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Selective Attachment of 4-Bromostyrene on the Si(111)-(7 × 7) Surface

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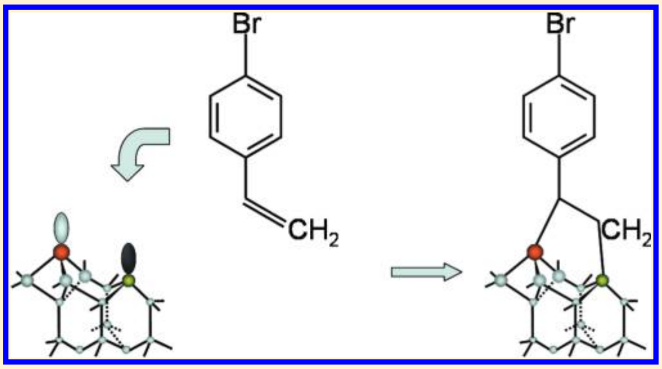
ABSTRACT: The covalent attachment of 4-bromostyrene on the Si(111)-(7 × 7) surface was investigated using X-ray photoelectron spectroscopy (XPS), high-resolution electron energy loss spectroscopy (HREELS), and density functional theory calculations. The HREELS spectra suggest that 4-bromostyrene covalently binds to the silicon surface through a [2 + 2]-like cycloaddition pathway between the external vinyl group and the adjacent adatom−rest atom pair of the Si(111)-(7 × 7) surface, forming 4-bromoethylbenzene-like binding configuration. The XPS results further confirm that only the vinyl double bond participates in the surface binding reaction, whereas the bromine atom remains unchanged during the adsorption process. The resulting 4-bromoethylbenzene-like structure on the Si(111)-(7 × 7) surface can be employed as a precursor for further chemical modification and functionalization.



1. INTRODUCTION

The covalent binding of organic molecules on semiconductor surfaces has been attracting much attention recently because of its fundamental scientific significance as well as potential applications in chemical and biological sensors and molecular electronics.[1−6] To achieve fine control in incorporating the desired organic functionalities into existing device technologies, fundamental research on the interface and surface chemistry of semiconductors is necessary to provide an essential understanding of molecular binding on semiconductor surfaces as well as to achieve controlled molecular attachment. In particular, the investigation of the selective attachment of multifunctional molecules on semiconductor surfaces is quite important since one of the functional groups can selectively bind onto semiconductor surfaces, and the others are reserved for further modification as well as the construction of covalent multilayers in vacuum.[7−11]

The (7 × 7) reconstruction of Si(111) is perhaps best known as the most complex and scientifically important semiconductor surface, which can serve as a model template for understanding the interaction between organic molecules and surface silicon atoms. Its structure, shown in Figure 1, can be described by the dimer−adatom−stacking fault (DAS) model.[12] A (7 × 7) structure unit cell can be divided into two triangular subunits (faulted and unfaulted) surrounded by nine silicon dimers, and contains nineteen dangling bonds associated with twelve adatoms, six rest atoms, and one corner hole. Chemical reactions are most likely to take place at these dangling bonds because of their unsaturated nature. The electron density is higher in the faulted half than in the unfaulted side. Within each half the three corner adatoms have a greater electron density compared to the center adatoms. This surface provides a number of chemically, spatially, and electronically inequivalent reactive sites, including the adatoms and rest atoms in both the faulted and unfaulted halves and the corner holes. The adjacent adatom−rest atom pair on the Si(111)-(7 × 7) surface can serve as a reactive functional group to readily react with unsaturated organic functionalities, leading to a di-σ binding mode through the cycloaddition-like strategy.[13−21]

4-Bromostyrene is an interesting multifunctional molecule, consisting of the π-conjugated phenyl ring ($-C_6H_5$), the vinyl group ($-CH{=}CH_2$), and the bromine (Br) atom. Its rich attachment chemistry on the Si(111)-(7 × 7) surface can be anticipated. It may selectively bind on the Si(111)-(7 × 7) surface through a typically [2 + 2] cycloaddition of the vinyl group with the adjacent adatom−rest atom pair, maintaining its phenyl ring skeleton and bromine atom in the addition product. Another possibility is that it can bind onto the surface through the phenyl ring in the binding modes similar to those of benzene and its derivatives.[19−23] The third possible binding mode is to form a styrene-like configuration through the cleavage of the C—Br bond. Thus, 4-bromostyrene was chosen as a model to demonstrate the selective attachment of multifunctional

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molecules on the Si(111)-(7 × 7) surface. Despite the interest of 4-bromostyrene on the Si(111)-(7 × 7) surface, only a few studies have dealt with the growth of Br-terminated monolayers by linking 4-bromostyrene on hydrogen-covered Si(111) and Si(100) surfaces, in which the bromine functionality is preserved at the top of the organic adlayer following reaction with hydrogen passivated silicon surfaces.[24,25]

In this paper, the adsorption of 4-bromostyrene on the Si(111)-(7 × 7) surface was investigated using X-ray photoelectron spectroscopy (XPS), high-resolution electron energy loss spectroscopy (HREELS), and density functional theory (DFT) calculations. The experimental and theoretical results clearly suggest that 4-bromostyrene adsorbs on the Si(111)-(7 × 7) surface through the vinyl group with an adjacent adatom−rest atom pair, maintaining its phenyl ring and C−Br bond protruding into the vacuum. The covalently bonded organic molecule with the intact C−Br bond could serve as a precursor for further photochemical modification and funtionalization.

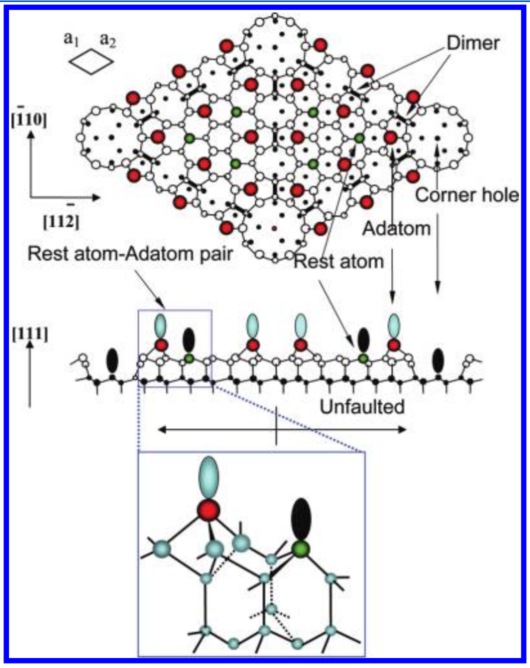

Figure 1. Top and side views of the DAS model for the Si(111)-(7 × 7) surface reconstruction. The (7 × 7) unit cell is outlined with the faulted half on the left and the unfaulted half on the right. The diradical reactive sites of an adjacent adatom−rest atom pair are also marked.

2. EXPERIMENTAL SECTION

XPS and HREELS studies were carried out in an ultrahigh vacuum (UHV) chamber with a base pressure lower than 2×10^{-10} Torr. This chamber is equipped with an X-ray source and a concentric hemispherical energy analyzer (CLAM2, VG) for XPS and a high-resolution electron energy loss spectrometer (LK-2000-14R, LK Technologies, Bloomington, IN). The XPS spectra were acquired using Al Kα radiation ($h\nu$ = 1486.6 eV) and a pass energy of 20.0 eV. The binding energy (BE) scale is referenced to the peak maximum of the Si 2p line (99.3 eV) of a clean Si(111)-(7 × 7) substrate.[26] The XPS peaks were fitted with Gaussian−Lorentzian sum functions using XPSPeak 4.1.[27] The bromine spectra were fitted with pairs of curves while imposing the necessary constraint for the Br $3d_{3/2}$ and $3d_{5/2}$ spin doublet (ΔE = 1.05 eV, 2:3 peak area ratio).[26] For HREELS experiments, the electron beam with an energy of 5.0 eV impinges on the Si(111)-(7 × 7) surface at an incident angle of 60° with a resolution of 6−7 meV (fwhm, 55 cm^{-1}).

The Si(111) samples (20 mm × 8 mm × 0.38 mm) were cut from p-type boron-doped silicon wafers (purity 99.999%, thickness 0.38 mm, resistivity 1−30 Ω cm, Goodfellow). A Ta-sheet resistive heater (thickness 0.025 mm, Goodfellow) was sandwiched between two Si(111) crystals held together using Ta clips and in turn spot-welded to Ta posts at the bottom of a Dewar-type liquid nitrogen (N_2) cooled sample holder. The crystals can be resistively heated to 1300 K and cooled to 110 K using liquid N_2. The clean Si(111)-(7 × 7) surfaces were prepared by overnight degassing at 850 K, cycles of Ar-ion sputtering

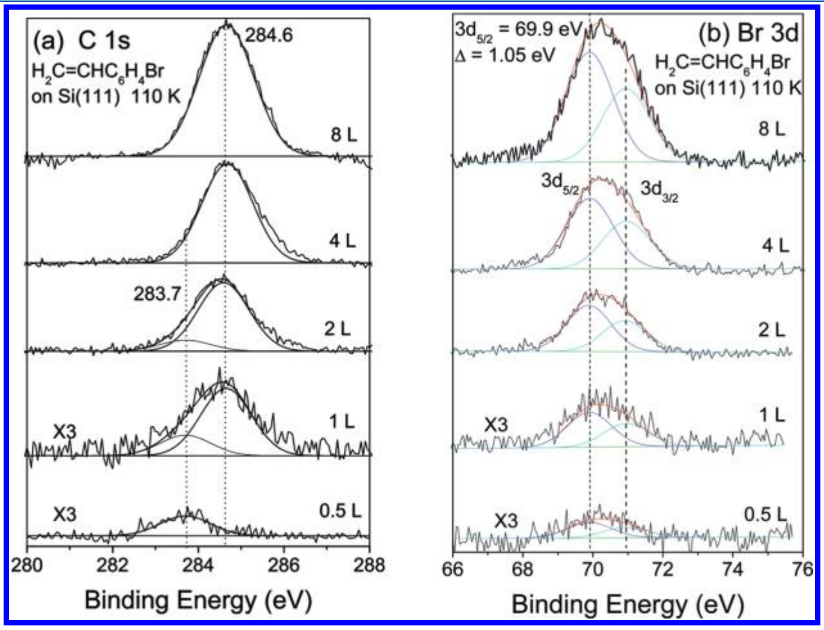

Figure 2. XPS spectra of (a) C 1s and (b) Br 3d regions for 4-bromostyrene adsorbed on the Si(111)-(7 × 7) surface as a function of exposure at 110 K.

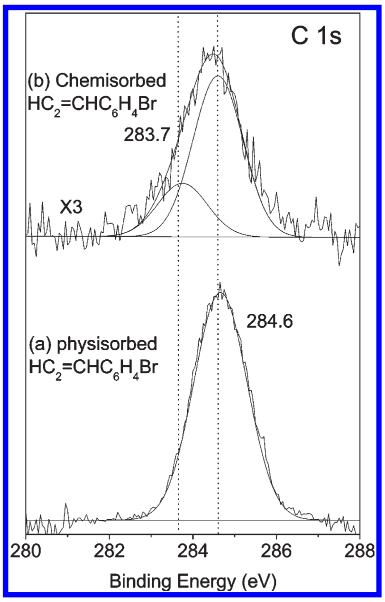

Figure 3. C 1s experimental spectra and their deconvolution results of physisorbed multilayer (a) obtained by exposing 8 L of 4-bromostyrene on the Si(111)-(7 × 7) surface at 110 K and saturated chemisorbed monolayer (b) obtained by annealing physisorbed sample to 300 K.

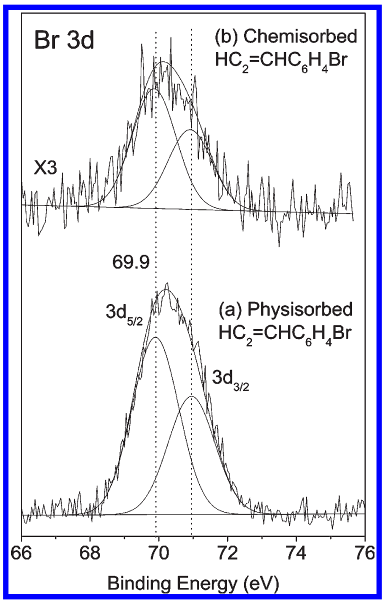

Figure 4. Br 3d experimental spectra and their deconvolution results for the physisorbed multilayer (a) and saturated chemisorbed monolayer (b) of 4-bromostyrene on the Si(111)-(7 × 7) surface. The spectra show a single Br spin doublet at 69.9 and 71.0 eV for both physisobed and chemisorbed molecules, which is attributed to carbon-bound bromine.

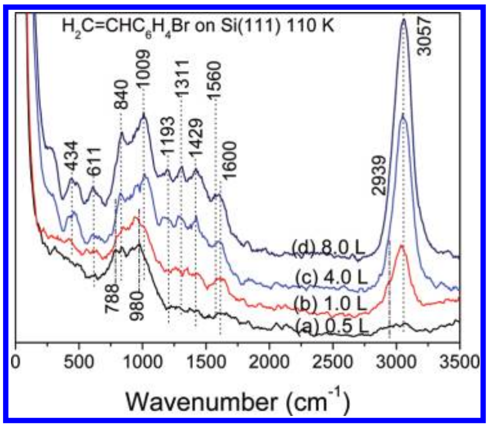

Figure 5. HREELS spectra as a function of 4-bromostyrene exposure on the Si(111)-(7 × 7) surface at 110 K.

(500 eV bombardment for 20 min with an ion current density of 10 μA cm^{-2}), and annealing to 1250 K for 5 min in UHV. The cleanliness of the samples was verified using XPS and HREELS.

4-Bromostyrene (98%, Sigma-Aldrich Chemical) was further purified through at least five freeze−pump−thaw cycles before being dosed onto the Si(111)-(7 × 7) surface at 110 K (liquid N_2 temperature). Dosing was performed through a dosing tube located at a few centimeters from the surface, and the exposures were reported in langmuirs (1 langmuir = 10^{-6} Torr·s) without the calibration of ion gauge sensitivity.

3. RESULTS AND DISCUSSION

A. XPS. XPS was employed to investigate the chemical shifts of C 1s and Br 3d core levels of 4-bromostyrene on the Si(111)-(7 × 7) surface. Figure 2a shows the C 1s XPS spectra of 4-bromostyrene adsorbed on the clean Si(111)-(7 × 7) surface at 110 K as a function of exposure. For 4-bromostyrene exposure less than 2 L, a C 1s photoemission feature centered at 283.7 eV (fwhm of 1.4 eV) was observed, ascribable to chemisorbed 4-bromostyrene. Increasing the exposure leads to the growth of the C 1s peak at 284.6 eV corresponding to the physisorbed molecules. The physisorption peak becomes dominant in the XPS spctra at exposures higher than 4 L. At 8 L, the photoemission from chemisorbed species is completely attenuated.

Figure 2b shows the Br 3d XPS spectra for 4-bromostyrene adsorbed on the clean Si(111)-(7 × 7) surface at 110 K as a function of exposure. Consistent with the Br $3d_{3/2}$ and $3d_{5/2}$ spin doublet, the fitted pairs of curves were subjected to the constraint of $\Delta E = 1.05$ eV and a peak area ratio of 2:3. As shown in Figure 3, the best fit for the Br 3d XPS spectra was obtained using only a single pair of peaks, indicating the existence of bromine in only one oxidation state. Since there is only one chemical state of Br $3d_{5/2}$ positioned at 69.9 eV for chemisorbed and physisorbed 4-bromostyrene, this state is attributed to carbon-bound bromine and confirms the presence of bromophenyl groups on the surface following monolayer formation.[24,25,28,29]

The fitted C 1s XPS spectra of physisorbed and chemisorbed 4-bromostyrene on the Si(111)-(7 × 7) surface are shown in Figure 3. The C 1s spectrum for the physisorbed multilayer, presented in Figure 3a, was obtained by exposing 8 L of 4-bromostyrene on the Si(111)-(7 × 7) surface at 110 K. The fitted results show that a single peak with binding energy of 284.6 eV can be readily resolved for the C 1s spectrum of the physisorbed multilayer, which shows that the C atoms in vinyl and phenyl groups have similar binding energies. Figure 3b is the C 1s spectrum for the saturated chemisorption monolayer on the Si(111)-(7 × 7) surface obtained by annealing the multilayer 4-bromostyrene-covered sample to 300 K to drive away physisorbed bromostyrene but retain chemisorbed molecules. The C 1s photoemission feature of chemisorbed molecules can be fitted into two peaks at 284.6 and 283.7 eV with an area ratio of 3:1.

Table 1. Vibrational Frequencies (cm^{-1}) and Their Assignments for Physisorbed and Chemisorbed 4-Bromostyrene on the Si(111)-(7 × 7) Surface

		HREELS of 4-bromostyrene on Si(111)-(7 × 7)		calculated vibrational frequencies of 4-bromostyrene on Si(111)-(7 × 7)	
vibrational assignment	IR of liquid 4-bromostyrene[30,31]	physisorbed	chemisorbed	physisorbed	chemisorbed
aromatic C—H stretching	3058	3057	3057	3039	3067
sp^3 C—H stretching			2939		2915
vinyl C=C stretching	1600	1600		1634	
ring C—C stretching	1560	1560	1560	1584	1578
aromatic C—H deformation	1416	1429	1429	1414	1469
vinyl CH_2 rocking	1308	1311	1311	1310	1310
ring breathing	1022	1009	1009	987	987
ring CH deformation			980		980
ring CH deformation	864	840	840	872	830
ring out of plane bending			788		807
Br-sensitive	572	611	611	640	640
ring deformation	420	434	434	471	471
Si—C stretching			700		696

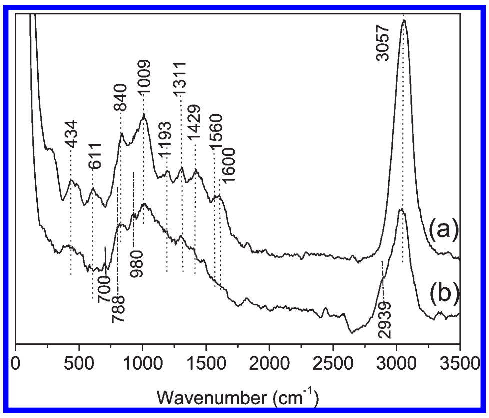

Figure 6. HREELS spectra of the physisorbed multilayer (a) obtained by exposing 8 L of 4-bromostyrene on the Si(111)-(7 × 7) surface at 110 K and saturated chemisorption monolayer (b) obtained by annealing physisorbed sample to 300 K.

The peak at 284.6 eV, similar to the C 1s peak of the physisorbed molecules, is assigned to C 1s of the phenyl ring, while the peak at 283.7 eV is assigned to the vinyl group binding on the silicon surface. For the chemisorbed 4-bromostyrene, six C atoms of the phenyl ring maintain their sp^2 hybridization upon chemisorption; the two C atoms in the vinyl group change to sp^3 hybridization from the original sp^2 when they are covalently linked to surface silicon atoms. Thus, the peaks at 284.6 and 283.7 eV can be reasonably assigned to the C atoms of the phenyl ring and those of the reacted vinyl group with sp^3 hybridization, respectively. Compared to physisorbed molecules, the C 1s core level of the phenyl ring does not display any significant chemical shift, which also suggests that the phenyl ring is not directly involved in the binding with the silicon surface.

Figure 4 presents the Br 3d XPS spectra for physisorbed (a) and chemisorbed (b) 4-bromostyrene on the Si(111)-(7 × 7) surface. The best fit for the Br 3d XPS spectrum was obtained using only a single pair of peaks, and the peak area ratio for $3d_{5/2}$ and $3d_{3/2}$ for both the physisobed and chemisorbed 4-bromostyrene is exactly 3:2, indicating the existence of bromine in one oxidation state. Specifically, this state is attributed to carbon-bound bromine because the binding energy for physisorbed and chemisorbed 4-bromostyrene remains unchanged, indicating that the C−Br bond remains intact after the surface reaction of 4-bromostyrene on the Si(111)-(7 × 7) surface.

B. HREELS. Vibrational studies were carried out to further examine the binding mechanism of 4-bromostyrene on the Si(111)-(7 × 7) surface. Figure 5 shows the high-resolution electron energy loss spectra of 4-bromostyrene exposed on the Si(111)-(7 × 7) surface at 110 K as a function of exposure. The vibrational frequencies and their assignments for physisorbed and chemisorbed molecules are summarized in Table 1. Vibrational signatures at 434, 611, 840, 1009, 1193, 1311, 1429, 1560, 1600, and 3057 cm^{-1} can be clearly identified in the spectra of physisorbed molecules. The vibrational features of physisobed 4-bromostyrene, shown in parts c and d of Figure 5, are consistent with the IR spectrum of liquid 4-bromostyrene.[30,31] Among them, the peak at 3057 cm^{-1} is assigned to the sp^2 aromatic ring CH stretching mode; the loss feature at 1600 cm^{-1} is attributed to the stretching mode of the vinyl C=C group; the peaks at 1560, 1429, 1009, and 420 cm^{-1} are associated with the characteristic vibrational modes of the phenyl ring; the peak at 611 cm^{-1} is related to the CH stretching and bending modes in the Br-sensitive CH:CHBr group.[30,31]

The vibrational features of chemisorbed 4-bromostyrene were obtained by annealing the physisorbed multilayer sample to 300 K to drive away all the physisorbed molecules and only retain the chemisorbed molecules, shown in Figure 6. There are several distinct differences between the spectra for the physisorbed and chemisorbed molecules. All the vibrational features related to the phenyl ring are retained in the spectrum for chemisorbed molecules in Figure 6b. These results point to the retention of the aromatic ring. The absence of the vinyl C=C strtching mode at 1600 cm^{-1} and the new vibrational feature at 2939 cm^{-1} corresponding to the sp^3 CH stretching mode suggest the presence of rehybridization of the vinyl C=C group for 4-bromostyrene di-σ bonded to the silicon surface. The new peaks at 980 and 788 cm^{-1} are related to the ring deformation and out-of-plane bending vibrations upon forming Si—C—C—Si bonds on the silicon surface, respectively.

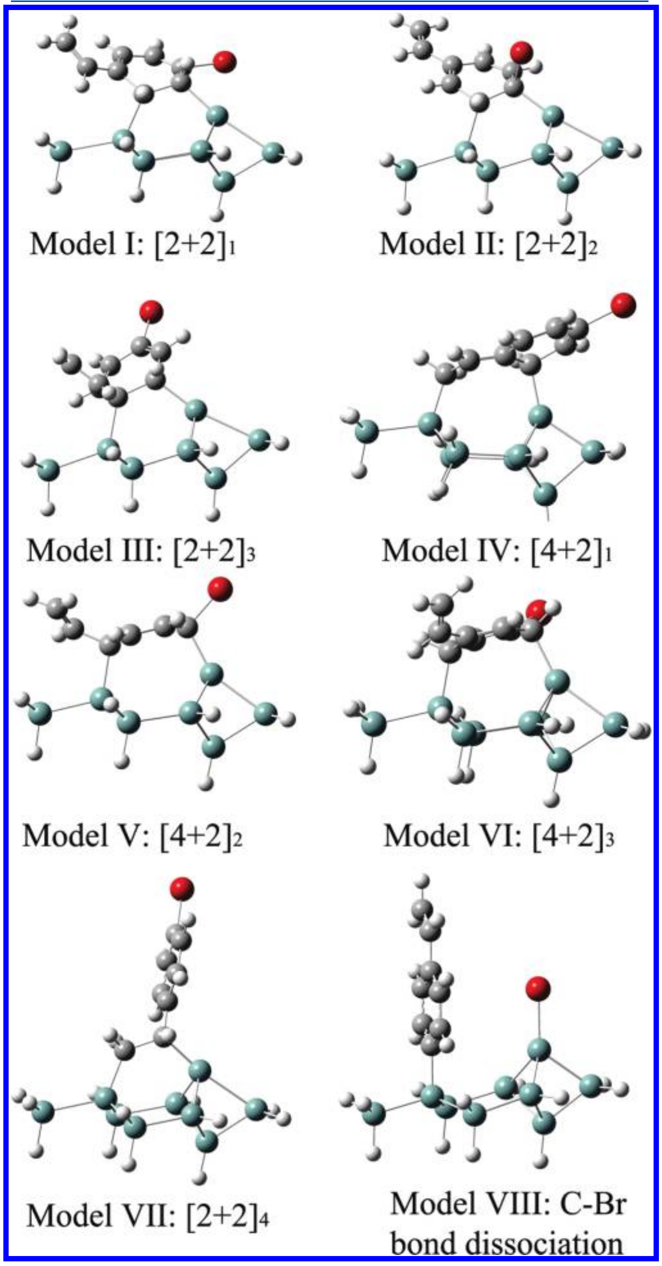

Figure 7. Possible binding configurations for 4-bromostyrene on the Si(111)-(7 × 7) surface.

C. DFT Calculations. In general, there are eight possible binding modes for 4-bromostyrene chemisorbed on the Si(111)-(7 × 7) surface, schematically illustrated in Figure 7. The first category involving the interaction between the phenyl ring and an adatom—rest atom pair is presented in modes I—V. The second possibility is the [4 + 2]-like cycloaddition involving both the phenyl and vinyl C═C double bonds (mode VI). The third is the direct [2 + 2] cycloaddition reaction of the vinyl group and the adatom—rest atom pair (mode VII). The last possibility is the dissociative reaction with the C—Br bond cleavage (mode VIII). Thus, DFT calculations were employed to obtain the optimized geometry and adsorption energy for the possible adsorption configurations to aid the understanding of the selectivity of 4-bromostyrene on the Si(111)-(7 × 7) surface.

We performed DFT calculations using the GAUSSIAN 09 software package[32] for a 4-bromostyrene molecule adsorbed on a starting cluster of Si_9H_{12}, which was previously proven to be successful in predicting the adsorption energy and binding configurations of organic molecules on the Si(111)-(7 × 7) surface.[14−17] On the basis of the possible binding modes shown in Figure 7, eight 4-bromostyrene bonded clusters were built to calculate the adsorption energies of 4-bromostyrene on the Si(111)-(7 × 7) surface. DFT B3LYP/6-31+G(d) level of theory was used to optimize the adsorption geometries and calculate the total energies. The results in Table 2 reveal that the product of [2 + 2]-like cycloaddition reaction occurring between the vinyl double bond and the adatom—rest atom pair (Mode VII) and the dissociative reaction involving the C—Br bond (Mode VIII) are thermodynamically favored, compared to the other cycloaddition reactions involving the phenyl ring, due to the retention of the aromatic phenyl ring. Although the dissociative adsorption involving the C—Br bond has a slightly larger adsorption energy compared to the [2 + 2]-like cycloaddtion with vinyl group, a higher transition state may exist in the formation of C—Si bond via C—Br bond breakage. Some DFT calculations support the conclusion that the addition of styrene on the silicon surface through the vinyl group is facile, with only a small barrier.[33,34] A recently published DFT study by Demirel et al.[35] showed that there was no energy barrier for 4-bromostyrene binding to the clean Si(100)-(2 × 1) surface through the [2 + 2]-like cycloaddtion reaction with the vinyl group and the silicon dimer. Our DFT calculations also showed that the dissociative reaction pathway with the C—Cl bond cleavage (80.4 kJ/mol) has a much higher energy barrier.[9] That may suggest that the cycloaddition reaction through the vinyl group is kinetically favored, which is also consistent with the XPS and HREELS experimental results. The calculated vibrational frequencies (Table I) for model VII are indeed in good agreement with the experimental vibrational spectra of the chemisorbed molecules, which support

Table 2. Adsorption Energies[a] of All Possible Binding Configurations for the 4-Bromostyrene/Si_9H_{12} Model System[b]

binding configurations in Figure 7	I	II	III	IV	V	VI	VII	VIII
functional group	phenyl ring	phenyl ring	phenyl ring	phenyl and vinyl C═C	phenyl ring	phenyl ring	vinyl group	C—Br
reaction model	[2 + 2]-like	[2 + 2]-like	[2 + 2]-like	[4 + 2]-like	[4 + 2]-like	[4 + 2]-like	[2 + 2]-like	C—Br bond cleavage
adsorption energy	180	150	201	258	182	231	342	381

[a] Adsorption energy is calculated by subtracting the energy of cluster C_8H_7Br/Si_9H_{12} from the total energy of free cluster Si_9H_{12} and gas-phase 4-bromostyrene C_8H_7Br. [b] All energies are in kcal mol^{-1}.

4-bromostyrene covalently binding to the Si(111) surface through reaction between the vinyl group and the adjacent adatom—rest atom pair. Since there are three rest atom—adatom pairs on each half unit cell and one 4-bromostyrene molecule binds on each pair, three 4-bromostyrene molecules can bond onto each half unit cell of the Si(111)-(7 × 7) surface at saturated coverage.

4. CONCLUSIONS

The adsorption of 4-bromostyrene was investigated with XPS, HREELS, and DFT calculations. 4-Bromostyrene selectively adsorbs on the Si(111)-(7 × 7) surface through the [2 + 2]-like cycloaddition reaction between the vinyl double bond and the adjacent adatom—rest atom pair. The resulting 4-bromoethylbenzene-like skeleton may be employed as a precursor for further chemical modification of silicon surfaces or as a monomer for fabrication of conductive polymer thin films on semiconductors.

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