New Approaches to Functionalize Silicon to Expand the Toolbox for Solar Fuel Generation

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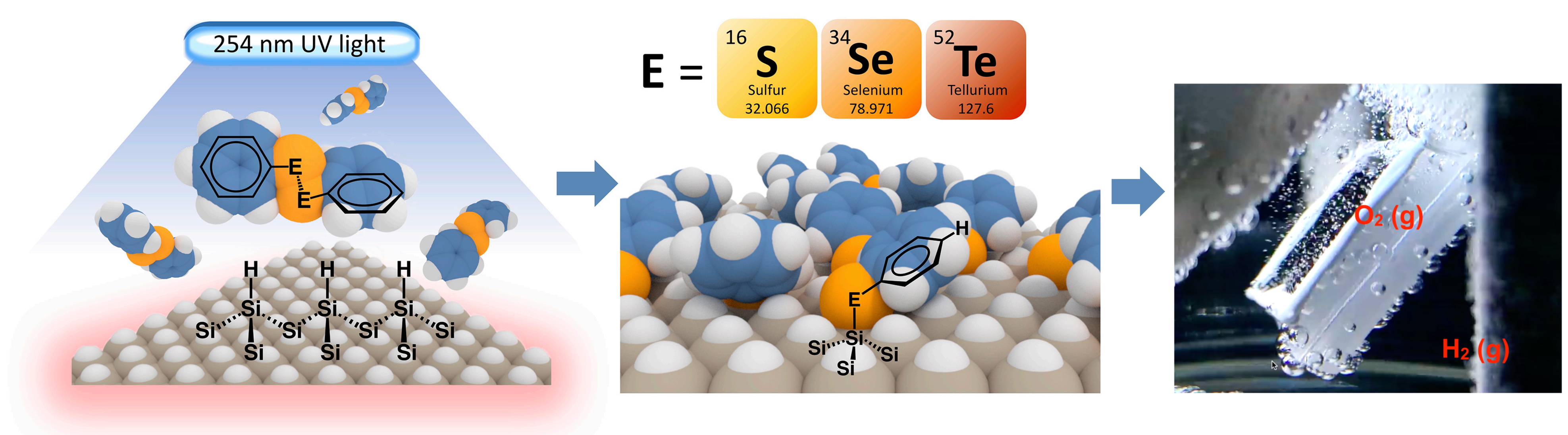
Introduction

Depletion of fossil fuels and increasing environmental concerns have triggered an urgent demand for sustainable alternative energy sources. Due to an abundant raw material supply and a nearly optimum bandgap for sunlight absorption, silicon-based light absorbers are being considered for solar energy conversion to solar fuels. Nano- and microcrystalline silicon-based light absorbers, in particular nanowire structures, are being functionalized with inorganic, organic, and bacterial catalysts for generation of hydrogen gas (H_2), a clean-burning fuel. Exquisite control over surface chemistry is critical to enable efficient charge transfer, and to stabilize the interfaces for extended periods of time under demanding conditions. While silicon-carbon bond formation on silicon surfaces has been extensively studied, including by our group, the interfaces tend to be resistive, blocking charge transfer. We are therefore studying other atomic linkers to develop more electrochemically active interfaces, based upon chalcogenides, to develop new interfaces for solar fuel generation.



Scheme 1. Overall reaction scheme summarizing the functionalization of silicon surface with silicon-chalcogen bonds (Si-S, SI-Se and Si-Te). The functionalized silicon can be assembled into device for water splitting.

Approaches to Functionalize Silicon

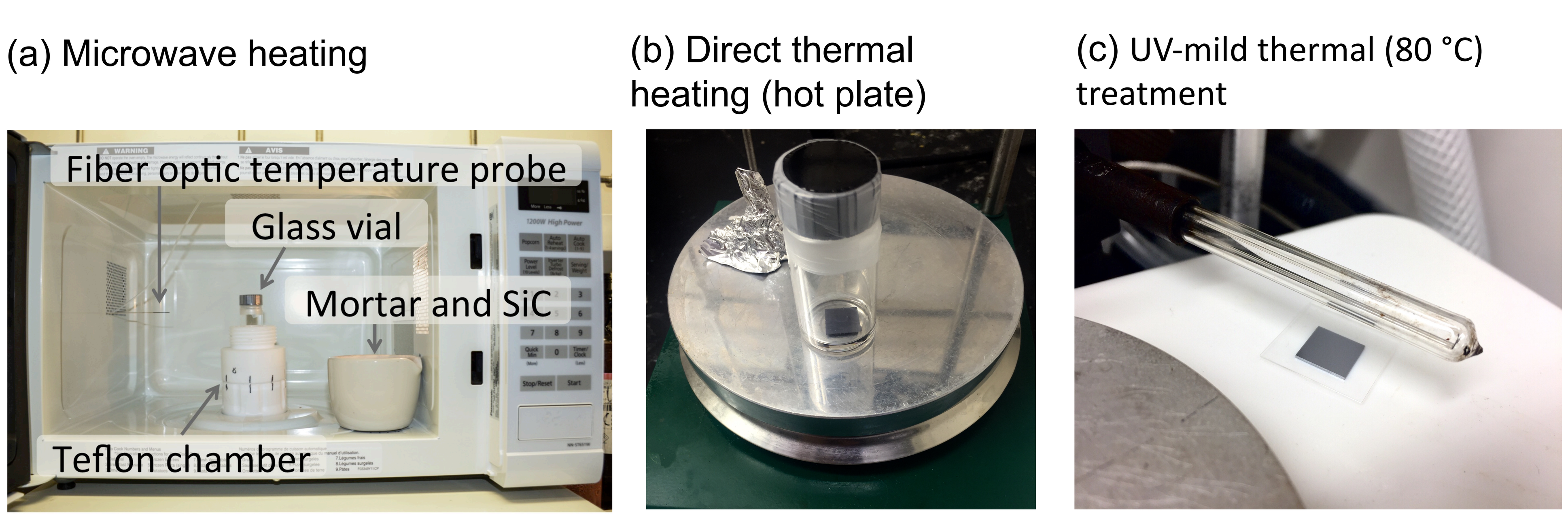


Figure 1. Three approaches to functionalize silicon surface, including (a) microwave heating, (b) direct thermal heating and UV-mild thermal (80 °C) treatment.

Surface Analysis: XPS

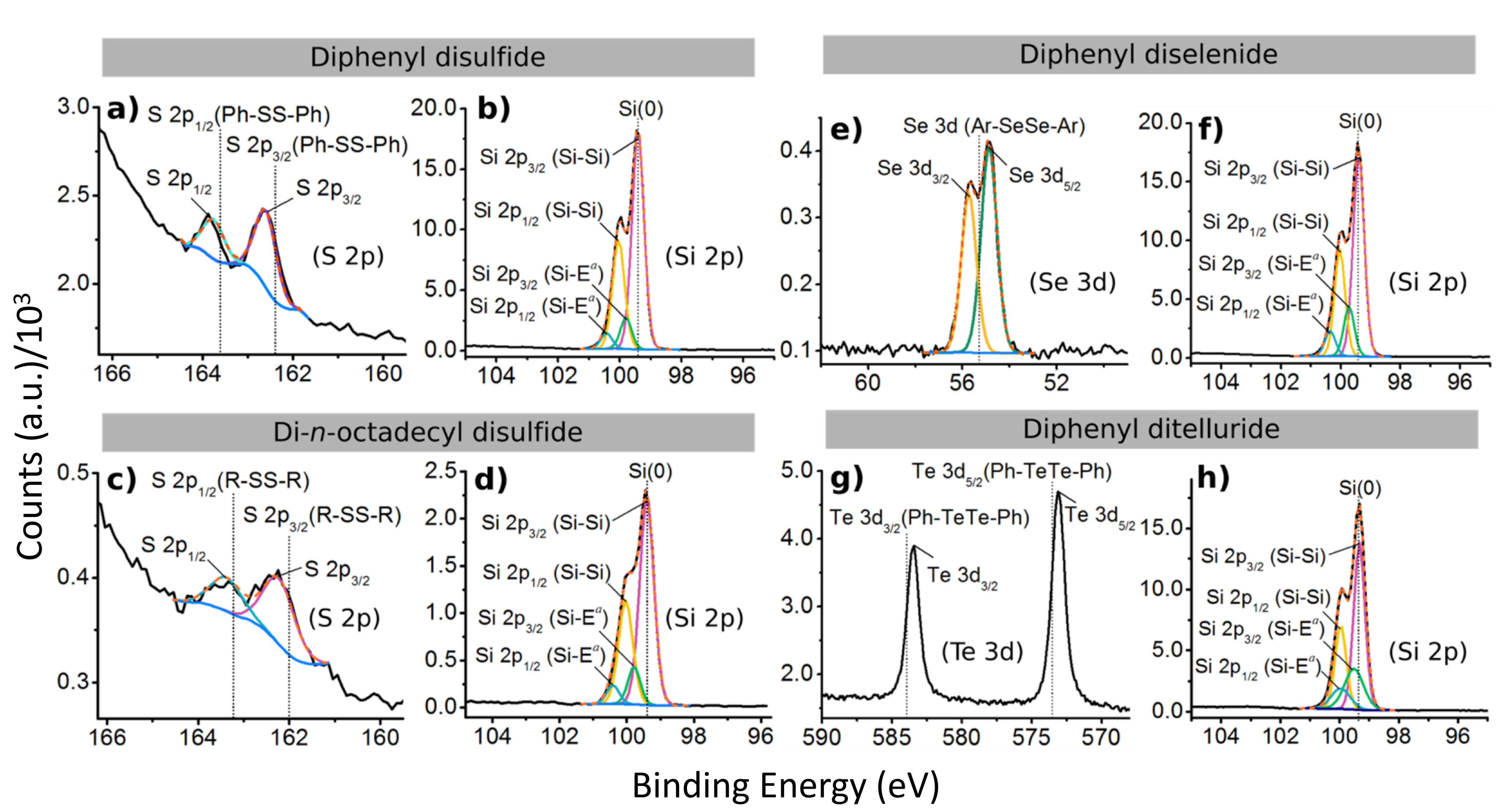


Figure 2. XPS spectra of Si(111) surfaces after the UV-mild thermal (80 °C) treatment with indicated diphenyl dichalcogenides and di-*n*-octadecyl disulfide reagents for 15 min.

Simulation and Model

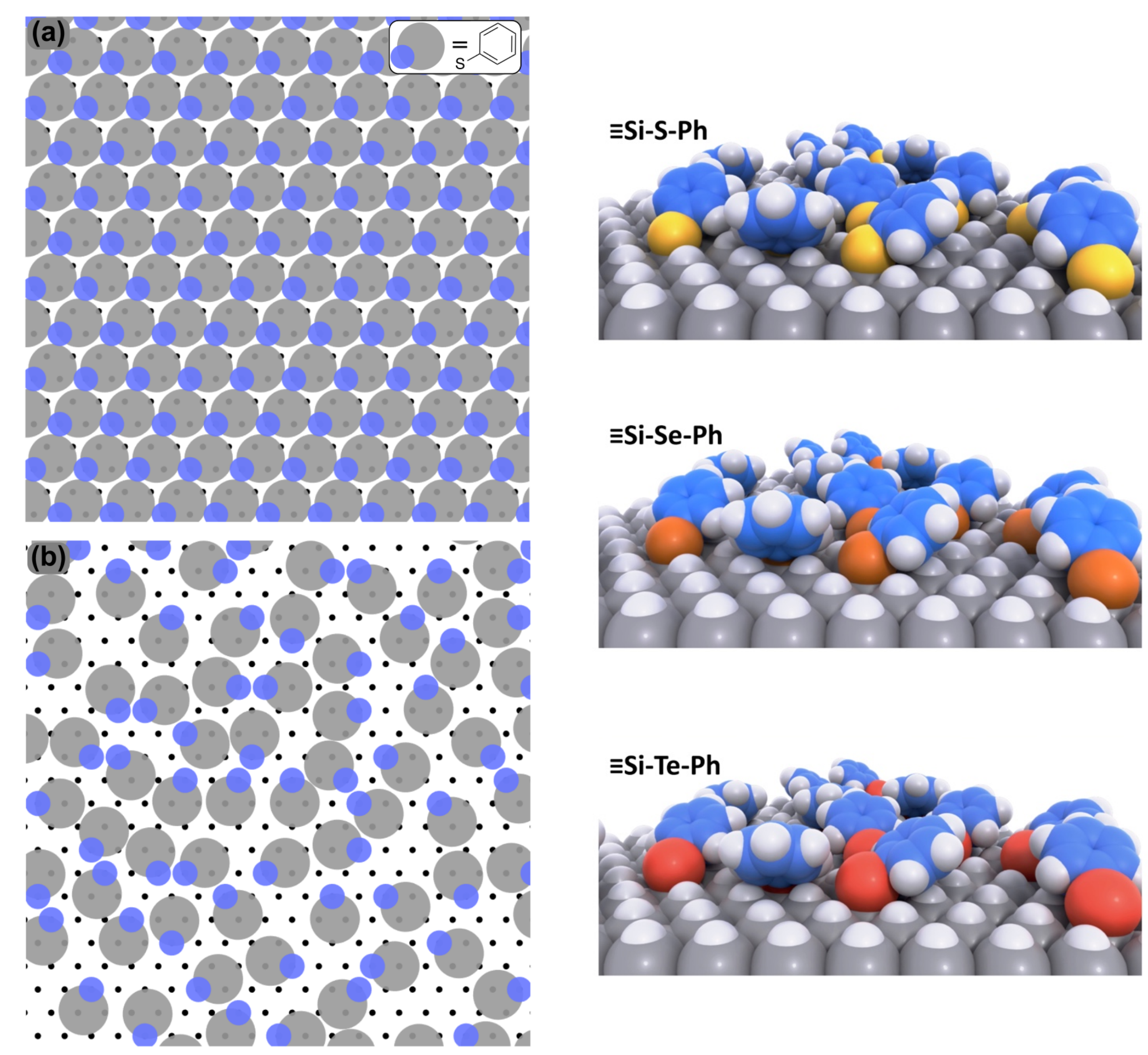


Figure 3. (Left) Simulation of stochastic packing of phenylchalcogenides: (a) Idealized close-packed configuration of ≡Si-S-Ph groups on a Si(111) surface. (b) Configuration resulting from a simulation of stochastically packed ≡Si-S-Ph groups on a Si(111) surface. (Right) Side-view space-filling model of the ≡Si-E-Ph (E = S, Se, Te) interfaces on a flat hydride-terminated Si(111) surface.

Band Diagram

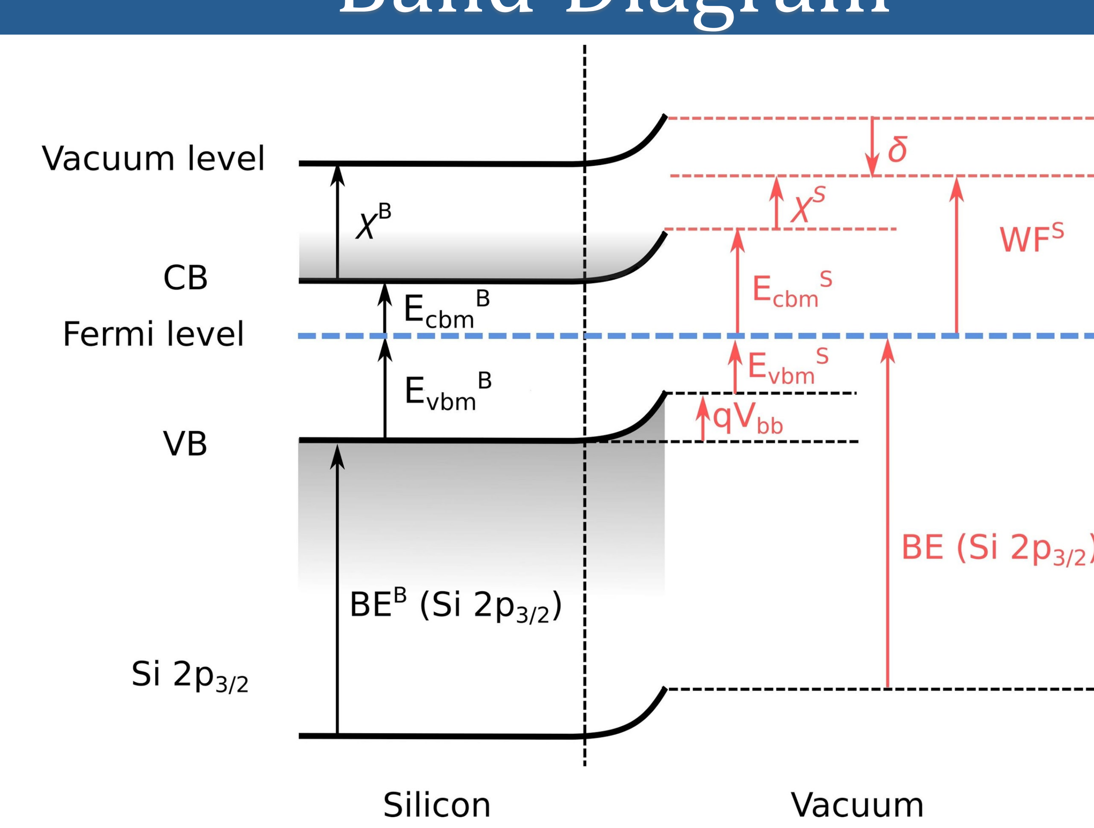


Figure 4. Energy band diagram of functionalized lightly doped n-type Si(111) with band bending, qV_{bb}, and surface dipole, δ.

Conclusions and Future Directions

Three straightforward approaches to form ≡Si−E−R (E = S, Se, Te) functionalities on Si(111)−H surfaces have been described using microwave heating, direct thermal heating or UV irradiation and gentle thermal heating, with synthetically practical dialkyl/diaryl chalcogenide precursors. The future directs will be the doping of the silicon using monolayer doping, which will induce the attached atoms on the silicon surface to diffuse into silicon, followed by the integration of catalysts, and assembly of water splitting devices for testing and optimization.

References

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FES Project Overview

T12-P04

More energy in the form of sunlight hits terrestrial earth in one hour than is used by humanity in an entire year. The first and most important challenge of using an energy source such as solar or wind is its inherent intermittency, necessitating efficient and inexpensive energy storage. Materials constraints are the single most formidable challenge facing solar energy conversion, storage, and conversion, the focus of this FES project.

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