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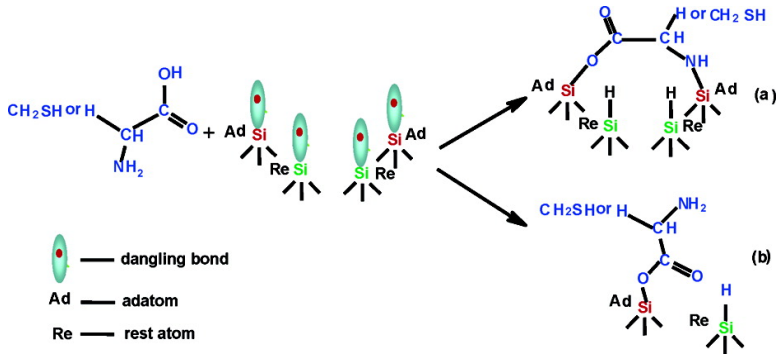

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Binding of Glycine and L-Cysteine on Si(111)-7×7

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The adsorption of glycine and L-cysteine on Si(111)-7×7 was investigated using high-resolution electron energy loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy (XPS). The observation of the characteristic vibrational modes and electronic structures of NH_3^+ and COO^- groups for physisorbed glycine (L-cysteine) demonstrates the formation of zwitterionic species in multilayers. For chemisorbed molecules, the appearance of ν(Si−H), ν(Si−O), and ν(C═O) and the absence of ν(O−H) clearly indicate that glycine and L-cysteine dissociate to produce monodentate carboxylate adducts on Si(111)-7×7. XPS results further verified the coexistence of two chemisorption states for each amino acid, corresponding to a Si−NH−CH_2−COO−Si [Si−NHCH(CH_2SH)COO−Si] species with new σ-linkages of Si−N and Si−O, and a NH_2−CH_2−COO−Si [NH_2CH(CH_2SH)COO−Si] product through the cleavage of the O−H bond, respectively. Glycine/Si(111)-7×7 and L-cysteine/Si(111)-7×7 can be viewed as model systems for further modification of Si surfaces with biological molecules.

1. Introduction

Organic modification of silicon surfaces is emerging as an important area in the development of molecular electronics, biosensors, and optical devices.[1−3] As the fundamental understanding on the reaction mechanisms of simple organic molecules on silicon surfaces was gained during the past decade,[4−6] the binding of complex compounds, especially biological molecules (proteins, peptides, etc.), is beginning to be of particular interest.

Using amino acids to gain information on the mode of protein adsorption is a common strategy, since amino acids are the building blocks of many proteins and peptides. Among them, glycine is the simplest in structure, containing an amino functionality and a carboxylic acid group attached to the same carbon. It is known that gaseous glycine molecules are present in their neutral form (NH_2CH_2COOH).[7,8] On the other hand, glycine at room temperature exists as an inner salt ($NH_3^+CH_2COO^-$) in the solid state and strong intermolecular hydrogen bonds affect its crystalline structure.[9] In previous studies, glycine was widely used as a model to investigate the interaction between biological molecules and solid surfaces. In the case of glycine adsorbed upon Cu(110), an anionic glycinate species was observed at room temperature.[10] After the sample was annealed to 400 K, the most stable binding geometry appears to involve both carboxylic and amino functional end groups.[11] Similarly, glycine binds to Pt(111) and nickel surfaces through −COOH and $-NH_2$ functionalities.[12,13] On a NiAl(110) alloy surface, glycine was found to adsorb molecularly in the zwitterionic state at 120 K and undergoes a dissociative reaction to yield an anionic species at room temperature (310 K).[14] In addition, the selective adsorption of glycine and deuterated glycine on clean Si(100)-2×1 and Na/Si(100)-2×1 was reported. Glycine chemisorbs on a clean Si(100)-2×1 through the carboxylate group in the monodentate coordination, while it produces a bidentate species on Na/Si(100)-2×1.[15] Density functional theory (DFT) simulations also indicated that the O−H dissociation is favored both thermodynamically and kinetically.[16]

Cysteine is another interesting amino acid, which bears three main functionalities—amino, carboxylic acid, and thiol groups. The side thiol group has a well-known affinity for some metals and also plays an important role in the stabilization of the secondary structure of the proteins.[17,18] It is worth noting that cysteine is often on the outer side of proteins, being a potential link to anchor these proteins to supports. The adsorption of cysteine on different metals, mainly on gold and copper, has been investigated.[17,19−26] L-Cysteine was attached to gold via the thiol group, whereas a more complex adsorption process seems

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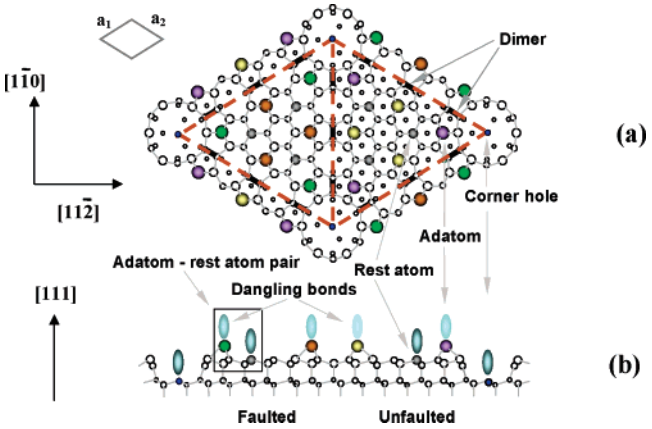

Figure 1. Top (a) and side (b) views of the detailed three-dimensional structure for one Si(111)-7×7 unit cell based on the dimer−adatom stacking (DAS) fault model.

to occur on copper, involving the coordination of both amino and carboxyl groups to the surface, in addition to chemisorption through S−H.[22] The recent study on the adsorption of S-cysteine on Cu(110) reported that the molecule interacts with the copper surface through the sulfur atom and two oxygen atoms of the carboxylate group placed equidistant to the surface under vacuum conditions.[23]

Si(111)-7×7 is one of the most important and well-understood semiconductor surfaces for investigating the reaction between organic compounds and silicon surfaces due to its unique electronic and spatial structures. Upon a 7×7 reconstruction, the number of dangling bonds on the (111) silicon surface reduces from 49 to 19 in each unit cell. On the basis of the dimer−adatom stacking (DAS) fault model (Figure 1),[27] the 19 dangling bonds are located at 12 adatoms, 6 rest atoms, and one corner hole. Furthermore, theoretical calculations[28] and experimental results[29] showed that each rest atom has a formal charge of −1 and each adatom has an electron occupancy of only 5/12, implying that rest atoms can act as electron donors whereas adatoms as acceptors in surface reactions.

In this paper, glycine/Si(111)-7×7 and L-cysteine/Si(111)-7×7 were employed to serve as model systems to explore the functionalization of Si(111)-7×7 with biological molecules. We examined the adsorption states of glycine and L-cysteine on Si(111)-7×7 both in multilayer and monolayer forms using high-resolution electron energy loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy (XPS). Our findings suggest that glycine and L-cysteine molecules adsorb predominantly in the zwitterionic state in physisorbed multilayers. The saturated chemisorption monolayer comprises of both Si−NH−CH_2−COO−Si [Si−NHCH(CH_2SH)COO−Si] and NH_2−CH_2−COO−Si [NH_2CH(CH_2SH)COO−Si] species at the glycine (L-cysteine)/Si(111)-7×7 interface.

2. Experimental Section

All the experiments were carried out in two ultrahigh vacuum (UHV) chambers, which are pumped by turbo-molecular, ion, and titanium sublimation pumps (base pressure ~2 × 10^{-10} Torr). One of them is equipped with a high-resolution electron energy loss spectrometer (HREELS, LK-2000) and a mass spectrometer (UTI-100) for gas analysis. An electron beam with the energy of 5.0 eV impinges on the surface at an incident angle of 60° with respect to the surface normal. Photoelectron studies were performed in another chamber equipped with an X-ray source and a concentric hemispherical energy analyzer (CLAM2, VG). XPS spectra were acquired using Al Kα radiation ($h\nu$ = 1486.6 eV) and 20 eV pass energy. The binding energy (BE) scale is referenced to the peak maximum of the Si(2p) line (99.3 eV calibrated to Au $4f_{7/2}$) of a clean Si(111) substrate.[30]

The samples (22 mm × 8 mm × 0.38 mm) were cut from the p-type boron-doped silicon wafers (99.999%, 1−30 Ω·cm, Goodfellow). A Ta foil (thickness ~0.025 mm, Goodfellow) was sandwiched between two experimental samples held together using Ta clips, and in turn spot-welded to Ta posts at the bottom of a Dewar-type liquid-N_2-cooled sample holder. The samples can be heated to 1250 K through the resistive heating of the Ta foil and cooled to 110 K using liquid nitrogen. To clean the samples, they were degassed at 850 K for overnight. Then, surface contaminants were removed by several cycles of Ar^+ bombardment (36 min at 500 eV and 5 $\mu A \cdot cm^{-2}$) and annealing at 1250 K. The cleanliness of the samples was verified using XPS and HREELS. The surface structure was examined using STM in a separate chamber.

The deposition source was a tantalum boat containing glycine (L-cysteine) powder (Sigma, 99% purity). The boat was first degassed in situ for about 1 h at 370 K and then heated to ~400 (glycine) or 420 K (L-cysteine) for depositing onto the silicon sample.[31] The exposures were reported in the unit of Langmuir (1 L = 10^{-6} Torr·s) without the calibration of ion gauge sensitivity and doser efficiency.

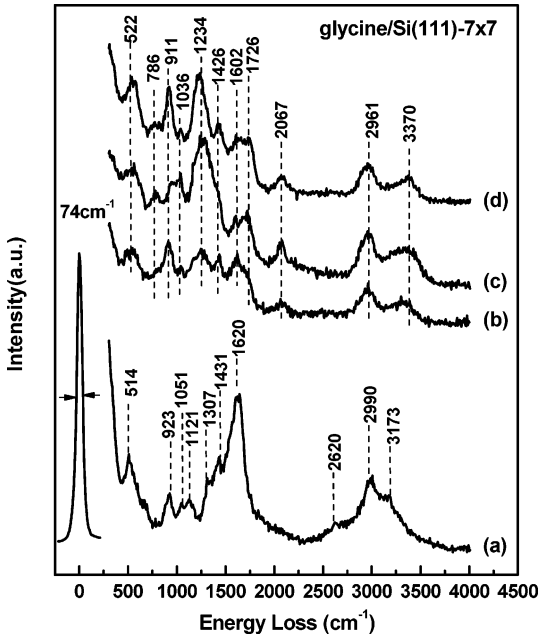

Figure 2. HREELS spectra of a Si(111)-7×7 sample exposed to 0.08 L of glycine at 110 K (a) and annealed to 250 (b) and 300 K (c). The spectrum taken after exposing the clean silicon sample to 0.10 L of glycine at room temperature is shown in a curve (d). E_p = 5.0 eV; specular mode.

3. Results

3.1. Binding of Glycine on Si(111)-7×7. The HREELS spectrum of physisorbed glycine on Si(111)-7×7 (Figure 2a) was taken after exposing the silicon sample to 0.08 L of glycine at 110 K, which shows loss peaks at 514, 923, 1051, 1121, 1307,

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Table 1. Assignments of HREELS Spectra for Physisorbed and Chemisorbed Glycine on Si(111)-7×7[a]

assignment	glycine in zwitterionic form[20]	crystalline glycine on copper[21]	glycine in acid form[42]	physisorbed glycine on Si(111)-7×7	chemisorbed glycine on Si(111)-7×7
O−H stretch			3566/3561		
N−H sym. stretch			3414/3411		3370
NH_3^+ asym. stretch		3186		3173	
CH_2 asym. stretch		2918		2990	2961
CH_2 sym. stretch					
NH_3^+ sym. stretch		2612		2620	
Si−H stretch					2067
C═O stretch			1792/1781		1726
NH_3^+ asym. deform.	1610	1626		1620	
N−H scissoring			1632		1602
CO_2^- asym. stretch	1594	1626		1620	
NH_3^+ sym. deform.	1523	1537			
CH_2 bend	1446	1446	1431/1429	1431	1426
CO_2^- sym. stretch	1415	1421			
C−O stretch			1389		1234
CH_2 wagging	1332	1340	1385	1307	
CH_2 twist	1314				
NH_3^+ rocking	1130,1112	1138		1121	
OH deform.			1101		
C−N stretch	1032	1042	1131	1051	1036
CH_2 rocking	911		882/880	923	911
C−C stretch	894		787		
N−H wagging			802/799		
CO_2^- bend	698				
CO_2^- wagging	608				
CO_2^- rocking	503			514	
Si−O stretch					786
Si−N stretch					522
CCN deformation	355				
COO torsion	226				

[a] All frequencies are given in cm^{-1}.

1431, 1620, 2620, 2990, and 3173 cm^{-1}. The detailed assignments of these vibrational frequencies are listed in Table 1. Among them, three peaks at 3173, 2620, and 1121 cm^{-1} can be assigned to the $-NH_3^+$ asymmetric, symmetric stretching, and rocking modes, respectively. $-NH_3^+$ asymmetric deformation and $-CO_2^-$ asymmetric stretching produce the intensity at 1620 cm^{-1}, which are not resolvable due to the resolution limit of the EELS spectrometer. Another characteristic vibrational signal related to the carboxylate ($-CO_2^-$) group is located at 514 cm^{-1}, attributable to the $-CO_2^-$ rocking mode. The features associated with $-NH_3^+$ and $-CO_2^-$ groups agree well with the values obtained in the IR spectrum of crystalline glycine,[32] thereby reflecting the zwitterionic configuration ($NH_3^+CH_2COO^-$) of physisorbed glycine on Si(111)-7×7. A similar vibrational spectrum of zwitterionic glycine on copper was previously reported.[33]

The vibrational features of chemisorbed glycine in Figure 2b and c were obtained by annealing the multilayer glycine-covered sample to 250 and 300 K to drive away all the physisorbed molecules, which are consistent with those of saturated chemisorption monolayer formed after exposure at room temperature (Figure 2d). Losses at 522, 786, 911, 1036, 1234, 1426, 1602, 1726, 2067, 2961, and 3370 cm^{-1} can be identified. The disappearance of vibrations corresponding to NH_3^+ and CO_2^- functionalities strongly demonstrates that the ionic structure of physisorbed glycine is not present in the chemisorption monolayer. The major spectroscopic change is the appearance of new peaks at 1726, 3370, and 1602 cm^{-1}, attributable to the C═O stretching, N−H symmetric stretching, and scissoring modes, respectively. Furthermore, the emergence of another new Si−H stretching feature at 2067 cm^{-1} indicates the dissociative nature of chemisorbed glycine on Si(111)-7×7.[34] The OH bond cleavage upon chemisorption is further supported by the absence of ν(OH) in the range of 3400−3600 cm^{-1} and the existence of ν(Si−O) at 786 cm^{-1}. An additional new feature at 522 cm^{-1} can be assigned to the Si−N stretching mode, consistent with the previous studies on the binding of N-containing organic molecules to Si surfaces through the Si−N linkage.[35,36] This result implies the concurrence of the dissociative reaction via the N−H bond. Our main vibrational features of chemisorbed molecules suggest the involvement of O−H and NH_2 groups in the interaction of glycine with Si(111)-7×7, leading to the formation of new Si−H, Si−O, and Si−N linkages.

XPS was employed to explore the electronic structure of adsorbed glycine on Si(111)-7×7. Figures 3, 4, and 5 present the C1s, O1s, and N1s XPS spectra of physisorbed and chemisorbed glycine ($NH_2C^1H_2C^2O^1O^2H$) on Si(111)-7×7, respectively. Two separate C1s intensities were observed for physisorbed molecules (Figure 3b), located at 287.1 and 289.4 eV with an intensity ratio of ∼1:1. The lower BE feature at 287.1 eV can be assigned to the alkyl carbon (C^1), while the other is attributable to the carboxyl carbon (C^2) due to its lower electron density. The highly electronegative oxygen considerably reduces the electron density on the adjacent carboxyl carbon, implying in turn a higher binding energy for this carbon. These assignments are consistent with the C1s data for condensed glycine on Pt(111).[12] The O1s spectrum of physisorbed molecules (Figure 4b) shows a symmetric peak at 532.3 eV with a typical fwhm of ∼1.6 eV under our XPS

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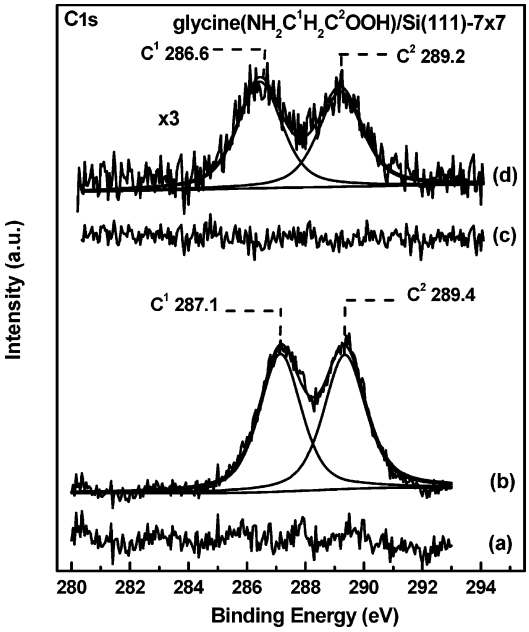

Figure 3. Decovoluted C1s XPS spectra of physisorbed and chemisorbed glycine on Si(111)-7×7. (a and c) Difference spectra between experimental results and the sum of the fitted peaks. (b and d) Experimental and fitted spectra of physisorbed glycine (0.08 L) at 110 K and chemisorbed molecules (0.10 L) at room temperature, respectively.

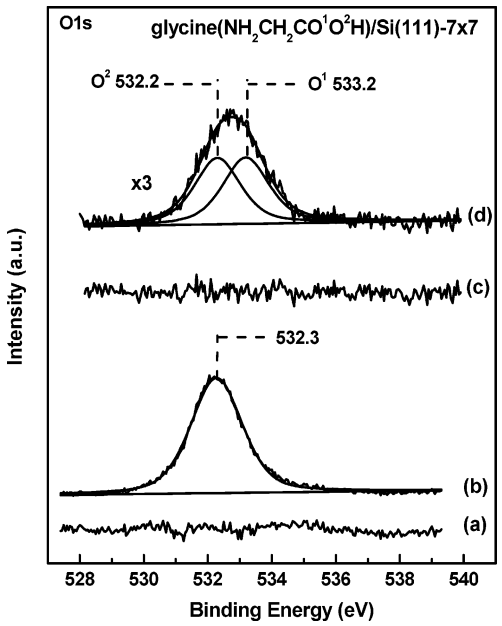

Figure 4. Decovoluted O1s XPS spectra of physisorbed and chemisorbed glycine on Si(111)-7×7. (a and c) Difference spectra between experimental results and the sum of the fitted peaks. (b and d) Experimental and fitted spectra of physisorbed glycine (0.08 L) at 110 K and chemisorbed molecules (0.10 L) at room temperature, respectively.

resolution, indicating that two O atoms in condensed glycine are chemically indistinguishable. The 532.3 eV binding energy observed here is close to that of oxygen atoms in the carboxylate ($-COO^-$) group.[12,33] In Figure 5b, the N1s feature at an unusually high binding energy (402.2 eV) for physisorbed glycine can be assigned to the N atom in NH_3^+, which is ~1.8 eV higher than the values (400.3−400.5 eV) obtained for physisorbed amines on nickel.[37] Previous studies also reported the binding energies

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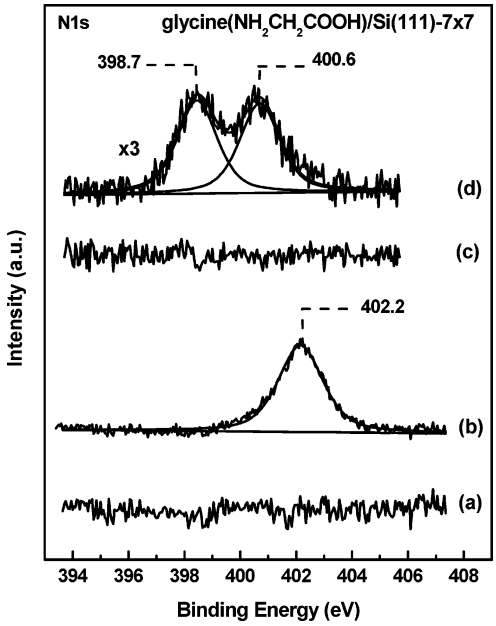

Figure 5. Decovoluted N1s XPS spectra of physisorbed and chemisorbed glycine on Si(111)-7×7. (a and c) Difference spectra between experimental results and the sum of the fitted peaks. (b and d) Experimental and fitted spectra of physisorbed glycine (0.08 L) at 110 K and chemisorbed molecules (0.10 L) at room temperature, respectively.

of 401.6 and 402.5 eV for the positively charged N atoms in $(CH_3)_4N^+Br^-$ and $(CH_3)_4N^+Cl^-$, respectively.[38,39] Thus, the C1s, O1s, and N1s photoemission features suggest a zwitterionic configuration of physisorbed glycine ($NH_3^+CH_2COO^-$) on Si-(111)-7×7, in agreement with HREELS results.

Upon exposing a Si(111)-7 × 7 sample to 0.10 L of glycine at room temperature (300 K), photoemission spectra for chemisorbed molecules were taken. In the C1s XPS spectrum of chemisorbed molecules (Figure 3d), two peaks at 286.6 and 289.2 eV are clearly resolved, slightly down-shifted from the values for physisorbed molecules. Two intensities at 532.2 and 533.2 eV were observed in the fitted O1s photoemission spectrum of chemisorbed glycine, indicative of two chemically inequivalent oxygen atoms. The feature at 532.2 eV is attributable to the oxygen atom (O^2) attached directly to the silicon atom and the other at 533.2 eV related to the retaining carbonyl O^1, in agreement with the binding energies of oxygen atoms in monodentate formate (HCO^1O^2-Si) on Si(111)-7×7.[40] Chemisorbed molecules also yield two N1s peaks at 398.7 and 400.6 eV with a separation of 1.9 eV, which implies the existence of two different chemisorption states for glycine binding on Si(111)-7×7. The N1s core level at 398.7 eV is related to the nitrogen atom directly bonded to the silicon atom, close to the values (~ 399.0 eV) of chemisorbed aniline, 1,4-phenylenediamine, and pyrrole on silicon surfaces via an N−H bond breakage.[41−43] The higher binding energy peak (400.6 eV) can be assigned to the N of neutral amino group ($-NH_2$), showing a down-shift by 1.6 eV compared to the data (402.2 eV) obtained for the positively charged nitrogen in

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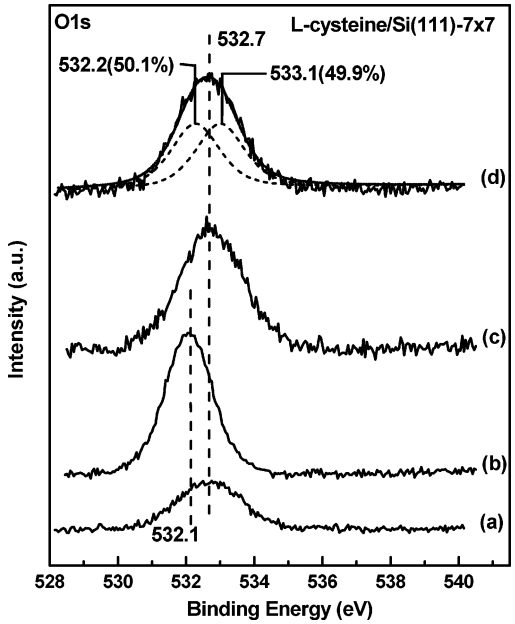

Figure 6. O1s XPS spectra of a Si(111)-7×7 sample exposed to 0.006 (a) and 0.06 L (b) of L-cysteine at 110 K and subsequently annealed to 300 K (c). The spectrum of L-cysteine (0.06 L) on Si-(111)-7×7 at room temperature is shown in a curve (d). The dashed lines represent the fitted spectra.

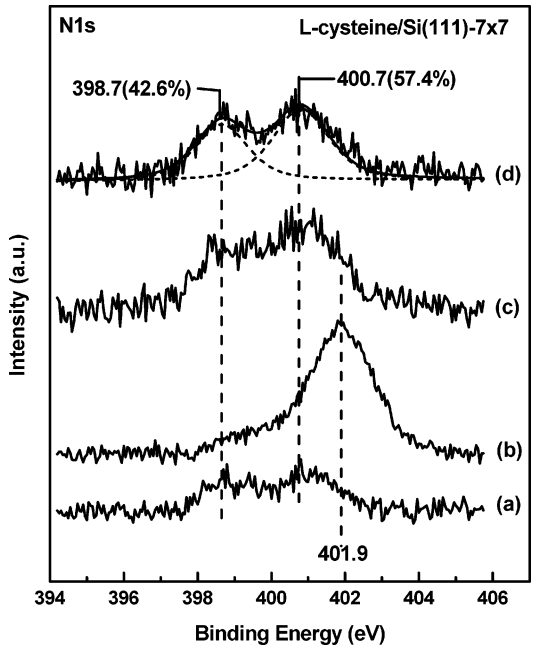

Figure 7. N1s XPS spectra of a Si(111)-7×7 sample exposed to 0.006 (a) and 0.06 L (b) of L-cysteine at 110 K and subsequently annealed to 300 K (c). The spectrum of L-cysteine (0.06 L) on Si-(111)-7×7 at room temperature is shown in a curve (d). The dashed lines represent the fitted spectra.

physisorbed molecules. This shift of 1.6 eV is quite close to the N1s binding energy difference (~1.8 eV) between $-NH_3^+$ and $-NH_2$ groups determined experimentally.[44]

3.2. Binding of L-Cysteine on Si(111)-7×7. Figures 6 and 7 show the O1s and N1s XPS spectra of physisorbed and chemisorbed L-cysteine [$NH_2C^1H(C^2H_2SH)C^3O^1O^2H$] on Si-(111)-7×7, respectively. The condensed multilayer L-cysteine was obtained after exposing the clean silicon sample to 0.06 L of L-cysteine at 110 K. The physisorbed molecules produce a symmetric O1s feature at 532.1 eV with a typical fwhm of ~1.7 eV under our XPS resolution, indicating the presence of only one type of oxygen (Figure 6b). This value is very close to those obtained for zwitterionic glycine and L-cysteine,[22,23,33,44] suggesting that the carboxylic group exists in the ionic ($-COO^-$) form. The N1s binding energy of physisorbed L-cysteine is found to be 401.9 eV, which is characteristic for the $-NH_3^+$ state of the amino group.[22,23,33,44] A binding energy of 401.4 eV was reported for the positive N atom in cysteine salt ($cystH_3^+Cl^-\cdot H_2O$).[45] The O1s and N1s photoemission features indicate that physisorbed L-cysteine on Si(111)-7×7 is in a zwitterionic structure [$NH_3^+CH(CH_2SH)COO^-$].

The photoemission spectra of chemisorbed molecules can be collected with three methods: (a) exposing Si(111)-7×7 to 0.006 L of L-cysteine at 110 K; (b) delivering 0.06 L of molecules to a Si sample at 110 K and then annealing the cysteine-covered sample to 300 K to drive away all physisorbed molecules; and (c) exposing the Si surface to 0.06 L of L-cysteine at room temperature. The O1s peak in Figure 6d was fitted into two features at 532.2 and 533.1 eV with comparable intensities, attributable to the oxygen atom (O^2) attached directly to the silicon atom and the preserved carbonyl O^1, respectively. There are two resolved peaks centered at 398.7 (42.6%) and 400.7 eV (57.4%) in the N1s XPS spectrum of chemisorbed molecules (Figure 7d), implying the existence of two different chemisorption states. The N1s binding energy at 398.7 eV corresponds to the nitrogen atom linked to the silicon atom directly, comparable to the values obtained for the chemisorbed N-containing molecules with the Si−N linkage.[41−43,46,47] The dissociation via cleaving two N−H bonds can be eliminated because a N1s core level at ~398.0 eV is expected for $R-N{=}(Si)_2$ species.[48] The other feature at 400.7 eV is due to the N in neutral amino group (NH_2) and close to the values of physisorbed amines.[12,37] The significant change of O1s and N1s binding energies upon chemisorption suggests that O and N atoms directly participate in the surface reaction of L-cysteine on Si(111)-7×7.

The C1s and S2s XPS spectra of physisorbed and chemisorbed L-cysteine on Si(111)-7×7 are presented in Figures 8 and 9, respectively. Two separate C1s peaks at 286.7 and 289.9 eV with an area ratio ~2:1 were detected for physisorbed molecules, which can be assigned to the alkyl carbon atoms (C^1, C^2) in C−N/C−S and the one (C^3) in the C═O group, respectively. These assignments are consistent with the C1s data for adsorbed L-cysteine on gold and copper.[22,23,49] For sulfur, the S2p spectrum was not attempted due to its overlapping with one of the plasma peaks of silicon substrates.[50] Figure 9b shows S2s XPS intensity at 228.3 eV, consistent with the S2s binding energies of physisorbed sulfur-containing organic molecules.[30,51] It is also noted that the C1s and S2s photoemission features of chemisorbed L-cysteine are similar to those of physisorbed molecules, indicating that the carbon and sulfur atoms are not directly involved in the interaction of L-cysteine with Si(111)-7×7. The

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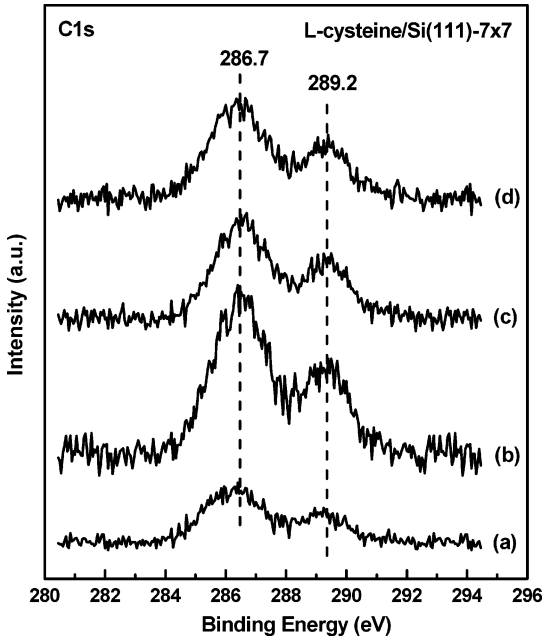

Figure 8. C1s XPS spectra of a Si(111)-7×7 sample exposed to 0.006 (a) and 0.06 L (b) of L-cysteine at 110 K and subsequently annealed to 300 K (c). The spectrum of L-cysteine (0.06 L) on Si-(111)-7×7 at room temperature is shown in a curve (d).

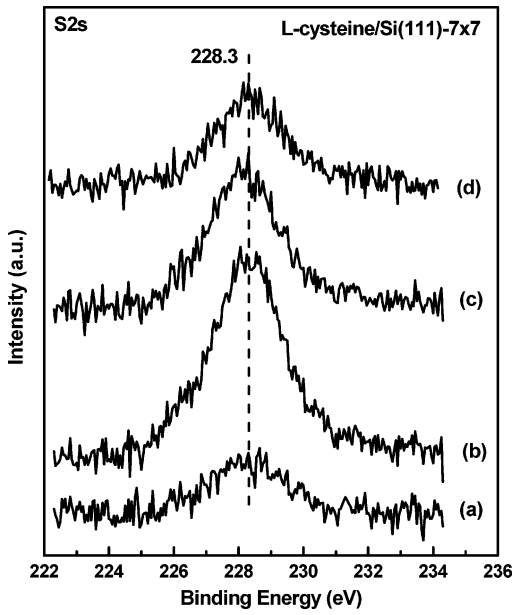

Figure 9. S2s XPS spectra of a Si(111)-7×7 sample exposed to 0.006 (a) and 0.06 L (b) of L-cysteine at 110 K and subsequently annealed to 300 K (c). The spectrum of L-cysteine (0.06 L) on Si-(111)-7×7 at room temperature is shown in a curve (d).

detailed assignments of the XPS features for physisorbed and chemisorbed molecules are summarized in Table 3.

In the HREELS spectrum of physisorbed L-cysteine on Si-(111)-7×7 (Figure 10b), loss peaks at 512, 679, 924, 1052, 1410, 1618, 2551, 2954, and 3189 cm^{-1} were observed, in excellent agreement with the experimental and calculated vibrational frequencies of solid-phase L-cysteine.[52] The features at 3189 and 1052 cm^{-1} can be ascribed to the NH_3^+ asymmetric stretching and rocking modes, respectively. The most intense band at 1618 cm^{-1} is related to the NH_3^+ asymmetric deformation and CO_2^-

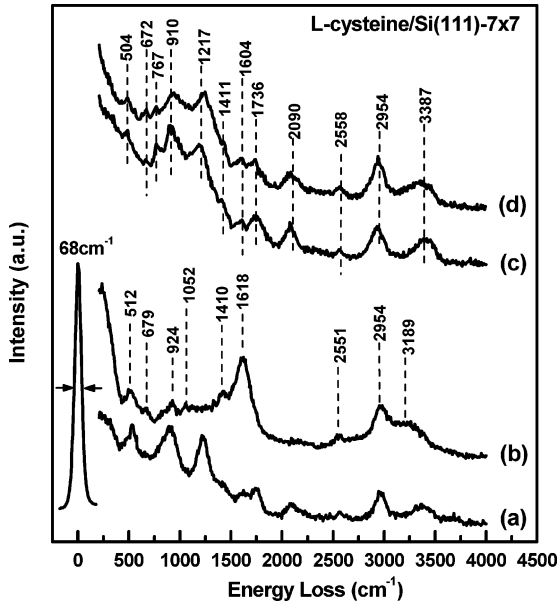

Figure 10. HREELS spectra of a Si(111)-7×7 sample exposed to 0.006 (a) and 0.06 L (b) of L-cysteine at 110 K and subsequently annealed to 300 K (c). The spectrum of L-cysteine (0.06 L) on Si-(111)-7×7 at room temperature is shown in a curve (d). $E_p = 5.0$ eV; specular mode.

asymmetric stretching, which are not resolved due to the resolution of the EELS spectrometer. The CO_2^- rocking vibration also produces the peak at 512 cm^{-1}. The characteristic feature of the S−H group is located at 2551 cm^{-1}, attributable to the S−H stretching mode. Due to the limitation of HREELS resolution, this high-intensity S−H vibrational feature makes the adjacent NH_3^+ symmetric stretching (∼2620 cm^{-1}) undistinguishable in Figure 10b, unlike that observed in the HREELS spectrum of physisorbed glycine on Si(111)-7×7 (Figure 2a). Furthermore, the absence of the vibrational features corresponding to carbonyl (C═O), hydroxyl (O−H), and amino (NH_2) groups rules out the presence of physisorbed L-cysteine in the neutral form on the Si surface.[53] We thus conclude that zwitterionic L-cysteine [$NH_3^+CH(CH_2SH)COO^-$] is formed in multilayers on Si(111)-7×7, consistent with the XPS result.

The vibrational spectra of chemisorbed molecules on Si(111)-7 × 7 are presented in Figure 10a, c, and d. Intensities at 504, 672, 767, 910, 1217, 1411, 1604, 1736, 2090, 2558, 2954, and 3387 cm^{-1} can be clearly identified. The new peaks at 1736, 3387, and 1604 cm^{-1} are assigned to the C═O stretching, N−H symmetric stretching, and scissoring modes, respectively. The appearance of the features related to the C═O and NH groups, together with the disappearance of vibrations corresponding to $-NH_3^+$ and $-CO_2^-$ functionalities, indicates that the zwitterionic structure of L-cysteine is perturbed upon chemisorption. Another important spectroscopic change is the emergence of a new peak at 2090 cm^{-1} due to Si−H stretching, suggesting the dissociative nature of chemisorbed L-cysteine on Si(111)-7×7.[34] It is noted that the S−H stretching is retained with the frequency of 2558 cm^{-1}, which excludes the breakage of the S−H bond in the chemisorption process. However, the dissociation occurring at the O−H and N−H groups is further supported by the absence of ν(OH) in the range of 3400−3600 cm^{-1} and the existence of ν(Si−O)/ν(Si−N) at 767 cm^{-1}/504 cm^{-1}.[35,36,54] The assignments

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Table 2. Fitted Results of XPS Spectra for Physisorbed and Chemisorbed Glycine ($NH_2C^1H_2C^2O^1O^2H$) on Si(111)-7×7[a]

			chemisorption	
		physisorption	$Si-N^1HC^1H_2C^2O^1O^2$ -Si	$N^2H_2C^1H_2C^2O^1O^2-Si$
O1s	COO^-	532.3 (fwhm=1.8 eV)		
	O^1		533.2 (fwhm=1.7 eV)	
	O^2		532.2 (fwhm=1.7 eV)	
N1s	NH_3^+	402.2 (fwhm=1.8 eV)		
	N^1		398.7 (fwhm=1.7 eV)	
	N^2			400.6 (fwhm=1.7 eV)
C1s	C^1	287.1 (fwhm=1.7 eV)	286.6 (fwhm=1.8 eV)	
	C^2	289.4 (fwhm=1.7 eV)	289.2 (fwhm=1.8 eV)	

[a] All energies are in eV.

Table 3. Fitted Results of XPS Spectra for Physisorbed and Chemisorbed L-Cysteine [$NH_2C^1H(C^2H_2SH)C^3O^1O^2H$] on Si(111)-7×7[a]

			chemisorption	
core level		physisorption	$Si-N^1HC^1H(C^2H_2SH)C^3O^1O^2-Si$	$N^2H_2C^1H(C^2H_2SH)C^3O^1O^2-Si$
O1s	COO^-	532.1 (fwhm=1.7 eV)		
	O^1		533.1 (fwhm=1.7 eV)	
	O^2		532.2 (fwhm=1.7 eV)	
N1s	NH_3^+	401.9 (fwhm=1.8 eV)		
	N^1		398.7 (fwhm=1.7 eV)	
	N^2			400.7 (fwhm=1.7 eV)
C1s	C^1,C^2	286.7 (fwhm=1.7 eV)	286.7 (fwhm=1.7 eV)	
	C^3	289.2 (fwhm=1.7 eV)	289.2 (fwhm=1.7 eV)	
S2s	S	228.3 (fwhm=1.8 eV)	228.3 (fwhm=1.8 eV	

[a] All energies are in eV.

Table 4. Assignments of HREELS Spectra for Physisorbed and Chemisorbed L-Cysteine on Si(111)-7×7[a]

assignment	Raman spectra of solid-phase L-cysteine[49]	calculated vibrational frequencies of solid-phase L-cysteine[49]	physisorbed L-cysteine on Si(111)-7×7	chemisorbed L-cysteine on Si(111)-7×7
ν (NH)				3387
ν_a (NH_3^+)	3166	3156, 3155	3189	
ν_s (NH_3^+)	3064	3064		
ν_a (CH_2)	2994	2996		
ν_s (CH_2)	2961	2976	2954	2954
ν (CH)	2961	2954		
ν (SH)	2551	2559	2551	2558
ν (SiH)				2090
ν (C=O)				1736
δ_a (NH_3^+)	1641	1645, 1642	1618	
δ (NH)				1604
ν_a (CO_2^-)	1575	1588	1618	
δ_s (NH_3^+)	1523	1524		
δ (CH_2)	1424, 1397	1439, 1410	1410	1411
δ (CH)	1344, 1303	1356, 1322		
C−O stretch				1217
γ (CH_2)	1269	1278		
t (CH_2)	1198	1258, 1180		
ρ (NH_3^+)	1140, 1106, 1004, 931, 868	1144, 1103, 1008, 922, 883	1052	
ρ (CH_2)			924	910
ν (SiO)				767
γ (CO_2^-)	826, 773	827, 795		
ν (CS)	691	687	679	672
δ (CO_2^-)	638, 535	635, 535	512	
ν (SiN)				504

[a] All frequencies are given in cm^{-1}.

for the vibrational features of physisorbed and chemisorbed L-cysteine on Si(111)-7×7 are listed in Table 4.

4. Discussion

4.1. Zwitterionic Structures of Physisorbed Glycine and L-Cysteine on Si(111)-7×7. Like all the amino acids, glycine and L-cysteine are amphoteric, containing both acidic carboxylic acid (−COOH) and basic amino ($-NH_2$) groups. Gaseous and solid glycine/L-cysteine molecules exist in neutral (nonionic) and zwitterionic (ionic) forms, respectively.[7−9] The major differences can be found in the vibrations associated with the carboxylic acid (−COOH) and amino ($-NH_2$) groups in the nonionic form and those of the carboxylate ($-COO^-$) and $-NH_3^+$ functionalities in the ionic state. In the HREELS spectra of physisorbed glycine and L-cysteine on Si(111)-7×7 (Figures 2a and 10b), the appearance of $-NH_3^+$ asymmetric (3173/3189 cm^{-1}) and symmetric (2620 cm^{-1}) stretching, as well as $-NH_3^+$ (1121/1052 cm^{-1}) and $-COO^-$ (514/512 cm^{-1}) rocking modes, indicates the coexistence of $-NH_3^+$ and $-COO^-$ on the surface. Moreover, no vibrational signals associated with $-NH_2$, −OH,

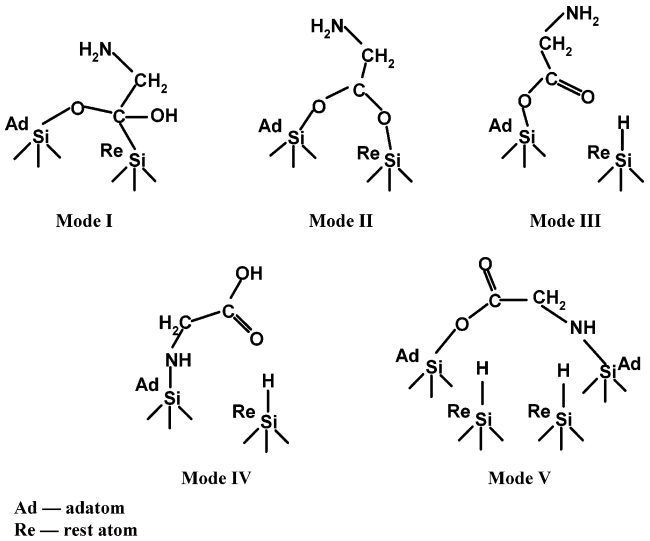

Figure 11. Schematic diagrams of five possible binding configurations for chemisorbed glycine on Si(111)-7×7.

and C═O groups were observed, excluding the presence of glycine and L-cysteine in the neutral forms.[53] XPS also provides strong evidence for the formation of zwitterionic glycine and L-cysteine on the Si surface. The N1s binding energies of 402.2 and 401.9 eV for physisorbed molecules are close to the value of ammonium salts.[38,39] The quaternary nitrogen atom is positively charged in $-NH_3^+$, leading to the low electron density on this nitrogen and its high binding energy. Similar N1s photoemission features of 402.2 and 402.5 eV were observed for the zwitterionic glycine on copper and Pt(111), respectively.[12,33] In addition, the XPS spectrum of nonionic glycine ($NH_2CH_2CO^1O^2H$), reported by Slaughter et al.,[55] showed two different O1s binding energy features with a separation of 1.8 eV, attributable to carbonyl (O^1) and hydroxyl (O^2) oxygen atoms, respectively. However, the ionic glycine produces only one type of oxygen.[44] The photoemission spectra of physisorbed glycine/L-cysteine present a single oxygen peak at 532.3/532.1 eV, consistent with the value of the zwitterionic glycine. From EELS and XPS findings, it is concluded that physisorbed glycine/L-cysteine molecules on Si(111)-7×7 are in the zwitterionic state.

4.2. Bonding of Chemisorbed Glycine and L-Cysteine on Si(111)-7×7. There are five possible reaction pathways of chemisorbed glycine on Si(111)-7×7, presented in Figure 11. The formation of a precursor state in the adsorption process of organic molecules on silicon surfaces was widely proposed in the previous calculation studies.[56,57] The electron-rich oxygen atom of hydroxyl or carbonyl in glycine may interact with the electron deficient Si− adatom to yield a dative bond in the intermediate state. If the dative bond is formed between the carbonyl oxygen and the silicon atom, a [2+2]-like cycloaddition is expected to occur through C═O (Mode I). On the other hand, the dative bonding via the hydroxyl oxygen leads to the occurrence of the dissociative reaction, which involves the cleavage of the OH group and the formation of glycinate species (Modes II and III). The emergence of the dative-bonded precursor via the N atom in NH_2 is another possibility since the nitrogen atom shows higher electronegativity in comparison with oxygen. This produces a Mode IV adsorbate through the breakage of the N−H group. When the dissociation occurs concurrently through both −OH and $-NH_2$ functionalities, the resultant chemisorbed species is shown in Mode V. In the HREELS studies of chemisorbed glycine on Si(111)-7×7 (Figure 2), the existence of the Si−H stretching at 2067 cm^{-1} and the lack of the OH stretching at ∼3560 cm^{-1}, together with the retaining C═O stretching (1726 cm^{-1}), show the cleavage of the OH bond and the formation of carboxylate species in the adsorption process, which clearly rules out the possibilities of the [2+2]-like C═O cycloaddition (Mode I) and the dissociation occurring only through the NH_2 group (Mode IV). The vibrational frequency difference between ν_s (OCO) and ν_{as} (OCO) [which correspond to the ν(C−O) and ν(C═O) modes of the monodentate carboxylate] is expected to distinguish bridging and monodentate carboxylate species.[58,59] The C═O and C−O stretchings produce the features at 1726 and 1234 cm^{-1} with a frequency difference of 492 cm^{-1}, indicating the presence of monodentate carboxylate species on the surface. This result is further supported by the existence of two chemically different O1s features for the chemisorbed species and the small shift (0.2 eV) in carboxyl C1s BEs upon chemisorption (Figures 3 and 4).[60] Although the N−H stretching of primary (Mode III) and secondary amines (Mode V) cannot be differentiated due to the quite weak peak intensity of secondary amine,[54] the coexistence of Modes III and V at the glycine/Si(111)-7×7 interface can be evidenced by the appearance of two N1s features in the XPS spectum chemisorbed glycine (Figure 5). The peak at 398.7 eV is related to the nitrogen atom directly bonded to the silicon atom in Mode V and the other at 400.6 eV is due to the N of neutral amino group ($-NH_2$) in Mode III. Therefore, glycine is dissociatively bonded to Si(111)-7×7 to form both Si−NH−CH_2−COO−Si (Mode V) and NH_2−CH_2−COO−Si species (Mode III).

Besides amino and carboxylic acid functionalities, L-cysteine bears another reactive thiol group. Although the sulfur atom shows a strong affinity to different metals, especially gold,[61−64] it is not active in the interaction of L-cysteine with Si(111)-7×7. The preservation of S−H stretching (2558 cm^{-1}) in the HREELS spectra of chemisorbed molecules and the little shift for S2s binding energies upon chemisorption both demonstrate that the thiol group is not involved in the surface reaction. In fact, the experimental results can be well explained considering the formation of Si−NHCH(CH_2SH)COO−Si and NH_2CH(CH_2-SH)COO−Si on the Si surface. In the vibrational spectra of chemisorbed L-cysteine, the appearance of ν(Si−H) at 2090 cm^{-1} and ν(Si−O) at 767 cm^{-1}, the absence of ν(O−H) between 3400 and 3600 cm^{-1}, and the existence of a large frequency difference (519 cm^{-1}) between the stretching modes of C═O and C−O, suggest the presence of monodentate carboxylate species in the chemisorbed species. Furthermore, there are two separate features in the N1s XPS spectra of chemisorbed molecules with binding energies at 398.7 and 400.7 eV, attributable to the N atoms in Si−NHCH(CH_2SH)COO−Si and NH_2CH(CH_2SH)COO−Si, respectively. It is concluded that L-cysteine undergoes a similar dissociative reaction as that of glycine on Si(111)-7×7. The terminal thiol group is retained in the adsorption process, unlike its strong affinity on gold with the formation of S−Au bond.[61−64] Furthermore, the selective adsorption of L-cysteine on Si(111)-7×7 demonstrates that the reactivity of carboxylic acid, amino,

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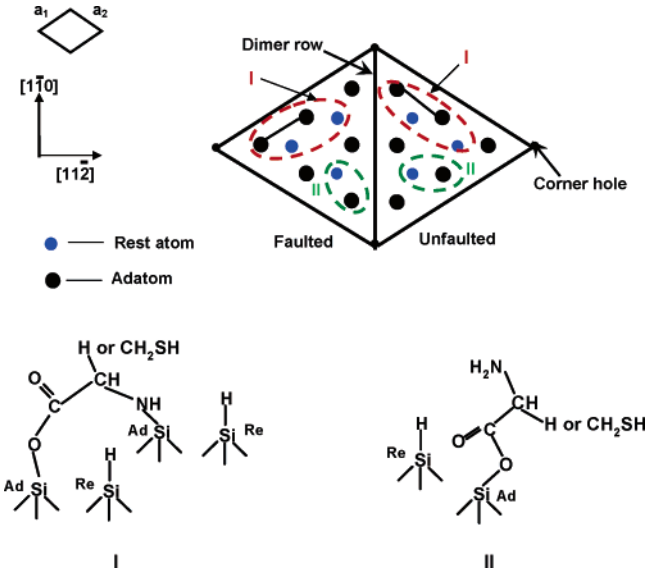

Figure 12. Possible configurations of Si−NH−CH_2−COO−Si [Si−NHCH(CH_2SH)COO−Si] and NH_2−CH_2−COO−Si [NH_2CH(CH_2SH)COO−Si] species on Si(111)-7×7.

and thiol groups on the Si surface is in the order of −COOH > −NH_2 > −SH.

The product ratio of Si−NH−CH_2−COO-Si to NH_2−CH_2−COO−Si species (glycine) and Si−NHCH(CH_2SH)COO−Si to NH_2CH(CH_2SH)COO−Si (L-cysteine) is estimated to be ∼1:1 on the basis of the XPS peak areas of two kinds of N atoms. This may be explained considering the existence of three adjacent adatom−rest atom pairs in one faulted or unfaulted half. At the low coverage, glycine (L-cysteine) is expected to be adsorbed via both −NH_2 and −OH groups, occupying two neighboring adatom−rest atom pairs in the half unit. Thus only one pair is available in the half unit for the binding via the OH group, resulting in the nearly equal ratio of these two products. The possible configurations of Si−NH−CH_2−COO−Si [Si−NHCH(CH_2SH)-COO−Si] and NH_2−CH_2−COO−Si [NH_2CH(CH_2SH)COO−Si] species on Si(111)-7×7 are shown in Figure 12. Further work is required to gain detailed understanding on the adsorption process of these two adsorbates on Si(111)-7×7.

5. Conclusion

The structures of physisorbed and chemisorbed glycine/L-cysteine on Si(111)-7×7 have been investigated using HREELS and XPS. The multilayer glycine and L-cysteine physisorbed on Si(111)-7×7 at 110 K exist in their zwitterionic states {[$NH_3^+CH_2COO^-$] and [$NH_3^+CH(CH_2SH)COO^-$]}. Chemisorption of glycine undergoes dissociative reactions on the Si surface, producing two surface intermediates species of Si−NH−CH_2−COO−Si and NH_2−CH_2−COO−Si. Similarly, two chemisorption states, including Si−NHCH(CH_2SH)COO−Si and NH_2CH(CH_2SH)COO−Si, coexist at the L-cysteine/Si(111)-7×7 interface. The remaining thiol group can act as an important reactive site for the further surface reactions. The investigations on the adsorption of simple amino acids on silicon surfaces are expected to establish the foundation for further studies in the interfacial phenomena between biological molecules, e.g., proteins, and solid surfaces at the molecular level, leading to wide applications in biosensors and biomaterials.

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