Chemical Physics Letters 482 (2009) 77–80

Contents lists available at ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Spectroscopic study of propargyl chloride attachment on Si(1 0 0) – 2 × 1

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ARTICLE INFO

Article history:
Received 19 August 2009
In final form 25 September 2009
Available online 30 September 2009

ABSTRACT

The vibrational and electronic features of propargyl chloride ($HC{\equiv}C{-}CH_2Cl$) attached on the Si(1 0 0) – 2 × 1 surface have been investigated using high resolution electron energy loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy (XPS). The disappearance of the C—Cl stretching mode and the existence of $\equiv C^{sp}{-}H$ and $-C{\equiv}C$ stretching modes in the HREELS spectra of chemisorbed molecules strongly demonstrate the cleavage of C–Cl bonds and the retention of $-C{\equiv}CH$ linkage upon the chemisorption, further supported by the changes of the electronic features in chemisorbed XPS spectra.

1. Introduction

Organic functionalization of semiconductor surfaces has been widely investigated in connection with its technological relevance in molecular electronics, biosensors and nanotechnology [1–3]. To realize these potential applications, it is necessary to gain a fundamental understanding of attachment chemistry of organic molecules on semiconductor surfaces at a molecular level. Si(1 0 0) has attracted a great deal of attention due to its extraordinary importance in the integrated chips manufacturing [4–13]. It 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 [14,15].

There are three possible reaction routes for the adsorption of propargyl chloride on Si(1 0 0) – 2 × 1, namely, (a) [2 + 2]-like cycloaddition through the $C{\equiv}C$ group (Fig. 1a); (b) simple dissociation of the C—Cl bond to form Si—Cl and $Si{-}CH_2{-}C{\equiv}CH$-like species (Fig. 1b); (c) end-like reaction leading to the formation of $Si{-}CH_2{=}C{=}CH_2$-like and Si—Cl species (Fig. 1c). In this communication, we report the formation of a $HC{\equiv}C{-}CH_2{-}$ structure through the dissociative reaction of the C—Cl bond in the attachment of propargyl chloride on Si(1 0 0) – 2 × 1 based on our investigations using high resolution electron energy loss spectroscopy (HREELS) and X-ray photoelectron spectroscopy (XPS).

2. Experimental

The experiments were performed in two separate ultra-high vacuum (UHV) chambers with a base pressure of $<2 \times 10^{-10}$ Torr. One of them is equipped with a high resolution electron energy loss spectroscopy (HREELS, LK-2000-14R, LK Technologies, USA). For HREELS experiments, the electron beam with an energy of 5.0 eV impinges on the Si(1 0 0) – 2 × 1 surface at an incident angle of 60° with a resolution of 6–7 meV (FWHM, 55 cm^{-1}). The XPS studies were carried out in another chamber equipped with an X-ray source and a concentric hemispherical energy analyzer (CLAM2, VG). The spectra were acquired using Al Kα radiation ($h\upsilon = 1486.6$ eV) and a pass energy of 20 eV. The binding energy (BE) scale is referenced to the peak maximum of the Si 2p line (99.3 eV) of a clean Si(1 0 0) – 2 × 1 substrate [16].

The Si(1 0 0) samples (20 mm × 8 mm × 0.38 mm) were cut from p-type boron-doped silicon wafers (purity ∼99.999%, thickness ∼0.38 mm, resistivity 1–30 Ω · cm, Goodfellow). A Ta-sheet resistive heater (thickness ∼0.025 mm, Goodfellow) was sandwiched between two Si(1 0 0) crystals held together using Ta clips, and in turn spot-welded to Ta posts at the bottom of a Dewar-type liquid nitrogen (N_2) cooled sample holder. The crystals can be resistively heated to 1300 K and cooled to 110 K using liquid N_2. The clean Si(1 0 0) – 2 × 1 surfaces were prepared by overnight degassed at 850 K, cycles of Ar-ion sputtering (36 min at 500 eV and 10 μA · cm^{-2}), and final annealing to 1250 K for 5 min in UHV. The cleanliness of the samples was verified using XPS and HREELS. The surface structure was examined using STM in a separate chamber, showing a defect density of ∼5–10%.

The propargyl chloride (Aldrich, 98%) were purified by several freeze–pump–thaw cycles before being dosed onto the Si(1 0 0) – 2 × 1 surface through an adjustable leak valve. The exposures are reported here in the unit of Langmuir ($1\ L = 1 \times 10^{-6}$ Torr · s) without the calibration of ion gauge sensitivity.

3. Results and discussion

The vibrational features of physisorbed and chemisorbed propargyl chloride on Si(1 0 0) – 2 × 1 are shown in Fig. 2. The physisorbed HREELS spectrum (Fig. 2a), which was obtained by preexposing 4 L propargyl chloride onto the Si(1 0 0) – 2 × 1 surface at 110 K, correlates well with the calculated normal vibrations

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doi:10.1016/j.cplett.2009.09.080

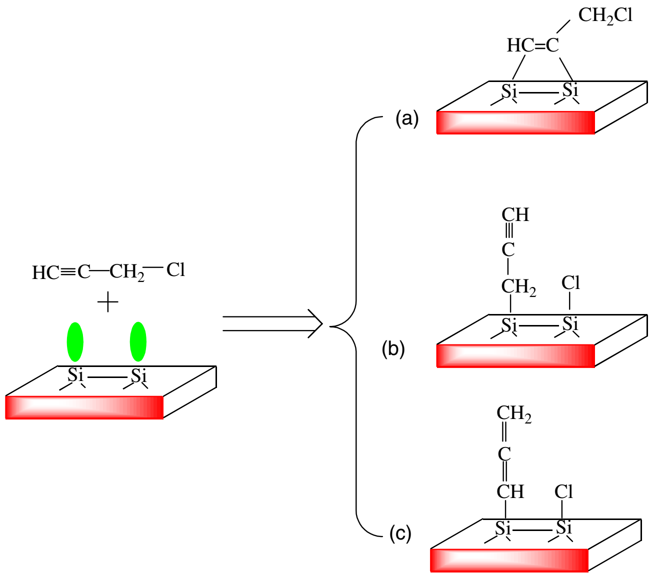

Fig. 1. Possible reaction pathways for the attachment of propargyl chloride on $Si(1\,0\,0)-2\times1$.

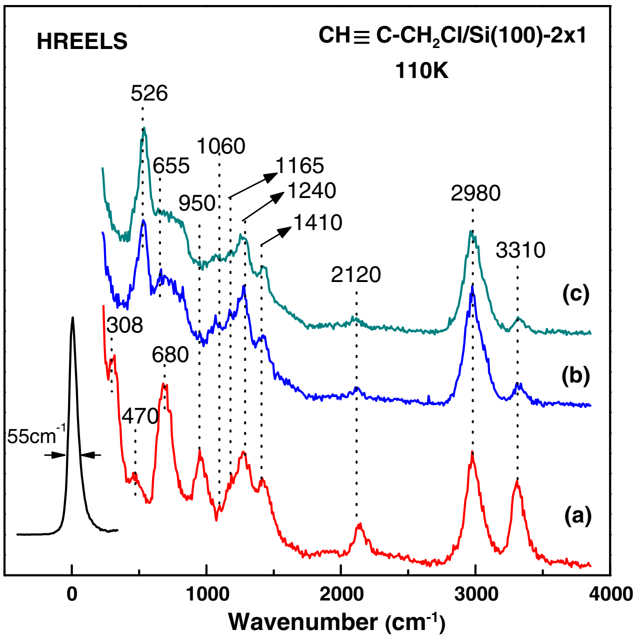

Fig. 2. The HREELS spectra obtained after pre-exposure of 4 L propargyl chloride on $Si(1\,0\,0)-2\times1$ at 110 K (a) and annealing the sample in (a) to 200 K (b) and 300 K (c). $E_p = 5.0$ eV; specular mode.

and FTIR spectra for propargyl chloride in liquid phase [17–20]. The loss peaks at 308, 470, 680, 950, 1060, 1165, 1240, 1410, 2120, 2980, and 3310 cm^{-1} are clearly resolved in the physisorbed HREELS spectrum. The intensities at 3310 and 1060 cm^{-1} can be assigned to the stretching and bending modes of the ≡CH group, respectively [18,19]. The vibrational frequency at 2120 cm^{-1} is related to the C≡C stretching mode [21,22]. The C—Cl stretching at 680 cm^{-1} agrees well with the previous studies [23]. The intensities at 308 and 470 cm^{-1} can be ascribed to the deformation of C—C—C skeleton and bending mode of C–C–Cl, respectively [17,19].

The sample covered with physisorbed propargyl chloride molecules was annealed to 200 and 300 K to obtain the spectra of saturated chemisorption monolayer (Figs. 2b and c). The loss features at 3310, 2980, 2120, 1410, 1240, 1165, 1060, 655, and 526 cm^{-1} are resolved in these two HREELS spectra of chemisorbed propargyl chloride. The value at 526 cm^{-1} is the characteristic Si—Cl stretching mode, which is consistent with that of the Si—Cl species produced by Cl_2 dissociative adsorption on $Si(1\,0\,0)-2\times1$ [24,25]. The disappearance of the C—Cl stretching mode (680 cm^{-1}), together with the formation of the Si—Cl bond, suggests the cleavage of C—Cl bond upon chemisorption. The CH_2 group is retained upon the chemisorption, indicated by its deformation (1410 cm^{-1}), wagging (1240 cm^{-1}), and twisting (1165 cm^{-1}) modes. The retained peaks at 3310 and 1060 cm^{-1} attributable to the stretching and bending modes of the ≡CH group indicate that the ≡CH group does not participate in the surface reaction, thus excluding the occurrence of the [2 + 2]-like cycloaddition through the C≡C group. The intensities of stretching mode of ≡CH group in chemisorption and physisorption spectra differ slightly, which is possibly due to the molecular orientation change [21,22]. This conclusion is further supported by the observation of the C≡C stretching mode at 2120 cm^{-1} and the Si—C stretching mode at 655 cm^{-1} [26–28] in the chemisorbed HREELS spectra. Thus, our vibrational studies of physisorbed and chemisorbed propargyl chloride strongly demonstrate that the chemisorption occurs through the dissociation of the C—Cl bond with the retention of the ≡CH group, as described in Fig. 1b. The Si—CH_2—C≡CH formed may be considered as a precursor for further organic synthesis and modification of silicon surfaces. The full frequency assignments for physisorbed and chemisorbed EELS spectra are listed in Table 1.

Fig. 3 shows the fitted Cl2p XPS spectra for physisorbed and chemisorbed propargyl chloride on $Si(1\,0\,0)-2\times1$. The Cl2p XPS spectrum of physisorbed propargyl chloride (Fig. 3b) was obtained by pre-exposing 4 L propargyl chloride on $Si(1\,0\,0)-2\times1$ at 110 K. The two peaks located at 200.5 and 202.2 eV with the same FWHM of 1.65 eV and an area ratio of 2:1 can be ascribed to $Cl2p_{3/2}$ and $Cl2p_{1/2}$, respectively. The binding energy for $Cl2p_{3/2}$ at 200.5 eV is comparable with the values obtained for physisorbed chloromethane on Pt [29], $SiCl_3CCl_3$ deposited on quartz [30] and chlorobenzene on Ag [31]. Compared to the $Cl2p_{3/2}$ binding energy (200.5 eV) in the physisorbed spectrum, the $Cl2p_{3/2}$ binding energy in the chemisorbed state is downshifted by 1.1 eV to 199.4 eV (Fig. 3a). This downshift of 1.1 eV indicates the dramatic change in the chemical environment of Cl-atom upon the chemisorption of propargyl chloride on $Si(1\,0\,0)-2\times1$. Indeed,

Table 1
Assignments of HREELS spectra for physisorbed and chemisorbed propargyl chloride on $Si(1\,0\,0)-2\times1$.[a]

Mode description	Calculated normal vibrations of propargyl chloride[b]	Physisorbed propargyl chloride on $Si(1\,0\,0)-2\times1$[c]	Chemisorbed propargyl chloride on $Si(1\,0\,0)-2\times1$[c]
$\nu(\equiv CH)$	3335	3310	3310
$\nu s(CH_2)$	3002	2980	2980
$\nu as(CH_2)$	2968	–	–
$\nu(C\equiv CH)$	2147	2120	2120
$\delta(CH_2)$	1441	1410	1410
$\omega(CH_2)$	1271	1240	1240
$\tau(CH_2)$	1179	1165	1165
$\beta(\equiv CH)$	–	1060	1060
$\nu(C—C)$	960	950	Not resolved
$\nu(CCl)$	650	680	–
$\nu(CCCl)$	451	470	–
$\delta(CCC)$	311	308	325
$\nu(Si—C)$	–	–	655
$\nu(Si—Cl)$	–	–	526

[a] All frequencies are in cm^{-1}.
[b] Ref. [11].
[c] Present work.

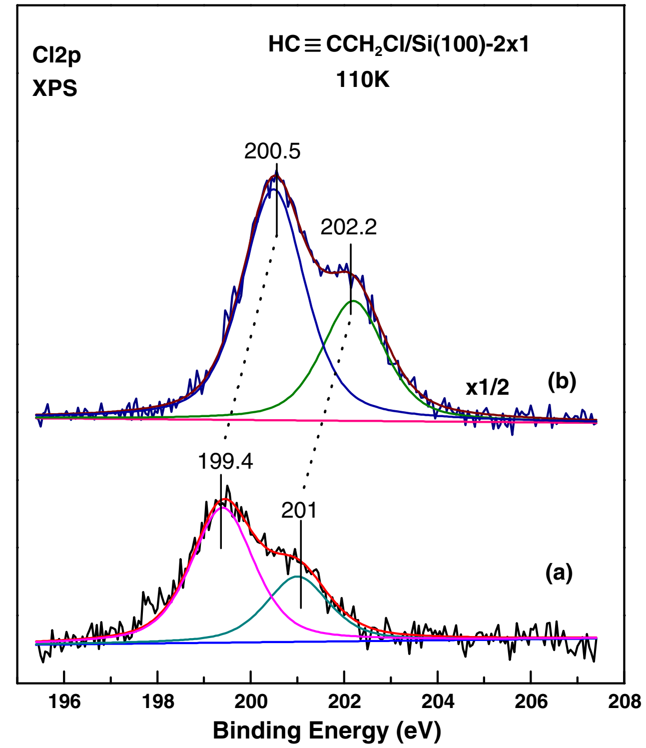

Fig. 3. Deconvoluted Cl2p XPS spectra of propargyl chloride on Si(1 0 0) – 2 × 1: (a) chemisorbed spectrum, obtained by annealing sample (b) to 300 K; (b) physisorbed spectrum, obtained by exposing 4 L propargyl chloride to Si surface at 110 K.

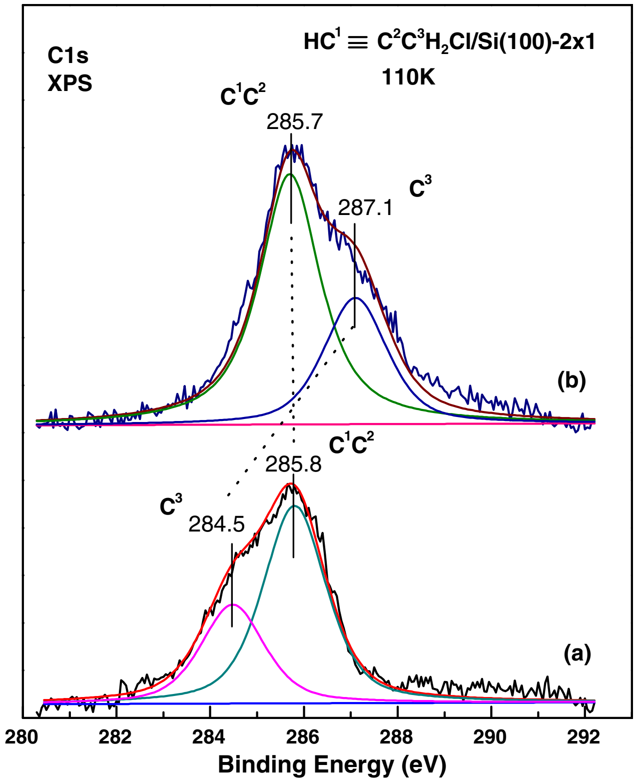

Fig. 4. Fitted C1s XPS spectra of propargyl chloride on Si(1 0 0) – 2 × 1: (a) chemisorbed spectrum, obtained by annealing sample (b) to 300 K; (b) physisorbed spectrum, obtained by exposing 4 L propargyl chloride to silicon surface at 110 K.

this $Cl2p_{3/2}$ peak at 199.4 eV is in excellent agreement with the typical value (199.3 eV) for the Si—Cl bonds [16,32], implying the formation of the Si—Cl bonds at the surface.

Table 2
The fitted XPS results for physisorbed and chemisorbed propargyl chloride on the Si(1 0 0) – 2 × 1 surface.[a]

$HC^1{\equiv}C^2C^3H_2Cl$	Physisorption	Chemisorption	Downshift
$Cl2p_{3/2}$	200.5	199.4	1.1
$C^1 1s$	285.7	285.8	0.1
$C^2 1s$	285.7	285.8	0.1
$C^3 1s$	287.1	284.5	2.6

[a] All energies are in eV.

The fitted C1s XPS spectra of physisorbed and chemisorbed propargyl chloride ($HC^1{\equiv}C^2C^3H_2Cl$) on Si(1 0 0) – 2 × 1 are displayed in Fig. 4. The physisorbed C1s XPS spectrum (Fig. 4b) is deconvoluted into two peaks at 285.7 and 287.1 eV with an area ratio of 2:1. The feature at 287.1 eV can be attributed to C^3 atom due to its direct bonding with the highly electronegative Cl-atom (3.2, Pauling scale) [33]. The value is close to the previous XPS studies about physisorbed CH_3Cl on Co [34]. The peak at 285.7 eV associated with C^1 and C^2 in the $HC^1{\equiv}C^2$-linkage, is in good agreement with the value (285.5–286.0 eV) for the sp hybridized C atoms [8,35–37].

However, the C1s XPS spectrum of chemisorbed molecules (Fig. 4a) is dramatically different, implying the significant changes in the electronic structures upon chemisorption of propargyl chloride on Si(1 0 0) – 2 × 1. The chemisorbed C1s XPS spectrum can be deconvoluted into two peaks at 285.8 and 284.5 eV with an area ratio of 2:1, which is consistent with the dissociative reaction mechanism evidenced in the HREELS and Cl2p XPS studies. The peak at 284.5 eV is attributed to the sp^3 hybridized C^3 atom covalently linked to the Si surface [8,38], demonstrating the cleavage of the C—Cl bond. Because the C^1 and C^2 atoms retain their sp hybridization in the chemisorption state, the binding energies (285.8 eV) are not expected to shift significantly from the value (285.7 eV) observed in the physisorbed state. The detailed assignments of C1s and Cl2p core levels for physisorbed and chemisorbed propargyl chloride on the Si(1 0 0) – 2 × 1 surface are listed in Table 2.

4. Summary

HREELS and XPS experimental results demonstrate that propargyl chloride dissociatively attaches onto Si(1 0 0) – 2 × 1 through the cleavage of the C—Cl bond and the retention of the —C≡CH linkage. The chemisorbed species containing one C≡C triple bond may be employed as an intermediate for further modification.

Acknowledgments

Yan Xia Shao expresses great appreciation for the award of Graduate Scholarship, National University of Singapore. The project was also supported by the Ministry of Education, Singapore. Grant No. R-143-000-377-112.

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