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Vibrational Sum-Frequency Spectroscopic Investigation of the Structure and Azimuthal Anisotropy of Propynyl-Terminated Si(111) Surfaces

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ABSTRACT

Vibrational sum-frequency generation (VSFG) spectroscopy was used to investigate the orientation and azimuthal anisotropy of the C–H stretching modes for propynyl-terminated Si(111) surfaces, Si–C≡C–CH_3. VSFG spectra revealed symmetric and asymmetric C–H stretching modes in addition to a Fermi resonance mode resulting from the interaction of the asymmetric C–H bending overtone with the symmetric C–H stretching vibration. The polarization dependence of the C–H stretching modes was consistent with the propynyl groups oriented such that the Si–C≡C bond is normal to the Si(111) surface. The azimuthal angle dependence of the resonant C–H stretching amplitude revealed no rotational anisotropy for the symmetric C–H stretching mode and a 3-fold rotational anisotropy for the asymmetric C–H stretching mode in registry with the 3-fold symmetric Si(111) substrate. The results are consistent with expectation that the C–H stretching modes of a –CH_3 group are decoupled from the Si substrate due to a –C≡C– spacer. In contrast, the methyl-terminated Si(111) surface, Si–CH_3, was previously reported to have pronounced vibronic coupling of the methyl stretch modes to the electronic bath of bulk Si. Vacuum-annealing of propynyl-terminated Si(111) resulted in increased 3-fold azimuthal anisotropy for the symmetric stretch, suggesting that removal of

propynyl groups from the surface upon annealing allowed the remaining propynyl groups to tilt away from the surface normal, into one of three preferred directions towards the vacated neighbor sites.

I. INTRODUCTION

Chemical functionalization of inorganic semiconductor surfaces has been used to tune the interfacial dipole, relative band-edge positions, manipulate surface-state densities, improve chemical stability, and alter the optoelectronic properties of the resulting materials.[1-8] The orientation and conformation of chemisorbed or physisorbed molecules can contribute to the electronic coupling between the bound adsorbate and semiconductor material, thereby regulating on a molecular scale interfacial electron transfer, charge injection and extraction, charge transport, and electron tunneling at the interface.[9-10] The energetics and coupling at the interface can be instrumental in controlling adsorbate-substrate energy transfer and in influencing reaction rates and mechanisms at the interface. A molecular-level understanding of functionalized semiconductor surfaces is thus necessary to elucidate interfacial chemistry and adsorbate-semiconductor interactions, which in turn can be used to inform device engineering.

Covalent attachment of organic moieties to oxide-free crystalline Si surfaces, while preserving the ideal electronic properties of H-terminated Si surfaces (H–Si(111)), would be an attractive route for the fabrication of highly passivated Si surfaces for applications in micro- and nanoelectronics,[6, 11] photonics, solar-energy conversion,[12] and chemical and biological sensors.[13-14] Methyl termination of Si(111) surfaces (CH_3–Si(111)) by a wet-chemical process yields atomically flat Si with all surface Si sites terminated.[15-18] Although CH_3–Si(111) surfaces exhibit enhanced resistance to air oxidation compared to H–Si(111) surfaces,[19-20] –CH_3 groups are limited by a lack of methods to impart secondary functionalization.

Functionalization of the Si(111) surfaces with alkynyl moieties, such as ethynyl and propynyl groups, has the advantage of allowing for elaboration through the unsaturated –C≡C– units while still, in principle, maintaining nearly full Si–C surface termination.[4, 21-24] Propynyl-

terminated Si(111) surfaces (CH_3CC–Si(111)) exhibit nearly complete termination of the Si(111) surface while maintaining a relatively low, air-stable, surface recombination velocity.[24-30] Previous characterization of CH_3CC–Si(111) surfaces has also indicated that the CH_3CC– groups are oriented normal to the surface by infrared spectroscopy, the surfaces exhibit a (1 × 1) surface unit cell by low-energy electron diffraction, and the surfaces exhibit broad atomic terraces by atomic-force microscopy.[24] However, a full understanding of the chemical and electronic structures of Si surfaces functionalized with alkynyl moieties is still lacking, owing to the paucity of surface-sensitive spectroscopic techniques suitable for the detailed characterization of molecular monolayers.

Vibrational sum-frequency-generation (VSFG) spectroscopy provides surface selectivity and submonolayer sensitivity for in-situ investigations of the molecular structure and dynamics at surfaces.[31-34] VSFG spectroscopy is a second-order nonlinear spectroscopic technique that, under the electric dipole approximation, occurs only in the region of the material in which the inversion symmetry is broken, specifically at the interface. The vibrational signatures of an adsorbate in the mid-IR region are sensitive to the local environment, so VSFG spectroscopy can be used in unraveling the adsorbate-adsorbate and adsorbate-substrate interactions.[35-40] The input and output beam polarizations of VSFG can be independently controlled to produce information about the molecular orientation of the surface species.[41]

The molecular structure and rotational dynamics of CH_3–Si(111) surfaces has been elucidated using polarization-selected VSFG spectroscopy.[42-43] The results indicated a strong electronic interaction between the –CH_3 vibrational modes and the Si surface, but the extent to which this coupling interaction is influenced by the proximity of the –CH_3 group to the Si(111) surface has not been investigated. While both CH_3CC–Si(111) and CH_3–Si(111) surfaces have

vibrational signatures arising from $–CH_3$ groups, the distance between the $–CH_3$ groups and the Si substrate is larger for $CH_3CC–Si(111)$ samples, allowing one to probe the dependence of adsorbate-substrate interactions on the distance between the terminal $–CH_3$ group and the Si(111) surface. The work reported herein describes a polarization-dependent VSFG study of the propynyl-terminated Si(111) surface, to elucidate the surface structure and the adsorbate-substrate interaction of this system.

II. EXPERIMENTAL

II.A. Materials and Methods. Water with a resistivity of ≥18.2 MΩ cm was obtained from a Barnstead E-Pure system. Ammonium fluoride (NH_4F(aq), 40%, semiconductor grade, Transene Co., Inc., Danvers, MA) was purged with Ar(g) (99.999%, Air Liquide) for 1 h prior to use. All other chemicals were used as received. Czochralski-grown n-type Si wafers (Virginia Semiconductor, Fredericksburg, VA) were double-side polished, doped with phosphorus to a resistivity of 1 Ω cm, 381 ± 25 μm thick, and oriented to within 0.1° of the (111) crystal plane.

II.A.1. Preparation of H–Si(111) Surfaces. The n-Si wafers were cut into 1 cm × 4 cm pieces and rinsed sequentially with water, methanol (≥99.8%, BDH), acetone (≥99.5%, BDH), methanol, and water. The wafers were oxidized and organic contaminants were removed by immersing the wafers for 10 min in a piranha solution (1:3 v/v of 30% H_2O_2(aq) (EMD): 18 M H_2SO_4 (EMD)) at 95 °C. The wafers were removed and then rinsed with copious amounts of water. The oxide was removed by immersing the wafers in buffered hydrofluoric acid (HF(aq), Transene Co. Inc., Danvers, MA) for 18 s, rinsing with water, and immediately placing the wafers for 9.0 min in an Ar(g)-purged solution of NH_4F(aq).[24, 44-45] The wafers were agitated at

the start of each minute of etching, to remove bubbles that formed on the surface. The samples were then removed from the etching solution, rinsed briefly with water, and dried under Ar(g).

II.A.2. Preparation of Cl–Si(111) Surfaces. The H–Si(111) samples were transferred to a N_2(g)-purged glove box with <10 ppm O_2(g). An initiating amount (<1 mg mL^{-1}) of benzoyl peroxide 98%, Sigma-Aldrich) was added to a saturated solution of PCl_5 (99.998% metal basis, Alfa Aesar) in chlorobenzene (anhydrous, 99.8%, Sigma-Aldrich). The wafers were rinsed with chlorobenzene and immersed in the PCl_5 solution at 90 ± 2 °C for 45 min.[24, 45-46] The wafers were removed from the reaction and rinsed with chlorobenzene followed by hexanes (anhydrous, mixture of isomers, 99%, Sigma-Aldrich).

II.A.3. Preparation of Propynyl-Terminated Si(111) Surfaces. The Cl–Si(111) surfaces were immersed in a 1.0 M solution of 1-propynyllithium (CH_3CCLi, BOC Sciences, Shirley, NY) at 45 ± 2 °C for 15 h inside foil-wrapped test tubes. The wafers were removed from the solution and rinsed with hexanes, followed by methanol (anhydrous, 99.8%, Sigma-Aldrich), submerged in methanol, and removed from the glove box. The samples were sonicated for 10 min in methanol, rinsed with water, and dried under Ar(g). The samples were broken into 1 cm × 1 cm squares, rinsed again with water, dried with Ar(g), and sealed under Ar(g) inside polypropylene centrifuge tubes, to enable transport from Caltech to the University of Southern California. X-ray photoelectron spectroscopy of the samples after preparation was consistent with results reported previously,[24] indicating complete termination of the surface by CH_3CC– groups and the absence of detectable levels of silicon oxide.

II.B. VSFG Spectroscopy. A detailed description of the VSFG apparatus can be found elsewhere.[42] In brief, the femtosecond mid-infrared and picosecond visible pulses used in the broadband SFG spectroscopy setup were generated by splitting the 4 W output of a

regeneratively amplified Ti:sapphire laser system (Spectra Physics Spitfire seeded by a KM Laboratories Oscillator) operating at 1 kHz repetition rate. The system delivered <100 fs pulses centered at ~800 nm. An optical parametric amplifier assembly (TOPAS-C, Light Conversion)-difference frequency generator (NDFG, Light Conversion) generated tunable femtosecond mid-IR pulses (fwhm 350 cm^{-1}). The narrowband visible pulses were generated from the uncompressed fundamental by passing the beam through an external compressor (Newport Corporation) and an etalon (TecOptics, fwhm 17 cm^{-1}).

To generate the SFG signal, the IR and visible pulses were spatially and temporally overlapped at the sample stage. SFG spectra were recorded using a triple-grating monochromator in conjunction with a CCD cooled by liquid nitrogen. SFG spectra were collected under an atmosphere of dry air obtained from a purge gas generator. To focus on the C–H stretching region of the CH_3CC–Si(111) samples, the IR pulse was centered at 3000 cm^{-1}. The beam was focused on the sample using a 25 cm focal length CaF_2 lens for the IR beam and a 45 cm focal length BK7 lens for the visible beam to yield a 200 μm diameter spot. The intensities of the visible and the IR beams were 6–7 mW and 6–9 mW, respectively. Prior to VSFG measurements, sample annealing was performed to remove surface impurities for 16–20 h under ultrahigh vacuum at the temperatures ranging from 200–320 °C (see text).

III. RESULTS

III.A. VSFG and Anisotropy Studies of CH_3CC–Si(111) Surfaces. Figure 1 presents SFG spectra of the C–H stretching region for PPP (SFG-visible-IR) and SSP polarization combinations, for as-prepared CH_3CC–Si(111) samples at room temperature. A 270 fs time delay between the IR and the visible pulses was used to collect both the PPP and the SSP spectra, to

suppress the nonresonant response of the silicon substrate.[42-43, 47-48] The PPP spectrum showed three resonant vibrational modes of the terminal $-CH_3$ group, which are assignable to the symmetric C–H stretch (r^+) at ~2865 cm^{-1}, the asymmetric C–H stretch (r^-) at ~2962 cm^{-1}, and the Fermi resonance (d^+_{FR}) of the r^+ mode with the C–H asymmetric bending overtone, at ~2933 cm^{-1}.[24, 42, 49-51] The SSP spectrum, which exhibited a significant reduction in signal intensity compared with the PPP spectrum, only showed signatures ascribable to the symmetric C–H stretch (r^+) at ~2863 cm^{-1} and the Fermi resonance (d^+_{FR}) at ~2935 cm^{-1}.

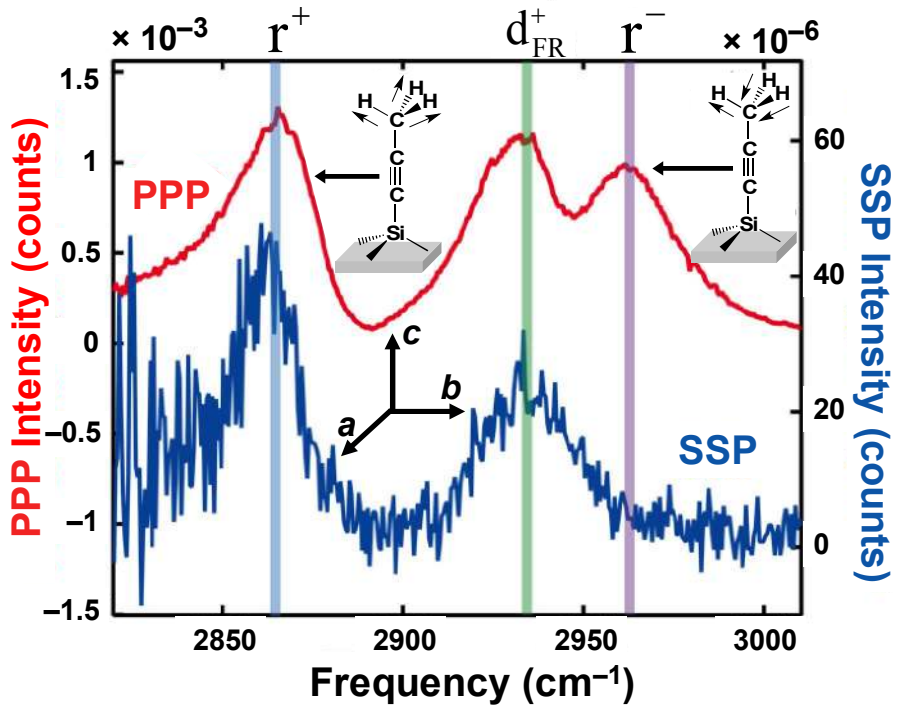

Figure 1. PPP (red, left axis) and SSP (blue, right axis) polarized VSFG spectra of the CH_3CC–Si(111) surface for the C–H stretching region. The time delay between the IR and the visible pulses was 270 fs. The corresponding molecular motions are shown alongside the VSFG spectra. The molecular frame of reference (*a*, *b*, *c*) used in this work is indicated in the figure relative to the proposed orientation of the CH_3CC– groups on the surface.

The azimuthal dependence of the resonant amplitudes of the r^+ and r^- modes of the CH_3CC–Si(111) samples was measured[42, 52-54] for azimuthal angles ϕ from 0° to 360°, and are shown for PPP polarization conditions in Figure 2. The data points represent the resonant C–H stretching mode amplitudes, which were obtained from the fits of the PPP spectra collected by in-plane rotation of the sample at 30° intervals (Table S2, Supporting Information). The polar plot for the r^+ mode (Figure 2A) showed only small changes in the amplitude of the resonant C–H stretching signal with ϕ, whereas the plot for the r^- mode showed a pronounced 3-fold dependence on the azimuthal angle (Figure 2B).

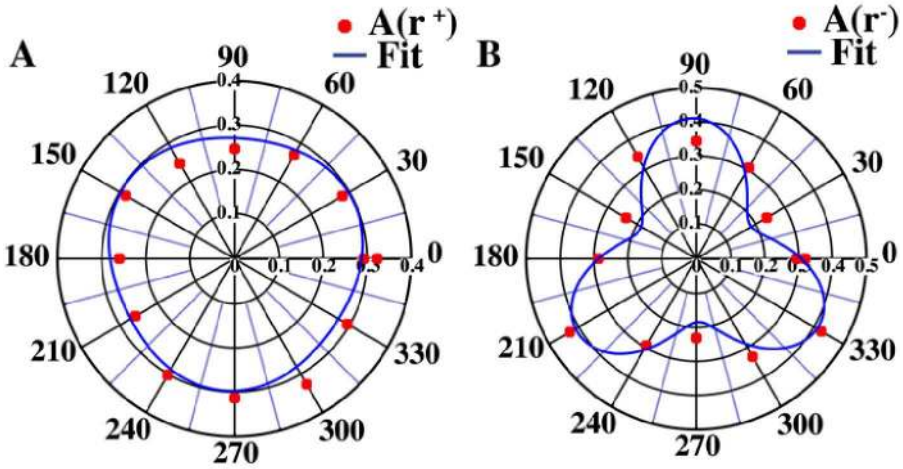

Figure 2. Polar plots showing the azimuthal dependence of the resonant amplitude of the C–H symmetric stretch r^+ (A) and C–H asymmetric stretch r^- (B), respectively, of the PPP spectra for as-prepared CH_3CC–Si(111) samples. Data points were collected from 0° to 360° in 30° increments, and the blue solid lines are fits described in the text (Eq. (2)).

III.B. Effects of Annealing on the Adsorbate-Substrate Coupling Interaction. The stability of the CH_3CC–Si(111) samples toward annealing in vacuum was investigated by VSFG spectroscopy. Samples were heated to 200–320 °C for 16–20 h under vacuum, and were then

allowed to cool to room temperature for characterization by VSFG spectroscopy. The VSFG spectra for the annealed samples (Figure 3) exhibited the same set of SFG transitions that were seen for the as-prepared samples, with the r^+ and the d^+_{FR} modes observed for both SSP and PPP polarizations, and the r^- mode only observed for the PPP polarization. After annealing, the peak intensities were reduced and the peak centers shifted by ~5–9 cm^{-1} to higher energy relative to the spectra obtained before annealing of the sample.

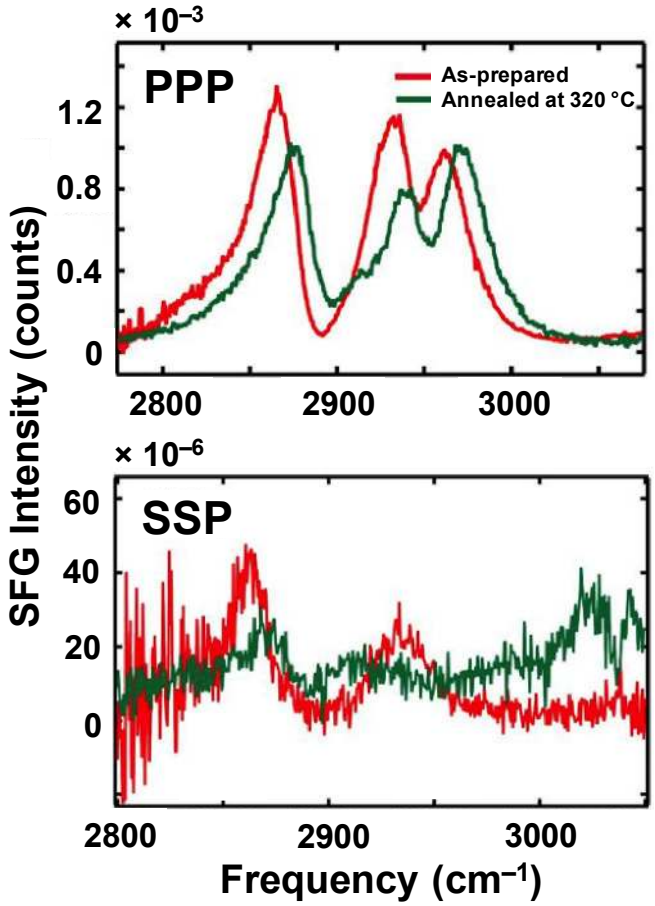

Figure 3. PPP and SSP spectra of the C–H stretching region of CH_3CC–Si(111) samples annealed at 320 °C for 16–20 h under vacuum. The decrease in intensity is consistent with the partial loss of the CH_3CC– units from the Si(111) surface upon annealing. The slight blue-shift of the peaks may be due to the changed local environment of the propynyl group remaining on the surface.

Figure 4 shows the dependence of the resonant amplitudes of the r^+ and r^- modes, respectively, of the annealed CH_3CC–Si(111) samples on the azimuthal angle ϕ for PPP polarization conditions. The fits of the azimuthal rotational anisotropy data, collected for in-plane rotation intervals of 10° (Table S3, Supporting Information), are shown superimposed on the data points. After annealing, a 3-fold rotational anisotropy of the symmetric stretch r^+ mode was readily observed, in contrast to the behavior prior to annealing. The 3-fold rotational anisotropy exhibited by the r^- mode was slightly enhanced by the annealing step. The rotational anisotropy of the resonant amplitudes of the r^+ and r^- modes was generally more pronounced after annealing, indicating a change in the interaction between the CH_3CC– adsorbates and the Si substrate.

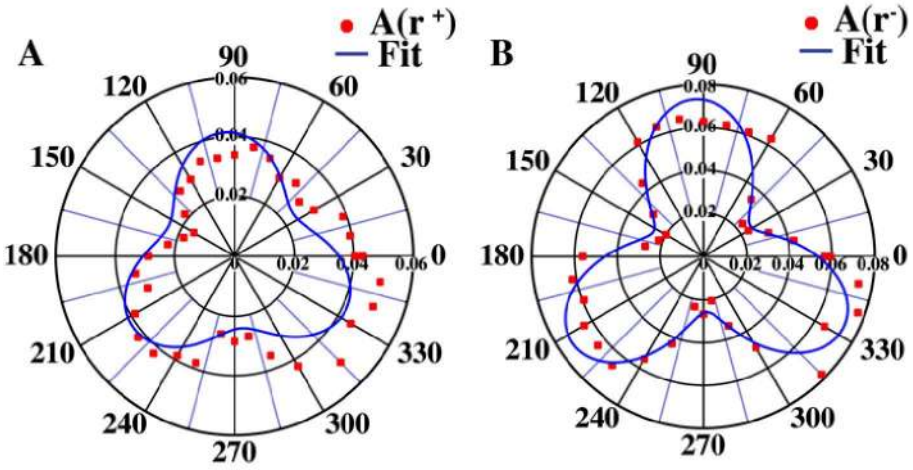

Figure 4. Polar plots showing the azimuthal dependence of the resonant amplitudes for PPP spectra of (A) the C–H symmetric stretch ($A(r^+)$) and (B) the C–H asymmetric stretch ($A(r^-)$) for CH_3CC–Si(111) samples annealed at 200 °C for 16–20 h under vacuum. Data points were collected from 0° to 360° in 10° increments, and the blue solid lines are fits described in the text (Eq. (2)).

IV. DISCUSSION

IV.A. VSFG Orientation Analysis of as-Prepared CH_3CC–Si(111) Samples. The sum frequency spectra of the CH_3CC–Si(111) samples were analyzed by macroscopic (ensemble) averaging of the resonant hyperpolarizability tensor elements ($\beta^{(2)}_{lmn}$, defined in the molecular frame (*a*, *b*, *c*)) that represent the methyl group vibrations (Figure 1).[41] $\beta^{(2)}_{lmn}$ for the *i*-th vibrational mode is expressed as a product of the vibrational transition dipole moment and the Raman polarizability tensor:

$$\beta^{(2)}_{lmn,i} \propto \frac{\partial \alpha_{lm}}{\partial q_i} \frac{\partial \mu_n}{\partial q_i} \qquad (1)$$

where q_i is the normal coordinate and the indices *l*, *m*, and *n* represent axes in the molecular frame of reference (*a,b,c*). Different vibrational modes have different symmetries, and the PPP and SSP polarization combinations sample different β tensor elements,[55-57] which are also governed by the molecular symmetries. Hence, the absence of the r^- mode in the SSP spectrum provides a qualitative indication of the orientation of the CH_3CC– moieties perpendicular to the Si(111) surface.

The terminating CH_3CC– group can be approximately described as having C_{3v} symmetry, with *c* being the C_3 symmetry axis and the *ac* plane lying on one of the σ_v symmetry planes.[55, 57] With respect to this molecule fixed coordinate system, the three C–H vibrational modes observed in the SFG spectra can be categorized into two different types of vibrations with different hyperpolarizability tensor elements.[58-59] The r^+ and the d^+_{FR} modes account for changes in the transition dipole moments along the *c* axis (perpendicular to the Si(111) surface plane), whereas the r^- mode accounts for changes along a direction that is perpendicular to the *c* axis (parallel to

the Si(111) surface plane). The corresponding β tensor elements for these modes can also be categorized into two groups: the totally symmetric r^+ mode corresponds to two isotropic independent β tensor elements, $\beta^{(2)}_{aac} = \beta^{(2)}_{bbc}$ and $\beta^{(2)}_{ccc}$, and the r^- mode corresponds to only one independent β tensor element $\beta^{(2)}_{aca} = \beta^{(2)}_{caa}$.

With the symmetries of the β tensor elements for the r^+ and r^- modes taken into account, along with knowledge of the input/output polarization combinations, the SSP spectra (which sample tensor element $\chi^{(2)}_{yyz}$ defined in the laboratory frame of reference (x, y, z)) would contain no peaks if the CH_3CC- units were all oriented parallel to the Si(111) surface plane. In contrast, if the CH_3CC- units were all oriented perpendicular to the Si(111) surface plane, the SSP spectrum would contain only peaks corresponding to vibrations perpendicular to the Si(111) surface plane. Because the SSP spectra in Figures 1 and 3 exhibit signals ascribed to the r^+ and d^+_{FR} modes, the data are thus consistent with the CH_3CC- groups being oriented perpendicular to the Si(111) surface. The PPP spectra in Figure 1 and Figure 3 contain peaks corresponding to both the parallel and perpendicular vibrations, as the spectrum is comprised of four different susceptibility tensor elements ($\chi^{(2)}_{xxz}$, $\chi^{(2)}_{xzx}$, $\chi^{(2)}_{zxx}$, and $\chi^{(2)}_{xzz}$) sampling molecular hyperpolarizabilities in all possible directions. The perpendicular orientation of the CH_3CC- groups with respect to the Si(111) surface plane is consistent with the conclusions from variable-angle transmission IR data on CH_3CC-Si(111) samples.[24]

IV.B. Azimuthal Dependence of the Resonant C–H Stretch Amplitudes for as-Prepared CH_3CC-Si(111) Samples. Both the adsorbate vibrational modes and the bulk Si crystal polarizability contribute to the effective second-order vibrational response from the functionalized Si(111) surface, as has been previously observed in VSFG studies of CH_3-Si(111) surfaces.[42] The coupling between the adsorbate vibrational modes and electronic bath of bulk Si

crystal, therefore, contributes to the azimuthal behavior of the resonant vibrational r^+ and r^- modes for as-prepared CH_3CC–Si(111) samples. Each of these contributions is comprised of an isotropic component and an anisotropic component dependent on the crystal symmetry. For the Si(111) surface, which has 3-fold rotational symmetry, the generated sum frequency field, E^{SFG}, has a form:

$$E^{SFG} = (A + C\cos(3\phi + \phi_0))E^{vis}E^{IR} \quad (2)$$

where A and C are the isotropic and anisotropic contributions to the response, respectively, ϕ is the azimuthal angle within the (111) plane with a phase correction of ϕ_0, and E^{vis} and E^{IR} are the input visible and mid-IR fields, respectively.

The observed azimuthal dependence of the VSFG signals can be connected to the resonant vibrational modes via the unique β tensor elements that describe the $-CH_3$ group vibrations. The non-zero β tensor elements for the r^+ mode are symmetric with respect to the C_3 axis ($\beta^{(2)}_{aac} = \beta^{(2)}_{bbc}$ and $\beta^{(2)}_{ccc}$) because the IR transition moment for the r^+ mode is along the C_3 axis (which is along c), and the Raman polarizability tensor is isotropic about the symmetry axis. Therefore, if the C_3 axis of the terminal $-CH_3$ group is normal to the surface, as evidenced by the results reported herein, no azimuthal anisotropy for the r^+ mode is expected regardless of the in-plane orientation of the $-CH_3$ group. The lack of clear rotational anisotropy for the r^+ mode under PPP polarization conditions (Figure 2A) is consistent with this expectation. In contrast, the β tensor elements for the r^- mode comprise the off-diagonal Raman polarizability tensor elements ($\alpha_{ac} = \alpha_{ca}$), which are not symmetric about the C_3 axis. Further, the vibrational transition dipole for the r^- mode is in-plane and also expected to be anisotropic, as long as the molecules do not freely rotate in-plane. As a result, the r^- mode shows a 3-fold rotational anisotropy (Figure 2B) that reflects the 3-fold symmetry of the crystalline Si(111) surface. The

3-fold anisotropy of the r^- mode also indicates that the $CH_3CC–$ groups do not rotate freely at room temperature, but spend most of their time in one of the three energetic minima in registry with the Si(111) surface, analogous to previously reported VSFG results for CH_3–Si(111) samples.[42] This is additionally consistent with steric considerations on CH_3–Si(111) or CH_3CC–Si(111) surfaces that predict the interlocking of adjacent $–CH_3$ on the surface.[18, 60] This observation supports a close packing structure of the $CH_3CC–$ groups on the Si(111) surface, suggesting that the surfaces are fully-terminated.

Previous VSFG studies on the CH_3–Si(111) surface showed a clear 3-fold azimuthal anisotropy for the r^+ mode,[42] in contrast to the results reported herein, which showed no such anisotropy of the r^+ mode for as-prepared CH_3CC–Si(111) samples. Because symmetry considerations suggest that the r^+ mode should not exhibit rotational anisotropy, the results for CH_3–Si(111) surfaces were attributed to coupling between the adsorbate vibrational modes and the above-band-gap Raman polarizability of the Si bulk.[42] In the CH_3–Si(111) system, the coupling between the C–H vibrational modes and the electronic structure of the Si bulk is strengthened by the close proximity of the $–CH_3$ group to the Si surface (the $–CH_3$ symmetric stretch mode involves displacement of the carbon atom, and thus likely the attached Si atom). Thus, the resultant Raman polarizability derivative for the $–CH_3$ group vibrations can be expressed as:

$$\frac{\partial \alpha_{lm}}{\partial q_i} = \frac{\partial \alpha_{\mathrm{Si}}}{\partial q_i} + \frac{\partial \alpha_{\mathrm{Me}}}{\partial q_i} \qquad (3)$$

where α_{Si} and α_{Me} are the electronic polarizability of the Si substrate and the $–CH_3$ group, respectively. The polarizability scales with volume, so α_{Si} is expected to be much larger than α_{Me}, and the measured VSFG signal is dominated by the above-band-gap electronic response of the Si substrate. Hence the molecular hyperpolarizabilities for the CH_3–Si(111) surface that correspond

to the r^+ and r^- modes show the same 3-fold anisotropy of the Si(111) bulk regardless of the orientations of their transition dipole moments with respect to the surface plane. The extent of the adsorbate-substrate coupling decreases as the $–CH_3$ groups are further removed from the Si(111) surface by the –C≡C– spacer. The hyperpolarizability tensor elements for the r^+ mode observed for CH_3CC–Si(111) samples thus only reflect the totally symmetric Raman polarizability tensor elements of the C–H symmetric vibrations of the methyl group uncoupled from the Si substrate. The results reported herein suggest that the distance provided by the –C≡C– group is sufficient to substantially suppress the vibronic interaction between the $–CH_3$ group vibrations and the Si bulk.

IV.C. Effects of Sample Annealing on the Structure of the CH_3CC–Si(111) Surface. The azimuthal anisotropy of the r^+ and r^- modes for CH_3CC–Si(111) was readily observed following sample annealing to 200–320 °C (Figure 4). The appearance of an azimuthal dependence for the r^+ mode and the increase in the observed anisotropy for the r^- mode can potentially be attributed to the loss of $CH_3CC–$ groups from the surface following annealing. Previous thermal stability studies of CH_3CC–Si(111) surfaces in vacuum have indicated loss of $CH_3CC–$ groups upon annealing to temperatures ≥200 °C, with ~0.76 ML remaining after annealing for 30 min at 200 °C.[24] The decrease in SFG signal intensity of the C–H stretching modes upon annealing in vacuum (Figure 3) supports the conclusion that $CH_3CC–$ groups are removed from the surface by this thermal process. The removal of a fraction of $CH_3CC–$ units results in vacancies on the Si(111) surface, which, in an otherwise closely packed structure, could allow the remaining $CH_3CC–$ groups adjacent to the defect sites to tilt away from the surface normal. Thus, a propynyl molecule after annealing could tilt in one of the three

azimuthal directions towards its neighbors. Figure 5 depicts the proposed removal of a $CH_3CC–$ unit by annealing and the subsequent reorganization of the surface structure.

As the direction of the C_3 symmetry axis of the $CH_3CC–$ group tilts away from the surface normal, the β tensor elements for the r^+ mode will have resolvable components parallel to the surface, and thus the SFG signal will exhibit 3-fold azimuthal anisotropy, as observed (Figure 4A). The observed decrease in SFG intensity is consistent with the partial loss of the $CH_3CC–$ units from the Si(111) surface upon annealing, and with tilting of the molecular axis away from surface normal. The tilt of the C_3 symmetry axis away from the surface normal also brings the $CH_3CC–$ units closer to the Si surface, which may result in an increased coupling between the $CH_3CC–$ groups and the Si surface. The higher modulation depth of the r^- azimuthal response (Figure 4B) is also consistent with this tilting.

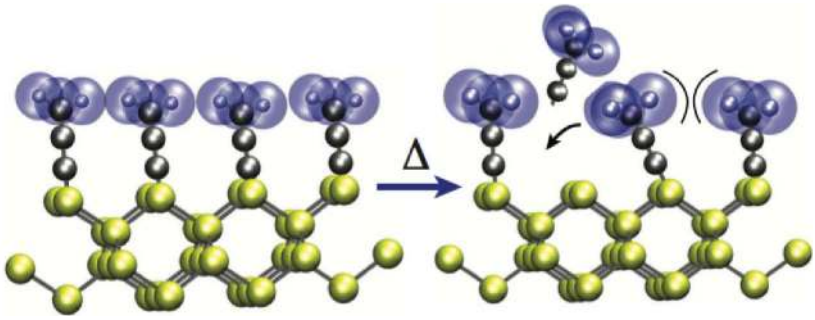

Figure 5. Annealing causes loss of $CH_3CC–$ units from the Si(111) surface creating vacancy defects. $CH_3CC–$ units adjacent to vacancies can tilt towards the Si(111) surface to relieve steric strain. As $CH_3CC–$ units tilt toward the Si(111) surface plane, the terminal $–CH_3$ group acquires in-plane component of the 2^{nd} order susceptibility, thus resulting in the 3-fold anisotropy observed in the VSDFG spectra.

V. CONCLUSIONS

The VSFG studies of the CH_3CC–Si(111) surface emphasize the importance of the molecular surface structure in determining the vibronic interactions between the semiconductor bulk and the terminating substituents. The observation of only vibrational modes with transition dipole moments oriented perpendicular to the surface plane for SSP polarization conditions provides evidence that the CH_3CC– groups are oriented perpendicular to the surface. The absence of azimuthal anisotropy observed for the r^+ mode, in addition to the observed 3-fold azimuthal anisotropy for the r^- mode, is consistent with expectations for C–H stretching vibrations for a $–CH_3$ group is decoupled from the Si substrate due to the distance introduced by the –C≡C– spacer group. This behavior stands in contrast to results observed for CH_3–Si(111) surfaces, which showed significant electronic coupling between C–H vibrational modes and the above-band-gap Raman polarizability of the Si bulk. The –C≡C– group present in CH_3CC–Si(111) surfaces thus appears to effectively isolate the terminal $–CH_3$ group from the Si surface, decoupling the C–H vibrational modes from the bulk electronic structure of the Si. Annealed CH_3CC–Si(111) surfaces exhibited a more pronounced azimuthal anisotropy for the r^+ and r^- modes compared with as-prepared samples. Loss of CH_3CC– groups from the surface upon annealing and subsequent tilting of the remaining bound CH_3CC– groups towards the neighbor vacancies and away from the surface normal results in the in-plane component of the hyperpolarizability of the tilted $–CH_3$ group which leads to the observed 3-fold asymmetry.

ASSOCIATED CONTENT

Supporting Information

The supporting information is available free of charge on the ACS publications website at DOI:

Fitting parameters used to analyze the rotational anisotropy of the resonant amplitudes for PPP spectra before and after annealing.

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Notes

The authors declare no competing financial interest.

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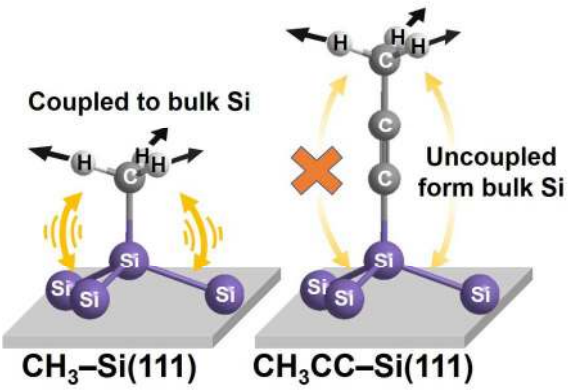
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