# Thermal and Photoinduced Covalent Attachment of 3-Chloro-1-propanol on Si(100)-2×1[†]

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3-Chloro-1-propanol (HO−CH₂−CH₂−CH₂−Cl) covalently binds onto Si(100)-2×1 through the thermal dissociation of the OH group to form Si−O−CH₂−CH₂−CH₂−Cl surface intermediates, evidenced by the appearance of the Si−H stretching mode (2110 cm⁻¹) and the retention of C−Cl stretching mode (654 cm⁻¹) in the high-resolution electron energy loss spectroscopy (HREELS) spectrum of chemisorbed 3-chloro-1-propanol molecules and the chemical downshift of O1s binding energy (BE) in the X-ray photoelectron spectroscopy (XPS) study. The C−Cl bonds in the chemisorbed 3-chloro-1-propanol can be cleaved upon 193 nm irradiation, resulting in Si−O−CH₂CH₂CH₂−CH₂CH₂CH₂−O−Si through lateral diradical coupling. Upon covering the chemisorbed 3-chloro-1-propanol with physisorbed molecules, photoinduced diradical coupling between physisorbed and chemisorbed molecules was also evidenced, achieving the secondary attachment of 3-chloro-1-propanol on the Si surface and forming Si−O−CH₂CH₂CH₂−CH₂CH₂CH₂−OH.

## Introduction

The construction of organic layers on semiconductor surfaces has been attracting much interest in the development of hybrid devices.[1−9] Recently, considerable efforts were devoted to graft multiple organic layers onto semiconductor surfaces with novel physical/chemical functionalities and desirable structures due to their potential technological applications. Bent et al.[10] and Bizter and Richardson[11] successfully demonstrated the feasibility of the continuous layer construction on Ge(100)-2×1 and Si(100)-2×1 surfaces through interfacial reactions of two bifunctional molecules. Cai and his co-workers demonstrated the photoinduced secondary organic attachment on Si(111)-7×7 surfaces.[12] In this work, we present a detailed study on the thermal and photoinduced chemical reactions of 3-chloro-1-propanol (Cl−CH₂CH₂CH₂−OH) on Si(100) to gain a better understanding of the secondary organic attachment on semiconductor surfaces.

Si(100) undergoes a (2×1) reconstruction involving the pairing of adjacent silicon atoms into dimers, forming rows of buckled surface dimers with the π-bond, zwitterionic, and diradical characters.[13,14] 3-Chloro-1-propanol (Cl−CH₂CH₂CH₂−OH) was selected to study photoinduced organic modification of the Si(100)-2×1 surface, because of its functionalities of C−Cl and C−OH groups. Experimentally, 3-chloro-1-propanol was found to react with the Si(100)-2×1 surface through the OH group dissociation, developing the well-defined Cl-terminated organic layer on the Si(100)-2×1 surface. The C−Cl bonds of chemisorbed species can be effectively dissociated using 193 nm photons and the newly formed surface C• radicals can undergo coupling reactions. In the case that physisorbed molecules are deposited on the chemisorption layer, the photoinduced radical coupling can also occur between the physisorbed and the chemisorbed molecules, resulting in secondary attachment.

## Experimental Methods

All experiments were performed in two separate ultrahigh vacuum (UHV) chambers with a base pressure of <2×10⁻¹⁰ Torr, achieved by turbo-molecular and ion pumps. One of them is equipped with a high-resolution electron energy loss spectrometer (HREELS, LK-2000-14R, LK Technologies, USA). For HREELS experiments, the electron beam with an energy of 5.0 eV impinges on the Si(100)-2×1 surface at an incident angle of 60° with a resolution of 7−8 meV [full width at half-maximum (fwhm), 60 cm⁻¹]. The X-ray photoelectron spectroscopy (XPS) studies were carried out in another chamber equipped with an X-ray source and a concentric hemispherical energy analyzer (CLAM2, VG). The XPS spectra were acquired using Al Kα radiation (*hν* = 1486.6 eV) and a pass energy of 20 eV. The binding energy (BE) scale is referenced to the peak maximum of the Si2p line (99.3 eV calibrated for Au4f₇/₂) of a clean Si(100)-2×1 sample with a fwhm of 1.2 eV.[15] Meanwhile, an ArF excimer laser (COMPex102 multigas *λ* Physik) was used as a UV light source in the surface photochemical reaction. During the course of the experiment, the laser with an intensity of 0.04 W·cm⁻² and frequency of 10 Hz was introduced into the UHV chamber through a quartz viewport (UV grade sapphire, MDC). The surface photoreaction can be normally followed by detecting the surface species or reaction products during or after irradiation.[16] In this study, the surface analysis techniques, such as HREELS and XPS, were employed to detect the products retained on the surface after irradiation.

The Si(100) samples with a dimension of 20 × 8 × 0.38 mm³ were cut from p-type boron-doped silicon wafers (purity ∼99.999%, thickness ∼0.38 mm, resistivity 1−30 Ω·cm, Goodfellow). A tantalum (Ta) sheet resistive heater (thickness ∼0.025 mm, Goodfellow) was sandwiched between two Si(100) crystals held together using Ta clips and in turn spot-welded to Ta posts at the bottom of a Dewar-type liquid nitrogen (N₂) cooled sample holder. The crystals can be resistively heated to 1300 K and cooled to 110 K using liquid N₂. The clean Si(100)-2×1 surfaces were prepared by degassing at 850 K, Ar ion sputtering (36 min, 500 eV, and 10 μA·cm⁻²), and final annealing to 1300 K for 5 min in UHV. The cleanliness of the samples was verified using XPS and HREELS. The surface
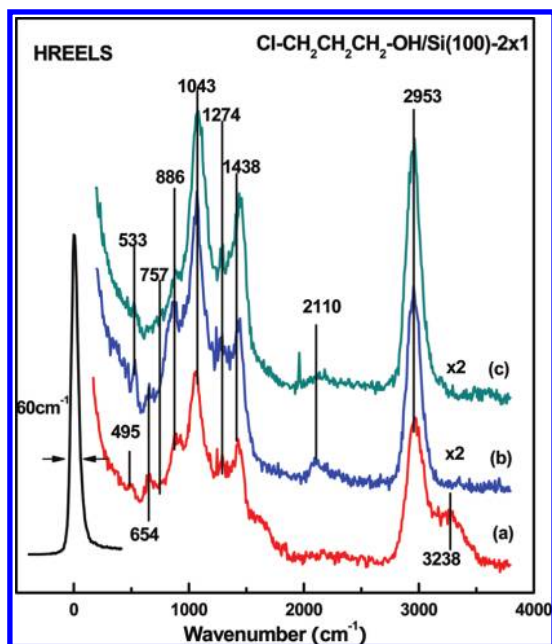
**Figure 1.** HREELS spectra obtained on the Si(100)-2×1 surface at 110 K: (a) condensed EELS spectrum, obtained by exposing 4 langmuir 3-chloro-1-propanol; (b) chemisorbed 3-chloro-1-propanol obtained by annealed sample a to 250 K; and (c) irradiating sample b for 30 min using the 193 nm laser.

structure was examined using scanning tunneling microscopy (STM) in a separate chamber.

The 3-chloro-1-propanol (98%, Merck) was purified by several freeze−pump−thaw cycles before being dosed onto the Si(100)-2×1 surface through an adjustable leak valve. The exposures reported here are in the unit of Langmuir (1 langmuir = $1 \times 10^{-6}$ Torr·s) without the calibration of ion gauge sensitivity. All of the HREELS and XPS spectra mentioned in this paper were collected at 110 K.

**Results and Discussion**

**1. Photoinduced Reaction of Chemisorbed 3-Chloro-1-propanol on Si(100)-2×1.** Figure 1 shows the vibrational spectra of 3-chloro-1-propanol on the Si(100)-2×1 surface. The HREELS spectrum of physisorbed molecules (Figure 1a) was obtained by exposing 4 langmuir 3-chloro-1-propanol onto the Si(100)-2×1 surface at 110 K. The loss peaks (Figure 1a) at 495, 654, 757, 886, 1043, 1274, 1438, 2953, and 3238 cm$^{-1}$ are readily resolved and are consistent with the Fourier transform infrared (FT-IR) spectrum for liquid 3-chloro-1-propanol.[17] Until now, the complete assignments of the vibrational features of 3-chloro-1-propanol were not available in the literature. We made the vibrational assignments for the physisorbed and chemisorbed molecules by referring to the FT-IR spectra, Raman spectra, and the frequency calculation of Cl−CH$_2$CH$_2$CH$_3$ and CH$_3$CH$_2$CH$_2$OH.[18,19] Among these vibrational features presented in Figure 1a, the intensity at 3238 cm$^{-1}$ is assigned to the stretching mode of the −OH group. The loss feature at 654 cm$^{-1}$ can be ascribed to the C−Cl stretching mode.[18,20,21] The C−O stretching band is visible at 1043 cm$^{-1}$, which is in the range of 1000−1100 cm$^{-1}$ of the C−O stretching mode for chemisorbed methanol on Fe$_2$O$_3$ powders and aluminum oxide.[22,23]

The chemisorbed spectrum of 3-chloro-1-propanol, obtained by annealing the physisorbed 3-chloro-1-propanol covered sample to 250 K, is presented in Figure 1b. The chemisorbed spectrum shows different spectral features with the absence of the O−H stretching mode at 3238 cm$^{-1}$ and with the appearance

of a new peak at 2110 cm$^{-1}$, which could be assigned to the stretching mode of the Si−H bond.[24−26] This indicates that the −OH group dissociates upon chemisorption. The appearance of another new peak at 533 cm$^{-1}$, which is attributable to the stretching of Si−O bond,[27] further supports the cleavage of the −OH group. The retention of the C−Cl stretching mode at 654 cm$^{-1}$ is indicative of the intact of C−Cl bonds on the surface. The loss peaks at 2953, 1438, 1274, and 757 cm$^{-1}$ can be attributed to the asymmetric stretching mode, deformation stretching mode, twisting mode, and rocking mode of the −CH$_2$− group, respectively, implying that the −CH$_2$− group is retained at the surface.[28] The C−C−C skeleton vibrational stretching mode appears at 886 cm$^{-1}$, suggesting the integrality of the main skeleton of 3-chloro-1-propanol upon chemisorption. The detailed vibrational assignments for physisorbed and chemisorbed 3-chloro-1-propanol on Si(100)-2×1 are presented in Table 1.

Figure 1c presents the vibrational features of chemisorbed 3-chloro-1-propanol on the Si(100)-2×1 surface after 193 nm laser irradiation for 30 min. Compared to the chemisorbed spectrum before laser irradiation (Figure 1b), most of the vibrational features in the photoinduced HREELS spectrum (Figure 1c) remain unchanged, except for the disappearance of the C−Cl stretching mode (654 cm$^{-1}$). This strongly suggests that only the C−Cl bond on the surface is cleaved during the laser irradiation. The newly generated C· radical would react with its neighboring C· radical to form the possible surface intermediate Si−O−CH$_2$CH$_2$CH$_2$−CH$_2$CH$_2$CH$_2$−O−Si or react with the dangling bonds on Si(100)-2×1 surface to form Si−O−CH$_2$CH$_2$CH$_2$−Si, which can be resolved in the following XPS studies. The existence of the Si−H stretching mode (2110 cm$^{-1}$) in Figure 1c implies that most of the Si−H linkages are retained. Pusel et al. reported a nonthermal H−Si dissociation from the H−Si(100) surface upon irradiation of photons at 7.9 eV.[29] Zhu and Vondrak subsequently reported that the irradiation energy of approximate 8 eV is attributed to the energy of H−Si $\sigma \rightarrow \sigma^*$ transition.[30] However, the photon energy at our surface is 6.4 eV (193 nm), which is less than the initial excitation energy of H−Si $\sigma \rightarrow \sigma^*$ transition (7.9 eV). This is also because the interaction of ·CH$_2$ radical and ·CH$_2$ radical is spontaneous and has no energy barrier. The reaction of the ·CH$_2$ radical capture of the H atoms from the surface is possible, but this reaction has steric hindrance as well as an energy barrier. So, the direct radical−radical coupling reaction will be predominant, and most of Si−H bonds remain on the surface. This is consistent with the existence of vibrational peaks at 2110 cm$^{-1}$ in Figure 1c, suggesting the retention of H−Si bonds at the surface upon irradiation. In the meantime, some subtle changes also appear in Figure 1c, such as the decreasing peak intensity of Si−O and Si−H bonds and the variable peak shapes in the range of 886−1438 cm$^{-1}$. It is well-known that the well-accepted dimer model of Si(100)-2×1 surface shows that the dimer rows are in parallel arrangement and dimers are alternating tilted. Thus, it is presumed that the adsorption of the first chemisorbed 3-chloro-1-proponal layer on the Si(100)-2×1 surface is compact and in the alternative arrangement by one hydrogen (H) atom and one −OCH$_2$−CH$_2$CH$_2$Cl species. The interaction of the photogenerated ·CH$_2$ radical with its neighboring ·CH$_2$ radical makes the surface H atoms become partially covered and makes the reflection probability lower; thus, the corresponding Si−H stretching peak intensity declines. In the same way, the interaction of radicals would also cover the part of Si−O bonds at the bottom layer on the surface, leading to the decreasing Si−O peak intensity after laser irradiation. In

**TABLE 1: Vibrational Assignments of Physisorbed and Chemisorbed 3-Chloro-1-propanol, Laser-Induced 3-Chloro-1-propanol, and Photo-Generated Construction of the Second 3-Chloro-1-propanol Layer on Si(100)-2×1[a]**

| vibrational assignment | IR for 1-chloropropane[b] | IR for 1-propanol[c] | physisorbed 3-chloro-1-propanol on Si(100)-2×1[d] | chemisorbed 3-chloro-1-propanol on Si(100)-2×1[d] | postlaser irradiated 3-chloro-1-propanol chemisorption on Si(100)-2×1[d] | second layer of 3-chloro-1-propanol construction on Si(100)-2×1[d] |
|---|---|---|---|---|---|---|
| $\nu$ (OH) | | 3687 | 3238 | | | 3238 |
| $\nu_{as}$ (CH$_2$) | 2956 | 2946 | 2953 | 2953 | 2953 | 2953 |
| $\nu_{s}$ (CH$_2$) | 2879 | 2876 | | | | |
| $\delta_{s}$ (CH$_2$) | 1433 | | 1438 | 1438 | 1438 | 1438 |
| $\omega$ (CH$_2$) | 1299 | 1393 | 1274 | 1274 | 1274 | 1274 |
| $\tau$ (CH$_2$) | 1263 | 1237 | 1274 | 1274 | 1274 | 1274 |
| $\nu$ (OC) | | 971 | 1043 | 1043 | 1043 | 1043 |
| $\nu_{s}$ (CCC) | 899 | 898 | 886 | 886 | 886 | 886 |
| $\rho$ (CH$_2$) | 789 | 758 | 757 | 757 | 757 | 757 |
| $\nu$ (C−Cl) | 658 | | 654 | 654 | | |
| $\beta$ (CCC) | 425 | 463 | 495 | | | |
| $\nu$ (Si−O) | | | | 533 | 533 | 533 |
| $\nu$ (Si−H) | | | | 2110 | 2110 | 2110 |

*[a]* All frequencies are in cm$^{-1}$. *[b]* Ref 18. *[c]* Ref 19. *[d]* Present work.
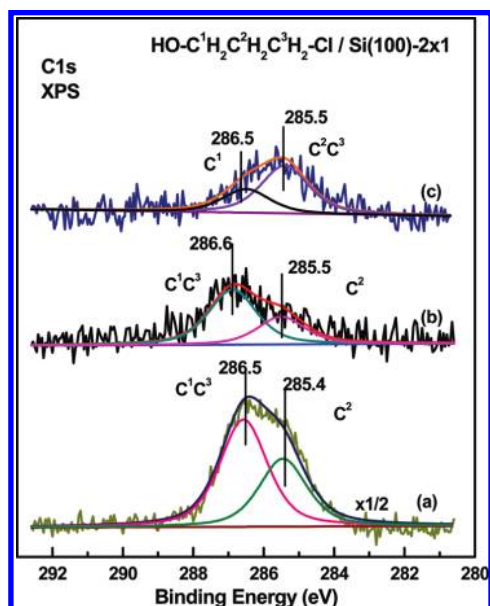


**Figure 2.** Fitted C1s XPS spectra on Si(100)-2×1 at 110 K: (a) physisorbed spectrum, obtained by pre-exposing 4 langmuir of 3-chloro-1-propanol onto Si(100)-2×1; (b) chemisorbed spectrum, obtained by annealing sample a to 300 K; and (c) irradiating sample b for 30 min using the 193 nm laser.

the meantime, the interaction of the •CH$_2$ radical with its neighboring •CH$_2$ radical in the same dimer row or neighboring dimer row also makes the surface irregular, resulting in the mirror scattering ratio becoming even smaller. Thus, the decreased resolution probability may result in some geometrical rearrangement on the surface, as well as changed peak positions.

XPS studies were also carried out, providing information on the changes of electronic properties of 3-chloro-1-propanol on Si(100)-2×1. The C1s XPS results for physisorbed and chemisorbed 3-chloro-1-propanol (Cl−C$^1$H$_2$−C$^2$H$_2$−C$^3$H$_2$−OH), as well as the photogenerated products on Si(100)-2×1, are shown in Figure 2. The C1s XPS spectrum for physisorbed molecules (Figure 2a) is deconvoluted into two peaks centered at 286.5 and 285.4 eV with an equal fwhm of 1.6 eV and an area ratio of approximately 2:1, in excellent agreement with the results for the condensed 3-chloro-1-propanol on the Si(111)-7×7 surface.[6] The detailed assignment for physisorbed and chemisorbed 3-chloro-1-propanol on the Si(100)-2×1 surface is tabulated in Table 2. Because of the higher electronegativities of O (3.5, Pauling scale) and Cl (3.2) atoms,[31] their neighboring

C atoms are expected to have a lower electron density and subsequently have a higher BE. Therefore, the C$^1$ and C$^3$ atoms attached to the O and Cl atoms in HO−C$^1$H$_2$C$^2$H$_2$C$^3$H$_2$−Cl contribute to the intensity at around 286.5 eV.[23,32] The photoemission feature at 285.4 eV is associated with the C$^2$ atom in the −CH$_2$− group. The C1s photoemission spectrum (Figure 2b) of the chemisorbed state can also be fitted into two peaks with comparable binding energies at 286.6 and 285.5 eV. Their similarities indicate that the local chemical environments for C atoms are not significantly different between the physisorption and the chemisorption states, implying the retention of the C−Cl and C−O bonds upon surface binding.

Figure 2c exhibits the C1s core level spectrum obtained after irradiating the chemisorbed 3-chloro-1-propanol on Si(100)-2×1 with 193 nm. Compared to the chemisorbed spectrum of 3-chloro-1-propanol on Si(100)-2×1 (Figure 2b), the laser irradiation caused significant spectrum changes. The reduction of the intensity at the higher BE (286.5 eV) is accompanied by the growth at the lower BE (285.5 eV). The peak area ratio (286.5 eV vs 285.5 eV) changes from 2:1 to 1:2. The BE at 286.5 eV is attributed to the C$^3$ atom adjacent to the O atom, while the value at 285.5 eV is assigned to the C$^1$ and C$^2$ atoms that are further away from the O atom in the C$^1$−C$^2$−C$^3$−O skeleton. The significant chemical downshift of 1.1 eV of the C$^1$ atom after laser irradiation suggests the photodissociation of the C−Cl bonds. The BE for the C$^1$ atom (285.5 eV) is significantly higher than that for the atom in the typical Si−CH$_2$− species (283.7−284.0 eV).[33,34] Thus, the newly formed •CH$_2$− from the cleavage of −CH$_2$−Cl bond is not directly bonded to the Si surface, but rather forming a Si−O−CH$_2$CH$_2$CH$_2$−CH$_2$CH$_2$CH$_2$−O−Si-like structure through the lateral C−C coupling of two neighboring molecular radicals. The identical areas of total C1s photoemissions before and after laser irradiation unambiguously exclude the possibility of photoinduced desorption.

Figure 3 exhibits the O1s XPS spectra of 3-chloro-1-propanol on Si(100)-2×1. The symmetric O1s peak at 533.1 eV for physisorbed molecules (Figure 3a) is consistent with the previous studies of physisorbed methanol on zinc oxide.[35] However, the O1s BE in the chemisorption spectrum (Figure 3b) downshifts to 532.2 eV, which strongly suggests the cleavage of the −OH group and the formation of Si−O linkage.[27,36] Compared to the chemisorbed spectrum (Figure 3b), the O1s photoemission feature in Figure 3c is almost unchanged,

**TABLE 2: Deconvoluted Results of XPS Spectra for Physisorbed and Chemisorbed 3-Chloro-1-propanol, Laser-Induced 3-Chloro-1-propanol Chemisorption, and Photo-Generated Construction of the Second 3-Chloro-1-propanol Layer on Si(100)-2×1[a]**

| $HO^2-C^6H_2C^5H_2C^4H_2-Cl/$ $ClC^3H_2C^2H_2C^1H_2O^1H$ | first layer physisorption | first layer chemisorption | postlaser irradiated chemisorption | second layer of 3-chloro-1-propanol |
|---|---|---|---|---|
| $C^1 1s$ | 286.5 | 286.6 | 286.5 | 286.6 |
| $C^2 1s$ | 285.4 | 285.5 | 285.5 | 285.2 |
| $C^3 1s$ | 286.5 | 286.6 | 285.5 | 285.2 |
| $C^4 1s$ | | | | 285.2 |
| $C^5 1s$ | | | | 285.2 |
| $C^6 1s$ | | | | 286.6 |
| $Cl(2p_{3/2})$ | 200.3 | 200.4 | N.A.[b] | N.A. |
| $O^1 1s$ | 533.1 | 532.2 | 532.3 | 531.9 |
| $O^2 1s$ | | | | 533.1 |

[a] All energies are eV. [b] N.A. stands for not available.
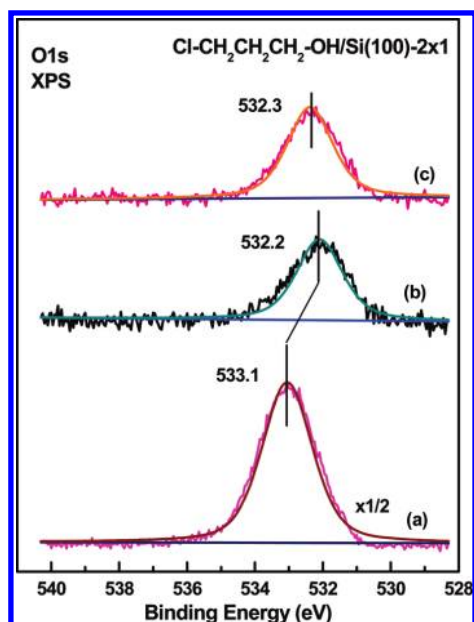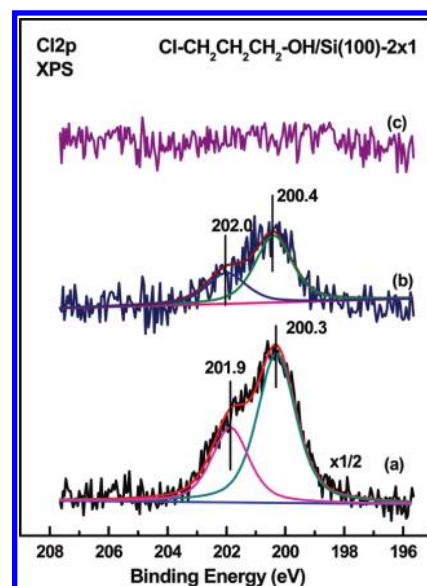


**Figure 3.** Deconvoluted O1s XPS spectra on Si(100)-2×1 at 110 K: (a) physisorbed spectrum, obtained by pre-exposing 4 langmuir of 3-chloro-1-propanol onto Si(100)-2×1; (b) chemisorbed spectrum, obtained by annealing sample a to 300 K; and (c) irradiating sample b for 30 min using the 193 nm laser.



**Figure 4.** Fitted Cl2p XPS spectra on Si(100)-2×1 at 110 K: (a) physisorbed spectrum, obtained by pre-exposing 4 langmuir of 3-chloro-1-propanol onto Si(100)-2×1; (b) chemisorbed spectrum, obtained by annealing sample a to 300 K; and (c) irradiating sample b for 30 min using the 193 nm laser.

suggesting that the Si—O bonds are intact at the surface after photon irradiation.

Figure 4 presents the Cl2p XPS photoemission features. The physisorbed 3-chloro-1-propanol molecules on the Si(100)-2×1 surface (Figure 4a) at 110 K give rise to Cl2p$_{3/2}$ and Cl2p$_{1/2}$ lines centered at 200.3 and 201.9 eV, respectively. The Cl2p$_{3/2}$ BE (200.3 eV) is consistent with the previous studies of the C—Cl bonds.[37–39] Upon chemisorption, no significant chemical downshifts of Cl 2p can be identified in Figure 4b, suggesting the retention of the C—Cl bonds. The disappearance of the Cl 2p intensity after 193 nm irradiation for 30 min (Figure 4c) implies that the Cl atoms resulting from the photodissociation of the C—Cl bonds eject into gaseous phase. This is indeed consistent with our HREELS results.

In summary, our results clearly demonstrate that 3-chloro-1-propanol (Cl—C$^1$H$_2$—C$^2$H$_2$—C$^3$H$_2$—OH) chemisorbs onto Si(100)-2×1 through a dissociative reaction of —OH, resulting in Si—H and Cl—C$^1$H$_2$—C$^2$H$_2$—C$^3$H$_2$—O—Si. This mechanism is supported by the large downshift (0.9 eV) of O1s and the O—Si vibration mode at 533 cm$^{-1}$. The comparable binding energies of the Cl and C atoms in the chemisorbed and physisorbed XPS spectra support the dissociation of the O—H group and the retention of the C—C—C skeleton and the C—Cl bond at the surface. The photodissociation of C—Cl bonds generates C· radicals on the surface, which combine to form Si—O—CH$_2$CH$_2$CH$_2$—CH$_2$CH$_2$CH$_2$—O—Si.

**2. Photoinduced Secondary Attachment of 3-Chloro-1-propanol on Si(100)-2×1.** As discussed above, the saturated chemisorption layer of 3-chloro-1-propanol molecules on the Si(100)-2×1 surface with the terminal C—Cl bonds protruding into the vacuum is formed through the dissociation of the —OH group. The subsequent 10 langmuir of 3-chloro-1-propanol molecules were then physisorbed onto the first chemisorbed layer at 110 K. The surface was subject to laser irradiation at 193 nm, followed by annealing the surface to 250 K to desorb the unreacted physisorbed molecules and retain the photoinduced 3-chloro-1-propanol layer attached on the Si(100) surface.

Figure 5 compares the vibrational features of chemisorbed molecules with the photogenerated layer of 3-chloro-1-propanol molecules on the Si(100)-2×1 surface. The vibrational losses at 533, 757, 886, 1043, 1274, 1438, 2110, 2953, and 3238 cm$^{-1}$ can be clearly observed in Figure 5b. When the physisorbed 3-chloro-1-propanol molecules (same exposure as for Figure 5b) were condensed on the 3-chloro-1-propanol modified Si(100)-2×1 surface without laser irradiation on the surface, the purely physisorbed EELS spectrum (identical to Figure 1a)
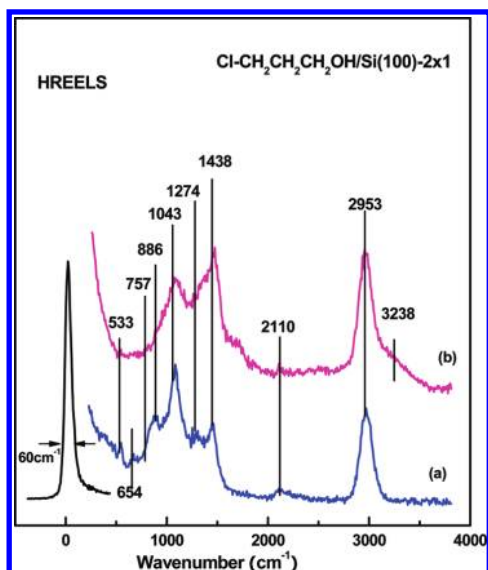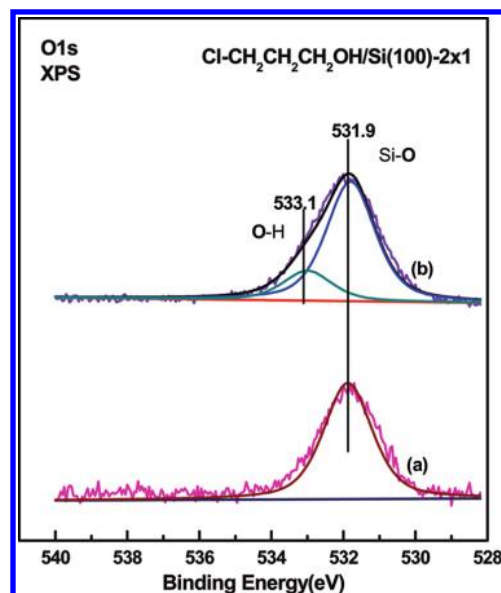
**Figure 5.** HREELS spectra on the Si(100)-2×1 surface at 110 K: (a) chemisorbed spectrum obtained by annealing the 3-chloro-1-propanol covered Si(100) surface to 250 K; (b) irradiating the condensed 3-chloro-1-propanol (10 langmuir) on sample a using the 193 nm laser for 30 min followed by annealing to 250 K.
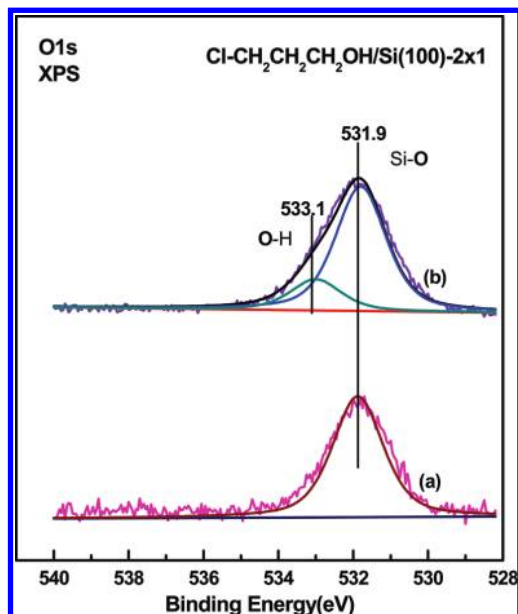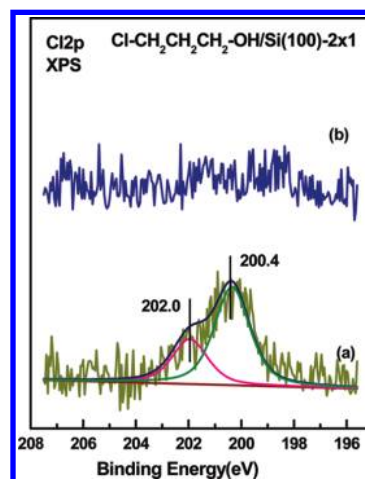


**Figure 6.** Fitted O1s XPS spectra on the Si(100)-2×1 surface at 110 K: (a) chemisorbed spectrum obtained by annealing the 3-chloro-1-propanol covered Si(100) surface to 250 K; (b) irradiating the condensed 3-chloro-1-propanol (10 langmuir) on sample a using the 193 nm laser for 30 min followed by annealing to 250 K.



**Figure 7.** Fitted C1s XPS spectra on the Si(100)-2×1 surface at 110 K: (a) chemisorbed spectrum obtained by annealing the 3-chloro-1-propanol covered Si(100) surface to 250 K; (b) irradiating the condensed 3-chloro-1-propanol (10 langmuir) on sample a using the 193 nm laser for 30 min followed by annealing to 250 K.



**Figure 8.** Deconvoluted Cl2p XPS spectra on the Si(100)-2×1 surface at 110 K: (a) chemisorbed spectrum obtained by annealing the 3-chloro-1-propanol covered Si(100) surface to 250 K; (b) irradiating the condensed 3-chloro-1-propanol (10 langmuir) on sample (a) using the 193 nm laser for 30 min followed by annealing to 250 K.

was presented. When the surface was subsequently annealed to 300 K, the purely chemisorbed EELS spectrum (identical to Figure 5a) was found, suggesting that the covalently bonded 3-chloro-1-propanol molecules were triggered by photons. Compared to the spectrum of the chemisorbed 3-chloro-1-propanol monolayer on a clean Si(100)-2×1 (Figure 5a), a new peak at 3238 cm$^{-1}$ appears after photoirradiation, which can be assigned to the OH stretching vibration mode. The presence of the OH group in the covalently bonded surface layer suggests the participation of physisorbed molecules in photoinduced surface reactions. The absence of the C−Cl stretching mode (654 cm$^{-1}$) in Figure 5b implies that the surface reactions may be initiated by the photodissociation of the C−Cl bonds in the physisorbed and chemisorbed molecules. The observation of the

−CH$_2$− asymmetric stretching mode (2953 cm$^{-1}$), deformation stretching mode (1438 cm$^{-1}$), twisting mode (1274 cm$^{-1}$), and rocking mode (757 cm$^{-1}$) at the surface (Figure 5b) points to a saturated carbon chain-like structure. The C−O stretching intensity in Figure 5b is relatively weaker compared with that in Figure 5a. Similar to our discussion on a postlaser irradiative EELS spectrum (Figure 1c), the photoinduced covalent attachment of a second layer on the 3-chloro-1-propanol modified Si(100)-2×1 surface may also cover part of Si−O−C bonds at the bottom layer and decrease its corresponding peak intensity; thus, the (Si)O−C stretch intensity in the EELS spectrum (Figure 5b) declines. The vibrational assignments for a photogenerated covalent layer of 3-chloro-1-propanol are listed in Table 1. Our HREELS results suggest the formation of the possible structure of Si−O−CH$_2$CH$_2$CH$_2$−CH$_2$CH$_2$CH$_2$−O−H induced by a photoreaction between the physisorbed and the chemisorbed molecules. However, the coexistence of Si−O−CH$_2$CH$_2$CH$_2$−
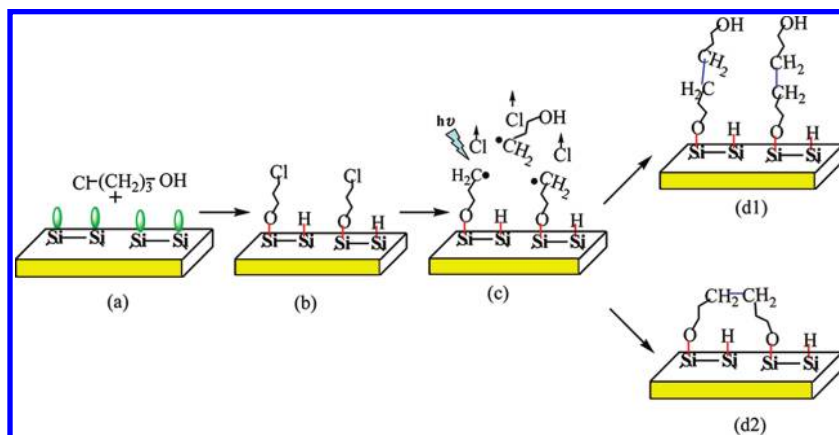
**Figure 9.** Proposed schematic reaction model: (a) 3-chloro-1-propanol pre-exposed onto Si(100)-2×1; (b) chemisorbed 3-chloro-1-propanol on Si(100)-2×1; (c) the interaction of the radicals by photodissociation of 3-chloro-1-propanol; and (d1) the formation of the second covalently bonded organic layer or (d2) the formation of a molecular loop on Si(100)-2×1.

$CH_2CH_2CH_2-O-Si$ resulting from the photoinduced lateral coupling of chemisorbed species cannot be excluded.

Figure 6b shows the O1s photoemission spectra for a photogenerated 3-chloro-1-propanol layer on the Si(100)-2×1 surface. Compared to the symmetric peak of Figure 6a, the O1s XPS features in Figure 6b are asymmetric and broader, suggesting the existence of two chemically inequivalent O atoms at the surface after laser irradiation. The spectra can be deconvoluted into two peaks at 531.9 and 533.1 eV with an area ratio of 3:1. The peak at 531.9 eV is assigned to the $O^2$ atom that is directly attached to the Si surface. This is in excellent agreement with the BE (531.8 eV) of $CH_3O-Si$ formed through the dissociative reaction of the hydroxyl group for methanol on the Si(100)-2×1 surface.[40] The existence of the higher BE at 533.2 eV, which is a typical O1s XPS value for the O atom in the dangling OH group, confirmed the formation of covalently grafted $Si-O^2-CH_2CH_2CH_2-CH_2CH_2CH_2-O^1H$-like structure. The additional intensity at 531.9 eV can be attributed to the coexistence of $Si-O-CH_2CH_2CH_2-CH_2CH_2CH_2-O-Si$. The ratio of these two species is ~1:1. This observation also suggests that about one-third of chemisorbed molecules reacted with the physisorbed layer to result in the secondary attachment, and the remaining two-thirds went through the lateral C−C coupling among themselves. This discussion is further supported by the C1s XPS results. Figure 7 depicts the C1s photoemission spectra for the chemisorbed and the photogenerated 3-chloro-1-propanol layer on the Si(100)-2×1 surface. Figure 7b was obtained by 193 nm photons, irradiating the condensed 3-chloro-1-propanol molecules on the chemisorbed layer for 30 min by annealing to 250 K, indicating the thermal stability of the photogenerated layer. The C1s photoemission spectrum for the photogenerated layer can be deconvoluted into two peaks at 285.2 and 286.6 eV with an area ratio of 2:1. The BE at 286.6 eV is attributed to the $C^1$ and $C^6$ atoms in the proposed structures of $Si-O^2$-$C^1H_2C^2H_2$ $C^3H_2-C^4H_2C^5H_2C^6H_2-O^1H$ and $Si-O-C^1H_2C^2H_2$ $C^3H_2-C^4H_2C^5H_2C^6H_2-O-Si$. The peak at 285.2 eV is assigned to the $C^2-C^5$ atoms that are not directly bonded to the O atom in the proposed structures. It is obvious that the peak area for the photogenerated layer (Figure 7b) is larger than that for a chemisorbed monolayer (Figure 7a), and their corresponding peak area ratio is about 4:3, which matches with O1s peak area ratio well. There is no noticeable amount of Cl remaining in the photogenerated layer (Figure 8), further confirming the C−C coupling reaction mechanism through the photoinduced C−Cl

bond dissociation. The proposed reaction process is schematically described in Figure 9.

## Conclusions

The experimental investigations demonstrate that 3-chloro-1-propanol selectively binds to Si(100)-2×1 through the dissociation of the OH group and the formation of the Si−O and Si−H linkages at the surface. The intact C−Cl group is cleaved by 193 nm irradiation, creating surface bound $Si-O-CH_2-CH_2-CH_2-CH_2\cdot$ radicals and Cl atoms (gas). The lateral C−C coupling of the radicals results in the formation of a molecular loop tied to the surface, $Si-O-CH_2CH_2CH_2-CH_2CH_2CH_2-O-Si$. The presence of physisorbed molecules on the chemisorbed layer opens an additional reaction pathway, coupling between $Si-O-CH_2-CH_2-CH_2-CH_2\cdot$ in the chemisorbed layer and $H-O-CH_2-CH_2-CH_2-CH_2\cdot$ present among physisorbed molecules, to form the $Si-O-CH_2CH_2CH_2-CH_2CH_2CH_2-OH$ standing on the surface.

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