An Investigation of Ethylene Attachment to Si(111)–7 × 7 in the Restatom—Adatom Bridging Geometry: Electronic and Vibrational Properties

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ABSTRACT: The adsorption of ethylene on the bridge adatom—restatom position of the Si(111)–7 × 7 surface was studied with scanning tunneling microscopy, photoelectron spectroscopy, and theoretical calculations. The electronic structure and the corresponding vibrational states were calculated for a single molecule adsorbed in different binding sites located within the 7 × 7 unit cell. We found that there is no significant difference in the electronic structure between the adsorption sites that were considered: center and corner adatom—restatom. Moreover, the different electron occupation of the restatoms and adatoms has a strong effect on the electronic structure of the adsorbed molecule near the Fermi level, and this leads to the reduction of the molecular symmetry to C₄ or even to C₁. In the case of the Si 2p core level, beside the previously reported continuous quenching of the restatom state, we found clear evidence of the existence of a peak corresponding to the Si—C bond separated by 0.44 eV from the bulk component. Furthermore, for the vibrational analysis, isotopic substitution of C₂H₄ with C₂D₄ gave us more insight into the correct assignment of the modes in the experiment. Specifically, exceptional care must be taken with the allocation of the C—H wagging, twisting, and C—C stretching modes.

I. INTRODUCTION

Ethylene serves as an invaluable “model system” in the study of adsorption on metal surfaces because it is a simple unsaturated, nonaromatic molecule. Among the metal surfaces that have been investigated, the Ni(110) surface has attracted the most attention: although Ni(110) has been studied from a number of complementary perspectives,¹,² there has been a particular focus on the adsorption-induced changes in the valence band region. Moreover, these adsorption studies have also been extended to the low-index semiconductor surfaces because of the importance of supported SiC, diamond films, and their chemical vapor deposition. In the case of Si(001)–2 × 1, several theoretical studies have sought to understand both the atomic and the electronic structure of the adsorbed system.³–⁶ However, because of the complexity of the Si(111)–7 × 7 surface reconstruction and the highly reactive nature of the same, this has turned out to be a highly nontrivial task.

One of the first studies of ethylene adsorption on Si(111)–7 × 7 was performed by Klámesch and coworkers.⁷ They proposed that the ethylene most probably adsorbs without dehydrogenation and found that compared with metal surfaces the dehydrogenation takes place at much higher temperature suggesting a strong and stable adsorption (chemisorption) mechanism. Further experiments with electron energy loss spectroscopy (EELS) demonstrated that the ethylene is predominantly adsorbed nondissociatively at room temperature and the C has a hybridization state that is close to sp³, indicating an additional adsorption mechanism.⁸ Piancastelli et al. reported a scanning tunneling microscopy (STM) experiment where ethylene exposures caused surface atoms to “disappear” and also introduced change in the local density of states around the Fermi level.⁹ This tendency was observed not only on the surface atoms directly involved in the adsorbate—substrate bonds but also on some of the neighboring atoms. On the basis of their observations, they proposed an adsorption model, where the molecule bridges an adatom and an adjacent restatom. Similar observation had been reported before for the acetylene molecule, and it had been suggested that this adsorption scheme is common for other
unsaturated molecules on $7 \times 7$.\textsuperscript{10} The fact that the adatoms and the restatoms are involved in the adsorption process was subsequently proved in a photoelectron spectroscopy (PES) study, where after depositing $\text{C}_2\text{H}_4$, the intensity corresponding to surface states simultaneously decreases in both the valence band and in the Si 2p core level spectra.\textsuperscript{11}

Until now, only Rochet and coworkers disagreed with the suggested adsorption process described above.\textsuperscript{5} On the basis of their combined LEED and PES experiment, an alternative adsorption mechanism was proposed involving the reconstruction of the $7 \times 7$ unit cell. This alternative mechanism would allow many more molecules to be adsorbed in a unit cell than was proposed in the adatom–restatom theory. The idea of adsorption-induced reconstruction was supported later also by Kim et al.\textsuperscript{12} From the Si 2p core level analyses, they also claimed that there are other adsorption sites involved in addition to bridging sites. Moreover, a similar configuration to the proposed one for the adsorption of acetylene (coupled-bridge) on the $7 \times 7$ surface\textsuperscript{13} must be considered for ethylene as well.

Interestingly, there is only one theoretical paper so far concerning the adsorption of ethylene on the Si(111)–$7 \times 7$ surface. Lu and coworkers published a detailed study of the cycloaddition-like reaction with small Si clusters representing the Si(111)–$7 \times 7$ for several molecules including ethylene.\textsuperscript{14} Their calculation did not show any intermediate or transition state along the reaction pathway supporting the previously accepted adatom–restatom adsorption model. In addition, they found that the substrate reconstruction has very low probability. The conclusions of this study depend critically on the degree to which the cluster, or unit-cell fragment, reproduces the behavior of the $7 \times 7$ unit cell.

Because of the recent discussion about the validity of the adatom–restatom model for the adsorption of ethylene on the Si(111)–$7 \times 7$ surface, we have investigated the adsorption of ethylene from low coverage until the saturation coverage when all bridging adatoms and restatoms are involved in the adsorption process was subse-

### II. METHODS

#### A. Scanning Tunneling Microscopy

All STM data were collected on an Omicron VT-STM operating at a base pressure of $1 \times 10^{-10}$ mbar or below. The bias voltage is applied to the sample; therefore, positive bias voltage refers to imaging empty states in this Article. Ethylene (Linde, Germany) was dosed from a precision leak valve. Depositions were performed by backfilling the chamber to $2 \times 10^{-16}$ mbar. Before each deposition, the cleanliness of the sample was checked with STM to ensure that no C atoms from previous depositions would affect results. All measurements were done at RT ($\sim 300$ K) and in the constant current mode.

#### B. Synchrotron Radiation Photoelectron Spectroscopy (SRPES)

The photoemission experiments were performed at the Materials Science Beamline at the Elettra synchrotron light source in Trieste. The beamline is equipped with a plane grating monochromator providing synchrotron light in the energy range of 40–800 eV, a Specs Phoibos 150 hemispherical electron energy analyzer, low-energy electron diffraction (LEED) optics, and dual-anode X-ray source. During the experiments, the base pressure in the main chamber was in the low $10^{-10}$ mbar range. Both STM and SRM chambers contain quadrupole mass spectrometers allowing the determination of the gas purity.

The Si 2p core level spectra were recorded at 150 eV of photon energy in normal emission geometry (NE, incidence/emission angles of $60^\circ/0^\circ$) and normal incidence geometry (NI, incidence/emission angles of $0^\circ/60^\circ$) with total energy resolution (both analyzer and beamline) of 0.15 eV. The C 1s XPS spectra were collected in the same geometries, and the photon energy and the total resolution were 330 and 0.45 eV, respectively. The valence band spectra were measured with the same Phoibos analyzer using angular resolution of $2^\circ$ and total energy resolution of 50 meV; spectra were measured in the interval between NE and NI with a step of $6^\circ$. The photon energy was 45 eV. The binding energy (BE) was calibrated by measuring the Fermi edge. The polarization of light from the beamline has not been measured but is believed to be between 80 and 90% linear, as the source is a bending magnet. The raw data were normalized to the intensity of the photon beam, measured by means of a high-transmission gold mesh and by corresponding spectra of the clean sample, and recorded under identical conditions.

#### C. Density Functional Theory Simulations

We have used the local orbital DFT code FIREBALL\textsuperscript{15,16} to optimize the atomic structure of ethylene molecules adsorbed on the Si(111)–$7 \times 7$ surface. The calculations were performed within the local-density approximation (LDA) for the exchange-correlation functional.\textsuperscript{15} The valence electrons have been described by optimized\textsuperscript{17} numerical atomic-like orbitals having the following cutoff radii (in a.u.): $R_c(s, s^*) = 3.8$ for H; $R_c(s) = 4.0, R_c(p) = 4.5$, and $R_c(d) = 5.4$ for C orbitals; and $R_c(s) = 4.8, R_c(p) = 5.4$, and $R_c(d) = 5.6$ for Si orbitals, respectively.

The clean Si(111) surface was modeled in a $7 \times 7$ supercell geometry, with an atomic slab of six Si layers, and the back-side of the slab was passivated by H atoms. The total number of atoms included in the calculation was $347$. The Si equilibrium bulk lattice constant of 5.46 Å was used to build the slab geometry. The five top Si layers of the slab were allowed to relax, whereas the rest of the atoms were kept fixed during the optimization process. Individual geometries have been converged until the respective criteria of $10^{-6}$ eV and 0.05 eV/Å for the accuracy in energy and force were satisfied. The structural optimization calculations were carried out using only the $\Gamma$-k-point sampling of the Brillouin zone.

The vibration states of the optimized adatom-restatom configuration were calculated within the harmonic approximation. The dynamical matrix elements were generated with the $\Gamma$-k-point sampling of the Brillouin zone with atomic displacement 0.03 Å. Characteristic harmonic frequencies and modes of the adsorbed molecule were determined by analyzing eigenmodes of the dynamical matrix. The theoretical STM images have been computed using the Green’s functions method. (For details, see refs 19 and 20.)

#### III. RESULTS AND DISCUSSION

#### A. Equilibrium Adsorption Geometry and Vibrational Properties

From our DFT calculations, we conclude that the ethylene molecule is adsorbed without decomposition in a bridge
The adsorption of ethylene on a 7 × 7 surface results in structural deformations of both the surface and the molecule. The substrate deformation due to adsorption of a single ethylene molecule in the Co–Re position is shown in Figure 2 (top), where only vertical displacements of adatoms and restatoms larger than ±0.02 Å are indicated. The restatom/adatom bonded to the molecule is displaced inward/upward by −0.42 and +0.02 Å, respectively. The other two adatoms near the molecule go upward from the surface by +0.14 Å. The structural changes for ethylene adsorption in the faulted and unfaulted subunit are the same. Calculations were also performed for two ethylene molecules (Figure 2, bottom panel) in the 7 surface. Vertical displacements below ±0.02 Å are not shown. Calculated STM images (filled state, −1 V) are used as a background to emphasize the impact of molecular adsorption on STM scans.

Table 1. Calculated Equilibrium Position of the Adsorbed Molecule*

<table>
<thead>
<tr>
<th>Bond Length (Å)</th>
<th>d(CαH)</th>
<th>d(CβH)</th>
<th>d(CαSi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CαH</td>
<td>1.11</td>
<td>1.11</td>
<td>1.99</td>
</tr>
<tr>
<td>CβH</td>
<td>1.11</td>
<td>1.11</td>
<td>1.98</td>
</tr>
<tr>
<td>CαSi</td>
<td>1.99</td>
<td>1.99</td>
<td>1.08</td>
</tr>
<tr>
<td>CReH</td>
<td>105.7</td>
<td>105.4</td>
<td>108.1</td>
</tr>
<tr>
<td>CReSi</td>
<td>107.7</td>
<td>108.2</td>
<td></td>
</tr>
<tr>
<td>CReCReH</td>
<td>108.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CReCReSi</td>
<td>124.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* All distances are in angstroms. The bond angles defined by the atoms in the brackets are represented by α, whereas φ represents the dihedral (torsion) angle.

(even C12) might occur.1−4,10 In contrast with metal surfaces, the molecule can easily form a strong covalent bond with the silicon substrate, resonant states or Bloch states (if symmetrically allowed), leading to distortions of the molecule geometry.3,4 In our case, the dangling bond state of the adatom and the restatom has different occupation including unsaturated dangling bonds on adatoms. The presence of these electronic states enhances the chemical reactivity of the surface. Molecules after adsorption no longer have two-fold symmetry (see Table 1 and C–C–Si angles) converting into C3v symmetry (strictly speaking, the mirror plane is gone as well, therefore Ci).

As a first evaluation of the adsorption mechanism, the vibrational spectra of the adsorbed molecules (C2H4, C2D4) in the bridge adatom–restatom position was calculated, and the...
characteristic vibrational modes are summarized in Table 2. In general, the frequencies of the calculated modes are in excellent agreement with the peak positions in the experimental EELS spectra presented by Yoshinobu et al.\textsuperscript{10} The CH\textsubscript{2} stretching mode has the characteristic energy of the sp\textsuperscript{3} hybridized group; however, the eigenstates are slightly different for the C\textsubscript{Ad}H\textsubscript{2} and C\textsubscript{Re}H\textsubscript{2} modes because of the asymmetry of the adsorbed molecule. The measured C–H stretching region shows an asymmetric (toward higher energies) peak at 2930 cm\textsuperscript{-1}.\textsuperscript{10} From our calculation, it is likely that the main components of this region can be assigned to the symmetric C–H stretching mode and the shoulder at higher frequencies is related to the asymmetric stretching. The calculated scissoring mode shows only 10 cm\textsuperscript{-1} splitting, and the average value is almost exactly equal to the measured one (1420 cm\textsuperscript{-1}). For lower frequencies, we have found some differences between the experimental assignments of the particular modes, for example, in the case of the CH\textsubscript{2} twisting and C–C stretching modes. In addition, our results are consistent with the recently published data by Kostov et al.\textsuperscript{22} for C\textsubscript{2}H\textsubscript{4} on Si(001)–2 × 1 in most of the cases. (Even the isotope ratios are nearly identical.) As an aside, our investigation ended with tailed information about the adsorption of ethylene on the Si(111) surface, we performed atomic-scale STM imaging of the ethylene exposed surface. Figure 3 contains two images that were collected after the Si(111)–2 × 1 surface had been exposed to 250 L of ethylene at room temperature. They were collected with bias voltages that probe filled and empty states (−1.0 and +1.0 V, respectively). Counterintuitively, the chemisorbed molecules do not produce protrusions in the constant-current topographical images. Instead, they produce depressions, closely resembling Si adatom vacancies: when alkenes and small aromatic molecules chemisorb to the Si(111)–7 × 7 surface, the process of covalent bond formation shifts surface electronic states out of the energy range, close to the Fermi level, which is normally accessed by the tunneling electrons.\textsuperscript{9,23} Consequently, the chemisorbed molecules image as depressions and the number of these features scales in a straightforward fashion with the ethylene exposure. For example, we found that the surface shown in Figure 3 had on average one Si adatom vacancy for every 14 7 × 7 unit cells before it was exposed to ethylene. After ethylene exposure, the average number of missing adatoms in each 7 × 7 cell increased to 1.33. In common with many other alkenes and small organic molecules, ethylene shows a preference for the faulted half on the 7 × 7 cell: the average number of missing adatoms after ethylene exposure divides unevenly into 1.17 and 0.15 for the faulted and unfaulted half unit cells, respectively. This uneven occupation of faulted/unfaulted half cells is known to be due to differences in the activation energy barrier for chemisorption from a mobile precursor (physisorbed) state.\textsuperscript{24–26}

To demonstrate that ethylene, like many other molecules, images as a depression, we calculated how an ethylene molecule located in the corner bridging position would appear in an STM image using a fully relaxed Si(111)–7 × 7 surface. For comparison, both the experimental high-resolution STM images (A–D) and the theoretical STM images (E,F) are presented in Figure 4. The Figure also includes cross-sectional cuts of the experimental occupied-state images of the 7 × 7 surface (from Figure 4A) and of an ethylene molecule chemisorbed in the unit cell (from Figure 4C). The arrows on Figure 4A,C indicate the position and direction of the line-profiles. To make the calculations tractable, the STM images were calculated using periodic boundary conditions and a 7 × 7 supercell. To facilitate comparison of the theoretical and experimental images, the simulated 7 × 7 cell was tiled to fill the same area. Consequently, in Figure 4E,F, each 7 × 7 unit cell contains an ethylene molecule located in the corner-bridging site. There is clearly good agreement between the theoretical and experimental images, indicating that ethylene forms a bridge between the corner adatom and the nearest neighbor restatom. The formation of the covalent bond between the Si adatom and the ethylene molecules produces a suppression of the corner adatom. Contrastingly, the intensity of the nearest neighboring (center) adatom increases by ∼75 pm while the next corner adatom in the half unit cell remains largely unperturbed. These observations are in good agreement with the previous STM study,\textsuperscript{9} where it was also reported that adatoms neighboring the ethylene adsorption sites appear brighter in filled-state STM images. Our calculations indicate that the presence of the ethylene molecule induces an upward movement of the nearest neighbor adatoms (Figure 2) and a small downward shift of the dangling bond state. Therefore, the enhanced contrast in the filled state images for the nearest neighbor adatoms is caused by

**Table 2. Theoretical Vibrational Frequencies in Inverse Centimeters for C\textsubscript{2}H\textsubscript{4} on Si(111) in the Adatom–Restatom Configuration**

<table>
<thead>
<tr>
<th>mode</th>
<th>energy (cm\textsuperscript{-1})</th>
<th>isotope ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{Ad}H\textsubscript{2} asymmetric stretch</td>
<td>3064</td>
<td>1.35</td>
</tr>
<tr>
<td>C\textsubscript{Re}H\textsubscript{2} asymmetric stretch</td>
<td>3017</td>
<td>1.35</td>
</tr>
<tr>
<td>C\textsubscript{Ad}H\textsubscript{2} symmetric stretch</td>
<td>3003</td>
<td>1.38</td>
</tr>
<tr>
<td>C\textsubscript{Re}H\textsubscript{2} symmetric stretch</td>
<td>2968</td>
<td>1.38</td>
</tr>
<tr>
<td>C\textsubscript{Ad}H\textsubscript{2} scissors</td>
<td>1424</td>
<td>1.35</td>
</tr>
<tr>
<td>C\textsubscript{Re}H\textsubscript{2} scissors</td>
<td>1412</td>
<td>1.37</td>
</tr>
<tr>
<td>CH\textsubscript{2} twist</td>
<td>1198</td>
<td>1.34</td>
</tr>
<tr>
<td>CH\textsubscript{2} wag</td>
<td>1084</td>
<td>1.40</td>
</tr>
<tr>
<td>CH\textsubscript{2} wag</td>
<td>1150</td>
<td>1.22</td>
</tr>
<tr>
<td>CC stretch</td>
<td>1070</td>
<td>1.49</td>
</tr>
<tr>
<td>CH\textsubscript{2} rocking</td>
<td>842</td>
<td>0.97</td>
</tr>
<tr>
<td>CH\textsubscript{2} rocking</td>
<td>723</td>
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</tr>
<tr>
<td>Si symmetric stretch</td>
<td>580</td>
<td>1.16</td>
</tr>
<tr>
<td>Si asymmetric Stretch</td>
<td>607</td>
<td>1.11</td>
</tr>
<tr>
<td>C\textsubscript{Si} symmetric stretch</td>
<td>533</td>
<td>1.03</td>
</tr>
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</table>
both vertical relaxation and changes in the electronic LDOS. The Si adatoms that form covalent bonds with the ethylene molecule image as depressions because the dangling bond states associated with the adatom/restatom are shifted downward in energy. (See Figure 8.) The impact of molecular adsorption on the surface electronic structures will also be discussed in the section following.

C. Valence Band. Because of the strong lifetime broadening and band dispersion caused mainly by electron phonon interaction near the Fermi level at the Si(111)–7 × 7,27 it is not a simple task to give a precise description for the adsorption effects in this region. The influence of the temperature on the adatom states has been investigated already, and it was found that the adatom peak clearly splits into two components (usually labeled as S1 and S01) that are separated by 0.20 to 0.25 eV: this is the difference in the dangling bond energy between the corner and the center adatoms.28,29 Moreover, a detailed analysis of the LDOS of 7 × 7 in real space made by the combination of phase-sensitive lock-in technique with STM was also in very good agreement with these photoemission findings.30

Figure 5. Angle-resolved valence band spectra taken at the temperature of 110 K from the clean 7 × 7 (top) and after 500 L of adsorption of ethylene (bottom). To obtain better resolution for the surface states, we cooled the sample to the temperature of 110 K during the data acquisition. The two well-known surface peaks, S1 (∼0.12 eV) and S2 (∼0.85 eV), correspond to adatoms and restatoms, respectively,31,32 and at the emission angle of 36°, the S′1 (0.22 eV from S1) surface state is clearly distinguishable. After a 500 L dose of ethylene, the intensity at the Fermi level strongly decreased, and also S2 dropped to approximately half of its initial value, which is in good agreement with previous studies.3,11 Note that the adsorption strongly affects the electron population at the Fermi level; therefore, the position of the restatom peak (fixed at 0.85 eV) should be used as an energy reference for all intermediate coverage. Furthermore, because of the effect of the temperature on the Fermi edge (shift and
broadening), the same fixed position for the restatoms was used at room temperature to get comparable and more accurate results.

Interestingly, the adsorption of ethylene has a less visible effect on the band around $S_1$. The $7 \times 7$ unit cell contains three (or five by separating the faulted and unfaulted halves) types of dangling bonds. In each unit cell, there are 6 dangling-bond electrons associated with the restatoms, 12 with the adatoms, and finally 1 dangling-bond electron with corner holes. We have already seen from the STM results that ethylene adsorbs preferably on the center adatoms. Therefore, the remaining population of electronic states at the Fermi level can be explained with the 2:1 ratio between the intact corner adatoms ($S'_1$) and center adatom $S_1$. In Figure 6, we present the evaluation of electronic structure of characteristic surface states with increasing coverage. The spectra were taken at room temperature after adding $C_2H_4$ sequentially to the surface and are shown for emission angles of 0 and 36°. From 2000 L, there is no more significant contribution from the $S_2$ state. Three adatom–restatom adsorption positions per half $7 \times 7$ unit cell are occupied by ethylene. The remaining dangling bonds located at the position of the intact adatoms are responsible for the nonzero electron density at the Fermi level.

Three sets of spectra recorded at 110 K using a photon energy of 45 eV for emission angles from 0 (up) to 60° (bottom) are shown in Figure 7. The first one on the left side corresponds to the clean Si(111)–$7 \times 7$ reconstructed surface, the center one to 500 L, and the one on the right side to 2000 L adsorption of ethylene. The dashed vertical lines correspond to the positions of the adsorption-induced states as well as to the 7 $\times$ 7 surface states that were discussed above. The adsorption related peaks are at the following positions with respect to the Fermi level: 1.0 ($A_1$), 4.0 ($A_2$), 5.8 ($A_2$), and 7.5 ($A_4$) eV. For comparison, the clean spectra are presented as well. The corresponding calculated projected density of states for the carbon and silicon atoms (restatom, adatom) is shown in Figure 8.

The first state assigned ($A_1$) is the closest one to the Fermi level and is predicted by our theoretical calculations to be a previously unreported resonant state between the upper carbon atom and, in this particular case, the center adatom. (See PDOS of the carbon atom and the adatom in Figure 8.) The position of peak $A_1$ makes its identification difficult because the broad peak, which corresponds to the restatoms ($S_2$) of the clean substrate, makes it impossible to clarify the validity of this prediction at any intermediate coverage. To overcome this problem, one has to saturate all restatoms within the unit cell by increasing the dose of molecules to 2000 L (see coverage dependence in Figure 6). At this coverage, a clear peak appeared at 1 eV ($A_1$) below the Fermi level (0° spectrum of 2000 L in Figure 7). All remaining assignments can be clearly made from the comparison with the clean spectra.

Figure 6. Series of valence band spectra collected from the Si(111)–$7 \times 7$ surface exposed to increasing doses of $C_2H_4$ at RT.

Figure 7. Angle-resolved photoemission spectra for clean Si(111)–$7 \times 7$ (left), after 500 L (center), and after 2000 L adsorption of ethylene. Three sets of spectra shown for emission angles from 0 (top) to 60° (bottom). The spectra were recorded at 110 K using a photon energy of 45 eV. The marked positions correspond to the adsorption-induced states; they are present on the clean spectra as well, and to facilitate comparison, they have also been added to the clean spectra.
surface and from the coverage dependence between 500 and 2000 L.

For differentiation, around peaks A2, A3 and A4 were also found and assigned as adsorption driven states in the work of Widdra et al. for C2H4/Si(001)\(^3\). In their study, they found a quite significant dispersion (\(\sim 0.8\) eV) at the position of A4 (marked as 1b_2g) due to the significant lateral interaction between the molecules and to the formation of adsorbate Bloch states. The reason that \(7 \times 7\) is different is related to the different adsorption geometries and large intermolecular distances, even at the saturation of all adatom–restatom sites. Therefore, in the case of the adatom–restatom model, the lateral interaction between the molecules is not significant, contrary to the densely packed molecular layer on C2H4/Si(001)\(^3\).

Finally, the origin of the molecular states can be understood by using the projected density of states shown in Figure 8. First of all, in good agreement with the experimental data, the adsorption clearly reduces the intensity of the \(S_2\) (restatom state). Moreover, also according to our calculations, the density at the Fermi level is strongly reduced because of the cycloaddition of the \(\pi\) bond to the adatom dangling bonds. Turning to the molecular driven states, A1 has the lowest BE, and according to the calculated intensities it is partially localized with an approximately \(1:1.2\) ratio on the C atom bonded to the adatom and on the bonded adatom itself. Beside the strong substrate contribution in this region, the delocalization makes even more difficult the identification in ARUPS. The formation of A2 is mainly due to changes in the density of states of the restatoms. Both experimental and theoretical data show modification of the intensity of bands between 2 and 5 eV, but there is no strong carbon state in this region. (See C PDOS in Figure 8.) Therefore, it can be concluded that in this regime the adsorption-induced surface state modifications (shifts) are dominant. The last two, A3 and A4, are strongly localized on the C atoms. Beside both states being strongly localized, A3 is less pronounced in the measured spectrum because of the intense surface contribution on the higher binding side. As a result, it gives only a shoulder in experiment.

In summary, our study has produced a better understanding of the adsorption-induced electronic effects. Specifically, A1 (instead of A3) is related to the donation of electrons to the lowest unoccupied state of the free ethylene molecule, LUMO (1b_3g). A3 originates from the interaction with highest occupied molecular orbital of the ethylene molecule, HOMO (1b_2u), and A4 is derived from the interaction with the lower lying 1b_2g state; in the case of the Si(111)–\(7 \times 7\) substrate, both remain strongly localized states on the C atoms.

D. Core Levels. A typical C 1s spectrum with fitted curves is presented in Figure 9. A constant Lorentzian width of 0.2 eV and Gaussian widths of 0.58 ± 0.1 eV were used for the Voigt fitting functions, and the energies of the presented peaks are given relative to the main component at the position of 283.95 eV.

![Figure 8](image82x566.png)  
**Figure 8.** Calculated projected density of states for the carbon and silicon atoms. The molecule bridged one of the center adatom and restatom positions. (See Figure 1.)

![Figure 9](image339x378.png)  
**Figure 9.** C 1s spectrum with curve fitting analysis obtained at room temperature after a 500 L dose of ethylene. The energies of the presented peaks are relative to the main component at the position of 283.95 eV.
in this work, and it needs further SXPS investigations. Lastly, a slight increase in the noise level appears on the low binding side of the main peak, suggesting that a very small portion of the molecules might undergo dissociative adsorption.

Because of the very complex nature of the Si 2p spectrum and the relatively low surface coverage, even at the saturation of all adatom—restatom pairs (0.2 ML), it is nearly impossible to give a correct description of the adsorption-induced changes in the Si 2p core levels with only nonlinear curve fitting analysis. To make it much easier to follow the adsorption-induced changes, we subtracted the clean spectrum from spectra taken after 250, 500, 1000, and 2000 L of adsorption of C\textsubscript{2}H\textsubscript{4} and presented at the top of Figure 10 with the reference spectrum of clean Si(111)–7 × 7 and its known fitted curves at the bottom. Usually the curve fitting analysis of the clean 7 × 7 results in a bulk (B) and five surface components (C\textsubscript{1}–C\textsubscript{5}).28 In our case, it was necessary to use two components (C\textsubscript{2} and C\textsubscript{5}) for the tail at the low binding side, similarly to the fitting result presented by Le Lay et al.30 Among all major studies, there is a good agreement about the assignment of C\textsubscript{4} (to restatoms) and C\textsubscript{5} (to adatoms), which are in main interest.28,37 From the difference spectra, it is clear that the C\textsubscript{2} state is quenched with the adsorption, and after a dose of 2000 L, it has almost completely vanished and is in good agreement with our previous assumption for the saturation coverage.

Beside the continuous drop of the restatom peak, a new peak (C\textsubscript{Si–C}) starts to appear, which is separated by 0.44 eV from the bulk component, and as the coverage increases, also the 2p\textsubscript{1/2} part is evident. We have to note here that none of the previous Si 2p core level studies reported any peak assigned to the Si—C bond in the Si 2p band for ethylene on Si(111)–7 × 7.5,11,12 Moreover, in the work of Kim et al., a slight shift was present for the surface peak related to adatoms (C\textsubscript{1}) in their fitting analysis, and the position of this component moved to 0.51 eV BE with respect to the bulk component.12 Because of the relatively small energy difference between C\textsubscript{1} and C\textsubscript{Si–C}, the new 0.51 eV (fitted) position of the C\textsubscript{1} can be obtained with a doublet filling the two components in the middle with slightly higher Gaussian width. This observation can evidently represent the possible arbitrariness of the fitting-based analyses for this system with moderately low-energy resolution. From our point of view, the change in this energy region is clearly related to the formation of the Si—C bond. This interpretation can be made based on the fact that the C\textsubscript{Si–C} peak grows continuously in the same position (no band bending) from very small coverage until the saturation of all adatom—restatom positions, and we observed no adsorption-induced reconstruction with STM. For alkyl-terminated Si(111) surfaces, the chemical shift of the Si—C bond was found to be 0.25 to 0.30 eV.35,38,39 Besides having in both situations an sp\textsuperscript{3} hybridized C atom attached to the silicon substrate, the load charge differs slightly, which leads to a variation of the chemical shift. Another correlation can be made with Si(001) supporting C\textsubscript{2}H\textsubscript{4}, where the surface core level shift is only 0.18 eV from the bulk Si 2p,6 representing also a difference in the electronic structure between the di-\textalpha bonded ethylene and adatom—restatom bonded on Si(111)–7 × 7.

Overall, besides the decreased intensity of the bulk component due to the formation of the molecular layer, only minor changes occur in the remaining surface components. A slight intensity drop can be noted from the negative slope at the position of C\textsubscript{5}, but this drop gets less pronounced at saturation because of the increased C\textsubscript{Si–C} component nearby. The adsorption seems to increase the intensity of the C\textsubscript{5} component, which is assigned to the contribution from dimer/second layer atoms, and the increased intensity can be related to slight changes in the position of the restatoms and adatoms upon adsorption. In our coverage range, there is no clear evidence of any significant change of the energy of the C\textsubscript{1} component.

**IV. CONCLUSIONS**

In summary, we have investigated the reliability of the adatom—restatom bridging scheme for ethylene on Si(111)–7 × 7. The calculated vibrational frequencies for the molecule bridging an adatom—restatom pair are in excellent agreement with the previously measured EELS spectra. Additionally, we clearly assigned individual modes to harmonic frequencies. Our STM measurements were in excellent agreement with previous findings in the sense that the reaction leads to a decrease in the number of observable adatoms on the surface.9 With our high-resolution images, it is clear that the restatom neighbors must also be directly involved in the reaction, and the simulated STM images suggest exactly the same behavior. On one hand, in the valence band PES spectra we have also seen quenching of the corresponding surface states in good agreement with previous studies.5 On the other hand, from low-temperature, angle-resolved photoemission spectra, it is clear that the S\textsubscript{1} surface components quench much faster than the S\textsuperscript{1} component (corner adatoms), especially at low coverage. The remaining electronic states close to the Fermi level originate from unsaturated adatoms. Although there is no significant energy difference between the adsorption sites, the center adatoms preferentially react during the adsorption process because the population of the central adatom—restatom adsorption configuration is two times higher than that.
of the corner adatom–restatom configuration. Furthermore, there is clearly a preference for the faulted half cell despite the fact that there is no difference in BE between the faulted and unfaulted half cells. This phenomenon is not uncommon and is normally explained in terms of different site-dependent activation energy barriers for chemisorption from the mobile precursor state.24–26

Additionally, our core level study has shown the existence of the peak clearly correlated with the formation of the Si–C bond, and we have seen good agreement for the C–H stretching loss feature in C 1s core level with the possibility of the existence of higher harmonic modes.

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