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UV-Initiated Si–S, Si–Se, and Si–Te Bond Formation on Si(111): Coverage, Mechanism, and Electronics

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S Supporting Information

ABSTRACT: Diaryl and dialkyl chalcogenide molecules serve as convenient precursors to silicon–chalcogenide bonds, $\equiv\text{Si}-\text{E}-\text{R}$ groups, on silicon surfaces, where E = S, Se, and Te. The 254 nm light, coupled with gentle heating to melt and liquefy the chalcogenide precursors for 15 min, enables formation of the resulting silicon–chalcogenide bonds. R groups analyzed comprise a long alkyl chain, octadecyl, and a phenyl group. Quantification of substitution levels of the silicon–hydride on the starting $\equiv\text{Si}(111)-\text{H}$ surface by an organochalcogen was determined by XPS, using the chalcogenide linker atom as the atomic label, where average substitution levels of $\sim 15\%$ were found for all $\equiv\text{Si}-\text{E}-\text{Ph}$ groups. These measured substitution levels were found to agree with 2-dimensional stochastic simulations assuming kinetically irreversible silicon–chalcogen bond formation. Due to the small bond angle about the chalcogen atom, the phenyl rings in the case of $\equiv\text{Si}-\text{E}-\text{Ph}$ effectively block otherwise reactive Si–H bonds, leading to the observed lower substitution levels. The linear aliphatic dialkyl disulfide version, $\equiv\text{Si}-\text{S}-n\text{-octadecyl}$, is less limited by steric blocking of surface Si–H groups as is the case with a phenyl group and has a much higher substitution level of $\sim 29\%$. The series, $\equiv\text{Si}-\text{S}-\text{Ph}$, $\equiv\text{Si}-\text{Se}-\text{Ph}$, and $\equiv\text{Si}-\text{Te}-\text{Ph}$, was prepared to determine the effect of chalcogenide substitution on the electronics of the silicon, including surface dipoles and work function. The electronics did not change significantly from the starting $\equiv\text{Si}-\text{H}$ surface, which may be due to the low level of substitution that is believed to be caused by steric blocking by the phenyl groups, as well as the relatively similar electronegativities of these elements relative to silicon.

■ INTRODUCTION

Control of the electronic properties of a semiconductor surface is critical for device applications.^{1–3} Functionalization of a semiconductor surface will affect various fundamental properties of the material, including band bending, an effect that has seen much attention for various semiconductor contacts ranging from metals, solutions, vacuum, and covalently bound molecules.^{4–7} When a semiconductor device becomes small (on the nanoscale), the surface:bulk ratio increases dramatically, and thus surface functionalization can dominate the electronic properties.^{8–10} For a given semiconductor, doping density and type determine the Fermi level relative to valence and conduction bands in the bulk.^{11,12} In the case of a molecular monolayer covalently bound to a semiconductor surface, a new energy level at the interface is created due to hybridization of the semiconductor and molecule. Band bending and alignment alter both work function and electron affinity of the surface, thus creating surface dipoles that can enhance or attenuate the ability to extract electrons from the surface.¹³ The complete energy band diagram can be determined using a combination of X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS).^{4,6,12,14}

Among various substrates developed for molecular electronics, silicon is of particular interest not only due to its ubiquity in microelectronics but also due to the feasibility of interfacing organic molecules through direct, covalent bonds on the silicon surface.¹⁵ Much attention has been focused on silicon surfaces functionalized with monolayers bound through Si–C bonds,^{16–18} and experimental results have been complemented by many theoretical studies.^{6,19,20} Systematic preparation and evaluation of other covalent bonds on silicon are, however, much more limited, but equally intriguing. Computational DFT work has suggested that the nature of the atom through which an organic monolayer is bonded to a silicon surface, the headgroup, can have profound effects on underlying electronics of the silicon.^{21–23} These predictions for chalcogenides have not yet been tested experimentally.

The chemistry of organic molecules bound to silicon surfaces through silicon–chalcogen bonds on surfaces is relatively new

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and has been focused for the most part on sulfur-containing molecules. Functionalization of silicon with organosulfur compounds, resulting in surface-bound silicon–sulfur bonds, was first initiated under ultrahigh vacuum conditions.²⁴ More recently, solution-phase approaches toward silicon–sulfur bound alkyl monolayers were shown to be accessible through reactions of alkanethiols, driven by UV,^{25,26} white light,²⁷ or heat.^{14,28} Using heat and supercritical carbon dioxide as an alkanethiol carrier fluid, monolayers on silicon surfaces bound through $\equiv\text{Si-SR}$ bonds were shown to be stable to prolonged exposure to ambient atmosphere.²⁹ To access silicon–selenium bonds, Bocian and co-workers used a very short (2 min), high-temperature (400 °C) baking procedure to covalently attach acetylchalcogenidoarene-derivatized (Ar-EAc, E = S, Se) porphyrins on Si(111) surfaces through Si–O, Si–S, and Si–Se linkages.^{30,31} However, until recently the complete series of S, Se, and Te linkers remained elusive due to the difficulty of making $\equiv\text{Si-TeR}$ bonds.

In order to secure the $\equiv\text{Si-Te}$ bond and complete the series of chalcogenides, we turned to diorganodichalcogenides (REER, where E = S, Se, Te) as synthetically useful molecular precursors.^{32,33} These molecules are readily available both commercially and synthetically and have a weak dichalcogenide bond that can be easily cleaved to enable silicon surface functionalization through radical-based mechanisms. Diorganodisulfides and diselenides react with porous silicon at room temperature with a diazonium radical initiator, but these conditions are incompatible with diphenyl ditelluride due to its lower solubility.³³ Diorganodichalcogenide molecules, however, very efficiently and cleanly form $\equiv\text{Si-ER}$ bonds (E = S, Se, and Te) on high surface area hydride-terminated porous silicon through microwave heating (10–15 s) or direct thermal heating (230 °C, 2 min), temperatures at which silicon radicals are generated directly through homolytic Si–H bond cleavage.³² Extension of this chemistry from porous silicon to flat Si(111)–H surfaces with these heat-driven approaches failed due to severe contamination with other decomposition products of the diorganodichalcogenide molecules (*vide infra*). In this work, we describe chemistry to functionalize Si(111)–H surfaces with $\equiv\text{Si-ER}$ bonds (E = S, Se, Te), in a manner that is fast and free from both oxidation and contamination from decomposition products of the starting diorganodichalcogenide molecules (Scheme 1). A combination of mild heating and UV irradiation resulted in a “sweet spot” of desired reactivity to enable clean functionalization of silicon with a series of $\equiv\text{Si-S-Ph}$, $\equiv\text{Si-Se-Ph}$, and $\equiv\text{Si-Te-Ph}$ groups. Both the substitution levels and electronic properties of these surfaces were analyzed via XPS. This method was also used with a saturated aliphatic variant, $\equiv\text{Si-S-}n\text{-octadecyl}$.

MATERIALS AND METHODS

General. Si(111) wafers (n-type, phosphorus doped, 1–10 $\Omega\cdot\text{cm}$, $525 \pm 25 \mu\text{m}$) were obtained from Virginia Semiconductor, Inc. Diphenyl disulfide (99%), diphenyl diselenide (98%), and diphenyl ditelluride (98%) were purchased from Sigma-Aldrich. Di-*n*-octadecyl disulfide (98%) was purchased from Alfa Aesar. All reagents were stored in a –20 °C freezer inside an argon-filled glovebox. Dichloromethane was purified by a solvent purification system (Innovative Technology, Inc.) and dried over molecular sieves for 24 h in glovebox prior to use. Molecular sieves (type 4A, 1/16 in. pellets, for selective adsorption), NH_4OH (aqueous, 30%), and HCl (aqueous, 37%) were purchased from Caledon Laboratories, Ltd. NH_4F

Scheme 1. Overall Reaction Scheme Summarizing the Formation of Si–S, Si–Se, and Si–Te Bonds on Si(111)–H Surfaces

(aqueous, 40%, semiconductor grade) was purchased from Transene Company, Inc. H_2O_2 (aqueous, 30%) and 2-propanol ($\geq 99.5\%$) were obtained from Sigma-Aldrich. $\text{KAuCl}_4 \cdot x\text{H}_2\text{O}$ was purchased from Strem Chemicals. HF (49% aqueous, semiconductor grade) was purchased from J. T. Baker.

Flat Si(111)–H Preparation. Silicon wafers were cut into 1 cm $\times$ 1 cm squares using a dicing saw (Disco DAD 321) and then sonicated in 2-propanol for 10 min. Each chip was cleaned by a standard RCA procedure: the chips were first immersed in a fresh solution of $\text{H}_2\text{O}/30\% \text{NH}_4\text{OH}$ (aq)/30% H_2O_2 (aq) (6:1:1) at 80 °C for 10 min, rinsed with water, and then immersed in a fresh solution of $\text{H}_2\text{O}/37\% \text{HCl}$ (aq)/30% H_2O_2 (aq) (5:1:1) at 80 °C for another 10 min. The chips were rinsed with water and dried with a stream of argon gas. The cleaned silicon chips were immersed in argon-saturated 40% NH_4F for 5 min and then dipped into deionized water for 10 s. After being dried with an argon stream, each chip was immediately transferred into a glovebox via a sealed argon-filled vial.

Reactions with Dichalcogenides. All reactions except for the etching of silicon surfaces were performed in the argon-filled glovebox. Each of the dichalcogenides, including diphenyl disulfide (PhSSPh), diphenyl diselenide (PhSeSePh), diphenyl ditelluride (PhTeTePh), and di-*n*-octadecyl disulfide ($\text{C}_{18}\text{SSC}_{18}$), was dissolved in dichloromethane to form a solution with a concentration of 20 mg/mL. The 1 cm $\times$ 1 cm silicon chip was placed on a hot plate heated to 80 °C, in the glovebox. 40 μL of a specific dichalcogenide solution was dropped onto the silicon and then covered with a UV grade quartz disc (from University Wafer), forming a sandwich of quartz coverslip–chalcogenide reagent–silicon wafer (assembly process is shown in Figure S1). The dichloromethane evaporated immediately upon contact with the silicon because of its low boiling point, and the small volume of the solution spread over a large area, leaving a solid film between the quartz and silicon. The melting points of PhSSPh, PhSeSePh, PhTeTePh, and di-*n*-octadecyl disulfide are 61 °C, 61 °C, 66 °C, and 62 °C, respectively, and thus the chalcogenide compounds melted to form a film. The samples were then irradiated with the light from a UVP Pen-Ray lamp (254 nm, model 11SC-1) held 1 cm above the samples for 15 min. The intensity of 254 nm light reaching the quartz surface was

measured to be $\sim 2 \text{ mW cm}^{-2}$. After reactions, the quartz coverslip was removed, and the silicon chips were soaked in dry dichloromethane for 3 min, followed by three rinses with a stream of dichloromethane from a pipet, to remove the unreacted reagents. The samples were removed from the glovebox in sealed vials, dried further under an argon gas stream, and analyzed immediately.

Analytical Techniques. X-ray photoelectron spectroscopy (XPS) spectra were taken on a Kratos Axis Ultra X-ray photoelectron spectroscopy system with a power of 14 kV, 12 mA, and 168 W using an Al source with an energy of 1487 eV, in the University of Alberta NanoFAB, with binding energies calibrated to $\text{Au } 4f_{7/2} = 84.0 \text{ eV}$. Photoelectrons were collected using a takeoff angle of 90° relative to the sample surface. Although samples were not rotated during XPS measurements (to eliminate photodiffraction effects), multiple measurements of identically prepared samples in separate XPS runs were used for all quantitative XPS calculations. From these results, it was found that there was generally less than a 10% difference in calculated substitution levels. Ultraviolet photoelectron spectroscopy (UPS) spectra were taken on a Kratos Axis Ultra XPS system with a power of 3 kV, 20 mA, and 60 W. Advancing and receding contact angle measurements were taken on an FTA200 video system. Sessile drop contact angles for the stability monitoring of the functionalized silicon surfaces were measured using $3 \mu\text{L}$ of water on a Ramé-Hart Mode 100–00 contact-angle goniometer. Film thicknesses were determined by contact mode atomic force microscopy (AFM) scribing. AFM scribing and images were captured using a Veeco/Digital Instruments Multi-Mode NanoScope IV. The intensity of the 254 nm UV light was measured by a Solo 2 energy and power meter with a XLPF12-3S-H2-D0 head (Gentec Electro-Optics Inc.). The resistivity of silicon wafers (oxide layer was removed by HF) was measured using a Keithley 2400 Source Meter in conjunction with a Jandel four-point probe (serial number LB25907) with 0.5 mm probe spacing.

Simulation. Stochastic packing of phenylchalcogenides on the Si(111) surface was simulated by assuming the steric interactions to be 2-dimensional, where the $\equiv\text{Si-E-Ph}$ groups were represented by the union of two hard disks. The respective radii of these disks were set by using the van der Waals radii of the chalcogen and the phenyl ring. Briefly, the packing algorithm works according to the following procedure. First, a sufficiently large Si(111) surface is generated (results were found to be effectively invariant for more than 14 000 Si atoms), and a random Si site is chosen. Then a $\equiv\text{Si-E-Ph}$ group is placed at this random Si site, at multiple random orientations with uniform spacing (results were found to be invariant for more than 7 different orientations), and checked to see if it overlaps with any of the other $\equiv\text{Si-E-Ph}$ groups on the surface. If an orientation with no overlaps is found, it is permanently left in that position and orientation. This process is then repeated at different randomly chosen Si surface sites until all silicon surface sites have been checked. The final substitution level is simply the number of $\equiv\text{Si-E-Ph}$ groups divided by the number of silicon sites. The substitution levels determined from simulation are the average of 150 independent simulation runs, each having a simulation size of 14 000 silicon sites and checking 13 different orientations for the $\equiv\text{Si-E-Ph}$ group at each silicon site. It is also noted that the sites at the edge of the simulation volume were not used to calculate the substitution level, as the amount of steric interactions will be lower in these regions. Specifically, sites within three silicon

lattice parameters of the simulation boundaries were not used. Nonetheless, given the large simulation volume, the edge effects were very small, leading to a less than $\sim 3\%$ difference after edge correction.

RESULTS AND DISCUSSION

Silicon–Chalcogen Bond Formation via UV Irradiation and Gentle Heating. To drive selective chemistry on Si(111)–H with dialkyl or diaryl dichalcogenides, low intensity 254 nm UV irradiation was coupled with gentle heating to enable the use of neat molecular reagents, with no additional solvent or other additives. A small volume ($40 \mu\text{L}$) of dichloromethane solution was placed on a 1 cm^2 chip of freshly etched Si(111)–H and then heated to 80°C to evaporate the solvent and melt the film (all four molecules have melting points below this temperature). A quartz window was pressed on top of the melted reagent to spread it evenly over the face of the silicon wafer, as shown in Figures S1 and S2. The sample was then irradiated by a Hg pen-lamp with a wavelength of 254 nm (intensity 2 mW cm^{-2}). X-ray photoelectron spectroscopy (XPS) was carried out on the silicon samples reacted with the PhSSPh, PhSeSePh, PhTeTePh, and di-*n*-octadecyl disulfide precursors to determine the nature of the bonding atom to the silicon (S, Se, or Te) and the level of oxidation. As shown in Figure 1, the narrow Si 2p feature of all four silicon samples reveals little oxidation, which would appear at a higher binding energy above 102 eV.^{3,34} Figure 1a,c shows the S 2p spectra, revealing the characteristic S $2p_{3/2}$ and S $2p_{1/2}$ peaks at 162.6 and 163.8 eV, for the PhSSPh-functionalized silicon surface, respectively, and 162.5 and 163.7 eV, for the di-*n*-octadecyl disulfide-functionalized silicon surface, respectively. The Se 3d spectrum (Figure 1e) also reveals a doublet of the Se 3d peak that has been fit to Se $3d_{5/2}$ and Se $3d_{3/2}$ peaks located at 54.9 and 55.7 eV, respectively. Two separate Te 3d peaks (Figure 1g) with binding energies of 573.1 and 583.5 eV correspond to Te $3d_{5/2}$ and Te $3d_{3/2}$, respectively. The binding energies for these chalcogens agree with the previous results for surfaces functionalized with Si–S, Si–Se, and Si–Te bonds on porous silicon surfaces.^{30,32} The features of the starting reagents, PhEEPh (E = S, Se, Te) and di-*n*-octadecyl disulfide, are shown in Figure 1 and are summarized in Tables S1 and S2.

Prior work in our group showed that dialkyl and diaryl dichalcogenides react very rapidly (seconds to minutes) and cleanly with hydride-terminated porous silicon at high temperatures in the range of $200\text{--}230^\circ\text{C}$ under inert atmosphere to form $\equiv\text{Si-E-R}$ (E = S, Se, Te) groups with no apparent oxidation.³² On flat Si(111)–H, however, contamination was determined by XPS to be a serious issue in the case of the tellurium derivative. Thermally driven reactions with diphenyl dichalcogenides on Si(111)–H were first carried out at 200°C for 90–120 s. The XPS spectra, shown in Figures S3a, b, c, and d, for the reactions with diphenyl disulfide and diphenyl diselenide on silicon surfaces proceed with little contamination or oxidation. For diphenyl ditelluride, however, the Te 3d XPS spectrum is complicated by two sets of Te 3d doublets, as seen in Figure S3e, as well as oxidation of the silicon surface (feature at 103 eV in Figure S3f). Lowering the temperature to 150°C also resulted in oxidation of the silicon surface (Figures S3g and h). The set of doublets with a higher binding energy is consistent with the formation of Te–O bonds.³⁵ Previous work has shown that phenylchalcogenides decompose upon heating to yield chalcogenide metal due to cleavage of the

Figure 1. 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. Orange dashed curves are the envelope fittings. The data from this figure and supporting literature are tabulated in Tables S1 and S2. E^a = S, Se, Te, as well as H.

chalcogenide–phenyl bond.³⁶ While the reactions were carried out in an inert atmosphere glovebox (O₂ < 1 ppm), if Te(0) was indeed formed under these conditions, brief exposure of the surfaces to air upon loading them into the XPS could result in oxidation of the tellurium metal. In order to keep the chemistry consistent across the sulfur, selenium, and tellurium derivatives, mild UV irradiation combined with gentle heating to 80 °C was used throughout this work.

Contact angle measurements of functionalized surfaces are typically used to obtain information regarding surface energy,³⁷ monolayer order,³⁸ and kinetics.³⁹ Static and dynamic (θ_a/θ_r) water contact angles of all the freshly prepared diphenyl dichalcogenide-functionalized samples fall between 80° and 83° (Table S3 and Figure S4), which are very close to that of the starting hydride-terminated silicon surface (~83°) and hence

not an informative metric to quantify surface functionalization. As such, the aliphatic disulfide, di-*n*-octadecyl disulfide, was used to provide insights into the rate of the reaction.^{39–41} As shown in Figure 2, the Si(111)–H surface reacted with di-*n*-

Figure 2. Water contact angles of di-*n*-octadecyl disulfide-functionalized silicon surfaces with different reaction times (black dots) and the fitting curve according to the contact angle data (red curve). Each black dot represents a unique sample that had been reacted for the indicated reaction time. The error bars represent the standard deviation of five measurements on the same sample.

octadecyl disulfide at 80 °C with UV irradiation appears to follow classic Langmuir kinetics,⁴² and a maximum contact angle of ~105° is reached after 10 min, a value similar to that of other silicon surfaces functionalized with long alkyl chains (contact angles range from ~105° to 110°).^{43–45} Representative contact angles of phenyl- and long alkyl chain-terminated silicon and gold surfaces from the literature are shown in Table S4. Control experiments, summarized in Table S5, showed that both heat and UV irradiation are necessary to reach this high contact angle with di-*n*-octadecyl disulfide. With only heat (80 °C) or UV irradiation, the contact angles fell within the range of 83–88°, indicating that both are required to enable the reaction to proceed to high coverage within 15 min. With hexadecane as the probe liquid for contact angle measurements, the contact angles of all ≡Si–E–Ph surfaces were low ($\theta < 10^\circ$), while for the ≡Si–S–*n*-octadecyl surface, the average contact angle was 43.4° (Table S3), a value that is consistent with previous work investigating monolayers on silicon,⁴⁶ gold,⁴⁷ or hydroxylated silicon surfaces.⁴⁸

Determination of Layer Thickness. Thicknesses of the resulting films were measured by scribing with an AFM tip, a commonly used technique that can be used to remove soft organic monolayers from the hard inorganic surface by scratching the surface with a (hard) silicon AFM tip.^{49–52} The scratched hydride-terminated silicon surface in Figure 3a reveals a small height difference of ~0.2 nm, most likely due to physisorbed hydrocarbon contaminants upon exposure to laboratory ambient. As shown in Figure 3b–d, the scribed areas of the diphenyl dichalcogenide-treated surfaces, capped with ≡Si–E–Ph groups, are ~0.8 nm deep, as determined from both line profiles and histogram analysis. For the ≡Si–S–*n*-octadecyl-terminated surface, the measured depth is ~2.5 nm; a smaller area could only be scribed due to buildup of residue on the AFM tip.

In order to calculate the predicted thickness of the molecular layer on the Si(111) surface, the ≡Si–E bond length, the size of the phenyl ring, and the ≡Si–E–C bond angle need to be known or assumed. The value with the greatest uncertainty is the bond angle about the chalcogen, the ≡Si–E–C bond angle; a table of comparable molecules is provided in Table S6.

Figure 3. AFM scribing of Si(111) surfaces. All scale bars are 400 nm. (a) Scribing on a hydride-terminated Si(111) surface. (b–d) Functionalized Si(111) surfaces reacted with PhSSPh, PhSeSePh, and PhTeTePh, respectively. (e) Functionalized Si(111) surfaces reacted with di-*n*-octadecyl disulfide. A smaller area was etched for the di-*n*-octadecyl disulfide molecule due to the rapid buildup of residue on the tip.

Only a small number of molecules with silicon–chalcogenide bonds has been sufficiently characterized to evaluate bond angles (by single-crystal X-ray diffraction, for instance). For instance, the Si–S–H bond angle in tri(mesityloxy)silanethiol has been reported to be 95.4° ,⁵³ and that of Si–S–CH₃ in the S-methyl ether of tri(*t*-butoxy)silanethiol is 106° ,⁵⁴ both of which were determined from crystal structures. For thioethers, the C–S–C bond angles for both Ph–S–CH₃ and Ar–S–Ar molecules are around 100° – 104° .^{55–59} Selenoethers, Ar–Se–Ar and C(sp³)–Se–C(sp²), have a C–Se–C bond angle of $\sim 101^\circ$.^{60,61} The C–Te–C bond angle for the telluroethers, Ph–Te–CH₃ and Ph–Te–Ph, is $\sim 96^\circ$.⁶² When $\equiv\text{Si–E–C}$ bond angles of 103° , 101° , and 96° were imposed upon $\equiv\text{Si–}$

S–Ph, $\equiv\text{Si–Se–Ph}$, and $\equiv\text{Si–Te–Ph}$ groups on the Si(111)–H surface, severe steric interference between underlying $\equiv\text{Si–H}$ groups and the overlying phenyl rings resulted. As shown in the space-filling representations in Figure 4, only

Figure 4. Side-view space-filling model of the $\equiv\text{Si–E–Ph}$ (E = S, Se, Te) interfaces on a flat hydride-terminated Si(111) surface. The chalcogenide-based functionalities were placed randomly on the surface, as would be the case for kinetically trapped, irreversible Si–E bond formation.

when the bond angle about the chalcogenide of the $\equiv\text{Si–E–Ph}$ was increased to 125° ($\equiv\text{Si–S–Ph}$), 124° ($\equiv\text{Si–Se–Ph}$), and 117° ($\equiv\text{Si–Te–Ph}$) there was no overlap of the van der Waals radii of the phenyl rings and the underlying $\equiv\text{Si–H}$ groups. The higher angle of the $\equiv\text{Si–S–Ph}$ group results from having the shortest $\equiv\text{Si–E}$ bond of the trio, as it needs to have a higher tilt to avoid overlap with the underlying silicon hydrides. These calculations are summarized in Scheme 2 and are shown with the smallest possible angle about the chalcogen atom. The calculated thicknesses for the $\equiv\text{Si–E–Ph}$ surfaces therefore represent the thinnest possible monolayer—with a higher angle about the chalcogenide linker atom, the monolayer could be thicker. For the aliphatic variant, the $\equiv\text{Si–S–}n$ -octadecyl-terminated surface, a tilt angle of the *n*-octadecyl group of 33° from the surface normal was used, based upon prior experimental results by Lou and co-workers for a similar surface formed via the reaction of 1-dodecanethiol on Si(111)–H.²⁶

The calculations in Scheme 2 differ to a small degree from the results observed by AFM scribing. To repeat, it must be stated that we cannot determine the exact bond angle about the chalcogenide for these $\equiv\text{Si–E–R}$ -functionalized surfaces, and thus the observed difference of ~ 0.2 nm between the calculated thicknesses and the measurements from AFM scribing could be due to physisorbed contamination but could also result from a higher $\equiv\text{Si–E–C}$ bond angle about the chalcogen. Indeed, it has been claimed that $\equiv\text{Si–O–Ph}$ -terminated surfaces have a Si–O–C bond angle close to 180° at high substitution levels,⁶³ but for the sulfur, selenium, and tellurium versions, the bond angle for RER molecules decreases going down the chalcogen group, so a bond angle closer to 180° about the chalcogen seems unlikely. Detailed quantification of substitution level by

Scheme 2. Theoretical Monolayer Thicknesses of $\equiv\text{Si-S-Ph-}$, $\equiv\text{Si-Se-Ph-}$, $\equiv\text{Si-Te-Ph-}$, and $\equiv\text{Si-S-n-Octadecyl-Modified Silicon Surfaces Calculated Based upon the Indicated Bond Lengths and Angles}$ ^a

^a H_{vdw} is the van der Waals radius of the hydrogen *para* to the chalcogenide. Red lines indicate steric hindrance between the phenyl ring and underlying hydrogen atoms on the silicon surface.

XPS, complemented by simulations that assume spatially stochastic covalent bonding (kinetic trapping), is described *vide infra*.

Quantification of Substitution Level of $\equiv\text{Si-H}$ with $\equiv\text{Si-ER}$ Groups. While the AFM scribing for all four $\equiv\text{Si-}$

E-R surfaces suggests uniform films, quantitative determination of the level of substitution of Si-H groups with chalcogenides was desired. XPS has been previously employed to estimate the substitution level of alkyl groups on silicon, bound through silicon-carbon bonds.^{64–66} In order to determine the substitution level, Θ , analytical expressions for the relative peak intensities (areas) of the silicon, carbon, and chalcogen signals were first derived. As is conventionally done, the silicon substrate and corresponding alkyl/phenyl molecular overlayers can be approximated by continuum layers that have a uniform atomic density, ρ , electron attenuation coefficient, λ , and thickness d . By making this continuum approximation, the measured intensity of photoelectrons can be calculated by simple application of the Beer-Lambert law. In the case of a silicon substrate (atomic density, ρ_{Si} , electron attenuation length, λ_{SiSi}) with a chalcogen overlayer (atomic density, ρ_{E} , electron attenuation length, λ_{EE}) capped by a phenyl/alkyl overlayer (atomic density, ρ_{C} , electron attenuation length, λ_{CC}), the total XPS intensity of the silicon peak is given by

$$I_{\text{Si}} = A\sigma_{\text{Si}}\rho_{\text{Si}} \left(\int_0^\infty \exp(-x/\lambda_{\text{SiSi}}) dx \right) \exp(-d_{\text{E}}/\lambda_{\text{SiE}}) \exp(-d_{\text{C}}/\lambda_{\text{SiC}})$$

$$I_{\text{Si}} = A\sigma_{\text{Si}}\rho_{\text{Si}}\lambda_{\text{SiSi}} \exp(-d_{\text{E}}/\lambda_{\text{SiE}}) \exp(-d_{\text{C}}/\lambda_{\text{SiC}}) \quad (1)$$

where A is the areal footprint of the X-ray beam and σ_{Si} is the relative sensitivity factor for silicon. Likewise, the signal from the chalcogen layer is given by

$$I_{\text{E}} = A\sigma_{\text{E}}\rho_{\text{E}} \left(\int_0^{d_{\text{E}}} \exp(-x/\lambda_{\text{EE}}) dx \right) \exp(-d_{\text{C}}/\lambda_{\text{EC}})$$

$$I_{\text{E}} = A\sigma_{\text{E}}\rho_{\text{E}}\lambda_{\text{EE}} (1 - \exp(-d_{\text{E}}/\lambda_{\text{EE}})) \exp(-d_{\text{C}}/\lambda_{\text{EC}}) \quad (2)$$

Lastly, the signal from the carbon layer is given by

$$I_{\text{C}} = A\sigma_{\text{C}}\rho_{\text{C}} \left(\int_0^{d_{\text{C}}} \exp(-x/\lambda_{\text{CC}}) dx \right)$$

$$I_{\text{C}} = A\sigma_{\text{C}}\rho_{\text{C}}\lambda_{\text{CC}} (1 - \exp(-d_{\text{C}}/\lambda_{\text{CC}})) \quad (3)$$

Taking the ratio of the silicon and carbon intensities (eqs 1 and 3) gives

$$\frac{I_{\text{Si}}}{I_{\text{C}}} = \frac{\sigma_{\text{Si}}\rho_{\text{Si}}\lambda_{\text{SiSi}} \exp(-d_{\text{E}}/\lambda_{\text{SiE}})}{\sigma_{\text{C}}\rho_{\text{C}}\lambda_{\text{CC}} (\exp(d_{\text{C}}/\lambda_{\text{SiC}}) - \exp(d_{\text{C}}(1/\lambda_{\text{SiC}} - 1/\lambda_{\text{CC}})))} \quad (4)$$

This expression can be simplified in two ways. First, we can assume that $\exp(d_{\text{C}}(1/\lambda_{\text{SiC}} - 1/\lambda_{\text{CC}})) \approx 1$ since the attenuation length of photoemitted electrons from the silicon layer passing through the carbon layer, λ_{SiC} , will be very close to that for photoemitted electrons from the carbon layer passing through the carbon layer, λ_{CC} . Second, we also assume that $d_{\text{E}}/\lambda_{\text{SiE}} \ll 1$ since the thickness of the chalcogen layer will be less than twice the van der Waals radius (~ 0.4 nm), while the attenuation length of the chalcogen will be on the order of 3–4 nm. From these simplifying assumptions, eq 4 becomes

$$\frac{I_{\text{Si}}}{I_{\text{C}}} = \frac{\sigma_{\text{Si}}\rho_{\text{Si}}\lambda_{\text{SiSi}}}{\sigma_{\text{C}}\rho_{\text{C}}\lambda_{\text{CC}} (\exp(d_{\text{C}}/\lambda_{\text{SiC}}) - 1)} \quad (5)$$

Finally, this expression can be used to calculate the substitution level by determining an effective thickness $d_{\text{C}}^{\text{eff}}$ of a carbon layer with attenuation length, $\lambda_{\text{SiC}}^{\text{Si}}$, and atomic density, $\rho_{\text{C}}^{\text{Si}}$, equal to that of a monolayer with 100% coverage of the silicon (111)

Table 1. Substitution Level Measured from XPS Data and Simulation

functional group	Si–S–Ph	Si–Se–Ph	Si–Te–Ph	Si–S– <i>n</i> -octadecyl	Si–S– <i>n</i> -octadecyl
substitution level (%) (XPS data)	15 ± 1 ^a	13.9 ± 0.6 ^a	16 ± 2 ^a	27 ± 6 ^a	30 ± 4 ^b
substitution level (%) (simulation)	14.9 ± 0.1	14.7 ± 0.1	13.2 ± 0.1	N/A	N/A

^{a,b}Calculated using eqs 12 and 9, respectively. Substitution levels are displayed as average ± standard deviation. Four identical samples were prepared for each type of silicon surface. For each sample, two spots were measured by XPS, leading to each functionalization of silicon surfaces containing eight measurements. Table S9 includes the substitution level for each measurement. Substitution levels measured from simulation are the mean of 150 independent simulation runs (14 000 Si atoms and 13 different possible orientations for each ≡Si–E–Ph group). Substitution levels marked.

surface. The values of $\lambda_{\text{SiC}}^{\text{Si}}$ and $\rho_{\text{C}}^{\text{Si}}$ can be estimated by scaling the values for gold surfaces with 100% coverage

$$\rho_{\text{C}}^{\text{Si}} = \frac{n_{\text{Si}}}{n_{\text{Au}}} \rho_{\text{C}}^{\text{Au}} \quad (6)$$

$$\lambda_{\text{SiC}}^{\text{Si}} = \frac{n_{\text{Au}}}{n_{\text{Si}}} \lambda_{\text{SiC}}^{\text{Au}} \quad (7)$$

$$\lambda_{\text{CC}}^{\text{Si}} = \frac{n_{\text{Au}}}{n_{\text{Si}}} \lambda_{\text{CC}}^{\text{Au}} \quad (8)$$

where n_{Si} and n_{Au} are the atomic surface densities of (111) silicon (7.8×10^{14} atoms/cm²) and the ($\sqrt{3} \times \sqrt{3}$)R30 surface of (111) gold (4.6×10^{14} atoms/cm²). Combining eqs 5, 6, 7 and 8 gives

$$d_{\text{C}}^{\text{eff}} = \frac{n_{\text{Au}}}{n_{\text{Si}}} \lambda_{\text{SiC}}^{\text{Au}} \ln \left(\frac{I_{\text{C}} \sigma_{\text{Si}} \rho_{\text{Si}}^{\text{Si}} \lambda_{\text{SiSi}}^{\text{Si}}}{I_{\text{Si}} \sigma_{\text{C}} \rho_{\text{C}}^{\text{Au}} \lambda_{\text{CC}}^{\text{Au}}} + 1 \right) \quad (9)$$

From eq 9, we can divide the effective thickness by the theoretical monolayer thickness (2.01 nm for ≡Si–S–*n*-octadecyl at a tilt angle of 33°) to obtain the substitution level. The average substitution level determined using eq 9 is 50 ± 2%, which agrees well with previously reported values for hydrosilylation of alkyl chains on the (111) silicon.^{64,67–70}

When using XPS data to determine the substitution level of alkyl chains on a silicon surface, analysis is typically limited to the silicon and carbon photoelectron signals. However, in the case of ≡Si–S–*n*-octadecyl, we can also utilize the silicon and sulfur peak intensities to derive a second expression for the substitution level. If we divide eqs 1 and 2 we arrive at the following expression

$$\frac{I_{\text{Si}}}{I_{\text{E}}} = \frac{\sigma_{\text{Si}} \rho_{\text{Si}}^{\text{Si}} \lambda_{\text{SiSi}}^{\text{Si}} \exp(-d_{\text{E}}/\lambda_{\text{SiE}}) \exp(-d_{\text{C}}/\lambda_{\text{SiC}})}{\sigma_{\text{E}} \rho_{\text{E}}^{\text{EE}} (1 - \exp(-d_{\text{E}}/\lambda_{\text{EE}})) \exp(-d_{\text{C}}/\lambda_{\text{EC}})} \quad (10)$$

If we again assume that $p(d_{\text{E}}(1/\lambda_{\text{SiE}} - 1/\lambda_{\text{EE}})) \approx 1$, $\exp(d_{\text{C}}(1/\lambda_{\text{SiC}} - 1/\lambda_{\text{EC}})) \approx 1$, and $d_{\text{E}}/\lambda_{\text{SiE}} \ll 1$, we arrive at the simplified expression of

$$\frac{I_{\text{Si}}}{I_{\text{E}}} = \frac{\sigma_{\text{Si}} \rho_{\text{Si}}^{\text{Si}} \lambda_{\text{SiSi}}^{\text{Si}}}{\sigma_{\text{E}} \rho_{\text{E}}^{\text{EE}} d_{\text{E}}} \quad (11)$$

Given that $\rho_{\text{E}} d_{\text{E}} = n_{\text{E}}$, where n_{E} is the atomic surface density of chalcogen atoms, and the substitution level is defined as $\Theta = n_{\text{E}}/n_{\text{Si}}$, we can solve for the substitution level

$$\Theta = \frac{\rho_{\text{Si}} \lambda_{\text{SiSi}}^{\text{Si}} \sigma_{\text{Si}} I_{\text{E}}}{n_{\text{Si}} \sigma_{\text{E}} I_{\text{Si}}} \quad (12)$$

The ≡Si–S–*n*-octadecyl substitution level determined using eq 12 are found to be 27 ± 6% (see Table 1), which appears to be significantly different from those determined using eq 9. However, this discrepancy can be resolved by adjusting for the

fact that unavoidable amounts of adventitious carbon will contribute to the integrated peak intensity of the C 1s signal. This can be done by first subtracting the effective thickness of the adventitious carbon layer from eq 9, then calculating the substitution level. Using eq 9 the thickness of the adventitious carbon layer is estimated by utilizing the silicon and carbon XPS spectra for hydride-terminated silicon, ≡Si(111)–H, which is found to be 0.42 ± 0.06 nm (Table S7). After correcting for the additional signal from the adventitious carbon, the substitution level determined using the silicon and carbon signals (eq 9) is found to be 30 ± 4% (Tables 1 and S8), which agrees very well with the values of 27 ± 6% determined using the silicon and sulfur signals [eq 12]. In the case of ≡Si–E–Ph-modified silicon surfaces, the substitution level can be determined using the silicon and chalcogen signals via application of eq 12. The average substitution levels are all found to be ~15% (Table 1). For more detailed information on these calculations, all of the utilized constants (Table S10) and intensity ratios measured from XPS can be found in the Supporting Information.

From these data it is found that the substitution level of the ≡Si–E–Ph-modified silicon surfaces (~15%) is low compared to the aliphatic variant, ≡Si–S–*n*-octadecyl (~30%). These lower substitution levels can be better understood by inspection of Figure 4, where the bulky phenyl rings are shown to be nearly parallel to the silicon surface. Such a molecular surface configuration would shield a significant number of Si–H bonds from further reactivity, thereby reducing the maximum possible ≡Si–E–Ph groups that can bind to the silicon surface. In order to better understand/validate the substitution levels measured by XPS, Figure 5a shows an idealized close-packed representation of ≡Si–S–Ph groups on a Si(111) surface. It can be seen from this tiling that the substitution level is 25%, which gives a useful reference for the upper theoretical limit of the substitution level. In reality, this close-packed configuration of ≡Si–E–Ph groups cannot be achieved due to the covalent nature of the silicon–chalcogen bond and the spatially stochastic nature of silicon–chalcogen bonding events. Once ≡Si–E–Ph groups are bonded to the silicon surface they are kinetically trapped and cannot diffuse to other sites in order to achieve a lower energy/more densely packed configuration. As such, there will be a significant fraction of silicon surface atoms that are not bonded to a chalcogen or directly underneath a phenyl ring and are unavailable to form silicon–chalcogen bonds.

This proposed mechanism of spatially stochastic covalent bonding of ≡Si–E–Ph groups on the silicon (111) surface was simulated, where a representative configuration is shown in Figure 5b. In these simulations, the surface packing is assumed to be a 2-dimensional problem, where the ≡Si–E–Ph groups are represented by the union of two hard disks with respective radii corresponding to the bond lengths shown in Scheme 2.

Figure 5. (a) Idealized close-packed configuration of $\equiv\text{Si-S-Ph}$ groups on a $\text{Si}(111)$ surface. (b) Configuration resulting from a simulation of stochastically packed $\equiv\text{Si-S-Ph}$ groups on a $\text{Si}(111)$ surface. Silicon-hydride groups are represented by small black dots, chalcogen atoms by medium blue disks, and phenyl rings by large gray disks. Movie S1 in the [Supporting Information](#) shows a time series visualization of this simulation.

Briefly, the stochastic bonding of $\equiv\text{Si-E-Ph}$ groups is simulated using the following method. First, a sufficiently large silicon (111) surface is generated (results were found to be effectively invariant for more than 14 000 Si atoms), and a random Si site is chosen. Then a $\equiv\text{Si-E-Ph}$ group is placed at this random Si site, at multiple random orientations with uniform spacing (results were found to be invariant for more than 7 different orientations), and checked to see if it overlaps with any of the other $\equiv\text{Si-E-Ph}$ groups on the surface. If an orientation with no overlaps is found, it is permanently left in that position and orientation. This process is then repeated at different randomly chosen Si surface sites until all silicon surface sites have been checked. A time series visualization of a stochastic simulation of $\equiv\text{Si-E-Ph}$ groups packing the $\text{Si}(111)$ surface is shown in Movie S1 in the [Supporting Information](#). The substitution levels measured from these simulations are shown in [Table 1](#) and found to be $\sim 15\%$, which is in excellent agreement with the experimentally measured values

derived from XPS data. These results support the claim of near-parallel configurations of the phenyl rings, as well as the stochastic nature of $\equiv\text{Si-E-Ph}$ groups bonding to the silicon surface.

Proposed Mechanism. As mentioned earlier, the reaction of a $\equiv\text{Si}(111)\text{-H}$ surface with di-*n*-octadecyl disulfide with only UV irradiation, or only 80°C heating, resulted in a small increase of contact angle versus the unfunctionalized hydride-terminated silicon surface ([Table S5](#)), indicating that successful functionalization requires that the UV illumination be coupled with gentle heating. The key intermediate in silicon–chalcogen bond formation is most likely a silicon radical formed via homolytic cleavage, as shown in [Figure 6](#), as has been postulated earlier on both surfaces and in silane molecules.^{27,32,33,44,71,72} This silicon radical can then add to the dichalcogenide through an $\text{S}_{\text{H}}2$ reaction, followed by collapse of the trivalent intermediate to product and an organochalcogen radical.^{32,33,71,72} The silicon radical could also react directly with an organochalcogen radical to form a silicon–chalcogen bond, although this pathway is expected to be less likely due to the improbability of having both species, present in low concentrations, in close proximity.

The central question is the driving force for homolytic cleavage of the surface silicon–hydride bond. The temperature required to initiate productive homolytic cleavage of the Si-H bond is typically in the range of $150\text{--}200^\circ\text{C}$, as shown through numerous studies on hydrosilylation of alkenes and alkynes on silicon surfaces.^{45,73,74} Similarly, heating to 80°C does not induce Si-EC bond formation, as shown by the control experiment with only heat (*vide supra*); heating to 80°C appears to only serve to liquefy the chalcogenide molecules to form an even layer on the silicon surface. The 254 nm UV light, however, is of sufficient energy (112.6 kcal/mol) to induce cleavage of both the diaryl/dialkyl dichalcogenide E-E bond^{75–77} and the Si-H bond.^{78–82} Because of the high absorption coefficients at 254 nm for the three diphenyl dichalcogenides as well as the di-*n*-octadecyl disulfide ([Figure S5](#), and corresponding calculations in [Supporting Information](#)), essentially all of the incident UV light would be absorbed by this molecular layer, and no UV light would directly impinge upon the silicon surface. The role of the 254 nm UV light, then, must be to cleave S-S , Se-Se , or Te-Te bonds (bond energies of 53–57, 40, and 30–35 kcal/mol, respectively)^{33,76,77} at the surface of the melted REER layer, in close proximity to the quartz coverslip, to yield thiyl, selenyl, or telluryl radicals, $\text{RE}\bullet$ ($\text{E} = \text{S}, \text{Se}, \text{and Te}$), respectively, as outlined in [Figure 6](#). Diffusion of these radicals throughout the layer could then lead to formation of silyl radicals, $\equiv\text{Si}\bullet$, at the surface, through removal of $\text{H}\bullet$ from surface-bound $\equiv\text{Si-H}$ groups ([Figure 6a](#)).

Upon formation of $\equiv\text{Si}\bullet$ species, two possible pathways would realize the formation of $\equiv\text{Si-ER}$ bonds, as has been previously described.³² The first route involves stepwise $\text{S}_{\text{H}}2$ addition of REER to a silyl radical, producing trivalent sulfuranyl, seleranyl, or telluranyl radical intermediates, followed by collapse of the intermediate to form the final $\equiv\text{Si-ER}$ product and an $\text{RE}\bullet$ radical ([Figure 6b](#)). This reaction pathway would most likely be favored due to the high abundance of REER molecules near the surface. The second pathway involves the direct combination of a surface silyl radical $\equiv\text{Si}\bullet$ and free chalcogenide radical $\text{RE}\bullet$ to produce $\equiv\text{Si-ER}$ ([Figure 6c](#)).³² Both may be in operation and would be difficult to distinguish.

Figure 6. “Photolysis–diffusion–abstraction–addition” mechanism leads to the $\equiv\text{Si}-\text{ER}$ bond formation. (a) Photolysis of REER molecules near the top of the organic layer results in $\text{RE}\bullet$ radicals. Because this film has been melted, and is thus a liquid, these radicals can diffuse throughout the film and can abstract a hydrogen from a surface $\equiv\text{Si}-\text{H}$ bond, leading to $\equiv\text{Si}\bullet$ radicals. (b) Addition of REER molecules to surface $\equiv\text{Si}\bullet$ radicals via $\text{S}_{\text{H}2}$ addition leads to $\equiv\text{Si}-\text{E}$ bond formation. (c) Direct combination of a $\equiv\text{Si}\bullet$ radical with a $\text{RE}\bullet$ radical can also yield $\equiv\text{Si}-\text{ER}$ bond formation.

Table 2. Binding Energy, Work Function, and Surface Dipole of Functionalized Silicon Surfaces^a

surfaces	BE ($\text{Si } 2p_{3/2}$) ^b (eV)	$E_{\text{vbm}}^{\text{S}}$ (eV)	qV_{bb} (eV)	WF^{Sb} (eV)	χ^{S} (eV)	δ^{b} (eV)
$\equiv\text{Si}-\text{H}$	99.44 ± 0.07	0.70	0.12	4.27 ± 0.03	3.85	-0.20 ± 0.08
$\equiv\text{Si}-\text{S}-\text{Ph}$	99.43 ± 0.06	0.69	0.13	4.16 ± 0.09	3.73	-0.32 ± 0.11
$\equiv\text{Si}-\text{Se}-\text{Ph}$	99.34 ± 0.06	0.60	0.22	4.26 ± 0.06	3.74	-0.31 ± 0.08
$\equiv\text{Si}-\text{Te}-\text{Ph}$	99.37 ± 0.05	0.63	0.19	4.31 ± 0.06	3.82	-0.23 ± 0.08

^aBE ($\text{Si } 2p_{3/2}$) is the binding energy of the $\text{Si } 2p_{3/2}$ peak at the surface as measured by XPS. $E_{\text{vbm}}^{\text{S}}$ is the energy difference from the valence band to Fermi level at the surface. Band bending energy is represented as qV_{bb} . WF^{S} is the dark work function at the silicon surface measured in the dark by UPS. χ^{S} and δ represent surface electron affinity and the surface dipole, respectively. ^bBinding energy, work function, and surface dipole are displayed as “average $\pm$ standard deviation”. The standard deviations of $E_{\text{vbm}}^{\text{S}}$ and qV_{bb} have the same values as the ones of BE ($\text{Si } 2p_{3/2}$), and the standard deviations of χ^{S} have the same values as the ones of δ . Four identical samples were prepared for each type of silicon surface. For each sample, two spots were measured by XPS as well as UPS, leading to each functionalization of silicon surfaces containing eight measurements. A gold-on-silicon sample was used as the reference for XPS.

Work Function and Surface Dipoles. The effect of surface functionalization was examined for the series, $\equiv\text{Si}-\text{S}-\text{Ph}$, $\equiv\text{Si}-\text{Se}-\text{Ph}$, and $\equiv\text{Si}-\text{Te}-\text{Ph}$, since these groups contain the same consistent phenyl termination. Functionalization of the silicon surface can alter its electronics, resulting from band bending due to charged surface states and surface dipoles,^{4,83,84} and thus we wished to examine the effect of the series of chalcogenide linkers on the properties of the silicon, since earlier predictions had suggested large effects.^{21–23} XPS can be used to determine the band bending, and work function can be obtained from UPS measurements.^{4,6,12,14} Measurements required multiple samples to account for measurement variability, as well as the use of gold-on-silicon as the reference for XPS, as outlined by Lewis and co-workers.⁴ Figure S6a,b shows the XPS spectra and cross-sectional SEM image of the Au reference used for binding energy calibration. Since the interfacial dipoles depend upon the doping level,¹¹ moderately doped n-type $\text{Si}(111)$ was chosen since it would be expected to have the greatest range of $\text{Si } 2p_{3/2}$ values depending upon surface functionality.⁴

Average values of electronic properties measured for the functionalized silicon surfaces are listed in Table 2. Raw data without normalization of all measurements including XPS and secondary electron He I UPS are shown in Figures S7 and S8, as well as calculations. The data for the $\equiv\text{Si}-\text{E}-\text{Ph}$ -terminated surfaces, as reported in Table 2, are similar to that of the

starting $\equiv\text{Si}-\text{H}$ -terminated surface. Figure S9 depicts the energy band diagram of $\text{Si } 2p_{3/2}$ binding energy with upward band bending, corresponding to the measured band bending values. The measured work function of the $\equiv\text{Si}-\text{H}$ -terminated surface is 4.27 ± 0.03 eV, which is similar to that reported earlier, 4.29 eV, for hydride-terminated $\text{Si}(111)$ of the same doping.⁴ Upon functionalization with the phenyl chalcogenide moiety, the work functions were relatively unchanged, in the range of 4.16 ± 0.09 eV for $\equiv\text{Si}-\text{S}-\text{Ph}$, to 4.31 ± 0.06 for $\equiv\text{Si}-\text{Te}-\text{Ph}$. Other electronic characteristics, including surface electron affinity (χ^{S}) and surface dipole (δ), are also largely unchanged compared to the starting $\equiv\text{Si}-\text{H}$ interface. A $\equiv\text{Si}-\text{CH}_3$ -terminated $\text{Si}(111)$ surface with similar (moderate n-type) doping, with full substitution of all $\equiv\text{Si}-\text{H}$ groups enabled by the small size of the methyl group, caused only a small drop of the work function to 4.04 eV.⁴ A large shift of work function compared to starting $\equiv\text{Si}-\text{H}$ was, however, observed upon substitution of hydrides with bromine atoms, $\equiv\text{Si}-\text{Br}$, to 4.86 eV.⁴ Thus, the chalcogenide terminations, which do not have the large dipole of the bromide termination and are more akin to the methyl termination in terms of electronegativity and surface dipole, do not induce much change. The small effect of $\equiv\text{Si}-\text{E}-\text{Ph}$ -termination may also result from the low substitution levels ($\sim 15\%$);^{1,85–88} the electronics of the silicon are thus dominated by the majority $\equiv\text{Si}-\text{H}$ termination.

CONCLUSIONS

A straightforward approach to form $\equiv\text{Si}-\text{E}-\text{R}$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) functionalities on $\text{Si}(111)-\text{H}$ surfaces has been described using UV irradiation and gentle thermal heating with synthetically practical dialkyl/diaryl chalcogenide precursors. The mechanism of reactivity of the dichalcogenides appears to be radical in nature and is closely related to observed reactivity in silane molecules. The substitution level of the phenyl chalcogenide derivatives, $\equiv\text{Si}-\text{E}-\text{Ph}$, was lower than that of the aliphatic chalcogenide ($\equiv\text{Si}-\text{S}-n\text{-octadecyl}$) group, most likely due to the fact that the phenyl group obscures neighboring silicon-hydride bonds and thus sterically prevents them from reacting. Use of larger flat aromatic precursors with dichalcogenide linkages could enable access to interesting interfaces that have few linker atoms to the surface of the silicon that shield the silicon surface with potentially electronically active moieties. Higher substitution levels will need to be achieved through use of less bulky dialkyl dichalcogenide groups in order to better study the effects of $\equiv\text{Si}-\text{E}$ bonds on the electronics of silicon.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.8b00910.

Estimation of light absorption by molecules; reaction apparatus; XPS spectra for reactions under thermal conditions; water contact angle images; XPS data and water contact angle data and their representative values from the literature; representative bond angles from the literature; UV absorption spectra for diphenyl and dialkyl dichalcogenides; XPS spectrum and SEM image for Au reference; substitution level calculations; XPS spectra of Si 2p peaks and UPS spectra of all Si(111) surfaces; silicon energy levels calculation (PDF)

Movie of time series visualization of a stochastic simulation of $\equiv\text{Si}-\text{E}-\text{Ph}$ groups packing the Si(111) surface (AVI)

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Notes

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