

# **Biofunctionalization of Si(111)7×7 by Renewable” L-Cysteine Transitional Layer**

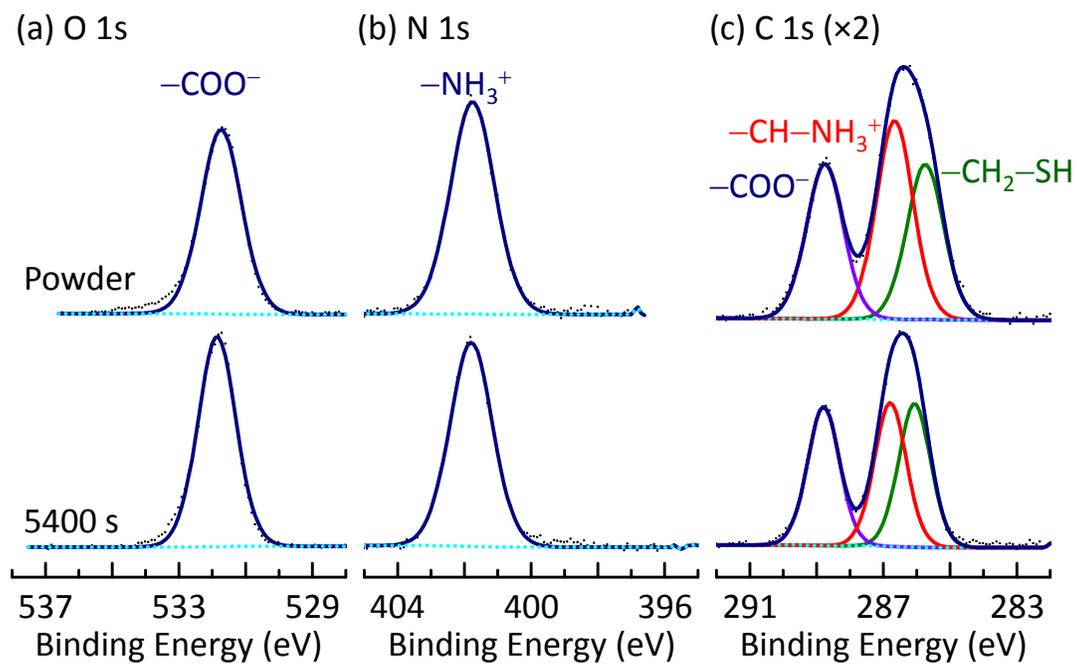
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## Supporting Information



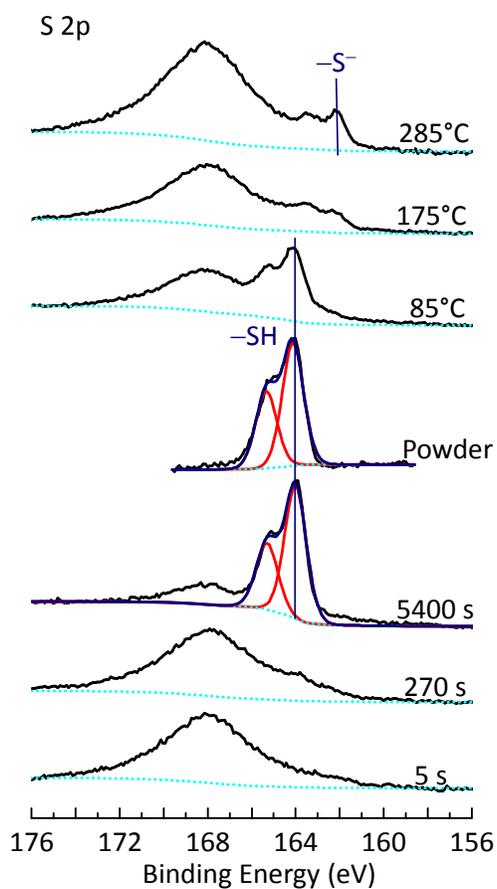
**Figure S1.** XPS spectra of (a) O 1s, (b) N 1s, and (c) C 1s regions for a multilayer film (with 5400 s exposure) on Si(111)7×7 and for cysteine powder. XPS data points are fitted with individual components (solid line) and a Shirley background (dotted line).

**Table S1.** Binding energies (in eV) of fitted peak maxima for various XPS core-level features and their assignments for different exposures of cysteine on Si(111)7×7 and for powder cysteine.

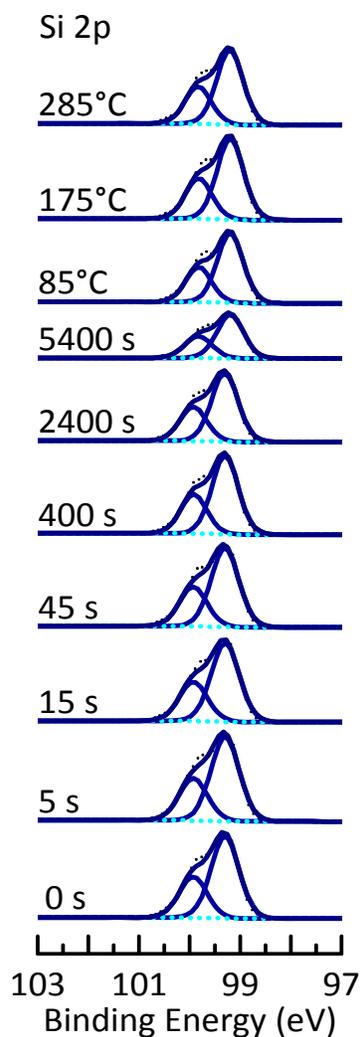
Core level	Interfacial-layer			Transitional-layer		Multi-layer	Powder	Assignment
	5 s	15 s	45 s	400 s	2400 s	5400 s		
<b>O 1s</b>	532.5	532.5	532.5	532.4	532.2	531.8	531.8	-C-OH/-C=O -COO <sup>-</sup>
<b>N 1s</b>	398.6	398.6	398.7 401.0	398.7 401.0	398.8 401.1	401.8	401.8	-NH-Si N··H-O -NH <sub>3</sub> <sup>+</sup>
<b>C 1s</b>	284.7	284.7	284.7	284.5	284.5	286.0	285.9	-CH <sub>2</sub> -S-Si -CH <sub>2</sub> -SH
	286.3	286.3	285.6 286.6	285.6 286.6	285.6 286.6			286.8
	289.2	289.2	289.2	289.2	289.2	288.8	288.8	
<b>S 2s</b>	227.4	227.4	227.4 228.4	277.4 228.4	228.4	228.4		-S-Si -SH
<b>S 2p</b>						164.1	164.1	-SH

**Table S2.** Binding energies (in eV) of fitted peak maxima for various XPS core-level features and their assignments for a multilayer film of cysteine on Si(111)7×7 after storage at room temperature under ultrahigh vacuum condition and upon annealing to 85, 175, and 285 °C for 10 min.

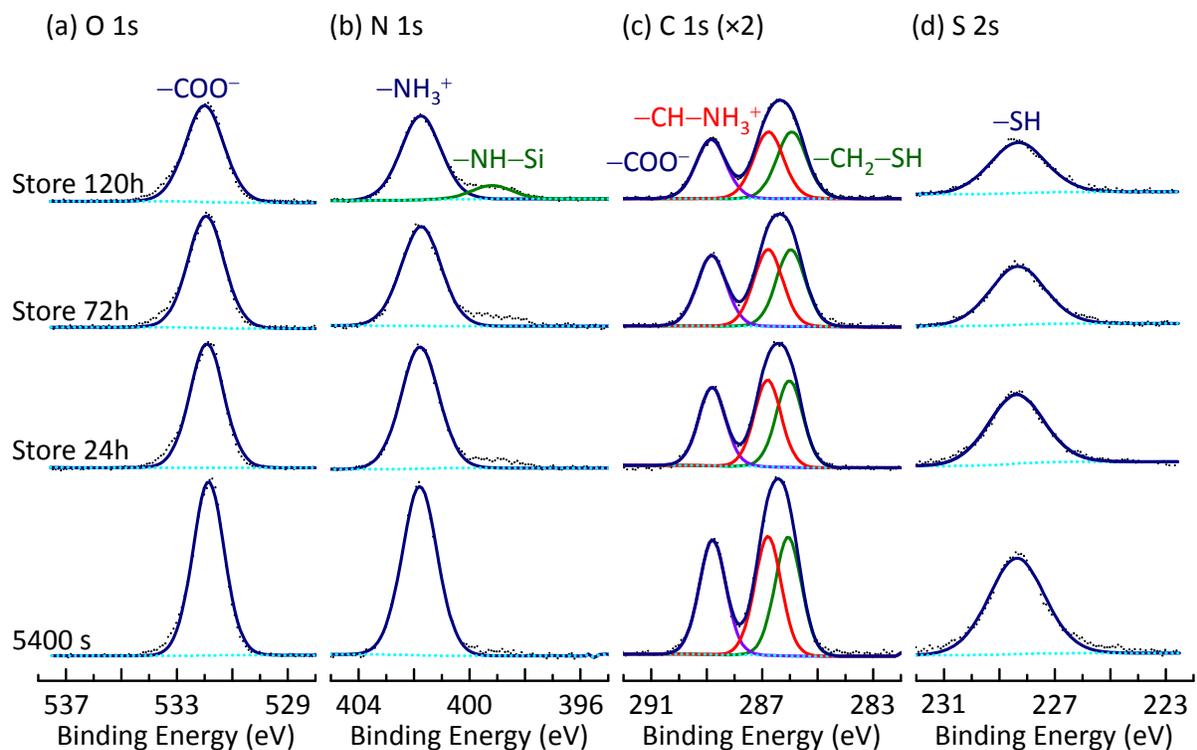
Core level	Multi-layer	Storage Time at 25 °C			Annealing Temperature for 10 min			Assignment
		5400 s	24 h	72 h	120 h	85°C	175°C	
O 1s	531.8	531.9	531.9	531.9	532.5	532.5	532.4	-C-OH/-C=O -COO <sup>-</sup>
					531.8			
N 1s	401.8	399.1 401.8	399.1 401.8	399.1 401.8	399.1	398.8 401.1	398.8	-NH-Si N...H-O -NH <sub>3</sub> <sup>+</sup> -NH <sub>2</sub>
					401.1			
					401.8	400.0	400.0	
C 1s	286.0 286.8 288.8	286.0 286.8 288.8	286.0 286.8 288.8	286.0 286.8 288.8	285.9	285.2	284.6	-CH <sub>2</sub> -S-Si -CH <sub>2</sub> -SH -CH-NH-Si -CH-NH <sub>3</sub> <sup>+</sup> -COOH -COO <sup>-</sup>
					286.8	286.2	286.2	
					286.8	289.1	289.1	
					288.8			
S 2s	228.4	228.4	228.4	228.4	228.4	227.4	226.8	-S-Si -SH -S <sup>-</sup>
S 2p	164.1							-SH



**Figure S2.** S 2p XPS spectra of cysteine deposited on Si(111)7×7 for 5 s, 270 s and 5400 s, and of cysteine powder, and the as-grown cysteine multilayer film (obtained with 5400 s) upon annealing at 85, 175, and 285 °C for 10 min. XPS data points are fitted with individual components (solid lines) on a Shirley background (dotted line). It should be noted that the S 2p spectrum partially overlaps with one of the plasmon peaks of Si (~ 168.0 eV).<sup>1</sup> The S 2p<sub>3/2</sub> peak is located at 164.1 eV binding energy for a thick cysteine film.<sup>2</sup>



**Figure S3.** XPS spectra of the Si 2p region for cysteine deposited on Si(111)7×7 as a function of exposure time (5 s to 5400 s); and of the as-deposited 5400 s cysteine film upon annealing to 85°C, 175°C and 285°C. XPS data points are fitted with individual Si 2p<sub>3/2</sub> and Si 2p<sub>1/2</sub> components (solid lines) on a Shirley background (dotted line).



**Figure S4.** XPS spectra of the (a) O 1s, (b) N 1s, (c) C 1s, and (d) S 2s regions of a cysteine zwitterionic multilayer film (obtained with 5400 s exposure) on Si(111)7×7, and as a function of storage time in ultrahigh vacuum condition. XPS data points are fitted with individual components (solid lines) on a Shirley background (dotted line).

## Detail of DFT Calculations

In order to determine the optimized equilibrium geometries and the adsorption energies for dissociative attachment of cysteine on Si(111)7×7, we use first-principle total energy calculations. These density functional theory (DFT)<sup>3,4</sup> calculations and DFT-D2 calculations (the latter include van der Waals interactions) are performed within the generalized gradient approximation<sup>5,6</sup> as defined by Perdew, Burke, and Ernzerhof (GGA-PBE),<sup>7</sup> based on the exchange-correlation functional and projector augmented-wave (PAW) potentials.<sup>8,9</sup> The Vienna Ab initio Simulation Package<sup>10,11,12</sup> (VASP, version 5.2) with the MedeA platform (Materials Design) is used. The plane wave cutoff energy is set to 400 eV and the surface Brillouin zone is sampled at the  $\Gamma$  point with k-point spacing of 0.5/Å. Conjugate-gradient algorithm is employed to optimize the geometry of the atomic structure, and all Si atoms are completely relaxed until the forces on all the atoms are less than 0.01 eV/Å. The energy convergence of the self-consistent field is set to  $1.0 \times 10^{-5}$  eV, with Methfessel-Paxton smearing of 0.2 eV. In this study, we use an optimized structure of the dimer-atom-stacking fault (DAS)<sup>13</sup> model for the Si(111)7×7 substrate (Figure S5a-5b), which contains a faulted (F) and an unfaulted (U) half unit cells, with 12 adatoms on the topmost layer and 6 restatoms (RA) on the second layer. A periodic repeating slab consisting of 200 Si atoms, distributed in two Si bilayers and a reconstructed layer (topmost layer) with a 5.419 Å lattice constant of the Si bulk, and a vacuum gap of 12 Å is used to simulate the Si(111)7×7 surface, and the bottom layer of the slab is terminated by 49 H atoms. During the geometry optimization, first all the H atoms positions are relaxed with all the Si atoms positions fixed. Then, the Si adatoms and two Si bilayers are relaxed while the H atoms are frozen. An adsorbate molecule, cysteine, is placed on the top face of the Si slab. The equilibrium geometry of an isolated (i.e. free) cysteine molecule is shown in Figure S5c. The adsorption energy  $E_{ad}$  is defined as  $E_{ad} = [E_{Total} - E_{Si\ Slab}] - E_{cysteine}$ , where  $E_{Total}$ ,  $E_{Si\ Slab}$  and  $E_{cysteine}$  are the total energies of the adsorbed cysteine on the Si slab, the Si slab, and the isolated cysteine molecule, respectively.

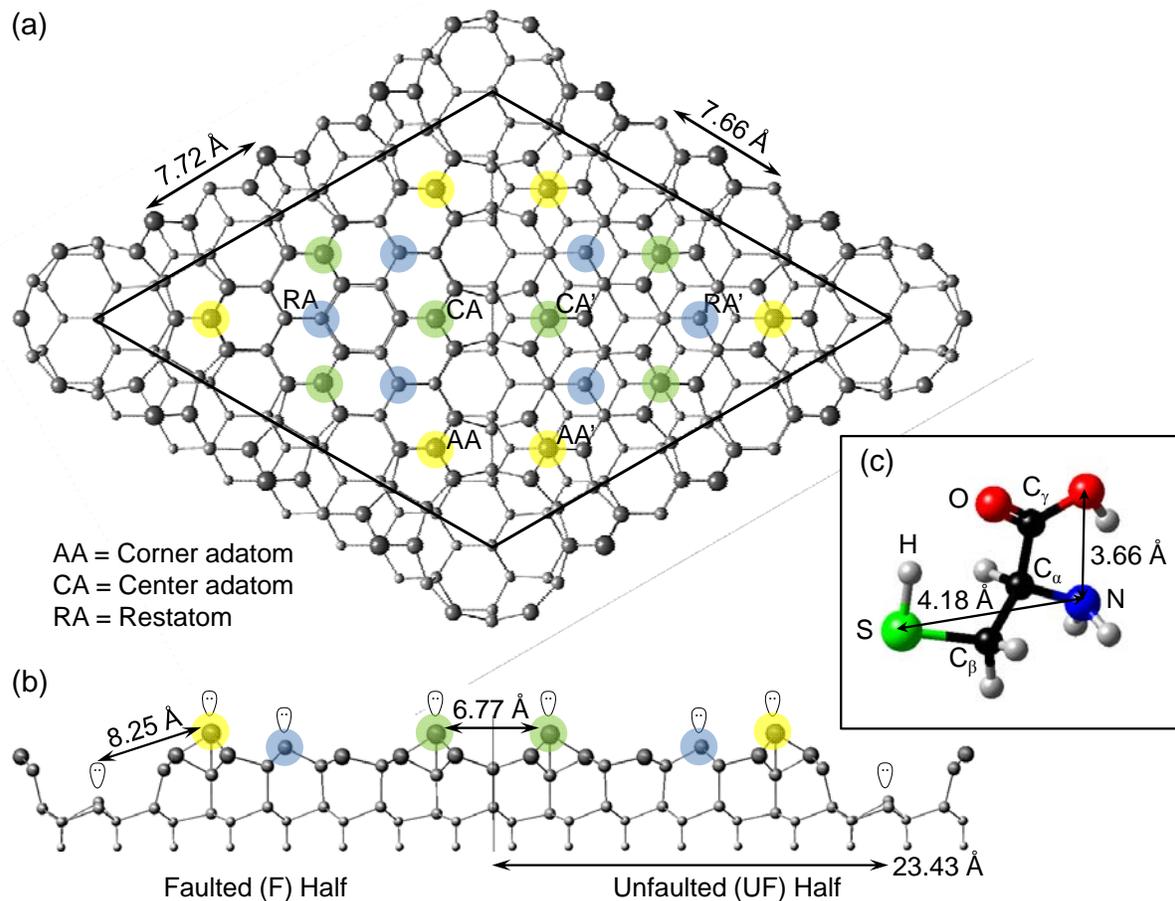
In the present calculation, a large variety of gas-phase conformations of cysteine adsorbed in unidentate and bidentate geometries (through three functional groups: carboxylic acid, amino and thiol) on specific sites on the Si(111)7×7 surface (corner and center adatom sites on both faulted and unfaulted half unit cells) are studied. The most stable equilibrium unidentate and bidentate configurations on the 7×7 model surface, as simulated by the Si<sub>200</sub>H<sub>49</sub> cluster, are

shown in Figure S6 and S7, respectively. Three kinds of upright adsorption configurations on the center adatom (CA) and corner adatom (AA) on both the faulted and unfaulted half unit cells of Si(111)7×7, via deprotonated functional groups (–SH, –NH<sub>2</sub>, –COOH), are considered. The results of adsorbed unidentate cysteine molecule on the CA or AA site of the 7×7 surface show that the adsorption energy on the CA site is lower than that on the AA site on both half unit cells. Furthermore, bonding through the deprotonated thiol group (Figure S6a) is 0.44 eV and 0.23 eV more stable than bonding through the amino (Figure S6c) and carboxylic acid (Figure S6b) groups, respectively.

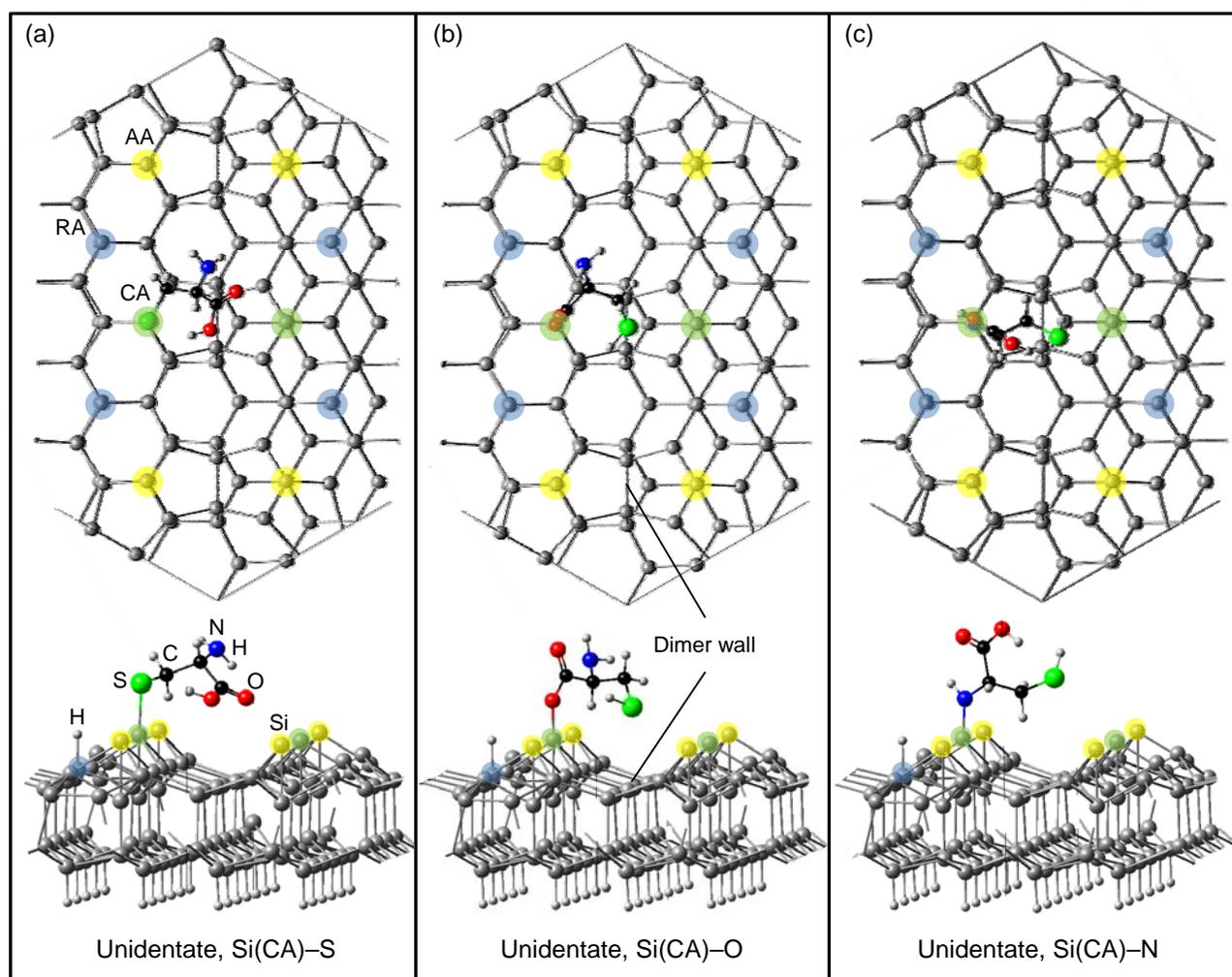
The other configuration considered here is cysteine adsorbed in a bidentate configuration on Si(111)7×7. Based on the DAS model of Si(111)7×7, two adjacent Si atoms with dangling bonds can be categorized as the following: (1) AA-CA, (2) CA-CA within a half unit cell; (3) CA-CA', (4) AA-AA', (5) AA-CA' across a dimer wall of adjacent half unit cells; (6) AA-corner hole, (7) AA-RA, and (8) CA-RA within a half unit cell. We use a prime symbol to denote substrate atom in the adjacent half unit cell. The corresponding separations between two Si atoms are 7.72, 7.66, 6.77, 6.71, 10.25, 8.25, 4.46, and 4.55 Å, respectively. Furthermore, typical bond lengths of Si–S, Si–N, and Si–O are 2.2, 1.7, and 1.7 Å, respectively. Given that the separation between the –NH<sub>2</sub> and –OH groups (3.66 Å) and that between the –OH and –SH groups (3.12 Å) in an isolated cysteine molecule are too short to bridge two neighboring Si adatom sites, the only feasible choice for such a bidentate configuration to the Si surface is the larger separation between N and S (4.18 Å) (Figure S5c), which could be obtained via N–H and S–H dissociative adsorption of cysteine. To form covalent linkages of the deprotonated –SH and –NH<sub>2</sub> groups, the separation between two adjacent Si dangling bond sites should be close to 6.9 Å, assuming a Si-to-adsorbate bond angle of 45°. This rules out cases 5 and 6 because their separations are too large and cases 7 and 8 because they are too small. The above possibilities can therefore be limited to cases 1 to 4. The results from our large-scale DFT-D2 calculations for a large variety of possible bidentate adsorption configurations show that the calculated adsorption energy of the bidentate cysteine on Si adatom-adatom pair across the dimer wall (i.e. CA-CA' and AA-AA') is at least 0.57 eV lower than that of the bidentate cysteine on CA-CA and CA-AA within a half unit cell. Moreover, the calculated adsorption energy of the bidentate cysteine on a CA-CA' pair (Figure S7b) is 0.13 eV lower than that of the adsorbed cysteine on a AA-AA' pair (Figure S7a), both across the dimer wall. Our large-scale DFT-D2 study also shows that the bidentate adstructure resulting from N–H and S–H dissociative adsorption of

cysteine (Figure S7) is considerably more stable (0.91 eV lower) than any unidentate adstructure (Figure S6).

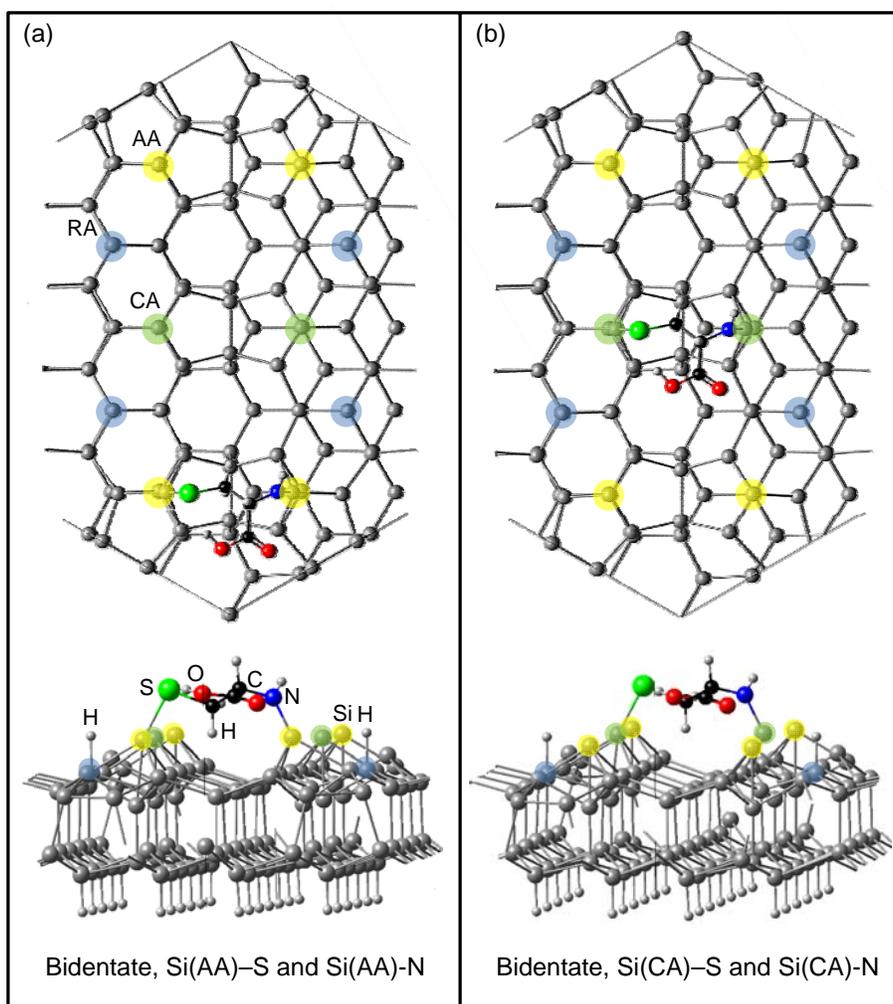
Hydrogen bonding interaction between amino acids is one of most important interactions that lead to self-assembled structures. We also investigate complexes formed by hydrogen bonding interactions between two cysteine molecules (i.e., a cysteine dimer) on Si(111)7×7 by putting two cysteine molecules in unidentate adsorption configurations at adjacent Si dangling bond sites in our DFT-D2 calculations. On the Si(111)7×7 surface, dimer formation is affected by steric hindrance on the adsorbed cysteine molecules exerted by the surface atoms. We have obtained the adsorption energies and equilibrium structures for a large number of different bonding combinations on a variety of Si dangling bond sites. Our DFT-D2 calculations suggest that the N···H–O hydrogen bond is a favorable hydrogen bond that would lead to acceptable cysteine dimer on adjacent CA-AA sites without torsion on the Si(111)7×7 surface. We overlay plausible configurations of such a cysteine dimer on the corresponding STM images of a CA-CA (Figure 5a) and a CA-AA pairs (Figure 5b). Perspective views of the corresponding equilibrium structures of these “torsion-free” dimer adsorption configurations are shown in Figure 5c and 5d.



**Figure S5.** (a) and (b) Top view and side view of the equilibrium dimer-adatom-stacking fault (DAS) model of a  $\text{Si}_{200}\text{H}_{49}$  cluster (included top adatoms layer, two Si bilayers, and terminated by H atoms) obtained by large-scale DFT-D2 calculations used as the model surface for  $\text{Si}(111)7\times 7$ . With increasing the distance from the surface, the sizes of the spheres used to represent the Si atoms were decreased. Si corner adatoms (AA), center adatoms (CA), and restatoms (RA) are highlighted by larger yellow, green, and blue circles for clarity, respectively. The dangling bonds represent on the top of adatoms, rest atoms, and corner hole. (c) Stick-and-ball models of an isolated cysteine molecule in neutral form.



**Figure S6.** Top and perspective views of the most stable equilibrium adsorption geometries of an unidentate cysteine molecule bonded through (a) S, (b) O, and (c) N atoms to the model Si(111)7×7 surface, a Si<sub>200</sub>H<sub>49</sub> cluster, obtained by large-scale DFT-D2 calculations. Si corner adatoms (AA), center adatoms (CA), and restatoms (RA) are highlighted by larger yellow, green, and blue circles, respectively. For clarity, only part of the unit cell with the relevant adatoms for bonding with cysteine is shown.



**Figure S7.** Top and perspective views of the most stable equilibrium adsorption geometries of a bidentate cysteine molecule bonded through the N and S atoms to the model Si(111)7×7 surface at an adatom-adatom pair across the dimer wall: (a) AA-AA', and (b) CA-CA'. Si corner adatoms (AA), center adatoms (CA), and restatoms (RA) are highlighted by larger yellow, green, and blue circles, respectively. For clarity, only part of the unit cell with the relevant adatoms for bonding with cysteine is shown.

## References for Supporting Information

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