Probing Surface-Adlayer Conjugation on Organic-Modified Si(111) Surfaces with Microscopy, Scattering, Spectroscopy, and Density Functional Theory

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Highly conjugated molecules bound to silicon are promising candidates for organosilicon electronic devices and sensors. In this study, 1-bromo-4-ethynylbenzene was synthesized and reacted with a hydrogen-passivated Si(111) surface via ultraviolet irradiation. Through an array of characterization and modeling tools, the binding configuration and morphology of the reacted molecule were thoroughly analyzed. Atomic force microscopy confirmed an atomically flat surface morphology following reaction, while X-ray photoelectron spectroscopy verified reaction to the surface via the terminal alkyne moiety. In addition, synchrotron X-ray characterization, including X-ray reflectivity, X-ray fluorescence, and X-ray standing wave measurements, enabled sub-angstrom determination of the position of the bromine atom with respect to the silicon lattice. This structural characterization was quantitatively compared with density functional theory (DFT) calculations, thus enabling the π -conjugation of the terminal carbon atoms to be deduced. The X-ray and DFT results were additionally corroborated with the vibrational spectrum of the organic adlayer, which was measured with sum frequency generation. Overall, these results illustrate that the terminal carbon atoms in 1-bromo-4-ethynylbenzene adlayers on Si(111) retain π -conjugation, thus revealing alkyne molecules as promising candidates for organosilicon electronics and sensing.

1. Introduction and Motivation

Functionalizing silicon surfaces with organic adlayers has generated significant interest from the scientific community.¹ Hybrid organosilicon materials have the potential to be used as substrates for highly sensitive chemical and biological sensors²⁻⁹ and show promise for enabling nonlinear charge transport in silicon-based molecular electronic devices.¹⁰⁻²⁴ To better understand and thus optimize the performance of these devices, thorough characterization with complementary experimental and theoretical techniques is required. Toward this end, we have previously investigated 4-bromostyrene adlayers on hydrogenpassivated silicon surfaces.^{25,26} This system was chosen because it forms a dense adlayer that preserves the bromine functionality on its terminal moiety. In particular, the bromine tag allows sub-angstrom precision structural characterization with X-ray surface-sensitive techniques, which can be directly compared to atomistic theoretical calculations.

To optimize molecular electronic charge transport, however, it is desirable to have delocalized π -conjugation throughout the entire organosilicon structure. Following reaction with silicon surfaces, the original alkene termination of 4-bromostyrene is converted to sp³ hybridization, thus compromising electronic

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coupling to the silicon substrate. Consequently, it is attractive to replace 4-bromostyrene with an alternative organosilicon adlayer that possesses π -conjugation throughout its structure. In particular, by migrating from the alkene-based 4-bromostyrene precursor to the alkyne-based 1-bromo-4-ethynylbenzene precursor, it may be possible to achieve an organic adlayer on silicon with improved π -conjugation. It has been suggested in the literature, however, that alkynes undergoing hydrosilylation with silicon can potentially bind to silicon in multiple configurations,²⁷ some of which lose π -conjugation upon reaction with the silicon surface.

In this paper, we present quantitative characterization of the conformation and conjugation of 1-bromo-4-ethynylbenzene adlayers on Si(111) with a diverse suite of experimental and theoretical techniques. Atomic force microscopy (AFM) is used to determine surface morphology, and X-ray photoelectron spectroscopy (XPS) is used to determine the chemical binding state of the bromine moiety. In particular, the presence of C-Br bonds and the absence of Si-Br bonds in XPS spectra verify that unintended Br abstraction by the silicon surface has not occurred.²⁶ XPS analysis also ensures that minimal Si oxidation has occurred during adlayer formation. X-ray fluorescence (XRF) and X-ray reflectivity (XRR) are employed to determine the packing density of the adlayer, while single-crystal X-ray standing wave (XSW) measurements enable the generation of three-dimensional maps of the Br atomic position with respect to the Si(111) lattice. When combined with XRR data, the position of the Br can be deduced with sub-angstrom precision. These experimental results are then directly compared with cluster and periodic density functional theory (DFT) calculations to reveal the conjugation of the terminal carbon atoms. To

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corroborate the X-ray and DFT results, sum frequency generation is also employed to interrogate the vibrational spectrum of the organosilicon adlayer. This comprehensive study strongly suggests that the 1-bromo-4-ethynylbenzene adlayer preserves π -conjugation at the original alkyne termination following chemisorption to the Si(111) surface, thus establishing a promising substrate for future organosilicon molecular electronics and sensing.

2. Experimental Methods

2.1. Organic Synthesis. All synthetic reactions were carried out at room temperature either in a N₂-filled glovebox or using standard Schlenk techniques, unless otherwise noted.

Materials. Tetrabutylammonium fluoride (TBAF, 1 M solution in THF, Aldrich), 1-bromo-4-iodobenzene (98%, Aldrich), trimethylsilylacetylene (GFS Chemicals), copper(I) iodide (CuI, Aldrich), and *trans*-dichloro(triphenylphosphine)palladium(II) (PdCl₂(PPh₃)₂, Alfa Aesar) were used as received. HPLC-grade triethylamine (400 mL, Fischer Scientific) was stirred with CaH₂ $(\sim 15 \text{ g}, +4 \text{ mesh}, \text{Aldrich})$ for 24 h, vacuum-transferred into a Strauss flask, and subjected to three freeze-pump-thaw cycles before use. Anhydrous benzene (99.8%, Aldrich) was further dried over 3-Å molecular sieves (Grade 564 3A, 8-12 mesh beads, Grace, preactivated in a 500 °C furnace overnight) overnight before use. Chloroform (99.9%, VWR Omnisolv grade) was washed with water (1:1 v/v) to remove any residual ethanol, dried over anhydrous Na₂SO₄ (Fischer Scientific) overnight, vacuum-transferred to a vacuum flask, subjected to three freeze-pump-thaw cycles, and further dried over 3-Å activated molecular sieves overnight before use. All other anhydrous solvents were dried over neutral alumina via the Dow-Grubbs solvent system.²⁸ Deuterated solvents were purchased from Cambridge Isotope Laboratories and used as received. All flash chromatography was carried out using silica gel (230-400 mesh, purchased from Sorbent Technologies, Atlanta, GA) under a positive pressure of laboratory air. Nanopure deionized water was obtained from a Millipore Milli-Q system (18 M Ω · cm resistivity).

Synthesis of (4-Bromophenylethynyl)trimethylsilane. In a N₂filled glovebox and into a 150-mL Kjeldahl-style Schlenk flask equipped with magnetic stir bar were added 4-bromo-1iodobenzene (2.83 g, 10 mmol), PdCl₂(PPh₃)₂ (0.15 g, 0.21 mmol), trimethylsilylacetylene (2.28 g, 23 mmol), and dry triethylamine (35 mL) (Scheme 1). After 5 min stirring, CuI (0.03 g, 0.16 mmol) was then added to the reaction flask to give a bright yellow solution. The reaction flask was capped, covered with aluminum foil, and allowed to stir overnight at room temperature during which time its color turned gray. The reaction flask was then removed from the glovebox. The reaction mixture was filtered over a Buchner funnel, and the solid residue that remained on the filter was rinsed with HPLC-grade triethylamine (2 \times 20 mL). The combined organics were concentrated to a minimum on a rotary evaporator to give a viscous oil, which was subjected to column chromatography $(7.5 \text{ cm} \times 40 \text{ cm}, \text{hexanes:methylene chloride } 9:1 \text{ v/v})$. The isolated product is a light yellow solid (2.47 g, 9.8 mmol, 98%). Spectroscopic data for (4-bromophenylethynyl)trimethylsilane was in good agreement with literature data.²⁹ ¹H NMR (500 MHz, CDCl₃): δ 0.26 (s, 9H) and δ 7.3–7.5 (AA'BB', 2H each). ¹³C NMR (125 MHz, CDCl₃): δ 0.2, 95.5, 103.8, 122.0, 122.7, 131.4, 133.4. GC-MS(EI): m/z = 254 and 252 observed for C₁₁Si₁Br₁H₁₃; 254 and 252 calculated.

Synthesis of 1-Bromo-4-ethynylbenzene. Modified from a published procedure:^{30,31} In a N_2 -filled glovebox and into a 150-mL Kjeldahl-style Schlenk flask equipped with a magnetic stir

SCHEME 1: Synthesis of (4-Bromophenylethynyl)trimethylsilane and 1-Bromo-4-ethynylbenzene



bar were added (4-bromophenylethynyl)trimethylsilane (2.53 g, 10 mmol), anhydrous THF (10 mL), and TBAF (15 mL of a 1-M solution in THF, 15 mmol) (Scheme 1). The reaction flask was capped and allowed to stir at room temperature for 2 h before being removed from the glovebox. The reaction mixture was concentrated on a rotary evaporator to give a purple residue, which was dissolved in deionized water (15 mL) and extracted with methylene chloride (3×15 mL). The combined organics were concentrated to a minimum on a rotary evaporator to give a viscous oil, which was subjected to column chromatography (7.5 cm \times 40 cm, hexanes:methylene chloride 9:1 v/v). The isolated product is a light yellow solid (1.44 g, 8 mmol, 80%). Spectroscopic data for 1-bromo-4-ethynylbenzene was in good agreement with literature data.^{30,31} ¹H NMR (500 MHz, CDCl₃): δ 3.13 (s, 1H) and δ 7.3–7.5 (AA'BB', 2H each). ¹³C NMR (125 MHz, CDCl₃): δ 78.3, 82.5, 121.0, 123.1, 131.6, 133.5. GC-MS(EI): m/z = 182 and 180 observed for C₈Br₁H₄; 182 and 180 calculated.

2.2. Monohydride Si(111) Sample Preparation. Monohydride termination of Si(111) was achieved using the procedure described by Higashi et al.³² Silicon samples were cut from single-sided polished Si(111) wafers (Virginia Semiconductor, 0.25° miscut in the $<110>\pm0.1^{\circ}$ direction, n-type, phosphorus doped, resistivity = $0.04-0.1 \ \Omega \cdot cm$). Samples were initially rinsed with acetone and methanol and then immersed in a 0.5% HF solution for 30 s in order to strip the as-received native oxide. The samples were then rinsed in Ar-sparged nanopure 18 M Ω ·cm water for 5 s. Next, the samples were placed into a 4:1 (v/v) $H_2SO_4/30\%$ H_2O_2 (aq) solution for 10 min at 90 °C. This step removes organic contaminants and grows a clean oxide on the surface. Subsequent to another 5-s rinse in Ar-sparged nanopure water, the samples were etched in Ar-sparged electronic grade 40% NH₄F (aq) for 30 min. Finally, the samples were rinsed for 1 min in Ar-sparged nanopure water, blown dry with a nitrogen air gun, and stored inside an inert-atmosphere glovebox (Nexus, Vacuum Atmospheres) that is maintained at a slightly positive N_2 pressure (<2 ppm O₂, <1 ppm H₂0).

2.3. Preparation of 1-Bromo-4-ethynylbenzene Adlayers on Si(111). Hydrogen-passivated Si(111) samples were loaded inside the inert atmosphere glovebox into a clear vial containing 1-bromo-4-ethynylbenzene dissolved in anhydrous benzene (0.2 M). Surface reaction was accomplished by irradiating the samples with a 254-nm Hg pen lamp (Spectroline 11SC-1 Short Wave UV Lamp) from a 1-cm distance for 20 h. The samples were then brought out of the glovebox, sonicated in chloroform for 5 min, and returned to the glovebox until further surface analysis was conducted.

2.4. Atomic Force Microscopy. Atomic force microscopy (AFM) images were taken following passivation and subsequent to monolayer growth. Imaging was accomplished with an Autoprobe CP Research AFM using Micromasch Ultrasharp NSC36 cantilever with force constants of 0.15-1.5 N/m and resonance frequencies of 50-105 kHz. Images were taken in intermittent contact mode under ambient air conditions.

2.5. X-ray Photoelectron Spectroscopy. An Omicron ESCA (Electron Spectroscopy for Chemical Analysis) probe was used for X-ray photoelectron spectroscopy (XPS) analysis at the Keck-II Interdisciplinary Surface Science Center of Northwestern University. A monochromated Al K α beam radiating at 1486.6 eV was incident on the sample at a 45° takeoff angle. A survey scan was initially performed with a pass energy of 50 eV with 500 meV steps to check for the presence of a bromine peak following adlayer formation. Subsequently, high-resolution spectra of the Br 3d peak and Si 2p peaks were checked by sweeping the relevant regions with a pass energy of 18 eV with steps of 20 meV. For these high-resolution spectra, eight sweeps were averaged in an effort to minimize noise. The results were calibrated relative to the C 1s peak.

2.6. X-ray Reflectivity. X-ray reflectivity (XRR), X-ray standing wave (XSW), and X-ray fluorescence (XRF) experiments were carried out following the same general procedures and analysis methods as described in greater detail in our earlier work for the case of 4-bromostyrene on the Si(111) surface.²⁵ A Rigaku ATX-G rotating-anode four-circle diffractometer was used for X-ray specular reflectivity measurements at the Northwestern University X-ray Facility. The experimental setup employs a multilayer parabolic collimating mirror followed by a Ge(111) asymmetric channel cut and a 0.1-mm-wide by 5-mmhigh incident beam slit to produce Cu K α_1 radiation with a flux of 4 \times 10⁷ p/s and instrumental resolution $\Delta Q = 1 \times 10^{-2}$ Å⁻¹. The reflectivity data was background subtracted, deadtime corrected, and normalized to the straight-through beam intensity. The XRR measurement is sensitive to the gradient of the electron density profile, $\rho'(z)$.³³ In the case of an organic adlayer, XRR analysis is sensitive to the molecular packing density, film thickness, interface roughness, and the height/ location of the Br layer relative to the Si/adlayer interface. The corresponding z-coordinates of the non-hydrogen atoms are used to determine the one-dimensional structure factor, F(Q), in the calculation of reflectivity.

2.7. X-ray Standing Wave and X-ray Fluorescence. The XSW analysis was carried out at the Advanced Photon Source (APS) 5ID-C undulator station. The 5ID-C experimental setup is more fully described elsewhere.³⁴ The incident photon energy was tuned to 14.98 keV to excite Br K fluorescence. XSW measurements require monitoring both reflectivity and XRF simultaneously while scanning through an H = hkl substrate Bragg peak.^{35–37} The (111), (333), (111), and (220) Bragg reflection XSW measurements were performed for the construction of a three-dimensional Br density map. A germanium solid-state detector was used for XRF, and the spectrum was dead-time corrected. The normalized Br fluorescence yield is given by

$$Y(\theta) = 1 + R(\theta) + 2\sqrt{R(\theta)}f_{\rm H}\cos[v(\theta) - 2\pi P_{\rm H}] \qquad (1)$$

where the reflectivity (*R*) and XSW phase (*V*) are derived from dynamical diffraction theory.^{35,36} Using the determined coherent fractions, $f_{\rm H}$, and coherent positions, $P_{\rm H}$, from specular and off-specular XSW measurements, a Br site relative to the Si lattice can be triangulated. A model-independent Br atomic three-dimensional map is also generated by Fourier inversion.^{25,38–40}

Direct comparison of the Br K α XRF yield to the As K β yield from an As-implanted standard provides the molecular coverage on the substrates. At 15.05 keV, the Br K α to As K β XRF cross-sectional ratio is 8.41. A 1-monolayer (ML) coverage corresponds to 7.83 atoms/nm², where each surface silicon atom is attached by one molecule.

To prevent surface oxidation and the creation of ozone that may cause film degradation, the samples were sealed within a dry-nitrogen-flow cell during X-ray exposure. X-ray radiation damage effects were closely monitored and minimized during exposure to the monochromatic undulator beam. Under the full undulator intensity of 1×10^{12} p/s per mm² of radiated surface area, the Br coverage showed an exponential decay with a half-life of 15 min.

2.8. Sum Frequency Generation. Detailed descriptions of the theoretical and experimental aspects of sum frequency generation (SFG) are available elsewhere,⁴¹ and the laser system, the sample cell, and the signal detection methods used in this work have been previously described.⁴²⁻⁴⁶ Briefly, we applied broadband sum frequency generation, pioneered by van der Ham et al.⁴⁷ and Richter et al.⁴⁸ For the current studies, the laser system consists of an 800-nm, 120-fs regeneratively amplified Ti:Sapphire system (1 kHz, 2.5 mJ/pulse, Spitfire Pro, Spectra-Physics), pumping an optical parametric amplifier (OPA-800CF, Spectra-Physics) to produce IR light around 3.4 μ m with a bandwidth (full width at half-maximum) of about 140 cm⁻¹. The energy of the incident light fields ranged between 1.5 and $2.5 \,\mu\text{J}$ for the infrared and between 1.4 and 1.6 μJ for the visible. The SFG, visible, and IR beams were all p-polarized. After polarization selection, the infrared and up-converter light fields are overlapped and focused onto the surface under investigation. The properly filtered SFG signal is dispersed with a 0.5-m spectrograph (Acton Research) and detected using a liquid nitrogen-cooled, back-thinned charge-coupled device (Roper-Scientific). All spectra are referenced to the 2955 cm⁻¹ C-H symmetric stretch of the methoxy groups in poly(methyl methacrylate) (PMMA) spin-coated on hydrogen-passivated Si(111). The reproducibility of the absolute SFG peak position is \pm 5 cm⁻¹, and the spectral resolution of the experiments is $\sim 10 \text{ cm}^{-1}$. Following the work of Esenturk and Walker,⁴⁹ we recorded broadband SFG spectra with several different input IR center frequencies to ensure that all vibrational modes in the C-H frequency region were probed. The spectra presented in this work are collected within about 1-2 min and represent a background-subtracted, power-normalized average over 2-3 spectra. Following Nihonyanagi et al.⁵⁰ and Ishibashi et al.,⁵¹ we defined the azimuthal angle as the angle between the incidence plane of the probe beams and the [112] direction of the Si(111) surface. The visible and IR beams were focused onto the sample with incident angles of 42° and 61° degrees from normal, respectively.

3. Theory

3.1. Cluster Density Functional Theory. To model the adsorption of 1-bromo-4-ethynylbenzene on the Si(111) surface, the structure of an isolated molecule on a silicon cluster was calculated. A Si₂₆H₃₁ cluster was chosen to represent the silicon substrate, consisting of three Si(111)-oriented double layers composed of 13, 9, and 4 silicon atoms within each respective layer. The silicon atoms were passivated with hydrogen to maintain the tetrahedral symmetry of the lattice. All isolated-molecule calculations were performed using density functional theory (DFT) within the QCHEM 2.1 software package.⁵² The hybrid B3LYP exchange-correlation functional was used, along with a 6-31G* all-electron basis set. The 1-bromo-4-ethynyl-benzene molecule was bonded to the (111) surface of this cluster in three distinct binding configurations.

The first binding configuration of 1-bromo-4-ethynylbenzene is analogous to that proposed previously for phenylacetylene.⁵³ In this case, the reaction initially involves the terminal alkyne carbon atom reacting with a silicon atom, thus resulting in a free radical on the neighboring carbon atom. Next, the radical



Figure 1. Binding geometry configurations for isolated-molecule cluster DFT calculations, showing a side view (upper image) and top-down view (lower image) of the molecule on the $Si_{26}H_{31}$ cluster. (a) Configuration proposed by Linford and Chidsey,⁵⁴ showing the 1-bromo-4-ethynylbenzene molecule after reacting with a single silicon atom and extracting one hydrogen atom from the surface. (b) "Double-bridge" configuration, showing the two end carbons bonded to two neighboring silicon T_1 sites. (c) "Single-bridge" configuration, showing the terminal carbon bonded with two neighboring T_1 sites. In (b) and (c), the molecule has extracted two hydrogen atoms from the surface.

is thought to extract a hydrogen atom from a neighboring silicon atom, leaving a styrene-like molecule bound to the surface. This geometry is shown in Figure 1a, which shows the molecule bonded to the passivated $Si_{26}H_{31}$ cluster after abstracting a hydrogen atom from the surface. Additionally, two alternate binding configurations were also considered, since the remaining carbon—carbon double bond can potentially further react with the silicon surface.

The second geometry is shown in Figure 1b, which we will refer to as a "double-bridge" configuration. In this instance, the molecule is bonded to neighboring T_1 sites on the silicon surface via two Si-C bonds, while the displaced hydrogen atoms are now bonded to the two end carbons of the molecule. An additional hydrogen atom has been abstracted from the surface to stabilize the radical.

The third configuration is shown in Figure 1c, which will be referred to as the "single-bridge" structure. In this binding geometry the terminal carbon of the molecule is simultaneously bound to two neighboring silicon T_1 sites. Additionally, the molecule has abstracted two hydrogen atoms from the surface, resulting in the complete saturation of the terminal alkynyl group. It should be noted that the silicon cluster in the latter two configurations exhibits some distortion, which is attributed to edge effects due to the limited size of the cluster.

The three aforementioned geometries predict substantially different orientations for 1-bromo-4-ethynylbenzene with respect to the surface, which allows for further clarification of the binding geometry in conjunction with experimental data. In the context of the experiment, it is particularly useful to compare the height of the terminal bromine atom above the silicon surface. The geometry from Figure 1a exhibits a height of 8.86 Å, while the configurations in Figures 1b and 1c show significantly lower heights of 5.82 and 5.08 Å, respectively. This significant difference in height allows for unambiguous discrimination between these potential binding configurations following comparison with experimental values obtained with XSW and XRR techniques.

3.2. Periodic Density Functional Theory. While the cluster DFT calculations yield clear differences between the different binding geometries, they do not account for effects resulting from molecule–molecule interactions within the organic adlayer.



Figure 2. Top view (a) and side view (b) of the relaxed periodic unit cells for the Si(111)-(1 × 1) T₄ 1-bromo-4-ethynylbenzene orientation calculated within SIESTA.⁵⁶ (a) The Si(111)-(1 × 1) hexagonal unit cell is outlined with black dashed lines, and the three high-symmetry sites T₁, T₄, and H₃ are labeled. (b) In this T₁-T₄ configuration, the carbon–carbon double bond in the alkene group at the bottom of the molecule is azimuthally aligned with the T₁-T₄ Si–Si bond just below.



Figure 3. Top view (a) and side view (b) of the relaxed periodic unit cells for the Si(111)-(1 × 1) H₃ 1-bromo-4-ethynylbenzene orientation calculated within SIESTA.⁵⁶ In comparison to the configuration shown in Figure 2, this T_1 -H₃ configuration has the molecule azimuthally rotated about the T_1 vertical axis by $180^\circ \pm 60^\circ$.

Consequently, periodic DFT calculations were performed to quantitatively determine the optimized geometry in the presence of molecule-molecule interactions. Two different periodicities were considered for 1-bromo-4-ethynylbenzene bonded to Si(111): the (1×1) case, where there is a 1-bromo-4ethynylbenzene molecule bonded to each T₁ silicon site, and the (2×1) case, where one-half of the silicon T₁ sites have a molecule attached.⁵⁵ The local density approximation was used,⁵⁶ and each geometry was converged to 0.01 eV/Å on a real-space grid corresponding to an energy cutoff of 300 Ryd. A double ζ polarized local atomic orbital basis set was employed, and each unit cell was periodically repeated in all calculations. Due to computational limitations, the periodic structural study was limited to the (2×1) and (1×1) configurations. Both unit cells were relaxed on slabs eight layers deep through the conjugate gradient method.

To minimize the repulsive forces between neighboring molecules, the benzene rings of 1-bromo-4-ethynylbenzene were optimized by the DFT calculation to align along either the T_1-T_4 direction (Figure 2) or T_1-H_3 direction (Figure 3). If the rings were instead aligned along the T_1-T_1 direction, the length of the rings with respect to the Si(111)-(1 × 1) hexagonal pattern would create significant nuclear overlap. Importantly, this was found to be true for both 1-bromo-4-ethynylbenzene and



Figure 4. Top view (a) and side view (b) of the relaxed periodic unit cells for Si(111)-(2 × 1) 1-bromo-4-ethynylbenzene in configuration 1 at the maximum tilt angle calculated within SIESTA.⁵⁶ (a) The 2 × 1 oblique-p unit cell is outlined with black dashed lines with H-occupied T₁ sites at the corners and molecule-occupied T₁ sites at the midpoints of the double-length edges. (b) Dashed lines are used to illustrate how the molecular tilt angle and Br height are defined.



Figure 5. Top view (a) and side view (b) of the relaxed periodic unit cells for Si(111)-(2 \times 1) 1-bromo-4-ethynylbenzene in configuration 2 at the maximum tilt angle calculated within SIESTA.⁵⁶

4-bromostyrene, where the lack of a double bond in the latter case allows the phenyl ring to freely rotate. Both T_1-T_4 and T_1-H_3 orientations have a height of 8.9 Å, measured from the T₁ bonding Si site to the Br atom. The absorption energy of the Si(111)-(1 × 1) T₄ orientation shown in Figure 2 is -1682.80 eV. The absorption energy of the Si(111)-(1 × 1) H₃ orientation shown in Figure 3 is -1682.73 eV. The absorption energy is defined as the total energy of a given calculation less the total energy of a Si(111)-(1 × 1):H eight-layer slab. The difference in energy between the two orientations is 70 meV, therefore the T₄ orientation is slightly more favorable with respect to thermal energy at room temperature ($k_BT = 25$ meV).

As shown in Figures 4 and 5, the (2×1) oblique-p unit cell contains two end-to-end hexagonal unit cells defined in the (1×1) model. The (2×1) has alternating rows of hydrogenpassivated T₁ sites and molecule-occupied T₁ sites. To minimize repulsive forces, the phenyl ring aligns to point toward a nearestneighbor unoccupied T₁ site. Although the direction of orientation is discrete, the molecule may lie at a tilt angle between 16° and 34° leading to large variations in the position of the Br atom above the underlying Si(111) crystal lattice. Due to computational constraints, we have sampled the height and absorption energies of only seven tilt angles as summarized in

TABLE 1: Relaxed Periodic Unit Cells for the Si(111)-(2 \times 1) for Seven Sampled Relaxed Configurations^{*a*}

configuration	abs. energy (eV)	tilt (deg)	height (Å)
1 (tilt-3)	-1686.32	34.32	6.51
1 (tilt-2) 1 (tilt-1)	-1686.27 -1686.27	29.34 25.31	7.31 7.74
2 (tilt-0)	-1686.25	16.94	8.32
2 (tilt-1) 2 (tilt-2)	-1686.25 -1686.25	15.92 18.52	8.37 8.29
2 (tilt-3)	-1686.25	21.07	8.18

 a It is apparent that variation is permitted in the monolayer tilt angle from approximately 16° to 34°. The two configurations are shown in Figures 4 and 5.



Figure 6. AFM intermittent contact mode images of Si(111) surfaces taken (a) immediately after passivation and (b) following a 20-h UV-induced hydrosilylation reaction with 1-bromo-4-ethynylbenzene. In both cases, steps are clearly visible indicating an atomically flat surface.

Table 1. The two tilt configurations are visualized in Figures 4 and 5. The tilt angle is affected by the underlying symmetry of the Si(111) surface but may go to the left or right with equal absorption energies. Figures 4 and 5 illustrate these two (2 \times 1) tilt configurations.

In tilt configuration 1 (see Table 1 and Figure 4), the phenyl ring is set at an angle with respect to the alkene group. On the other hand, tilt configuration 2 (see Table 1 and Figure 5) features a direct alignment of the phenyl ring with the alkene group. The seven sampled angles in Table 1 are labeled with respect to configuration 1 or 2. Heights range from 8.4 Å at a tilt of approximately 16° to 6.5 Å at a maximum tilt of approximately 34° (as measured from the T₁ bonding Si site to the bromine atom). These results are in direct contrast to the (1 \times 1) adlayer geometry where tight packing constrains the molecules to an upright orientation. The absorption energy, which is defined as the total energy of a given calculation less the total energy of an eight-layer Si(111)-(2 \times 1):H slab, decreases slightly as the tilt angle increases (see Table 1). Given that the transition energy from one tilt angle to the next is less than or only slightly greater than the thermal energy at room temperature ($k_{\rm B}T = 25$ meV), it is likely that all tilt angles from 16° to 34° are accessible. The mean absorption energy of sampled configurations is -1686.27 eV, which is 3.5 eV less than the (1×1) configuration. Therefore, the periodic DFT calculations suggest that a more dispersed coverage is preferred and that the dense (1×1) packing is less likely to be observed experimentally.

4. Results and Discussion

AFM images of the Si(111) surface taken after hydrogen passivation show atomically flat steps that are characteristic of monohydride-passivated Si(111) (Figure 6a). Following UV attachment of 1-bromo-4-ethynylbenzene, the samples were sonicated for 5 min in chloroform to remove loosely bound adsorbates and contamination. AFM was then performed again



Figure 7. High-resolution (20-meV pass energy) XPS scan of the Br 3d peak, revealing the presence of Br-C bonds and the absence of Br-Si bonds. This spectrum shows a single bromine 3d spin doublet with peaks located at 71.3 and 70.3 eV.

to verify that step edges were visible after sonication (Figure 6b). The observation of step edges shows that spurious physisorption has been minimized and suggests the presence of a uniform adlayer at the surface.

XPS measurements were performed to verify the absence of any undesired reaction products. In particular, the XPS spectrum of Figure 7 shows that the Br 3d peak possesses a Br–C doublet at 71.3 and 70.3 eV and no Si–Br doublet at 70.3 and 69.3 eV.⁵⁷ Consequently, it is concluded that the Br has remained attached to the phenyl ring and has not reacted with the Si surface. It should also be noted that examination of the Si 2p peak (not shown) reveals that minimal surface oxidation has occurred.

In addition to allowing chemical analysis by XPS, the presence of Br on 1-bromo-4-ethynylbenzene enables further structural characterization by XRR and XSW techniques. In Figure 8a, XRR experimental results are compared to three model calculations with different molecular packing densities. In these model calculations, the film thickness (t) is allowed to vary by changing the tilt angle η of the molecule with respect to the surface normal about the T1 Si site. The cluster DFT predicted film thickness from Figure 1a (with $\eta = 10^{\circ}$) is t =8.9 Å. The best-fit curve to the data is labeled A1 and has (1) the molecule tilted further inward to $\eta = 14^{\circ}$ (corresponding to t = 8.7 Å), (2) the molecular packing at a coverage of $\Theta =$ 0.65 ML, (3) a static Gaussian vertical displacement distribution for all atoms in the molecule characterized by a width $\sigma = 2$ Å, and (4) the interface roughness parameter⁵⁸ at $\beta = 0.5$, which corresponds to $\sigma_{\rm rms} = 4.4$ Å. From curves A1, A2, to A3, the packing density has been changed from 0.65 to 0.5 and 0.8 accordingly. As can be seen, the strength of the antireflection around Q = 0.30 Å⁻¹ changes with coverage, and the χ^2 increases from 0.56 (A1) to 0.80 (A2) and 7.62 (A3). In Figure 8b, the XRR data are compared with XRR simulations for the DFT-predicted configurations shown in Figures 1b, 1c, and 4. None of these alternative binding configurations agree with the observed XRR data.

The Br atomic coverage was determined to be $\Theta_{Br} = 0.68(4)$ ML by XRF, which is in close agreement to the previously described XRR-measured coverage of the 1-bromo-4-ethynylbenzene molecules made independently on the same sample. The XSW results listed in Table 2 are the values obtained from a second identically prepared sample. The (111) XSW data and theoretical fit from eq 1 are shown in Figure 9. The top of the Si bilayer is chosen as the referential origin for all the coherent positions in this analysis.

The Br three-dimensional atomic density map with twodimensional cuts shown in Figure 10 was obtained by a summation of the Fourier components whose XSW measured amplitudes $(f_{\rm H})$ and phases $(P_{\rm H})$ are listed in Table 2. Since this map is produced by allowed Si reflections, it has the same periodicity as the Si primitive unit cell. A hexagonal unit cell is used because of the diamond-cubic (111) surface. Three symmetry equivalent maxima²⁵ in the Br atomic density map show up at (1) $z = P_{111} * d_{111} = 2.32(6)$ Å (laterally above the T₁ site), (2) $z = (1 + P_{111})d_{111} = 5.45(6)$ Å (laterally above the H₃ site), and (3) $z = (2 + P_{111})d_{111} = 8.59(6)$ Å (laterally above the T₄ site). With the previously described XRR result of $z \sim$ 8.7(5) Å for Br height, the Br atoms are determined to be centered above the T₄ site. This orientation requires a molecular tilt of 14°, which agrees with the tilt angle used in the best fit of the XRR data. Furthermore, this tilt angle sits between the 21° predicted by the (2 × 1) periodic DFT case (Figure 5) and the nearly upright (1×1) periodic DFT case (Figures 2 and 3), suggesting that a combination of the (2×1) and (1×1) cases are present on the surface. A combination of (2×1) and (1×1) is also consistent with the measured coverage of 0.65 ML, which sits between the maximum coverage of 0.5 and 1.0 ML for the (2×1) and (1×1) cases, respectively.

If the equilibrium state of the 1-bromo-4-ethynylbenzene molecules on Si(111) surface has only one configuration, then all Br atoms will be at a single height, and the expected P_{111} and P_{333} measured values would follow the relationship $P_{333} = Mod[3P_{111}]$.³⁸ However, if one compares the results from the (111) and (333) XSW measurements, it can be seen that the measured value for $P_{333} = 0.32$ is greater than $Mod[3P_{111}] = 0.22$, which demonstrates that the Br atomic distribution is not consistent with a single height model. In fact, relating the measured (111) and (333) coherent positions demonstrates that the projected Br distribution is asymmetric and furthermore top heavy (i.e., the mode is greater than the mean).

Overall, the X-ray measurements rule out the single-bridge and double-bridge configurations for 1-bromo-4-ethynylbenzene on Si(111). Consequently, in contrast to 4-bromostyrene, the terminal carbon atoms in 1-bromo-4-ethynylbenzene preserve π -conjugation following reaction to Si(111). To verify this conclusion, broadband vibrational sum frequency generation (SFG) was employed to compare the conjugation of 1-bromo-4-ethynylbenzene and 4-bromostyrene on Si(111). Since the carbon-carbon double bond of 4-bromostyrene reacts with the silicon surface to form a carbon-carbon single bond, its SFG spectrum should only contain CH stretches below 3000 cm^{-1,59-61} The SFG spectra displayed in Figures 11A and B show that this is indeed the case. This fact is demonstrated further in the upper spectrum of Figure 12, which shows the backgroundsubtracted and power-normalized sum of the SFG spectra displayed in Figures 11A and B. While the asymmetric and symmetric CH stretches are self-apparent, the SFG does not show signal intensity in the aromatic and olefinic CH stretching region (>3000 cm⁻¹).^{62–70} This finding indicates that the aromatic CH stretches of the benzyl ring are associated with transition moments that are oriented mainly parallel to the interface, which is orthogonal to the main probe direction of the ppp-polarized SFG experiments. An upright orientation for the benzyl ring is consistent with the aforementioned X-ray and DFT analyses.

Unlike 4-bromostyrene, the bottom SFG spectrum displayed in Figure 12, which is the background-subtracted and powernormalized sum of the SFG spectra exhibited in Figures 11C and D, shows that Si(111) surfaces functionalized with 1-bromo-4-ethynylbenzene display strong ppp-polarized SFG signal intensity at 3080 cm⁻¹. Given the fact that the aromatic CH



Figure 8. (a) Specular XRR data (filled circles) and model simulations using a molecule structure factor with atomic coordinates based on the cluster DFT calculation of Figure 1a. The best-fit simulation is labeled A1. The A1 model has a molecular coverage of 0.65 ML, an inward molecular tilt of 14° (t = 8.7 Å), a Si surface roughness parameter of $\beta = 0.5$, and a $\sigma = 2$ Å Gaussian distribution to the vertical displacements of the atoms in the molecule. Model A2: same as A1, except it assumes a 0.5-ML coverage. Model A3: same as A1, except it assumes 0.8-ML coverage. (b) Fits to alternate binding configurations compared to the best fit. The Alt1 fit depicts the single-bridge configuration height obtained by cluster DFT, Alt2 describes the double-bridge configuration, and Alt3 represents the 34° tilting angle, 6.5-Å bromine-height minima discovered in the (2 × 1) periodic DFT case.

TABLE 2: XSW Measured Values for the Br Coherent Fractions $(f_{\rm H})$ and Coherent Positions $(P_{\rm H})^a$

	measure	measured values		DFT	
hkl	$f_{\rm H}$	P _H	a_{H}	P_{H}	
111	0.61(2)	0.74(2)	1	0.82	
333	0.29(4)	0.32(4)	1	0.47	
$11\overline{1}$	0.15(2)	0.29(2)	0.21	0.53	
220	0.10(2)	0.92(3)	0.21	0.36	

^{*a*} Also listed are the model calculated values for geometrical factor $(a_{\rm H})$ and $P_{\rm H}$ for the Br distribution as predicted by the DFT model shown in Figure 1a.



Figure 9. Single-crystal (111) XSW results for the 1-bromo-4ethynylbenzene adlayer on Si(111). Shown are the angle dependence of the Si(111) Bragg reflectivity rocking curve and the Br K α XRF yield data. Symbols are measured data, and solid lines are the best fits (including eq 1) to the data. The f_{111} and P_{111} parameters determined by this fit are listed in Table 2.

stretches are spectroscopically silent, the mode at 3080 cm⁻¹ is attributed to the CH stretches of the terminal carbon–carbon double bond. This spectral assignment is supported by the notion that the infrared vibrational transition moments of asymmetric CH stretches involving carbon–carbon double bonds are generally strong^{66,71–74} and that Raman and infrared vibrational modes for the olefinic CH stretches appear in the same frequency region (between 3010 and 3100 cm⁻¹). Interestingly, while the carbon–carbon double bond that gives rise to the SFG signal intensity above 3000 cm⁻¹ is expected to be trans-oriented, which would result in destructive interference and thus spectral silence in SFG, its CH stretches are clearly observable using



Figure 10. XSW-generated Br atomic map with respect to the Si hexagonal unit cells that exhibits the threefold symmetry of the Si(111)- (1×1) surface. These two-dimensional cuts through the three-dimensional Br atomic density map coincide with the Br maxima in the three-dimensional map. The upper image is a top view cut parallel to the (111) surface at a height of z = 8.70 Å above the top bulklike Si(111) atomic layer. The lower image is a side view cut perpendicular to the (111) surface that coincides with the T₁, T₄, and H₃ high-symmetry sites of the Si(111)- (1×1) surface. For reference, the bulklike Si positions for the top bilayer of the Si(111) surface are shown as open and filled circles at the bottom of the lower image. The T₁ site is directly above the bottom Si (filled circle) in the Si bilayer. The lateral position for the H₃ hollow site is also indicated.

SFG. This finding is attributed to the asymmetry surrounding the olefinic carbon–carbon double bond, which is a key requirement for SFG.^{75–81} Under these conditions, SFG allows confirmation of the presence of sp² hybridization in 1-bromo-4-ethynylbenzene on Si(111).

5. Summary and Conclusion

Through the use of a complementary suite of X-ray tools, scanning probe microscopy, vibrational spectroscopy, and



Figure 11. (a, b) SFG spectra for a 4-bromostyrene adlayer on Si(111) (black trace) using the ppp-polarization combination and an infrared center frequency of (a) 3050 cm^{-1} and (b) 2950 cm^{-1} . (c, d) Same as (a, b) but for 1-bromo-4-ethynylbenzene on Si(111). The differences between the SFG spectra and a Gaussian are shown as gray traces in the spectra.



Figure 12. SFG spectra at ppp polarization for a 4-bromostyrene adlayer (top) and 1-bromo-4-ethynylbenzene adlayer (bottom) on Si(111) after the non-resonant Gaussian background was subtracted.

computational modeling, 1-bromo-4-ethynylbenzene adlayers on the Si(111) surface have been thoroughly characterized. AFM confirmed an atomically flat surface morphology, while XPS verified the absence of any unintended chemical reactions. Subsequently, by comparing structural XRR and XSW experimental data to DFT calculations, it was concluded that 1-bromo-4-ethynylbenzene forms a single bond to the Si(111) surface from its original alkyne group, thus retaining π -conjugation in its terminal carbon atoms. In support of this conclusion, SFG was used to compare 1-bromo-4-ethynylbenzene to 4-bromostyrene on Si(111). The SFG measurements provide direct evidence of a retained nonaromatic carbon-carbon double bond only in the case of 1-bromo-4-ethynylbenzene. While this study focused on the specific case of 1-bromo-4-ethynylbenzene on Si(111), it is likely that the experimental and theoretical methodology outlined in this paper can be applied to a diverse range of other surface functionalization chemistries. Overall, the ability to quantitatively assess the conformation and conjugation of organic adlayers on silicon surfaces presents opportunities for optimal design and quality control of organosilicon molecular electronic and sensing devices.

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