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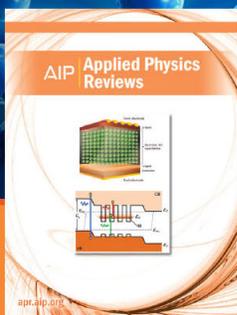
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# Cycloaddition chemistry of thiophene on the silicon (111)-7×7 surface

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The mechanism of the cycloaddition reaction between thiophene and Si(111)-7×7 has been investigated using thermal desorption spectroscopy (TDS), high resolution electron energy loss spectroscopy (HREELS), electronic electron energy loss spectroscopy (EELS), scanning tunneling microscopy (STM), and PM3 semiempirical calculations. The results show that thiophene binds on Si(111)-7×7 through a [4+2] cycloaddition reaction between the 2, 5 C-atoms of thiophene and the adjacent adatom-rest atom pairs on Si(111)-7×7. Semiempirical PM3 calculations based on the cluster model further confirm this di- $\sigma$  bonding configuration. A stepwise surface diradical mechanism has been proposed to account for the regioselective [4+2] cycloaddition reaction. © 2001 American Institute of Physics. [DOI: 10.1063/1.1386435]

## I. INTRODUCTION

The desire to design and create new molecular scale devices has driven the studies of the monolayers and multilayers of organic molecules on silicon surfaces. The organic molecules offer great opportunities to combine high chemical, mechanical, and thermal stability with tailored electronic or optical properties into the existing devices.<sup>1-3</sup> Among them, thiophene is particularly interesting since the polymeric materials, such as conjugated polythiophene or oligothiophene are promising candidates for a wide range of applications including advanced optics, microelectronics, and sensors.<sup>4-6</sup> In order to gain the control needed to incorporate the organic functionalities into the molecule-based hybrid organic molecule/silicon devices,<sup>3,7</sup> it is of considerable importance to know about the adsorbed monolayer structure as well as the microscopic details of the reaction mechanism prior to the device realisation.

There are relatively few fundamental studies of thiophene adsorption on silicon surfaces. Using photoemission and electron energy loss spectroscopy, Piancastelli *et al.* investigated the desulfurization of thiophene on a cleaved Si(111) surface with (2×1) reconstruction at room temperature.<sup>8,9</sup> It was proposed that the adsorption states of thiophene at low temperature involve a  $\pi$ -bonded geometry as well as a  $\sigma$ -bonded configuration resulting from the breakage of C $_{\alpha}$ -H bond. MacPherson and co-workers investigated the interactions of thiophene, furan, and pyrrole with Si(111)-7×7 using thermal desorption spectroscopy (TDS)

and photoelectron emission techniques.<sup>10,11</sup> Based on their experimental results, two molecular states, corresponding to a  $\sigma$ -bonded state through the lone pair electrons of the heteroatom (S) and a  $\pi$ -bonded geometry, was proposed. Recently, the molecular adsorption of thiophene on Si(111)-2×1 at 300 K was investigated by Jeong *et al.* using low-energy electron diffraction (LEED), Auger electron spectroscopy (AES), ultraviolet photoelectron spectroscopy (UPS).<sup>12</sup> Coupled with the semiempirical PM3 calculation results, they proposed that thiophene molecule adsorbs on the surface by forming di- $\sigma$  bonds between two adjacent carbon atoms of thiophene and the silicon dimer with the sulfur atom interacting with the neighboring silicon dimer. These previous results indicate that the adsorption behavior of thiophene on the silicon surface is strongly surface specific.

In this paper we present the combined experimental and theoretical results of the [4+2] cycloaddition reaction of the heterocyclic thiophene molecule on a Si(111)-7×7 surface. The brief report of such reaction system has been presented in Ref. 13. Previous works have shown the feasibility of a [4+2] cycloaddition of butadienes on the dimer-rows Si(111)-2×1 surface.<sup>14-16</sup> A surface diradical mechanism was proposed to describe the adsorption reaction between 1,3-dienes and the silicon dimer on the surface.<sup>16</sup> In contrast to 1,3-dienes, thiophene has been well documented as one of the least reactive dienes in solution cycloaddition reaction due to its high aromaticity.<sup>17</sup> Nevertheless, a few experimental and theoretical studies have suggested that the cycloaddition of thiophene as a diene can be facilitated by the use of highly reactive electron-deficient dienophiles or undertaking reactions at a high pressure.<sup>18-20</sup> Thiophene has a high

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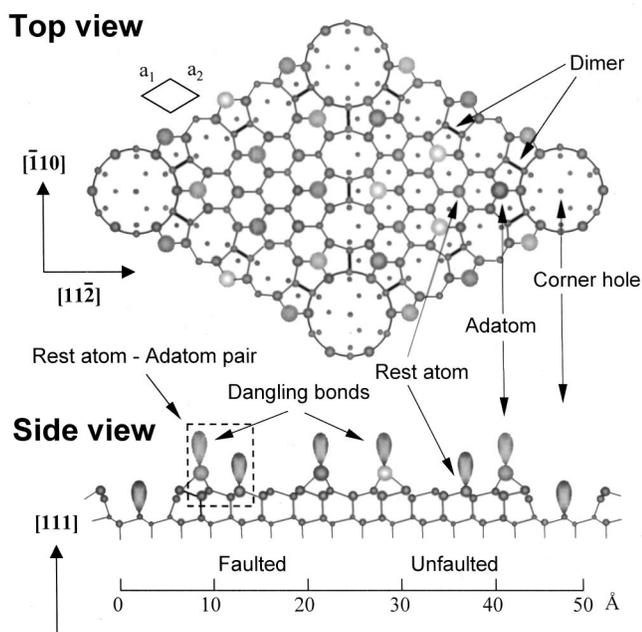


FIG. 1. Dimer-adatom-stacking-fault (DAS) model of the Si(111)- $7\times 7$  unit cell proposed by Takayanagi *et al.* (Ref. 49). The faulted half of the unit-cell is at left and the unfaulted right. Only adatoms, rest atoms, and corner hole atoms have dangling bonds. The adatoms are divided into the corner adatoms and the center adatoms.

$\pi$ -electron density. In addition, the electron density of the highest occupied molecular orbital (HOMO) is mostly concentrated at its  $\alpha$ -positions. These electronic characteristics make it highly susceptible to electrophilic attack at the 2, 5-positions.<sup>21</sup> On the other hand, it has been shown that the electron occupancies for the spatially isolated rest atoms and adatoms on Si(111)- $7\times 7$  are 1.5–2 and about 0.5 electrons, respectively.<sup>22,23</sup> The unique geometric and electronic features of the adjacent adatom-rest atom pair (see Fig. 1) on Si(111)- $7\times 7$  imply a reactive “diradical site” for surface reaction.<sup>13,24,25</sup>

Our studies investigate the cycloaddition chemistry including binding configuration, thermal stability, and specific adsorption sites of thiophene molecules on Si(111)- $7\times 7$ . Results were obtained using a combination of thermal desorption spectroscopy (TDS), high resolution electron energy loss spectroscopy (HREELS), electron energy loss spectroscopy (EELS), scanning tunneling microscopy (STM) and PM3 semiempirical calculations. We show that the covalent binding of thiophene molecules onto the silicon surface can be readily achieved by vacuum vapor adsorption. The combined STM and HREELS data clearly show the [4+2] cycloaddition of thiophene molecules to the adjacent adatom-rest atom pairs on the Si(111)- $7\times 7$  surface. The resultant 2, 5-dihydrothiophenelike surface intermediate is di- $\sigma$  bonded to an adjacent adatom-rest atom pair through the  $\alpha$ -carbons in thiophene with the remaining C=C group and C-S-C linkage tilted from the silicon surface.

## II. EXPERIMENT

The experiments were performed in two separate ultra-high vacuum (UHV) systems. The HREELS and TDS studies

were carried out in a three-level chamber with a base pressure lower than  $2\times 10^{-10}$  Torr.<sup>24,25</sup> The STM images were collected in a second chamber equipped with a low-energy electron diffraction (LEED) (Perkin Elmer) and a scanning tunneling microscopy (STM) (Omicron).<sup>13</sup> The EEL spectrometer consists of a double-pass 127° cylindrical deflector analyzer (CDA) for the monochromator and a single-pass 127° CDA for the analyzer. Vibrational HREELS was performed on both clean and dosed samples with a primary beam energy of 5.0 eV. Resolutions, measured by the full width at half-maximum (FWHM), varied from about 45  $\text{cm}^{-1}$  (5.5 meV) to 100  $\text{cm}^{-1}$  (~12 meV). EEL spectra in the electronic excitation region were recorded in the same scattering geometry as those in the vibrational region, but with an incident beam energy of 15.0 eV. In this case, the resolution was lowered to allow the examination of the low-intensity losses above 0.5 eV.<sup>26</sup> A temperature ramping rate of  $dT/dt=2\text{ K s}^{-1}$  employed in the experiment is provided by a RHK temperature controller which is capable of producing a reproducible and linear temperature ramp in the region between 110 K and 1200 K.

The Si(111) samples (9 mm $\times$ 18 mm $\times$ 0.38 mm) were cut from *n*-type (*P*-doped) silicon wafers with a resistivity of 1–15  $\Omega\text{ cm}$  (Goodfellow, Cambridge). A Ta foil (thickness ~0.025 mm) was sandwiched between two experimental samples with a set of Ta clips, and in turn was spot-welded to two Ta posts (diameter ~1.5 mm) at the bottom of a Dewar-type LN<sub>2</sub>-cooled sample holder. The sample was heated through resistive heating of the Ta foil. Its temperature was measured by a W/Re5%–W/Re26% thermocouple (C-type) attached to the edge of the sample using a high temperature ceramic adhesive (Aremco 516), and confirmed with an optical pyrometer (Minolta,  $\epsilon=0.74$ ). The sample surface was carefully cleaned by cycles of Ar<sup>+</sup> sputtering and annealing to 1200 K for 10 min.<sup>24,25</sup> Surface cleanliness was routinely checked by HREELS, showing a featureless background in the range of 240–4000  $\text{cm}^{-1}$ . The (7 $\times$ 7) structure was confirmed by LEED and STM equipped on a separate chamber.

Thiophene (99.8%) was purchased from Aldrich. 2, 5-Dideuteriothiophene was prepared from 2, 5-dibromothiophene via the Grignard technique.<sup>27</sup> The purity of the final product is above 96% as determined by GC-MS and NMR.<sup>28</sup> All chemicals were further purified by several freeze–pump–thaw cycles with liquid nitrogen before being dosed onto the crystal through a doser. The organic vapours were admitted into the vacuum chamber through a doser (i.d.~6 mm) attached to a Varian adjustable leak valve. The thiophene exposures (in Langmuirs, 1 L=10<sup>-6</sup> Torr s) quoted here are normalized to background exposures by comparing the respective thermal desorption spectra after doser and background exposures.

## III. RESULTS

### A. Thermal desorption spectroscopy

Thermal desorption spectra after thiophene adsorption at 110 K on the Si(111)- $7\times 7$  surface are shown in Fig. 2. With increasing exposure three desorption peaks are observed. At low exposure, only single molecular desorption peak at 414

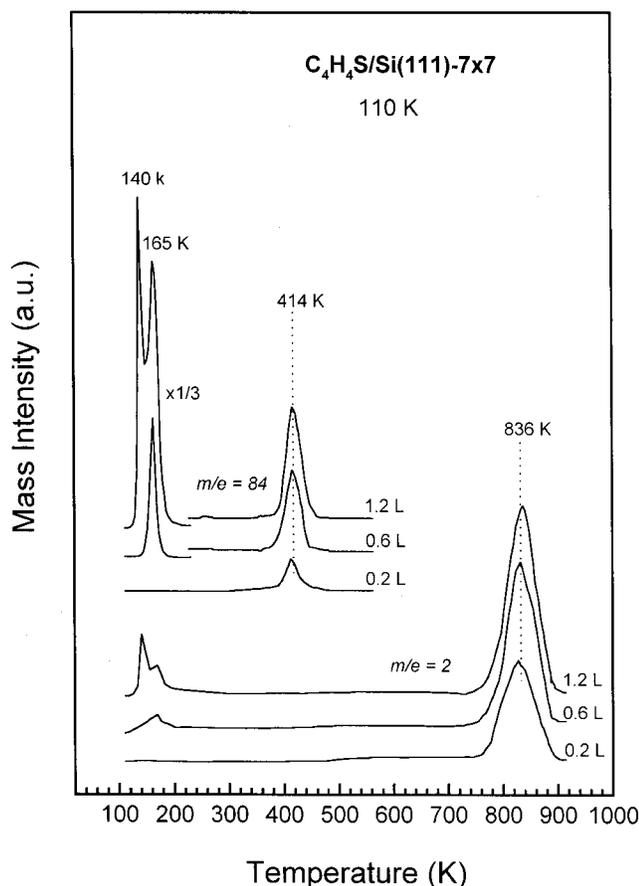


FIG. 2. Thermal desorption spectra for thiophene ( $m/e = 84$ ) and  $H_2$  ( $m/e = 2$ ) desorbing from the Si(111)-7×7 surface as a function of exposure. The adsorption temperature was 110 K and a heating rate of 2 K/s was used.

K corresponding to chemisorbed thiophene is observed from the spectra. As increasing exposure of thiophene, the peak increases in intensity. In addition, a new low temperature peak located at 165 K appears, which is assigned to the first physisorbed layer that is on top of the chemisorbed species on Si(111)-7×7. The growth of multilayers on top of the first physisorbed layer takes place with large exposures, which desorbs at a low temperature of 140 K. At multilayer exposure, the chemisorbed state at 414 K is saturated. By assuming first order desorption kinetics and a pre-exponential factor of  $10^{13} s^{-1}$ , the desorption energy of the chemisorbed state was estimated to be  $\sim 110 kJ mol^{-1}$ .<sup>29</sup>

Besides the desorption of molecular thiophene on Si(111)-7×7 shown above, further analysis of the accompanied molecular hydrogen signal ( $H_2^+$ , 2 amu) is shown to be more informative. Other than low temperature states corresponding to physisorbed thiophene desorption, hydrogen desorption at  $\sim 836$  K is observed (see Fig. 2). The observation of the hydrogen desorption around  $\sim 800$  K indicates the presence of thiophene decomposition in addition to the molecular desorption.<sup>26</sup> A semiquantitative analysis by comparing the desorption yield of molecular hydrogen product with that of atomic H-saturated Si(111)-7×7 has been made, showing that about 10% of chemisorbed thiophene undergoes thermal decomposition upon annealing.

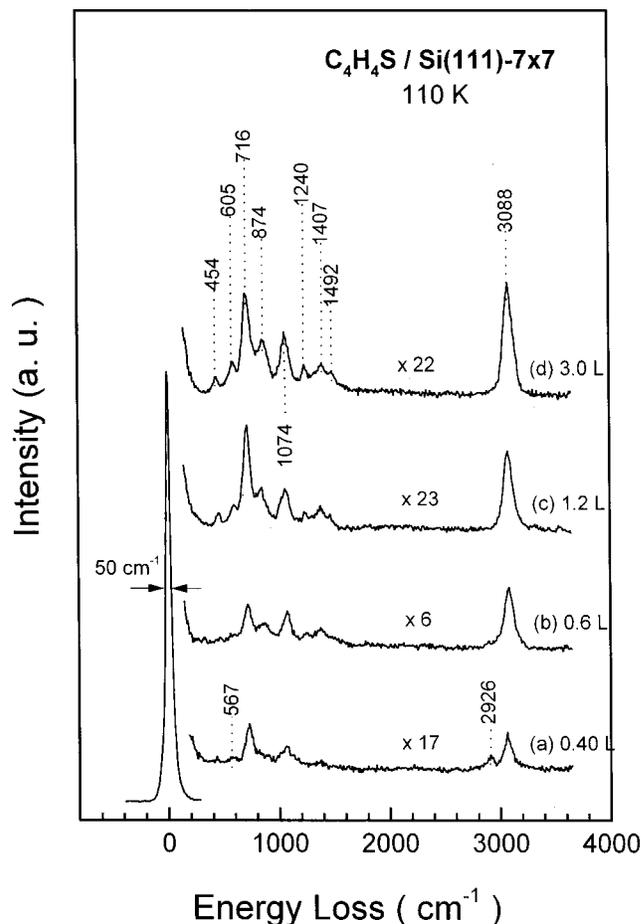


FIG. 3. HREEL spectra obtained after exposing the Si(111)-7×7 surface to various exposures of thiophene at 110 K: (a) 0.4 L, (b) 0.6 L, (c) 1.2 L, and (d) 3.0 L.

### B. Vibrational high resolution electron energy loss spectroscopy

Figure 3 displays the HREEL spectra recorded as a function of  $C_4H_4S$  exposure. Figure 3(d) presents the HREEL spectrum for multilayer thiophene (3.0 L) on the Si(111)-7×7 surface at 110 K, and the spectrum shows loss features at 3088, 1492, 1407, 1240, 1074, 874, 716, 605, and 454  $cm^{-1}$ . The corresponding loss energies compare well with the vibrational energies of liquid-phase thiophene within  $\sim 20 cm^{-1}$ .<sup>30</sup> The detailed assignments for physisorbed thiophene are summarized in Table I. For the low  $C_4H_4S$  exposure at 0.40 L, features corresponding to chemisorbed thiophene are observed in Fig. 3(a) as evidenced by the presence of two additional features at 2926 and 566  $cm^{-1}$ .

To further study the chemisorbed thiophene, the surface was preexposed to 1.2 L thiophene at 110 K, and then annealed to 300 K to drive all the physisorbed thiophene away so that only chemisorbed thiophene is left on the surface. The HREEL spectrum for the chemisorbed thiophene is shown in Fig. 4(c) and the peak assignments are summarized in Table II. Losses at 566, 754, 827, 925, 1088, 1174, 1319, 1595, 2926, and 3048  $cm^{-1}$  can be resolved for chemisorbed thiophene. The two separate vibrational features at 2926 and 3048  $cm^{-1}$ , corresponding to the C–H stretching modes for  $sp^3$  and  $sp^2$  carbons, respectively, clearly suggest the pres-

TABLE I. Vibrational modes assignment for thiophene physisorbed on Si(111)-7×7. IR data for liquid thiophene (Ref. 30) are included for comparison. (The vibrational frequencies are given in cm<sup>-1</sup>.)

Mode	Mode No. and symmetry	Liquid phase thiophene	Multilayer C <sub>4</sub> H <sub>4</sub> S /Si(111)-7×7 <sup>110</sup> K
C-H str.	$\nu_2(a_1)$	3126/3098	3088
C-H str.	$\nu_{13}(b_1)$	3086	...
C-C str.+CH rock	$\nu_{14}(b_1)$	1504	1492
CH=C str.+CH rock	$\nu_3(a_1)$	1409	1407
C-H ip-bending	$\nu_{15}(b_1)$	1256	1240
C-H ip-bending	$\nu_5(b_1)$	1083	1074
C-H op-bending	$\nu_9(a_2)$	903	874
C-H op-bending	$\nu_{20}(b_2)$	712	716
Ring def.+C-S str.	$\nu_8(a_1)$	608	605
Ring torsion	$\nu_{21}(b_2)$	452	454

ence of rehybridization of carbon atoms in chemisorbed thiophene. The 1595 cm<sup>-1</sup> loss is attributed to the C=C stretching vibration. The 1319, 1174, and 1088 cm<sup>-1</sup> peaks can be assigned to the CH in-plane bending modes. The loss at 925 cm<sup>-1</sup> is ascribed to C-C stretching. The intensity at 827 cm<sup>-1</sup> is associated with C-S-C stretching mode. The C-H out-of-plane bending and Si-C stretching modes can account for the peaks at 754 and 565 cm<sup>-1</sup>, respectively. The vibrational frequencies of 2, 5-dihydrothiophene are also included in Table II for comparison.<sup>31</sup> It is clear that the vibra-

TABLE II. Vibrational modes assignment for chemisorbed thiophene on Si(111)-7×7 as well as the gas phase IR data for 2,5-dihydrothiophene (Ref. 31) (the vibrational frequencies are given in cm<sup>-1</sup>). The dominant electron scattering mechanism is included.

Mode	Gas phase 2,5-dihydrothiophene	Chemisorbed C <sub>4</sub> H <sub>4</sub> S on Si(111)-7×7	Dominant mechanism
≡C-H str.	3065	3048	Impact
-C-H str.	2936	2926	Impact
-C-H str.	2866	...	Impact
C=C str.	1647	1595	Impact
CH <sub>2</sub> deformation	1451	...	Impact
CH ip-bending	1273	1319	Impact
C-H ip-bending	1227	1174	Impact
C-H ip-bending	1112	1088	Impact
C-C str.	953	925	Impact
C-S-C str.	824	827	Impact
C-H op-bending	...	754	Dipole
C-Si str.	...	566	Dipole

tional structure of chemisorbed thiophene and free 2, 5-dihydrothiophene molecule correlates very well, suggesting a 2,5-dihydrothiophene-like structure for chemisorbed thiophene on Si(111)-7×7.

The off-specular spectrum, taken at -20° ( $\Delta\theta$ ), is shown in Fig. 4(b). It is well known that the off-specular geometry would screen out most of the dipole transition related vibrational modes.<sup>32</sup> The intensification of the C-H stretching peaks at 3048 and 2926 cm<sup>-1</sup> shows the large contribution of impact scattering. We also observed the sharp attenuation of 566 and 754 cm<sup>-1</sup> losses, indicating a dipole scattering mechanism (Table II). It should be noted that the losses at 566 and 754 cm<sup>-1</sup> are associated with the Si-C stretch and C-H out-of-plane bending mode, respectively, suggesting the nearly flat orientation of the chemisorbed thiophene molecule on the Si(111)-7×7 surface.<sup>24</sup>

To confirm the regio-selective reaction of thiophene molecules with the Si(111)-7×7 surface, 2,5-*d*<sub>2</sub>-thiophene was further studied in our HREELS experiments. The multilayer (3.0 L) HREEL spectrum for 2,5-*d*<sub>2</sub>-thiophene on Si(111)-7×7 at 110 K is given in Fig. 5(a) Loss peaks at 3088, 2324, 1471, 1399, 1308, 1222, 1046, 889, 825, 762, 590, and 421 cm<sup>-1</sup> can be resolved. These vibrational features correlate very well with the liquid phase IR data<sup>33</sup> and the vibrational features for multilayers 2,5-deuterated-thiophene on Fe(100) in a range of ±20 cm<sup>-1</sup> (Table III), suggesting the free-molecular nature for multilayers 2,5-deuterated-thiophene on Si(111)-7×7.

The HREELS spectra for chemisorbed monolayer 2,5-*d*<sub>2</sub>-thiophene produced by annealing the multilayer covered Si(111)-7×7 surface to 300 K are presented in Fig. 5(b). As expected, drastic spectral changes are observed for the chemisorbed monolayer compared to multilayer 2,5-*d*<sub>2</sub>-thiophene on Si(111)-7×7. The loss features at 3048, 2193, 1586, 1330, 1180, 1024, 921, 835, 753, 700, and 554 cm<sup>-1</sup> can be observed. The detailed assignment is also given in Table III. The vibrational loss at 2324 cm<sup>-1</sup> associated with the C(sp<sup>2</sup>)-D stretching vibration in Fig. 5(a) is shifted to 2193 cm<sup>-1</sup> (sp<sup>3</sup>C-D) in the corresponding monolayer spectrum [Fig. 5(b)]. The red shift of about 131 cm<sup>-1</sup>

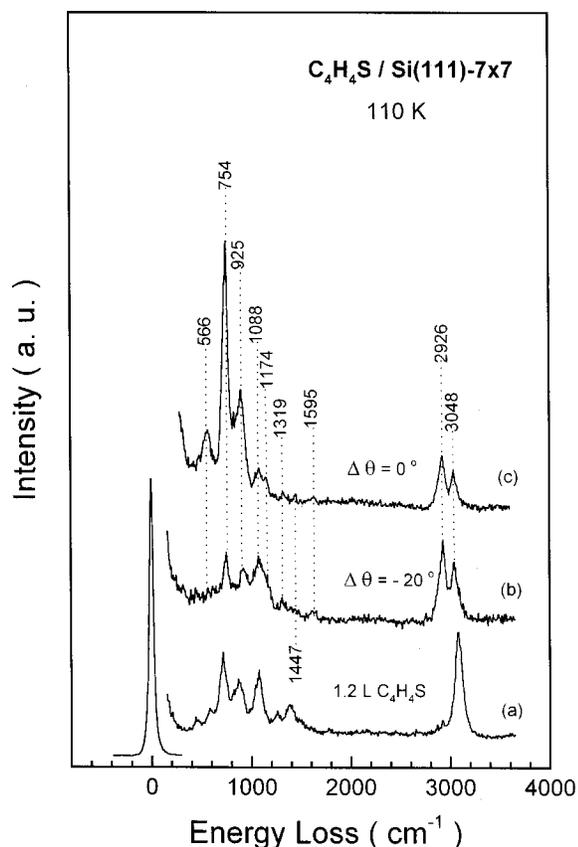


FIG. 4. HREEL spectra obtained after (a) exposing Si(111)-7×7 to 1.2 L thiophene 110 K; (b) annealing (a) to 300 K; (c) off-specular spectrum of (b) with  $\Delta\theta = -20^\circ$ .



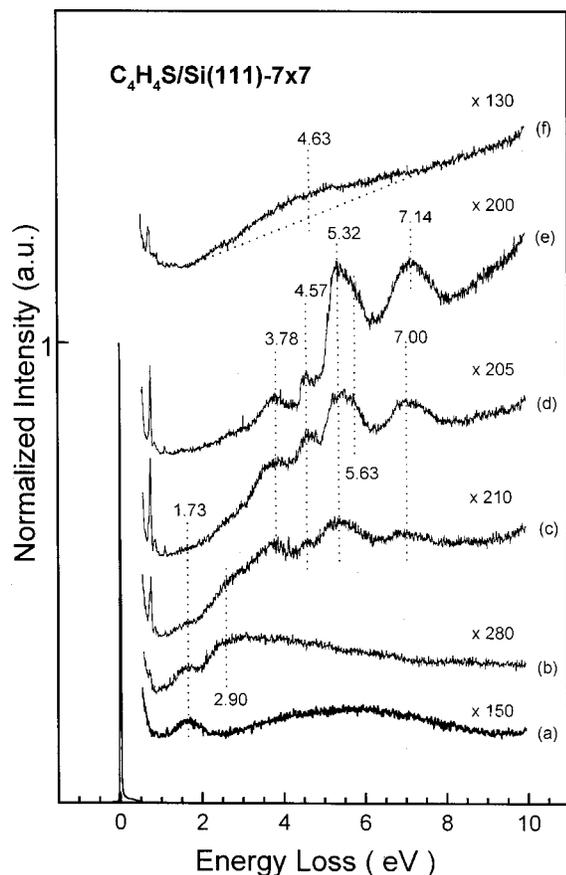


FIG. 7. Electronic EEL spectra of thiophene adsorbed on Si(111)-7 $\times$ 7 at  $T=110$  K performed with  $E_0=15.0$  eV in specular geometry for (a) clean surface; (b) 0.2 L; (c) 0.6 L; (d) 1.2 L; (e) 3.0 L; (f) monolayer thiophene by annealing (e) to 300 K.

Si-C stretching motion suggests the possible occurrence of a thermal decomposition of the molecularly chemisorbed thiophene. Further annealing to 600 K results in the appearance of two new loss peaks at 490 and 2150  $\text{cm}^{-1}$  associated with the vibrational excitation of Si-S<sub>2</sub> and Si-H species, respectively.<sup>26</sup>

After annealing to 800 K, loss features at 2952, 947, and 754  $\text{cm}^{-1}$  associated with C-H species are observed for the remaining adsorbates. The feature at 490  $\text{cm}^{-1}$  corresponding to Si-S<sub>2</sub> species is attenuated. There is also a blue-shift for the Si-H stretching vibration from 2111 to 2150  $\text{cm}^{-1}$  in the 800 K spectrum. At 1000 K, the only feature on the Si(111)-7 $\times$ 7 surface is the broad peak centered at 880  $\text{cm}^{-1}$  assigned to Si-C species,<sup>35</sup> suggesting the complete dissociation of the C-H species as well as the complete desorption of hydrogen.

### C. Electronic electron energy loss spectroscopy

The electronic transitions of thiophene adsorbed on Si(111)-7 $\times$ 7 have been measured by EELS using a primary beam energy of 15 eV with a 10–15 meV resolution. Figure 7 shows the EEL spectra of the Si(111)-7 $\times$ 7 surface as a function of thiophene exposure at 110 K. On the clean Si(111)-7 $\times$ 7 surface, a weak loss feature can be observed at

TABLE IV. Energy (eV) of electronic transition from the thiophene multilayer condensed on the Si(111)-7 $\times$ 7 surface at 110 K. Energy of thiophene gas phase transitions, from various sources, is also given.

State	Electron impact spectrum <sup>a</sup>	Electron impact spectrum <sup>b</sup>	Optical observation	C <sub>4</sub> H <sub>6</sub> S/Si(111)-7 $\times$ 7 <sup>110</sup> K
<sup>3</sup> B <sub>2</sub>	3.75	3.80	3.90 <sup>c</sup>	3.78
<sup>3</sup> A <sub>1</sub>	4.62	4.70	4.64 <sup>d</sup>	4.57
<sup>1</sup> A <sub>1</sub>	5.48	...	5.41 <sup>e</sup>	5.32
<sup>1</sup> B <sub>2</sub>	5.93	5.65	5.53 <sup>e</sup>	5.63
<sup>1</sup> B <sub>2</sub>	7.05	7.05	6.90 <sup>f</sup>	7.14

<sup>a</sup>Reference 36.

<sup>b</sup>Reference 37.

<sup>c</sup>Reference 38.

<sup>d</sup>Reference 39.

<sup>e</sup>Reference 40.

<sup>f</sup>Reference 41.

1.73 eV, which was previously observed by Chakarov *et al.*<sup>26</sup> and assigned to the transition with the surface states.

A low exposure of 0.2 L thiophene causes a loss change, shown in Fig. 7(b). The peak at 1.73 eV decreases in intensity and an additional broad band between 2 and 4 eV can be observed, indicative of the strong modification to the surface electronic structure of Si(111)-7 $\times$ 7 upon thiophene adsorption. The appearance of the additional broad transition band is possibly due to the charge transfer in the adsorbate-substrate complex, as will be discussed in more detail in the following section.

With increasing exposure of thiophene, the intensity of the loss between 2 and 4 eV increases and four new losses at 3.78, 4.57, 5.32, and 7.00 eV appear [Fig. 7(c)]. A shoulder around 5.63 eV is detected for 1.2 L thiophene exposure [Fig. 7(d)]. Table IV gives the assignments of the transition energies in our experiments as well as the values of the electronic<sup>36</sup> and optical transitions<sup>37–41</sup> for gas phase thiophene from the literature. For multilayer thiophene the losses at 3.78, 4.57, 5.32, 5.63, and 7.14 eV [in Fig. 5.7(e)] are assigned to <sup>3</sup>B<sub>2</sub>←<sup>1</sup>A<sub>1</sub>, <sup>3</sup>A<sub>1</sub>←<sup>1</sup>A<sub>1</sub>, <sup>1</sup>A<sub>1</sub>←<sup>1</sup>A<sub>1</sub>, <sup>1</sup>B<sub>2</sub>←<sup>1</sup>A<sub>1</sub>, and <sup>1</sup>B<sub>2</sub>←<sup>1</sup>A<sub>1</sub>, respectively. All the above excitations involve only the  $\pi$ - $\pi^*$  orbital transitions.

Figure 7(f) displays the electronic transition EEL spectrum for a monolayer of chemisorbed thiophene on the silicon surface. The most striking feature of the present results is the absence of similarity between EELS of the adsorbed molecules and the corresponding gas phase data. This is in accordance with the vibrational HREELS results showing the strong interaction between adsorbed thiophene molecules and the silicon substrate. The intense intramolecular  $\pi$ → $\pi^*$  like transitions characteristic for free-molecular thiophene seem to be missing. The spectrum of chemisorbed monolayer only shows a broad band centered at 4.63 eV. It is also clear that the absence of sharp adsorbate features in the loss spectra can not be due to the experimental resolution of this study ( $\leq 0.5$  eV). The present observation clearly reflects the changes in the electronic structures of thiophene upon chemisorption.

### D. Scanning tunneling microscopy

In order to further elucidate the nature of thiophene chemisorption on Si(111)-7 $\times$ 7, we employed scanning tunneling microscopy (STM) to investigate the extent and spa-

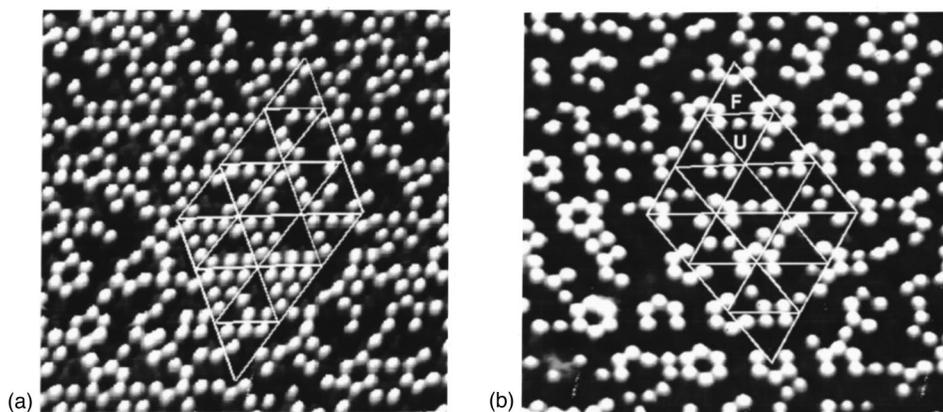


FIG. 8. STM images ( $\sim 160 \text{ \AA} \times 160 \text{ \AA}$ ,  $V_s = 1.7 \text{ V}$ ,  $I_T = 0.15 \text{ nA}$ ) of the unoccupied states of the Si(111)-7×7 surface exposed with (a) 0.1 L, and (b) 5.0 L thiophene at 300 K. A unit cell is outlined with the faulted (F) and unfaulted (U) subunits labeled. The darkened regions are due to the chemisorbed thiophene quenching the dangling bonds on surfaces.

tial distribution of the present surface reaction system with atomic resolution. In Fig. 8(a) we show a STM constant current topograph (CCT) of a Si(111)-7×7 surface that has been exposed to 0.1 L of thiophene at room temperature. Both reacted and unreacted adatoms are discernible. Comparison with the clean surface (not shown) reveals that the (7×7) reconstruction is preserved overall after thiophene adsorption reaction. We see that part of the surface adatoms becomes invisible as a result of the surface reaction. This apparent formation of darkened sites, whose number increases as a function of the exposure, was also observed during the adsorption of other small molecules, such as  $\text{H}_2\text{O}$ ,<sup>42</sup>  $\text{NH}_3$ ,<sup>43</sup>  $\text{C}_2\text{H}_2$ ,<sup>44</sup>  $\text{C}_2\text{H}_4$ ,<sup>45</sup>  $\text{C}_6\text{H}_6$ ,<sup>46</sup> and  $\text{C}_6\text{H}_5\text{Cl}$ ,<sup>47</sup> on Si(111)-7×7. In all cases, the darkness of the adatoms in the STM images was attributed to the saturation of the adatom dangling bonds due to the surface-adsorbates bond formation.

A statistical counting of darkened dangling bond sites can provide the information regarding the spatial selectivity for thiophene adsorption. Figure 8(a) reveals that there are 140 center adatoms and 54 corner adatoms among the 194 darkened adatoms. In addition, 138 of them are located in the faulted subunits while 56 are in the unfaulted subunits. According to the inspection of several different regions on the same sample, the situations are similar; the center adatoms have a reactivity of about two times greater than that of the corner adatoms and the adatoms in faulted subunits react preferentially over those in unfaulted subunits with a 2.4:1 ratio. It is noted that real vacancy defects may be included in the account. However, the amount of vacancies is only  $\sim 1\%$ .

Figure 8(b) shows a CCT of a Si(111)-7×7 surface after a saturation exposure of 5.0 L thiophene at room temperature. It is observed that more adatoms have become darkened, manifesting the greater number of adatom dangling bonds that have reacted with thiophene. Meanwhile, substantial adsorption also occurs on unfaulted halves. In addition, “rings,” which are formed by the remaining unreacted corner adatoms, are easily identified. The  $\sim 2:1$  ratio between the number of darkened center and corner adatoms is similar to that observed at lower exposures. However, at this saturation coverage, the ratio of reacted adatoms in the faulted and unfaulted subunits reduces to 1:1, as one would expect. The preferential binding of thiophene with the ada-

tom sites on the faulted halves of a Si(111)-(7×7) unit cell can be understood by considering the higher electrophilicity of the faulted subunits.<sup>48</sup> On the other hand, the DAS (7×7) model shows that reaction at a corner adatom will strain two dimer bonds, while the reaction at the center adatom will affect only one. Therefore, a smaller strain induced by adsorbed thiophene at a center adatom site would decrease the energy of the transition state, leading to a higher reaction rate at the center adatom site.<sup>43</sup>

By counting up the darkened sites for adsorbed thiophene, the saturation coverage (5.0 L thiophene exposure) of thiophene on Si(111)-7×7 at room temperature is estimated to be about 0.13 ML (where  $1 \text{ ML} = 7.8 \times 10^{14} \text{ molecules/cm}^2$ ). This corresponds to three thiophene molecules per half unit-cell. The equal number of adsorbed thiophene molecules and the rest atoms present on the surface strongly suggests the involvement of the rest atoms in binding thiophene to the Si(111)-7×7 surface.

#### IV. DISCUSSION

The present results of thiophene adsorption on the Si(111)-7×7 surface are markedly different from previous work on the same surface by MacPherson *et al.* Using combined techniques of TDS and XPS. MacPherson *et al.* have investigated the molecular adsorption and desorption behavior of thiophene on both clean and bombarded Si(111)-7×7 surface at 300 K.<sup>10,11</sup> They proposed that the intense peak at 405 K in their TDS spectra is due to the geometry  $\sigma$  bonded through lone pair electrons of sulfur atom while the weak peak at 350 K corresponds to  $\pi$ -bonded geometry. In present investigation, only the stable chemisorbed state of thiophene located at 414 K in the TDS spectra is identified for thiophene on Si(111)-7×7 adsorbed at 110 K. Moreover, we notice that chemisorbed thiophene molecules undergo both molecular desorption ( $\sim 90\%$ ) and thermal decomposition ( $\sim 10\%$ ) upon thermal annealing, which is quite different from the totally molecular desorption behavior for thiophene on Si(111)-7×7 as observed by MacPherson *et al.*<sup>10,11</sup>

In addition to TDS, we have employed several additional surface analysis techniques to further investigate the binding of thiophene on Si(111)-7×7. The STM CCTs show that the



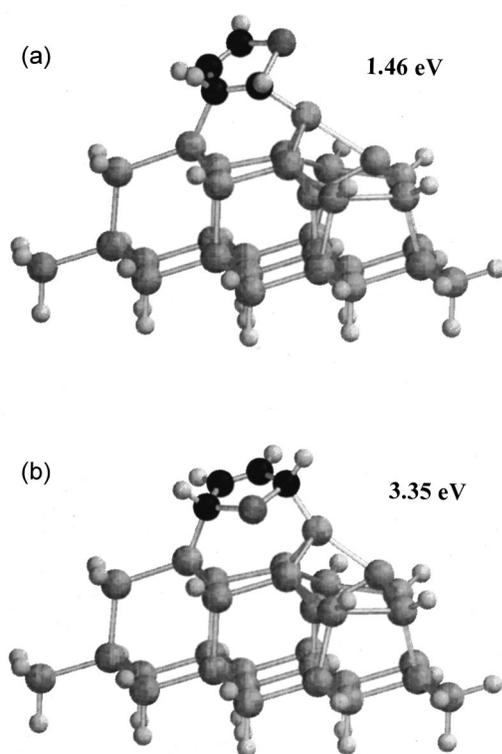


FIG. 9. Two possible adsorption geometries for thiophene on Si(111)-7  $\times$  7. (a) the [2+2] product; (b) the [4+2] product. Shown are the results of the energy optimization of the PM3 calculations. Also given is the calculated binding energy of the configurations.

majority of the (7  $\times$  7) subunits have three darkened sites on the thiophene-saturated surface. Since there are only three rest atoms with dangling bonds in each half of the unit cell, this finding strongly suggests that the binding of one thiophene per neighboring adatom-rest atom pair in line with previous results for unsaturated hydrocarbons such as acetylene and ethylene on the Si(111)-7  $\times$  7 surface.<sup>44,45</sup> Moreover, from our TDS and HREELS results, we know that chemisorbed thiophene did not undergo dissociation on Si(111)-7  $\times$  7 upon chemisorption. Our HREELS data unambiguously demonstrate the rehybridization of carbon atoms in chemisorbed thiophene and the participation of the thiophene  $\alpha$ -positions in bond formation with the surface. Furthermore, the absence of strong  $\pi$ - $\pi^*$  transitions characteristic for free-molecular thiophene in the electronic EELS of the monolayer thiophene demonstrates that both filled and

empty  $\pi$  states of chemisorbed thiophene have been strongly modified by the surface chemical bond and therefore lose their free-molecular character. Coupled with the STM results, we therefore have strong evidences to show that thiophene is di- $\sigma$ -bonded to a pair of neighboring adatom and rest atom on Si(111)-7  $\times$  7, forming a 2,5-dihydrothiophene-like structure shown schematically in Fig. 9.

According to the dimer-adatom-stacking fault (DAS) model of Si(111)-7  $\times$  7 as depicted in Fig. 1(a), the direct distance between two adjacent adatom and rest-atom is  $\sim$ 4.5  $\text{\AA}$ ,<sup>49</sup> the closest Si-atom pair with dangling bonds. On the other hand, the distance between the two  $\alpha$ -positions in thiophene is 2.47  $\text{\AA}$ ,<sup>28</sup> and the typical bond length of SiC is 1.8–2.1  $\text{\AA}$ .<sup>50</sup> Thus, it is reasonable to make the di- $\sigma$  bond between the thiophene molecule and the adjacent adatom and rest-atom without inducing much strain in the adsorption complex. The energy loss in forming our proposed structure can be well compensated by the formation of two Si–C bonds. In organo-silicon chemistry, the typical bond energy for Si–C( $D_{\text{Si-C}}$ ) is 318  $\text{kJ mol}^{-1}$ ,<sup>51</sup> much greater than 186  $\text{kJ mol}^{-1}$  [(resonance energy<sup>52</sup>+1 double bond) 2=(121+251)/2  $\text{kJ mol}^{-1}$ ].<sup>53</sup> Hence, The di- $\sigma$  bonding of thiophene to the adjacent adatom and rest-atom pair is energetically favorable.

Compared to benzene or chlorobenzene on Si(111)-7  $\times$  7,<sup>24,25</sup> the present thermal desorption results show that the binding of thiophene is much stronger. It is known that the resonance energy for benzene, chlorobenzene, and thiophene are 172, 151, and 121  $\text{kJ mol}^{-1}$ , respectively.<sup>52</sup> The energy loss during the formation of the di- $\sigma$  bonded surface adsorption complex associated with a thiophene molecule would be much smaller, resulting a stronger binding to the Si(111)-7  $\times$  7 surface.

From the adsorption geometry of thiophene on Si(111)-7  $\times$  7, one can easily conclude that thiophene interacts with the neighboring adatom-rest atom pairs on the Si(111) surface via the surface [4+2] cycloaddition reaction. The selective cycloaddition of thiophene on Si(111)-7  $\times$  7 leads to the direct attachment of a functional C–S–C linkage onto the surface. The as attached C–S–C linkage is involved in a stretched bicyclic surface-complex, which would induce ring strains on the surface attached C–S–C group. Although the  $\text{CH}_2$ –S– $\text{CH}_2$  group is known to be rather inert in conventional organosulfur chemistry,<sup>53</sup> the existence of ring strains may activate the present surface at-

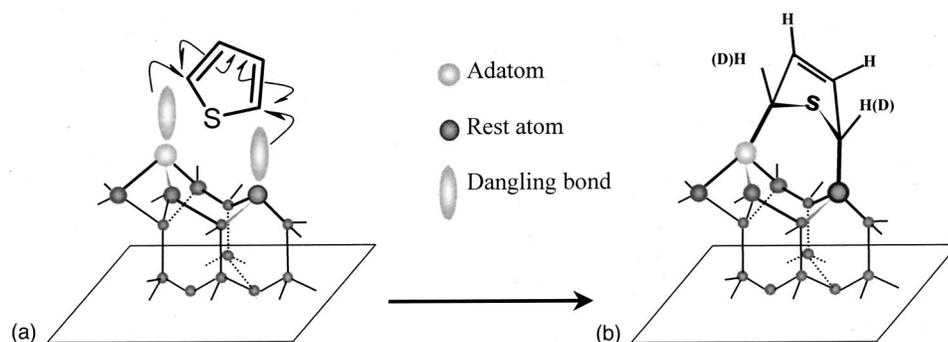


FIG. 10. Schematic diagram for [4+2] cycloaddition reaction of thiophene with Si(111)-7  $\times$  7. Note that the thiophene molecule is di- $\sigma$  bonded to an adjacent adatom-rest atom pair with the direct attachment of a reactive C–S–C linkage.

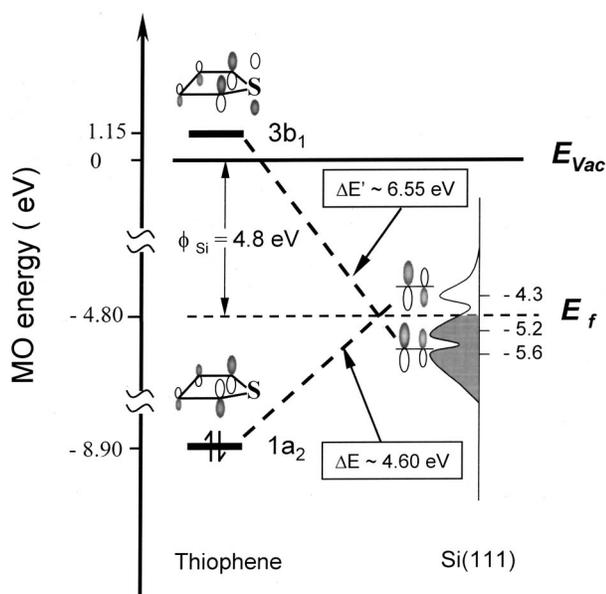


FIG. 11. Frontier orbital energy correlation between thiophene and Si(111)-7×7. The MO energy for thiophene is taken from Schäfer *et al.* (Ref. 60) and the  $\phi$  value for Si(111)-7×7 is 4.8 eV (Ref. 48).

tached C–S–C linkage. This novel surface reaction was also observed for furan adsorption on the Si(111)-7×7 surface at room temperature.<sup>54</sup>

Previous experimental and theoretical studies have shown the feasibility of a Diels–Alder-type [4+2] cycloaddition reaction occurring on Si(100)-2×1,<sup>14,15</sup> where the “Si=Si” can serve as a dienophile in analogy of “C=C.” Further experimental evidences from the combined STM and FTIR data showed that the *conjugate addition* reaction between the 1,3-dienes and the silicon dimers of Si(100)-2×1 can be described using a diradical model.<sup>16</sup> In the present study, an electron deficient dienophile can be formed for an adatom–rest atom pair on Si(111)-7×7 since the rest atom undergoes a reverse charge transfer to the adatom.<sup>43</sup> These electrophilic sites would serve as reactive diradical sites to attack the electron-rich 2,5-positions of an incoming thiophene to form the Diels–Alder cycloadduct. Since the adatoms and rest atoms are both spatially and electronically inequivalent in nature, the present heterogeneous [4+2] cycloaddition reaction may not be a concerted process although the concerted reaction is common in the gas or liquid phase.<sup>55</sup> A precursor-mediated chemisorption may be involved, similar to the case of benzene or chlorobenzene.<sup>24,25</sup> The reaction probably occurs through a short-lived mono- $\sigma$  bonded state, subsequently the stable di- $\sigma$  bonded thiophene on Si(111)-7×7.<sup>25</sup>

Previous theoretical calculations of 1,3-dienes adsorption on Si(100)-2×1 have predicted that the [4+2] and [2+2] products would have a formation energy difference of about 15 kJ mol<sup>-1</sup>, predicting a preferential reaction pathway through a [4+2] process.<sup>15,56</sup> However the latest experiment has demonstrated the formation of comparable amounts of both [4+2] and [2+2] products.<sup>16</sup> A diradical mechanism was proposed to account for the observed low reaction selectivity for alkenes on Si(100) surface. In our case, it is also

possible to form a [2+2] cycloadduct by the reaction of the 2,3 carbons in thiophene with the surface diradical. We have performed semiempirical calculations at the PM3 level using the SPARTAN package<sup>57</sup> for thiophene adsorption on a Si<sub>30</sub>H<sub>28</sub> cluster. This cluster represents an adjacent adatom–rest atom pair on a Si(111)-7×7 surface (see Fig. 10). The binding energies for the [4+2] and [2+2] cycloadducts using PM3 calculations are found to be -323 and -141 kJ mol<sup>-1</sup>, respectively. This result clearly indicates that the 2,5-dihydrothiophene-like surface product is the stable surface intermediate, supporting the conclusions from the HREELS and STM data.

At low coverage or monolayer case, the absence of the intensities of all the characteristic free-molecular thiophene transitions in electronic EELS may be explained by the loss of aromaticity in the surface complex. The adsorbate derived loss intensity between 2 and 4 eV in Fig. 7(b) is associated with the whole adsorbate complex, and is likely attributable to the charge-transfer excitations from the filled states of chemisorbed thiophene to the empty states of silicon. This argument is valid for electronic excitation of benzene and pyridine adsorption on transition metal surfaces,<sup>58</sup> where  $d \rightarrow \pi^*$  charge-transfer bands were observed in the region 2.5–5 eV. A number of silicon empty states can be involved in the excitations on a silicon surface and this may explain the broad nature of the charge-transfer loss band.

The charge transfer behavior can also be understood by employing the frontier molecular orbital (FMO) approach.<sup>59</sup> Figure 11 illustrates the frontier orbital energy correlation between thiophene<sup>60</sup> and the adjacent adatom–rest atom pair on Si(111)-7×7. The adatom–rest atom pair can be viewed as a dienophile in this case, and the empty and filled states of Si(111)-7×7 are the corresponding LUMO and HOMO, respectively. The frontier molecular orbital energies of thiophene and the surface are referenced to the vacuum level, and a work function,  $\phi$ , of 4.8 eV is taken for Si(111).<sup>48</sup> It is clear that the energy difference (4.5 eV) between LUMO<sub>Si(111)</sub> and HOMO<sub>thiophene</sub> is about 2.05 eV smaller than the value (6.55 eV) for LUMO<sub>thiophene</sub>–HOMO<sub>Si(111)</sub>. This is in excellent agreement with the normal electron demand in a Diels–Alder reaction.<sup>61</sup> As a thiophene molecule approaches the Si(111)-7×7 surface, the requirement for better molecular orbital overlap would steer the electron-rich  $\alpha$ -positions of thiophene toward rest atom–adatom pair, leading to the formation of a stable [4+2] cycloadduct on Si(111)-7×7.

In the present reaction system, electron excessive thiophene molecule serves as an electron donor, while the silicon substrate as the acceptor. This can well explain the observation of a broad transition in a higher energy region of 2–4 eV as shown in Fig. 7(b). According to Fig. 11, the HOMO for thiophene molecule is located at about 4.1 eV below the Fermi energy level compared to the average ~0.6 eV for the filled state of the silicon. It is reasonable that the transition from the HOMO of chemisorbed thiophene molecule to the empty state of the substrate will appear at a energy loss region between the weak 1.73 eV loss corresponding to the surface states on clean surface and the region

corresponding to  $\pi-\pi^*$  transitions in free-molecular thiophene.

## V. CONCLUSIONS

In this combined experimental and theoretical study we have presented the first detailed investigation of the cycloaddition chemistry of thiophene on the Si(111)- $7\times 7$  surface. We have shown that thiophene molecules undergo a facile heterogeneous [4+2] cycloaddition reaction as dienes with the adjacent adatom-rest atom pairs on Si(111)- $7\times 7$ . The resultant 2,5-dihydrothiophene-like surface intermediate is di- $\sigma$  bonded to an adjacent adatom-rest atom pair through the  $\alpha$ -carbons in thiophene with the remaining C=C group and C-S-C linkage tilted from the silicon surface. In addition, atomic-resolved STM data have shown the preferential chemisorption of thiophene molecules on the faulted subunits and the center adatoms within each subunit. Furthermore, a diradical reaction mechanism through the formation of mono- $\sigma$  bonding species has been proposed. The elucidation of the molecular mechanism involved in the present adsorption system provides a better understanding of the surface reactions proceeding on semiconductors, and, more significantly, offers a new methodology for further modification of semiconductor surfaces.

## ACKNOWLEDGMENT

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