Surface Functionalization of Reconstructed Si(111) with Methionine

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ABSTRACT: Understanding the fundamental interactions between biological and inorganic systems enables better control of the molecular adsorption and nanofilm growth processes, allowing the manipulation of interfacial phenomena for potential applications in nanobiotechnology and biomedical sciences. Here, we provide the first study of coverage-dependent adsorption behavior of L-methionine molecules on the Si(111)7×7 surface by using X-ray photoelectron spectroscopy (XPS) and large-scale ab initio density functional theory (DFT)-D2 calculations (that include van der Waals corrections), particularly to follow the evolution of the adsorption structures and growth mechanisms as a function of coverage. Our DFT-D2 calculations show that the most stable adsorption configuration involves a dehydrogenated methionine adspecies N-bonded on Si with its S atom undertaking long-range interaction with Si at the early growth stage. XPS analysis further reveals a three-stage growth process, from a chemisorbed interfacial layer (first stage) to a transitional layer (second stage) and finally to a zwitterionic multilayer film (third stage), upon increasing methionine exposure. In the interfacial layer, a single prominent N 1s feature corresponding to the formation of a Si–N covalent-bonded structure involving a dehydrogenated amino group is observed. At a higher coverage, the presence of two N 1s peaks corresponding to NH–H–O hydrogen bonding and protonated amino (–NH3+) group supports the formation of a transitional layer and a zwitterionic layer. In contrast to cysteine, which has been observed to unidentately attach through either the dehydrogenated amino or thiol group, methionine [obtained by replacing a thiol (–SH) group in cysteine with a terminal methylthio methylene (–CH3SCH3) group] is found to exhibit remarkably different bonding interaction involving S dative bond. The discernibly longer molecular backbone in methionine also leads to unique bonding features that significantly affect the details of the nanofilm growth.

INTRODUCTION

Functionalization of biomolecules on a semiconductor or metal surface is a growing field of interest because of the many synergetic advantages of combining organic and inorganic materials.1–3 Understanding the adsorption process at the atomic level has enabled manipulation of biomolecules on an inorganic surface and control of fundamental interfacial phenomena for potential applications in nanobiotechnology and biomedical sciences.4,5 Determining the adsorption structures of amino acids on a solid surface (such as a single-crystal semiconductor or metal surface) is particularly important not only to practical applications in biochips and sensors but also to basic research on the relative efficacy of multiple functional groups in amino acids (specially sulfur-containing amino acids) toward different surface reactions. Each aliphatic amino acid consists of a carboxyl group (–COOH), an amino group (–NH2), a hydrogen atom (–H), and a side-chain group (–R) attached to the α-carbon. Because amino acids contain a variety of functional groups, various adsorption structures can be obtained as a result of intra- and/or intermolecular competition among interactions between the functional groups and the solid surface. Studies of the adsorption structures and chemical reactions of functional groups in amino acids adsorbed on solid surfaces are therefore fundamentally important to the development of biochemical applications. Of the 20 proteinogenic amino acids of the standard genetic code, methionine (COOHC6H5HNH2CH2CH2SCH3) is one of two sulfur-containing aliphatic amino acids. Methionine contains a terminal methylthio methylene group (–CH3SCH3), while the other sulfur-containing amino acid, cysteine (COOHC6H5HNH2CH2SH), contains a thiol group (–SH). Methionine is a neutral amino acid, while cysteine is basic, and both methionine and cysteine are gluconeogenic. Methionine is fundamentally interesting because it is one of the nine essential amino acids and the only sulfur-containing one that serves as a precursor for all other sulfur-containing amino acids and their derivatives. It is part of the coenzyme S-adenosyl methionine, which impregnates and adjusts the enzymatic activity and DNA duplication process.6

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Of all the semiconductors, silicon is the most prominent material in microelectronics and nanoelectronics applications, as it continues to serve as the primary platform/substrate for device fabrication in the past few decades. In the past 20 years, silicon surfaces have attracted even more attention with advances in chemical functionalization making oxide-free silicon surfaces a reality. As a result, fundamentally new electronic properties and chemical reactivity have become available, and the focus of chemical research now turns more toward targeting specific chemical bonds and inducing selectable functionalities on silicon. The silicon surfaces that have attracted the most attention are Si(100)×2×1 and Si(111)×7×7. The Si(111)×7×7 surface is well known as a highly reactive surface for chemisorption of organic molecules because of the 18 directional dangling bonds [at six center and six corner electrophilic adatom (AA) sites, and six nucleophilic restatom (RA) sites] plus one dangling bond shared among the four corner-hole sites per unit cell. The surface has been investigated in adsorption of organic molecules on Si(111)×7×7 and Si(100)×2×1 surfaces, particularly focusing on the surface modification and functionalization, by using ultra-high-vacuum surface science techniques and wet chemistry methods. These experiments are complemented by large-scale ab initio computational studies at the same time. Recently, we have reported the adsorption and nanofilm growth of l-cysteine on the Si(111)×7×7 surface and followed its thermal evolution.1

Here, we study the room-temperature nanofilm growth mechanisms of methionine on Si(111)×7×7 and determine their adsorption structures by combining our data from X-ray photoelectron spectroscopy (XPS) with results from large-scale calculations based on the density functional theory (DFT). By comparing the adsorption structures between l-cysteine and l-methionine on the Si(111)×7×7 surface, we determine the important roles of the thiol group (—SH) vs the methylthio methylene group (—CH₂SCH₃) in the adsorption process of these amino acids. Of the few available studies on methionine, all of the focus has been on its self-assembly on single-crystal noble-metal surfaces [e.g., Au(111), Cu(111), and Ag(111)]15, while only one investigation on its adsorption on a semiconductor surface, Ge(100), has been reported.17 Recently, we have examined the self-organized adsorption structures of methionine on the Si(111)×7×7 surface using scanning tunneling microscopy (STM) and compared to supported clusters obtained by DFT calculations.15 Given that the overall length of the methionine molecules (∼7.4 Å) is closely matched to the adatom-to-adatom separation on the 7×7 surface (∼7.7 Å), methionine could potentially grow epitaxially on the 7×7 surface. Understanding the initial growth stage of methionine is therefore extremely important to realizing the formation of self-organized cluster structures and ultimately “aligned” or ordered nanofilms on a semiconductor surface.

## METHODS

The experiments were performed in a custom-built five-chamber ultra-high-vacuum system (Omicron Nanotechnology, Inc.) with a base pressure lower than 5×10⁻¹¹ mbar. The analysis chamber was equipped with a variable-temperature scanning probe microscope for atomic-resolution scanning tunneling microscopy (STM) imaging, and a high-performance photoelectron spectrometer consisting of a monochromatized Al Kα source (1486.7 eV photon energy), an SPHERA hemispherical electron analyzer (operated with a pass energy of 20 eV), and a 7-Channeltron detector assembly for X-ray photoelectron spectroscopy (XPS) analysis.9,15–17 A low-temperature organic effusion cell (Dr. Eberl MBE-Komponenten GmbH) was used to deposit l-methionine in an organic molecular beam epitaxy chamber (with a base pressure of 1×10⁻¹⁰ mbar). Single-side polished n-type Si(111) chips (11×2 mm², 0.3 mm thick, with a resistivity of 5 Ω cm, from Virginia Semiconductor Inc.) were used as the substrates. A contaminant-free, well-reconstructed Si(111)×7×7 substrate was prepared by flash annealing at ~1200 °C for 10 s after direct-current resistive heating at 400 °C overnight, and its surface cleanliness was validated by both XPS and STM. After outgassing thoroughly overnight at 100 °C, l-methionine powder (99.5% purity, Fluka), with a normal melting point at 280 °C, was exposed to the 7×7 surface at room temperature with the effusion cell held at 130 °C18 and the deposition chamber pressure at 2×10⁻⁹ mbar. The amount of exposure time was used to indicate the relative amount of methionine deposition. The molecular identity and integrity of methionine during exposure were confirmed in situ by using a quadrupole mass spectrometer (Stanford Research Systems, RGA-300) and found to be in good accordance with the literature.19 After the methionine exposure on the Si surface, XPS spectra of the Si 2p, N 1s, C 1s, O 1s, and S 2s regions were recorded with an energy resolution of 0.7 eV full width at half-maximum (for the Ag 3d₅/₂ photoline at 368.3 eV). It should be noted that we have chosen to use the S 2s spectrum for quantification because the S 2p feature partially overlaps with one of the Si plasmon peaks located at ~168.0 eV.20 The spectra were fitted with Gaussian–Lorentzian line shapes (70% Gaussian and 30% Lorentzian) along with the Shirley background using the Casa-XPS software, and the binding energies were referenced to the Si 2p₃/₂ peak of bulk Si at 99.3 eV. We have also measured the core-level spectra of l-methionine powders, in which case an electron neutralizer was employed to compensate the minor charging during the measurement. The binding energy scale of the powder spectra was calibrated with respect to that of the corresponding multilayer films by aligning the main N 1s feature. For the thermal evolution experiments, as-grown thick methionine nanofilms (obtained with a 2400 s exposure) were annealed sequentially by resistive heating of the sample holder to 85 or 175 or 285 °C, each for 600 s. After the sample has been cooled back to room temperature, the chemical-state compositions of the remaining layers were then characterized by XPS analysis.

## DFT-D2 COMPUTATIONAL DETAILS

To complement our experimental results, we performed DFT-D2 calculations21 with the inclusion of van der Waals interactions to model the equilibrium geometries of plausible adsorption structures of l-methionine on one complete unit cell of Si(111)×7×7 in the early growth stage. The DFT-D2 calculations also provided more accurate simulation of hydrogen bonds involved in dimolecular configurations of l-methionine on the 7×7 surface (and in the gas phase). The first-principles total energy calculations were performed within the generalized gradient approximation,22,23 as defined by Perdew, Burke, and Ernzerhof,24 and were based on the exchange–correlation functional and projector augmented-wave potentials25,26 to describe the effect of core electrons on the valence shells together with a plane-wave basis set used to span the valence electronic states. The Vienna Ab initio Simulation Package27–30 (version 5.4) with the MedeA platform (Materials Design, version 2.18) was used. The plane-wave expansion cutoff energy was set to 400 eV, and the surface Brillouin zone was sampled at
the Γ point with a k-point spacing of 0.5 Å⁻¹. Conjugate-gradient algorithm was employed to optimize the geometry of the atomic structure, and all Si atoms were completely relaxed until the forces on all of the atoms were less than 0.01 eV/Å. The energy convergence of the self-consistent field was set to 1.0 × 10⁻⁵ eV, with a Methfessel–Paxton smearing of 0.2 eV.

An optimized structure of the dimer–adatom–stacking fault model was used to represent the Si(111)7×7 substrate. The 7×7 structure contained a faulted and an unfaulted half unit cells, each of which included three corner adatoms and three center adatoms in the topmost layer, and three restatoms in the second layer (Figure S1, Supporting Information). A periodic repeating slab consisting of 200 Si atoms, distributed in the reconstructed topmost layer and two underlying Si bilayers with the lattice constant of the Si bulk (5.42 Å), and a vacuum gap of 12 Å was used to represent the Si(111)7×7 surface, and the bottom layer of the Si slab was terminated by 49 H atoms. We have categorized a dangling bond pair between adjacent Si sites (including center adatom (CA), corner adatom (AA), and restatom (RA)) into the following two groups, with their respective separations between two Si atoms indicated in parentheses and the prime sign to identify Si site on the unfaulted half unit cell:

(A) Two Si sites within a half unit cell: CA−CA′ (7.72 Å), CA−CA (7.66 Å), CA−RA (4.55 Å), AA−RA (4.46 Å), and AA′−corner hole (8.25 Å) and

(B) Two Si sites across the dimer wall of adjacent half unit cells: CA−CA′ (6.77 Å), AA−AA′ (6.71 Å), and CA−CA′ (10.25 Å).

These separations represent the available “pitch” spacings on the 7×7 surface registry for constructing covalent bonding with appropriate functional groups of the biomolecules.

An adsorbate methionine molecule was placed on the topmost layer of the Si slab to simulate covalent binding to a Si adatom in the interface layer. To find the most stable equilibrium configuration, we first calculated a large variety of plausible adsorption configurations of methionine in an unidentate geometry (bonding through the amino or carboxyl group) on specific sites on the Si(111)7×7 surface (AA and CA sites on both the faulted and unfaulted half unit cells, and across the dimer wall). A selection of the most stable geometries was then made on the basis of their adsorption energies after geometry optimization. The positions of all adsorbed molecules and Si atoms were relaxed during the DFT-D2 calculations. The adsorption energy \( E_{\text{ad}} \) for \( n \) molecules (\( n = 1 \) or 2) is defined as

\[
E_{\text{ad}} = (E_{\text{M+Si}_200H_{49}} - E_{\text{Si}_200H_{49}} - nE_{\text{M}}) - E_{\text{M}}
\]

and \( E_{\text{M}} \) are the total energies of \( n \) methionine molecule(s) adsorbed on the Si200H49 slab, the Si200H49 slab, and the isolated methionine molecule, respectively. The H-bond energy \( E_{\text{H-bond}} \) for a dimolecule in the gas phase is defined as

\[
E_{\text{H-bond}} = (E_{\text{M+M}} - 2E_{\text{M}})/m
\]

where \( E_{\text{M-M}} \) and \( E_{\text{M}} \) are the total energies of dimethionine and isolated methionine, respectively, and \( m \) is the number of H bonds.

### RESULTS AND DISCUSSION

Figure 1 shows the O 1s, N 1s, C 1s, and S 2s spectra of methionine as a function of exposure time at room temperature and upon annealing the thickest methionine film to an elevated temperature. The corresponding peak positions and assignments obtained for the fitted features are summarized in Table S1 (Supporting Information), while the changes in their relative intensities are given in Figure 2. Instead of one dominant feature for the lowest exposure (30 s), a second N 1s peak is found to emerge at a higher binding energy for the 90 s exposure (Figure 1b). This is in good accord with the presence of the O−H···N hydrogen bond at 401.0 eV (where we use “…” to denote a H-bond), which is found to be quite common in the chemisorption of \( \alpha \)-amino acids. As indicated by the N−Si N 1s feature located at a lower binding energy (398.7 eV), methionine is found to undergo N−H dissociative adsorption on Si(111)7×7.
surface at room temperature via N–H bond cleavage. The absence of any feature related to the neutral amino group (−NH₂) at ∼400.0 eV³² also supports the N–H dissociative chemisorption. Although methionine and cysteine are both sulfur-containing amino acids, bidentate chemisorption of cysteine via additional cleavage of the thiol group at very low exposure⁹ is not observed for methionine. The corresponding S 2s feature for various methionine exposures observed at the same binding energy position is consistent with an intact methylthio methylene (−CH₂−S−CH₃) group (Figure 1d and Table S1). With two strong C−S bonds in the methylthio methylene group, the sulfur atom in methionine could still undergo long-range interaction through its lone-pair electrons with a Si adatom or restatom, which could perturb the final equilibrium configuration. The C 1s spectrum (Figure 1c) is best fitted with four components (from low to high binding energy): −CH₂−, −CH₁−S−CH₃, −CH−NH−, and −COOH, with atomic ratios of 1:2:1:1, in excellent accord with the stoichiometric composition and with the chemical state of the neutral dehydrogenated methionine adspecies. Finally, the O 1s spectrum for exposure below 90 s is consistent with the carbonyl

Figure 2. Peak areas of various O 1s and N 1s features (a) for different methionine exposure times and (b) for a multilayer methionine film (obtained with a 2400 s exposure) upon annealing to increasing temperature from room temperature (open triangle and open square).

Figure 3. (a1−a3) Top and side views of the three most stable equilibrium adsorption geometries of an unidentate methionine molecule bonded through the N atom in accordance with our XPS results, with various orientations of the methylthio methylene group over the dimer wall on the model Si(111)7×7 surface, as represented by a Si₂₀₀H₴₉ cluster, obtained by large-scale DFT-D2 calculations. (b1−b5) Top and side views of the most stable equilibrium adsorption geometries of an unidentate methionine molecule bonded through the N atom within a half unit cell with various methylthio methylene orientations at different Si CA and AA sites. Equilibrium geometries of (c1) free methionine molecule and the most stable adsorption configurations of methionine (c2) across the dimer wall and (c3) within a half unit cell of the 7×7 surface. For clarity, the entire 7×7 unit cell is shown, along with the Si adatoms and restatoms highlighted by yellow and green circles, respectively. The adsorption energies of the respective geometries are given in square parentheses, while the S−to−Si separations are indicated in parentheses. The straight (∧) and curly horizontal bars (∼) are used to indicate covalent bonding between a N and a Si surface atom and long-range interaction between a S and a Si surface atom, respectively. The structures supported by STM results (for the early growth stage) are marked by asterisks.
component (−C=O) at 532.2 eV and hydroxyl oxygen (−OH) at 533.1 eV.

The XPS spectra of the methionine multilayers obtained for the 1080 s exposure on Si(111)7×7 (Figure 1) are found to be similar to those for methionine powder in the solid phase (Figure S2, Supporting Information). The single O 1s and N 1s features represent, respectively, the carboxylate (−COO\(^{−}\)) and protonated amino groups (−NH\(_3^{+}\)) in the zwitterionic state for methionine (NH\(_3\)CH\(_2\)CH\(_2\)SCH\(_2\)COO\(^{−}\)). Similar zwitterionic features have also been observed for other benchmark proteinogenic biomolecules (including glycine and cysteine).\(^{9,33}\) The −NH\(_3^{+}\) N 1s feature for the zwitterionic layer obtained for the 1080 s exposure also nearly doubles in intensity with respect to that for the transitional layer for the 540 s exposure (Figure 2a). Upon further doubling the methionine exposure from 1080 to 2160 s, the intensity of the −NH\(_3^{+}\) N 1s feature increases only by ∼10% (Figure 2a), which indicates that the zwitterionic layer obtained for 1080 s has reached a sufficiently large film thickness above the electron mean free path of the photoelectrons.

We also study the thermal stability of the methionine nanofilm (obtained with the 2400 s exposure) on the 7×7 surface by annealing the film for 600 s to successively elevated temperatures (85, 175, and 285 °C) and perform XPS analysis after the sample has been cooled back to room temperature. Evidently, annealing the film at 85 °C completely removes the zwitterionic methionine multilayer features, as indicated by the reemergence of two N 1s features related to the interfacial layer and to the H-bond formation and by the shift in the O 1s feature back to the position for the carboxylic acid group (Figure 1). The overall spectral intensities of O 1s and N 1s peaks (Figure 2b) decrease with increasing annealing temperature to 175 °C, indicating reduction in the amount of physisorbed methionine in the film. For methionine, the S 2s position of the methylthio methylene group is unchanged for the interfacial, transitional, and zwitterionic layers, but it shifts to a lower binding energy upon annealing at 285 °C, indicating partial dissociation of the two methyl groups, resulting in the adsorption of the remaining fragment to the substrate to form Si–S. By analogy to the thermal evolution of thiophene on Si(100)\(^{34}\) and Pt(111),\(^{35}\) we could attribute the S 2s shift to the adsorption of atomic S to the Si surface as a result of double C–S bond cleavages.

From the observed thermal stabilities of the thick amino acid nanofilms (methionine, cysteine, and glycine)\(^{36}\) on the Si(111)7×7 surface, we conclude that the stabilities of zwitterionic multilayer and transitional layer depend on the extent and strength of the intralayer and interlayer hydrogen bonding. Moreover, the interfacial layer secured through the dehydrogenated amino group of proteinogenic biomolecules on Si dangling bond sites is stable until decomposition of amino acids begins to occur above 200 °C, which confirms the strength of the −HN−Si covalent bond between the adsorbate and Si surface.

Given the XPS result for adsorbed methionine in the interfacial layer (the first adlayer), we have considered a large variety of unidentate geometries involving bonding through the dehydrogenated amino group on specific sites within a half unit cell and across the dimer wall of the 7×7 surface. The equilibrium unidentate adsorption configurations on the 7×7 model surface obtained by DFT-D2 calculations, along with their respective adsorption energies, are shown in Figure 3. The two most stable configurations are found to involve methionine overhanging the dimer wall (Figure 3a1) and within a half unit cell (Figure 3b1). For the adsorption configurations involving bonding through the dehydrogenated amino group with the rest of the adsorbate overhanging across the dimer wall, we find that the geometry with the S atom closest to the CA′ site across the dimer wall (Figure 3a1, with a separation of 2.55 Å between a Si adatom and S) to be 0.189 and 0.335 eV, respectively, more stable than that with the molecular plane near parallel (Figure 3a2, with a CA′-to-S separation of 4.26 Å) and near perpendicular to the Si adatom surface plane (Figure 3a3, with a CA′-to-S separation of 5.12 Å). (We define the molecular plane as the plane containing the C–S–C backbone, and we use the prime sign to denote an adatom or a restatom in the unfaulted half unit cell.) Our calculations further show the configuration with the S atom atop of a Si restatom to be the most stable configuration (Figure 3b1, with a separation of 2.33 Å between a Si restatom and S), among all other unidentate configurations involving methionine on the CA site within a half unit cell (Figure 3b1−b4). The stabilization energy of this configuration (Figure 3b1) is also 0.224 eV more negative (i.e., more stable) than the unidentate configuration across the dimer wall (Figure 3a1). As expected, the results of the unidentate methionine adsorbate on the CA site vs those on the AA site show that the adsorption energy on the CA site (Figure 3b1) is generally slightly more negative than that on the AA site (Figure 3b5). While the S atom in methionine is not involved in direct covalent bonding with the 7×7 surface, the separation between the S atom and Si adatom/restatom (as also indicated in Figure 3) controls the strength of the latter weak long-range interaction, which ultimately governs the stability of the final adsorption geometry. Furthermore, the plausible unidentate adsorption configurations have been confirmed by our recent STM study for the initial growth stage\(^{15}\) and these configurations (Figure 3a1−3a3,3b1) are identified by the asterisks in Figure 3. We compare the equilibrium geometry of a free methionine (Figure 3c1) with the most stable geometry of adsorbed methionine across the dimer wall (Figure 3c2,3a1) and within the half unit cell of the Si(111)7×7 surface (Figure 3c3,3b1), with their respective bond lengths, bond angles, and dihedral angles summarized in Table S2 (Supporting Information). Evidently, there is a minimal change in the geometry from the “free” state to the “adsorbed” state for bond lengths (less than 1.2% for 3c2 and 3.4% for 3c3) and bond angles (less than 3.4% for 3c2 and 2.7% for 3c3). This is consistent with methionine requiring only minimal energy to adjust part of the molecular structure as the molecule becomes more stable upon adsorption by forming chemical bond with the surface. The most notable change between the free methionine and adsorbed methionine structures overhanging the dimer wall involves the S atom, particularly the dihedral angle C3−C4−S−C5 (Figure 3c2), while that between the free methionine and adsorbed methionine structures within the half unit cell involves the carboxylic acid group, particularly the dihedral angle H1−O1−C1−O2 (Figure 3c3). Evidently, the molecule expends a minimal amount of energy by rotating the respective part of its structure along the molecular long axis to achieve the more stable adsorption geometry with the Si surface atom, depending on its adsorption across the dimer wall or within the half unit cell.

Ab initio calculations alone, even the large-scale ones employed here, could provide only plausible adsorption configurations based on the total energies. STM studies have therefore been used to provide complementary information about the site-specific adsorption process. To understand the STM results, we consider the importance of site-specific electric...
Figure 4. Top and side views of equilibrium dimolecular configurations of methionine molecules for the most stable (a1−a2) flat and (b1−b12) lateral and near-vertical H-bonding on the Si200H49 model 7×7 surface, obtained by large-scale DFT-D2 calculations. The lengths of the respective H-bonds are indicated, along with the corresponding adsorption energies shown in square parentheses. Si adatoms and restatoms are highlighted, respectively, by larger yellow and green circles for clarity. Each panel heading describes the orientation of the >C−COOH backbone in the admolecules with respect to the Si surface (flat, tilt, or twist) at specific Si adatom sites, with the double bar (∥) and semicolon (;) indicating the second admolecule H-bonded, respectively, across the dimer wall and within the same half unit cell. The structures not supported by the XPS results are grayed out, while the plausible
configuration (for early growth stage) supported by STM results is marked by an asterisk (a2). (c1) Configuration of a methionine trimer via formation of triple O−H−O hydrogen bonds in a ring configuration at the center of a faulted half unit cell on an expanded model 7×7 surface.

field density as imposed by the surface registry in directing the initial adsorption of the incoming molecules. As the CA site (with a formal charge of ca. +1) is more electrophilic than the AA site (with a formal charge of ca. +7/12), while the RA site (with a formal charge of ca. −1) is nucleophilic, the incident molecule would more likely be guided by the electrostatic field provided by the CA site rather than AA site and would thereby orient itself appropriately to attach to the CA site. Furthermore, given that adsorption on the CA site in the faulted half unit cell is also more energetically stable than on the unfaulted half unit cell (with an energy difference of 0.05−0.08 eV), adsorption is expected to be more favorable on the CA site than the CA′ site, which has also been illustrated in our large-scale calculations. The present work therefore demonstrates the importance of our three-pronged approach to seeking better understanding of such a complex surface chemistry problem, i.e., first by using chemical-state-specific XPS data to characterize and to narrow down the bonding possibilities; second by using large-scale ab initio calculations to identify potential adsorption geometries; and finally by using STM data to validate some of the model geometries.

In contrast to single-crystal metal surfaces, such as Au(111) and Ag(111) surfaces, 13 on which methionine adsorbs in the zwitterionic form, methionine chemisorbs on Ge(100) and Si(111)7×7 in the neutral form to produce the interfacial layer for submonolayer coverage. This is similar to that found for other proteinogenic biomolecules such as glycine and cysteine. 9,33 For cysteine with three functional groups, 9 we determine that the thiol group is generally more reactive than other proteinogenic biomolecules such as glycine and cysteine. 9,33 For cysteine adsorbed on Au(110) surface by STM. 43 This double H-bond configuration is followed by a slightly less stable configuration containing a single O−H−O H-bond with one methionine molecule anchored to a CA site while the second methionine molecule hovered over a CA′ site across the dimer wall (Figure 4a1). Similar dimerization involving two carboxylic acid groups has also been found for cysteine adsorbed on Au(110) surface by STM. 43 This double H-bond configuration is followed by a slightly less stable configuration containing a single O−H−O H-bond with one methionine molecule anchored to a CA site while the second methionine molecule hovered over a CA′ site across the dimer wall (Figure 4a2). The low intensity of the broad O 1s spectrum for films obtained with a low exposure (<30 s, Figure 1c), for which the presence of O−H−O H-bonds is expected, does not provide a definitive fit to isolate the O−H−O H-bond feature at 532.2 eV. 44 Our STM results for the interfacial layer (obtained with a 5 s exposure) support the presence of the single O−H−O H-bond configuration shown in Figure 4a2. 15 We have also evaluated other adsorption geometries with two methionine molecules in a single half unit cell and found that anchoring the second molecule to an adjacent Si adatom site within the same half unit cell is much less likely because of the considerable length of methionine (7.40 Å). We therefore conclude that aliphatic long-chain amino acids (such as methionine) that are adsorbed through a unidentate Si−N linkage on the 7×7 surface could only make intralayer O−H−O H-bonds across the dimer wall (flat configuration) due to the size effect. In the remaining DFT-D2 calculations, we consider a large variety of interlayer H-bond with “lateral” and “near-vertical” configurations between two methionine molecules that correspond to the molecular backbone of the second molecule oriented away from the first adsorbed molecule closer to the surface plane or to the surface normal, respectively. The resulting more stable adsorption geometries are shown in Figure 4b1−4b12. We designate these dimolecular geometries using CA or AA as the anchoring sites of the first adsorbed molecule and a double bar (||) or semicolon (;) sign to indicate the position of the second adsorbed molecule in the adjacent half unit cell or in the same half unit cell, respectively. The orientation of the second adsorbed molecule relative to the first adsorbed molecule is identified in parentheses as “flat”, “twist”, or “tilt”. Our DFT-D2 results show that the most stable lateral configurations to accommodate interlayer H-bonds include double O−H−O H-bonds between the carboxylic acid groups of two methionine molecules (Figure 4b1,4b2). These attachment through either the dehydrogenated amino or thiol group, 9 a methionine molecule could make a unidentate anchor on a Si dangling bond site only through the dehydrogenated amino group. Formation of intralayer O−H−N “flat” (head-to-tail) H-bonding among methionine molecules in the interfacial layer is therefore much less likely than cysteine molecules (“head” and “tail” are usually referred to the carboxylic acid and amino terminal groups, respectively). This is because in the methionine case, there is no free amino group available for H-bonding with an adjacent carboxylic acid group, unlike the cysteine case, in which an intact amino group not involved in bonding to the surface is freely available to form a flat O−H−N H-bond.

Interestingly, our calculations show that the most stable configuration to accommodate flat H-bonds in the interfacial layer involves double O−H−O H-bonds between two vicinal carboxylic acid groups of two methionine molecules (head-to-head) at the CA−AA′ sites across the dimer wall (Figure 4a1). This feature at 532.2 eV. 44 Our STM results for the interfacial layer (obtained with a 5 s exposure) support the presence of the single O−H−O H-bond configuration shown in Figure 4a2. 15 We have also evaluated other adsorption geometries with two methionine molecules in a single half unit cell and found that anchoring the second molecule to an adjacent Si adatom site within the same half unit cell is much less likely because of the considerable length of methionine (7.40 Å). We therefore conclude that aliphatic long-chain amino acids (such as methionine) that are adsorbed through a unidentate Si−N linkage on the 7×7 surface could only make intralayer O−H−O H-bonds across the dimer wall (flat configuration) due to the size effect. In the remaining DFT-D2 calculations, we consider a large variety of interlayer H-bond with “lateral” and “near-vertical” configurations between two methionine molecules that correspond to the molecular backbone of the second molecule oriented away from the first adsorbed molecule closer to the surface plane or to the surface normal, respectively. The resulting more stable adsorption geometries are shown in Figure 4b1−4b12. We designate these dimolecular geometries using CA or AA as the anchoring sites of the first adsorbed molecule and a double bar (||) or semicolon (;) sign to indicate the position of the second adsorbed molecule in the adjacent half unit cell or in the same half unit cell, respectively. The orientation of the second adsorbed molecule relative to the first adsorbed molecule is identified in parentheses as “flat”, “twist”, or “tilt”. Our DFT-D2 results show that the most stable lateral configurations to accommodate interlayer H-bonds include double O−H−O H-bonds between the carboxylic acid groups of two methionine molecules (Figure 4b1,4b2). These attachments through either the dehydrogenated amino or thiol group, 9 a methionine molecule could make a unidentate anchor on a Si dangling bond site only through the dehydrogenated amino group. Formation of intralayer O−H−N “flat” (head-to-tail) H-bonding among methionine molecules in the interfacial layer is therefore much less likely than cysteine molecules (“head” and “tail” are usually referred to the carboxylic acid and amino terminal groups, respectively). This is because in the methionine case, there is no free amino group available for H-bonding with an adjacent carboxylic acid group, unlike the cysteine case, in which an intact amino group not involved in bonding to the surface is freely available to form a flat O−H−N H-bond.

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configurations can, however, be ruled out because free carboxylic acid is observed by our XPS results, again validating the importance of our three-pronged approach to examining complex surface and interface systems. These are followed by lateral and near-vertical configurations involving interlayer O–H···N H-bonds. The lateral configurations of the interfacial layer and an amino group in the transitional layer, which are similar to those found for the smaller amino acids (e.g., glycine) (Figure 4b3,4b4,4b12). The adsorption energies of the lateral configurations are generally more negative than those of the near-vertical configurations due to the long-range interactions with the surface to form the transitional layer in the former, while the adsorption energy of the flat configuration is the most negative one. On the other hand, an amino acid with a thiol group, such as cysteine, could produce O–H···N H-bonds through both flat and lateral/near-vertical configurations because of the free amino groups in the interfacial layer within the half unit cell or/and across the dimer wall (Figure S3, Supporting Information).

To go beyond dimer calculation, we expand the size of the model 7×7 surface by employing a supercell with a total of four unit cells (i.e., a Si160H396 cluster) and then strategically position three methionine adspecies and their corresponding dissociated H atoms at the respective CA’ and RA’ sites. These ultra-large-scale DFT-D2 calculations reveal that trimer formation of methionine adspecies could occur within the unfaulted half unit cell. A methionine trimer feature (Figure 4c1) can be regarded as a combination of three of the most stable adsorbed methionine molecules overlapping the dimer wall, each located at the center adatom of a half unit cell, by creating a trimolecular ring with threefold symmetry using three O–H···O H-bonds. The present calculation suggests the viability of using large-scale and indeed ultra-large-scale ab initio calculations to explore the formation of plausible adsorption configurations of triply or multiply H-bonded adspecies.

**CONCLUSIONS**

In the present work, we focus on the recent progress in the development of hybrid interfaces between silicon and organic materials, particularly the notable surface chemical effects introduced by a larger S-containing terminal group, methylthio methylene, relative to the more common thiol group. Given that the overall length of the methionine molecules (∼7.4 Å) is closely matched to the adatom-to-adatom separation on the 7×7 surface (∼7.7 Å), this raises the possibility of potential epitaxial growth of methionine on the 7×7 surface. The room-temperature bonding configurations and growth mechanism of methionine on the Si(111)7×7 surface have been investigated by combining XPS chemical-state specific data with large-scale DFT-D2 calculations. The “three-stage” growth process of methionine adsorbed on the silicon surface, from the interfacial layer to the transitional layer and to the zwitterionic multilayer film, has been observed through the spectral analysis. In particular, the interfacial layer is formed by anchoring methionine molecules to specific dangling bond sites on the 7×7 reconstruction surface via short strong-range Si–N covalent bonds in unidentate arrangement. This is then followed by the formation of the transitional layer and finally of the zwitterionic film, both of which are driven by intralayer and interlayer hydrogen bonding. As supported also by large-scale DFT-D2 calculations, the most stable adsorption configuration in the interfacial layer can be described as a dehydrogenated methionine adspecies N-bonded to Si with its S atom undergoing long-range interaction to the substrate. Our calculations also reveal that the formation of the transitional layer is driven by interlayer N–H···O hydrogen bonding between a free carboxylic acid group and an amino group. Despite the closely matched molecular length of methionine (7.4 Å) to the adatom-to-adatom separation (7.7 Å) on the 7×7 surface, the rather unreactive methylthio methylene terminal group (relative to the thiol group as in cysteine) serves as a natural “spacer” among methionine and indeed other plausible adspecies, thus disrupting any epitaxy-like growth on the 7×7 registry. The absence of direct S bonding to the substrate also suggests that the adsorption of methionine is mainly through the N–Si bond formation and that interlayer, and not intralayer, hydrogen bonding is favored, thus promoting the formation of the transition layer. Large-scale computational studies of the adsorption configurations of biomolecules therefore provide crucial information for collaborating with results from XPS (and STM) studies. Understanding of the film growth mechanism and the driving force for the formation of the adsorbed biomolecular layers on a semiconductor surface is essential to exploring potential applications in nanobiotechnology and biomedical sciences.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.9b07226.

XPS peak-fitting data; bond lengths; bond angles; dihedral angles of equilibrium structures (DFT-D2 calculations); and equilibrium structures obtained by large-scale DFT-D2 calculations (PDF)

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**Notes**

The authors declare no competing financial interest.

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