Selective Dissociation of 4-Chloroaniline on the Si(111)-7×7 Surface through N−H Bond Breakage

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The covalent attachment of 4-chloroaniline on the Si(111)-7×7 surface was investigated by using a combination of X-ray photoelectron spectroscopy (XPS), high-resolution electron energy loss spectroscopy (HREELS), and density functional theory (DFT) calculations. The HREELS spectra suggest that one of the N−H bonds dissociates to form Si−N and Si−H bonds with the phenyl ring and the C−Cl bond unperturbed upon chemisorption. The XPS results confirm that only the NH_2 group participates in the surface binding. This binding mode and surface reaction pathway are further supported by the DFT calculation. The resulting chlorobenene-like structure on Si(111)-7×7 can be employed for further photochemical modification and functionalization.

Introduction

The binding of organic molecules on semiconductor surfaces has attracted much attention due to its potential applications in the development of molecular electronics, biosensors, and nanotechnology.[1−3] To integrate organic functionalities onto semiconductor surfaces for fine-tuning the chemical, physical, and mechanical properties of organic-semiconductor interfaces, previous studies were focused on understanding the reaction mechanisms of unsaturated organic molecules on semiconductor surfaces.[4−6] The interest in this area has been extended to the investigation of reactivities and selectivities of multifunctional organic molecules to develop molecular templates for further modification and functionalization, such as the construction of covalently attached organic multilayers.[7−9] Recently, the successful construction of a second covalently bonded organic layer with use of the photochemical method has been demonstrated on the silicon surface,[10] implying the importance of fundamental understandings on the silicon surface chemistry of Cl-containing organic molecules.

Among the semiconductor surfaces of interest, the Si(111)-7×7 surface, adopting the dimer−adatom-stacking (DAS) faulted structure,[11,12] is of great scientific importance. This surface provides a number of chemically, spatially, and electronically inequivalent reactive sites, including the adatoms and rest atoms in the inherently different faulted and unfaulted halves. When the Si(111)-7×7 surface reacts with organic molecules, the adjacent adatom−rest atom pair acts as a diradical to facilitate a wide range of chemical reactions.[7] For example, benzene[13,14] and chlorobenzene[15] were demonstrated to molecularly adsorb on the Si(111)-7×7 surface via a [4+2]-like cycloaddition reaction, and pyrrole[16] adsorbs dissociatively with the N−H bond cleavage on the Si(111)-7×7 surface.

Compared to the extensive work on the dissociative reactions of amines on Si(100),[17−20] few studies were conducted on Si(111)-7×7. However, the adsorption of N-containing organic molecules on the Si(111)-7×7 surface is attractive, because the electron lone pair of the nitrogen atom always plays an important role in the adsorption process,[19−22] which provides the basis for the high selectivity in the covalent binding of molecules containing NH_2 groups on Si(111)-7×7. On the other hand, the Cl-containing organic molecules are known to be photoactive in the gas phase and on metal surfaces.[23−25] The integration of intact C−Cl bonds in the surface-bound molecular template may enable us to fabricate multilayer organic structures through photoinduced surface reactions.[10] Thus, 4-chloroaniline containing both the NH_2 group and C−Cl bond conjugating with the phenyl ring was chosen in this experiment to build a surface-linked functional organic template.

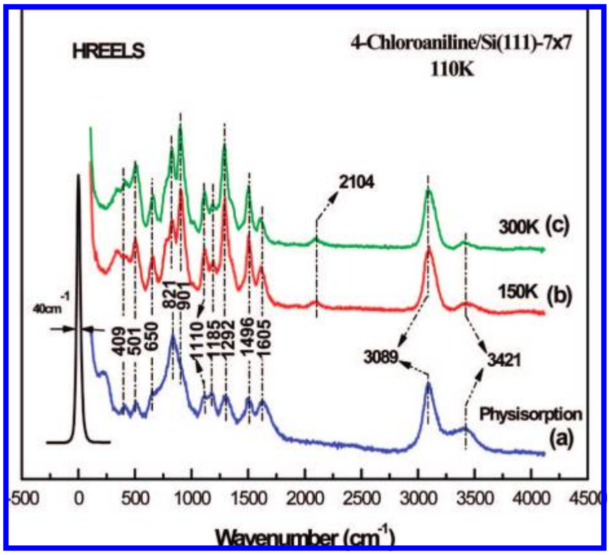

Figure 1. HREELS spectra for physisorbed 4-chloroaniline obtained after condensing the 4-chloroaniline multilayer on the Si(111)-7×7 surface at 110 K (a) and chemisorbed 4-chloroaniline prepared after annealing the multilayer 4-chloroaniline-covered sample to 150 (b) and 300 K (c).

In this work, the adsorption of 4-chloroaniline on the Si(111)-7×7 surface was studied with use of high-resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) calculations. The experimental and theoretical results suggest that 4-chloroaniline dissociatively adsorbs on the Si(111)-7×7

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TABLE 1: Vibrational Assignment for Physisorbed and Chemisorbed 4-Chloroaniline on Si(111)-7×7[a]

vibrational assignment	IR of crystal 4-chloroaniline[b]	Raman of 4-chloroaniline[b]	HREELS of physisorbed 4-chloroaniline on Si(111)-7×7[c]	HREELS of chemisorbed 4-chloroaniline on Si(111)-7×7 [c]
$\nu_a(NH_2)$	3469		3421	3421
$\nu_s(NH_2)$	3378			
ν(CH)	3058	3059	3089	3089
ν(CC)	1597	1602	1605	1605
ν(CC)	1500		1496	1496
β(CH)	1291		1292	1292
β(CH)	1117		1110	1110
β(CH)	1091	1090		
γ(CH)	929	939		901
γ(CH)	835		821	821
ring breathing + trigonal ring mode	826	826		
ν(CCl)	642	637	650	650
γ(CH)	513		501	501
γ(CCC)	423	407	409	409
β(CCC)	381	379		
ν(Si−N)				501
ν(Si−H)				2104

[a] The vibrational frequencies are given in cm^{-1}. [b] From refs 27 and 28. [c] Present work.

surface via one N−H bond cleavage, leaving intact the C−Cl bond protruding to the vacuum. The remaining (Si)NH-C_6H_4-Cl-like structure on the Si(111)-7×7 surface would serve as a precursor for further photochemical modification and functionalization.

Experimental Section

The experiments were performed in two separate ultrahigh 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 spectrometer (EELS3000, LK Technologies, USA). An electron beam with energy of 5.0 eV impinged on the surface at an incident angle of 60° and the scattered electrons were detected at the specular angle with a resolution of about 40 cm^{-1}. 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 with Al Kα radiation ($h\nu = 1486.6$ 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(111)-7×7 substrate.[26]

The Si(111) samples (22 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(111) crystals held together by Ta clips, and in turn spot-welded to Ta posts at the bottom of a Dewar-type liquid N_2-cooled sample holder. The crystals can be resistively heated to 1300 K and cooled to 110 K with liquid nitrogen. The sample was degassed and carefully cleaned by cycles of Ar^+ sputtering (36 min at 500 eV and 5 $\mu A \cdot cm^{-2}$) and annealing to 1200 K. Sample temperatures ($T > 800$ K) were determined by an infrared pyrometer ($\epsilon = 0.74$, TR-630, Minolta), which showed a good temperature distribution within ±10 at 1000 K. The cleanliness of the samples was verified by using XPS and HREELS. 4-Chloroaniline (Aldrich, 98%) vapor was dosed onto the Si(111)-7×7 surface through a variable leaking valve. The exposures were reported here in units of Langmuir (1 L $=1 \times 10^{-6}$ Torr·s) without the calibration of ion gauge sensitivity.

Results and Discussion

Figure 1 shows the HREELS spectra for physisorbed and chemisorbed 4-chloroaniline on the Si(111)-7×7 surface. The vibrational features of the physisorbed multilayer of 4-chloroaniline (Figure 1a) were obtained after exposing 1 L (1 L = 1 × 10 $^{-6}$ Torr·s) of 4-chloroaniline molecules onto the Si(111)-7×7 surface at 110 K. The energy losses at about 409, 501, 650, 821, 1110, 1185, 1292, 1496, 1605, 3089, and 3421 cm^{-1} can be readily resolved, which agree well with the vibrational features of 4-chloroaniline observed in IR studies.[27,28] Among the vibrational features, the peak at 650 cm^{-1} is assigned to the C−Cl stretching mode. The intensities at about 1496 and 1605 cm^{-1} are attributed to the characteristic C−C stretching modes of the phenyl ring, and the broad peak at about 3421 cm^{-1} is associated with the N−H stretching modes. The detailed assignments for the physisorbed and chemisorbed 4-chloroaniline are summarized in Table 1.

On the other hand, the spectra (Figure 1b,c) for chemisorbed 4-chloroaniline obtained after annealing the above sample to 150 and 300 K, respectively, to drive away physisorbed molecules, are different. Energy loss at about 409, 501, 650, 821, 901, 1110, 1185, 1292, 1496, 1605, 2104, 3089, and 3421 cm^{-1} can be identified. The appearance of the Si−H stretching mode at about 2104 cm^{-1} indicates that the C−H and/or N−H bonds break upon the chemisorption of 4-chloroaniline on the Si(111)-7×7 surface.[16,17,29] As the C−H bonds are relatively strong compared to the N−H bonds, benzene, chlorobenzene, and other aromatic molecules have been shown to adsorb on the Si(111)-7×7 surface without C−H dissociation,[14,15,30] while amines and pyrrole were found to bind on the Si(111)-7×7 surface via the N−H bond breakage.[6,22,31] Besides, aniline adsorbs on Si(100)-2×1 with the dissociation of one N−H bond, not C−H.[8,17,32] Considering the diradical-like properties of dimers on Si(100) and adatom−rest atom pairs on Si(111)-7×7, it is probable that upon chemisorption of 4-chloroaniline on Si(111)-7×7, one of the N−H bonds dissociates to form new Si−N and Si−H bonds with other molecular parts unperturbed. This binding configuration is supported by the retained, but reduced N−H stretching peak width and relative intensity in Figure 1b,c compared to the spectrum for physisorbed molecules. This observation is consistent with the fact that the $-NH_2$ group in physisorbed molecules has symmetric and asymmetric stretching vibrations while the −NH− group in chemisorbed species only has one stretching mode. In addition, the binding configuration is further supported by the observation of vibrational peaks at about 650, 1292, 1496, and 1605 cm^{-1}, together

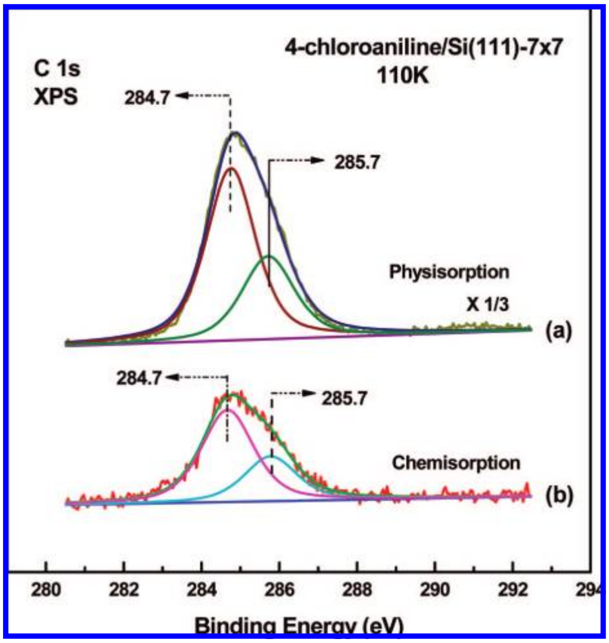

Figure 2. C 1s XPS spectra for physisorbed and chemisorbed 4-chloroaniline on Si(111)-7×7.

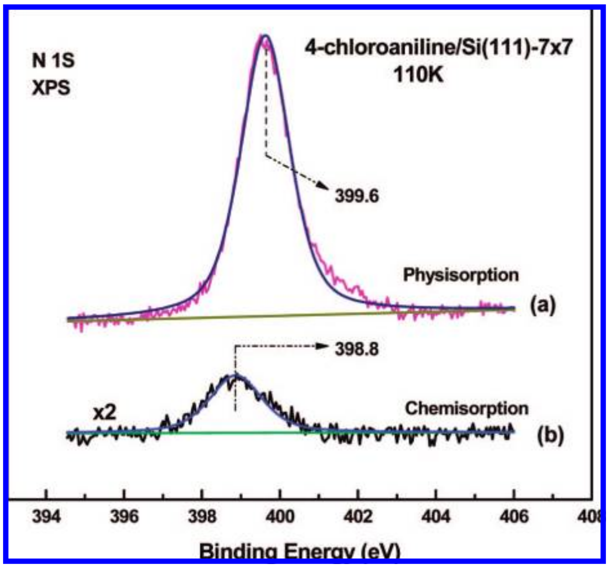

Figure 3. N 1s XPS spectra for physisorbed and chemisorbed 4-chloroaniline on Si(111)-7×7.

with the absence of (sp^3)C−H stretching modes, indicating the retention of the C−Cl bond and the phenyl ring after the surface reaction. The stretching vibration of the newly formed Si−N bond is probably coupled with the peak at about 501 cm^{-1}.[16,29,33] Compared to physisorbed molecules, intensity changes for retained vibrational modes in chemisorbed species can be noticed, which may be attributable to their difference in orientation.

For further understanding the binding mechanism of 4-chloroaniline on the Si(111)-7×7 surface, X-ray photoelectron spectroscopy (XPS) was employed to study the electronic properties of 4-chloroaniline upon adsorption. Figure 2a shows the C 1s XPS spectrum for the condensed multilayer of 4-chloroaniline on the Si(111)-7×7 surface. In comparison, Figure 2b presents the C 1s photoemission features of chemisorbed 4-chloroaniline, which was obtained after annealing the

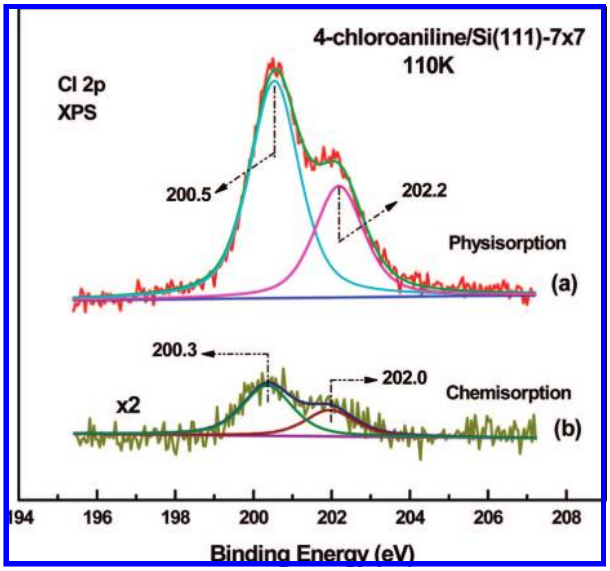

Figure 4. Cl 2p XPS spectra for physisorbed and chemisorbed 4-chloroaniline on Si(111)-7×7.

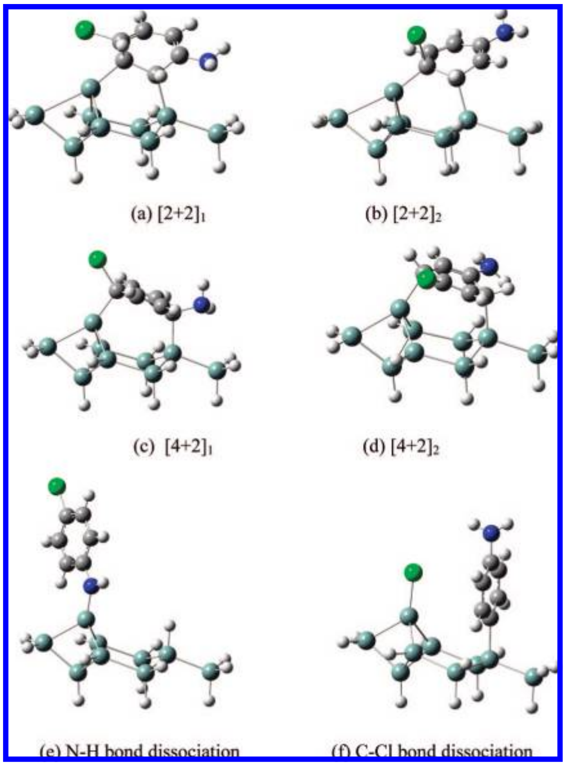
(a) $[2+2]_1$
(b) $[2+2]_2$
(c) $[4+2]_1$
(d) $[4+2]_2$
(e) N-H bond dissociation
(f) C-Cl bond dissociation

Figure 5. Six possible binding configurations for 4-chloroaniline on the Si(111)-7×7 surface (a−f).

TABLE 2: Deconvoluted Results of XPS Spectra for Chemisorbed and Physisorbed 4-Choroaniline on the Si(111)-7×7 Surface[a]

$H_2NC^1(C^2HC^3H)_2C^4Cl$	physisorption	chemisorption	downshift
Cl ($2p_{3/2}$)	200.5	200.3	0.2
C^1	285.7	285.7	0
C^2	284.7	284.7	0
C^3	284.7	284.7	0
C^4	285.7	285.7	0
N	399.6	398.8	0.8

[a] All energies are in eV.

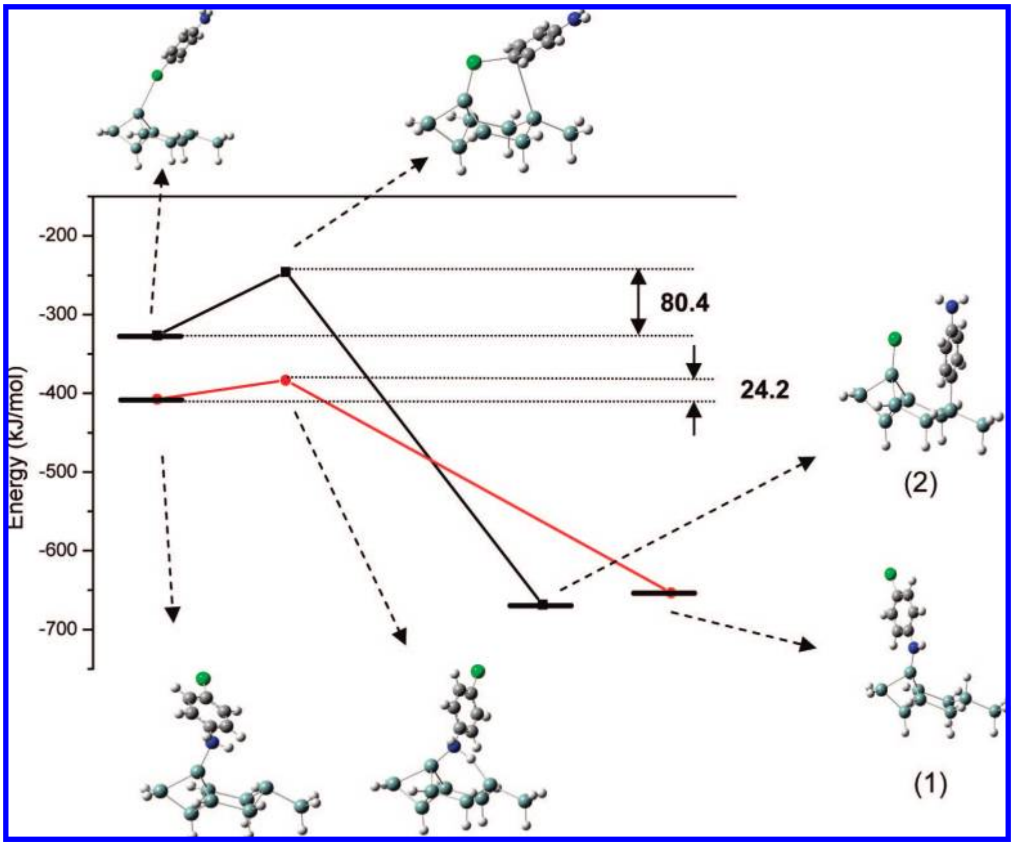

Figure 6. Critical points of the calculated reaction pathways for the reaction of 4-chloroaniline on a Si_9H_{12} cluster at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory: (1) N−H dissociation and (2) C−Cl dissociation.

TABLE 3: Adsorption Energies of the Local Minimums in the $ClC_6H_4NH_2/Si_9H_{12}$ Model System[a]

reaction model	$[2+2]_1$	$[2+2]_2$	$[4+2]_1$	$[4+2]_2$	N−H bond cleavage	C−Cl bond cleavage
functional group	phenyl ring	phenyl ring	phenyl ring	phenyl ring	NH_2	C−Cl
configuration[c]	a	b	c	d	e	f
adsorption energy[b]	371	362	441	488	653	668

[a] All energies are in kJ/mol. [b] Adsorption energy: $\Delta E = E(Si_9H_{12}) + E(C_6H_6NCl) - E(C_6H_6NCl/Si_9H_{12})$. [c] Corresponding to configurations illustrated in Figure 5.

same sample to 300 K to drive away all the physisorbed molecules. The C 1s XPS peaks in these spectra are obviously asymmetric and broader than the instrumental resolution, indicating the presence of chemically inequivalent carbon atoms in chemisorbed and physisorbed molecules. Both spectra can be deconvoluted into two peaks centered at the binding energies of 284.7 and 285.7 eV, with an area ratio of about 2:1. The C 1s peak in both spectra with a higher binding energy can be assigned to the C atoms adjacent to the electronegative Cl atom and N atom, and the peak with a lower binding energy is attributable to the carbon atoms connected to H atoms. These assignments are consistent with the C 1s binding energy differences between inequivalent carbon atoms observed for the gas phase aniline and chlorobenzene.[34] Furthermore, these C 1s photoemission peak positions agree well with that reported for physisorbed aniline on Ag(110) and Ni(100) surfaces, as well as that for physisorbed chlorobenzene on Ag(111).[25,35,36] The similarity between the C1s photoemission features for physisorbed and chemisorbed 4-chloroaniline molecules in peak positions and area ratios suggests that the phenyl ring is unperturbed upon chemisorption on the Si(111)-7×7 surface with C−N and C−Cl bonds intact.

Figure 3 shows the N 1s core level photoemission spectra for physisorbed and chemisorbed molecules. The FWHM of the N 1s XPS peaks for both spectra are identical, suggesting that there is only one chemically distinguishable form of N atoms in the chemisorbed 4-chloroaniline molecules. The most obvious difference is the downshift of the peak position of about 0.8 eV from 399.6 to 398.8 eV, indicating the change of electronic environment of the N atom upon chemisorption. The N 1s binding energy for physisorbed molecules at about 399.6 eV is comparable with that observed for NH_2-C_6H_5-like species on the Si(100) surface and the condensed aniline multilayer on Ni(100).[8,35] In contrast, the N 1s XPS peak position at 398.8 eV for chemisorbed 4-chloroaniline is close to the value for Si-NH-C_6H_6-like species formed by the dissociative adsorption of aniline on Si(100),[17] suggesting the dissociation of one N−H bond upon chemisorption of 4-chloroaniline and the formation of a new Si−N bond. In addition, the value of 398.8 eV for N 1s is significantly higher than that for $-NSi_2$ species (∼397.9 eV),[8] suggesting that the N atom of 4-chloroaniline is bonded to the Si(111)-7×7 surface with only one Si−N bond.

Figure 4 presents the Cl 2p XPS spectra for physisorbed and chemisorbed 4-chloroaniline on the Si(111)-7×7 surface. The Cl 2p XPS spectrum splits into two peaks, which are Cl $2p_{1/2}$ and Cl $2p_{3/2}$. The Cl $2p_{3/2}$ peak position at 200.5 eV displayed in Figure 4a is consistent with the values obtained for physisorbed chlorobenzene condensed on Ag(111) and is a typical

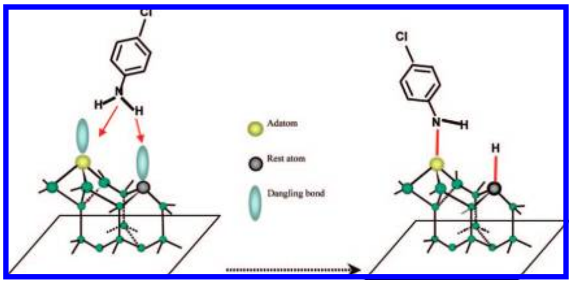

Figure 7. Schematic model of 4-chloroaniline chemisorbed on the Si(111)-7×7 surface.

value for C−Cl species.[25,26,37] On the other hand, the binding energy of Cl $2p_{3/2}$ for the chemisorbed species at about 200.3 eV is comparable to the value for physisorbed molecules, but significantly higher than that for Si−Cl species (about 199.3 eV),[38,39] indicating that the C−Cl bond remains intact after the surface reaction of 4-chloroaniline on the Si(111)-7×7 surface. The detailed assignments of the XPS features for physisorbed and chemisorbed molecules are listed in Table 2.

To obtain a better understanding of the experimental results, the density functional theory (DFT) method was used to obtain the optimized geometry and adsorption energy for the possible adsorption configurations and to investigate the reaction pathways. The DFT calculation was performed with Gaussian 03[40] on the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level. Moreover, the primitive Si cluster (Si_9H_{12}) was previously proven to be successful in predicting the adsorption energies and binding configurations of organic compounds on Si(111)-7×7,[7,13] and the adsorbed clusters are fully optimized without constraints. The possible adsorption configurations and their adsorption energies of 4-chloroaniline on the Si(111)-7×7 surface are summarized in Figure 5 and Table 3, respectively. These results revealed that both dissociative reaction pathways with the C−Cl or N−H bond cleavage are thermodynamically favored, compared to the cycloaddition reactions, due to the retention of the aromatic phenyl ring.

Similar to the adsorption of other organic molecules on the silicon surfaces, the adsorption of 4-chloroaniline on Si(111)-7×7 may take a stepwise process, starting with a dative bonding precursor in which the electron was donated from the lone pair electrons of the nitrogen atom or chlorine atom to the electron-deficient adatom site, followed by N−H bond or C−Cl bond cleavage.[22,41−44] The calculation results of the dissociative reaction pathways of 4-chloroaniline on the Si_9H_{12} cluster are summarized in Figure 6. It is clear that the $Si\leftarrow NH_2C_6H_4Cl$-like dative bonded precursor state is more stable than the $Si\leftarrow ClC_6H_4NH_2$-like species, implying that the formation of the former is preferred and it has a longer residence time. Although the transition states for both dissociative reactions are lower than the entrance channel, the energy barrier for the N−H dissociation (24.2 kJ/mol) is much lower than that for the C−Cl dissociation (80.4 kJ/mol), suggesting that the N−H dissociation pathway is kinetically favored.

Thus, the experimental and theoretical results strongly indicate that the chemisorbed 4-chloroaniline molecule covalently binds to the Si(111)-7×7 surface through the cleavage of one N−H bond to form new Si−N and Si−H bonds involving one adjacent adatom−rest atom pair with the phenyl ring and C−Cl bond intact protruding to the vacuum, as illustrated in Figure 7.

These results are consistent with the previous studies about the adsorption of chlorobenzene and aniline on silicon surfaces. It was found that chlorobenzene bonds to the Si(111)-7×7 surface via a [4+2]-like cycloaddition with the C−Cl bond intact,[25] indicating that the cycloaddition of the phenyl ring is more favorable than the C−Cl dissociation. Meanwhile, the investigations about the reactions of amines on the silicon surfaces imply that the cleavage of the N−H bond in the NH_2 group readily happens on silicon surfaces.[16−19] It is expected that 4-chloroaniline would adsorb on the Si(111)-7×7 surface through the breakage of one N−H bond with other molecular parts unaffected. Moreover, previous STM studies suggested that the dissociation of amines involves the adatom−rest atom pair with the preference of center adatoms,[45,46] and the N-atom intends to interact with the positively charged adatom site (especially the center adatoms),[22] the dissociative binding configuration of 4-chloroaniline with the N-atom linking to the adatom and H atom sitting on the neighboring rest atom is proposed, as described in Figure 7.

Conclusion

The adsorption of 4-chloroaniline was investigated with XPS, HREELS, and DFT calculations. The experimental and theoretical results showed that 4-chloroaniline dissociatively adsorbs on the Si(111)-7×7 surface with one N−H bond cleavage on one adjacent adatom−rest atom pair to form Si-NH-C_6H_4-Cl-like and Si−H species with other molecular parts intact. In this way, the intact C−Cl bond can be integrated onto the Si(111)-7×7 surface to serve as a precursor to facilitate further photoinduced silicon surface modification or material synthesis under vacuum conditions.

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Supporting Information Available: Schematic diagram of the sample manipulator and sample assembly and simulation details. This material is available free of charge via the Internet at http://pubs.acs.org.

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