

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

Thesis by
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In Partial Fulfillment of the Requirements for
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Doctor of Philosophy

The logo for the California Institute of Technology (Caltech), featuring the word "Caltech" in a bold, orange, sans-serif font.

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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 $\equiv\text{C-H}$, $\text{C}\equiv\text{C}$, 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 $\text{C}\equiv\text{C}$ stretching with $\Phi_{\text{Si-CCCH}_3} = 1.05 \pm 0.06$ 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.

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