Spectroscopic, Electronic, and Mechanistic Studies of Silicon Surfaces Chemically Modified with Short Alkyl Chains

Thesis by

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I have been lucky enough to have one of the most experienced and supportive committees possible in graduate school. Bill Goddard has been supportive and provided valuable advice during committee meetings and exams. Thank you, Bill, for working with me though this process! Harry Gray served as the chair of my committee, and has been incredibly encouraging throughout graduate school. Through the National Science Foundation Center for Chemical Innovation: Solar Fuels program, I have had the fantastic opportunity of working with Harry on outreach programs like Juice from Juice. Thanks to Harry, I was also supported through the CCI for my last year and some months of graduate school. Thank you Harry for supporting me and giving me a place to work on community outreach!

Bruce Brunschwig has been my fourth committee member since my props exam, but he has been my friend and surrogate advisor since I joined the Lewis group. I have worked with Bruce since I started as a GLA in the MMRC shortly after we purchased the Dimension Icon AFM. After about 6 months with the AFM, I was moved to the much more labor-intensive XPS instruments. While I have been slowly retiring my XPS responsibilities over the last year, this job had a substantial impact, mostly good and some bad, on my experience in graduate school. Bruce always remained an invaluable resource when doing these jobs, and I really valued his support through the times when the instruments were misbehaving. Additionally, Bruce has been incredibly patient with me, particularly when it comes to charge transfer kinetics at interfaces, and I have learned so much from working with him over the years. Thank you, Bruce, for making my experience in the Lewis group better a great one!

As an XPS GLA, I got to work with some of the best Lewis group members. Taking over responsibilities from Joseph Beardslee and Judy Lattimer was quite an initial shock. Thank you to Joseph and Judy for making the transition as painless as possible! I started my GLA responsibilities with Adam Nielander and Amanda Shing, both of who remain my good friends. Thanks, Adam and Amanda! You made it fun to be a GLA and have all the power!!! Now, I'm handing responsibilities to the seasoned Jonathan Thompson, the somewhat less experienced Annelise Thompson, and the brand new Ellen Yan. All of you have helped make being a GLA, even as I drift farther away from the day-to-day responsibilities, a very positive experience. Best of luck to Jonathan, Annelise, and Ellen!

As a first year getting started in the Lewis group, I remember being overwhelmed with the range of different work that the Lewis group was doing. Coming from a background in Vitamin B_{12} kinetics, which I studied as an undergraduate, I had to find an area that interested me in a very diverse and large research group. Initially, I worked with Shane Ardo, who has been an inspiration to me since. A few months into working with Shane, Leslie O'Leary, then a graduating 5th year, approached me about taking on some collaborative projects involving Si surface chemistry. I had initially anticipated working with both Leslie and Shane, but the time-sensitive nature of the collaborations took priority and I soon discovered that Si surface chemistry is a full-time project. As Leslie departed for Dow Chemical a couple months after teaching me the ropes, Ron Grimm became an informal mentor in the lab. Anyone who knows Ron knows that he is truly unique and extremely multi-talented. From how to make a temperature-controlled hot plate to how to review manuscripts, Ron taught me so many of the little skills that I am so grateful to have now. Thank you Ron, Shane, and Leslie for guiding my initial few years in graduate school and providing me with the foundation to succeed!

The Lewis group, by my estimation, is by far one of the most cohesive and fun groups at Caltech, despite being spread out over 3 campus buildings. I have made such an enormous group of phenomenal friends over the years! As academia is structured around the constant revolving door of people, particularly postdocs who come and go faster than the graduate students, one has the advantage of constantly meeting new people. The disadvantage, of course, is the slow but constant stream of friends leaving for greener pastures. When I joined the Lewis group, there were 8 of us, which soon reduced to 7 and the 6. Our giant year was only rivaled and surpassed by the year that came 2 after ours. Azhar Carim, Michael Lichterman, Fadl Saadi, Nick Batara, and Victoria Dix are now all my good friends – I couldn't have done it without you!

I always enjoyed my conversations with James Blakemore, and when we got Adam Nielander, Aaron Sattler, or Wes Sattler involved, something good and possibly crazy was bound to happen. I look back on trips I went on to Las Vegas with Adam, James, Aaron, Wes, Rob Corridan, Mita Dasog, and Sonja Francis with great fondness. I'll never ever forget the trouble we got into at the Paris club the last time we were there. I also will never forget my darling Sonja Francis, who went with me to Italy! We had such an amazing time, and I have the photos to prove it! I would go visit anywhere with you by my side!

I had the good fortune in graduate school of working with two amazing undergraduate students. Allison Lim came from Harvey Mudd College to work with me in Summer of 2014. She came from working with Ron Grimm while he was a temporary faculty member there, and she was very eager to learn all about semiconductor interfaces. Thank you, Allison, for making my experience as a first-time mentor a positive one. Anshul Ramachandran was my second attempt at mentoring an undergraduate, and his project picked up where Allison's left off. I was lucky to work with both Allison and Anshul, and I am so pleased that we got to write a paper together! Good luck with graduate school, Allison, and good luck with your last couple years at Caltech, Anshul. Also, Anshul, keep up the break dancing!

I also had the great pleasure of working with Mita Dasog on the work presented in Chapter 5 of this thesis. Thank you, Mita, for working with me on this project. Without your influence, I wouldn't have made it through that project. I also want to thank Paul Kempler, who spent some time doing a little bit of surface chemistry and looking for ferrocene in Big Bird. I know you'll put the surface chemistry skills to good use with your microwire project! Miguel Caban-Acevedo is carrying the silicon surface chemistry torch in the Lewis group, with Ellen, Annelise, and Josh Wiensch developing new ways to do chemistry on tricky 2-dimensional materials. Another indispensible person who must be thanked is Barbara Miralles. Barbara, I am so glad to have your support on the administrative end of things! Your understanding and patience have benefited us all in the Lewis group, and you really do make the world go around as far as I'm concerned.

I also want to devote a quick sentence or two to thank Azhar, Kyra Lee, and Dan Torelli + Susie Haubner for consistently serving as fantastic hosts for house parties. I had so much fun hanging out at your respective places! We will definitely be having a few more parties before I am out of here for good! The atmosphere that you created in the Lewis group has helped dull a lot of the stress and tension that is built into Caltech, and your influence on the group has been invaluable. I honestly have a hard time coming to the realization that our parties left together are limited.

Lastly, I want to thank my family, who has always encouraged me to do my best and find the career I love. Dad always provided me with level headed advice and has not steered me wrong yet! Mom always was a great listener whenever I had something that was bothering me or when I just needed to talk about something. I truly adore my parents, and I hope I can be like them someday. My sister, Rachel, is absolutely without a doubt my favorite person in the world. Somehow, she and I have developed a nearly identical sense of humor, and all of our conversations leave me in such a good mood. Thank you, mom, dad, and Rachel, for all of your support over the years and also keeping up with me all the way from Ohio! I love you all!

ABSTRACT

The chemical, structural, and electronic properties of semiconductor surfaces are known to strongly influence the energetics at semiconductor interfaces. Inexpensive and scalable wet chemical modification of semiconductor surfaces provides a means to impart a desired functionality at semiconductor interfaces for the development of new devices based on precise and cost-effective chemistry. This thesis is composed of three studies that focused on identifying the spectroscopic, electronic, and mechanistic properties of reactions at Si surfaces. First, ethynyl- and propynyl-terminated Si(111) surfaces were prepared and characterized by vibrational and photoelectron spectroscopy as well as electrochemical scanning-tunneling microscopy. Ethynyl-terminated Si(111) exhibited ≡C−H, C≡C, Si−C stretching signals and a fractional monolayer (ML) coverage (Φ) of $\Phi_{\text{Si–CCH}} = 0.63 \pm 0.08$ ML and $\Phi_{\text{Si–OH}} = 0.35 \pm 0.03$ ML. Propynyl-terminated Si(111) showed $(\text{C–H})_{\text{CH}_3}$ bending, Si−C stretching, and C≡C stretching with $\Phi_{\text{Si–CCH}_3} = 1.05 \pm 0.06$ ML. Deprotonation of ethynyl-terminated Si(111) surfaces formed a unique surface-bound lithium acetylide that acted as nucleophile. This work provides definitive spectroscopic and microscopic evidence for the covalent attachment of ethynyl and propynyl groups to the Si(111) surface.

Second, Si(111) surfaces were modified with 3,4,5-trifluorophenylacetylene (TFPA) groups to impart a positive dipole at the Si(111) surface. This negative surface dipole provides the necessary band-edge shift at the Si surface to maximize the interface between p-type Si and the proton reduction half reaction. Vibrational and photoelectron spectroscopy provided evidence for the attachment of TFPA groups to the Si(111) surface. Mixed methyl/TFPA monolayers were prepared and characterized using electrochemical and photoelectrochemical methods to show that the band-edge positions and open-circuit voltages were shifted positive with increasing fractional TFPA coverage on the surface. This work demonstrates that monolayer chemistry can be used to manipulate the band-edge positions of Si surfaces as a function of surface composition.

Finally, mechanistic studies of the reaction of liquid methanol with hydride-terminated Si(111) surfaces in the presence of an oxidant were carried out. Vibrational and photoelectron spectroscopy showed that acetylferrocenium, ferrocenium, and dimethylferrocenium could serve as oxidants to promote an increased rate of methoxylation of the H–Si(111) surface in the dark. Illumination of intrinsic and n-type surfaces resulted in an increased rate of methoxylation, resulting from a positive shift in energy of the electron quasi-Fermi level in the presence of light. The results are described in the context of a kinetic charge transfer formalism that is consistent with the experimentally observed results. This work provides a general framework to describe the kinetics of charge transfer reactions that occur on semiconductor surfaces.

PUBLISHED CONTENT AND CONTRIBUTIONS

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Plymale, N. T. participated in the conception of the project, performed the sample preparation, collected the majority of the data, performed the data analysis, and participated in writing the manuscript.

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Plymale, N. T. participated in the conception of the project, the sample preparation, the data collection, the data analysis, and the writing of the manuscript.

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