

**EFFECTS OF SURFACE MODIFICATION ON CHARGE-
CARRIER DYNAMICS AT SEMICONDUCTOR INTERFACES**

Thesis by
Agnes Juang

In Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy

California Institute of Technology

Pasadena, California

2003

(Defended July 16, 2002)

© 2003

Agnes Juang

All Rights Reserved

Acknowledgments

The past five years have been the most incredible time of my life. Graduate school has changed the way I learn, the way I think, and the way I see things. I have gained so much more than what I had anticipated throughout the course of my study at Caltech, and I am glad that I chose to come here and stayed even when things got tough. Along the way, many people have landed their helping hands and gave me the strength to hang on. Without them, this thesis would not have been born.

I am grateful to have had a chance to learn electrochemistry first hand from Prof. Nathan Lewis. He is not only an exceptional scientist, but also one of the best in the field. I have learned a lot from Nate over the years including his high standard for research and persistent scientific honesty; his scientific intuition has not ceased to amaze me. I truly appreciate his forbearance and trust for allowing me to become an independent researcher.

I am thankful to have started my graduate work with a bunch of talented group members. Among all, Dr. Arnel Fajardo was the one whom I followed around the most, and the one who showed me how to hook up my electrochemical cell to the potentiostat. I am lucky to have Dr. Rob Rossi around for most of my time here at Caltech. He had provided me with lots of help and encouragement in and out of the lab. He was also the one who dragged me to the top of the snow-covered Bear Mountain and introduced me to the wonderful world of skiing, which had become my passion and had kept me sane during the winter time. To many others like Florian Gstrein, Dr. Nicholas Prokopuk, and Dr. William Royea, from whom I have learned a trick or two that made my work easier, my thanks go to them. As for the late comers, many have impressed me with their hunger for knowledge and their ambitions to make difficult projects work. Some of them have also let me use their instrument time during the last few months, which allowed me

to finish up on time, and I have to thank them for that. I am also very thankful to have a great collaborator Oren Scherman for the work included in Chapter 4. He saved me from having to do many organic synthesis, and I could always count on him for the best home-made chemicals.

Although Caltech is a wonderful place to be for researchers, it can sometimes make individuals feel trapped or isolated. Without my two closest friends at Caltech, Heather Cox and Dr. Anne Fu, and the almost-weekly lunch meetings we had, I would not have had many chances to talk about something other than science and politics when I am on campus. I also thank all of Nate's administrative assistants, especially Nannette Pettis, who had offered me help and an open door for small chats and complaints. Many people in Chemistry Department and Caltech administrative offices had also made my life easier when I was the head TA for Chem 1, and for that I gratefully thank them.

Best of all, I have met someone who understands not only my research, but also my heart. I thank Nick for his caring, patience, and love. He has shown me the true meaning of partnership through his constant support and understanding. He has also brought endless joy and laughter into my life; with him, life is always fun, fun, fun!

I would like to dedicate this thesis to my parents, Stephen and Sophia, who had bought me my first volume of science book and introduced me to the science at an early age. They had made me believe that I can do anything I want, and never stop having faith in me. Because of their hard work and sacrifices, I never had to worry about anything. Their unconditional love and support throughout my life is immeasurable, and I am forever indebted to that.

Abstract

Understanding the basic concepts of semiconductor junctions is an important step towards the development of efficient solar energy conversion devices. The work described in this dissertation includes both the investigation of semiconductor/liquid junctions and the modification of semiconductor surfaces for achieving chemical control over physical properties.

The interfacial charge-carrier dynamics of *n*-GaAs/CH₃CN junctions has been investigated. Differential capacitance barrier height measurements and steady-state current density–potential (*J–E*) measurements were used to evaluate the degree of partial Fermi-level pinning. The presence of irreversible chemical and/or electrochemical changes on *n*-GaAs electrodes immersed in CH₃CN-CoCp₂⁺⁰ solutions was examined using x-ray photoelectron spectroscopy (XPS) and cyclic voltammetric studies that were designed to probe surface reactions.

Chemical modifications of semiconductor surfaces can provide a reliable mean to control physical properties of semiconductor interfaces. The growth of robust polymer films that are covalently attached to Si surfaces via a Si-C linkage was demonstrated. Uniform polymer overlayers of different thicknesses were formed using a general method combining chlorination/Grignard reaction with ring-opening metathesis polymerization (ROMP). The surfaces of these modified Si were characterized by x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), ellipsometry, and/or profilometry. The charge-carrier dynamics at these modified Si/air interfaces was investigated using transient photoconductivity decay method. Time-dependent photoconductivity measurements further confirmed the ability for polymer-terminated Si to maintain low surface recombination velocities once exposed to the air.

Table of Contents

Acknowledgments.....	iii
Abstract.....	v
Table of Contents	vi
List of Figures.....	ix
List of Tables	xii

Chapter 1 Introduction 1

1. Overview.....	2
2. Charge-Transfer Equilibration at Semiconductor Heterojunctions.....	5
3. Current–Voltage Properties of a Semiconductor Diode	12
4. Charge-Carrier Recombination Mechanisms.....	14
4.1. Interfacial Electron Transfer/Thermionic Emission.....	17
4.2. Electron Tunneling.....	18
4.3. Surface-State Recombination.....	19
4.4. Depletion-Region Recombination.....	23
4.5. Bulk-Region Recombination	24
5. Surface States	26
6. References.....	28

Chapter 2 Photoelectrochemical Behavior of *n*-GaAs in Acetonitrile Solutions 29

1. Introduction.....	30
2. Background	32
2.1. Determination of the Electron-Transfer Rate Constant at the Semiconductor/Liquid Interface.....	32
2.2. Fermi-Level Pinning.....	34
3. Experimental	37
3.1. Electrode Material and Etching.....	37
3.2. Solvents and Reagents.....	38
3.3. Electrochemical Measurements	39
3.3.1. Impedance Measurements	39
3.3.2. Steady-State Current Density vs. Potential Characteristics.....	41
3.4. Surface Analysis of <i>n</i> -GaAs in Contact with CH ₃ CN-CoCp ₂ ⁺⁰ Solution.....	44
3.4.1. X-ray Photoelectron Spectroscopy.....	44
3.4.2. Cyclic Voltammetry	45

4.	Results.....	46
4.1.	Differential Capacitance vs. Potential Results and the Barrier Height of n -GaAs/CH ₃ CN-CoCp ₂ ⁺⁰ Contacts.....	46
4.2.	Steady-State J - E Behavior of n -GaAs/CH ₃ CN-CoCp ₂ ⁺⁰ Contacts.....	55
4.2.1.	J - E Data for n -GaAs electrodes in CH ₃ CN-CoCp ₂ ⁺⁰ solutions	55
4.2.2.	Photoresponses of n -GaAs electrodes in CH ₃ CN-CoCp ₂ ⁺⁰ and CH ₃ CN-Fc ₂ ⁺⁰ solutions	55
4.2.3.	Effects of Exposure to CH ₃ CN-CoCp ₂ ⁺⁰ Solutions on the Behavior of n -GaAs/CH ₃ CN-Fc ₂ ⁺⁰ Contacts.....	56
4.3.	X-Ray Photoelectron Spectroscopy and Cyclic Voltammetry Data of n -GaAs Surfaces in Contact with the CH ₃ CN-CoCp ₂ ⁺⁰ Electrolyte	62
5.	Discussions.....	66
5.1.	Electrochemical Properties of n -GaAs/CH ₃ CN Contacts.....	66
5.2.	Interfacial Rate Constant Determinations Using n -GaAs/CH ₃ CN Contacts	67
6.	Summary	70
7.	Acknowledgments	70
8.	References and Notes	71

Chapter 3 Fabrication and Characterization of n -Si(111) Based Metal-Insulator-Semiconductor Diodes 74

1.	Introduction.....	75
2.	Experimental	80
2.1.	Solvents and Reagents.....	80
2.2.	Semiconductor Material and Etching	81
2.3.	Surface Modification	82
2.4.	Metal Deposition and Device Fabrications.....	85
2.4.1.	The First-Generation MIS Device.....	85
2.4.2.	The Second-Generation MIS Device	86
2.4.3.	The Third-Generation MIS Device	86
2.4.4.	The Fourth-Generation MIS Device	87
2.5.	Surface Characterization.....	93
2.6.	Electrical Measurements.....	94
3.	Results.....	97
3.1.	Surface Modification	97
3.2.	The J - E Behaviors of MIS Diodes	100
4.	Discussions.....	107
5.	Summary	110
6.	References.....	110

Chapter 4 Transient Photoconductivity Decay Measurements of Polymer-Terminated Silicon Surfaces 113

1.	Introduction	114
2.	Experimental	119
2.1.	Chemicals.....	119
2.2.	Preparation of Substrates	120
2.3.	Surface Modification	121
2.3.1.	Chlorination	121
2.3.2.	Terminal-Olefin Addition via Grignard Reaction.....	122
2.3.3.	Catalyst Addition	123
2.3.4.	Polymerization	123
2.4.	Surface Characterizations	124
2.4.1.	X-ray Photoelectron Spectroscopy.....	124
2.4.2.	Overlayer Thickness Measurements: Ellipsometry and Profilometry	125
2.4.3.	Scanning Electron Microscopy	126
2.5.	Photoconductivity Decay Measurements	130
3.	Results.....	138
3.1.	Surface Modifications	138
3.1.1.	Polynorbornene-Terminated Si.....	139
3.1.2.	PolyDCPD-Terminated Si	139
3.1.3.	ROMP of COD and COT	140
3.1.4.	Control Experiments	140
3.2.	Surface Characterizations	148
3.2.1.	Polymer Thickness Measurements.....	148
3.2.2.	Scanning Electron Microscopy	148
3.3.	Photoconductivity Decay Measurements	156
3.3.1.	C3 Olefin-Terminated and C3 Olefin-Polymer-Terminated Si Surfaces	156
3.3.2.	Effects of Olefin Linker Chain Length.....	158
3.3.3.	C5 Olefin-Terminated and C5 Olefin-Polymer-Terminated Si Surfaces	158
3.4.	Time-Dependent XPS Studies: Oxidation of Modified Si surfaces in Air.....	172
4.	Discussions.....	180
4.1.	Surface Modifications and Characterizations	180
4.2.	Surface Recombination Velocity and Oxidation	184
5.	Summary	188
6.	Acknowledgments	188
7.	References	189

List of Figures

Chapter 1

Figure 1.1	A band bending diagram for an ideal n -type semiconductor/liquid junction.	8
Figure 1.2	A band bending diagram for an ideal n -type semiconductor/metal junction.	10
Figure 1.3	Various types of recombination pathways for an n -type semiconductor/liquid junction.	16
Figure 1.4	A schematic depicting the microscopic balance between electron and hole capture and emission processes at recombination centers in the semiconductor.	22

Chapter 2

Figure 2.1	Open-circuit photovoltage vs. equilibrium cell potential for the n -GaAs/CH ₃ CN-LiClO ₄ system at $J_{ph} = 1.0 \text{ mA cm}^{-2}$	36
Figure 2.2	Circuit diagrams for a semiconductor/liquid junction.	43
Figure 2.3	(a) A representative Bode plot for the n -GaAs/CH ₃ CN-CoCp ₂ ⁺⁰ junction.	49
	(b) A plot of phase angle vs. $\log f$ for the n -GaAs/CH ₃ CN-CoCp ₂ ⁺⁰ junction.	50
	(c) A representative Nyquist plot for the n -GaAs/CH ₃ CN-CoCp ₂ ⁺⁰ junction.	51
Figure 2.4	(a) Mott-Schottky plot of the n -GaAs/CH ₃ CN-CoCp ₂ ⁺⁰ junction.	53
	(b) Linear extrapolations of the Mott-Schottky data shown in (a).	54
Figure 2.5	Representative J - E behaviors of n -GaAs electrodes in contact with CH ₃ CN-CoCp ₂ ⁺⁰ solution.	57
Figure 2.6	Representative J - E behaviors of n -GaAs electrodes in contact with slightly wet CH ₃ CN-CoCp ₂ ⁺⁰ solution.	58
Figure 2.7	(a) The J - E behavior of n -GaAs electrode in contact with CH ₃ CN-Fc ⁺⁰ solution.	60
	(b) The J - E behavior of n -GaAs electrode in contact with CH ₃ CN-Fc ⁺⁰ solution after performing J - E scans in CH ₃ CN-CoCp ₂ ⁺⁰ solution.	61
Figure 2.8	XP survey spectra of n -GaAs before and after 10 minutes of J - E scans in a CH ₃ CN-CoCp ₂ ⁺⁰ solution.	64
Figure 2.9	Cyclic voltammogram of n -GaAs in CH ₃ CN-0.7 M LiClO ₄ in the absence of a redox species.	65

Chapter 3

Figure 3.1	A band bending diagram of a metal/insulator-semiconductor (MIS) junction.....	79
Figure 3.2	An illustration of the first-generation MIS device.....	89
Figure 3.3	An illustration of the second-generation MIS device.....	90
Figure 3.4	An illustration of the third-generation MIS device.....	91
Figure 3.5	An illustration of the fourth-generation MIS device.....	92
Figure 3.6	XP survey spectra of H-terminated, Cl-terminated, C3-terminated, C6-terminated, and C10-terminated Si.....	98
Figure 3.7	(a) $J-E$ behavior of H-terminated Si in contact with 450 Å of Ni..... (b) $J-E$ behavior of C3-terminated Si in contact with 450 Å of Ni.....	102 102
Figure 3.8	$J-E$ behaviors of a series of C_nH_{2n+1} -terminated Si/Ni ($n = 2, 4, 6,$ and 8) and an H-terminated Si/Ni junctions in the dark.....	104
Figure 3.9	Photoresponses of a series of C_nH_{2n+1} -terminated Si/Ni ($n = 2, 4, 6,$ and 8) and an H-terminated Si/Ni junctions in the dark.....	105
Figure 3.10	Time-dependent $J-E$ behaviors of a C_8H_{17} -terminated Si/Ni junction in the dark	106

Chapter 4

Figure 4.1	Polymer-terminated Si surfaces reported in literature	117
Figure 4.2	Experimental approach to produce a variety of covalently attached polymer overlayers on Si surfaces	127
Figure 4.3	A schematic of the radio frequency (rf) apparatus used to perform photoconductivity decay measurements.....	133
Figure 4.4	(a) A schematic of the controlled-environment chamber for sample storage	136
	(b) A photograph of the controlled-environment setup.....	137
	(c) A detailed photograph of the chamber interior.....	137
Figure 4.5	XP survey spectra of each step of the surface modification.....	142
Figure 4.6	XP survey spectra of polyDCPD-terminated Si.	144
Figure 4.7	XP survey spectra of control experiments.....	146
Figure 4.8	(a) A partial profilometric surface profile of a polynorbornene-terminated Si surface.....	151
	(b) A SEM image of the same surface at 30× magnification	151
Figure 4.9	SEM top-view images of polynorbornene-terminated Si surfaces.	153
Figure 4.10	A cross-sectional SEM image of a polynorbornene-covered Si surface	155
Figure 4.11	Time-resolved photoconductivity decay curves of C3 olefin-terminated, C3 olefin-polynorbornene-terminated, and C3 olefin-polyDCPD-terminated Si surfaces in an $N_2(g)$ ambient.....	161

Figure 4.12	Time dependence of the mean carrier lifetimes for C3 olefin-terminated, C3 olefin-polynorbornene-terminated, and C3 olefin-polyDCPD-terminated Si in air	162
Figure 4.13	Time dependence of the mean carrier lifetimes for mixed methyl/C3 olefin-terminated, C3 olefin-terminated, C5 olefin-terminated, and C6 olefin-terminated Si surfaces in air.....	163
Figure 4.14	Time-resolved photoconductivity decay curves of C5 olefin-terminated, C5 olefin-polynorbornene-terminated, and C5 olefin-polyDCPD-terminated Si surfaces in an N ₂ (g) ambient.....	164
Figure 4.15	(a) Time dependence of the mean carrier lifetimes for C5 olefin-terminated Si surfaces exposed to high temperature/humidity and low temperature/humidity conditions	166
	(b) Time dependence of the mean carrier lifetimes for C5 olefin-polynorbornene-terminated Si surfaces exposed to high temperature/humidity and low temperature/humidity conditions.....	167
	(c) Time dependence of the mean carrier lifetimes for C5 olefin-polyDCPD-terminated Si surfaces exposed to high temperature/humidity and low temperature/humidity conditions.....	168
Figure 4.16	Time dependence of the mean carrier lifetimes for C5 olefin-terminated, C5 olefin-polynorbornene-terminated, and C5 olefin-polyDCPD-terminated Si surfaces exposed to a low temperature/humidity condition.....	169
Figure 4.17	Time dependence of the mean carrier lifetimes for C5 olefin-terminated, C5 olefin-polynorbornene-terminated, and C5 olefin-polyDCPD-terminated Si surfaces exposed to a high temperature/humidity condition.....	170
Figure 4.18	Time-dependent high-resolution XP spectra of C5 olefin-terminated Si under low temperature/humidity condition.....	174
Figure 4.19	Time-dependent high-resolution XP spectra of C5 olefin-terminated Si under high temperature/humidity condition.....	175
Figure 4.20	Time-dependent high-resolution XP spectra of C5 olefin-polyDCPD-terminated Si under low temperature/humidity condition	176
Figure 4.21	Time-dependent High-resolution XP spectra of C5 olefin-polyDCPD-terminated Si under high temperature/humidity condition	177
Figure 4.22	Time-dependent high-resolution XP spectra of H-terminated Si under low temperature/humidity condition	178
Figure 4.23	A space-filling model of a Ru catalyst and a Si surface.....	183
Figure 4.24	The aged Si 2p high-resolution XP spectra of H-TERMINATED, C5 olefin-terminated, and C5 olefin-polyDCPD-terminated surfaces.....	187

List of Tables

Chapter 3

Table 3.1	A summary of reaction time, overlayer thickness, and air stability of alkyl-terminated Si.....	84
-----------	--	----

Chapter 4

Table 4.1	List of reagents and reaction conditions for Si surface modification	129
Table 4.2	Dependence of the polymer overlayer thickness on the concentration of norbornene in the solution.....	150
Table 4.3	Time-dependent measured carrier recombination lifetimes and surface recombination velocities for various modified Si surfaces	171
Table 4.4	Time dependence of the silicon oxide growth for polymer-terminated Si.....	179