Thermal Reactions of Methanethiol and Ethanethiol on Si(100)

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We investigated adsorption and thermal decomposition of methanethiol (CH_3SH) and ethanethiol (C_2H_5SH) on a Si(100) surface by means of temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) with synchrotron radiation. At an adsorption temperature of 115 K, CH_3SH and C_2H_5SH dissociate to form thiolates and hydrogen at a small coverage (<0.2 monolayer), whereas molecular chemisorption occurs at a greater coverage; all chemisorbed molecules either deprotonate to form thiolate or desorb intact up to 400 K. Adsorption and decomposition of thiols occur on the dangling bonds of a dimer without breaking the Si−Si dimer bond, resulting in preservation of a 2×1 LEED pattern. Thiolates further decompose to evolve hydrocarbons via scission of the C−S bond to form a sulfur adatom on the surface at a temperature above 550 K. Maximum desorption of surface sulfur as SiS occurs at 820 K. CH_3 generated from CH_3S reacts with surface hydrogen to evolve CH_4, whereas the C_2H_5 moiety of C_2H_5S undergoes β-hydride elimination to form C_2H_4. To a small extent, the alkyl moiety transfers onto the surface and undergoes dehydrogenation, resulting in desorption of hydrogen and deposition of carbon on the surface.

Introduction

Reactions to modify a surface are important not only for engineering of surface energy and composition but also for attaching molecules with varied physical and chemical properties.[1,2] A number of studies have reported deposition of self-assembled monolayers (SAM) formed from organosulfur compounds via bonding of the sulfur atom to various surfaces; surfaces of noble metals such as Au and Ag have been much investigated.[3,4] Like adsorption of alkanethiols that occurs on noble metals, a SAM film might be prepared on a Si surface that can modify the chemical and physical properties of that surface and become potentially adaptable for such applications as protecting and insulating layers.[5−7] Organic monolayers with known orientation and controllable properties on a semiconductor surface have prospective applications as bio- or chemical sensors, and as molecular electronic and optoelectronic devices.[8,9] Organic/bio-molecules containing a sulfhydryl group (−SH) have been attached to a Si surface with the sulfur atom as the tether.[10,11] The chemical behavior of thiols on a silicon surface is thus fundamentally important in the field of molecular electronics and has relevance to fields as diverse as biological science.

We report here an investigation of the mechanism of adsorption and decomposition of alkanethiols on a Si(100) surface, utilizing temperature- programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS); such spectral examination elucidates pathways of this surface reaction. In principle, the length of the carbon chain of an alkanethiol might exert a significant influence on the thermal stability and reaction mechanism due to the presence of β-hydrogen and the interaction between a Si surface and an alkyl group. We thus undertook a comparison of thermal reactivity and reaction products for alkanethiols with varied lengths of alkyl chain (i.e., RSH with R═CH_3 and C_2H_5), thus probing the formation and thermal stability of an alkanethiolate adlayer on the Si surface.

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Experimental Section

Experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure 2×10^{-10} Torr. The system was equipped with a quadrupole mass filter (EPIC, Hiden), low-energy electron diffraction (LEED), and an electron-energy analyzer (HA100, VSW). The Si(100) samples (n-type, 1−10 Ω· cm) for our work had thickness 0.3 mm. To eliminate possible organic residues, the Si surface was cleaned with acetone, methanol, and hot HNO_3 solution (1 M) in a sequence, and was followed by rinsing with distilled water. A Ta strip (thickness 0.025 mm) was uniformly pressed between two Si samples by Ta foils at two ends, which were in turn mounted on a copper block. The sample could be cooled to 115 K with liquid nitrogen via conduction through the copper block, and heated by resistive heating of the Ta strip and the Si sample. The sample temperature was monitored with a K-type thermocouple spot-welded onto a thin Ta foil that was inserted between the two Si samples. The Si surface was initially cleaned by means of resistive heating in situ slowly to 1200 K. After each experimental run, the surface was cleaned through Ar^+ ion sputtering and annealed to 1200−1300 K; according to LEED, the surface then exhibited sharp 2×1 and dim $c(4 \times 2)$ patterns revealing two domains.[12] The cleanliness of the Si surface was verified with XPS measurements. To diminish effects of surface damage caused by ion sputtering we replaced Si samples after 3−4 experimental runs.

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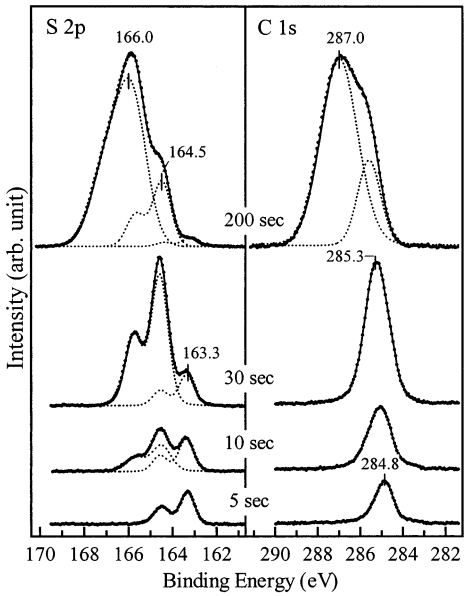

Figure 1. XPS spectra of S 2p and C 1s recorded for a Si surface with varied duration of exposure to CH_3SH at 115 K. Dots represent data collected after background subtraction; solid lines are fitted curves, and various components are shown in dashed lines. The photon energy used to collect these spectra is 400 eV.

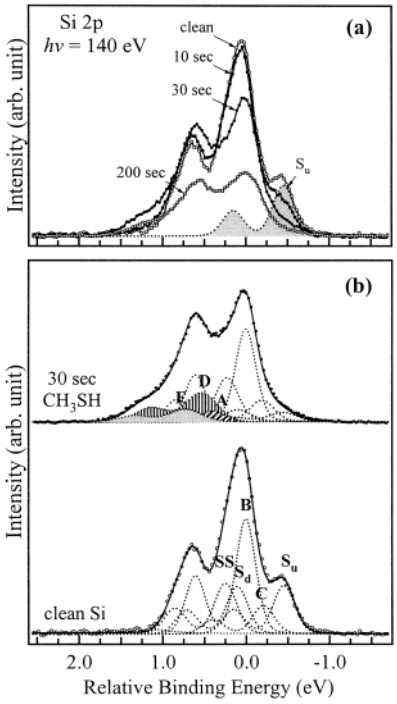

Figure 2. (a) XPS spectra of Si 2p recorded for a Si surface with varied duration of exposure to CH_3SH at 115 K; (b) decomposition of Si spectra from a clean surface and a surface exposed to CH_3SH for 30 s.

Before use, C_2H_5SH (>99%, Merck) and C_4H_9SH (>98%, Merck) liquids were subjected to several freeze−pump−thaw cycles. CH_3SH (>99.5%, Matheson) was used without further purification. Alkanethiols were introduced onto the Si surface via a stainless steel tube with a pinhole (diameter 250 μm). During dosing, partial pressures of alkanethiols were controlled at 2×10^{-9} Torr and the sample surface was placed ~20 mm in front of the doser pinhole to minimize contamination of the UHV system with thiols.

XPS were measured at the wide-range and LSGM beamlines of SRRC (Synchrotron Radiation Research Center, Taiwan); the angle of incidence of photons was 45° from the surface normal. Emitted photoelectrons were collected with an electron analyzer at an angle 10° from the surface normal in an angle-integrated mode. Collected spectra were numerically fitted with a Gaussian-broadened Lorentzian function after Shirley background subtraction with a third-order polynomial to each side of the feature. The Si and S 2p spectra were fitted with a branching ratio 0.5 ± 0.02 between $p_{1/2}$ and $p_{3/2}$; the spin−orbit splittings were 0.60 and 1.18 eV, respectively. The onset of photoemission from an Au foil attached to the sample holder served as the Fermi level, corresponding to zero binding energy.

A quadrupole mass filter served for analysis of desorption products in the TPD measurement. The mass analyzer was enclosed in a differentially pumped cylinder, at the end of which is a skimmer with an entrance aperture (diameter 2 mm). For TPD measurement, the sample surface was placed about 2 mm before the aperture and in line of sight of the ionizer of the mass spectrometer; TPD scans were recorded on ramping the sample at a linear rate ~2 K/s.

Results and Discussion

Surface species upon adsorption and thermal fragmentation of CH_3SH on a Si surface were identified chemically using XPS measurement. Figure 1 shows spectra in S 2p and C 1s regions collected from a Si(100) surface exposed to CH_3SH at 115 K for varied duration. After brief exposure (5 s), only an S 2p spin−orbit doublet is observed with the $p_{3/2}$ binding energy at 163.3 eV, which is attributed to surface methyl thiolate (CH_3S) and discussed further below. Two additional S $2p_{3/2}$ components at 164.5 and 166.0 eV develop with increasing duration of exposure. The intensity of the former component reaches a maximum at an exposure of duration ~30 s, whereas the intensity of the latter component does not saturate upon extended exposure of CH_3SH. These S $2p_{3/2}$ components are thus assigned to CH_3SH molecules chemisorbed and physisorbed on the surface, respectively.

XPS data indicate that on initial adsorption CH_3SH molecules dissociate to form surface CH_3S and hydrogen ($CH_3SH \rightarrow CH_3S + H$). CH_3SH can also adsorb molecularly on the surface at large coverage with increasing coverage of CH_3S. For a saturated monolayer, 15−20% of adsorbed CH_3SH deprotonates to form thiolate at adsorption temperature 115 K. CH_3SH molecules can condense on the surface after adsorption sites become saturated, but the sticking coefficient is greatly decreased. Parallel to these S 2p spectra, corresponding C 1s chemical states of methyl groups have 1s binding energies at 285.3 and 287.0 eV. The former feature is assigned to dissociative CH_3S and chemisorbed CH_3SH, and the latter feature is due to physisorbed CH_3SH. These assignments of XPS features are consistent with an observation that intensities of S 2p and C 1s signals due to chemisorbed CH_3SH and CH_3S become attenuated by physisorbed CH_3SH molecules on protracted exposure (>30 s).

Figure 2a shows core level spectra of Si 2p taken before and after a clean Si surface is exposed to CH_3SH at 115 K. The Si 2p binding energy is referred to the bulk $2p_{3/2}$ component so that complication resulting from the variation of surface band bending can be eliminated after adsorption and thermal decomposition of CH_3SH. Without curve fitting, we find that Si 2p spectra show broadening at the side of greater binding energy because of interaction of the Si surface and CH_3SH. It is generally accepted that the Si 2p spectrum of a clean Si(100)−2 × 1 surface is fitted with four surface components (S_u, S_d, SS, and C) with the bulk component (B) as shown in Figure 2b;

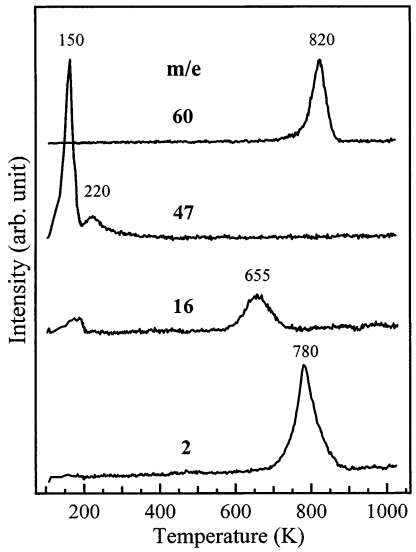

Figure 3. Composite temperature-programmed desorption scans collected from a Si(100) surface exposed to CH_3SH at 115 K for 200 s.

components S_u and S_d correspond to upward and downward buckled Si atoms of asymmetric dimers, respectively; component SS is assigned to the second layer Si atoms, and component C is likely due to third-layer Si atoms or defects.[13−15] The energy shifts relative to the bulk component are −0.46, −0.21, 0.09, and 0.25 eV, repectively, in agreement with previous results except for a small difference in the energy shifts.

For simplicity and clarity, only the upward buckled Si of a dimer at −0.46 eV for the clean surface is shown in Figure 2a. This component is gradually attenuated upon increasing exposure of CH_3SH, indicating that a reaction occurs between CH_3SH and surface Si atoms of dimers. The ordered (2 × 1) LEED pattern is maintained after adsorption of CH_3SH at 115 K, although its intensity decreases. We assume that at 115 K the molecular CH_3SH and the dissociative H and CH_3S species are likely bound to existing dangling bonds of a Si dimer without major disruption of Si surface structure. As shown in Figure 2b, taken from a Si surface exposed to CH_3SH for 30 s, the four surface components of Si 2p decrease in intensity and three new Si 2p components (labeled as components A, D, and E) appear at the side of large binding energy with energy shifts 0.42, 0.53, and 0.70 eV relative to the bulk component. As mentioned above, dissociation of CH_3S-H produces surface hydrogen and CH_3S. On the basis of infrared reflection spectroscopy, it has been reported that CH_3OH dissociates to form surface $Si-OCH_3$ and Si−H without breaking the Si−Si dimer bond at 150 K. The Si−H species resulting from dissociation of CH_3O-H has a chemical shift of Si 2p at 0.435 eV with respect to the bulk Si.[15] Thus, component A is assigned to surface Si bonded to hydrogen. Components D and E at large binding energy are assigned to surface Si atoms of a dimer bonded to molecular CH_3SH and dissociative CH_3S via electron-withdrawing S atoms, respectively.

Figure 3 shows TPD scans for a Si(100) surface exposed to CH_3SH at 115 K for 200 s. To detect possible products evolving during thermal decomposition of CH_3SH on the surface, we observed several possible fragments. Desorption features of molecular CH_3SH ($m/e = 47$) are observed at 150 and 220 K, and are attributed to desorption of physisorbed and chemsiorbed CH_3SH. Most chemisorbed CH_3SH undergoes thermal decomposition, resulting in desorption of hydrogen ($m/e = 2$), CH_4 ($m/e = 16$), and SiS ($m/e = 60$). Desorption of hydrogen results in an intense feature at 780 K and resembles the β_1 states of

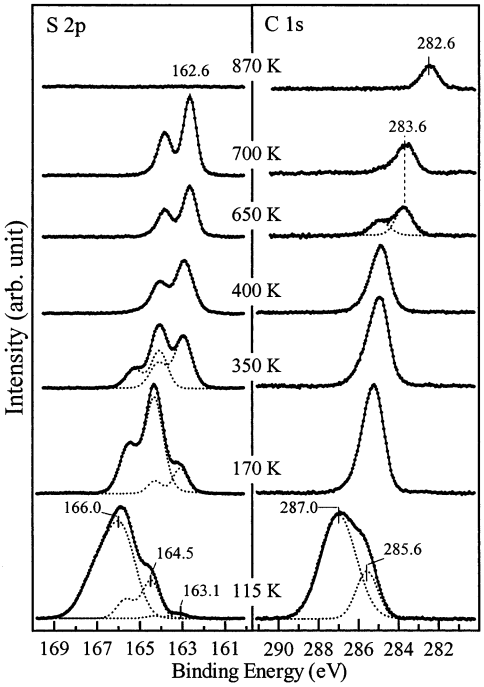

Figure 4. XPS spectra of S 2p and C 1s for a Si(100) surface exposed to CH_3SH for 200 s at 115 K and subsequently heated to the indicated temperatures. The photon energy used to collect these spectra is 400 eV.

hydrogen desorption observed after adsorption of atomic hydrogen on Si(100), which are attributed to recombination of surface hydrogen in a form of Si monohydride.[16] Maximum desorption of CH_4 occurs at 655 K, due to the hydrogenation of CH_3 moiety. Formation of C_2H_6 via coupling of CH_3 groups of CH_3SH is not observed, unlike the case of transition metals.[17] Desorption of SiS is observed with a feature at 820 K, as observed for adsorption of elemental sulfur and H_2S on a Si surface.[18,19] Hence, for the decomposition of CH_3SH, SiS is desorbed via formation of atomic sulfur on a Si surface.

The thermal evolution of XPS spectra is used to characterize the variation of surface composition during thermal decomposition of CH_3SH on a Si surface and correlates with TPD results to elucidate the reaction intermediates. Figures 4 and 5 show core-level spectra of S 2p, C 1s, and Si 2p obtained from a Si(100) surface that is exposed to CH_3SH at 115 K for 200 s, then warmed to the indicated temperatures. All XPS spectra were recorded for samples at 115 K after the sample was heated to a desired temperature at a linear rate ∼1 K/s and cooled immediately on abrupt termination of heating. The S $2p_{3/2}$ (166.0 eV) and C 1s (287.0 eV) features due to physisorbed CH_3SH disappear upon heating the sample to 170 K. Between 170 and 400 K, the S 2p peak assigned to CH_3S gradually increases, whereas the S $2p_{3/2}$ peak at 164.5 eV due to chemisorbed CH_3SH decreases. Thermal dissociation of chemisorbed CH_3SH occurs to form CH_3S in this temperature range. In addition, the total integrated area of S 2p decreases because a proportion of chemisorbed CH_3SH is desorbed intact as shown in TPD data.

A previous study of infrared reflection spectroscopy showed that all chemisorbed CH_3OH molecules dissociate to form surface hydrogen and methoxy species (CH_3O) on Si(100)−2 × 1 at 150 K.[20] Our XPS results show that the dissociation temperature of chemisorbed CH_3S-H is higher than that of CH_3O-H, although the bond strength of S−H (80 kcal/mol) is less than that of O−H (102 kcal/mol).[21] Thus, we propose that the dissociation temperatures of CH_3S-H and CH_3O-H on Si-

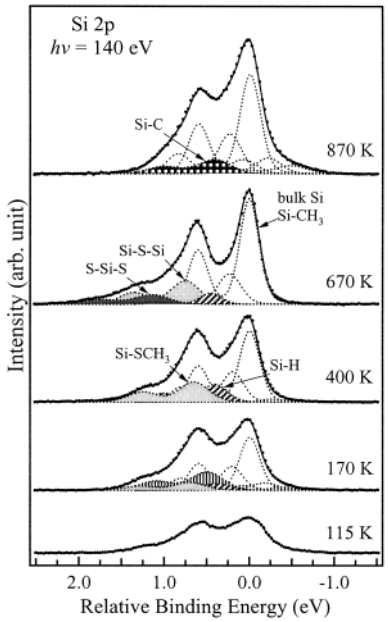

Figure 5. XPS spectra of Si 2p for a Si(100) surface exposed to CH_3SH for 200 s at 115 K and subsequently heated to the indicated temperatures. The photon energy used to collect these spectra is 140 eV.

(100) are mainly determined by the formation of Si−S (148 kcal/mol) and Si−O (190 kcal/mol) bonds, respectively. On the other hand, the dissociative adsorption of both CH_3SH and CH_3OH molecules do not break the Si−Si dimer bond and preserve the 2 × 1 surface pattern.[15]

Upon annealing the sample above 650 K, the S 2p spin−orbit doublets ($p_{1/2}$ and $p_{3/2}$) become better resolved (having a smaller fwhm) and shift slightly to smaller binding energy. This behavior reflects that CH_3S further decomposes to form sulfur adatom ($S_{(ad)}$) and liberates the CH_3 group via breaking the CH_3−S bond. A new C 1s feature that appears at 283.6 eV is thus assigned to surface CH_3.[22] As shown in Figure 3, desorption of CH_4 is observed in this temperature range and corresponds to the decreasing total intensity of C 1s. CH_4 is formed via reaction between the CH_3 moiety and surface hydrogen that originates from the dissociation of CH_3S−H at low temperature. We thus conclude that the CH_3 moiety generated on breaking the CH_3−S bond either transfers onto the surface or hydrogenates to desorb as CH_4.

At 700 K, all CH_3S species dissociate completely to form sulfur adatoms and leave a portion of the CH_3 moiety on the surface. The intensity of S 2p increases significantly after decomposition of CH_3S. Because the CH_3 group is liberated from the sulfur atom after decomposition of CH_3S, the scattering of photoelectrons emitted from S 2p by the CH_3 moiety is diminished and the intensity of S 2p in XPS measurements thus increases. Between 650 and 870 K, the C 1s feature shifts down toward 282.6 eV. Previous observations of vibrational spectra indicated that surface CH_3 on a Si surface dissociates to form SiH near 700 K.[23−26] We thus attribute this C 1s peak to surface carbon that results from dehydrogenation of surface CH_3.[27,28] Surface hydrogen is also formed during dehydrogenation of CH_3 and is subsequently desorbed with an intense feature at 780 K, as shown in Figure 3.[29] The S 2p peak disappears in this temperature range because sulfur is removed from the surface with a maximum effect at 820 K as shown in TPD data.

Figure 5 shows Si 2p core-level spectra as a function of temperature. A surface exposed to CH_3SH at 115 K for 200 s is covered with chemisorbed and physisorbed CH_3SH. Upon heating to 170 K, the spectral intensity of Si 2p becomes higher because of desorption of physisorbed CH_3SH, and the decomposition of the Si 2p spectrum is similar to that observed for a Si surface exposed to CH_3SH at 115 K for 30 s as shown in Figure 2b, for a surface saturated with chemisorbed CH_3SH and dissociative CH_3S. At 400 K, chemisorbed CH_3SH decomposes completely into surface CH_3S and H, and the Si 2p spectra are thus fitted with two components with chemical shifts at 0.41 and 0.67 eV due to Si−H and Si−SCH_3, respectively, as shown in Figure 4.

At 670 K, the CH_3S species decomposes further into surface sulfur and desorbs as CH_4 or forms surface CH_3 via cleavage of the CH_3−S bond. Decomposition of the Si spectrum yields two S−induced Si 2p components at 0.75 and 1.15 eV attributed to surface Si bound to sulfur atoms with oxidation states +1 and +2, respectively. Theoretical work indicates that a surface S atom absorbs at a bridge position above the topmost Si atoms, as the most energetically stable conformation.[30] Accordingly, we propose that the S-induced Si peak at 0.75 eV is due to surface Si atoms bound to bridge-bonded sulfur (Si−S−Si). Formation of Si−S−Si might occur on Si atoms of a dimer on breaking the Si−Si bond or with Si atoms between two Si dimers. According to the LEED observation, the 2 × 1 pattern persists after the Si surface exposed to CH_3SH at 115 K is heated to 670 K, although its intensity becomes small. Hence, adsorption and decomposition of CH_3SH might occur on dangling bonds of a Si dimer without breaking the Si−Si bond of that dimer. Thus, the Si−S−Si species is proposed to be formed mainly on two Si atoms of adjacent dimers. The large chemical shift of Si $2p_{3/2}$ at 1.15 eV is near that observed for Si(100)−1 × 1−S, for which the surface Si atom is terminated with bridge-bonded sulfur and has an oxidation state +2.[31] The Si $2p_{3/2}$ component is thus attributed to a surface S−Si−S species that we propose to form from decomposition of two adjacent CH_3S. The intensity ratio of the component at 0 eV to the second-layer Si is significantly greater than that of the bulk Si to the second-layer Si for a clean Si surface. On the basis of C 1s spectra shown in Figure 4, a portion of CH_3 groups liberated from dissociation of CH_3S transfers onto the surface in this temperature range. Thus, the component at 0 eV is attributed to bulk Si and surface Si bonded to the CH_3 group (Si−CH_3).

After annealing the sample to 870 K, the surface S is removed in a form of SiS and a well-defined 2 × 1 LEED pattern is recovered. However, a proportion of CH_3 moiety dehydrogenates to produce surface carbon. At 870 K, the Si 2p spectrum consists of a $p_{3/2}$ component with chemical shift at ∼0.45 eV due to the SiC species, and four surface components as obtained for a clean Si surface.[14]

On the basis of TPD and XPS results, the mechanism of decomposition of CH_3SH on Si(100) is summarized as follows:

$$CH_3SH_{(ad)} \rightarrow CH_3S_{(ad)} + H_{(ad)} \quad 115-400\ K \qquad (a)$$

$$CH_3S_{(ad)} + H_{(ad)} \rightarrow CH_{4(g)} + S_{(ad)} \quad 550-670\ K \qquad (b)$$

$$CH_3S_{(ad)} \rightarrow CH_{3(ad)} + S_{(ad)} \quad 550-670\ K \qquad (c)$$

$$CH_{3(ad)} \rightarrow CH_{x(ad)} + (3-x)H_{(ad),}\ (x \leq 2) \quad 670-870\ K \qquad (d)$$

$$2H_{(ad)} \rightarrow H_{2(g)} \quad 700-870\ K \qquad (e)$$

$$S_{(ad)} + Si_{(s)} \rightarrow SiS_{(g)} \quad 740-870\ K \qquad (f)$$

Our XPS data indicate that thiolate species on the Si surface sustain up to 550 K and is more stable than those formed on transition metals. The dissociation temperature of the CH_3−S

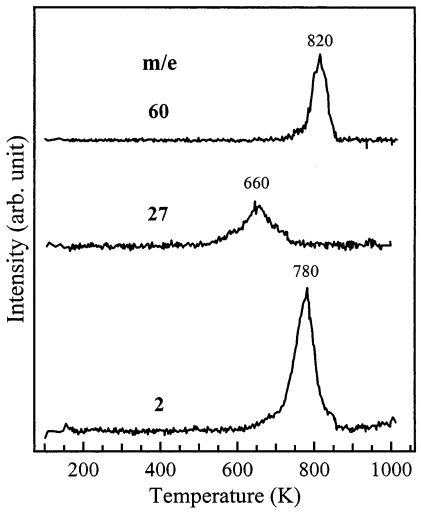

Figure 6. Composite temperature-programmed desorption scans collected from a Si(100) surface exposed to C_2H_5SH at 115 K for 30 s.

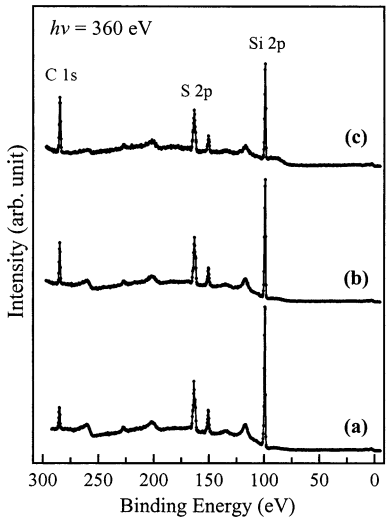

Figure 7. Comparison of XPS spectra recorded for Si surfaces exposed to (a) CH_3SH, (b) C_2H_5SH, and (c) C_4H_9SH for 200 s at 115 K and heated to ~170−200 K.

bond is less than that of CH_3-O by ~150 K.[32] H_2, CH_4, and SiS are products of desorption, and only carbon is left on the Si surface after decomposition of CH_3SH on annealing the sample to 870 K.

To understand the effect of length of alkyl chain on the reactions of thiols on a Si surface, we studied adsorption also of C_2H_5SH. Figure 6 shows TPD scans for a Si surface exposed to C_2H_5SH for 30 s. H_2 ($m/e = 2$) and C_2H_4 ($m/e = 27$) are desorption products of C_2H_5SH decomposition with maximum signals at 660 and 780 K, respectively. Desorption of C_2H_6 ($m/e = 30$), a hydrogenation product, is not observed. To avoid background interference from residual gas (e.g., CO and N_2) in the chamber, we recorded the intensity of a signal for C_2H_4 desorption at $m/e = 27$, rather than at $m/e = 28$. C_2H_4 is formed via β-hydride elimination of surface C_2H_5 moiety of C_2H_5S ($C_2H_5S \rightarrow C_2H_4 + H + S$), as generally observed for transition metals.[33,34] Dissociation of the C−H bond is catalyzed by the metallic surface to form metal−H species,[33,35] but the desorption temperature of C_2H_4 is near that of CH_4 obtained from decomposition of CH_3SH. Hence, the reaction of alkanethiolate on a Si surface seems to be determined by the cleavage of the C−S bond. This behavior is consistent with an observation that the temperature of dissociation of the CH_3-S bond is significantly less than that of CH_3-O, for which the bond energy of C−O is greater than that of C−S. Desorption of hydrogen with a maximum at 780 K reflects recombination of surface hydrogen produced on dissociation of the C_2H_5S-H bond and β-hydride elimination of C_2H_5 groups. This observation is consistent with previous results with a C_2H_5 group from C_2H_5Br adsorption on Si(100) proceeding through a β-elimination reaction on the surface to form C_2H_4.[36−38]

For a comparison of adsorption density of alkanethiols with varied lengths of alkyl chain, Figure 7 shows XPS spectra recorded for Si surfaces exposed to CH_3SH, C_2H_5SH, and C_4H_9SH for 200 s at 115 K and subsequently heated to 170−200 K to remove physisorbed molecules. Assuming that the adsorption density of alkanethiol/ alkanethiolate is proportional to the ratio of S 2p-to-Si 2p intensity, we find that the ratio varies less than the chain length of an alkyl group. Hence, alkanethiols (CH_3SH, C_2H_5SH, and C_4H_9SH) adsorb on the Si surface with the alkyl group away from the surface, instead of lying on the surface. This deduction is consistent with an argument that dissociation of thiolate is determined by the C−S cleavage and

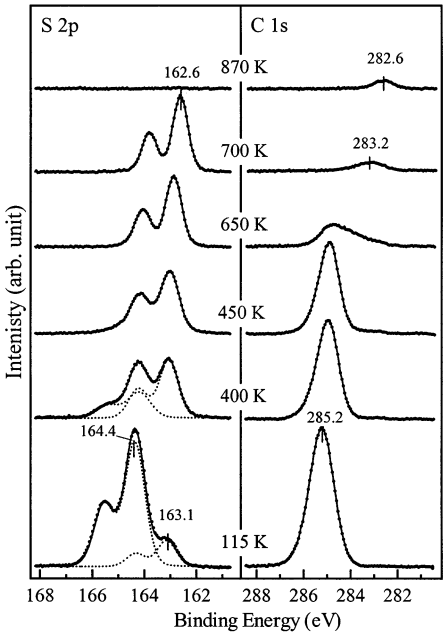

Figure 8. XPS spectra of S 2p and C 1s for a Si(100) surface exposed to C_2H_5SH for 30 s at 115 K and subsequently heated to the indicated temperatures.

is little affected by the interaction between the Si surface and an alkyl group as observed on a metallic surface.

Figure 8 shows S 2p and C 1s XPS spectra of a Si(100) surface exposed to C_2H_5SH at 115 K for 30 s, so that it became saturated with chemisorbed C_2H_5S and C_2H_5SH, as a function of surface temperature. The S 2p spectrum at 115 K contains two S $2p_{3/2}$ features at 163.1 and 164.4 eV due to adsorbed C_2H_5SH and C_2H_5S. C_2H_5SH to a small proportion (15%) decomposes into C_2H_5S on the Si surface at the temperature of exposure, 115 K; C_2H_5SH seems slightly less reactive than CH_3SH. Between 170 and 450 K, the intensity of S $2p_{3/2}$ at 162.4 eV gradually increases, indicating deprotonation of chemisorbed C_2H_5SH. Annealing the sample to 650 K causes a rapid decrease of C 1s intensity, accompanied by formation and desorption of C_2H_4. In addition, the spin−orbit doublet of S 2p becomes sharper, although its binding energy does not significantly alter. Consistent with TPD data, C_2H_5S decomposes to form surface sulfur and to desorb C_2H_4 via a concerted mechanism of

breaking of the C_2H_5-S bond and β-hydride elimination. At 700 K, all C_2H_5S decomposes into surface sulfur. The C 1s feature becomes weaker and shifts to 283.2 eV, because a small proportion of C_2H_5 moiety transfers onto the surface. At 870 K, surface sulfur is desorbed from the surface as SiS and the surface C_2H_5 group dehydrogenates to form surface carbon with C 1s at 282.6 eV. The coverage of surface carbon remaining after decomposition of C_2H_5SH is less than for the case of CH_3SH, indicating that most C_2H_5 moieties undergo β-hydride elimination, rather than dehydrogenation.

Conclusion

TPD results show that H_2, CH_4, and SiS are desorbed from a Si surface during thermal decomposition of CH_3SH. XPS data indicate that dissociative adsorption of CH_3SH yields surface CH_3S and H on Si(100) at 400 K. The resulting CH_3S and H bind to dangling bonds without breaking the Si−Si bond of a dimer; the (2×1) surface structure is consequently preserved. Surface CH_3S dissociates further to form Si−S−Si and S−Si−S intermediates at temperatures above 550 K. Si monohydride is proposed to be the surface intermediate, corresponding to desorption of hydrogen peaking at 780 K. C_2H_5SH shows similar behavior of adsorption and dissociation, although C_2H_5SH is slightly less reactive to deprotonation on the Si surface. At 550 K, decomposition of both CH_3S and C_2H_5S thiolates proceeds, to form surface S and to desorb CH_4 and C_2H_4, respectively; the rate of this reaction is determined by breaking of the C−S bonds. Formation of CH_4 results from reaction between surface H and the CH_3 moiety of CH_3S, and desorption of C_2H_4 occurs via β-hydride elimination of the C_2H_5 moiety of C_2H_5S.

Our results provide information about the adsorption and thermal reaction of alkanethiol/alkanethiolate on a Si surface, when introduced onto the Si surface through vapor deposition in UHV conditions. As expected from reaction mechanisms of CH_3SH and C_2H_5SH, other thiol molecules with inert alkyl groups (R−SH) can deprotonate and form a thiolate layer on heating to ~400 K. The resulting thiolate is incorporated with surface hydrogen and can sustain up to ~550 K, and might provide a passivation layer in the fabrication of electronic devices. This surface modification might extend potentially to immobilization of proteins and bio-molecules in the manufacture of biochips and biosensors, in which the thiol molecule with a second functional group, instead of the inert alkyl moiety, acts as a link to the Si surface via a covalent Si−S bond.

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