

Tetra- $\sigma$  attachment of allyl cyanide on Si(111)-7 $\times$ 7

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The investigation of allyl cyanide adsorption on Si(111)-7 $\times$ 7 using high-resolution electron-energy-loss spectroscopy (HREELS), x-ray photoelectron spectroscopy (XPS), and ultraviolet photoelectron spectroscopy (UPS) reveals a *tetra- $\sigma$*  binding mode through two [2+2]-like cycloaddition reactions. The HREELS spectra of chemisorbed monolayer show the absence of C=C, C $\equiv$ N, and C(*sp*<sup>2</sup>)-H stretching modes coupled with the appearance of C=N stretching mode at  $\sim 1590$  cm<sup>-1</sup>, demonstrating that both the C=C and C $\equiv$ N of allyl cyanide directly participate in binding with the surface to form C—C and C=N bonds, respectively. This binding configuration was further confirmed in our XPS and UPS studies. The imine-containing skeleton formed on the surface can possibly be employed as a molecular template for a further modification of Si surfaces and syntheses in vacuum.

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## I. INTRODUCTION

The binding of organic molecules on silicon surfaces may have potential applications in developing advanced optics, microelectronics, and sensors.<sup>1-3</sup> Among the silicon single crystal surfaces, of great fundamental interests is Si(111)-7 $\times$ 7. As schematically presented in Fig. 1, Si(111) undergoes a 7 $\times$ 7 reconstruction,<sup>4,5</sup> reducing the number of unsaturated surface Si atoms in every unit cell from 49 to 19. The 19 Si atoms with a dangling bond on each consist of six "rest atoms," 12 "adatoms," and one "corner hole." Most importantly, this structural reconstruction results in the electronic redistribution. Among the 19 electrons, 14 are located on the six rest atoms and one corner hole, and the remaining five are distributed on the 12 adatoms. The obvious unequal electron densities on adatoms and rest atoms make them both electrophilic and nucleophilic.

The diversity in structural and electronic arrangements of reactive sites on Si(111)-7 $\times$ 7 provides great opportunities for surface attachment of various functional organic molecules.<sup>5,6</sup> Previous studies showed that the *neighboring adatom-rest atom pair* can serve as active reaction sites in the covalent binding of simple unsaturated organic molecules including ethylene,<sup>7,8</sup> acetylene,<sup>9-13</sup> benzene,<sup>14,15</sup>

thiophene,<sup>16,17</sup> etc. The high reactivity observed in these chemical systems is attributable to the coexistence of electrophilic adatom and its neighboring nucleophilic rest atom with a reasonable spatial separation, leading to the feasible occurrence of [2+2]-like or/and [4+2]-like cycloaddition reactions on Si(111)-7 $\times$ 7.

In order to construct organic monolayers with available functionalities for further reaction to form multilayer organic films,<sup>1-3</sup> an understanding of the attachment mechanism of multifunctional molecules becomes essential. For multifunctional molecules, the attachment can be complex. Different functional groups in the molecule may compete for active sites on the surface. It is also possible that more than one functionality in the molecule simultaneously bind to the surface. Acrylonitrile containing conjugated C=C and C $\equiv$ N groups can be bound to Si(111)-7 $\times$ 7 through a [4+2]-like cycloaddition reaction.<sup>18</sup> In its attachment, both conjugated C=C and C $\equiv$ N are involved in the interaction with the neighboring adatom-rest atom pair to form a (Si)CH<sub>3</sub>-CH=C=NH(Si)-like structure. For allyl cyanide CH<sub>2</sub>=CH-CH<sub>2</sub>-C $\equiv$ N, however, the reactive C=C and C $\equiv$ N groups are separated by -CH<sub>2</sub>-, not being able to interact through conjugation. Thus, allyl cyanide displays a combined chemical structure of ethylene and acetonitrile. Recent studies showed that both ethylene and acetonitrile can covalently bind to the neighboring adatom and rest atom pair through a [2+2]-like addition mechanism.<sup>7,8,19</sup> The reactive C=C or/and C $\equiv$ N groups of allyl cyanide may possibly bind to Si(111)-7 $\times$ 7 separately or simultaneously via ethylene-like or/and acetonitrile-like reaction channels. Our studies focus on the vibrational features: C 1s and N 1s core-levels, and a valence-band structure of allyl cyanide on Si(111)-7 $\times$ 7. Experimental results show that allyl cyanide is mainly covalently bound to the Si surface with a *tetra- $\sigma$*  linker via two [2+2]-like addition reactions.

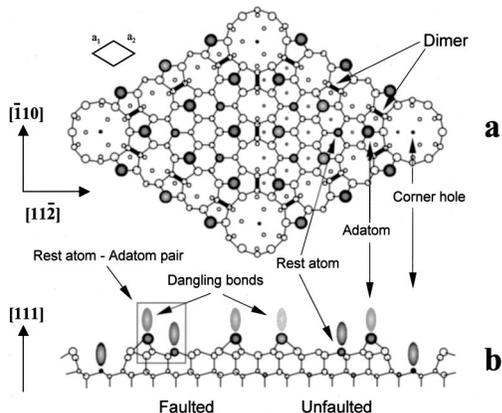


FIG. 1. Top (a) and side (b) views of the detailed three-dimensional structure for one Si(111)-7 $\times$ 7 unit cell based on the dimer-adatom-stacking (DAS) faulted model.

## II. EXPERIMENT

Experimental measurements were performed using high-resolution electron-energy-loss spectroscopy (HREELS) x-ray photoemission spectroscopy (XPS), and ultraviolet

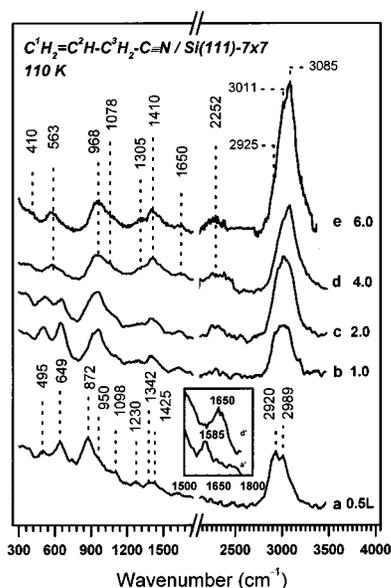


FIG. 2. HREELS spectra of allyl cyanide on Si(111)-7 $\times$ 7 as a function of exposure at 110 K.  $E_p = 5.0$  eV, specular geometry.

photoemission spectroscopy (UPS) in two separate ultrahigh-vacuum chambers with a base pressure of  $< 2 \times 10^{-10}$  Torr.

The vibrational studies were carried out in a HREELS chamber mounted with a quadrupole mass spectrometer (UTI-100) for gas analyses. The EELS spectrometer (LK-2000-14R) consists of a double-pass 127 $^\circ$  cylindrical deflector analyzer (CDA) for the monochromatorization and a single-pass 127 $^\circ$  CDA for detection. The vibrational HREELS measurements were taken with a primary beam of 5.0 eV in a specular configuration (incident angle  $\theta_i = 60^\circ$  from the surface normal) and a resolution of 5.5–7.0 meV [full width at half maximum (FWHM) of the elastic peak].

The electronic structures of the adsorption system were characterized in the other chamber equipped with an x-ray source, a He discharge lamp, and a concentric hemispherical electron energy analyzer (CLAM2, VG). XPS spectra were acquired using Al  $K\alpha$  radiation ( $h\nu = 1486.6$  eV) with a pass energy of 10 eV. For XPS, the binding-energy (BE) scale is referenced to the peak maximum of the Si(2p) line [the BE is 99.3 eV calibrated for Au 4f $_{7/2}$  (Ref. 20)] of the Si(111) substrate with a FWHM of less than 1.2 eV. He II

TABLE I. The vibrational signatures of physisorbed C<sup>1</sup>H<sub>2</sub>=C<sup>2</sup>H-C<sup>3</sup>H<sub>2</sub>-C<sup>4</sup>≡N and chemisorbed molecules on Si(111)-7 $\times$ 7 together with those of solid phase allyl cyanide. All the frequencies are in cm<sup>-1</sup>. \* Possibly attributed to the formed —C=N group.

Mode no.	Assignment	Solid phase	Physisorption	Chemisorption	
				0.5 L 110 K	Annealing to 300 K
$\nu_1$	=CH <sub>2</sub> asym stretch	3093	3085		
$\nu_2$	=CH stretch	3032			
$\nu_3$	=CH <sub>2</sub> sym stretch	2989	3011		
$\nu_{17'}$	CH <sub>2</sub> asym stretch	2966		2989	2965
$\nu_{17}$	CH <sub>2</sub> asym stretch	2933	2925	2920	2910
$\nu_4$	CH <sub>2</sub> sym stretch	2919			
$\nu_5$	C≡N stretch	2249	2252		
$\nu_6$	C=C stretch	1645	1650	1585	1595
$\nu_7$	CH <sub>2</sub> deformation	1422	1410	1425	1425
$\nu_8$	=CH <sub>2</sub> scissors	1403			
$\nu_9$	CH <sub>2</sub> wag	1327		1342	1363
$\nu_{10}$	=CH bend	1305	1305		
$\nu_{10'}$	=CH bend	1288			
$\nu_{18}$	CH <sub>2</sub> twist	1215		1230	1232
$\nu_{11'}$	=CH <sub>2</sub> rock	1075	1078	1098*	1100*
$\nu_{19}$	=CH <sub>2</sub> twist	990			
$\nu_{20}$	CH <sub>2</sub> rock	949	968	950	955
$\nu_{21}$	=CH <sub>2</sub> wag	933			
$\nu_{12}$	C—C—C asym stretch	914			
$\nu_{13}$	C—C—C sym stretch	867		872	878
	Si—N stretch			649	646
$\nu_{22}$	OH=wag	557	563		
	Si—C stretch			495	497
$\nu_{15}$	C=C—C bend	407	410		

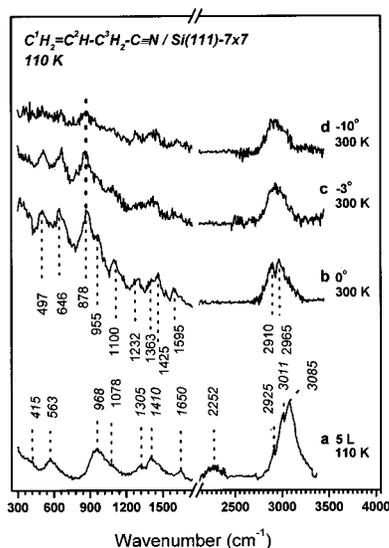


FIG. 3. HREELS spectra obtained after (a) exposing Si(111)-7 $\times$ 7 to 5.0-L allyl cyanide at 110 K; (b) annealing (a) to 300 K; (c) off-specular spectrum of (b) with  $\Delta\theta = -3^\circ$ ; and (d) off-specular spectrum of (b) with  $\Delta\theta = -10^\circ$ .

( $h\nu = 40.8$  eV) was selected for obtaining the valence band spectra due to its wider energy window.

The Si(111) samples were cut from *n*-type phosphorus-doped Si(111) wafers (99.999%, 1–30  $\Omega$  cm, Goodfellow) and mounted with the following procedures. Two pieces of Si(111) single crystals of the same dimension (18 $\times$ 10 $\times$ 0.38 mm<sup>3</sup>) were first deposited with a thin Ta layer on their unpolished backs for better thermal contact. A piece of Ta foil (0.025 mm thick, Goodfellow) was sandwiched between the Ta-covered backs of the two silicon samples as a heater. The samples were clamped together using two Ta clips. The Ta foil was then spot welded to Ta rods connected

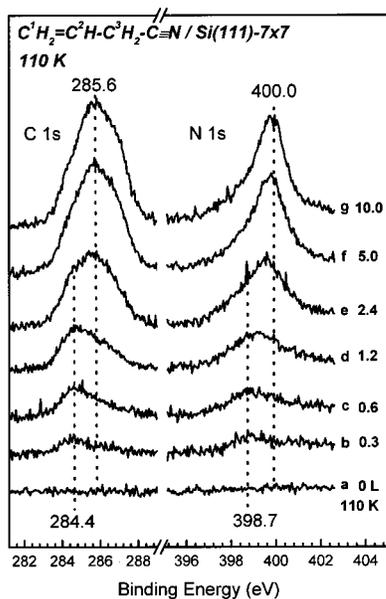


FIG. 4. XPS spectra of allyl cyanide on Si(111)-7 $\times$ 7 at 110 K as a function of exposure.

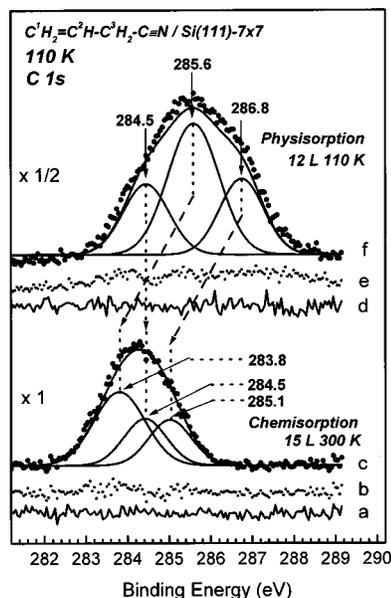


FIG. 5. The decoupled XPS spectra of chemisorbed and physisorbed allyl cyanide on Si(111)-7 $\times$ 7. Curves *a* and *d*: the C 1s spectra of a clean Si(111)-7 $\times$ 7 surface before dosing allyl cyanide. Curves *b* and *e*: the difference spectra between experimental results and the sum of fitted peaks. Curves *c* and *f*: the experimental and fitted spectra of chemisorbed allyl cyanide and physisorbed molecules, respectively.

to the feedthroughs of the manipulator. A 0.003" W-5% Re/W-26% Re thermocouple was attached to the center of one of silicon samples using a high-temperature ceramic adhesive (Aremco 516) for temperature measurement and control. The silicon sample mounted in such a way can be resistively heated to 1400 K and conductively cooled to 110 K using liquid nitrogen. The temperature distribution on the sample is within  $\pm 10$  K at 1000 K, as determined by an IR pyrometer ( $\epsilon = 0.74$ , TR-630, Minolta).

After being inserted into the chamber, the silicon sample was then thoroughly degassed at 900 K overnight under an ultrahigh vacuum. Surface contaminants, such as carbide and oxide, were removed by repeated Ar<sup>+</sup> bombardment and annealing to 1200 K for 20 min. Surface cleanliness was confirmed using HREELS, XPS, and UPS. Allyl cyanide (99+%, Aldrich) was purified by freeze-pump-thaw cycles prior to use. Dosing was accomplished by backfilling the chamber through a variable leak valve without ion gauge sensitivity calibration.

The spectra for chemisorbed allyl cyanide are collected with two methods: (a) expose Si(111)-7 $\times$ 7 to allyl cyanide of low exposure at 110 K, or (b) deliver molecules of high exposure to a Si sample at 110 K and anneal the allyl cyanide-exposed sample to 300 K to drive away all physisorbed molecules and only retain the chemisorbed molecules on the Si surface, and then collect spectra. The vibrational (HREELS) and electronic properties (XPS and UPS) for physisorbed molecules are obtained by collecting spectra upon exposing Si sample to allyl cyanide of high exposure at 110 K.

TABLE II. The fitted results and assignments of physisorbed and chemisorbed  $C^1H_2=C^2H-C^3H_2-C^4\equiv N$  on Si(111)- $7\times 7$ . All energies are in eV.

Core level	Physisorption	Intensity	Chemisorption	Intensity	Chemical shift	Rehybridization
$C^1 1s$	$\sim 285.6$	$\sim 50.4\%$	$\sim 283.8$	$\sim 49.0\%$	$\sim 1.8$	$sp^2 \rightarrow sp^3$
$C^2 1s$						
$C^3 1s$	$\sim 284.5$	$\sim 24.4\%$	$\sim 284.5$	$\sim 25.8\%$	0	$sp^3 \rightarrow sp^3$
$C^4 1s$	$\sim 286.8$	$\sim 25.2\%$	$\sim 285.1$	$\sim 25.2\%$	$\sim 1.7$	$sp \rightarrow sp^2$
N $1s$	$\sim 400.0$		$\sim 398.7$		$\sim 1.3$	$sp \rightarrow sp^2$

### III. RESULTS AND DISCUSSION

#### A. High-resolution electron-energy-loss spectroscopy

Figure 2 shows the HREELS spectra recorded as a function of allyl cyanide ( $C^1H_2=C^2H-C^3H_2-C^4\equiv N$ ) exposure. Figures 2(d) and 2(e) display the vibrational features for physisorbed multilayer allyl cyanide after exposing 4.0 and 6.0 L onto the Si(111)- $7\times 7$  surface at 110 K, respectively. The energy-loss peaks at 410, 563, 968, 1078, 1305, 1410, 1650, 2252, 2925, 3011, and 3085  $cm^{-1}$  are readily resolved, which are in good agreement with the vibrational energies of liquid-phase allyl cyanide within  $\sim 20 cm^{-1}$ . The peaks at 3085 and 3011  $cm^{-1}$  are assigned to the  $C(sp^2)-H$  stretching modes of  $C^1H_2=$  and  $=C^2H-$ , respectively. The intensity at 2263  $cm^{-1}$  is associated with the  $C\equiv N$  stretching mode. The loss at 1650  $cm^{-1}$  is attributable to the  $C=C$  stretching. The detailed assignments for physisorbed and chemisorbed allyl cyanide on Si(111)- $7\times 7$  together with the IR data of liquid phase allyl cyanide<sup>21</sup> are summarized in Table I. At a low exposure of 0.50 L, features corresponding to chemisorbed molecules [see also Fig. 3(b)] are clearly observed. Compared to physisorbed allyl cyanide, the  $C-H$  stretching features are red-shifted to  $< 3000 cm^{-1}$ , suggesting the rehybridization of C atoms of the vinyl group from  $sp^2$  to  $sp^3$  upon chemisorption. This is further sup-

ported by the absence of the  $C=C$  stretching mode at 1650  $cm^{-1}$  in the spectra of chemisorbed molecules. In addition, the absence of the  $C\equiv N$  stretching mode at  $\sim 2200-2300 cm^{-1}$  in chemisorbed molecules is accompanied by a feature appearing at 1585  $cm^{-1}$  attributable to the  $C=N$  stretching, clearly demonstrated in the enlargement of Fig. 2. These spectroscopic changes strongly suggest the direct participation of both the  $C=C$  and  $C\equiv N$  groups in the interaction with the Si surface. The changes in the region of  $\leq 1200 cm^{-1}$  are also noticeable. The peak around 563  $cm^{-1}$ , corresponding to the  $C^2H=$  wagging observed for physisorbed multilayer, is not present in the spectra of chemisorbed molecules, consistent with the involvement of  $C=C$  in surface binding. The peaks at 495 and 649  $cm^{-1}$  are attributable to the formation of Si-C and Si-N linkages upon chemisorption.<sup>22,23</sup> The absence of spectrum intensity of the Si-H stretching around 2000–2150  $cm^{-1}$  (Ref. 24) indicates the associative chemisorption nature of allyl cyanide on Si(111)- $7\times 7$ . Similar results, shown in Fig. 3(b) and Table I, were also obtained for a saturated chemisorption monolayer prepared by exposing a clean Si(111)- $7\times 7$  surface to 5.0-L allyl cyanide at 110 K, and then annealing the surface to 300 K to drive away all the physisorbed molecules. In addition, off-specular HREELS spectra [Figs. 3(c) and 3(d)]

TABLE III. Assignments of the valence band energy-level of physisorbed and chemisorbed  $C^1H_2-C^2H-C^3H_2-C^4\equiv N$  on Si(111)- $7\times 7$  and the calculated ionization potentials of gas-phase allyl cyanide. All energies are in eV.

Band	Orbital character	Calculated ionization potentials	Average value	Physisorbed allyl cyanide on Si(111)- $7\times 7$	Chemisorbed allyl cyanide on Si(111)- $7\times 7$
1	$\pi_{CC} (3a'')$	10.47	12.47	2.84 (A)	
2	$\pi_{CN} (15a')$	12.69	12.73	5.20 (B)	3.22 (B')
3	$\pi_{CN} (2a'')$	12.76			
4	$n_N (13a')$	14.97	14.58	7.27 (C)	7.80 (C')
5	$\sigma_{CH} (14a')$	14.20			
6	$\sigma_{CC} (12a')$	16.14			
7	$\sigma_{CH} (1a'')$	17.46			
8	$\sigma_{CH} (11a')$	17.90	17.67	10.63 (D)	10.42 (D')
	$\sigma_{CC} (11a')$	17.90			
9	$\sigma_{CH} (10a')$	18.99			
10	$C_{2s} (9a')$	21.65	21.65	14.68 (E)	14.60 (E')

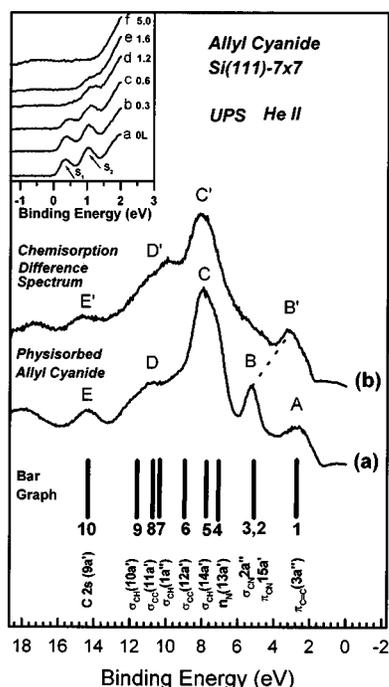


FIG. 6. The valence-band spectrum of physisorbed allyl cyanide (a) and the difference spectrum of chemisorbed allyl cyanide (b) on Si(111)-7 $\times$ 7.

were collected to screen out the dipole transition related vibrational modes.<sup>25</sup> The relative intensification of the C—H stretching peak around 2950  $\text{cm}^{-1}$  at off-specular angles possibly indicates a parallel configuration of chemisorbed molecules on the Si surface. On the other hand, the sharp attenuation of the 497- and 646- $\text{cm}^{-1}$  losses [Figs. 3(c) and 3(d)] correlated to Si—C and Si—N stretching modes shows their nearly perpendicular nature to the surface. Based on our HREELS results, it is concluded that both the C $\equiv$ N and C=C groups are bound to Si(111)-7 $\times$ 7 through [2+2]-like cycloadditions with neighboring adatom-rest atom pairs, forming a CH<sub>3</sub>—CH<sub>2</sub>—CH<sub>2</sub>—CH=NH-like surface intermediate.

### B. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy was employed to investigate the shifts of C 1s and N 1s core levels for allyl cyanide on Si(111)-7 $\times$ 7. The C 1s and N 1s spectra of allyl cyanide following a sequence of exposures at 110 K are shown in Fig. 4. For exposures  $\leq 1.2$  L, peaks at 284.4 eV (C 1s) and 398.7 eV (N 1s) are observed, attributable to chemisorbed allyl cyanide. Further increase in the exposure results in new photoemission intensities on the higher binding energy sides of the C 1s and N 1s peaks of chemisorbed allyl cyanide together with a gradual attenuation of chemisorbed features. At high exposures of 10 L, a broad feature at 285.6 eV (C 1s) and a symmetric peak at 400.0 eV (N 1s) become dominant due to physisorbed allyl cyanide. In order to assign C 1s peaks of physisorbed and chemisorbed allyl cyanide, software VGX900 was employed to deconvolute the photoemission features from C 1s and N 1s core levels. The fitting

results are shown in Fig. 5. Figure 5(f) shows that the C 1s feature for physisorbed allyl cyanide can be reasonably deconvoluted into three peaks at 286.8, 285.6, and 284.5 eV with an area ratio of  $\sim 1:2:1$ . The peak at 286.8 eV can be assigned to the C atom of cyano due to its *sp* hybridization, similar to the value obtained for acetonitrile.<sup>26</sup> The photoemission feature at 285.6 and 284.5 eV are associated with C<sup>1</sup>H<sub>2</sub>=C<sup>2</sup>H- and -C<sup>3</sup>H<sub>2</sub>-, respectively, in good agreement with the C 1s BEs determined for the C atoms with *sp*<sup>2</sup> and *sp*<sup>3</sup> hybridizations in alkenes.<sup>27</sup> The spectrum of chemisorbed molecules with a narrower FWHM was also fitted into three peaks at 285.1, 284.5, and 283.8 eV with an area ratio of  $\sim 1:1:2$  [Fig. 5(c)]. The peak at 285.1 eV can be attributed to the C atom of -C<sup>4</sup>(Si)=N(Si), which was evidenced in acetonitrile chemisorption on Si(111)-7 $\times$ 7 through a *di*- $\sigma$  binding mode.<sup>19</sup> The photoemission at 283.8 eV is ascribed to -C<sup>2</sup>H(Si)-C<sup>1</sup>H<sub>2</sub>(Si), well in line with *di*- $\sigma$  bonded ethylene on Si(100).<sup>27,28</sup> The actual assignments and relative intensities of fitted spectra for chemisorbed and physisorbed molecules are listed in Table II. The significant down shifts of C<sup>4</sup> and N atoms of the cyano group and C<sup>1</sup> and C<sup>2</sup> atoms of the vinyl group strongly suggests that both C<sup>1</sup>=C<sup>2</sup> and C<sup>4</sup> $\equiv$ N functionalities are involved into the direct reaction with the Si surface, which is consistent with the evidences shown in our HREELS experiments (see Table III).

### C. Ultraviolet photoelectron spectroscopy

Allyl cyanide, a typical unsaturated multifunctional molecule, contains two reactive functional groups, C=C and C $\equiv$ N. The valence-band structure of gaseous allyl cyanide was previously investigated with *ab initio* self-consistent field calculations with 4-31 G basis functions and experimental He I UPS and He\* (*2*<sup>3</sup>S) penning ionization electron spectroscopy.<sup>29</sup> Nine ionization energy levels were reported. They are shown in the forms of bar graphs together with the valence band spectra of physisorbed allyl cyanide and the difference spectrum of chemisorbed molecules on Si(111)-7 $\times$ 7 (Fig. 6), but shifted to account for work-function and final-state relaxation effects when condensed on solid-state surfaces. Figure 6(a) presents the valence-band spectrum obtained after exposing a clean Si(111)-7 $\times$ 7 surface to 6.0 L of allyl cyanide at 110 K. Its close resemblance to the gas phase spectrum clearly demonstrates the formation of physisorbed allyl cyanide multilayer. The surface state of adatoms at  $\sim 0.3$  eV disappears more rapidly as a function of the exposure compared to that of rest atom at  $\sim 0.8$  eV. This observation can possibly be attributed to the concurrent occurrence of physisorption of allyl cyanide molecules on the surface through the interaction of the lone-pair electrons at the N atom of allyl cyanide with individual adatoms. However, the possibility of electron redistribution on adatoms due to the existence of neighboring chemisorbed molecules cannot be ruled out. Further experimental and theoretical work is required to fully understand this result.

To obtain the spectral changes upon chemisorption, a saturated chemisorption monolayer was prepared by annealing a multilayer allyl cyanide precovered Si(111)-7 $\times$ 7

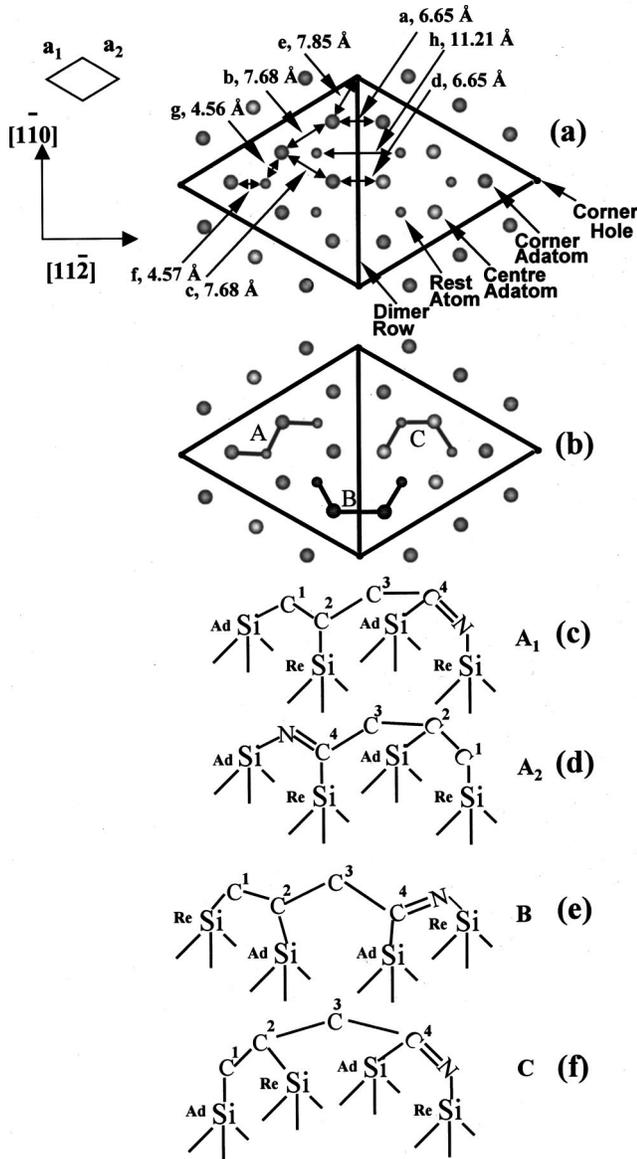


FIG. 7. (a) The distribution of reactive adatoms, rest atoms, and corner holes in a Si(111)-7 $\times$ 7 unit cell. (b) The configurations (A, B, and C) of two adjacent “neighboring adatom-rest atom pairs” in a unit cell. (c), (d), (e), and (f). The possible *tetra- $\sigma$*  binding configurations of allyl cyanide on Si(111)-7 $\times$ 7.

sample to 300 K to desorb physisorbed molecules. The difference spectrum [Fig. 6(b)] was obtained by subtracting the photoemission of a clean surface from that of a fully chemisorbed allyl cyanide Si(111)-7 $\times$ 7. The emission features at  $\sim$ 3.22, 7.80, 10.42, and 14.60 eV can be readily resolved. Our main focus is to closely examine the variation of bands A and B upon chemisorption as these two valence bands are relevant to the reactive  $\pi_{C=C}$  and  $\pi_{C\equiv N}$  bonds. In view of the fact that  $\sigma_{C-C}$  and  $\sigma_{C-H}$  do not participate directly in the interaction with Si surface dangling bonds, we align these deep levels in the spectra of physisorbed and chemisorbed molecules to observe the changes in shallow bands. Compared to physisorbed molecules [Fig. 6(a)], two major changes are noticed in the difference spectrum of chemi-

sorbed molecules, namely, the disappearance of the  $\pi_{C=C}$  photoemission feature and the significant down shift of the  $\pi_{CN}$  energy level by  $\sim$ 2.0 eV. In addition, the photoemission intensity of  $\pi_{CN}$  displays some attenuation upon chemisorption. The observation of photoemission from  $\pi_{CN}$  in chemisorbed molecules excludes the possibility of the *tetra- $\sigma$*  bonding between the C $\equiv$ N group and the Si surface. These results are indeed consistent with the above HREELS and XPS observations. The involvement of surface dangling bonds in the covalent attachment of allyl cyanide is evidenced in the inset of Fig. 6. On a clean Si(111)-7 $\times$ 7 surface, two peaks at  $\sim$ 0.3 ( $S_1$ ) and  $\sim$ 0.8 eV ( $S_2$ ) below  $E_F$  are clearly identified, due to the dangling bond surface states of adatoms and rest-atoms, respectively, according to scanning tunneling microscopy (STM) studies.<sup>30,31</sup> Increasing allyl cyanide exposures results in the gradual attenuation of these states due to the redistribution of their electron density in the formed adsorbate-substrate complex.

#### D. Possible binding configurations

Previous STM studies showed that unsaturated hydrocarbons containing two C=C groups at their two ends bind to Si(111)-7 $\times$ 7 through the formation of four  $\sigma$  bonds at the two C=C of these molecules.<sup>32</sup> In this experiment, our results show that allyl cyanide is mainly covalently attached to Si(111)-7 $\times$ 7 with a *tetra- $\sigma$*  binding mechanism through two [2+2]-like cycloaddition reactions between the C=C and C $\equiv$ N groups and the surface. Considering the feasible [2+2]-like cycloaddition between C=C of ethylene<sup>7,8</sup> (the C $\equiv$ N group in acetonitrile<sup>19</sup>) and the neighboring adatom-rest atom pair, it is reasonably deduced that allyl cyanide is bound to two neighboring adatom-rest atom pairs of the Si surface with four newly formed  $\sigma$  bonds. Figure 7(a) shows the spatial distribution of reactive adatoms, rest atoms and corner holes on Si(111)-7 $\times$ 7.<sup>33,34</sup> The spatial configurations of *adjacent* neighboring adatom-rest atom pairs (A, B, and C) are presented in Fig. 7(b). All of them involve two adatoms and two rest atoms. Although the terminal separations of configurations A (A1 and A2) and B are similar, the distances between the two middle dangling bonds are 4.56 and 6.65 Å, respectively.<sup>33,34</sup> A smaller strain is expected in configuration A [Figs. 7(c) and 7(d)] compared to configurations B [Fig. 7(e)]. With a comparable separation between the two middle dangling bonds, Configuration C has a shorter distance between the two terminal atoms than configurations A and B. Considering the molecular dimension of allyl cyanide, it is expected to be thermodynamically preferred compared to A and B.

#### IV. SUMMARY

The covalent attachment of allyl cyanide on Si(111)-7 $\times$ 7 has been investigated using high-resolution electron energy loss spectroscopy (HREELS), x-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS). The HREELS results demonstrate that the attachment of allyl cyanide mainly involves two [2+2]-like

cycloadditions of the C=C and C $\equiv$ N groups to two adjacent neighboring adatom-rest atom pairs, forming a *tetra- $\sigma$*  bonded intermediate. The CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH=NH-like skeleton attached on Si(111)-7 $\times$ 7 can be useful as a mo-

lecular template for further modification and functionalization of Si surfaces or employed as an intermediate for syntheses in vacuum through a large number of possible reactions of an imine group.<sup>35,36</sup>

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