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Selective Binding of the Cyano Group in Acrylonitrile Adsorption on Si(100)-2 × 1

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Abstract: The covalent binding of acrylonitrile ($CH_2{=}CH{-}C{\equiv}N$) and the formation of a $C{=}C{-}C{=}N$ structure on Si(100) have been investigated using high-resolution electron energy loss spectroscopy (HREELS), X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and density functional theory (DFT) calculations. For chemisorbed acrylonitrile, the absence of $\nu(C{\equiv}N)$ at 2245 cm^{-1} and the appearance of $\nu(C{=}N)$ at 1669 cm^{-1} demonstrate that the cyano group directly participates in the interaction with Si(100), which is further supported by XPS and UPS observations. Our experimental results and DFT calculations unambiguously demonstrate a [2 + 2] cycloaddition mechanism for acrylonitrile chemisorption on Si(100) through the binding of $C{\equiv}N$ to Si dimers. The resulting chemisorbed monolayer with a $C{=}C{-}C{=}N$ skeleton can serve as a precursor for further chemical syntheses of multilayer organic thin films in a vacuum and surface functionalization for in situ device fabrication.

I. Introduction

The covalent binding of organic molecules on semiconductor surfaces has recently become an increasingly important aspect of surface modification and functionalization for potential applications in semiconductor and microelectronic technologies.[1,2] To gain the control needed for incorporating organic function into existing technologies, there are growing efforts dedicated to the fundamental understanding of molecular adsorption on semiconductor surfaces.[3−5] Surface modification may offer ways to fine tune the chemical and physical properties of interfaces.[3,6]

One particularly interesting semiconductor surface is Si(100), which undergoes a 2 × l reconstruction involving the pairing of surface atoms into dimers. These dimers are formally held together with a Si═Si double bond,[7,8] suggesting a possible similarity between the chemical properties of Si(100) and organic alkenes. Previous investigations in this area mainly focused on the covalent attachment chemistry of some unsaturated hydrocarbons.[9−23] These unsaturated hydrocarbons can be covalently bonded onto Si(100) through the [2 + 2] or/and [4 + 2] cycloaddition reactions of C═C, C≡C, and dienes with surface dimers.

In organic syntheses, vinyl and cyano groups are two of the most important building blocks for many organic molecules.[24] Acrylonitrile, a typical monomer with both vinyl and cyano groups, is a valuable polyfunctional heteroatomic molecule having single, double, and triple bonds. The cyano group modifies the electronic structure of the vinyl group through conjugation. The conjugative effect delocalizes the $\pi_{C{=}C}$ orbital over the molecule, lowering the electronic density at the vinyl group. Regarded as a substituted ethylene because of conjugative and inductive effects, acrylonitrile possesses both electron-withdrawing and electron-donating properties,[25] indicative of its rich chemistry. Thus, acrylonitrile can be chosen as a template

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(1) Yates, J. T., Jr. *Science* **1998**, *279*, 335−336.

(2) Lopinski, G. P.; Moffatt, D.; Wayner, D. D. M.; Wolkow, R. A. *Nature* **1998**, *392*, 909−911.

(3) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413−441.

(4) Waltenberg, H. N.; Yates, J. T., Jr. *Chem. Rev.* **1995**, *95*, 1589−1673.

(5) Hamers, R. J.; Coulter, S. K.; Ellison, M. D.; Hovis, J. S.; Padowitz, D. F.; Schwartz, M. P.; Greenlief, C. M.; Russell, J. N., Jr. *Acc. Chem. Res.* **2000**, *33*, 617−624.

(6) Crooks, R. M.; Ricco, A. J. *Acc. Chem. Res.* **1998**, *31*, 219−227.

(7) Schlier, R. E.; Farnsworth, H. E. *J. Chem. Phys.* **1959**, *30*, 917−920.

(8) Appelbaum, J. A.; Baraff, G. A.; Hamann, D. R. *Phys. Rev. B* **1976**, *14*, 588−596.

(9) Liu, H.; Hamers, R. J. *J. Am. Chem. Soc.* **1997**, *119*, 7593−7594.

(10) Hamers, R. J.; Hovis, J. S.; Lee, S. *J. Phys. Chem. B* **1997**, *101*, 1489−1492.

(11) Teplyakov, A. V.; Kong, M. J.; Bent, S. F. *J. Am. Chem. Soc.* **1997**, *119*, 11100−11101.

(12) Hovis, J. S.; Hamers, R. J. *J. Phys. Chem. B* **1997**, *101*, 9581−9585.

(13) Lopinski, G. P.; Fortier, T. M.; Moffatt, D. J.; Wolkow, R. A. *J. Vac. Sci. Technol., A* **1998**, *16*, 1037−1042.

(14) Hovis, J. S.; Liu, H.; Hamers, R. J. *J. Phys. Chem. B* **1998**, *102*, 6873−6879.

(15) Padowitz, D. F.; Hamers, R. J. *J. Phys. Chem. B* **1998**, *102*, 8541−8545.

(16) Hovis, J. S.; Hamers, R. J. *J. Phys. Chem. B* **1998**, *102*, 687−692.

(17) Liu, H.; Hamers, R. J. *Surf. Sci.* **1998**, *416*, 354−362.

(18) Teplyakov, A. V.; Lai, P.; Noah, Y. A.; Bent, S. F. *J. Am. Chem. Soc.* **1998**, *120*, 7377−7378.

(19) Lopinski, G. P.; Moffatt, D. J.; Wolkow, R. A. *Chem. Phys. Lett.* **1998**, *282*, 305−312.

(20) Hovis, J. S.; Hamers, R. J.; Greenlief, C. M. *Surf. Sci.* **1999**, *440*, L815-L819.

(21) Lai, P.; Teplyakov, A. V.; Noah, Y. A.; Kong, M. J.; Wang, G. T.; Bent, S. F. *J. Chem. Phys.* **1999**, *110*, 10545−10553.

(22) Hovis, J. S.; Lee, S.; Liu, H.; Hamers, R. J. *J. Vac. Sci. Technol., B* **1997**, *15*, 1153−1158.

(23) Clemen, L.; Wallace, R. M.; Taylor, P. A.; Dresser, M. J.; Choyke, W. J.; Weinberg, W. H.; Yates, J. T., Jr. *Surf. Sci.* **1992**, *268*, 205−216.

(24) Morrison, R. T.; Boyd, R. N. *Organic Chemistry*; Allyn and Bacon: Boston, 1959.

(25) El-Sayed, M. F. A.; Sheline, R. K. *J. Inorg. Nucl. Chem.* **1958**, *6*, 187−192.

10.1021/ja010574j CCC: $20.00

to demonstrate the selectivity and reactivity of functional groups coexisting in a multifunctional molecule on Si(100).

In this paper, the covalent attachment chemistry of acrylonitrile on Si(100) was studied with the aim of elucidating the nature of acrylonitrile/silicon interfacial chemistry and fabricating a functional intermediate suitable for further organic syntheses and functionalization. HREELS was used to characterize the vibrational properties of acrylonitrile on Si(100). XPS provides information on chemical shifts of the C 1s and N 1s core levels. The valence bands of the adlayer were probed with UPS. DFT (density functional theory) calculations (pBP/DN** in Spartan 5.1 and B3LYP/6-31G* in Gaussian 98) were employed to optimize the chemisorption geometries and calculate their total energies. Our experimental results and theoretical calculations show that acrylonitrile is covalently bonded to Si(100) through a [2 + 2] cycloaddition of the cyano group with the Si═Si dimer. The resulting chemisorbed species, $C{=}C{-}C{=}N$, can be considered as a precursor for realizing "dry" organic syntheses on the Si(100) surface and further functionalization.

II. Experimental Section

Experiments were performed in two ultrahigh vacuum (UHV) systems with base pressures lower than 2×10^{-10} Torr. One of them is equipped with a high-resolution electron energy loss spectrometer (HREELS LK-2000-14R). HREELS measurements were taken in a specular geometry. The electron beam with an energy of 5.0 eV impinges on the surface at an incident angle of 60° with respect to the surface normal. A typical instrumental resolution of 50 cm^{-1} is achieved. The other chamber was equipped with an X-ray source, a differentially pumped helium resonance lamp, and a concentric hemispherical electron energy analyzer (CLAM2, VG), as well as a quadrupole mass spectrometer (SRS-200). In the XPS experiments, the Mg X-ray source ($h\nu = 1253.6$ eV) was used. All spectra reported in this paper are referenced to the binding energy (BE) of 99.3 eV for the bulk Si 2p XPS peak.[26] To obtain a wider flat energy window, He II UV radiation was employed in our UPS studies.

A p-type, B-doped Si(100) wafer from Goodfellow (U.K.) was cut into samples with dimensions of $8 \times 18 \times 0.38$ mm^3, which were cleaned with a hot 5% HF solution and then rinsed with deionized water. The clean Si(100) samples were prepared by Ar ion bombardment (1 keV, 30 min, ~5–10 $\mu A \cdot cm^{-2}$) and final annealing at 1300 K in the ultrahigh vacuum (UHV) systems. No C, O, and N impurities could be detected on the clean surfaces by XPS and HREELS.

Acrylonitrile (99%) purchased from Aldrich Chemical was further purified through at least five freeze–pump–thaw cycles before being dosed onto the clean Si(100) surface at 110 K. Dosing was performed by backfilling the chamber, and the exposures were reported in Langmuirs ($1\ L = 10^{-6}$ Torr·s). The absolute coverage of chemisorbed acrylonitrile was calibrated independent of its exposure by comparing the C 1s peak areas of chemisorbed benzene and acrylonitrile, assuming identical C 1s cross section and scattering for both molecules.

III. Results

III.A. High-Resolution Electron Energy Loss Spectroscopy. Figure 1 shows the high-resolution electron energy loss spectra of Si(100) exposed to acrylonitrile at 110 K. The inset is the enlargement of vibrational features in the 1500–1750 cm^{-1} range. The vibrational frequencies and their assignments for physisorbed and chemisorbed acrylonitrile on Si(100) are listed in Table 1. From this table, it can be seen that loss features of physisorbed molecules (Figure 1c–e) are in good agreement with the infrared spectrum of solid-state acrylonitrile as well as the previous IR studies of physisorbed acrylonitrile on transition metals.[27–29]

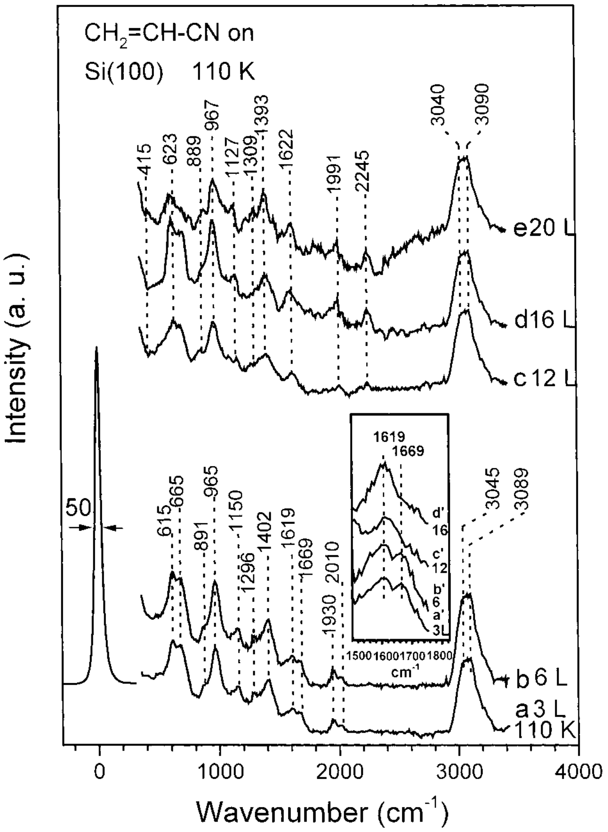

Figure 1. HREEL spectra as a function of acrylonitrile exposure on Si(100) at 110 K.

Table 1. Vibrational Assignments of Physisorbed and Chemisorbed Acrylonitrile on Si(100) at 110 K[a]

vibrational assignments	solid state[27] $CH_2{=}CH{-}CN$	physisorbed $CH_2{=}CHCN$ on Si(100)	chemisorbed $CH_2{=}CHCN$ on Si(100)
$=CH_2$ asymmetric stretch	3093	3090	3089
$=CH$ stretch	3039	3040	3045
$=CH_2$ symmetric stretch	2989		
CH_2 asymmetric stretch	2933		
CH_2 symmetric stretch	2919		
$C{\equiv}N$ stretch	2249	2245	
twice $=CH_2$ twist			2010
twice CH_2 (twist + rock + wag)		1991	1930
$C{=}N$ stretch			1669
$C{=}C$ stretch	1645	1622	1619
CH_2 deformation	1422		
$=CH_2$ scissors	1403	1393	1402
CH_2 wag	1327		
$=CH$ bend	1305	1309	1296
$=CH$ bend	1288		
CH_2 twist	1215	1127	1150
$=CH_2$ rock	1075		
$=CH_2$ twist	990		
CH_2 rock	949	967	965
$=CH_2$ wag	933		
$C{-}C{-}C$ asymmetric stretch	914	889	891
$C{-}C{-}C$ symmetric stretch	867		
$Si{-}C$ stretch			665
$C{-}C{-}C$ bend	621	623	615
CH wag	557		
$C{=}C{-}C$ bend	407	415	

[a] Vibrational frequencies (cm^{-1}) of solid acrylonitrile are also included for comparison.

The vibrational characteristics of chemisorbed acrylonitrile at low exposures (Figure 1a,b), however, are significantly different. One of the most important differences between chemisorbed and physisorbed acrylonitrile is the absence of the

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(26) Moulder, J. F.; Stickle, W. F.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Corporation: Minnesota, 1992.

ν(C≡N) stretching mode at 2245 cm^{-1} for chemisorbed acrylonitrile at 3 and 6 L exposures. Moreover, a new peak at 1669 cm^{-1}, close to the stretching mode of the C=C bond at 1619 cm^{-1}, is observed, being gradually attenuated with increasing physisorbed acrylonitrile. We assign the new peak at 1669 cm^{-1} to the stretching mode of the C=N bond. Because of the nearly parallel configuration of the C=N bond on Si(100), its intensity is relatively weak,[30] but the inset of Figure 1 still clearly demonstrates the coexistence of the stretching modes of C=C and C=N. The absence of ν(C≡N) coupled with the concurrent emergence of ν(C=N) in the HREEL spectra of chemisorbed acrylonitrile is the direct evidence for the participation of the cyano group in the interaction with surface silicon dimers. On the other hand, the stretching modes of C(sp^2)—H do not display obvious variations in the corresponding peak shape and peak position, indicating that C atoms of the vinyl are not rehybridized. This is consistent with the fact that the stretching mode of C=C remains constant for both chemisorbed and physisorbed molecules. If the vinyl was involved in binding with Si surface dangling bonds, a peak of C(sp^3)—H, red-shifted by 80−100 cm^{-1} from the C(sp^2)—H stretching mode, would be expected. Thus, our HREEL spectra clearly demonstrate that the carbon atoms of the vinyl group do not directly interact with Si(100). The negligible loss at ∼2050−2150 cm^{-1} corresponding to ν(Si—H) [31] rules out the possibility of dissociative chemisorption of acrylonitrile by forming a σ-bonded species which involves C—H bond scission and Si—H bond formation.

III.B. X-ray Photoelectron Spectroscopy. Figure 2 shows the N 1s and C 1s XPS spectra of acrylonitrile adsorbed on Si(100) at 110 K. For exposures < 8 L, a broad C 1s peak with a large fwhm (full width at half-maximum of height) of ∼3.6 eV centered at 285.5 eV and a nearly symmetrical N 1s peak at 398.2 eV are observed, attributable to chemisorbed acrylonitrile. With increasing exposure, an asymmetrical C 1s peak at 286.8 eV and the N 1s peak at 399.9 eV due to the physisorbed molecules grow up and dominate the XPS feature at exposures higher than 16 L. The contribution from chemisorbed acrylonitrile is completely attenuated at an exposure of 40 L.

The area ratio $A_{\mathrm{C1s}}/A_{\mathrm{Si2p}}$ is plotted as a function of acrylonitrile exposure in the inset of Figure 2. The value for each point was obtained by averaging three separate measurements to reduce possible errors. A_{C1s} is the XPS peak area of chemisorbed acrylonitrile at 300 K. The saturation of the $A_{\mathrm{C1s}}/A_{\mathrm{Si2p}}$ ratio indicates the completion of chemisorption. To estimate its absolute saturation coverage, XPS measurements for acrylonitrile-saturated Si(100) are compared with those of chemisorbed benzene. The saturation coverage of benzene, $\theta_{\mathrm{benzene}}$, the number of benzene molecules per surface Si atom, is known to be ∼0.27.[32] The peak area ratio ($A_{\mathrm{C1s}}/A_{\mathrm{Si2p}}$) for acrylonitrile-saturated Si(100) is 0.236, whereas the value for benzene is determined to be ∼0.268. After taking into consideration the numbers of carbon atoms in these two molecules, the saturation coverage, $\theta_{\mathrm{acrylonitrile}}$, is estimated to be ∼0.46 [$= 0.27 \times (0.236/0.268) \times (6/3)$], showing that each acrylonitrile molecule approximately reacts with one silicon surface dimer (two silicon atoms).

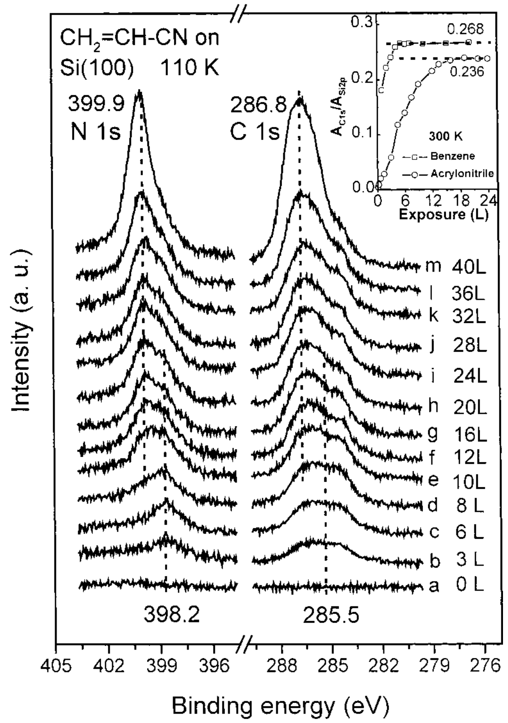

Figure 2. C 1s and N 1s XPS for acrylonitrile adsorbed on Si(100) as a function of exposure at 110 K. The inset plots the XPS peak area ratio, $A_{\mathrm{C1s}}/A_{\mathrm{Si2p}}$, for acrylonitrile and benzene on Si(100) as a function of exposure at 300 K, where the dotted line represents the saturation chemisorption.

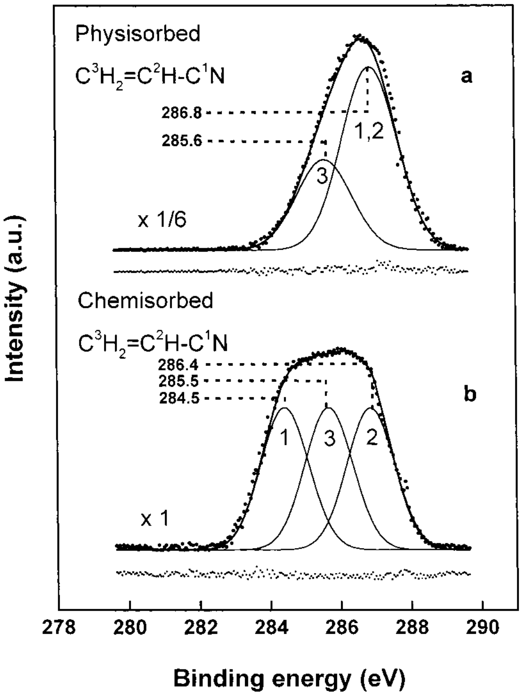

Figure 3. Fitted C 1s spectra for physisorbed and chemisorbed acrylonitrile. The bottom panels of parts a and b are the plots of the differences between experimental data and fitted curves for physisorbed and chemisorbed acrylonitrile, respectively.

Figure 3 shows the fitted C 1s XPS spectra for chemisorbed and physisorbed acrylonitrile on Si(100). The C 1s spectrum of physisorbed acrylonitrile is fitted into two peaks with equal fwhm centered at 285.6 and 286.8 eV and an area ratio of ∼1:2 (Figure 3a). The separation between the two fitted peaks is ∼1.2 eV. The result shown in Figure 3a is in good agreement with the experimental XPS results of physisorbed acrylonitrile on

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(27) Durig, J. R.; Guirgis, G. A.; Drew, A. S. *J. Raman Spectrosc.* **1994**, *25*, 907−921.

(28) Kubota, J.; Kondo, J.; Domen, K.; Hirose, C. *J. Electron Spectrosc. Relat. Phenom.* **1993**, *64/65*, 137−144.

(29) Parent, Pa.; Laffon, C.; Tourillon, G. *J. Phys. Chem.* **1995**, *99*, 5058−5066.

(30) Ibach, H.; Mills, D. L. *Electron Energy Loss Spectroscopy and Surface Vibrations*; Academic Press: New York, 1982.

(31) Wagner, H.; Butz, R.; Backes, U.; Bruchmann, D. *Solid State Commun.* **1981**, *38*, 1155−1157.

Table 2. Peak Assignments of Valence Band Spectral Features for Chemisorbed and Physisorbed Acrylonitrile on Si(100)[a]

	gas phase		physisorbed acrylonitrile		chemisorbed acrylonitrile		
MO type	orbital	average	peak	energy	8 L	4 L	1 L
$\pi_{C=C}$	2a″ (10.91)	10.91	A	6.06	5.85	5.78	5.78
$\pi_{C\equiv N}$	12a′ (12.36)	13.34[b]	B	8.24[c]	7.58[c]	7.40[c]	7.35[c]
$\pi_{C=C}$, $\pi'_{C\equiv N}$	1a″ (13.04)						
σ_{CN}	11a′ (13.53)						
π_{CH_2}	10a′ (14.44)						
σ_{C-C}	9a′ (16.17)	16.17	C	11.45	11.25	11.20	11.20
C_{2s}(CN)	8a (17.62)	17.62	D	13.10	12.95	12.90	12.90

[a] Ionization energies of the gas-phase molecular orbitals are shown in parentheses. All energy values are in electronvolts. [b] 13.34 is the average value of energy corresponding to $\pi_{C\equiv N}$(12a′), $\pi_{C=C}$(1a″) and $\pi'_{C\equiv N}$(1a″), σ_{CN}, and π_{CH_2}. [c] This value is the energy of the central point of peak B.

Cu(100), Pt(111), and Au(111).[29,33] It is also consistent with the density functional theory calculation result obtained by Crispin et al.,[33] showing that the BEs of C^1 and C^2 separated by 0.19 eV are ~1.1 eV higher than that of the C^3 atom. Resolving the C 1s BE difference of ~0.2 eV of C^1 and C^2 by further deconvolution was not attempted because of the limitation of our XPS resolution. Thus, the peak at 286.8 eV can be assigned to C^1 and C^2, while the other one at 285.6 eV can be assigned to C^3 of physisorbed molecules.[29,33]

The XPS result for chemisorbed acrylonitrile is shown in Figure 3b. The C 1s spectrum can be fitted into three peaks at BEs of 286.4, 285.5, and 284.5 eV with the same fwhm. The ratio of the peak intensities is approximately 1:1:1, indicative of three kinds of chemically inequivalent carbon atoms in the chemisorbed species. The significant differences in the C 1s spectra of chemisorbed and physisorbed acrylonitrile show the changes in the electronic structure of acrylonitrile upon chemisorption on the silicon surface. The detailed discussion for the differences of C 1s spectra between the chemisorbed and physisorbed acrylonitrile and the detailed assignments of the three fitted peaks in Figure 3b will be presented in Section IV.

III.C. Ultraviolet Photoelectron Spectroscopy. The acrylonitrile molecule is planar in its neutral ground electronic state and is of C_s symmetry. The valence band structure of gaseous acrylonitrile molecules was extensively investigated with high-resolution He I photoelectron spectroscopy and penning ionization techniques.[34−36] Lake and Thompson[34] first investigated its He I photoelectron spectrum and reported seven ionization energy levels. The first band of the spectrum is located at 10.91 eV, attributable to the ionization of the orbital from the vinyl group.[36] The second at 12.36 eV was assigned to the ionization of electrons from the π_{CN}(12a′) orbital of the cyano group.[33] The narrow and intense peak at 13.04 eV is contributed by the electrons from the 1a″ molecular orbital with a mixed character of π'_{CN} and $\pi_{C=C}$. The other four bands at 13.53, 14.44, 16.17, and 17.62 eV were related to σ_{CN}, σ_{CH_2}, σ_{C-C}, and C_{2s}(CN), respectively.

Previous valence band spectra of acrylonitrile show that π_{CN} splits into two levels, π_{CN}(12a′) and π'_{CN}(1a″), with an energy separation of 0.68 eV, as shown in Table 2.[37] The π'_{CN}(1a″) of the C≡N group is perpendicular to the plane of the acrylonitrile molecule, forming a conjugated orbital with $\pi_{C=C}$(a″). The other $\pi_{C\equiv N}$(12a′) is in the molecular plane. Figure 4 presents the correlation diagram of the molecular orbitals of CH_2═CH─CN, CH_2═CH_2, and HCN.[36,38,39] The schematic diagram of gaseous acrylonitrile molecular orbitals is presented in the top panel of Figure 4. In view of the fact that the inductive effect of the CN group is larger than the conjugation effect,[37] Figure 4 shows that the induction effect of the CN group stabilizes the $\pi_{C=C}$(2a″) orbital (its ionization energy is 10.91 eV instead of 10.51 eV for CH_2═CH_2), and the π'_{CN}(1a″) is destabilized by the increase of electron density and has an ionization energy lower than expected, if only considering a pure conjugation effect.

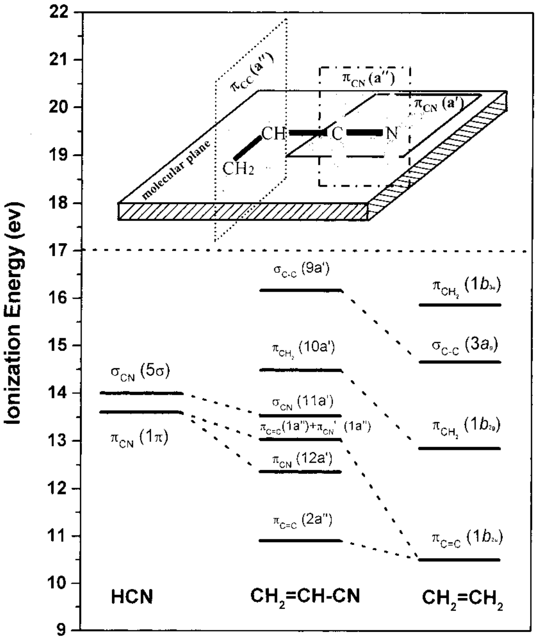

Figure 4. Energy level correlation diagram for the molecular orbitals of HCN, CH_2═CH─CN, and CH_2═CH_2. The top panel is the schematic diagram of acrylonitrile molecular orbitals.

Figure 5 shows the He II photoelectron spectra of physisorbed and chemisorbed acrylonitrile on Si(100). The inset (Figure 5) shows that increasing exposure leads to the attenuation of the dangling bond surface state and to the total quenching at 8 L of acrylonitrile, correlating well with the saturation of chemisorption revealed by XPS. Upon 40 L exposure at 110 K, a physisorbed multilayer results in four dominant features at 6.06 (A), 8.24 (B), 11.45 (C), and 13.10 (D) eV below the Fermi level, E_f. It can be seen from Table 2 that, for physisorbed acrylonitrile, the energy separations between two successive levels agree well with those of gas-phase UPS.[34−38] The peak

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(32) Taguchi, Y.; Fujisawa, M.; Takaokat, T.; Okada, T.; Nishijima, M. *J. Chem. Phys.* **1991**, *95*, 6870−6876.

(33) Crispin, X.; Bureau, C.; Geskin, V. M.; Lazzaroni, R.; Salaneck, W. R.; Bredas, J. L. *J. Chem. Phys.* **1999**, *111*, 3237−3251.

(34) Lake, R. F.; Thompson, H. *Proc. R. Soc. London, Ser. A* **1970**, *317*, 187−195.

(35) Ohno, K.; Harada, Y.; Imai, K.; Matsumoto, S. *J. Phys. Chem.* **1984**, *88*, 206−209.

(36) Delwiche, J.; Gochel-Dupis, M.; Collin, J. E.; Heinesch, J. *J. Electron Spectrosc. Relat. Phenom.* **1993**, *66*, 65−74.

(37) Ohoo, M.; Niessen, W. V.; Gochel-Dupuis, M.; Delwiche, J.; Heinesch, J. *J. Electron Spectrosc. Relat. Phenom.* **1996**, *77*, 149−154.

(38) Perreau, J.; Reyuaud, C.; Lecayon, G.; Ellinger, Y. *J. Phys. B: At. Mol. Opt. Phys.* **1986**, *19*, 1497−1505.

(39) Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Itawa, S. *Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules*; Japan Scientific Societies Press: Tokyo, 1981.

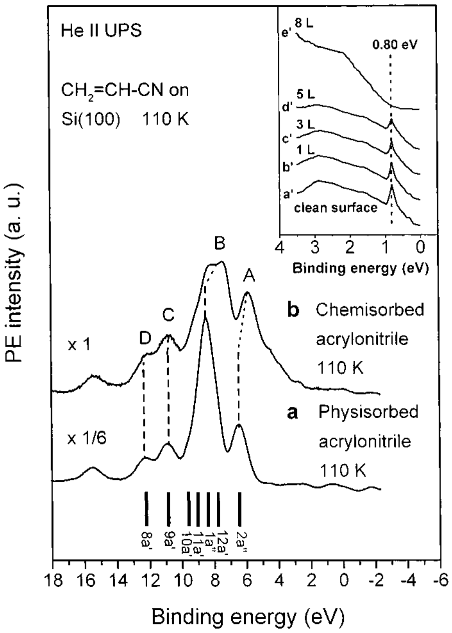

Figure 5. UP spectra of physisorbed and chemisorbed acrylonitrile on Si(100). The inset shows the influence of acrylonitrile exposure on the dangling bond surface state of the Si(100) surface at 110 K.

broadening and spectrum shift in energy are due to the solid-state effects and the change in reference levels. Thus, the four bands A, B, C, and D observed in our experiment can be assigned to $\pi_{C=C}(2a'')$, [$\pi_{CN}(12a') + \pi_{C=C}(1a'') + \pi'_{C\equiv N}(1a'')$ + $\sigma_{CN}(11a') + \pi_{CH_2}$], σ_{C-C}, and C_{2s}(CN), respectively.

The UPS of chemisorbed acrylonitrile was obtained after annealing the sample pre-exposed to 40 L of acrylonitrile at 110 K to 200 K to drive away all physisorbed molecules. Because π_{CN} and $\pi_{C=C}$ mainly contribute to peaks A and B, we focus on these two bands of the physisorbed and chemisorbed acrylonitrile, shown in Figure 5. As σ_{C-C} (peak C) does not take part in the interaction with the Si surface, its intensity was taken as a reference to calculate relative changes in intensities of other orbitals. From Figure 5, it is noted that the relative intensity of peak A, $I[\pi_{C=C}(2a'')]/I(\sigma_{C-C})$, is almost the same for both the physisorbed and chemisorbed acrylonitrile, indicating the similar nature of the orbital of C=C in these differently adsorbed molecules. In the UPS spectrum of physisorbed acrylonitrile, peak B, shown in Figure 5a, is nearly symmetric and sharp, assigned to the combination of π_{CH_2}, $\sigma_{CN}(11a')$, $\pi'_{C\equiv N}(1a'')$, $\pi_{C=C}(1a'')$, and $\pi_{C\equiv N}(12a')$. However, the corresponding peak of chemisorbed acrylonitrile (Figure 5b) appears as a flattop. The significant reduction of peak B for chemisorbed acrylonitrile shows that some constituent orbitals directly participate in the interaction with the Si surface state, consistent with the disappearance of the dangling bond surface state with increasing exposure (the inset of Figure 5). The possible orbitals in peak B involved in the binding with Si surface dangling bonds are $\pi_{C\equiv N}(12a')$, $\pi'_{C\equiv N}(1a'')$, or/and $\pi_{C=C}(1a'')$. The $\pi_{C=C}(1a'')$ orbital (a part of peak B) is known to have the same symmetry as $\pi_{C=C}(2a'')$ (peak A), but a higher binding energy. On the basis of the fact that the relative intensity of peak A, $I[\pi_{C=C}(2a'')]/I(\sigma_{C-C})$, as mentioned above, remains the same for chemisorbed and physisorbed acrylonitrile, the $\pi_{C=C}(1a'')$ orbital of chemisorbed acrylonitrile is expected to maintain the same chemical nature and contribution for the valence orbital photoemission as that of physisorbed molecules. Therefore, it is reasonable to attribute the dramatic decrease in the intensity of peak B of the chemisorbed monolayer to the participation of $\pi_{C\equiv N}$ in the chemisorption. A similar analytical method as above, comparing the contributions of different valence orbitals for UPS after chemisorption, was employed by Parent et al.[29] They concluded that acrylonitrile chemisorbs on Pt(111) through the nitrogen lone pair orbital on the basis of the absence of the contribution from the nitrogen lone pair orbital in the UPS spectra of chemisorbed acrylonitrile, compared to that of physisorbed molecules.[29]

III.D. Density Functional Theory Calculations. In general, there are four possible binding modes for acrylonitrile chemisorbed on Si(100): (a) typical [2 + 2] cycloaddition through the two carbon atoms of the vinyl; (b) interaction of the lone pair electrons of the N atom with the Si dangling bond, similar to the case of acetonitrile on Cu(100);[40] (c) [4 + 2] cycloaddition through both the N atom of the cyano and the C^3 atom of the vinyl group; and (d) [2 + 2] cycloaddition of the cyano group. Considering the large BE shifts of *both* C 1s and N 1s observed in our XPS studies, the reduction in the contribution of the π orbitals of the cyano in the UPS spectrum, and the coexistence of C=C and C=N vibrational features in chemisorbed species, binding modes a and b can be readily excluded. The C 1s and N 1s core level shifts from XPS and variation of valence bands in UPS cannot conclusively deduce which one of modes c and d is the main reaction pathway. However, the retention of sp^2 hybridized vinyl C atoms in chemisorbed molecules, suggested by the C—H stretching vibration, is consistent with mode d, that is, [2 + 2] cycloaddition between the cyano group and Si=Si dimers. Our DFT modeling focuses on the geometry optimization and total energy calculation of modes c and d to make the theoretical prediction and also to confirm the experimental conclusion.

The interaction of acetylene with Si(100) was recently investigated using photoelectron holography (PH) and high-resolution photoemission spectroscopy (HRPES) with synchrotron radiation.[41,42] The C≡C triple bond possibly was suggested to form four σ bonds with two adjacent Si=Si dimers in the same row. A similar tetra-σ bonding mode is not considered in our modeling, because of an absolute saturation coverage of $\theta \sim 0.46$ and the observation of a C=N vibration feature in the chemisorbed molecules.

The substrate clusters employed in this modeling are (1) cluster I, Si_9H_{14}, the smallest cluster representing a Si(100) surface; and (2) cluster II, $Si_{17}H_{22}$, with a dimer and four layers of bulk Si atoms.

Density functional theory (pBP/DN** in Spartan 5.1 and B3LYP/6-31G* in Gaussian 98) was used to optimize the adsorption geometries and calculate the total energies.[43,44] To confirm the validity, Si_9H_{12}/1,3-butadiene and $Si_{17}H_{20}$/1,3-butadiene were modeled using the above-mentioned clusters and calculation methods. The results, not described here, are in good agreement with those based on other modeling methods.[45,46]

Figure 6 displays the possible adsorption geometries optimized by density functional theory (pBP/DN**). The relative

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[40] Sexton, B. A.; Hughes, A. E. *Surf. Sci.* **1984**, *140*, 227−248.

[41] Xu, S. H.; Yang, Y.; Keefee, M.; Lapeyre, G. J. *Phys. Rev. B* **1999**, *60*, 11586−11592.

[42] Wu, H.; Lapeyre, G. J. *Phys. Rev. B* **1995**, *51*, 14549−14553.

[43] *SPARTAN 5.1*; Wavefunction, Inc.: Irvine, CA, 1998.

[44] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *Gaussian 94*, Revision C; Gaussian, Inc.: Pittsburgh, PA, 1995.

[45] Teraishi, K.; Takaba, H.; Yamada, A.; Endou, A.; Gunji, I.; Chatterjee, A.; Kubo, M.; Miyamoto, A.; Nakamura, K.; Kitajima, M. *J. Chem. Phys.* **1998**, *109*, 1495−1504.

[46] Konecny, R.; Doren, D. J. *Surf. Sci.* **1998**, *417*, 169−188.

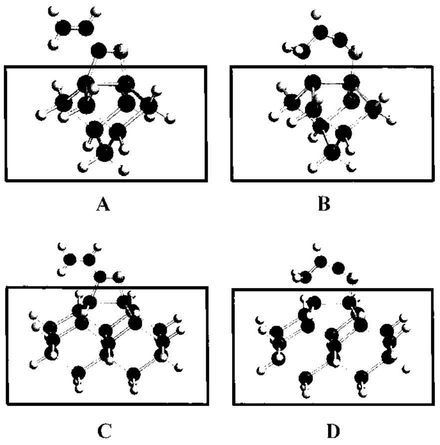

Figure 6. Possible adsorption geometries optimized by density functional theory (pBP/DN**) for acrylonitrile on the Si(100) surface: acrylonitrile/Si_9H_{12} through [2 + 2] (A) and [4 + 2] cycloaddition reaction (B); and acrylonitrile/$Si_{17}H_{20}$ through [2 + 2] (C) and [4 + 2] cycloaddition reaction (D).

Table 3. Differential Values of Total Energies between [2 + 2] and [4 + 2] Cycloadducts on the Basis of Clusters I and II and Different Calculation Methods[a]

	cluster I		cluster II
cycloaddition mode	PBP/DN** OPT	B3LYP/6-31G* OPT	PBP/DN** OPT
[2 + 2]	−3.0	−4.2	−5.6
[4 + 2]	0	0	0

[a] OPT: geometry optimization. All energy values are in kcal·mol^{-1}.

total energies of the [2 + 2] and [4 + 2] cycloaddition products are listed in Table 3. It is interesting to note that the total energies of the [2 + 2] cycloadducts are always lower than those of the [4 + 2] cycloaddition products by ~3−6 kcal·mol^{-1}. The energetically preferred reaction mechanism for acrylonitrile seems to be different from that of the typical conjugated dienes. For 1,3-cyclohexadiene[46,47] and 1,3-butadiene,[46] the $C^1C^2C^3$ angle in the six-membered ring (Si−C^1H_2−C^2H=C^3H−C^4H_2−Si) formed in [4 + 2] cycloaddition is nearly 120°. However, for the [4 + 2] cycloadduct of acrylonitrile, the C^2C^1N angle in the six-membered ring (Si−C^3H_2−C^2H=C^1=N−Si) is nearly 180°, because of the presence of the two consecutive double bonds C^2=C^1 and C^1=N. Therefore, a large structural strain is expected in the [4 + 2] cycloadduct of acrylonitrile with Si=Si dimers, compared to the [2 + 2] cycloadduct through the cyano group.

III.E. Thermal Stability. The thermal stability of chemisorbed species was monitored with HREELS. Figure 7 presents the vibrational features of adsorbed acrylonitrile as a function of surface temperature. The spectrum in Figure 7b was collected after annealing the multilayer acrylonitrile covered surface to 250 K. The most important change observed is the disappearance of the C≡N stretching mode at 2245 cm^{-1} of physisorbed acrylonitrile (Figure 7a). The features related to chemisorbed species remain constant until around 450 K, above which they become weakened and the frequencies of the C−H stretching modes are obviously red-shifted, indicating the occurrence of partial desorption and decomposition of the chemisorbed species. The red shift of ν(C−H) can be caused by the rehybridization of carbon atoms from sp^2 to sp^3, possibly because of the binding of vinyl to the surface. A distinctive ν(Si−H) loss peak appears at 2080 cm^{-1} upon annealing at 700 K, suggesting C−H bond scission in chemisorbed species or further decomposition of the carboneous moieties. At 1000 K, the HREEL spectrum is dominated by a broad hump from 400 to 850 cm^{-1}, corresponding to ν(Si−C) and ν(Si−N) modes of silicon carbide and silicon nitride.[48]

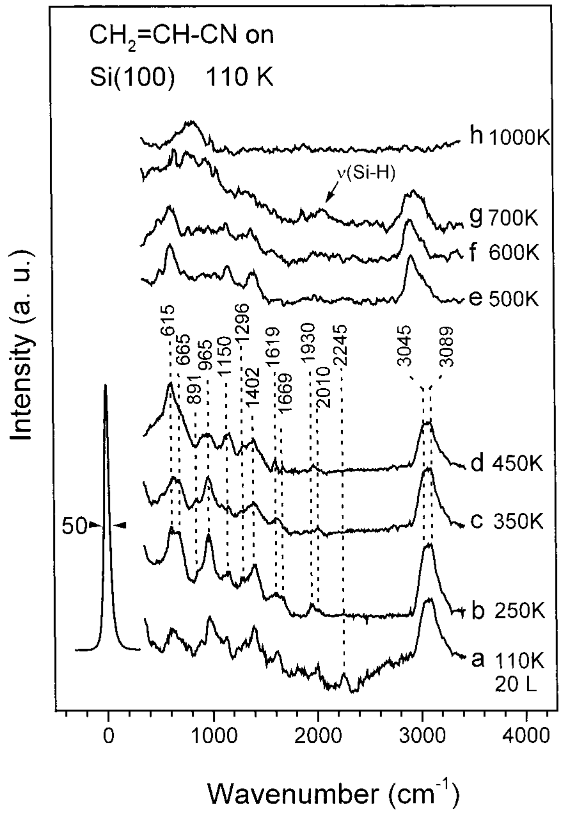

Figure 7. HREEL spectra obtained after annealing the Si(100) pre-exposed to 20 L acrylonitrile at 110 K to indicated temperatures.

Similar observations were also made in our XPS and UPS studies. All of them show that the chemisorbed species with a C=C−C=N conjugated structure is stable to ~450 K.

IV. Discussion

As mentioned earlier, in section III.D, there are four possible binding modes of acrylonitrile on Si(100). The corresponding surface reactions are schematically described in Figure 8. The [2 + 2] cycloaddition through the vinyl group in reaction 1 forms a surface intermediate of (Si)C^3H_2−C^2H(Si)−C^1≡N, where the C^2 and C^3 atoms rehybridize from sp^2 to sp^3, while C≡N is retained. For reaction 2, the interaction of the lone pair electrons on the N atom of acrylonitrile with the surface Si dangling bond is expected to be weak. The resulting configuration of C=C−C≡N···Si retains the basic structure of acrylonitrile molecules. The [4 + 2] cycloaddition through the terminal N and C atoms (reaction 3) leads to the formation of (Si)C^3H_2−C^2H=C^1=N(Si) and rehybridization of the C^3 atom from sp^2 into sp^3. Reaction 4 gives a surface intermediate with a C=C−C=N conjugated structure through [2 + 2] cycloaddition of the C≡N to a surface Si dimer.

In the cycloadducts formed through reactions 1 and 3, the conversion of one or two carbon atoms in the vinyl group from C(sp^2) to C(sp^3) is expected. However, our HREEL spectra of chemisorbed acrylonitrile show that all the vibrational modes related to C(sp^2)−H remain unchanged after chemisorption, excluding these two possibilities. Both the absence of the C≡

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(47) Konecny, R.; Doren, D. J. *J. Am. Chem. Soc.* **1997**, *119*, 11098−11099.

(48) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 3rd ed.; Collection I; John Wiley & Sons: New York, 1975; p 374.

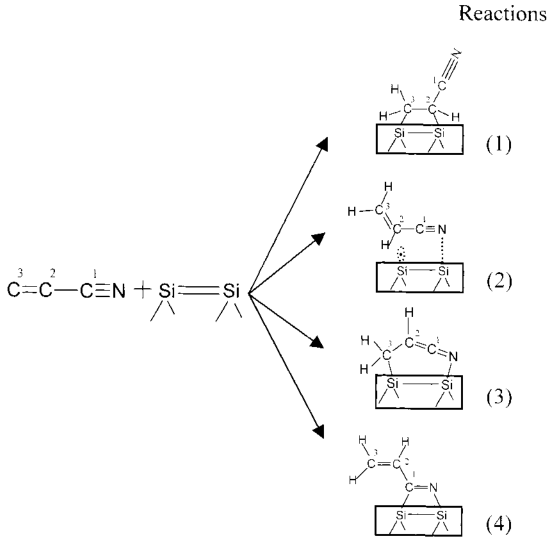

Figure 8. Schematic diagram for the possible reactions of acrylonitrile on Si(100).

Table 4. Fitted Result of XPS Spectra for Chemisorbed and Physisorbed Acrylonitrile[a]

$C^3H_2{=}C^2H{-}C^1N$	physisorbed acrylonitrile	chemisorbed acrylonitrile	chemical shift	rehybridization
N	399.9	398.2	1.7	$sp{-}sp^2$
C^1	~286.8	284.5	2.3	$sp{-}sp^2$
C^2	~286.8	286.4	0.4	$sp^2{-}sp^2$
C^3	285.6	285.5	0.1	$sp^2{-}sp^2$

[a] All energy values are in electronvolts.

N stretching mode and appearance of the stretching mode of C=N clearly rule out the possibility of reaction 2 and obviously support reaction 4. Hence, the vibrational characteristics allow us to make the conclusion that acrylonitrile covalently bonds to Si(100) through one π bond of the cyano with a Si=Si dimer to form Si—C and Si—N σ bonds via the [2 + 2] cycloaddition mechanism. This is also in good agreement with the prediction of DFT calculations.

The deconvoluted C 1s XPS data shown in Figure 2b can be reasonably explained by reaction 4. In line with this mode, the experimental C 1s spectrum consists of the contributions from both C atoms of the vinyl group ($C^3H_2{=}C^2H$), with high BEs at 285.5 (C^3) and 286.4 (C^2) eV, and the C^1 of $(Si)C^1{=}N(Si)$, with a low BE at 284.5 eV. Table 4 summarizes the detailed assignments of C 1s core levels for physisorbed and chemisorbed acrylonitrile on Si(100). The binding energy (284.5 eV) of the C^1 atom [$(Si)C^1{=}N(Si)$] is very close to the values for acetonitrile chemisorbed on Pt(111) and Ni(111), where both C and N atoms of the cyano group bond on the surface through the di-σ bonding mode.[40,49,50] The C 1s core levels of C^2 and C^3 only display slight chemical shifts, because of the absence of the direct interaction of vinyl groups with Si dimers. The different C 1s BEs between C^2 and C^3 atoms of the chemisorbed species $C^3H_2{=}C^2H{-}(Si)C^1{=}N(Si)$ are mainly due to the inductive effect of the $(Si)C^1{=}N(Si)$ group, resulting in a decrease of the final state screening of the carbon atom C^2 and, consequently, an increase in its binding energy. In fact, a greater difference between the BEs of C^2 and C^3 for physisorbed acrylonitrile than that for chemisorbed molecules is attributable to the larger inductive effect of the $C^1{\equiv}N$ in physisorbed acrylonitrile than that of the $(Si)C^1{=}N(Si)$ in the chemisorbed acrylonitrile.

By analyzing the UPS of physisorbed and chemisorbed acrylonitrile, we found that the photoemission of the π orbitals of the CN group in the chemisorption species is greatly reduced and the contribution of the $\pi_{C=C}$ remains the same for both chemisorbed and physisorbed molecules, indicative of the direct interaction of the cyano group with Si dimers and consistent with the observations of HREELS and XPS.

The selective binding of the cyano group on Si(100) can also be understood from the viewpoint of the polarization of organic functional groups and buckling Si=Si dimers. Previous experiments showed that the reactive sticking probabilities of cyclopentene are 1.0 on Si(100),[10] 0.1 on Ge(100), [51] and on the order of 10^{-3} on C(100),[52] correlating the extent of surface dimer buckling with the reactivity in cycloaddition. The dimers on Si(100) and Ge(100) are experimentally and theoretically shown to be buckled.[52−54] However, no buckling dimers are present on C(100).[55−57] The electron transfer from the "down" atom to the "up" atom results in polarized Si=Si and Ge=Ge bonds, making the buckled-down atom electrophilic and the buckled-up atom nucleophilic.[52,53] These results clearly demonstrated that the polarization in surface dimers significantly enhances their reactivity with the C=C group of organic molecules. A similar approach may also be employed to understand the selectivity in acrylonitrile adsorption on Si(100). Compared to that of C=C, the large dipole moment of the C≡N group in the molecule makes it both electrophilic (C^1 atom) and nucleophilic (N atom). Thus, a lower transition state is expected for the cylcoaddition between the polarized cyano group and the buckling dimer on Si(100). This is consistent with our experimental conclusion that acrylonitrile selectively binds on Si(100) through the [2 + 2] cycloaddition between cyano groups and Si dimers.

V. Conclusion

Both experimental results and theoretical calculations show that acrylonitrile interacts with Si(100) through a [2 + 2] cycloaddition reaction between the Si=Si dimer and a bond of the cyano group to form two new σ bonds. The cycloadduct containing a C=C—C=N conjugated structure is thermally stable to 450 K and will be useful for further chemical modification and syntheses at the interface. The "free" vinyl group may react further with chosen organic functionalities through typical vinyl reactions, such as addition, cyanoethylation, and polymerization.[58,59]

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(49) Sexton, B. A.; Avery, N. R. *Surf. Sci.* **1983**, *129*, 21−36.

(50) Friend, C. M.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981**, *103*, 767−772.

(51) Hamers, R. J.; Hovis, J. S.; Greenlief, C. M.; Padowitz, D. F. *Jpn. J. Appl. Phys.* **1999**, *38*, 3879−3887.

(52) Hovis, J. S.; Coulter, S. K.; Hamers, R. J.; D'Evelyn, M. P.; Russell, J. N., Jr.; Butler, J. E. *J. Am. Chem. Soc.* **2000**, *122*, 732−733.

(53) Liu, Q.; Hoffman, R. *J. Am. Chem. Soc.* **1995**, *117*, 4082−4092.

(54) Chadi, D. J. *Phys. Rev. Lett.* **1979**, *43*, 43−47.

(55) Hukka, T. I.; Pakkanen, T. A.; D'Evelyn, M. P. *J. Phys. Chem.* **1994**, *98*, 12420−12430.

(56) Kuang, Y. L.; Wang, Y. F.; Lee, N.; Badzian, A.; Badzian, T.; Tsong, T. T. *Appl. Phys. Lett.* **1995**, *67*, 3721−3723.

(57) Mercer, T. W.; Pehrsson, P. E. *Surf. Sci.* **1998**, *399*, L327−L331.

(58) Bruson, B. A. In *Organic Reactions V*; Adams, R., Bachmann, W. E., Fieser, L. F., Johnson, J. R., Snyer, H. R., Eds.; Wiley & Sons: New York, 1952; p 80.

(59) Venuto, P. B.; Landis, P. S. *Adv. Catal.* **1968**, *18*, 259−273.