clear from this data, and in one case the measurement actually increases when placed in solution. Methanol, while less effective than benzoquinone, is known to show some mild passivation effect on silicon surfaces, so it is initially unclear whether this chemistry is having an additional effect on the measurement.⁵⁹

To attempt to control for any chemical effects on the lifetime, a wafer (Sample N4) with a thermally grown oxide layer of thickness 110nm, was tested. This thick oxide layer should effectively block any passivating effects caused by organic molecules from the solution. Lifetime measurements were performed for this wafer in and out of solution when contained in either a plastic petri dish or plastic bag. The data shown in Figure 2.4 show the combined effects of factors independent of optical constant, such as placing the wafer in a petri dish, and factors which affect only the optical constant, such as covering the petri dish with a lid. It is expected that the methanol filled bag represents a combination of both types of factors. Again the bag was shown to cause a smaller decrease in the measured lifetime than the petri dish, with further decreases in measured lifetime for both containers when immersed in methanol. A repeated measurement with the wafer placed directly on the instrument surface was performed shortly after removal from the methanol solution, which showed no change to the lifetime of the wafer. The same tests were performed on a

wafer with only a thin natively formed oxide, which showed the same trends with no increase in lifetime from the brief methanol treatment.

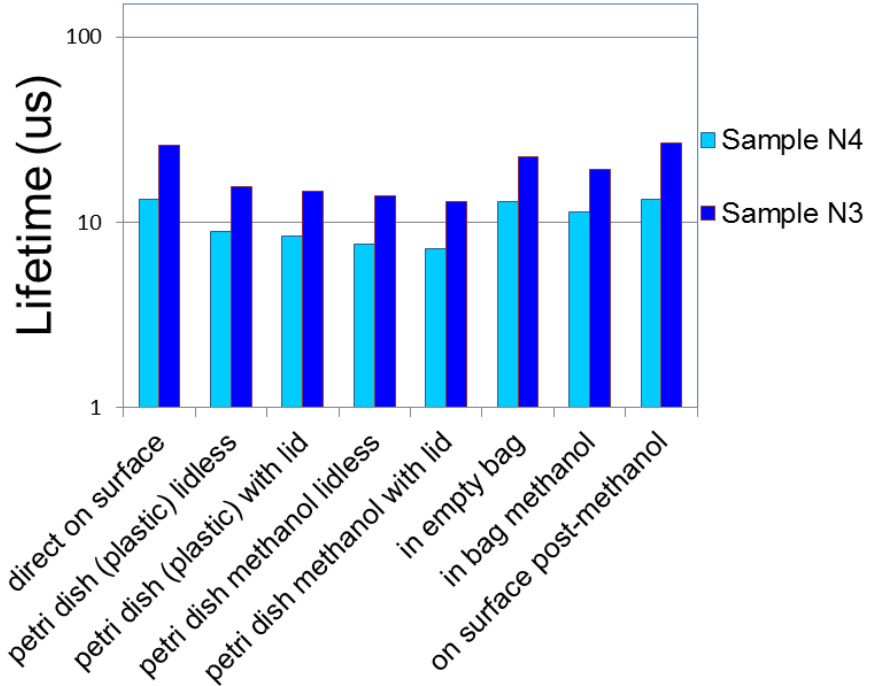


Figure 2.4. Measurements of a wafer with thermally grown oxide (N4) and native oxide (N3) (Note the logarithmic axis). Decreases in measured lifetime are seen due to thickness of containers, light blocking lids, and immersion in methanol. The last measurement is a repeat of the first measurement following immersion in methanol and shows no significant change. © 2015 IEEE

The presence of a liquid solution is likely to affect both the value of the optical constant and the bridge voltage scaling factor K_B . While these effects generally tend to decrease the reported carrier lifetime, recalibration is recommended to ensure accuracy of measurements. In most cases, the optical constant can be estimated reasonably well for a particular type of sample and environmental setup and can be kept fixed for the duration of the experiment. At sufficiently high lifetime values in the millisecond range, the transient photoconductance mode or generalized mode can be used for data analysis, and the choice of optical constant becomes unimportant.

The more complicated source of error in measured lifetimes comes from changes in the relationship between wafer conductance and measured bridge voltage. An increase in distance between the wafer and inductive coil will tend to decrease the measured lifetime due to an underestimation of the photoconductance and corresponding minority carrier concentrations.⁶⁰ This effect is seen to be relatively strong even for small displacements from the instrument surface. Placing the wafer in a plastic petri dish was seen to decrease the measured lifetime up to 42%. For samples that must be placed in containers, thinner materials such as a plastic bag minimize this introduced error. A better solution is to recalibrate the instruments for the new environmental setup, finding a new scaling factor K_B for the bridge voltage, as described by Lago-Aurrekoetxea et al.⁶¹

A wafer with a thick thermally grown oxide layer has been shown to be useful in separating the physical and chemical passivating effects of the liquid. It is expected that the use of similarly chemically inert wafers will enable the removal of the effect of the experimental setup on the measured lifetimes.

In this section, variations in the optical constant and inductive coupling of the wafer, as well as the presence of a liquid solution, are shown to lead to discrepancies in the measured lifetime of the wafers. The accuracy of optical constant is more important in the quasi-steady state photoconductance testing mode than in the transient photoconductance decay or generalized mode. Since optical constants typically range from around 0.63 to 1.03 for standard test setups, even gross misjudgment of the optical constant will still result in measurements accurate within a factor of 2. The changes in the relationship between wafer conductance and measured bridge voltage are more complicated and can cause up to a 40% decrease of lifetime (for example, if

a petri dish is used). In this work, for samples that must be placed in containers, thinner materials such as a plastic bag are used to minimize the introduced error.

2.4 Experimental Methods

2.4.1 Wafer Cleaning

N-type Si(100) samples (doped with phosphorus, FZ, DSP) from Topsil GlobalWafers were used in this work. The specified resistivity is 1-5 ohm_{cm} and wafer thickness is 280±20µm. A bulk minority carrier lifetime minimum of 9.18ms is certified by the vendor.

All wafers were cleaned following the procedures described by Opila and Teplyakov et al.: Substrates were cleaned using a Piranha etch (H₂SO₄:H₂O₂= 4:1) for five minutes, followed by a five minute DI water rise and a two-minute immersion in hydrofluoric acid (HF, 2wt%) to obtain hydrogen terminated surfaces.¹⁰ After cleaning, the substrates were quickly dried with a nitrogen gun and immediately placed in the passivation solution to be tested.

2.4.2 Wafer Thinning

Silicon wafers were thinned in steps of 20nm with an HNA (hydrofluoric acid/nitric acid/acetic acid) etching procedure, where the wafer is immersed in HNA solution for three minutes, followed by five minute DI water bath and another five minutes DI water bath. The HNA solution is a mixture of 17mL acetic acid (Fisher Scientific), 73mL nitric acid (J.T. Baker, 69.5%) and 10mL hydrofluoric acid (J.T. Baker, 49%). After HNA thinning, wafers were dried and weighed. The change in thickness is calculated by weight loss. Piranha and HF were used to clean the etched surface and terminate surface with hydrogen, as described previously. These thinned

Si:H wafers were then put in passivation solution immediately and lifetimes were recorded.

2.4.3 Passivation Treatment

0.01M passivation solutions of the following molecules with methanol (ME, J.T. Baker CMOS grade, as-is) as the solvent were prepared, unless otherwise noted, shown in Figure 2.5. The passivation solutions were freshly mixed and contained within sealed acid resistant plastic bags at room temperature. The concentration, 0.01M, was chosen based on a previous quinhydrone concentration study.³⁶

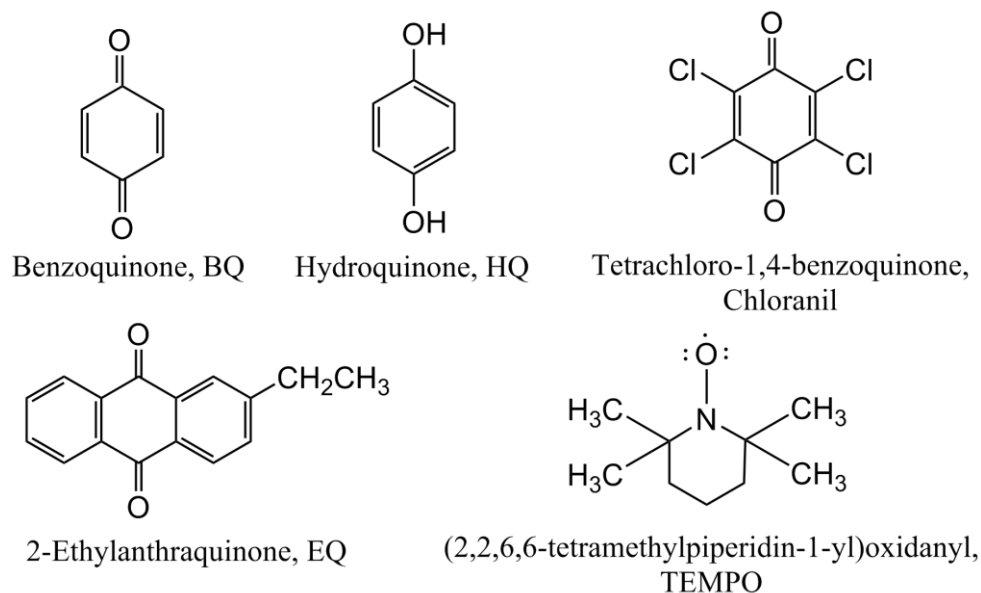


Figure 2.5. Passivants used in this paper are BQ (98+% Sigma-Aldrich), HQ (99% Acros Organics), Chloranil (99% Sigma-Aldrich), EQ (97% Acros Organics) and TEMPO (98+% Sigma-Aldrich). All chemicals are used as received from the vendor.

2.4.4 Lifetime Measurements

A Sinton WCT-120 Lifetime tester was used to measure the lifetime that began immediately following immersion in solution.⁵⁷ An optical constant of 0.7 was used

for all experiment based on the in-solution lifetime measurement study.⁶²

Measurements were taken every 15 minutes, and the substrates remained in solution over the duration of the experiment. Based on the study of quasi-steady-state and quasi-transient measurements, lifetime higher than 200 μ s is reported in transient photoconductance decay (PCD) mode at MCD= $1 \times 10^{15} \text{cm}^{-3}$, and lifetime below 200 μ s is reported in quasi steady state photoconductance (QSSPC) mode at MCD= $1 \times 10^{14} \text{cm}^{-3}$.^{63,64} All lifetime comparisons of different passivation techniques in the same plot are performed on pieces cut from the same stock wafer to minimize any variation of the substrate, unless otherwise specified.

2.4.5 Photoinitiation Set-up

A home-built system in Figure 2.6 was used for photoinitiation study. A 300W xenon lamp (300nm-700nm) was used as the light source. Light was directed by a silver mirror and then through a longpass filter (380nm longpass for I819 and 470nm longpass for CQ). The intensity on the sample surface measured by a light meter is 13mW/cm² around 470nm and 40mW/cm² around 380nm for I819 and CQ respectively. In addition, the ambient room light intensity is on the order of 100 W/cm².

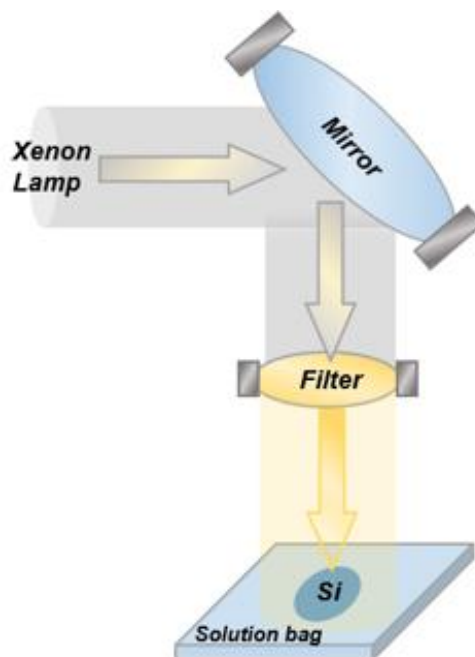


Figure 2.6. Photoinitiation set-up. Xe light was directed by a silver mirror and then went through a longpass filter (380nm longpass for I819 and 470nm longpass for CQ). Wafers were kept in the solution during this irradiation treatment.

2.4.6 Electrochemical Cell Set-up

The electrochemical measurements were carried out using a VersaStudio (Princeton Applied Research) computer-controlled electrochemical measurement system equipped with a potentiostat (PARSTAT 3000, Princeton Applied Research).

The measurements were carried out using a conventional three-electrode configuration: a working electrode (WE, silicon modified sample), a counter electrode (CE, platinum foil) and a reference electrode (RE, Ag/Ag⁺), as shown in Figure1. The silicon electrodes were single side polished wafers of 0.01-0.02 Ω .cm resistivity, boron-doped, (100) oriented, single-crystal material obtained from MEMC Electronic Materials. Typical electrodes consisted of 1cm² on each side. Prior to use, Si electrodes were cleaned with piranha and HF as described in section 2.4.1, and Ga-In eutectic were rubbed on the unpolished side to form an ohmic contact. Ag/Ag⁺ non-

aqueous reference electrodes were home assembled using a Ag wire dipping in 0.1 M AgNO_3 /methanol solution. Tip of the reference electrode was sealed with a voycor glass.

Methanol, from J.T. Baker, was bubbled with dry nitrogen for 30 minutes before use. TBAPF_6 , from Acros Organics, was added as the supporting electrolyte. iR compensation was automatic detected by the potentiostat and applied in all measurements.

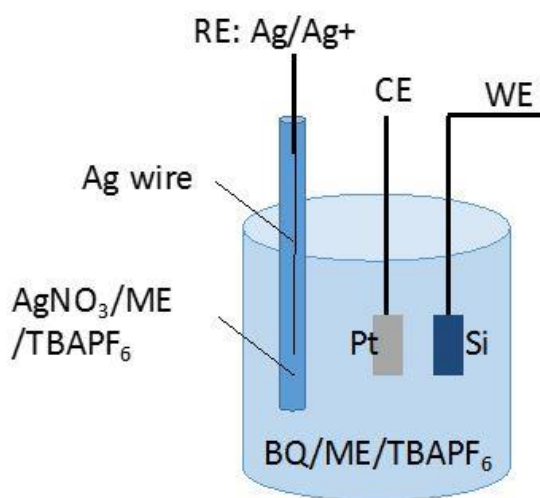


Figure 2.7. Electrode configuration for BQ/ME reaction on Si electrode

2.5 Results and Discussion

2.5.1 Passivation using BQ, HQ and Methanol

After piranha and HF cleaning, wafers were placed in BQ/ME, HQ/ME and ME solution immediately, and lifetime data were collected as a function of time while the wafers remained in solution, as illustrated in Figure 2.8. It can be seen here that BQ/ME provides nearly instantaneous improvement of lifetime reaching the highest around $4500\ \mu\text{s}$ in around 30 mins, and then starts to decline (H terminated Si is found to have a lifetime lower than $40\ \mu\text{s}$ in this work). HQ/ME and ME passivation shows a

gradually increase with HQ/ME plateauing around 2500 μs and ME solution plateauing around 1300 μs .

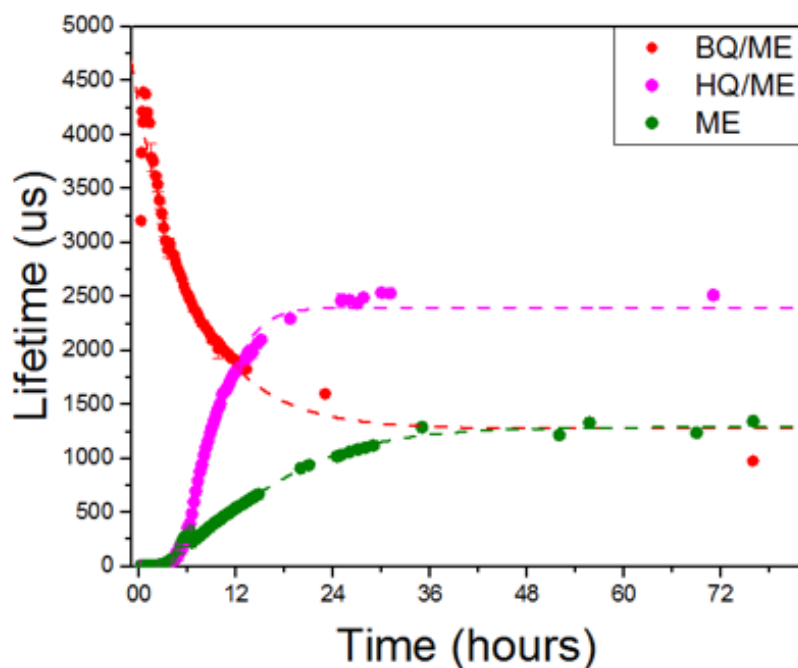


Figure 2.8. Passivation results of BQ/ME(0.01M), HQ/ME(0.01M) and the control sample, methanol. Solid points are measured data, while dash lines are trend lines. The error bars are smaller than the symbol size unless indicated otherwise.

The lifetime behavior can be explained by the redox reaction illustrated in Figure 2.9. In BQ/ME solution, BQ abstracts H atoms from the solvent methanol to form QH^* and MEO^* , and these radicals bond to the reactive silicon surface providing passivation effects. According to the study by Forbes and Lewis et al., the excitation of QH^* and MEO^* in BQ/ME mixture under ambient light is more energetically favorable than the formation of MEO^* in pure ME, which explains why BQ/ME has a faster response and much higher lifetime than ME.^{59,65} In pure ME solution, shown in green dots in Figure 2.8, the improvement of lifetime implies the bonding of methanol molecules on the surface. Bonding of methanol on silicon surfaces in pure anhydrous

methanol has also been observed by Lewis et al. via XPS and FTIR, where a sharp Si-OCH₃ stretch peak is observed after three hours wafer immersion.⁵⁹ In HQ/ME solution, the equilibrium still exists and QH* slowly releases. The behavior of radicals will be further confirmed in the following sections.

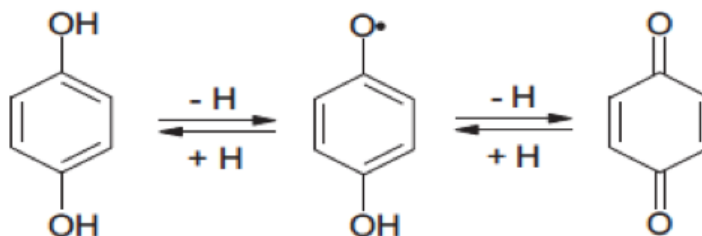


Figure 2.9. Reversible redox reaction of BQ/QH*/HQ system.⁶⁶

Surface recombination velocity (SRV) is extracted from Equation 1.2, where the effective lifetime τ is a function of bulk lifetime τ_b , SRV and wafer thickness W . $\tau_b = 9.18\text{ms}$ is certified by the vendor. This gives a SRV of 1.6cm/s for BQ/ME passivation and 4.1cm/s for HQ/ME passivation on polished N-type wafers at $\text{MCD} = 1 \times 10^{15}\text{cm}^{-3}$.

HNA is a commonly used etching process.⁶⁷ The SRV of HNA treated surfaces is also studied. N-type silicon wafers were thinned five times using the HNA procedure described in the experimental section. Lifetimes of wafers with different thicknesses were recorded at two injection levels (1×10^{14} and $1 \times 10^{15}\text{cm}^{-3}$) in Figure 2.10. Using a linear fit is performed with a fixed bulk minority carrier lifetime of 9.18ms . Results show that for the HNA treated surfaces, at the injection level of $1 \times 10^{15}\text{cm}^{-3}$, $\text{SRV} = 6.7\text{ cm/s}$ (adj. $R^2 = 0.98$), and at the injection level of $1 \times 10^{14}\text{cm}^{-3}$, $\text{SRV} = 7.3\text{ cm/s}$ (adj. $R^2 = 0.99$). The SRV is equivalent to other existing passivation techniques, like thermal SiO_2 , a-SiN_x:H, a-Si:H, and Al_2O_3 .¹⁷

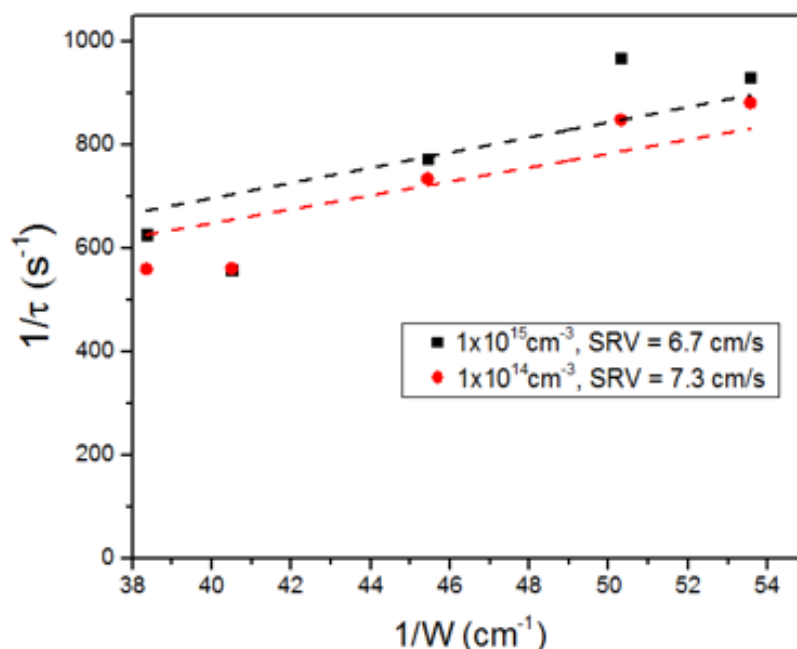


Figure 2.10. Inverse of the effective lifetime after BQ/ME treatment plotted vs. the inverse of thickness for extrapolation of SRV from the fit of data at each injection level. The linear fit is performed with a fixed bulk minority carrier lifetime of 9.18ms

2.5.2 Impact of External Radicals

To investigate the role radicals play in the quinone and H terminated Silicon system, a free radical trap, TEMPO, was introduced. TEMPO, (2,2,6,6-tetramethylpiperidin-1-yl) oxidanyl, shown in Figure 2.5, was discovered by Lebedev and Kazarnowskii in 1960 and is known as a stable radical.⁶⁸ The steric effects in TEMPO create stability against light and heat and promote the capture of other radicals.

Following the same cleaning procedure, four solutions were made: ME, HQ/ME (0.01M), TEMPO/ME(0.01M), and HQ/TEMPO/ME (0.01M). The concentrations of HQ and TEMPO were each 0.01M in the HQ/TEMPO/ME solution. Wafers were immersed in the solutions immediately after cleaning, and lifetime data were collected as a function of time, as illustrated in Figure 2.11.

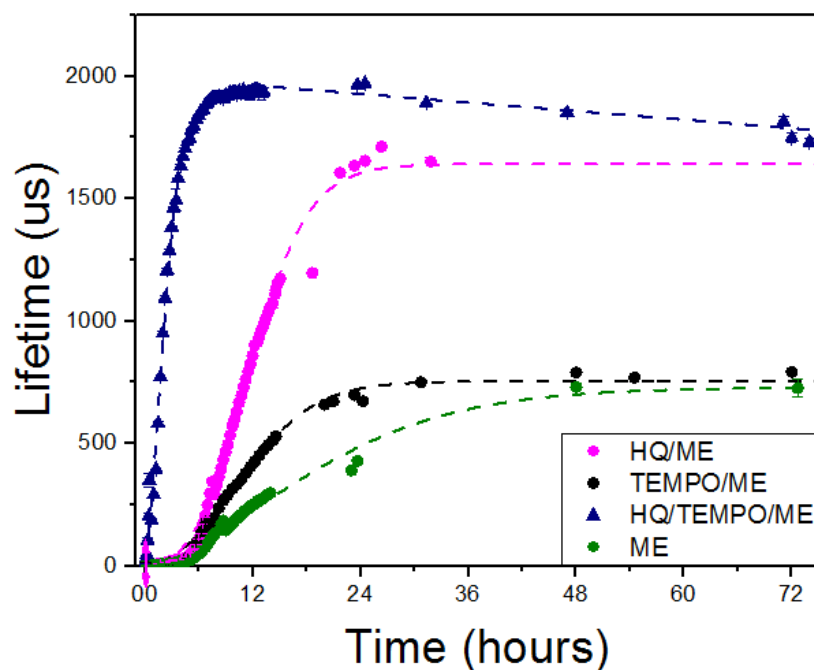


Figure 2.11. External radical effects on HQ passivation. Wafers were kept in four solutions: HQ/ME (0.01M), TEMPO/ME (0.01M), HQ/TEMPO/ME (0.01M) and a ME control. Solid points are measured data, while dashed curves are trend lines.

Comparing quinone containing solutions (HQ/ME in pink and HQ/TEMPO/ME in dark blue) and non-quinone solution (ME in green and TEMPO/ME in black), the quinone solutions eventually plateau at a much higher level than the non-quinone solutions. This further confirms that the quinone facilitates passivation, presumably by more QH* and MEO* bonded to the Si surfaces.

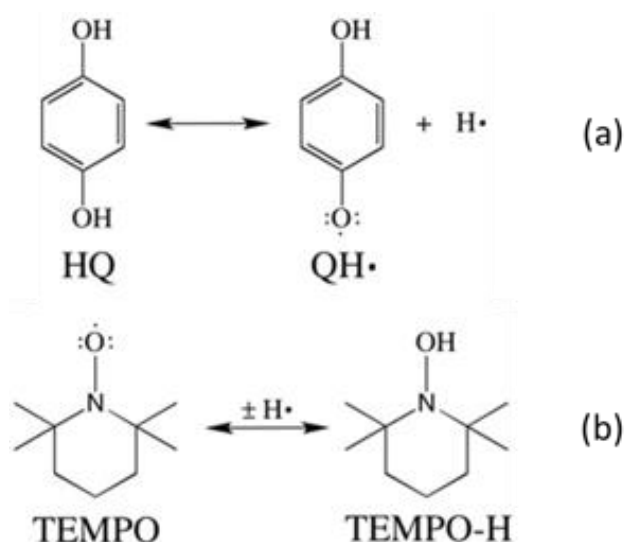


Figure 2.12. Reactions of HQ (a) and TEMPO (b) with hydrogen atoms.

ME, TEMPO/ME and HQ/ME all require at least six hours before significant passivation effects are shown, and the lifetime plateaus after around 24 hours. However, when HQ is mixed with TEMPO, the result changes completely: lifetime of the mixed solution increases dramatically in the first hour, and plateaus quickly at the saturation level. As sketched in Figure 2.12(a), we hypothesize that HQ releases a hydrogen atom becoming QH*, and QH* then bonds to the surface achieving a longer carrier lifetime. By adding TEMPO to the system, hydrogen atoms are consumed by TEMPO. Although it has been known that the O-H bond in TEMPO-H is 30% weaker than a typical O-H bond, TEMPO will still capture some of the hydrogen atoms, shown in Figure 2.12(b), and promote the reversible reaction to go to the right, leading to an accumulation of QH*. ⁶⁹ Thus, more QH* is available in solution and longer lifetimes are observed. As soon as the surface is saturated with QH* molecules, the lifetime levels out.

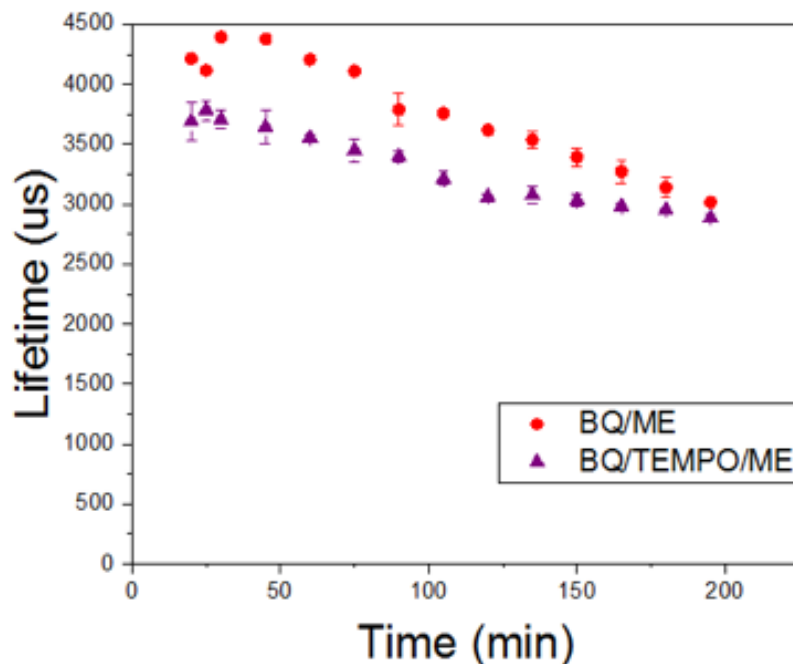
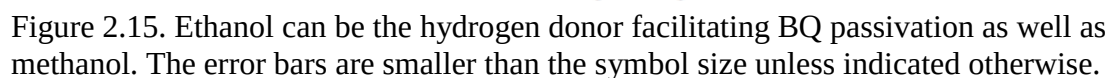


Figure 2.13. External radical effects on BQ passivation. Data indicates the lifetime after treatments of two passivation solutions: BQ/ME (0.01M) and BQ/TEMPO/ME (0.01M). Wafers were kept in solution for the duration of the experiment.

However, contrary results are observed in BQ/TEMPO/ME, as seen in Figure 2.13. The mixture solution, BQ/TEMPO/ME, has a lower lifetime than BQ/ME. This can be explained by the reaction in Figure 2.14, where BQ abstracts a hydrogen atom from the solvent methanol to transfer into QH*. QH* and MEO* radicals are responsible for the bonding on the silicon surface, and the rate of the passivation mechanism slows down when adding the free radical trap, TEMPO, in BQ/ME. Alcohol's role as a hydrogen donor is confirmed by ethanol, shown in Figure 2.15, and a previous study in our group where no passivation was shown from BQ in aprotic solution, diethyl ether.³⁹



39

2.5.3 Passivation Using Quinone Derivatives

The electronegative groups on the benzene ring affect the reactivity of the molecule. A group of benzene congeners with different oxidability are compared in the following section. Structures of the passivants are shown in Figure 2.5. All solutions were prepared at 0.01M using methanol (ME) as the solvent, except for chloranil. For chloranil, a saturated solution of around 0.005M is used because of the low solubility of chloranil in methanol. In all of the tests, wafers were immersed in solution at ambient room light for up to four days.

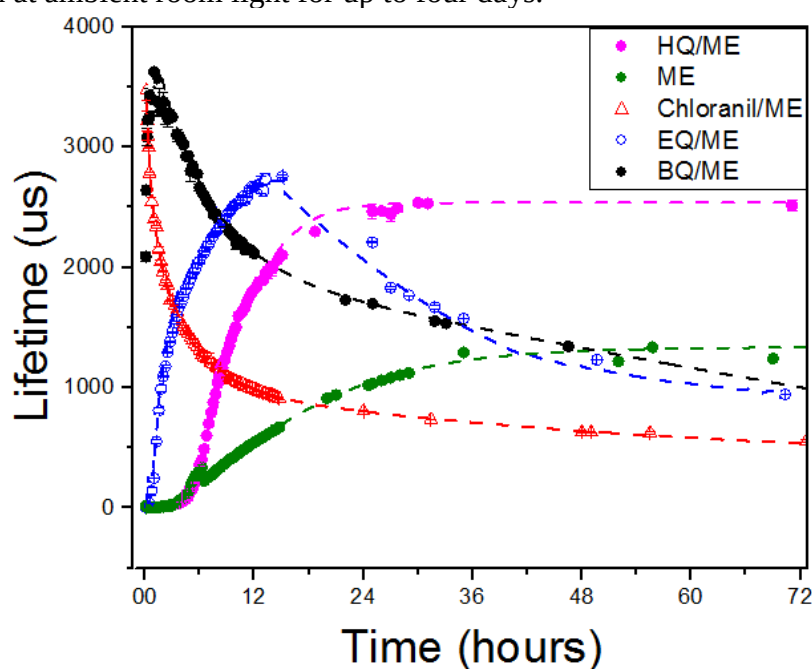


Figure 2.16. Lifetime performance of alternative passivants. Concentration for all solution is 0.01M, except for the 0.005M chloranil/ME. The error bars are smaller than the symbol size unless indicated otherwise.

Figure 2.16 shows the lifetime comparison of all passivant molecules. It can be seen that BQ and chloranil follow a similar trend in that the best passivation effects are obtained in the first hour when the wafers contact the solution, and then start to degrade. EQ and HQ show a gradual increase in passivation. In addition, TEMPO slows down the rate of passivation mechanism in both BQ/ME (Figure 2.13) and

chloranil/ME, and promotes the passivation in both HQ/ME (Figure 2.11) and EQ/ME. (TEMPO's effect on chloranil and EQ data is not included here)

Comparing the structures of all molecules, the ones with a more electronegative group (as the Cl- and O= in chloranil and BQ) abstract H atoms from the solvents more easily to become semi-quinone radicals, form bonds with the surface and have the large, instantaneous increase in lifetime. This agrees with the hypothesis in the previous section that radicals are responsible for bonding.

2.5.4 Passivation Using Radical Photoinitiators

Photoinitiators are good sources of radicals, which presumably can bond to silicon surfaces and induce passivation effects. Two commercial radical photoinitiators were studied in this work, bis(2,4,6-trimethylbenzoyl)-phenylphosphineoxide (I819) and camphorquinone (CQ), which undergo Norrish type I and type II radical formation, respectively.

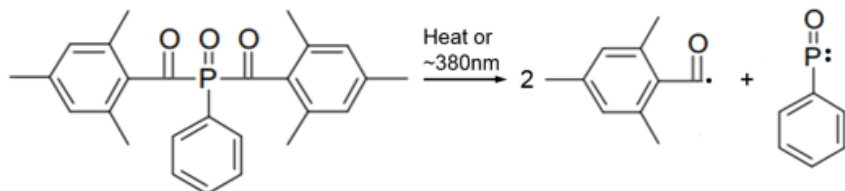


Figure 2.17. I819 radical formation, Norrish type I reaction.

In a Norrish type I reaction, the molecules in excited states, S_1 or T_1 , undergo a hemolytic bond cleavage forming two or more free radical fragments, as illustrated in Figure 2.17.⁷⁰ The size and nature of these fragments depend on the stability of the generated radicals. Benzoin and its derivatives are common compounds in this category. When applying radical photoinitiators for silicon passivation, the photoinitiators' absorption spectra should also be considered. For example, benzoyl peroxide, in Figure 2.18, another widely used commercial photoinitiator, would not be

a good candidate for passivation because the absorption λ is around 240 nm, which is likely to cause damage on silicon surfaces.^{71,72} In a Norrish type II reaction, the free radicals are formed by abstracting hydrogen from a hydrogen donor such as alcohol or amine upon absorption of light, as show in Figure 2.19.^{70,73} Presumably, the generated free radicals can bond to the reactive silicon surface sites and passivate the surface.

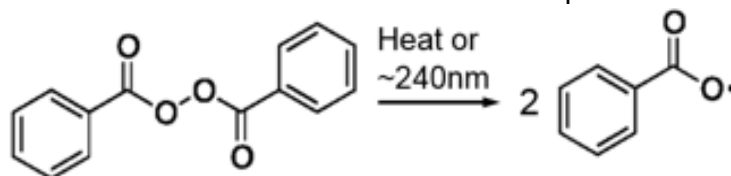


Figure 2.18. BPO radical formation.

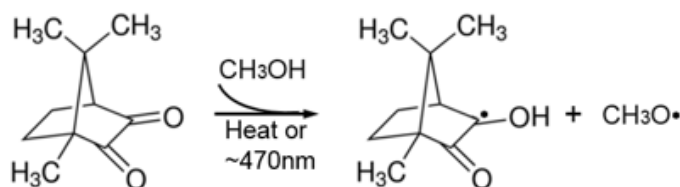


Figure 2.19. CQ radical formation, Norrish type II reaction.

In the home-built set-up illustrated in Figure 2.6, hydrogen terminated silicon samples were kept immersed in I819/ME or CQ/ME solutions while exposed to filtered Xe light for a time interval of 30mins or one hour, before performing lifetime measurements. This irradiation treatment was repeated several times over the course of seven hours, as indicated by the solid lines in Figure 2.20. Samples were kept in solution for the duration of the experiment, and stayed on the Sinton measurement stage between irradiation periods, which is held at 28°C. Compared with the room light condition indicated by triangles in Figure 2.20, the irradiation treatment in both I819 and CQ solution increases silicon lifetime. Lifetime of samples in I819/ME plateaus at around 900 μ s in about five hours. CQ/ME reaches 750 μ s in three hours.

This improvement of lifetime introduced by irradiation is consistent with the free radical bonding and passivation mechanism.

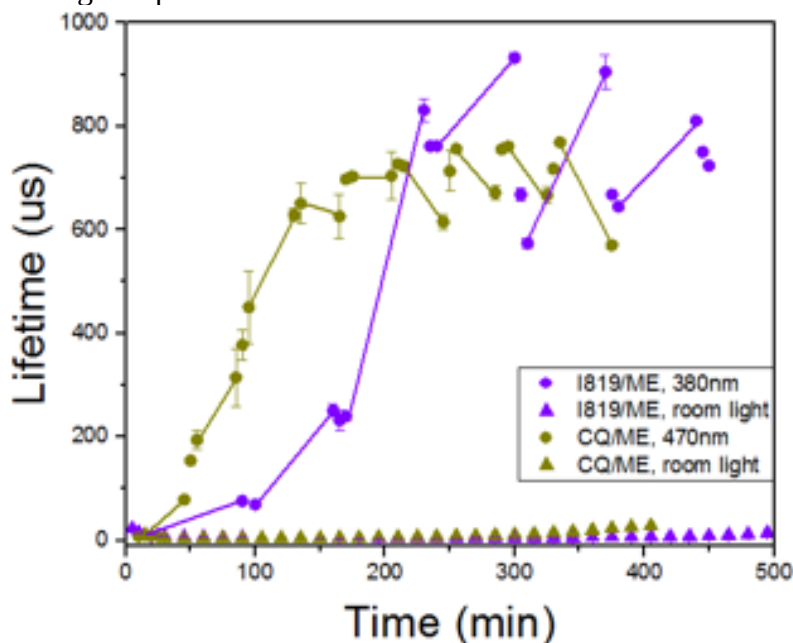


Figure 2.20. Si lifetime performance in I819/ME and CQ/ME with irradiation treatment for up to seven hours. A 380nm Xe longpass filter is used for I819 and a 470nm Xe longpass filter for CQ. Solid lines indicate the 30mins or one hour sample irradiation treatment duration. Dotted data that are not connected record lifetime measurements between irradiation periods in ambient room light. The error bars are smaller than the symbol size unless indicated otherwise.

Measured lifetime for I819/ME passivation, 900μs, is much lower than the average BQ/ME result, typically over 3ms. There are couple of possible explanations for these results. First, in BQ/ME, both QH* and the resulting methanol radical, MEO*, can react with the active silicon sites. While in I819/ME, only the benzylic radicals contribute to bonding. In CQ/ME, shown in Figure 16, presumably only MEO* radicals contribute to passivation, and CQ radicals are less likely to bond with silicon due to the large steric hindrance, which may account for the overall lower lifetime of wafers in CQ/ME than in BQ/ME. Another theory developed by Cahen et al. stated that radicals residing on the oxygen component of the organic molecules

formed by nucleophilic substitution (SN) are sensitive to the reactivity of Si surface sites, and the reactions take place rapidly on the more reactive sites (silicon defect sites), but much slower on the less reactive Si sites (H terminated Si sites). As a result, SN provides better electronic passivation by saturating the reactive surface defect sites.⁷⁴ BQ/ME falls in this category with QH* and MEO* both being oxygen radicals. On the other hand, α -carbon radicals, like benzylic radicals from I819, are more likely to follow the radical chain reaction (RCR) mechanism, where the bonding reaction proceeds through the migration of the radicals from one Si atom to the neighboring Si atom and forms a closed-packed monolayer in its vicinity. However, RCR is not very site-specific, and thus silicon dangling bonds are less uniformly saturated than in the case of oxygen radicals.⁷⁴

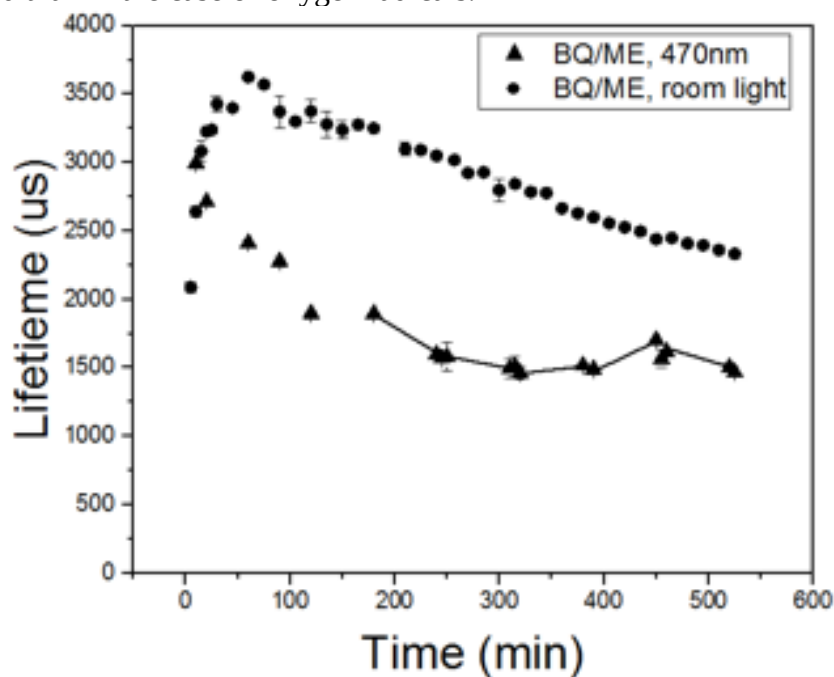


Figure 2.21. Si lifetime performance in BQ/ME with irradiation treatment. Solid lines indicate the 30mins or one hour sample irradiation treatment. Dotted data record the lifetime between irradiation treatment when wafers in solution bags were sitting on the Sinton stage in ambient room light. Two wafers are from different stock wafers. The error bars are smaller than the symbol size unless indicated otherwise.

BQ, though not commonly used as a photoinitiators, is also photosensitive. It has been shown that BQ, stable in solid phase, can be photolyzed by light with wavelengths around 450nm in alcohol.⁶⁵ Kotulak, et al. have observed that ambient room light facilitates BQ/ME passivation.⁴⁰ Irradiation treatment with 470nm light was also performed on BQ/ME solution, and results are shown in Figure 2.21. The degradation of BQ/ME passivation when substrates are still immersed in solution in ambient room light condition is most likely caused by the addition of ME on the surface where ME competes or even replaces BQ, as discussed in the following XPS section. Note that the two wafers used here are from different stock wafers, which means the bulk quality might affect the overall lifetime. On the other hand, the fact that the degradation propagates in both light conditions proves that the irradiation treatment shows no significant improvement of lifetime as for I819 and CQ. This could be due to the passivation mechanism saturating in BQ/ME because of the high efficiency of QH* and MEO* bonding on silicon surface.

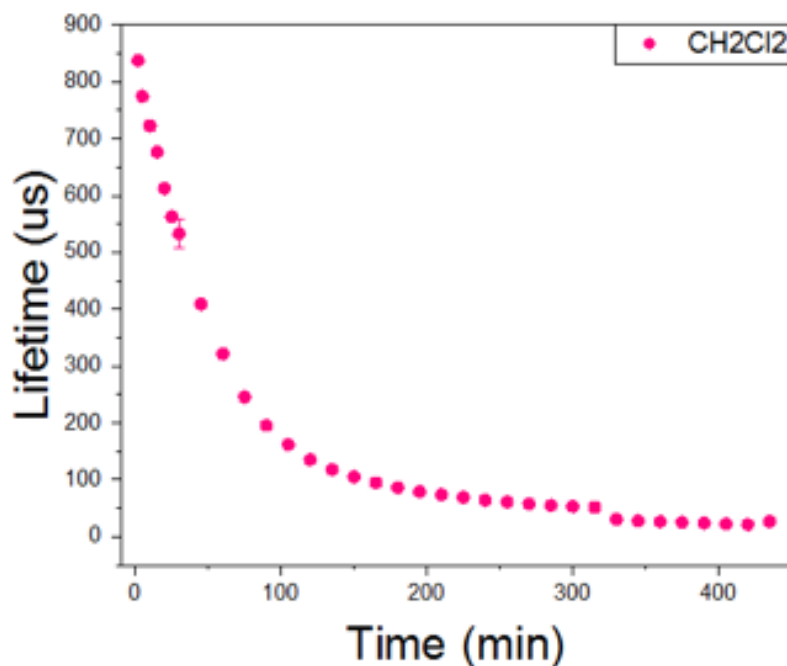


Figure 2.22. Passivation of CH_2Cl_2 in ambient room light versus time.

Not only compounds containing benzene groups can be the radical source, weak bonds like Cl-Cl and C-Cl, (bond energy of Cl-Cl is 242kJ/mol, and C-Cl is 350kJ/mol), can undergo homolytic cleavage giving free radicals as well when supplied with heat or light.⁷⁵ Silicon wafers were immersed in CH_2Cl_2 solution (>99.5%) in a closed Teflon zip bag immediately after HF cleaning. Minority lifetime in ambient room light along with time is recorded in Figure 2.22. Results show that CH_2Cl_2 passivates the silicon surface instantly reaching a peak lifetime of 837 μs (H terminated Si has a lifetime <40 μs). But this passivation is not stable; lifetime decreases to half in an hour while the wafer is still immersed in CH_2Cl_2 solution.

Experiments in this section investigated the effectiveness of different radical sources. Photoinitiators I819 and CQ were proven to passivate silicon surfaces when irradiated with light at the corresponding reaction energy. Weak bonds like C-Cl can also generate radicals and passivate silicon. These support the proposed free radical

bonding and passivation mechanism. However, irradiation treatment of BQ/ME shows no significant further improvement of lifetime compared with the room light condition.

2.5.5 BQ Reaction on Si in an Electrochemical Cell

First, we looked in to the potential of the Ag/Ag⁺ reference electrode using ferrocene couple (Fc/Fc⁺) as a standard. Methanol (ME) was used as solvent, and Pt as both the working and counter electrodes, illustrated in Figure 2.23.

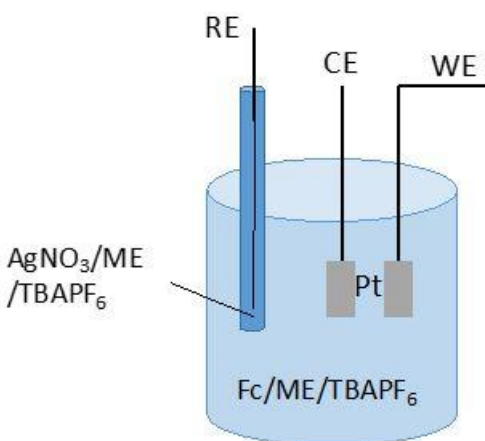


Figure 2.23. RE calibration with Fc/Fc⁺ couple.

Figure 2.24 shows the cyclic voltammetry (CV) of Fc/Fc⁺ couple on Pt electrodes in methanol in three scan rates, 0.1V/s, 0.05V/s and 0.02V/s. From the detailed number listed in Table 2.1, the peak separation is the smallest for the lowest scan rate, 0.02V/s. However, the intensity of the current decreases as the decrease of scan rate. The best CV testing condition for Fc/Fc⁺ in methanol was 0.05V/s, and the Fc/Fc⁺ potential is found to be -0.13V vs. Ag/Ag⁺. Koepp et al. reported that the potential of Fc/Fc⁺ in methanol was 0.41V vs. Ag/AgCl.⁷⁶ Thus, the Ag/Ag⁺ RE used in this work is 0.54V vs Ag/AgCl.

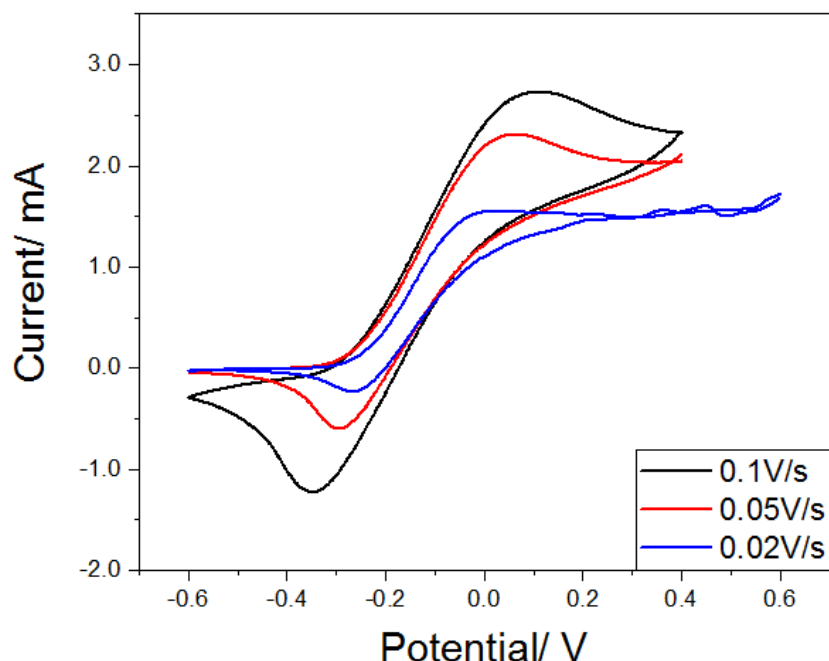


Figure 2.24. CV of Fc/Fc⁺ couple on Pt electrodes in methanol using Ag/Ag⁺ as reference electrode.

Table 2.1. Scan rate comparison of Fc/Fc⁺ potential on Pt electrode in methanol.

	E _{pc}	E _{pa}	E	ΔE
0.1v/s	-0.34	0.1	-0.12	0.44
0.05v/s	-0.29	0.04	-0.13	0.33
0.02v/s	-0.26	0	-0.13	0.26

After validation of the home-built electrochemical cell, the linear sweep voltammetry (LSV) was performed to study the Si electrode behavior in both BQ/ME solution and the ME control, using the set-up described in Figure 2.7. Potentials positive of 0 V were avoided to eliminate the possible changes of the silicon surface properties, like dissolution and oxidation, shown in Figure 2.25.⁷⁷ The highlighted areas in Figure 2.25 indicate the electrode electron transfer efficiencies. A current enhancement in LSV is observed in the BQ/ME solution compared with pure ME, indicating that the electron transfer on the surface is more efficient in BQ/ME than in ME.

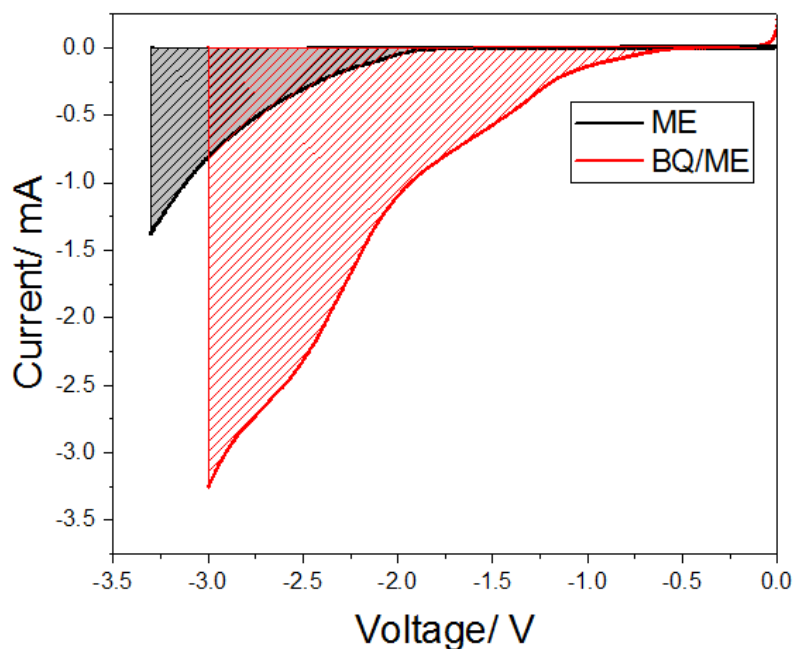


Figure 2.25. Linear sweep voltammetry (LSV) of BQ/ME and ME solutions using Si as WE, Pt as CE and Ag/Ag⁺ as RE. Scan rate is 0.05 V/s. WE area is around 1.0cm².

In addition, Fc/Fc⁺ was used as the internal standard in the CV scan for BQ/ME reaction on Si electrode. Results of the BQ/Fc/ME and the Fc/ME control samples are shown in Figure 2.26. The reduction and oxidation peaks attributed to Fc/Fc⁺ are observed in -0.3V and 0.09V respectively. However, no redox peak rising from BQ observed, indicating the BQ reaction on Si doesn't involve electron transfer if there is any.

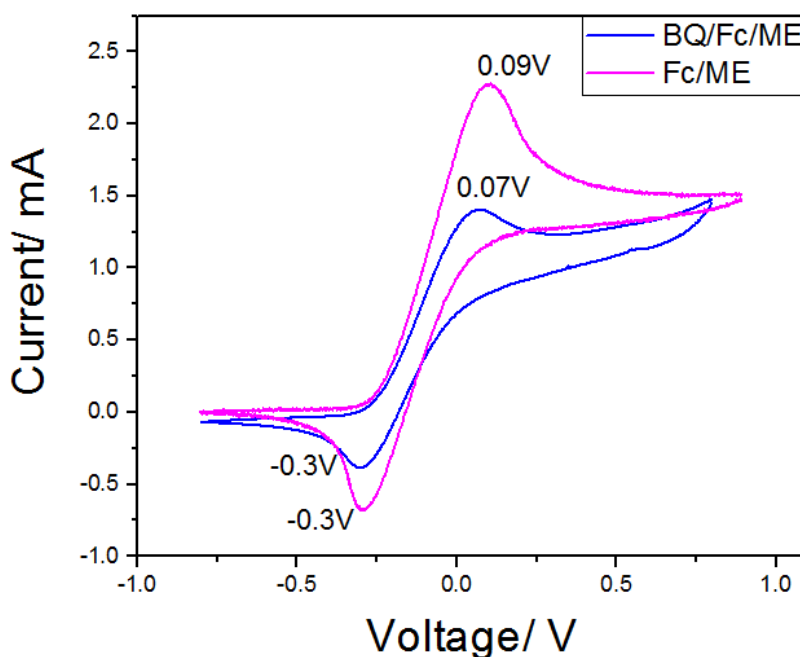


Figure 2.26. CV of BQ/ME on Si electrode using Fc/Fc⁺ as internal standard. CE is Pt. RE is Ag/Ag⁺. Scan rate is 0.05V/s.

2.6 Conclusions

This chapter investigated the passivation behavior study of free radicals in BQ, HQ, under the impact of external radicals, radiation and electronegative groups substitution in quinone molecules, and other radical sources like photoinitiators and chloromethane compounds. Quinone radicals and methanol radicals are believed to be responsible for the improvement of minority carrier lifetime.

Comparing the passivation effects of EQ, chloranil, BQ and HQ molecules, the molecules containing electronegative groups can abstract H atoms from the solvents more easily to form radicals, bond to silicon and show large, nearly instantaneous increases in lifetime.

Photoinitiators I819 and CQ can passivate silicon surfaces when applying light with the corresponding activation energy. This is further evidence of a free radical-

based bonding and passivation mechanism. Weak bonds like C-Cl can also generate radicals and passivate silicon. However, irradiation treatment of BQ/ME shows no significant improvement of lifetime compare with the room light condition.

In addition, this section investigated the BQ/ME reaction on silicon surface through electrochemical tools. The measurements were carried out using a conventional three-electrode configuration using non-aqueous Ag/Ag⁺ reference electrode (0.54V vs. Ag/AgCl). The current enhancement in LSV indicates that the electron transfer to the surface is more efficient in BQ/ME than in ME. In addition, no redox peak rising from BQ observed, indicating the BQ reaction on Si doesn't involve electron transfer if there is any.

Work in this chapter confirms the significant role that radicals play in H-Si surface passivation reactions. BQ is believed to abstract hydrogen atoms from methanol to become QH*, and both QH* and the resulting methanol radical are responsible for the nearly instantaneous improvement of minority carrier lifetime ($\tau=4500\mu\text{s}$, with SRV=1.6cm/s on polished surfaces; SRV=6.7cm/s on HNA etched surfaces). In HQ/ME solution, HQ loses a hydrogen atom to become QH*. QH*, the methanol radical and other radicals can bond to silicon and act as passivants.

Chapter 3

SURFACE COMPOSITION STUDY*

3.1 Introduction

X-ray photoelectron spectroscopy (XPS) is a widely used quantitative spectroscopic technique that measures the surface elemental composition, and can be used to study the silicon surfaces after passivation in this work. XPS spectra are obtained by exciting a samples surface with X-rays causing photoelectrons to be emitted from the topmost few nm of the sample surfaces. An electron energy analyzer is used to measure the kinetic energy and number of the emitted photoelectrons. The energies and intensities of the photoelectrons allow identification and quantification of the surface elements. In this chapter, I will investigate the bonding of quinones on silicon via XPS, the surface monolayer quinone coverage, as well as the time evolution of the bonding.

3.2 Experiment

Following the same cleaning procedure described in the experimental methods section, N-type Si(100) wafers were immersed in BQ/ME for 1, 7 and 24 hours. After the surface treatment, the wafers were taken out of the solution, briefly rinsed with

* Reprinted with permission from Chen, M.; Hack, J. H.; Iyer, A.; Jones, K. J.; Opila., R. L. *J. Phys. Chem. C*. **2017**, 121 (39), 21364. Copyright 2017 American Chemical Society.

methanol, blown dried with a nitrogen gun, and then loaded immediately into the XPS chamber.

A Physical Electronics model 5600 X-ray photoelectron spectrometer was used for the XPS studies. The spectra were collected with a pass energy of 23.5 eV in high resolution with a monochromatic aluminum $K\alpha$ X-ray source ($h\nu=1486.6$ eV).

3.3 Results

3.3.1 Time Evolution of BQ/ME Bonding to Si

Silicon surfaces treated by 1 hour, 7 hours and 24 hours BQ/ME were measured by XPS to study the time evolution of BQ/ME bonding to Si, shown in Figure 3.1.

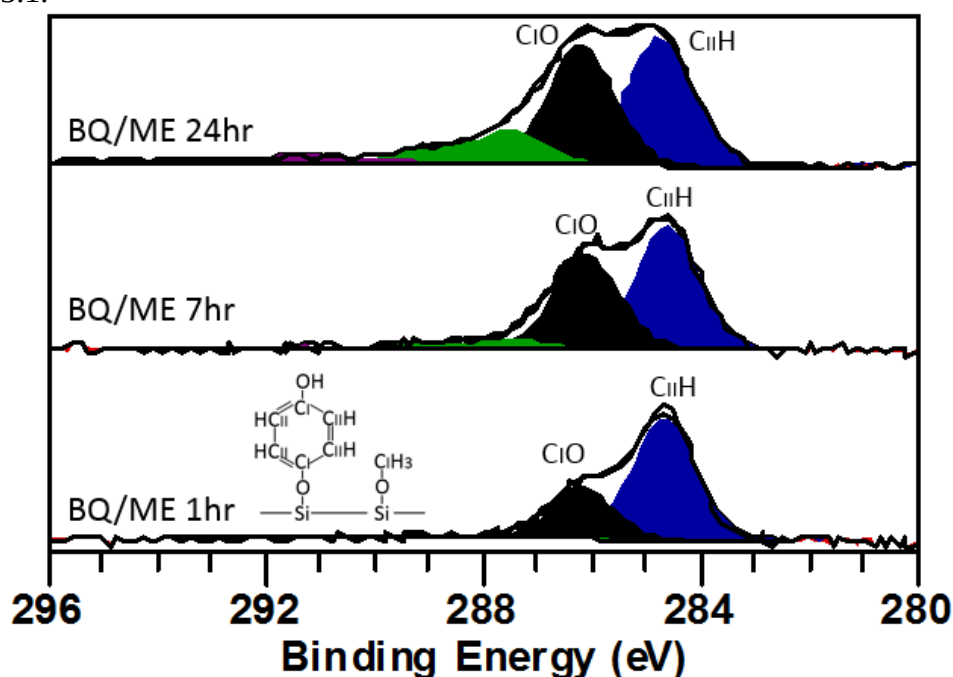


Figure 3.1. Carbon 1s peak evolution of the substrates after 1 hour (bottom), 7 hours (middle) and 24 hours (top) BQ/ME treatment. The peaks in blue, black and green are assigned to C₁H bonded to hydrogen, C₁O bonded to oxygen, and adventitious carbon, respectively. The increasing of C₁ fraction along with time indicates an increasing contribution from methanol bonding.

For the wafer after one hour BQ/ME treatment, illustrated in Figure 3.1(bottom), two types of carbon are assigned based on the bonding; C_I from the benzene complex, as well as in methanol, bond with oxygen, and C_{II} in the benzene ring bonded only with carbon and hydrogen. Because the intensity of the component from 287 to 288 eV, usually attributed to adventitious carbon, is so small, adventitious carbon is assumed to be negligible for analysis on this one hour treatment. Without adventitious carbon, peaks at 284.6eV and 286.2eV can be assigned to C_I and C_{II} , respectively. The fraction of C_{II} to C_I is roughly 2:1 for the one hour treated surface, indicating that it is mostly BQ bonding after one hour BQ/ME immersion.

Comparing the one hour treatment with 7 hours and 24 hours treatment, it shows that the fraction of C_I increases along with time, indicating an increasing contribution from methanol bonding. This is consistent with the minority carrier lifetime measurement in Figure 2.8, that the highest lifetime in BQ/ME is achieved within the first one hour when BQ bonding to the surface is dominant, and then starts to decline with time, which might be attributed to the addition of ME on the surface. ME competing with, or replacing, BQ decreases the lifetime because ME is less effective as a passivant than BQ; BQ tends to repel negative charges that can induce a field effect on the Si surface, as discussed in Figure 4.7. The time evolution in Figure 3.1 also shows an increasing amount of the part attributed to adventitious carbon (in green).

3.3.2 Quantification of Surface Coverage

More detailed carbon 1s peak fitting of the 24 hours BQ/ME treated sample is shown in Figure 3.2. A low intensity peak located at 291.4eV with a 2.9% intensity is observed. This is the shake-up satellite caused by the delocalized electrons from the

aromatic ring. Based on this satellite signal, one carbon signal from the aromatic ring, C_{II}, is fixed 7eV lower at 284.7eV with a intensity 12.5 times stronger.⁷⁸ The peak at 286.2 is assigned to C_I, and the rest of the peaks are fitted into more oxidized carbon peaks. Assuming each BQ has two parts C_I and four parts C_{II}, while ME has only one part C_I, the ratio of C_I to C_{II} is 1.1, listed in Table 3.1, gives a ratio of methanol bonding to aromatic bonding of roughly 2.4 after 24 hours BQ/ME immersion, Equation 3.1. A large amount of methanol bonding on silicon surfaces is also observed by Chabal et al. in pure methanol via FTIR.⁷⁹

Table 3.1. XPS Data for BQ/ME-24hr Sample

	Name	Position/eV	Component con%
C1s	C+3	289.1	4.4
	C+2	287.5	10.5
	CO(CI)	286.2	41.9
	CH(CII)	284.7	37.6
	C-C	284.6	5.5
O1s	SiOSi	532.7	52.4
	SiOC	531.8	47.6
Si2p	SiOx	102.0	7.1
	Si 2p _{1/2}	100.0	31.0
	Si 2p _{3/2}	99.3	61.9

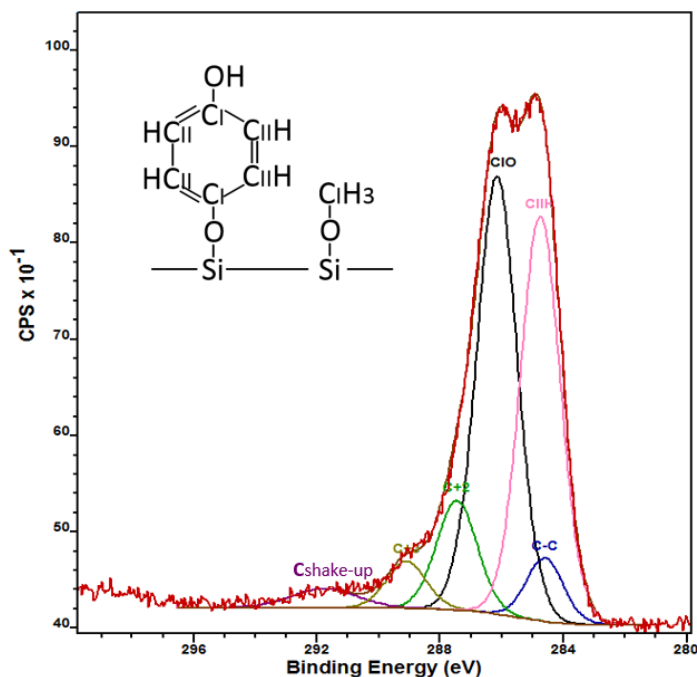


Figure 3.2. Carbon 1s spectra of the substrate after 24 hours BQ/ME treatment. Shake-up satellite peak implies the presence of aromatic groups on the silicon surface.

$$\text{Si} - \text{ME} : \text{Si} - \text{BQ} = 2.4 \quad \text{Equation 3.1}$$

Si signals in Figure 3.3 show a broad peak of Si in +1, +2 and +3 oxidation states (SiO_x) around 102.0eV. Using Lewis' quantification model, one can derive the coverage of the oxidized silicon on the surface.^{80,81} In Lewis' model, where the system is modeled as a flat Si surface terminated with a monolayer of alkoxy and aryloxy groups, the coverage of oxidized Si can be calculated from the relative areas of the bulk Si 2p and oxidized Si 2p peaks. If 100% of surface silicon atoms are oxidized, the measured atomic concentration ratio of oxidized Si to bulk Si is given by Equation 3.2, where I is the silicon intensity, n is the atomic number density (6.9×10^{14} atoms/cm² for Si (100)), σ is the Si atomic photoionization cross section and λ is the escape depth.

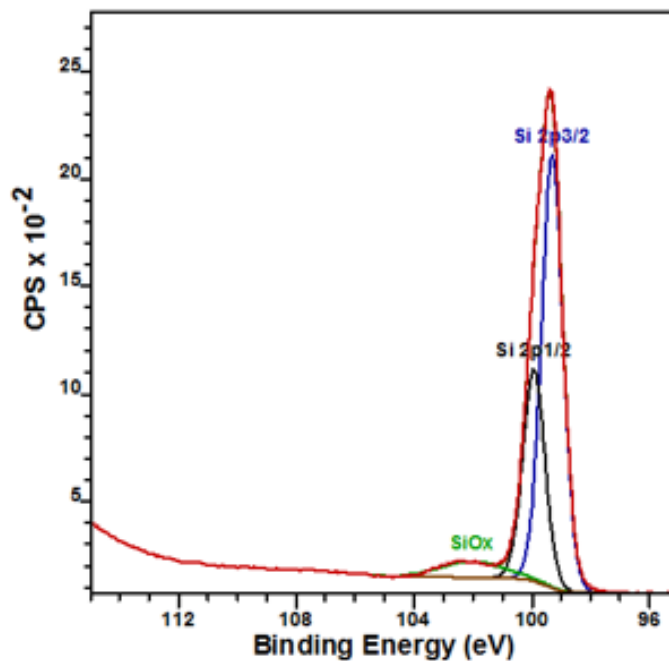


Figure 3.3. Silicon 2p spectra of the substrate after 24 hours BQ/ME treatment.

Using Equation 3.2, a surface to bulk concentration ratio of 0.18 is calculated for 100% oxidized monolayer on Si (100).⁸⁰ Comparing with our Si signals, where oxidized Si intensity is 0.07, yields roughly 40% total oxidized Si surface coverage, including contributions from SiOSi bond (including SiOH) and SiOC bond (SiO-alkoxy/aryloxy).

$$\frac{I_{\text{surface}}}{I_{\text{bulk}}} = \frac{I_{\text{surface}}}{I_{\text{total}} - I_{\text{surface}}} = \frac{n_{\text{surface}}\sigma}{n_{\text{total}}\sigma\lambda - n_{\text{surface}}\sigma} \quad \text{Equation 3.2}$$

The SiOSi (and SiOH) bond and SiOC bond can be further separated by assistance of the oxygen spectra in Figure 3.4, where SiOSi and SiOC bond are fitted into peaks at 532.7eV and 531.8eV respectively.⁸² Atomic concentration listed in Table 3.1 gives a ratio of 1.1 for these two components, Equation 3.3

$$\text{SiOSi} : \text{SiOC} = 1.1 : 1 \quad \text{Equation 3.3}$$

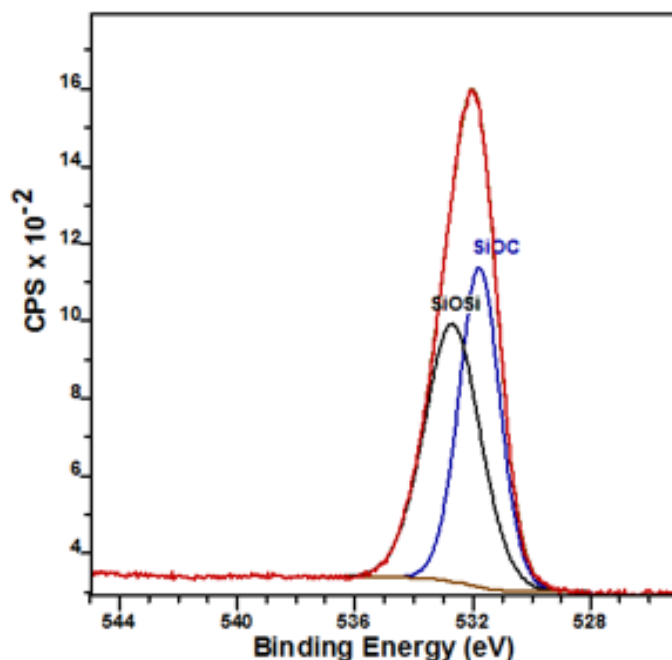


Figure 3.4. Oxygen 1s spectra of the substrate after 24 hours BQ/ME treatment.

Therefore, the 40% oxidized Si surface is constituted by 21% SiOSi and 19% SiOC. Since Si-ME is 2.4 times of Si-BQ, Equation 3.1, the 19% SiOC contains 13% Si-ME and 6% Si-BQ. Overall, the silicon surfaces after 24 hours BQ/ME treatment contains roughly 21% SiOSi, 13% ME and 6% BQ top surface monolayer coverage.

3.4 Conclusions

The surface study in this section confirms the bonding of aromatic groups to the surface. The time evolution study of the BQ/ME bonding mechanism shows that BQ bonding dominates for a one hour BQ/ME treated sample, and methanol bonding to the surface increases with increasing immersion time. This is consistent with the minority carrier lifetime measurement that the highest lifetime in BQ/ME is achieved within the first one hour when BQ bonding to the surface is dominant, and then starts to decline with time, which might be attributed to the addition of ME on the surface.

ME competing with, or replacing, BQ decreases the lifetime because ME is less effective as a passivant than BQ, which will be discussed in detail in chapter 4 and 5. The time evolution also shows an increasing amount of adventitious carbon and silicon oxidation with increasing immersion time.

In addition, quantitative analysis shows that the 24 hours BQ/ME treatment gives roughly 21% SiOSi, 13% ME and 6% BQ top surface monolayer coverage.

Chapter 4

BONDING THERMODYNAMIC STUDY BY DENSITY FUNCTIONAL THEORY*

4.1 Introduction

Hydrogen terminated silicon surface morphologies have been intensively studied in the past. At least three reconstructions exist on Si (100) surface under different preparation procedures, as shown in cross section in Figure 4.1. The chemical etch method used in our experiment will end up with an atomically rough surface with a combination of mono- and di-, or even tri-hydride species.^{83,84} Here both the monohydride and dihydride Si(100) surfaces are modeled to presents the system.

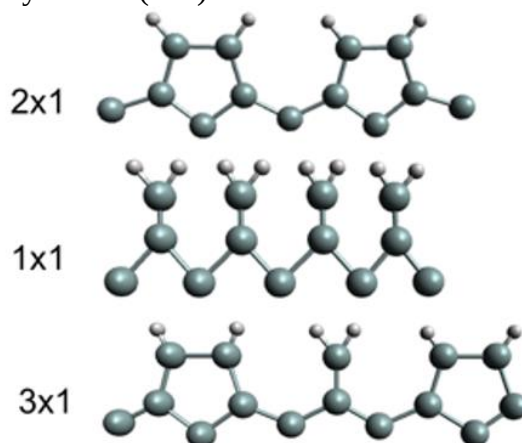


Figure 4.1. 2x1(monohydride), 1x1(dihydride), and 3x1(mixture of mono and dihydride) silicon surface reconstruction. Grey balls denote H atoms, and green balls denote silicon atoms.

* Reprinted with permission from Chen, M.; Hack, J. H.; Iyer, A.; Jones, K. J.; Opila., R. L. *J. Phys. Chem. C*. **2017**, 121 (39), 21364. Copyright 2017 American Chemical Society.

Thermodynamics calculations of BQ bonding on hydrogen terminated Si(100) surfaces are performed using both a monohydride cluster model and a dihydride surface slab approach of the Si surface. The cluster calculations employ the B3LYP/6-31+G(d,p) basis set approach as implemented within the Gaussian program.⁸⁵ A $\text{Si}_{35}\text{H}_{40}$ cluster formed by four monohydride dimers represents the system in Gaussian. Previous work has shown that B3LYP function is reliable to represent the silicon (100) surface, and 6-31+G (d, p) can be performed to give a relatively accurate calculation result with less time.^{86,87} The surface slab approach employs the Vienna Ab Initio software package (VASP), along with the generalized gradient approximations (GGA) to describe exchange and correlation.^{88–90} While the cluster model simplifies considerably the calculation of ionic states and the construction of full potential energy surfaces, the surface slab approach is more reliable. In this chapter, both Gaussian and VASP are employed to compare the BQ bonding on H-Si.

4.2 Experiment

The 2x1 monohydride structure is modeled using the Gaussian 09 package with the B3LYP/6-31+G(d,p) basis set. A $\text{Si}_{35}\text{H}_{40}$ cluster formed by 4 dimers represents the system, as illustrated in Figure 4.2. All silicon atoms at the edge of the cluster are saturated by hydrogen to achieve sp^3 hybridization. In the surface interaction study, bulk atoms (atoms in shadow) are fixed to mimic reality, while four silicon atoms in the first layer, together with four hydrogen atoms bonded to them are free to move.

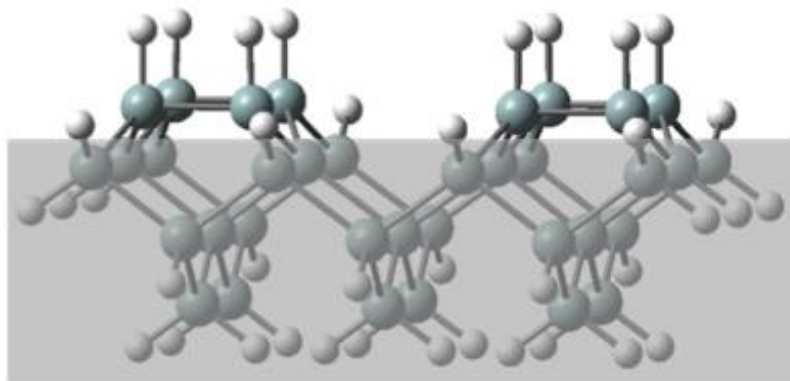


Figure 4.2. A $\text{Si}_{35}\text{H}_{40}$ monohydride cluster with bulk atoms fixed (atoms in shadow). All silicon atoms are saturated by hydrogen.

Dihydride DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP).⁹¹ The interaction between ions (nuclei) and electrons were described using projector augmented wave pseudopotentials.⁹² Electron-electron exchange and correlation interactions were described using the gradient corrected Perdew-Burke-Ernzerhof (PBE) functional.⁹³ The Brillouin-zone (BZ) integrations were performed using the Monkhorst-Pack (4x4x1) K-point set. The unit cell was a 4x4 periodic slab containing eight atomic layers. The coordinates of the Si atoms in the bottom six layers Si were kept fixed after silicon slab relaxation. The vacuum region was approximately 26Å and the energy cut-off was 300 eV. For the H-terminated Si, all top and bottom layer silicon atoms were terminated with two hydrogen atoms per silicon, as shown in Figure 4.3. This 1x1 canted-row dihydride structure is found to be energetically favorable with respect to the symmetric 1x1 dihydride, in good agreement with literature.⁸³ For the BQ-adsorbed Si, one of the two hydrogens adsorbed on Si was replaced by a BQ radical, QH^* , per unit cell. The coverage of QH^* was one QH^* per eight surface Si atoms.

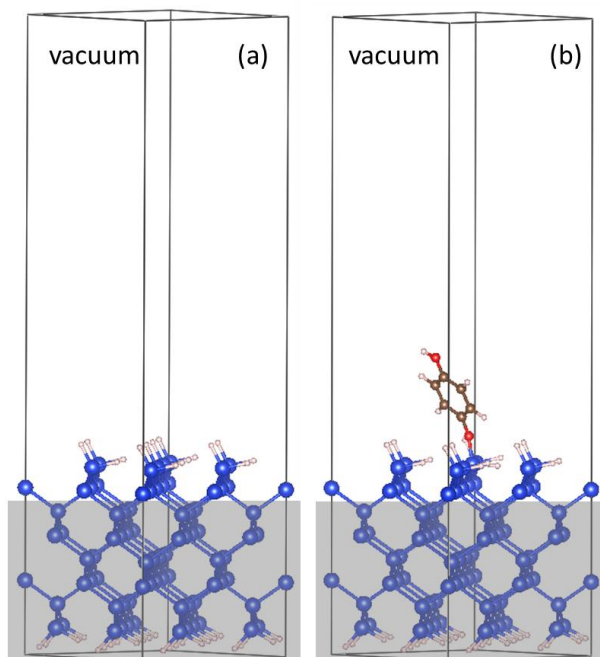


Figure 4.3. A dihydride-passivated (a) and BQ-adsorbed (b) Si slab with bulk atoms fixed (atoms in shadow) modeled using periodical boundary condition in VASP. The vacuum region was approximately 26Å.

4.3 Results

4.3.1 Thermodynamic Possibility of QH* Bonding

Based on our hypothesis, the QH* radical is the most likely species that bonds to the surface and improves the passivation. So, the first study in Gaussian was the thermodynamic possibility of this reaction. The final product is optimized using a Gaussian fitting, and the system energy is acquired. Comparing this energy with the energy of the starting configuration of the system, which is BQ and H-Si as illustrated in Figure 4.4, a negative energy for the reaction, -1.96 eV is obtained.

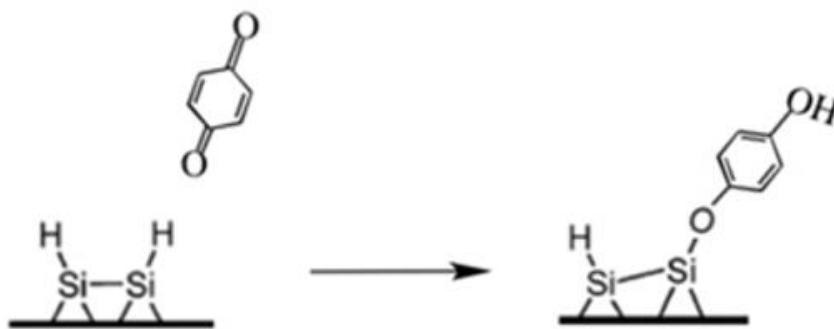


Figure 4.4. Proposed BQ reaction schematic on monohydride Si surfaces. QH* bonding can lower the system energy by 1.96 eV.

The negative free energy supports our previous results in that it is thermally possible for QH* to bond to the surface by allowing the system energy of 1.96 eV. However, the detailed reaction process is not provided at this point, e.g. the mechanism for the removal of hydrogen atoms from the surface, or the possible transition states studies. The dihydride Si surfaces were also modeled in VASP, and QH* bonding lowers the system energy by 2.23 eV.

4.3.2 Interface Bonding Structure

Adsorption energy is strongly associated with the molecular structure. The final products with the aromatic groups in different molecular orientations have varied adsorption energies. It has been reported by Xu et al. that [6+2]-like cycloaddition, across a dimer is the most exothermic over several other structures.⁹⁴ However, our DFT simulation gives different results.

We study the single-bonded “edge-on” and the double-bonded “face-on/cycloaddition Buckle” structure shown in Figure 4.5. The “edge-on” mode shows a 54.4° angle to the silicon surface, while the “face-on” has a 19.5° angle. In the “face-on” configuration, the aromatic ring is very close to fitting in the dimer, but still needs

to bend 19.5° to lower the geometric strain, which adds extra potential energy to the system.

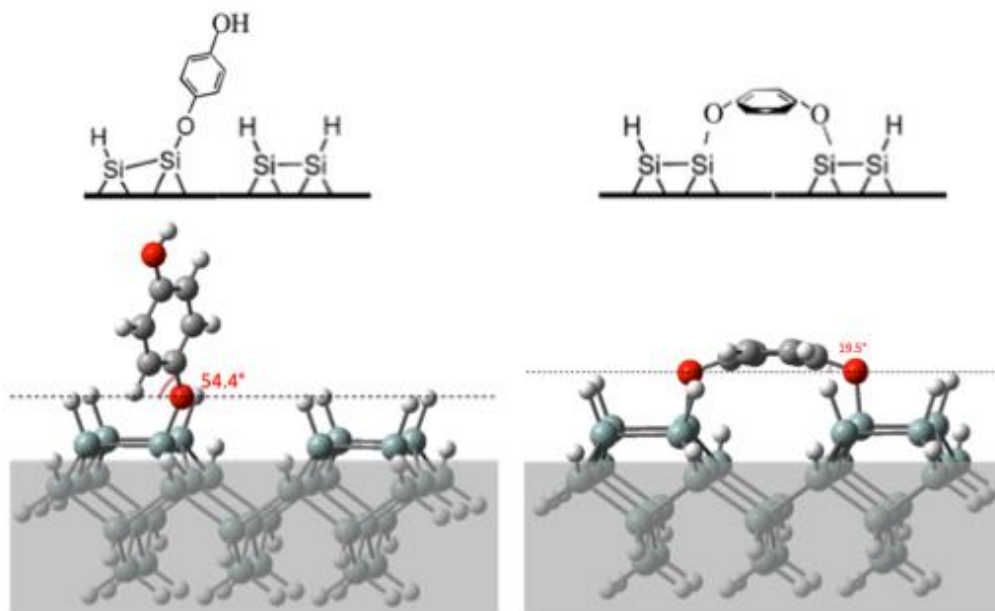


Figure 4.5. The "edge-on" mode (left) is 1.32 eV lower in energy than the "face-on" mode (right).

Data shows that “face-on” mode has an energy 1.32 eV higher than the “edge-on” mode. Compared with Xu’s previous work, these contradictory results are caused by the fixed structure of atoms in the bulk, which is closer to reality, while in Xu’s work, the whole cluster was allowed to relax substantially.⁹⁴

Transition states have not been considered at this point. Initial structures are very important in transition states study, but as mentioned before, the H-Si surface after chemical etching is complex, so a more complete model of the initial structure would be needed before a robust kinetic analysis could be addressed.

The dihydride Si surface modeled in VASP agrees with the results on monohydride Si site by showing that the “face-on” mode is 0.45 eV higher in energy

than the “edge-on” mode. Thus, the “edge-on” QH* bonding configuration is the preferred structure on both monohydride and dihydride silicon sites.

4.3.3 Competing Process Study

Previous sections strongly suggest that QH* is an important component of the passivation mechanism. On the other hand, research by Cahen et al. and Lewis et al. also observed the bonding of methanol to the surface and consumption of H-Si sites over time.^{50,59} Presumably, competing processes exist among BQ, QH* and MEO*. Here we calculate the energetic favorability of these three species by comparing their adsorption energies.

Adsorption energy is the energy difference between reactants and products, shown in Equation 4.1.

$$\Delta E_{adsorption} = E_{products} - E_{surface\ cluster} - E_{react\ molecules} \quad \text{Equation 4.1}$$

Three reactions on both monohydride and dihydride Si surfaces are sketched in Figure 4.6. Configurations in all reactions are optimized. All six reactions are thermodynamically possible, while MEO* is the most favorable species to bind to Si monohydride and dihydride defect sites, rather than QH* and BQ, which agrees with the XPS data showing a large presence of Si-methoxy groups on the surface. Steric effects might be an explanation for this result. From this competing process study, we can conclude that MEO* as well as QH* are the active and important species in bonding with silicon surfaces.

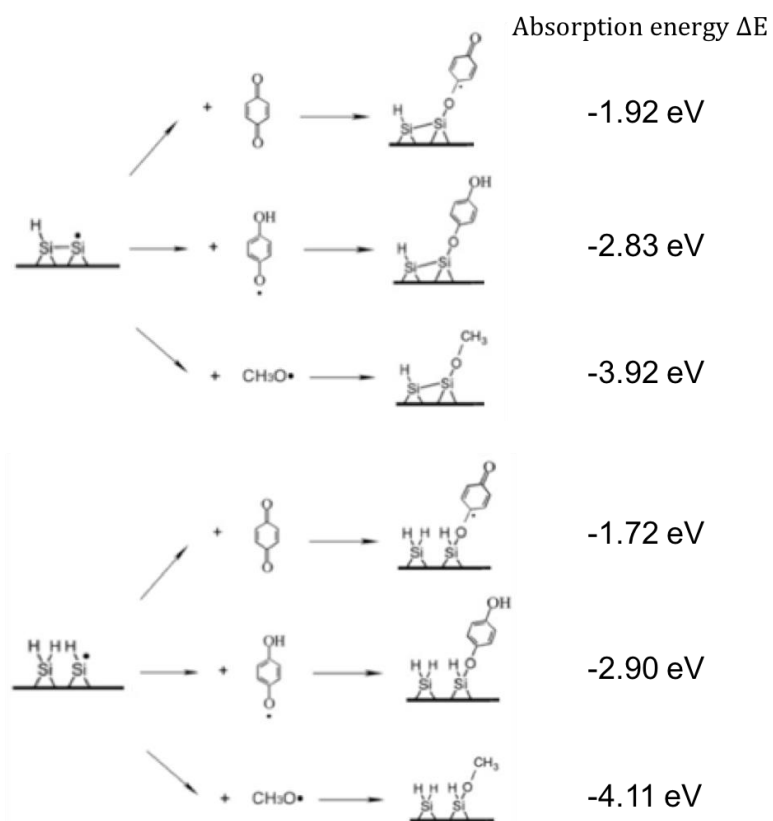


Figure 4.6. Competing processes in the BQ/ME passivation solution on Si monohydride and dihydride defect sites. Adsorption energy is calculated using Equation 4.1

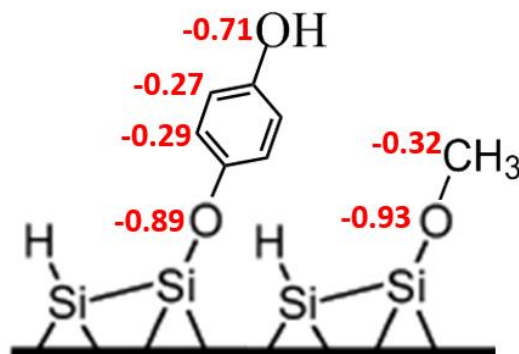


Figure 4.7. Electron distribution of bonded MEO* and QH* molecules. Larger numbers indicate greater electronegativity of each atom.

Additionally, the electron distribution in Figure 4.7 indicates that both QH* and MEO* might induce dipole moment on silicon surface, which will be discussed in more details in chapter 5.

4.4 Conclusions

In this chapter, monohydride and dihydride Si(100) surfaces have been modeled with Gaussian and VASP respectively, to study the thermodynamics of BQ bonding on Si(100) surfaces. It has been found out that it is thermally possible for QH* to bond to the surface by allowing the system energy of 1.96 eV on monohydride silicon free sites and 2.23 eV on dihydride sites.

Moreover, the bonding geometry has been studied, wherein the single-bonded “edge-on” configuration is more energetically favorable than double-bonded “face-on” configuration on both monohydride and dihydride silicon surfaces.

The competing processes among BQ, QH* and MEO* show that methanol radical MEO* has the most favorable adsorption energy for bonding to free monohydride and dihydride silicon sites, followed by QH* and then BQ molecule.

Dihydride silicon free sites are more reactive than monohydride silicon sites for radical bonding.

Chapter 5

ELECTRONIC STRUCTURE CHARACTERIZATION*

5.1 Introduction

The previous several chapters have been focused on understanding the chemical passivation mechanism by studying the BQ bonding on Si defect sites. In this chapter, we will discuss the electronic structure of BQ/ME passivated Si (BQ-Si). The work function of the BQ modified Si surface is determined by a combination of the surface band bending and electron affinity/ dipole.^{95,96} The quinone-induced silicon band bending will be explored using Scanning Kelvin Probe Microscopy (SKPM) and XPS, and surface dipole will be calculated by VASP.

5.1.1 Band Bending

The electronic properties of a semiconductor are dominated by the highest partially empty valence band (E_V), and the lowest partially filled conduction band (E_C). Fermi level, E_f , is the energy level at which there is a 50% probability that the level will be occupied. As demonstrated in Figure 5.1 (left), the more electron-rich materials, n-type, will have E_f closer to E_C , while the more hole-rich materials, p-type, will have E_f closer to E_V . An explanation of interfacial band bending was developed

* Reprinted with permission from Chen, M.; Hack, J. H.; Iyer, A.; Lin, X.; Opila, R. L. In *Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*; Elsevier Inc., 2017. Copyright 2017 Elsevier Inc.

by Schottky and Mott to explain the fermi level alignment when metals and semiconductors with different work functions contact, shown in Figure 5.1 (right).⁹⁷⁻⁹⁹

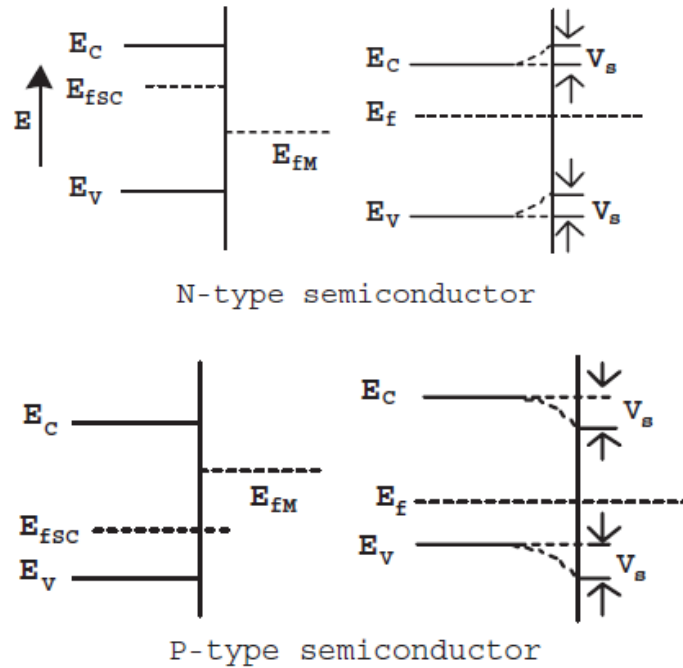


Figure 5.1. Plots showing the formation of semiconductor surface band bending when a semiconductor contacts a metal (E_C : the bottom of conduction band; E_V : the top of valence band; E_f : the Fermi energy level; SC: semiconductor; M: metal; V_s : the surface barrier). Copyright 2002 Elsevier Science.⁹⁹

In addition to metal/semiconductor contact induced band bending, band bending can also be induced by surface states, adsorption and field effect.¹⁰⁰ Take surface-state-induced band bending for an example. Surface states are electronic states found at the surface of materials. The surface states of a clean surface, the dangling bonds resulting from the termination of the periodic bulk structure at the surface, are called “intrinsic surface states”. These are found only at the atom layers closest to the surface. Additionally, “non-intrinsic surface states” can often form due to adsorbed impurities at the surface. The existence of these surface states induces electron and hole transfer from the bulk to surface, resulting a surface space charge region (SCR)

where a built-in electric field, V_s , is established and the valence and conduction band are bended, shown in Figure 5.2. V_s is also called surface potential barrier. Generally, the width of the SCR is of the order of $1\text{--}10^3$ nm, depending on the doping and dielectric constant of the material.¹⁰¹ In the case of solution passivation, like BQ/ME passivation, band bending may exist on semiconductor surfaces due to the different chemical environment between surface and bulk, such as the termination of lattice periodicity at the surface, absorption of molecules, or contact with other materials.^{99,100,102}

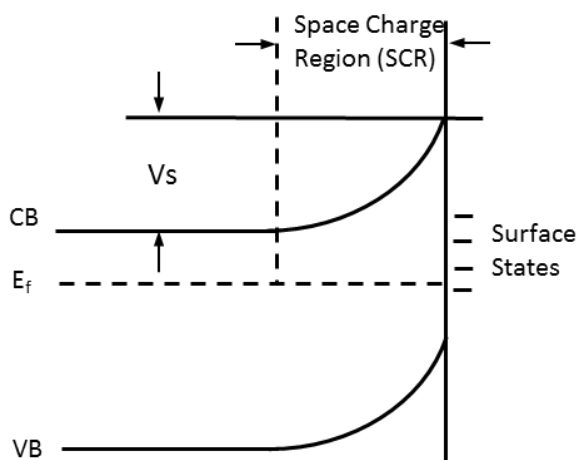


Figure 5.2. Upward band bending on n-type semiconductor surface. CB: the bottom of conduction band; E_f : the fermi energy level; VB: the top of valence band; V_s : the surface potential barrier.

5.1.2 Band Bending Measurements

Band bending can be probed with the surface photovoltage (SPV) technique. The SPV measurement is a contactless and non-destructive technique to characterize band bending by measuring light induced changes on the semiconductor surfaces.^{99,102} For passivation samples, it can offer important information about surface and interface such as surface band bending, and carrier transport rate.

In SPV measurement, when a semiconductor is excited by light with sufficient energy, the absorbed photons will generate free charge carriers by creating electron–hole pairs. Figure 5.3 shows that electrons and holes travel in opposite direction due to the built-in potential. When a new equilibrium is established, the degree of band bending will also change. The difference in V_s before and after illumination is the surface photovoltage signal. When SPV reach saturation, the charge can completely flatten the surface band.¹⁰³ Therefore, band bending can be probed by changing the illumination conditions.

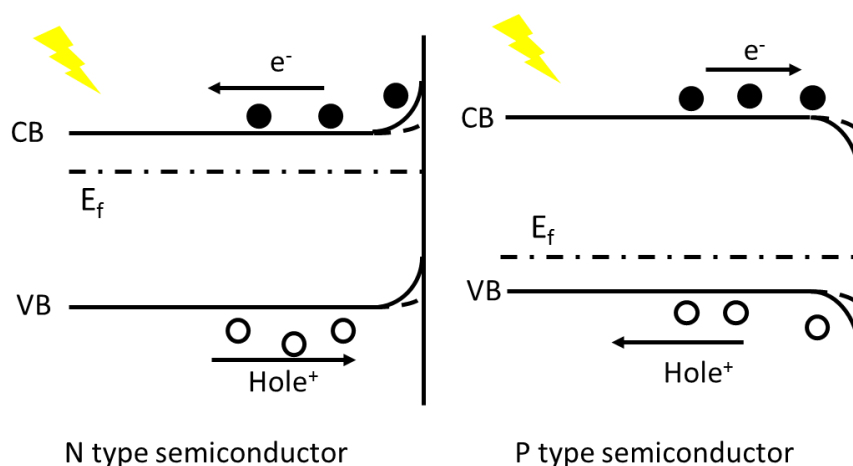


Figure 5.3. The charge behavior on exposure to light.

The band bending at solid interfaces is usually estimated from various optical and electrochemical measurements. The Kelvin probe is a traditional method for measuring relative changes in work functions. This method was first designed by Tomas, and later modified by Lord Kelvin.¹⁰⁴ Now the Kelvin probe can also work with atomic force microscopy and perform high spatial resolution measurements.¹⁰² In the Kelvin probe measurement, two surfaces of different material are considered as two sides of a parallel capacitor. When a metal plate has back contact with a

semiconductor, a MIS structure is formed, and the contact potential difference (CPD) will be affected by the surface band bending as shown Figure 5.4. The change of CPD under illumination can also be used to measure the surface photo voltage. Michael Grätzel had used this method to measure the SPV of a metal oxide electrode in dye sensitized solar cell, and get the relative energy level configurations for semiconductor/dye interfaces.¹⁰⁵ This modification also shows that the Kelvin probe can measure samples in liquid.

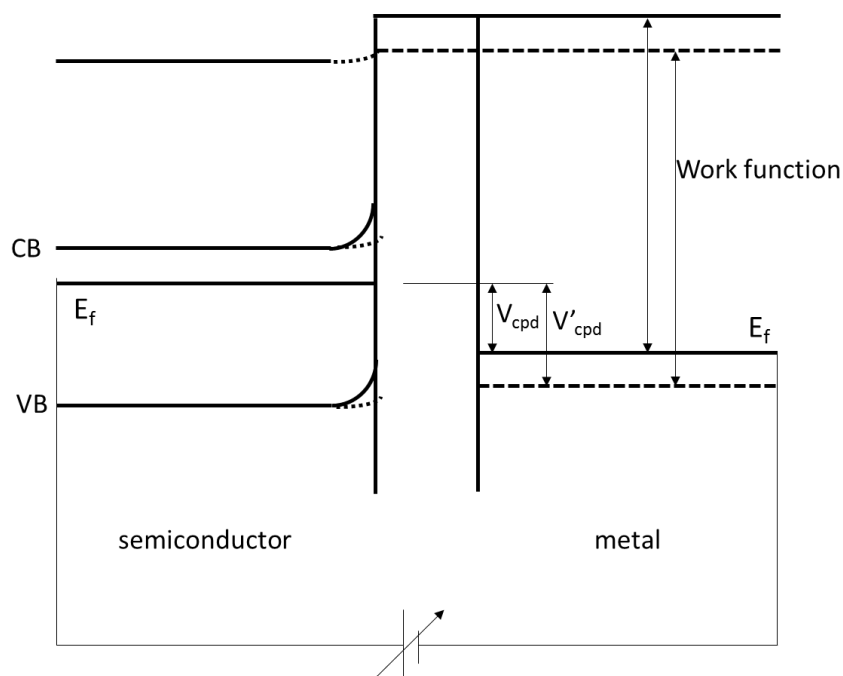


Figure 5.4. The basic structure of the Kelvin probe for surface photovoltage by measuring the contact potential difference between two surfaces.

As shown in Figure 5.5, photoelectron spectroscopy (PES) can also measure the binding energy of semiconductors. Since PES is a very surface sensitive technique, the changing band bending region from surface photovoltage will change surface charging, and then change the binding energy of valence band and core level peaks. In photoelectron spectroscopy, electrons with a binding energy of EB are excited by

incident photons with energy $h\nu$, ultraviolet photons or X-ray, and escaped from the top 0 to 10nm of the material surface. Detector captures the photoelectrons and measures the kinetic energy E_{kin} and number of the electrons. The binding energy, E_B , can be calculated with the equation below,

$$E_B = h\nu - E_{\text{kin}} - \phi_{\text{det}}, \quad \text{Equation 5.1}$$

Where ϕ_{det} is the work function of the detector. SPV can be calculated by directly measuring the valence band maximum with ultraviolet photoelectron spectroscopy (UPS) where 10–45 eV ultraviolet incident photons are used to excite the valence electrons. On the other hand, core electrons on the sample surfaces that excited by incident X-ray with energy 200–2000 eV in X-ray photoelectron spectroscopy (XPS) can also be used to study SPV.

Recently, Sezen and Suzer group reported a series of studies on $\text{Si}^{106,107}$ and GaN^{108} surface using XPS as a probe for SPV under ultrahigh vacuum conditions. They used element core level peak shifts to detect the charging change from illumination. The binding energy shift is repeatable when turning light on and off. They also discovered that a SiO_2 layer on a Si surface can increase the band bending in P-doped Si and decrease the band bending in N-doped Si.

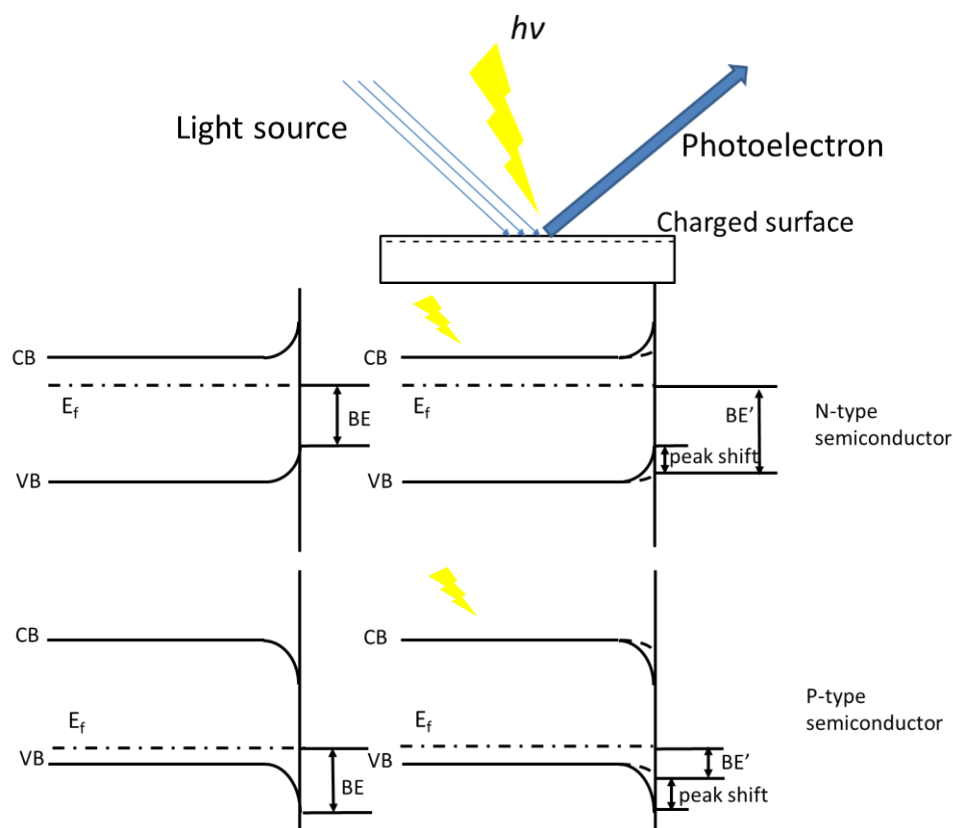


Figure 5.5. Surface photovoltage experiments with PES. The binding energy (BE) of the valence band maximum (VBM) can be defined as the energy between the VBM and the Fermi level. Illumination can flatten the band bending at the surface. The core-level binding energy will increase for an N-type semiconductor and decrease for a P-type semiconductor.

5.1.3 Surface Dipole

The second component of the work function is the surface electron affinity χ . A dipole induced by an adsorbed polar molecule can alter the surface electron affinity and result in a change in the work function. The dipole contribution can be independently determined through density functional theory (DFT) calculations.¹⁰⁹ Since DFT calculations do not include doping and, therefore, the band-bending component of the work function is not included, then the difference in the calculated work function Φ can be attributed to the dipole δ , Equation 5.2.

$$\delta_{BQ-Si} = \Phi_{BQ-Si}^{DFT} - \Phi_{H-Si}^{DFT} \quad \text{Equation 5.2}$$

In this study, the conduction and valence band bending on BQ and methanol treated n-type silicon surfaces will be characterized using both Kelvin Probe and X-ray photoelectron spectroscopy (XPS). The surface dipole will be calculated using DFT in the Vienna Ab initio Simulation Package (VASP). The work function of the BQ-Si surface relative to the H-Si surface can then be calculated from the band bending and dipole behaviors.

5.2 Experiment

The wafers used in this work were double side polished n-type silicon (100) FZ wafers with a resistivity of 1-5 ohm-cm and $280 \pm 20 \mu\text{m}$ thickness.

The same cleaning procedure described in chapter 2.4 was used for every trial to achieve hydrogen termination: The first step was a piranha clean consisting of a 5-minute bath in a 4:1 solution of sulphuric acid and hydrogen peroxide. Piranha solutions were freshly made and cooled at room temperature for 10 minutes before use. Subsequently the wafers were given a 5 minute DI water submersion and then followed by a 2-minute HF (2%) immersion. These H-Si wafers were then briefly rinsed with DI water and blown dry with N_2 .

The cleaned H-Si wafers were quickly placed in a sealed plastic bag containing a 0.01 mol/L BQ/ME solution or pure methanol solution to achieve BQ or ME termination. Samples were kept in BQ/ME for one hour and 24 hours in ME before SPV testing for an optimal passivation effect based on the immersion time study in Figure 2.8.

SPV was measured using a Physical Electronics model 5600 X-ray photoelectron spectrometer (XPS) with an overall accuracy of 0.05 eV. A 300W Xenon lamp was used for illumination, where the light was focused on the sample surface through a quartz window on the XPS chamber. Silicon samples were grounded with carbon tape on the stage. The XPS chamber was kept in ultra-high vacuum and cooled to around 17°C.

Scanning Kelvin Probe Microscopy (SKPM), equipped in an Asylum Research MFP-3D AFM was also used to study SPV. The silicon tips coated with Pt were calibrated with freshly peeled HOPG. Illumination of the sample carrier excitation was done by a 650nm red laser with a power output of 20mW. Measurements were taken under nitrogen purge in ambient room condition.

Dipole calculations were performed for a dihydride-passivated and an BQ-adsorbed Si (100) surface, Figure 4.3, using VASP with the same settings described in chapter 4. Absorption of BQ is chosen to happen only on the front surface of the silicon to match the surface measurements in Kelvin Probe and XPS.¹¹⁰

5.3 Results

5.3.1 SPV Measurements by XPS

Band bending on three n-type Si(100) wafers were studied via XPS: H-terminated Si (H-Si), BQ/ME passivated Si (BQ-Si) and methanol treated Si (ME-Si). The hydrogen termination was achieved by using the piranha/HF cleaning procedure described in the experimental section. BQ-Si and ME-Si were achieved by immersing H-Si in BQ/ME or ME solution for one hour and 24 hours respectively before testing,

based on the immersion time study in Figure 2.8 where the BQ/ME is observed reaching the highest passivation in one hour and ME passivation takes 24 hours.

Figure 5.6 shows the shift of Si 2p peak of H terminated Si and BQ treated Si with xenon light on and off. Si 2p shifts to lower binding energy on both samples in the light condition, while BQ/ME-Si shifts more than the H-Si sample. Repetitive light and dark conditions were performed on Si samples with three different treatments, recorded in Figure 5.7. It can be seen that a repeatable energy shift to lower binding energy in the illumination condition exists on all three samples, which indicates a downward band bending.

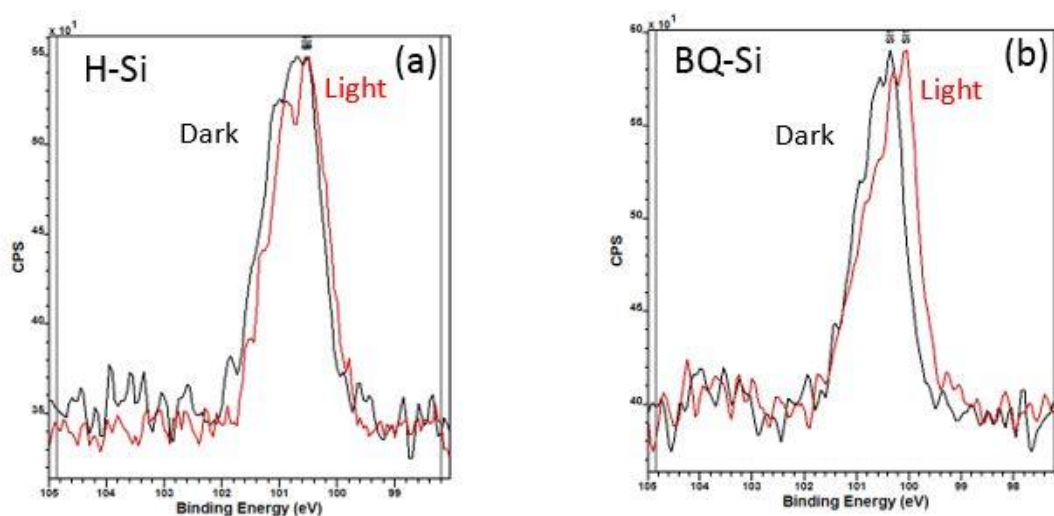


Figure 5.6. N type silicon peak shift with light on and off for H-Si (a) and BQ-Si (b).

5.3.2 SPV Measurements by SKPM

N-type Si(100) wafers with three different surface treatments, H-Si, BQ-Si and ME-Si as described in the previous section, were studied in SKPM. The contact potential difference (CPD) between the Kelvin probe tip and the grounded samples' surface were recorded in a scan size of $3\mu\text{m} \times 3\mu\text{m}$, shown in Figure 5.9. An initial scan found high spatial homogeneity of the contact potential difference, with less than 5mV of variation across the area of the sample.

For all samples, a reproducible shift of CPD is observed when the 650nm light source is switched on and off during the scan. The average CPD values in each $0.5\mu\text{m} \times 3\mu\text{m}$ region are reported relative to the HOPG reference in Figure 5.10. It can be seen that the shift in potential between the light and dark conditions is consistent across the area of each sample with an error bar smaller than 5mV. Comparing the 10mW (depicted in red) and 20mW (depicted in blue) light irradiation on BQ-Si, both reach an illuminated CPD of around 450mV. This suggests that the 20mW 650nm laser illumination is close to approach a flat-band condition of around 450mV on this sample. Similar results are found for the H-Si sample. However, the illuminated CPD of the ME-Si surface is observed to be 200mV higher. This could be explained by a change in grounding or differing surface dipoles between the treatments, but would not affect the magnitude of the surface photovoltage.

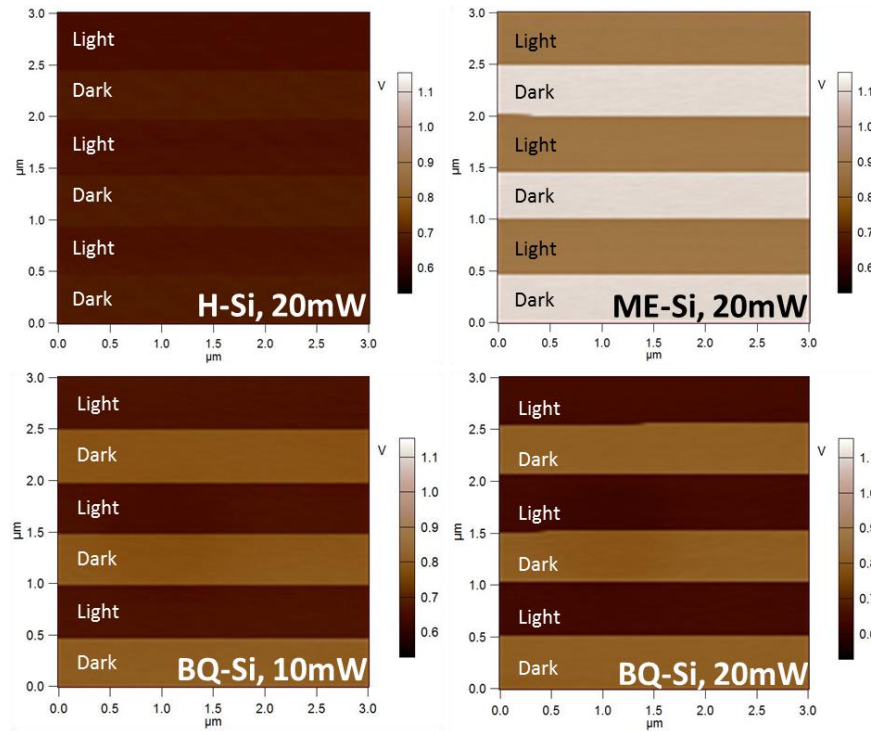


Figure 5.9. CPD map of n-type silicon wafers under three surface treatments: H-Si, BQ-Si and ME-Si. The Kelvin probe scan size was $3\mu\text{m} \times 3\mu\text{m}$. Tip potential was -217mV with respect to an HOPG reference. Surface contact potential of all samples shift when the 650nm laser (10mW or 20mW) was switched on and off during the scan.

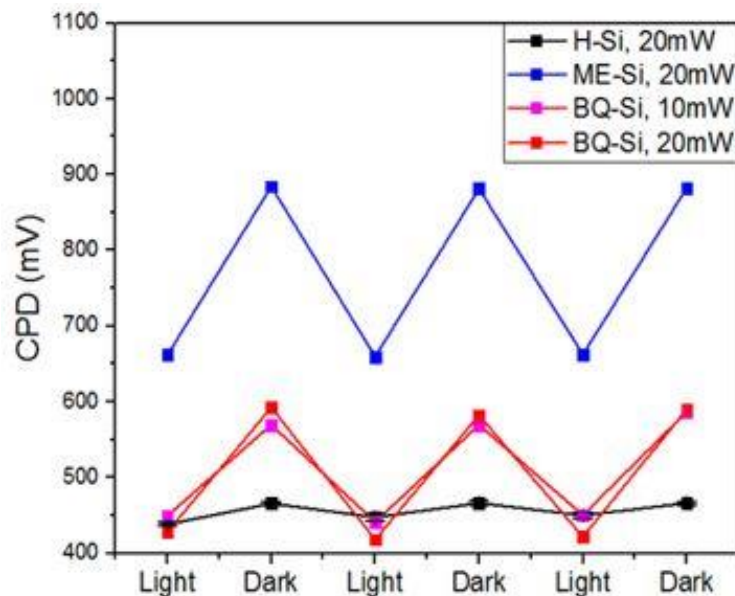


Figure 5.10. CPD values measured by Kelvin probe for n-type silicon wafers under three surface treatments, H-Si, BQ-Si and ME-Si, with respect to HOPG. A

reproducible shift of CPD is observed when the 650nm light was switched on and off during scan.

Surface photovoltage (SPV) is obtained by calculating the difference of CPD between light and dark conditions, shown in Figure 5.11. The negative SPV values confirm a downward band bending for n-type Si with all three surface treatments. However, band bending on ME-Si is observed higher than BQ-Si, in contrast to the XPS results, which might be caused by the interference of oxygen oxidization on BQ-Si caused by inefficient N₂ purge.

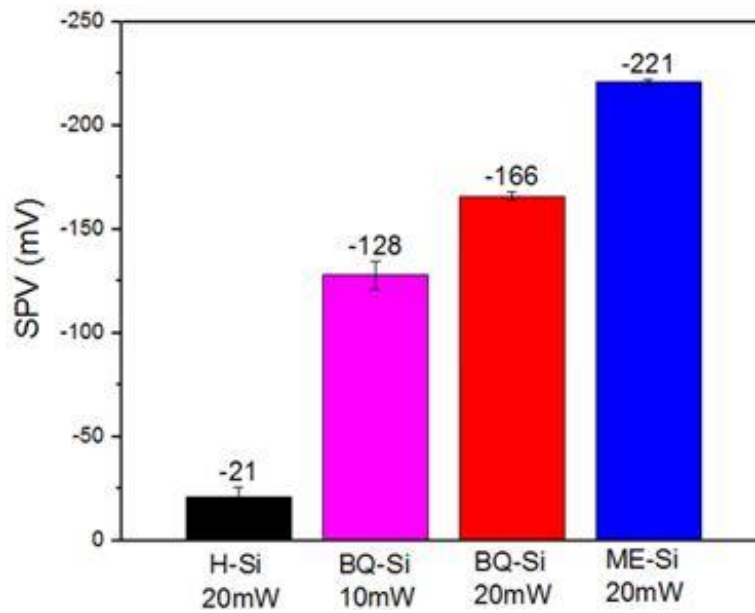


Figure 5.11. SPV values measured by Kelvin probe for n-type silicon wafers under three surface treatments, H-Si, BQ-Si and ME-Si.

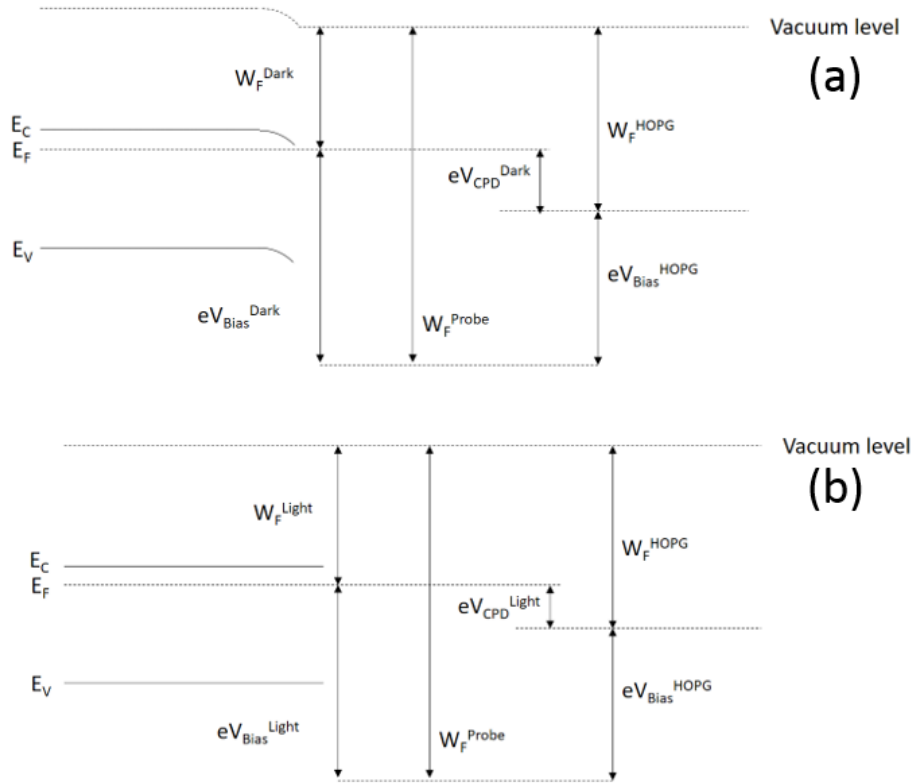


Figure 5.12. Energy levels measured in a dark Kelvin probe measurement (a) and light Kelvin probe measurement in the flat-band condition (b).

The energy levels measured in dark and light condition in Kelvin probe are illustrated in Figure 5.12. The applied bias voltage V_{Bias} is equal to the difference in work functions of the probe ($W_{\text{F}}^{\text{Probe}}$) and sample ($W_{\text{F}}^{\text{Light}}$ or $W_{\text{F}}^{\text{Dark}}$). To remove the effect of the unknown probe work function, the contact potential difference V_{CPD} is reported relative to the bias measured on an HOPG reference sample. The difference in $V_{\text{CPD}}^{\text{Light}}$ and $V_{\text{CPD}}^{\text{Dark}}$ gives the surface photovoltage, SPV. The work function of the BQ passivated n-Si surface is thus found out to be 4.15 eV.

With SKPM, it further confirms that immersing H terminated Si in BQ and ME solutions increases the downward band bending, which agrees with the band bending

reported by XPS in Figure 5.7. Additionally, the work function of the BQ passivated n-Si surface is calculated to be around 4.15 eV by SKPM.

5.3.3 Surface Dipole and Work Function Calculation

The second component of the work function is the surface electron affinity χ^S , which is defined as the energy required to excite a surface electron from the bottom of the conduction band to the local vacuum level.¹¹¹ The surface dipole (δ) equals the difference between the surface electron affinity χ^S and the bulk electron affinity χ^B (4.05 eV for χ^B), Equation 5.3.^{112,113} Depending on the dipole size and direction, the molecular dipole can increase or decrease χ^S . A negative dipole with respect to surface normal decreases χ^S and Φ because an emitted electron is accelerated within this dipole field on its way from the conduction band at the surface into the local vacuum, and vice versa.

$$\delta = \chi^S - \chi^B \quad \text{Equation 5.3}$$

Surface dipole introduced by the bonding of the BQ radical were calculated using VASP. The computed electrostatic potential difference is the change in the surface dipole component of the work function, since the potential contribution from the bulk to the work function remains the same for both H-Si and BQ-Si surfaces. In VASP, the work function Φ is the difference between the vacuum potential E_{vac} and fermi level ε_F :

$$\Phi = E_{vac} - \varepsilon_F \quad \text{Equation 5.4}$$

The calculated electrostatic potential profiles for H-Si and BQ-Si surfaces are shown in Figure 5.13. A decrease in work function due to a surface dipole $\delta =$

−0.04 eV upon BQ adsorption is observed. The dipole energy shift observed agrees with our previous DFT calculation in Gaussian, shown in Figure 4.7, where the BQ bonding group was shown to be an electron-rich system.

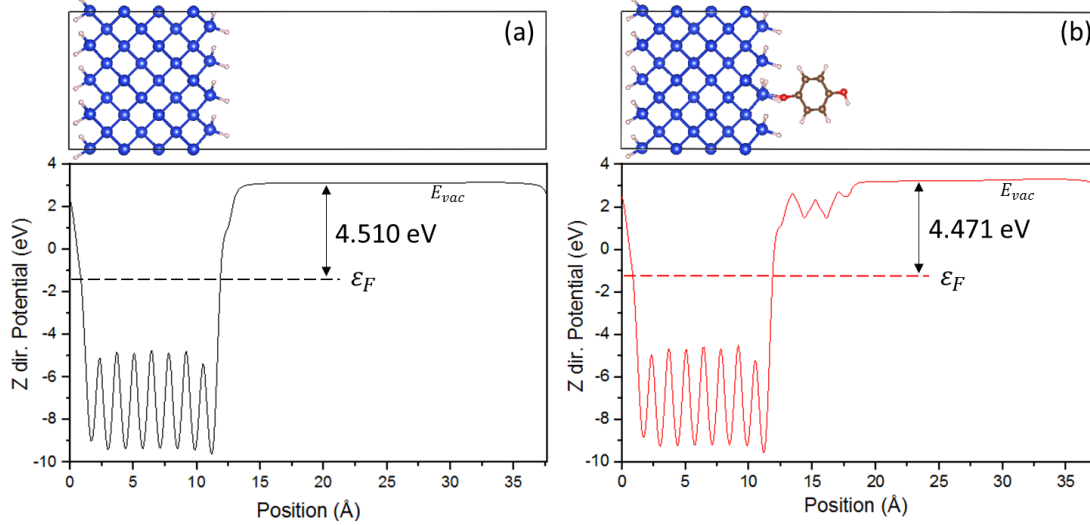


Figure 5.13. Cross-section of a unit cell and the corresponding laterally averaged electrostatic potential profile for the H-Si (a) and BQ-Si (b) slab. The potential difference between the fermi level and the vacuum is denoted.

The work function of the BQ passivated n-Si surface, shown in Figure 5.14, can thus be calculated using the following equations:

$$\begin{aligned}\chi^S &= \chi^B + \delta = 4.05 \text{ eV} - 0.04 \text{ eV} = 4.01 \text{ eV} \\ E_{CBM} &= CB - \varepsilon_F - E_{BB} = 0.27 \text{ eV} - 0.17 \text{ eV} = 0.10 \text{ eV} \\ \Phi &= \chi^S + E_{CBM} = 4.11 \text{ eV}\end{aligned}$$

where $CB - \varepsilon_F = 0.27 \text{ eV}$ is based on the Si doping level of 10^{15} cm^{-3} , and the band bending energy $E_{BB} = 0.17 \text{ eV}$ is obtained from the SKPM results in Figure 5.11. The work function of the BQ passivated n-Si surface is thus found out to be 4.11 eV, in agreement with the 4.15 eV found in SKPM when using HOPG as a reference. It should be noted that the coverage of QH* simulated here is larger than experimental coverage, and QH* bonding is not the only component of the surface dipole,

methanol, oxidation and other surface irregularities contribute to the experimentally measured value of the surface dipole as well. The electronic structure of BQ passivated n-Si surfaces in Figure 5.14 further explains the BQ passivation mechanism, where both the dipole δ and the downward band bending E_{BB} contribute to the decrease of the Si surface work function, resulting in accumulation, a more electron-rich surface. With the chemical bonding mechanism found in previous work, we conclude that BQ passivation on n-Si decreases the surface defect states, as well as forms an electron accumulation layer decreasing the minority carrier density on the surface.

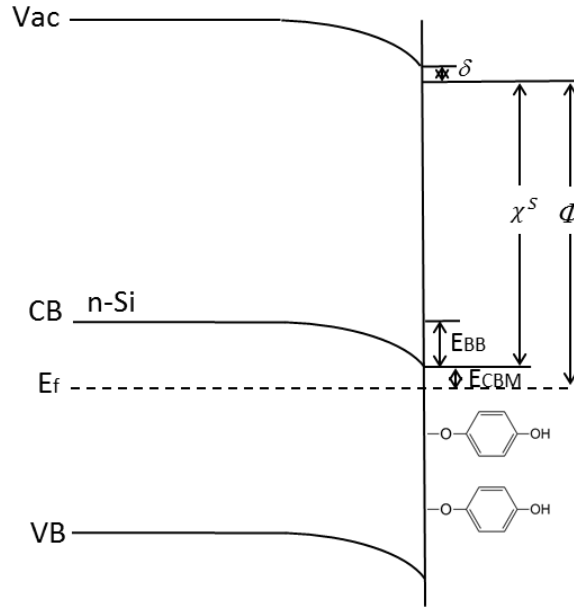


Figure 5.14. Electronic structure of BQ passivated n-Si surfaces. Both the dipole δ and the downward band bending E_{BB} contribute to the decrease of the Si surface work function upon bonding of BQ radicals.

5.4 Conclusions

Surface photovoltage measurements via both the photoemission and SKPM techniques indicate a downward band bending of H-Si and BQ and ME treated

samples. This suggests the creation of an accumulation layer of majority carriers near the surface, with a significant field-effect contribution to the observed surface passivation. It is seen that subsequent treatment of hydrogen terminated Si with solutions of methanol and benzoquinone further increases the magnitude of band bending. It is expected that variations between samples in the amount of oxide formation at the surface could explain some of the variation in SPV values recorded between the two measurement methods. The highest SPV values recorded for the ME-Si and BQ-Si samples of about -220mV are approaching the fermi level – conduction band crossover. The similar magnitudes of surface band bending observed with both the BQ-ME and ME treatments is consistent with the expected mechanism of the surface modification, in which both BQ radicals and methanol radicals adhering to the surface. This work, verified by two measurement techniques, is contrary to the suggestion of Cahen et al. that BQ-Si exhibits an upward band-bending, suggesting a different method of field-effect passivation.⁵⁰

DFT calculations observe a decrease in work function due to formation of the dipole upon bonding of BQ radicals on the surface, decreasing the surface electron affinity. Considering the 0.04 eV shift due to the dipole δ and the 0.17 eV downward band bending E_{BB} , the work function of BQ-Si is found to be 4.11 eV. Both the dipole and downward band bending contribute to the formation of electron accumulation on n-Si passivated by BQ.

With the chemical bonding mechanism found in chapter 2-4, we can conclude BQ passivation on n-Si mechanism, that BQ radicals bonding on n-Si decreases the surface defect states, as well as forms an electron accumulation layer, decreasing the minority carrier density on the surface.

Chapter 6

ORGANIC-INORGANIC HYBRID DEVICE*

6.1 Introduction

The search for low cost photovoltaics has brought up great interests in organic materials because of the low costs of organics, easy solution processing, high throughput and possible recyclability. Organic photovoltaics (OPV) have been fabricated with organic materials that are donor-acceptor blends with both conducting and semiconductor properties.

The most common mechanism of OPV devices consists light absorption, exciton diffusion, charge separation and charge transport and collection, Figure 6.1. The excitons are formed on absorption of light, and then diffuse towards the donor-acceptor interface. At the interface, the exciton undergoes a charge transfer reaction, forming a hole and electron in the donor and acceptor layers, respectively. In this process an electron is transferred from the donor to the acceptor, in an exothermic process. After the hole and electron are generated, they are conducted through the donor and acceptor materials and extracted by the electrodes and the photocurrent is generated. A poor generation and transportation of electrical charges are the common limitations of the OPV efficiency. The efficiency record of OPV devices is still low, 13.2% by Heliatek in Feb 2016, comparing with the efficiency of over 25% for silicon

* Reprinted with permission from Hack, J. H.; Iyer, A.; Chen, M.; Opila, R. L.; In *IEEE Photovoltaic Specialists Conference.*; 2017; pp 1–6.. Copyright 2017 IEEE.

based solar cells.¹¹⁴ A further problem is lifetime, where photo induced degradation of organic materials is still a major downfall of this technology.

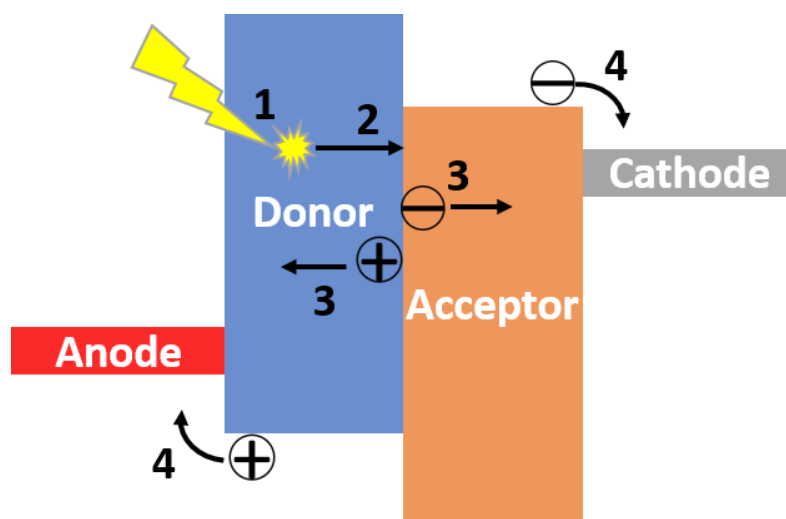


Figure 6.1. OPV device operating principle. Step 1, light absorption; step2, exciton diffusion; step3, charge separation; step4, charge collection.

One good approach in solving the problems is organic-inorganic hybrid solar cells that incorporate both material groups.^{115,116} Inorganic semiconductor materials are generally better light absorbers than organics, and have better electronic properties, like a high dielectric constant, a high charge mobility and environmental stability.^{117–}
¹¹⁹ Incorporating semiconductor materials with organics will take advantage of the solution-processability of organics and enhanced charge generation and transportation in inorganics.

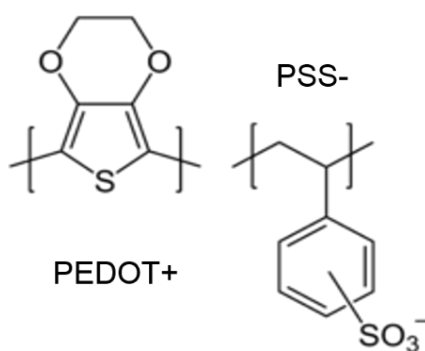


Figure 6.2. PEDOT:PSS is a polymer mixture of two ionomers.

A lot of research have been done in looking for good combinations of organics and inorganics.^{120–124} PEDOT:PSS (Poly(3,4-ethylenedioxy-thiophene):poly-(styrenesulfonate)) has been widely used as hole-collecting layers in hybrid solar cells due to its high light transmission, hole extraction, long-term stability and solution processability.^{125,126} PEDOT:PSS is a mixture of two ionic polymers, PEDOT-rich conductive cores and PSS-rich outer shells, Figure 6.2. PEDOT is an insoluble polymer, but by adding PSS as the charge balancing counter ion, an aqueous mixture is possible. With a deep work function of ~ 5.0 eV in PEDOT:PSS film, a well-defined Schottky junction with silicon can be formed in the interface.¹²⁷ PEDOT:PSS/Si based heterojunction has been extensively investigated as one of the potential techniques to realize low-cost PV application^{122–124,127}, and further improvements in the PEDOT:PSS/Si interface are needed in order to reduce the carrier recombination lose and increase the efficiency. Here we will apply BQ in the PEDOT:PSS/Si interface to confirm the passivation effect in the hybrid device.

6.2 Experiment

An n-type silicon wafer with textured surfaces was used as substrate. Texturing was achieved by a low concentration (<2%) KOH etch, that etches silicon anisotropically in the $\langle 100 \rangle$ plane, creating a random pyramidal textured surface

(provided by Arizona State University). Back surface field (BSF) were created by POCl_3 diffusion reaching $100 \, \Omega/\square$ sheet resistance. This BSF region creates band bending which reduce the rear side surface recombination.

The textured wafer was cleaned using a Piranha etch ($\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2 = 4:1$) for five minutes, followed by a five-minute DI water rise and a two-minute immersion in hydrofluoric acid (HF, 2wt%) to obtain hydrogen terminated surfaces. After cleaning, the substrates were quickly dried with a nitrogen gun and immediately placed in the 0.01M BQ/ME passivation solution. Wafers are kept in the solution for one hours to achieve the maximum passivation based on the carrier lifetime study in chapter two.

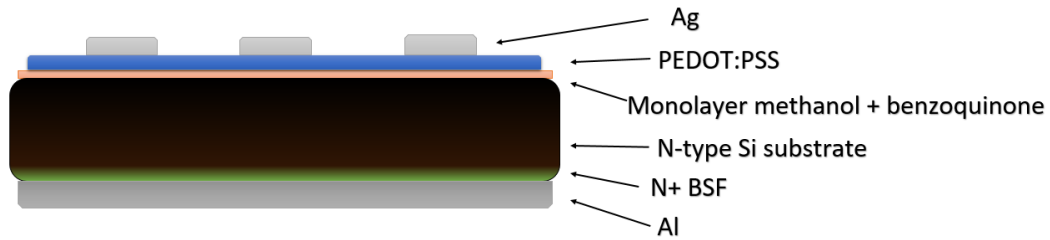


Figure 6.3. Device structure of the PEDOT:PSS-BQ-Si solar cell. Surface texturing not depicted. © 2017 IEEE

PEDOT:PSS is then spin coated onto the front surface, in which 7% dimethyl sulfoxide (DMSO) is added to increase the conductivity and 0.25% Triton X-100 (from Sigma Aldrich) acting as a surfactant. Aluminum back contact and silver front contact are then deposited via electron beam vapor deposition. Device structure is shown in Figure 6.3.

6.3 Results

Several optimizations on the device structure were performed in this work. First, we looked at the substrate resistivity, which has been demonstrated having a

large impact on open circuit voltages. Cahen et al, has reported that diodes made from hydroquinone on c-Si display an increase of approximately 70mV in open circuit voltages for every order of magnitude decrease in substrate resistivity.³⁸ Kotulak et al, has seen decreases in fill factor for device with lower resistivity that potentially caused by higher bulk recombination.¹²⁸ In this work, substrates with resistivity less than 25 $\Omega\cdot\text{cm}$ were studied and the best performance was found for wafers with resistivity around 1 $\Omega\cdot\text{cm}$.

Different front and rear contacts were studied to achieve the best ohmic contact in the device to reduce resistive losses. Ti/Pd/Ag stacks are commonly used for n-type contacts, however transmission line measurements yielded higher resistance values for these contacts and in some cases showed a non-linear voltage dependence. Aluminum was found out being a better back contact for our device comparing with Ti/Pd/Ag, which might attribute to the better ohmic contact created by Al and prevention of additional junction. Ti/Pd/Ag was also compared to Ag as an alternative front contact. Of the metals tested, Ag remained the best choice for the front contact. Results of the preliminary hybrid device are shown in Table 6.1 and Figure 6.4, published by Hack, et al.¹²⁹

Table 6.1. Results of the hero hybrid device. © 2017 IEEE

Jsc (mA/cm ²)	Voc (V)	n (%)	FF (%)	Rs(Ohm cm ²)	Rsh (Ohm cm ²)	Area (cm ²)
28.6	.545	9.6	61.6	1.769	425.336	1

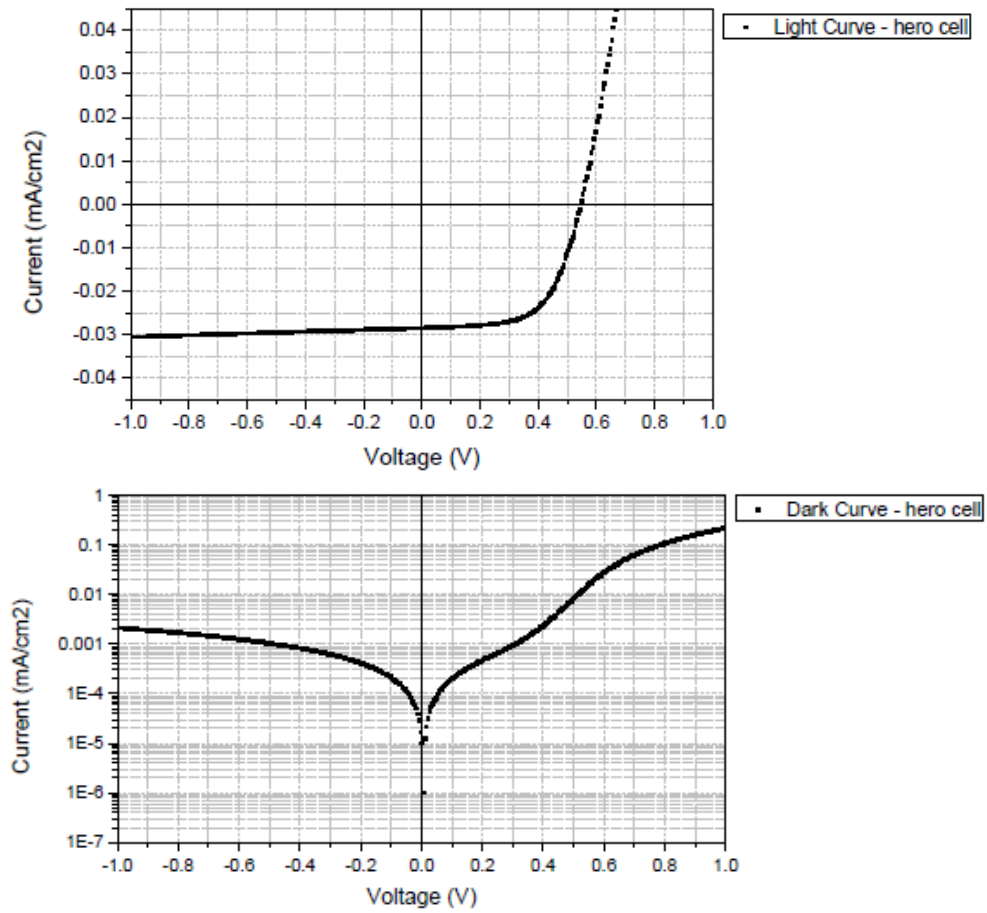


Figure 6.4. IV curve of hero device. (top) light IV curve, (bottom) dark IV curve.¹²⁹ © 2017 IEEE

As a proof of concept, the first implementation of BQ as a device layer is successful. BQ is able to be used as a device layer with carriers able to pass through the BQ from the Si to the PEDOT:PSS for collection. A device efficiency of 9.6% has been achieved. A high V_{oc} is expected resulting from the high quality BQ passivation, however this may require further optimization of the BQ-PEDOT:PSS interface. The relatively high series resistance might be attributed to a bad ohmic contact.

The external quantum efficiency data, Figure 6.5, shows a good absorption at short wavelengths, in comparison with a diffused junction silicon cell. This indicates a well-passivated front surface since short wavelength light is absorbed near the front of

the cell. The relatively low absorption across the middle wavelength is likely caused by reflection, which can be potentially improved by optimized PEDOT:PSS layer.

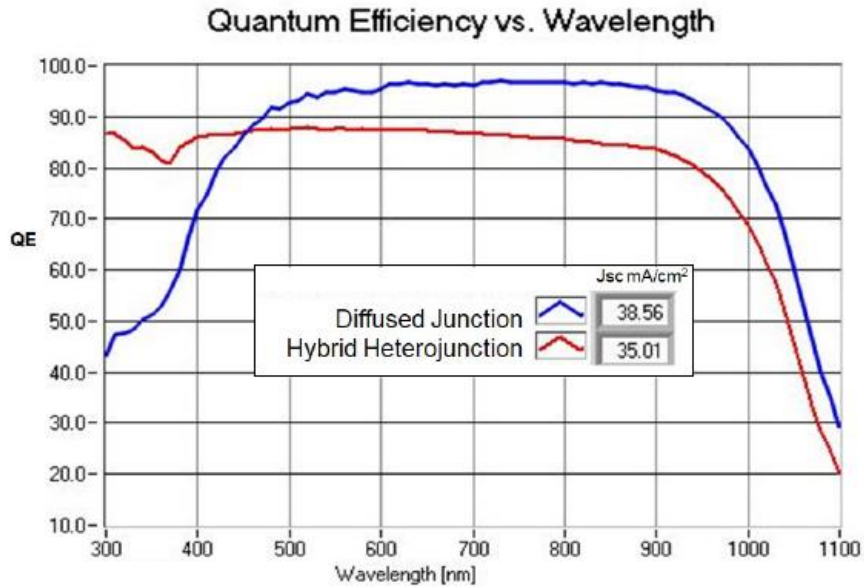


Figure 6.5. External quantum efficiency measurements with integrated short circuit current of devices. Hybrid device on KOH textured wafer with BSF (blue), Conventional diffused junction silicon device for comparison (blue).¹²⁹ © 2017 IEEE

6.4 Conclusions

The structure of the proof of concept device combining PEDOT:PSS on Si with BQ/ME as a surface passivant was demonstrated. The introduction of the benzoquinone passivating layer does not provide a barrier to charge transfer. A hero device efficiency of 9.6% was achieved. Quantum efficiency data showed a good light absorption near the front of the cell indicating a well-passivated front surface. Further optimization of PEDOT:PSS layer is needed in order to lower the series resistance and improve fill factor, as well as better understanding of the energy levels and charge transport across the Si, BQ and PEDOT:PSS interfaces.

Chapter 7

INORGANIC PASSIVANTS- SiOC by PLASMA-FREE ALD*

7.1 Introduction

The conventional passivation layers for silicon solar cells are silicon oxide or silicon nitride. Silicon oxide is normally thermally grown, and it requires a high thermal budget using temperatures greater than 1000°C. Plasma-enhanced chemical vapor deposition (PECVD) is widely used for silicon nitride deposition, but one disadvantage is plasma induced surface damage, which can cause a strong decrease of lifetime due to the defects created on the surface.^{16,130–133} Hence, passivation materials are needed that can be deposited without plasma and at relatively low temperatures.

This chapter discusses about SiOC films using carbosilane compound precursors with plasma-free ultra-low-temperature ALD. This work is collaborated with K.K. Air Liquide Laboratories, Japan. The elimination of plasma and high temperature ensures the high quality of the substrate surface and also greatly decreases the thermal budget. Composition and bonding of the SiOC films are studied using XPS and FTIR. The surface passivation by the SiOC film, as well as its in-air and thermal stability are also studied and compared with the quinone passivation.

* Reprinted with permission from Chen, M.; Noda, N.; Rochat, R.; Iyer, A.; Hack, J.; Ko, C.; Dussarrat, C.; Opila, R. L. In *IEEE Photovoltaic Specialists Conference*; 2017; pp 1–6. Copyright 2017 IEEE.

7.2 Experiment

Substrates used in this work are p-type Silicon (100) Cz wafers, with a resistivity of 1-100 Ωcm , and thickness of 700-750 μm . Two types of surface treatments were performed prior to ALD: Hydrogen termination is obtained by 1 wt% HF, and OH termination by SPFM solution (details described in reference ¹³⁴). Samples were then loaded into the reactor immediately for the SiOC deposition. Three precursors (PRECs) were deposited in ULT-ALD in this work: BTCSM and BDCSM (Gelest 95% and Aldrich 97%, respectively) and R#2 shown in Figure 7.1, among which R#2 is a novel, proprietary compound synthesized in Air Liquide Laboratories.



Figure 7.1. PREC structures © 2017 IEEE

The home-built ALD system and the gas supply sequences are shown in Figure 7.2. The silicon precursors and water are introduced into the reactor in sequence with a precursor to water ratio around 1:15. Amines (pyridine or trimethylamine), introduced with the precursor serve as the catalyst for both precursor and water steps. The reactants are supplied through bubblers where the flow rates of each gas supply line are controlled separately by the flow rate and temperature of the nitrogen bubbling gas. Deposition rate of R#2, BTCSM and BDCSM were found to be around 0.7 $\text{\AA}/\text{min}$, 1.5 $\text{\AA}/\text{min}$ and 3 $\text{\AA}/\text{min}$ respectively, under these conditions.

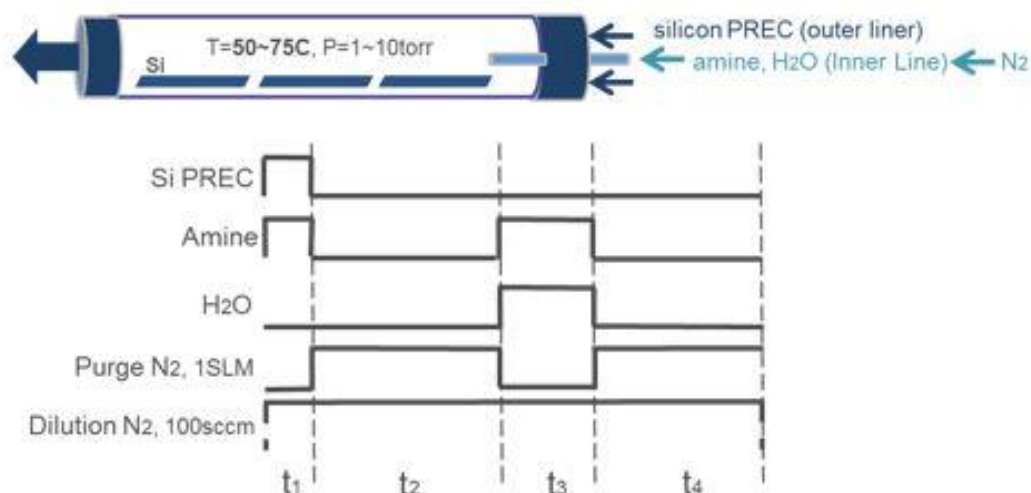


Figure 7.2. The home-built ALD reaction system and gas delivery sequences. © 2017 IEEE

After deposition, samples were loaded into an X-ray photoelectron spectrometer (XPS, Thermo scientific K-alpha) or FTIR spectrometer (Thermo Fisher Nicolet) immediately. Lifetime data was acquired with a Sinton WCT-120 Lifetime tester at $MCD=1 \times 10^{14} \text{ cm}^{-3}$ using quasi-steady-state conductance decay (QSSCD). The thickness of the SiOC film is measured by an ellipsometer (Semilab, SE-2000).

7.3 Results

7.3.1 Influence of Surface Treatment Prior to ALD

It is essential to study different surface features since both ALD and passivation are surface sensitive processes.¹³⁵ Three surfaces are studied here, hydrogen terminated Si (HSi), hydroxyl terminated Si (OH-Si) and silicon with native oxide surfaces.

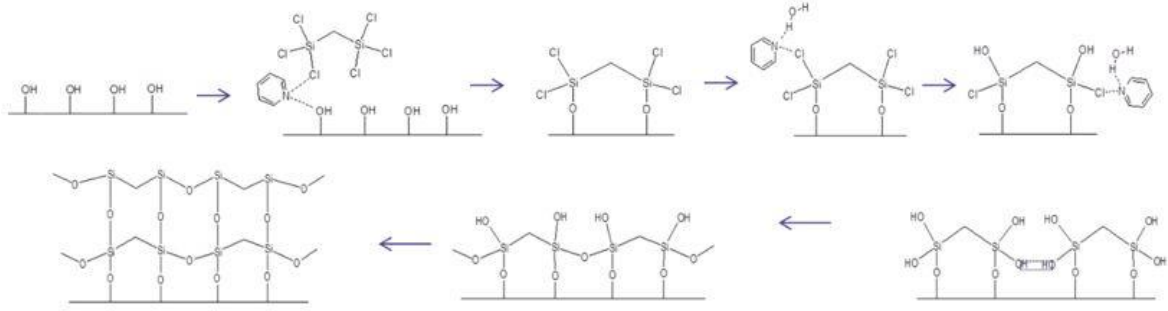


Figure 7.3. ALD mechanism. © 2017 IEEE

BTCSM was deposited on these three types of wafers using the same ALD conditions. It was found that the deposition rate for H-Si substrates is 15% lower than for OH-Si and Si-native oxide substrates. This can be explained by the proposed mechanism in

Figure 7.3. The oxygen on the substrate surfaces is the active site that bonds with silicon precursors to deposit the first monolayer, with amine as the catalyst; as water exposure follows, more chlorine is substituted by oxygen creating reaction sites for the next layer deposition. BDCSM and R#2 presumably follow a similar mechanism based on the precursor structures. For the rest of this work, the OH-Si surface is used, unless otherwise specified. The activity of Si-native oxide surfaces in this ULT-ALD method indicates that, in production, wafers can be loaded directly into the fabrication line without a surface precleaning, which will greatly shorten the processing time.

Lifetime tests show that the films deposited on both OH-Si and Si native oxide substrates can passivate the surface with an increase in lifetime from less than 20 μs to around 120 μs , while BTCSM films deposited on H-Si do not passivate the surface. It needs to be noted that the SiOC depositions here have not been optimized for passivation, and it will be shown in the following sections that the longest carrier lifetime observed was 349 μs .

7.3.2 Lifetime Performances

The deposition conditions for R#2 and BTCSM are optimized, while BDCSM is more of a CVD-like process, and is still under study. It can be seen from Figure 7.4 that, comparing with bare silicon, which has a lifetime under 20 μs , the SiOC film deposited by both R#2 and BTCSM can passivate the p-Si substrates; the film deposited by R#2 with a thickness of 26.2nm, noted as sample R#2_1, gives the highest lifetime of 349 μs . The lifetime has a weak dependence on thickness for all samples.

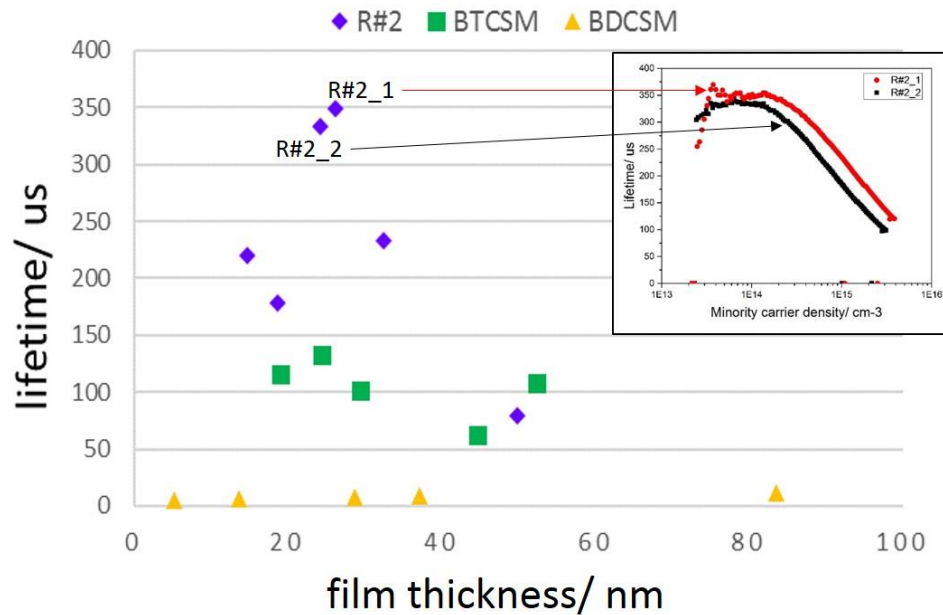


Figure 7.4. Lifetime performance of the films deposited by three PRECs as a function of film thickness (nm). © 2017 IEEE

BDCSM might be expected to give a higher lifetime than BTCSM because of a higher hydrogen incorporation in the PREC molecules. However, the opposite results are shown here, and it may be because the deposition conditions for BDCSM are not yet optimized. In this process the PREC vapors are mixed in the gas phase and then deposited without further reaction on the silicon substrates; as a result, the reactive

surface defects sites are less likely to be saturated by PREC molecules. FTIR of the deposited film shows the presence of unreacted precursor. (data not shown here) As a comparison, BQ/ME passivation was applied on the same substrate wafer following the procedure described in Chapter 2.4, and a lifetime of 1172 μs was observed.

The study of the composition as a function of depth in Figure 7.5 shows that the best passivation sample R#2_1, has around 10%C, 40%O and 50%Si. Si-O, C-O and Si-C bonding are observed in all films from XPS and FTIR.

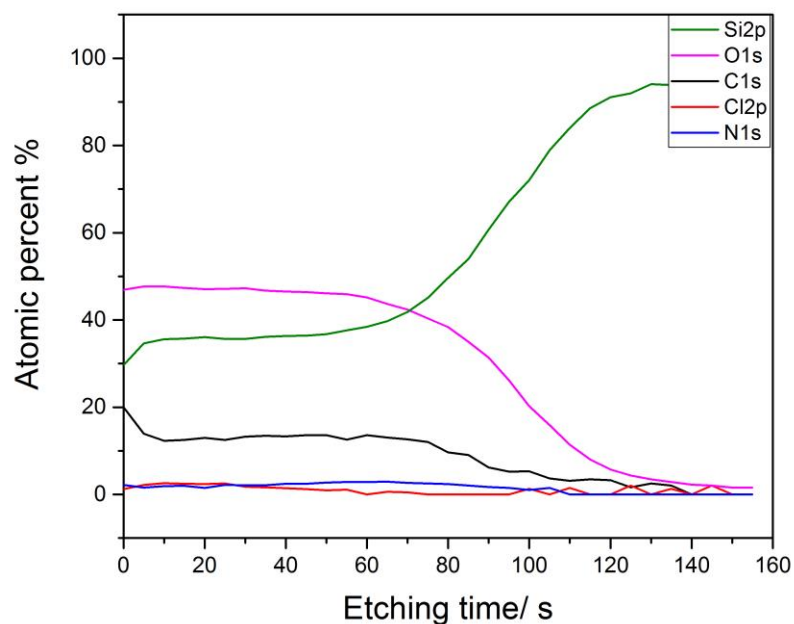


Figure 7.5. XPS depth profiles of R#2_1. © 2017 IEEE

7.3.3 Stability – In-air Degradation

The in-air stability of SiOC was examined. R#2 samples were kept in ambient room condition for up to three weeks after deposition. The change in lifetime is recorded in Figure 7.6.

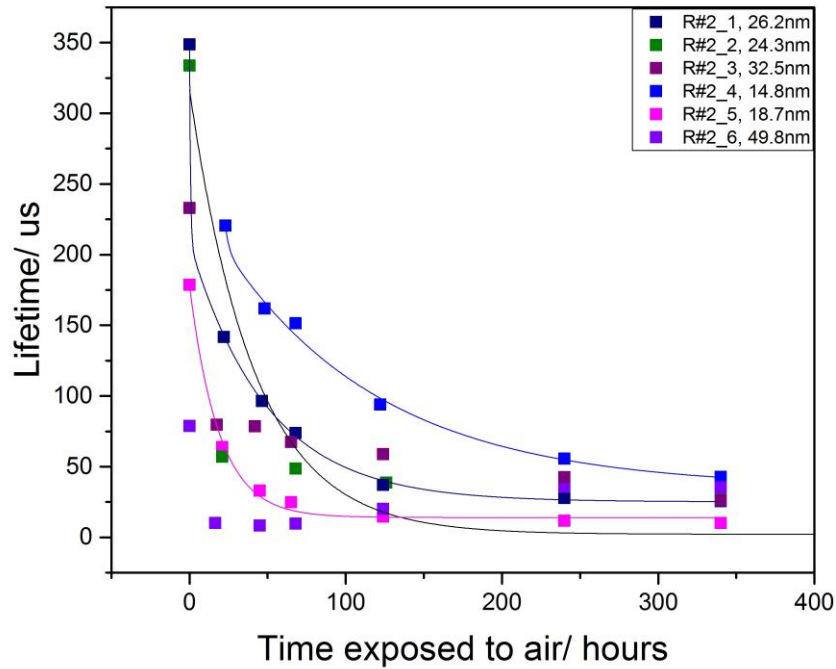


Figure 7.6. Lifetime as a function of time in air of R#2 samples. © 2017 IEEE

Figure 7.6 indicates that most films' lifetime follows an exponential decay when the films are exposed to air. Some samples degrade much slower than others; R#2_4(220 μ s initially), can maintain 80% performance for 2 days. The degradation rate slows in samples with relatively thin SiOC layers. One hypothesis is that among the thinner samples, oxygen diffuses to the interface more easily, which introduces negative charges and decreases the number of interface state defects.^{136–138} It can be seen that even though the SiOC passivation lifetime is lower than BQ/ME passivation, SiOC is more stable in air than the BQ/ME layer on Si.

7.3.4 Stability – Heating Effect

To characterize the temperature dependence of the degradation, BTSCM samples were heated up to 100°C on a Sinton tester (WC-120 TS) equipped with a thermal probe in ambient room condition, and then cooled down. The heating takes place in a period of a few minutes, and the cooling requires several hours. The corresponding lifetimes are shown in Figure 7.7.

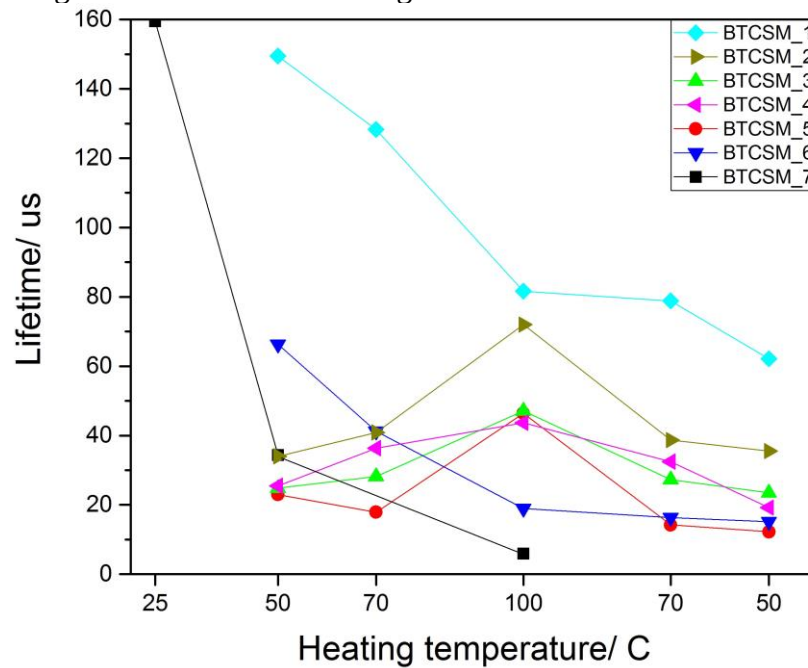


Figure 7.7. Lifetime performances of BTSCM samples in high temperature. © 2017 IEEE

It can be seen here that the lifetime of four samples increased when heating the films to 100°C, and decreased when cooled down. One hypothesis is that heating facilitates hydrogen diffusion from dielectric films to the interface, and terminates Si dangling bonds, which decreases the interface state density and thus gives a higher lifetime.^{136–138} Figure 7.7 also indicates that the impact of hydrogen or oxygen is more significant on relatively low lifetime samples; for samples with a lifetime longer than 80 μ s, the improvement is not strong enough to compensate the oxidation of the

passivation layer, and the overall lifetime degrades dramatically at an elevated temperature, like for samples BTSCM_1,6,7.

7.4 Conclusions

SiOC thin films have been successfully deposited by carbosilane precursors using ULT-ALD at 50 °C to 70 °C. The plasma-free ultra-low temperature process eliminates the damage of silicon surfaces due to plasma and high temperature processing. This ALD can be performed on both OH terminated Si and Si-native oxide surfaces. This demonstrates another advantage of the SiOC film: wafers can be loaded directly into the deposition chamber without a surface cleaning, which will greatly shorten the processing time.

Lifetime tests show that the SiOC film deposited by R#2 and BTSCM can passivate the p-Si substrates; the film deposited by R#2 with a thickness of 26nm gives the highest lifetime of 349 μ s. Surface analysis shows that the film has around 10%C, 40%O and 50%Si with trace amounts of N and Cl.

Most of the films lifetime performances follow an exponential decay when exposed to air. Some of the relatively thinner samples degrade much slower than other thicker films. This can be explained by the diffusion of oxygen to the interface more easily in thinner samples, which introduces negative charges and lowers the interface state defect density. Even though the SiOC passivation lifetime is lower than BQ/ME passivation, SiOC is more stable in air than the BQ/ME layer on Si.

Moreover, an increase in lifetime is observed with an elevated storage temperature up to 100°C, which may be related to hydrogen migration.

Overall, SiOC has been found to be a good alternative in passivating silicon solar cells. This SiOC plasma-free ULTALD process can also be used in thin film fabrication where plasma and high temperature are critical factors.

Chapter 8

CONCLUSIONS AND FUTURE WORK

Throughout this work, experimental and theoretical investigations were carried out for the passivation of Si surfaces with organic molecules and the implementation of those molecules in a hybrid organic/silicon solar cell device. While these findings have led to some conclusions, they have also presented paths forward for future work. These conclusions and improvement opportunities are presented in the following sections.

8.1 Conclusions

This work consists of three main components: chemical passivation mechanism studies, electrical passivation mechanism studies and device fabrication.

Beginning with a study of the passivation behavior of free radicals in BQ, HQ, under the impact of external radicals and radiation, a radical-driven passivation mechanism was proposed: BQ is believed to abstract hydrogen atoms from methanol to become QH*, and both QH* and the resulting methanol radical are responsible for the nearly instantaneous improvement of minority carrier lifetime ($\tau=4500\mu\text{s}$, with SRV=1.6cm/s on polished surfaces; SRV=6.7cm/s on HNA etched surfaces). In HQ/ME solution, HQ loses a hydrogen atom to become QH*. QH*, the methanol radical and other radicals can bond to silicon and act as passivants.

Other radical sources like photoinitiators can passivate silicon surfaces when applying light with the corresponding activation energy. This is further evidence of a

free radical-based bonding and passivation mechanism. Weak bonds like C-Cl can also generate radicals and passivate silicon. The radical-driven mechanism also got confirmed via electrochemistry where no redox peak rising from BQ is observed, indicating the BQ reaction on Si doesn't involve electron transfer.

The chemical passivation mechanism was further investigated by XPS, which confirmed the bonding of aromatic groups to the surface. The time evolution study of the BQ/ME bonding mechanism showed that BQ bonding dominates for a one hour BQ/ME treated sample, and methanol bonding to the surface increases with increasing immersion time. In addition, quantitative analysis showed that the 24 hours BQ/ME treatment gives roughly 21% SiOSi, 13% ME and 6% BQ top surface monolayer coverage.

DFT results further support the possibility of QH* bonding from a thermodynamic perspective. The methanol radical has the most favorable adsorption energy for bonding, followed by QH* and then BQ molecule. Electron distribution results, specifically the large negative charge on the adsorbed moiety, indicate a field-effect passivation effect by methanol. Moreover, the bonding geometry has been studied, wherein the single-bonded "edge-on" configuration is more energetically favorable than double-bonded "face-on" configuration.

Surface photovoltage measurements via both the photoemission and SKPM techniques indicate a downward band bending of H-Si and BQ and ME treated samples. This suggests the creation of an accumulation layer of majority carriers near the surface, with a significant field-effect contribution to the observed surface passivation. The highest SPV values recorded for the ME-Si and BQ-Si samples of about -220mV are approaching the fermi level – conduction band crossover. The

similar magnitudes of surface band bending observed with both the BQ-ME and ME treatments is consistent with the expected mechanism of the surface modification, in which both BQ radicals and methanol radicals adhering to the surface. DFT calculation shows that a dipole is formed upon bonding of BQ radicals on the surface, decreasing the surface electron affinity and work function. The work function of BQ-Si is found to be 4.11 eV. Both the dipole and downward band bending contribute to the formation of electron accumulation on n-Si passivated by BQ.

After investigations on the passivation mechanism, hybrid organic/silicon devices using quinones were fabricated. The structure of the proof of concept device combining PEDOT:PSS on Si with BQ/ME as a surface passivant. The introduction of the benzoquinone passivating layer does not provide a barrier to charge transfer. A device efficiency of 9.6% was achieved. Quantum efficiency data showed a good light absorption near the front of the cell indicating a well-passivated front surface. Further optimization of PEDOT:PSS layer is needed in order to lower the series resistance and improve fill factor, as well as better understanding of the energy levels and charge transport across the Si, BQ and PEDOT:PSS interfaces.

At last, another alternative passivation method -- SiOC passivation was studied, where the SiOC films were deposited with plasma-free ultra-low-temperature ALD. Composition and bonding of the SiOC films were studied using XPS and FTIR. The surface passivation effect and stability of the SiOC films are studied and compared with the quinone passivation.

8.2 Future Work

Future work for the organic passivation will focus on examining the passivation degradation mechanism, improved understanding on the energy band bending, and optimizing the hybrid solar cell structure.

The first topic to look at is the passivation degradation mechanism. It has been observed in Figure 2.8, that the lifetime of wafers in BQ/ME solution starts to degrade after couple hours, while HQ/ME can maintain the passivation results for days even though it takes longer for HQ/ME to reach a maximum passivation. One hypothesis is that oxidation still happens in the closed passivation bag, since the zip bags containing the solution and wafers are not high air proof. Another hypothesis is that the decline of Si lifetime in BQ/ME might be attributed to the addition of ME on the surface. Methanol bonding to the surface increases with increasing immersion time has been observed in Figure 3.1. ME competing with, or replacing, BQ decreases the lifetime because ME is less effective as a passivant than BQ. Further analysis on the degradation mechanism will assist the understanding of the organic passivation.

In addition to the chemical passivation mechanism, a better explanation of the energy band structure on the silicon-organic interface is needed. Surface photovoltage on BQ and ME treated n-type Si samples was measured in Chapter 5, however, it is still not clear why BQ/ME passivation works on p-type as well, and if there are ways to further bend the band introducing an even higher lifetime.

The next step would be optimization of the hybrid solar cell structure. The current champion device has a relatively high series resistance of 1.7 Ohm cm^2 , which might be attributed to a bad ohmic contact, and needs further optimization of the BQ-PEDOT:PSS interface. In addition, from the quantum efficiency data that a relatively low absorption across the middle wavelength is observed, which is likely caused by

PEDOT:PSS layer reflection. Thus, more work on improving the PEDOT:PSS layer light absorption and conductivity critical in bringing up the device performances.

Ultimately, utilizing this low-cost organic passivation with optimized hybrid device structure will result in a low-cost high-efficiency next generation PV technology.

8.3 Disseminations

This material is based upon work primarily supported by the Engineering Research Center Program of the National Science Foundation and the Office of Energy Efficiency and Renewable Energy of the Department of Energy under NSF Cooperative Agreement 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 the National Science Foundation or Department of Energy.

The radical-driven organic passivation mechanism study was published in Journal of Physical Chemistry, C.¹³⁹ The study of lifetime QSST measurement of samples immersed in solutions was presented in 2015 IEEE Photovoltaics Specialists Conferences. An accompanying paper was then published in the conference proceedings.⁶² The study on hybrid device fabrication and SiOC passivation were also published in 2017 IEEE Photovoltaics Specialists Conferences.^{129,140}

REFERENCES

- (1) Dimroth, F.; Tibbits, T. N.; Niemeyer, M.; Predan, F.; Beutel, P.; Karcher, C.; Oliva, E.; Siefert, G.; Lackner, D.; Fuß-Kailuweit, P.; Bett, A. W. *IEEE J. Photovoltaics* **2016**, 6 (1), 343.
- (2) Fraunhofer ISE: Photovoltaics Report, 2017 July
<https://www.ise.fraunhofer.de/content/dam/ise/de/documents/publications/studies/Photovoltaics-Report.pdf>.
- (3) World record CIGS lab cell efficiency of 22.6%, 2016 June <https://www.pv-tech.org/news/zsw-achieves-world-record-cigs-lab-cell-efficiency-of-22.6>.
- (4) Kamada, R.; Yagioka, T.; Adachi, S.; Handa, A.; Tai, K. F.; Kato, T.; Sugimoto, H. In *Photovoltaic Specialists Conference (PVSC)*; 2016; p 1287.
- (5) New world efficiency record with perovskite solar cells, 22.1%, 2017 July <https://www.sciencedaily.com/releases/2017/07/170725122105.htm>.
- (6) Quantum dot solar cells hit record efficiency, 2016 July
<http://cen.acs.org/articles/94/i28/Quantum-dot-solar-cells-hit.html?type=paidArticleContent>.
- (7) Green, M. A.; Emery, K.; Hishikawa, Y.; Warta, W.; Dunlop, E. D. *Prog. Photovoltaics Res. Appl.* **2016**, 24 (7), 905.
- (8) Röder, T. C.; Eisele, S. J.; Grabitz, P.; Wagner, C.; Kulushich, G.; Köhler, J. R.; Werner, J. H. *Prog. Photovoltaics Res. Appl.* **2010**, 18 (7), 505–510.
- (9) Chabal, Y. J.; Higashi, G. S.; Raghavachari, K. *MRS Online Proc. Libr. Arch.* **1988**, 131.
- (10) Tian, F.; Yang, D.; Opila, R. L.; Teplyakov, A. V. *Appl. Surf. Sci.* **2012**, 258 (7), 3019–3026.
- (11) Jin, H.; Weber, K. J.; Dang, N. C.; Jellett, W. E. *Appl. Phys. Lett.* **2007**, 90 (26), 262109.
- (12) Hezel, R.; Jaeger, K. *J. Electrochem. Soc.* **1989**, 136 (2), 518–523.

- (13) Lauinger, T.; Schmidt, J.; Aberle, A. G.; Hezel, R. *Appl. Phys. Lett.* **1996**, *68* (9), 1232–1234.
- (14) Leguijt, C.; Lölgen, P.; Eikelboom, J. A.; Weeber, A. W.; Schuurmans, F. M.; Sinke, W. C.; Alkemade, P. F. A.; Sarro, P. M.; Maree, C. H. M.; Verhoef, L. A. *Sol. Energy Mater. Sol. Cells* **1996**, *40* (4), 297–345.
- (15) Warren, W. L.; Rong, F. C.; Poindexter, E. H.; Gerardi, G. J.; Kanicki, J. J. *Appl. Phys.* **1991**, *70* (1), 346–354.
- (16) Schmidt, J. and Aberle, A. G. *J. Appl. Phys.* **1999**, *85*, 3626.
- (17) Hoex, B.; Schmidt, J.; Pohl, P.; Sanden, M. C. M. Van De; Kessels, W. M. M. *J. Appl. Phys.* **2008**, *104*, 44903.
- (18) Agostinelli, G.; Delabie, A.; Vitanov, P.; Alexieva, Z.; Dekkers, H. F. W.; De Wolf, S.; Beaucarne, G. *Sol. Energy Mater. Sol. Cells* **2006**, *90* (18), 3438–3443.
- (19) Hoex, B.; Heil, S. B. S.; Langereis, E.; Van de Sanden, M. C. M.; Kessels, W. M. M. *Appl. Phys. Lett.* **2006**, *89* (4), 42112.
- (20) Solar Cell Production Equipment
http://www.ensolar.com/directory/equipment/cell_diffusion.
- (21) Aberle, A. G. *Prog. Photovoltaics Res. Appl.* **2000**, *8* (5), 473–487.
- (22) Nagel, H.; Aberle, A. G.; Hezel, R. *Prog. Photovoltaics Res. Appl.* **1999**, *7* (4), 245–260.
- (23) Kimura, K. *Tech. Dig. Int. PVSEC-1, Kobe* **1984**, 3741.
- (24) Yates, J. T. *Science* (80-.). **1998**, *279* (5349), 335–336.
- (25) Linford, M. R.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1993**, *115* (26), 12631–12632.
- (26) Linford, M. R.; Fenter, P.; Eisenberger, P. M.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1995**, *117* (11), 3145–3155.
- (27) Buriak, J. M. *Chem. Rev.* **2002**, *102* (5), 1271–1308.
- (28) Nemanick, E. J.; Hurley, P. T.; Brunschwig, B. S.; Lewis, N. S. *J. Phys. Chem. B* **2006**, *110* (30), 14800–14808.

- (29) Yu, H.; Webb, L. J.; Ries, R. S.; Solares, S. D.; Goddard, W. A.; Heath, J. R.; Lewis, N. S. *J. Phys. Chem. B* **2005**, *109* (2), 671–674.
- (30) O’Leary, L. E.; Johansson, E.; Brunschwig, B. S.; Lewis, N. S. *J. Phys. Chem. B* **2010**, *114* (45), 14298–14302.
- (31) Nemanick, E. J.; Hurley, P. T.; Webb, L. J.; Knapp, D. W.; Michalak, D. J.; Brunschwig, B. S.; Lewis, N. S. *J. Phys. Chem. B* **2006**, *110* (30), 14770–14778.
- (32) Angermann, H.; Henrion, W.; Rebien, M.; Röseler, A. *Sol. energy Mater. Sol. cells* **2004**, *83* (4), 331–346.
- (33) Takato, H.; Sakata, I.; Shimokawa, R. *Jpn. J. Appl. Phys.* **2002**, *41* (Part 2, No. 8A), L870–L872.
- (34) Horanyi, T. S.; Pavelka, T.; Tüttö, P. *Appl. Surf. Sci.* **1993**, *63* (1–4), 306–311.
- (35) Takato, H.; Sakata, I.; Shimokawa, R. In *Photovoltaic Energy Conversion, 2003. Proceedings of 3rd World Conference on*; IEEE, 2003; Vol. 2, pp 1108–1111.
- (36) Chhabra, B.; Bowden, S.; Opila, R. L.; Honsberg, C. B. *Appl. Phys. Lett.* **2010**, *96* (6), 63502.
- (37) Regeimbal, J.; Gleiter, S.; Trumpower, B. L.; Yu, C.-A.; Diwakar, M.; Ballou, D. P.; Bardwell, J. C. A. *Proc. Natl. Acad. Sci.* **2003**, *100* (24), 13779–13784.
- (38) Har-Lavan, R.; Yaffe, O.; Joshi, P.; Kazaz, R.; Cohen, H. and Cahen, D. *AIP Adv.* **2012**, *2*, 12164.
- (39) Kotulak, N.; Chen, M.; Schreiber, N.; Opila, R. L. In *Photovoltaic Specialist Conference*; 2014; pp 1529–1533.
- (40) Kotulak, N. A.; Chen, M.; Schreiber, N.; Jones, K.; Opila, R. L. *Appl. Surf. Sci.* **2015**, *354*, 469–474.
- (41) Chhabra, B.; Weiland, C.; Opila, R. L.; Honsberg, C. B. *Phys. Status Solidi. a.* **2011**, *208* (1), 86–90.
- (42) Avasthi, S.; Qi, Y.; Vertelov, G. K.; Schwartz, J.; Kahn, A.; Sturm, J. C. *Surf. Sci.* **2011**, *605* (13), 1308–1312.
- (43) Avasthi, S.; Vertelov, G.; Schwartz, J.; Sturm, J. C. In *Photovoltaic Specialists Conference (PVSC), 2009 34th IEEE*; IEEE, 2009; pp 1681–1685.
- (44) Grant, N. E.; McIntosh, K. R. In *24th European Photovoltaic Solar Energy*

Conference; 2009; Vol. 30, p 922.

- (45) M'saad, H.; Michel, J.; Lappe, J. J.; Kimerling, L. C. *J. Electron. Mater.* **1994**, 23 (5), 487–491.
- (46) M'saad, H.; Michel, J.; Reddy, A.; Kimerling, L. C. *J. Electrochem. Soc.* **1995**, 142 (8), 2833.
- (47) Opila, R. L.; Yang, D.; Kotulak, N.; Costello, L.; Chhabra, B. In *38th IEEE Photovoltaic Specialists Conference*; 2011; pp 2583–2587.
- (48) Guin, P. S.; Das, S.; Mandal, P. C. *Int. J. Electrochem.* **2011**, 2011, 1–22.
- (49) Bausche M; Mntele W. *J. Phys. Chem.* **1992**, 96 (26), 11101–11108.
- (50) Har-lavan, R.; Schreiber, R.; Yaffe, O.; Cahen, D. *J. Appl. Phys.* **2013**, 113, 84909.
- (51) Jablonski, A. *Nature* **1933**, 131, 839–840.
- (52) Douglas A. Skoog; Nieman, T. A.; Holler, F. J. *Principles of Instrumental Analysis*; Brooks/Cole, 1998.
- (53) Crivello, J. V; Reichmanis, E. *Chem. Mater* **2014**, 26, 533–548.
- (54) A. Ravve. *Light-Associated Reactions of Synthetic Polymers*; Springer Science & Business Media: New York, 2007.
- (55) Glöckner, P. *Radiation curing: Coatings and printing inks; technical basics, applications and trouble shooting*; Vincentz Network GmbH & Co KG, 2008.
- (56) Baldacchini, T. *Three-dimensional Microfabrication Using Two-photon Polymerization: Fundamentals, Technology, and Applications*; William Andrew, 2015.
- (57) Sinton, R. A.; Cuevas, A. *Appl. Phys. Lett.* **1996**, 69 (17), 2510.
- (58) R. Lago Aurrekoetxea, I. Tobias, C. del Cannizo, A. L. *J. Electrochem. Soc.* **2001**, 148 (4), 200.
- (59) Michalak, D. J.; Rivillon, S.; Chabal, Y. J.; Estève, A.; Lewis, N. S. *J. Phys. Chem. B.* **2006**, 110 (41), 20426–20434.
- (60) J. Krausse. *Solid. State. Electron.* **1972**, 15 (12), 1377.

- (61) Lago-Aurrekoetxea, R., Tobías, I., del Cañizo, C. and Luque, A. *J. Electrochem. Soc.* **2001**, *148* (4), 200.
- (62) Chen, M.; Hack, J. H.; Iyer, A.; Opila, R. L.; Delaware, U. In *IEEE Photovoltaic Specialists Conference.*; 2015; pp 1–6.
- (63) Nagel, H.; Berge, C.; Aberle, A. G. *J. Appl. Phys.* **1999**, *86* (11), 6218–6221.
- (64) Kerr, M. J.; Cuevas, A. *J. Appl. Phys.* **2002**, *91* (4), 2473.
- (65) Leighton, P. A.; Forbes, G. S. *J. Am. Chem. Soc.* **1929**, *51* (12), 3549–3559.
- (66) Foster, R.; Forman, M. I. *The Chemistry of Quinoid Compounds*; Wiley: New York, 1974.
- (67) Bernardini, S.; Nærland, T. U.; Coletti, G.; Ding, L.; Blum, A. L.; Mariana, I.; Sample, A. In *Photovoltaic Specialists Conference.*; 2016; pp 2863–2867.
- (68) Lebedev, O. L.; Kazarnovskii, S. N. *Zhur. Obs. Khim* **1960**, *30* (5), 1631–1635.
- (69) Galli, C. *The Chemistry of Hydroxylamines, Oximes and Hydroxamic Acids 2*; John Wiley & Sons Ltd, 2009.
- (70) McNaught, A. D.; Wilkinson, A. *Compendium of Chemical Terminology, 2nd ed*; Blackwell Scientific Publications: Oxford, 1997.
- (71) Terry, J.; Mo, R.; Wigren, C.; Cao, R.; Mount, G.; Linford, M. R.; Chidsey, E. D. *Nucl. Instruments Methods Phys. Res. B* **1997**, *133*, 94–101.
- (72) Gupta A, Gulati M, P. N. K. *Rasayan J. Chem.* **2009**, *2* (3), 649–654.
- (73) Norrish, R. G. W.; Bamford, C. H. *Nature.* **1937**, *140*, 195–196.
- (74) Ya, O.; Ely, T.; Har-lavan, R.; Egger, D. A.; Johnston, S.; Cohen, H.; Kronik, L.; Vilan, A.; Cahen, D. *J. Phys. Chem. C.* **2013**, *117* (43), 22351–22361.
- (75) Ramsden E N. *A-Level Chemistry.*; Nelson Thornes, 2000.
- (76) Koepp, H. M., Wendt, H. and Strehlow, H. *Reports Bunsen Soc. Phys. Chem.* **1960**, *64* (4), 483.
- (77) Laser, D. and Bard, A. J. *J. Phys. Chem.* **1976**, *80* (5), 459.
- (78) Brune, D., Hellborg, R., Whitlow, H. J., Hunderi, O. *Surface Characterization: A Users Sourcebook*; John Wiley & Sons Ltd, 2008.

- (79) Michalak, D. J.; Amy, S. R.; Este, A.; Chabal, Y. J. *J. Phys. Chem. C* **2008**, *112*, 11907–11919.
- (80) Haber, J. A.; Lewis, N. S. *J. Phys. Chem. B* **2002**, *106*, 3639–3656.
- (81) Webb, L. J.; Nemanick, E. J.; Biteen, J. S.; Knapp, D. W.; Michalak, D. J.; Traub, M. C.; Chan, A. S. Y.; Brunschwig, B. S.; Lewis, N. S. *J. Phys. Chem. B* **2005**, *109*, 3930–3937.
- (82) Ohta T., Yamada M., K. H. *Bull. Chem. Soc. Jpn.* **1974**, *47* (5), 1158–1161.
- (83) Northrup, J. E. *Phys. Rev. B* **1991**, *44*, 1419.
- (84) Perrine, K. A.; Teplyakov, A. V. *Chem. Soc. Rev.* **2010**, *39*, 3256–3274.
- (85) Petersson, A.; Bennett, A.; Tensfeldt, T. G.; Al-Laham, M. A.; Shirley, W. A.; Mantzaris, J. *J. Chem. Phys.* **1988**, *89*, 2193.
- (86) Nachtigall, P.; Smith, K. D. J.; Jónsson, H.; Smith, A.; Jo, H. *J. Chem. Phys.* **1996**, *104* (148).
- (87) Santos, H. R. R.; Ramos, M. J.; Gomes, J. A. N. F. *C. R. Chinmie* **2005**, *8*, 1461–1468.
- (88) Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, *47* (1), 558.
- (89) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45* (23), 13244.
- (90) Vanderbilt, D. *Phys. Rev. B* **1990**, *41* (11), 7892.
- (91) Kresse, G.; Furthmüller, J. *Phys. Rev. B* **1996**, *54* (16), 11169.
- (92) Blöchl, P. E.; Jepsen, O.; Andersen, O. K. *Phys. Rev. B* **1994**, *49* (23), 16223.
- (93) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77* (18), 3865.
- (94) Ning, Y. S.; Shao, Y. X.; Xu, G. Q. *J. Phys. Chem. C* **2010**, *114* (23), 10455–10462.
- (95) He, T.; Ding, H.; Peor, N.; Lu, M.; Corley, D. A.; Chen, B.; Ofir, Y.; Gao, Y.; Yitzchaik, S.; Tour, J. M. *J. Am. Chem. Soc.* **2008**, *130* (5), 1699.
- (96) Gleason-Rohrer, D. C.; Brunschwig, B. S.; Lewis, N. S. *J. Phys. Chem. C* **2013**, *117* (35), 18031.

- (97) Mott, N. F. *Math. Proc. Cambridge Philos. Soc.* **1938**, 34 (4), 568.
- (98) Schottky, W. *J. Phys. A Hadron. Nucl.* **1939**, 113 (5), 367.
- (99) Jing, L.; Sun, X.; Shang, J.; Cai, W.; Xu, Z.; Du, Y.; Fu, H. *Sol. Energy Mater. Sol. Cells* **2003**, 79 (2), 133.
- (100) Zhen, Hang; Yates, J. T. *J. Chem. Rev.* **2012**, 112 (10), 5520.
- (101) Ishibashi, K. I.; Fujishima, A.; Watanabe, T.; Hashimoto, K. *J. Photochem. Photobiol. A Chem.* **2000**, 134 (1), 139.
- (102) Kronik, L.; Shapira, Y. *Surf. Sci. Rep.* **1999**, 37, 1.
- (103) Sell, K.; Barke, I.; Polei, S.; Schumann, C.; von Oeynhausen, V.; Meiwes-Broer, K. H. *Phys. Status Solidi* **2010**, 247 (5), 1087.
- (104) Kelvin, L. V. *Philos. Mag.* **1898**, 46, 82.
- (105) Lenzmann, F.; Krueger, J.; Burnside, S.; Brooks, K.; Grätzel, M.; Gal, D.; Rühle, S.; Cahen, D. *J. Phys. Chem. B* **2001**, 105 (27), 6347.
- (106) Sezen, H.; Suzer, S. *J. Chem. Phys.* **2011**, 135, 141102.
- (107) Çopuroğlu, M.; Sezen, H.; Opila, R. L.; Suzer, S. *ACS Appl. Mater. Interfaces* **2013**, 5, 5875.
- (108) Sezen, H.; Ozbay, E.; Aktas, O.; Suzer, S. *Appl. Phys. Lett.* **2011**, 98, 111901.
- (109) Magid, I.; Burstein, L.; Seitz, O.; Segev, L.; Kronik, L.; Rosenwaks, Y. *J. Phys. Chem. C* **2008**, 112 (18), 7145.
- (110) Natan, A.; Kronik, L.; Shapira, Y. *Appl. Surf. Sci.* **2006**, 252 (21), 7608.
- (111) Cahen, D.; Kahn, A. *Adv. Mater.* **2003**, 15 (4), 271.
- (112) Sze, S. M. *Physics of Semiconductor Devices*; Wiley: New York, 1981.
- (113) Hunger, R.; Fritsche, R.; Jaeckel, B.; Jaegermann, W.; Webb, L. J.; Lewis, N. S. *Phys. Rev. B* **2005**, 72 (4), 45317.
- (114) Heliatek sets new Organic Photovoltaic world record efficiency of 13.2%
<http://www.heliatek.com/en/press/press-releases/details/heliatek-sets-new-organic-photovoltaic-world-record-efficiency-of-13-2>.

- (115) Zhou, Y., Eck M., K. M. *Energy Environ. Sci.* **2010**, 3, 1851.
- (116) Xu, T., Q. Q. *Energy Environ. Sci.* **2011**, 4, 2700.
- (117) Ruchuan Liu. *Materials (Basel)*. **2014**, 7, 2747.
- (118) Dayal, S., Kopidakis, N., Olson, D.C., Ginley, D.S. and Rumbles, G. *Nano Lett.* **2009**, 10, 239.
- (119) Nicolaidis, N.C., Routley, B.S., Holdsworth, J.L., Belcher, W.J., Zhou, X. and Dastoor, P. C. *J. Phys. Chem. C* **2011**, 115 (7801).
- (120) Ishwara, T. *Energy Procedia* **2017**, 110, 109.
- (121) Hofstetter, Y. J., Hopkinson, P. E., Bakulin, A. A., & Vaynzof, Y. *J. Mater. Chem. C* **2016**, 4 (5), 1111.
- (122) Sharma, M., Pudasaini, P. R., RuizZepeda, F., Elam, D., Ayon, A. A. *Appl. Mater. Interfaces* **2014**, 6, 4356.
- (123) Pudasaini, P. R., Ayon, A. A. *J. Phys. Conf. Ser.* **2013**, 476, 12140.
- (124) He, L., Jiang, C., Wang, H. and Lai, D. *Appl. Mater. Interfaces* **2012**, 4, 1704.
- (125) Hu, Z., Zhang, J. and Zhu, Y. *Renew. Energy* **2014**, 62, 100.
- (126) Chang, S.H., Chiang, C.H., Kao, F.S., Tien, C.L. and Wu, C. G. *IEEE Photonics J.* **2014**, 6 (4), 1.
- (127) Zhang J, Zhang Y, Song T, Shen X, Yu X, Lee ST, Sun B, J. B. *Appl. Mater. Interfaces* **2017**.
- (128) Kotulak, N. A. Developing novel hybrid heterojunctions for high efficiency photovoltaics, University of Delaware, 2014.
- (129) Hack, J.H., Iyer, A., Chen, M., Opila, R. L. *IEEE Photovolt. Spec. Conf.* **2017**.
- (130) Elmiger, J. R. *MRS Proceedings, Cambridge Univ. Press* **1996**, 426, 1709.
- (131) Schmidt, J., Schuurmans, F.M., Sinke, W.C., Glunz, S.W. and Aberle, A. G. *Appl. Phys. Lett.* **1997**, 71, 252.
- (132) Steingrube, S., Altermatt, P.P., Steingrube, D.S., Schmidt, J. and Brendel, R. *J. Appl. Phys.* **2010**, 108, 14506.

- (133) Tachibana, T., Takai, D., Kojima, T., Kamioka, T., Ogura, A. and Ohshita, Y. *ECS J. Solid State Sci. Technol.* **2016**, 5 (9), 253.
- (134) Ljungberg, K., Jansson, U., Bengtsson, S. and Söderbärg, A. *J. Electrochem. Soc.* **1996**, 143 (5), 1709.
- (135) Moshe, H., Mastai, Y. In *Materials Science Advanced Topics*; InTech, 2013; p 6384.
- (136) Zhou, C., Zhu, J., Zhou, S., Tang, Y., Foss, S.E., Haug, H., Nordseth, Ø., Marstein, E.S. and Wang, W. *Prog. Photovolt Res. Appl.* **2016**, 10 (1002), 2803.
- (137) Keipert-Colberg, S., Barkmann, N., Streich, C., Schütt, A., Suwito, D., Schäfer, P., Müller, S. and Borchert, D. *26th EU PVSC* **2011**, 1770.
- (138) Schmidt, J., Werner, F., Veith, B., Zielke, D., Steingrube, S., Altermatt, P.P., Gatz, S., Dullweber, T. and Brendel, R. *Energy Procedia* **2012**, 15, 30.
- (139) Chen, M.; Hack, J. H.; Iyer, A.; Jones, K. J.; Opila., R. L. *J. Phys. Chem. C.* **2017**, 121 (39), 21364.
- (140) Chen, M.; Noda, N.; Rochat, R.; Iyer, A.; Hack, J.; Ko, C.; Dussarrat, C.; Opila., R. L. In *IEEE Photovoltaic Specialists Conference.*; 2017; pp 1–6.

Appendix A

COPYRIGHT



[Home](#) [Account Info](#) [Help](#) 

 **ACS Publications**
Most Trusted. Most Cited. Most Read.

Title: Radical-Driven Silicon Surface Passivation by Benzoquinone- and Hydroquinone-Methanol and Photoinitiators
Author: Meixi Chen, James H. Hack, Abhishek Iyer, et al
Publication: The Journal of Physical Chemistry C
Publisher: American Chemical Society
Date: Oct 1, 2017
Copyright © 2017, American Chemical Society

Logged in as:
Meixi Chen
University of Delaware
[LOGOUT](#)

PERMISSION/LICENSE IS GRANTED FOR YOUR ORDER AT NO CHARGE

This type of permission/license, instead of the standard Terms & Conditions, is sent to you because no fee is being charged for your order. Please note the following:

- Permission is granted for your request in both print and electronic formats, and translations.
- If figures and/or tables were requested, they may be adapted or used in part.
- Please print this page for your records and send a copy of it to your publisher/graduate school.
- Appropriate credit for the requested material should be given as follows: "Reprinted (adapted) with permission from (COMPLETE REFERENCE CITATION). Copyright (YEAR) American Chemical Society." Insert appropriate information in place of the capitalized words.
- One-time permission is granted only for the use specified in your request. No additional uses are granted (such as derivative works or other editions). For any other uses, please submit a new request.

[BACK](#)[CLOSE WINDOW](#)

Copyright © 2017 [Copyright Clearance Center, Inc.](#) All Rights Reserved. [Privacy statement](#). [Terms and Conditions](#).
Comments? We would like to hear from you. E-mail us at customercare@copyright.com



RightsLink®

[Home](#)
[Account Info](#)
[Help](#)


Title: Minority carrier lifetime measurements: An electrical passivation study

Conference Proceedings: Photovoltaic Specialist Conference (PVSC), 2015 IEEE 42nd

Author: Meixi Chen

Publisher: IEEE

Date: June 2015

Copyright © 2015, IEEE

Logged in as:
Meixi Chen
University of Delaware

[LOGOUT](#)

Thesis / Dissertation Reuse

The IEEE does not require individuals working on a thesis to obtain a formal reuse license, however, you may print out this statement to be used as a permission grant:

Requirements to be followed when using any portion (e.g., figure, graph, table, or textual material) of an IEEE copyrighted paper in a thesis:

- 1) In the case of textual material (e.g., using short quotes or referring to the work within these papers) users must give full credit to the original source (author, paper, publication) followed by the IEEE copyright line © 2011 IEEE.
- 2) In the case of illustrations or tabular material, we require that the copyright line © [Year of original publication] IEEE appear prominently with each reprinted figure and/or table.
- 3) If a substantial portion of the original paper is to be used, and if you are not the senior author, also obtain the senior author's approval.

Requirements to be followed when using an entire IEEE copyrighted paper in a thesis:

- 1) The following IEEE copyright/ credit notice should be placed prominently in the references: © [year of original publication] IEEE. Reprinted, with permission, from [author names, paper title, IEEE publication title, and month/year of publication]
- 2) Only the accepted version of an IEEE copyrighted paper can be used when posting the paper or your thesis online.
- 3) In placing the thesis on the author's university website, please display the following message in a prominent place on the website: In reference to IEEE copyrighted material which is used with permission in this thesis, the IEEE does not endorse any of [university/educational entity's name goes here]'s products or services. Internal or personal use of this material is permitted. If interested in reprinting/republishing IEEE copyrighted material for advertising or promotional purposes or for creating new collective works for resale or redistribution, please go to http://www.ieee.org/publications_standards/publications/rights/rights_link.html to learn how to obtain a License from RightsLink.

If applicable, University Microfilms and/or ProQuest Library, or the Archives of Canada may supply single copies of the dissertation.

[BACK](#)
[CLOSE WINDOW](#)

Copyright © 2017 [Copyright Clearance Center, Inc.](#) All Rights Reserved. [Privacy statement](#). [Terms and Conditions](#).
Comments? We would like to hear from you. E-mail us at customercare@copyright.com

ELSEVIER ORDER DETAILS

Dec 22, 2017

Order Number	501340287
Order date	Nov 27, 2017
Licensed Content Publisher	Elsevier
Licensed Content Publication	Elsevier Books
Licensed Content Title	Reference Module in Chemistry, Molecular Sciences and Chemical Engineering
Licensed Content Author	M. Chen, J. Hack, A. Iyer, X. Lin, R.L. Opila
Licensed Content Date	2017
Licensed Content Volume	n/a
Licensed Content Issue	n/a
Licensed Content Pages	1
Start Page	
End Page	
Type of Use	reuse in a thesis/dissertation
Portion	full chapter
Format	both print and electronic
Are you the author of this Elsevier chapter?	Yes
Will you be translating?	No
Title of your thesis/dissertation	RADICAL-DRIVEN SILICON SURFACE PASSIVATION FOR ORGANIC-INORGANIC HYBRID PHOTOVOLTAICS
Expected completion date	Dec 2017
Estimated size (number of pages)	100
Requestor Location	University of Delaware 201 Dupont Hall NEWARK, DE 19716 United States Attn: University of Delaware
Publisher Tax ID	98-0397604
Total	Not Available