Adsorption configurations and thermal chemistry of acetylene on the Ge(100) surface

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The adsorption structures and thermal desorption behavior of C$_2$H$_2$ on Ge(100) were studied in ultrahigh vacuum by scanning tunneling microscopy (STM) and temperature programmed desorption (TPD). The STM investigation revealed that, at low coverage, C$_2$H$_2$ initially adsorbs onto the Ge(100) surface with two types of configurations: (i) a di-$\sigma$ configuration on top of a single Ge–Ge dimer (on-top) and (ii) a tetra-$\sigma$ configuration parallel to the dimer axes, bridging two neighboring Ge dimers ($p$-bridge). TPD measurements show that chemisorbed C$_2$H$_2$ desorbs from Ge(100) nondissociatively with two different desorption features, denoted as $\alpha$ (520 K) and $\beta$ (560 K). In addition, it was found that the desorption of C$_2$H$_2$ follows first order kinetics for both states and that the desorption energies of the $\alpha$ (520 K) and $\beta$ (560 K) states are 1.3 and 1.4 eV, respectively. STM studies of the adsorption of C$_2$H$_2$ at various Ge surface temperatures indicate that the $\alpha$ and $\beta$ features correspond to the on-top and $p$-bridge configurations, respectively. © 2002 American Institute of Physics. [DOI: 10.1063/1.1521162]

I. INTRODUCTION

The adsorption, reaction, and desorption of organic molecules on semiconductor surfaces have been investigated in numerous studies aimed at understanding the microscopic details of covalently attached molecule-semiconductor systems. The chemistry of these systems determines the fundamental and technological aspects that must be taken into account when developing molecular electronics and optoelectronic devices. Therefore, the organic functionalization of semiconductors, which imparts specific molecular properties to the semiconductor device, has been a growing field in the development of new molecule-based devices. This hybrid approach, combining organic molecules with semiconductor materials, provides the development of new semiconductor device by the incorporation of electronic property, optical response, chemical functionalization, and biological activity.

Over the last few decades, numerous experimental1–6 and theoretical7–10 studies have investigated the interaction of organic molecules on the Si(100)–2×1 surface, but only a few have considered the Ge(100) surface. Recently, the interaction of organic molecules on Ge(100) has received attention due to the different reactivities of molecules on a Ge surface compared to a Si surface, as well as to the application of GeSi alloys in optoelectronic devices.11–14 The Si(100) and Ge(100) surfaces have very similar atomic structures, but the slight differences in their lattice constants and electronic structures cause organic molecules to have different reactivities on the two surfaces.

On a semiconductor surface, the majority of reactions with organic molecules occur at or near dangling bonds of the reconstructed surface. The dangling bonds of Si(100) and Ge(100) surfaces are arranged in surface dimers which consist of a strong $\sigma$ bond and a weak $\pi$ bond. The surface dimer $\pi$ bond induces a structure similar to the $\pi$ bond of unsaturated hydrocarbons. The addition of a carbon $\pi$ bond to a surface dimer leads to a [2+2] cycloaddition reaction,15–20 which is symmetry forbidden in organic chemistry.21 Furthermore, both Si(100)–2×115,22–24 and Ge(100)–2×113,14 surfaces participate in a [4+2] cycloaddition reaction, widely known as a Diels–Alder reaction, where the $\pi$ bond of the surface dimer acts as a dienophile in a reaction with a conjugated diene. Recently, a retro-Diels–Alder reaction between conjugated butadiene and a Ge(100) surface, leading to the evolution of the original butadiene molecules, has been observed.13 This behavior of the Ge surface differs from that of Si(100)–2×1, on which the butadienes decompose. These results provide the motivation for further studies to understand the reactivity of hydrocarbons on the Ge(100) surface.

The interaction of unsaturated hydrocarbons with the Si(100) surface has been the subject of considerable interest in recent years. In particular, chemical reactions of small unsaturated hydrocarbon molecules such as acetylene25–30 or ethylene31–33 with Si(100) have been investigated to understand the fundamental reaction mechanism of organic molecule-semiconductor systems. Through a study of the initial adsorption of acetylene on Si(100), it was found that acetylene adsors via a mobile precursor state with an initial probability of unity at low temperatures.34 Furthermore, results obtained using scanning tunneling microscopy (STM) as well as low-energy electron diffraction (LEED) showed that adsorption of acetylene occurs at the dimer sites without breaking (2×1) reconstruction.27,35,36 Although the system of acetylene on the Si(100)–2×1 surface has been extensively studied, no experimental results have been reported...
for the behavior of acetylene on the Ge(100) – 2 × 1 surface.

With regard to the adsorption geometries of C₂H₂ on Group IV(100) surfaces, four possible configurations should be considered as shown in Fig. 1: two di-σ configurations in which C₂H₂ resides on top of a dimer (on-top) or bridges two adjacent dimers (end-bridge) and two tetra-σ configurations in which the molecular axis of C₂H₂ is parallel (p-bridge) or perpendicular (r-bridge) to the dimer axis. Recently, on-top and end-bridge di-σ configurations have been proposed as the adsorption geometry of C₂H₂ on Si(100) on the basis of STM measurements[37] and theoretical calculations;[38] however, this is still a subject of debate.

In this paper, we investigate the initial adsorption geometries of C₂H₂ on the Ge(100) – 2 × 1 surface using STM measurements. In addition, the energetics and mechanism for thermal desorption of C₂H₂ from Ge(100) are studied by temperature programmed desorption (TPD) and compared with the results for the C₂H₂/Si(100) system. Furthermore, the thermal stability of C₂H₂ adsorption structures is studied by directly counting the number of each type of adsorption configuration in STM images taken at different surface temperatures.

II. EXPERIMENTAL DETAILS

All experiments were carried out in two separate ultra-high vacuum (UHV) chambers with base pressures of less than 1 × 10⁻¹¹ Torr. One UHV chamber was used to study the thermal desorption. This chamber was equipped with a differentially pumped quadrupole mass spectrometer (QMS), an Auger electron spectrometer (AES), LEED optics, an ion sputter gun for sample cleaning, and a doser with a hexagonal array of seven parallel capillaries. The other UHV chamber was equipped with a scanning tunneling microscope to investigate the adsorption structure of acetylene molecules. The sample was introduced into the STM chamber through a load-lock transfer system.

The Ge(100) crystal (0.1–0.39 Ω cm, p-type, B-doped) was cut to a size of 3 × 15 mm² and mounted between tantalum foil clips for resistive heating. The sample was cleaned by Ar⁺ ion sputtering (2.5 μA of 1.0 keV) at the sample temperature, Tₜ = 700 K, for 30 min, followed by thermal annealing (heating rate 5.0 K/s and cooling rate 1.0 K/s) at Tₜ = 900 K for 10 min. After several cleaning cycles, surface cleanliness was confirmed by AES, which showed no detectable surface impurities. The (2 × 1) structure of the crystal was confirmed by LEED and STM.

Acetylene gas was purchased from Matheson 99.6% pure and further purified using the method described previously[35] before being exposed onto the crystal. The purity of the acetylene was checked by gas chromatography and further verified in situ by mass spectrometry. For all experiments, purified acetylene was exposed onto Ge(100) – 2 × 1 at 298 K through a variable leak valve. The pressure during acetylene exposure was measured using the uncorrected ion gauge reading. A direct doser with a seven-capillary array was used to reduce the chamber background pressure and interactions with the equipment.

A differentially pumped quadrupole mass spectrometer (UTI–100C) was used to study the thermal desorption. The thermal desorption experiments were performed by subjecting the sample exposed to acetylene at 300 K to an almost linear heating rate of 2 K/s over the temperature range 300–900 K. The acetylene-exposed crystal surface was placed approximately 2 mm from the 3 mm aperture of the QMS shield. Sample temperature was monitored by a chromel–alumel (type-K) thermocouple glued to the back of the sample with a high-temperature ceramic adhesive and calibrated by measuring the desorption temperature of hydrogen from monohydride-adsorbed Ge(100) – 2 × 1. The possibility of surface reaction such as the oligomerization and dissociation of acetylene was checked by a thorough search of the desorbing species between 2 and 80 amu. During the thermal desorption experiments, mass peaks recorded were C₂H₂ +, C₂H⁺, CH⁺, and H₂⁺. All STM measurements were performed on an OMICRON VT–STM at room temperature using electrochemically etched W-tips with subsequent annealing in a vacuum. STM images shown here were taken at a constant current mode with a tunneling current of 100 pA. For effective imaging of molecules, sample bias voltages of −1.0 to −1.6 V were employed.

III. RESULTS AND DISCUSSION

A. Initial adsorption geometries and voltage-dependent STM images

Figure 2(a) shows a filled-state STM image (Vₛ = −1.5 V, Iₜ = 100 pA) taken after adsorption of 0.04 ML C₂H₂ onto a clean Ge(100) – 2 × 1 surface. Unreacted Ge dimers are imaged as bean-shaped protrusions for the symmetric dimers and zigzag-shape chains for the buckled dimers. In Fig. 2(a), two distinctive features of the reacted dimer sites can be identified, denoted as A and B. Feature A is imaged as a slightly darker and narrower spot in the dimer row direction. The cross-section line profile of feature A [Fig. 2(b)] shows a single maximum in the position of a
single Ge dimer. A very similar feature has been previously found in STM images of C$_2$H$_2$ adsorption on Si(100), and was attributed to the on-top (di-$\pi$) configuration. Thus, feature A is attributed to the di-$\pi$ structure in which C$_2$H$_2$ resides parallel to and on top of the Ge–Ge dimer.

On the other hand, feature B is located between two Ge dimers along the direction of the dimer axis. This STM image indicates that the C$_2$H$_2$ molecule corresponding to feature B interacts with the two Ge dimers. Three configurations could potentially be responsible for feature B: two tetra-$\sigma$ configurations and a paired end-bridge configuration interacting with four Ge atoms as shown in Fig. 1. The tetra-$\sigma$ structure is considered simply in order to explain the interaction with four Ge atoms. The two possible configurations with a tetra-$\sigma$ bond structure are the $p$-bridge [Fig. 1(c)] and $r$-bridge [Fig. 1(d)] configurations oriented parallel and per-
increasing dose of \( \text{C}_2\text{H}_2 \); however, this is a minor factor compared with the number of chemisorbed \( \text{C}_2\text{H}_2 \) molecules. Therefore, the bright spots should be disregarded.

The results of a recent STM experiment\(^{17}\) and theoretical calculation\(^{38}\) on the system of \( \text{C}_2\text{H}_2 \) on \( \text{Si}(100) \) led to the reassigning of a feature that resembles feature \( B \) to a paired end-bridge configuration, which is a pair of \( \text{C}_2\text{H}_2 \) molecules bound across two neighboring dimers in the same dimer row. Such a paired end-bridge configuration could also potentially give rise to feature \( B \) in the system of \( \text{C}_2\text{H}_2 \) on \( \text{Ge}(100) \). However, the single end-bridge configuration, which is the initial state for the paired end-bridge configuration in the case of \( \text{C}_2\text{H}_2 \) on \( \text{Si}(100) \), is not observed in the STM images at very low exposure for the Ge system. Therefore, we conclude that \( \text{C}_2\text{H}_2 \) molecules adsorb onto the \( \text{Ge}(100) \) surface in two distinctive configurations: on-top (di-\( \sigma \)) and \( p \)-bridge (tetra-\( \sigma \)). We note that bright spots on the STM images are considered to be impurities that remain in the \( \text{C}_2\text{H}_2 \) gas after cleaning. The number of bright spots increases as with increasing dose of \( \text{C}_2\text{H}_2 \); however, this is a minor factor compared with the number of chemisorbed \( \text{C}_2\text{H}_2 \) molecules. Therefore, the bright spots should be disregarded.

Figure 3 shows filled-state STM images (\( V_s = -1.5 \text{ V}, I_T = 100 \text{ pA} \)) as a function of \( \text{C}_2\text{H}_2 \) coverage. The series of STM images was recorded during real-time dosing of \( \text{C}_2\text{H}_2 \) onto the \( \text{Ge}(100) \) surface. Four STM images taken of the same surface region (22×22 nm\(^2 \)) show two configurations, as shown in Fig. 2. The STM image at 0.22 ML of \( \text{C}_2\text{H}_2 \) contains some white spots, which are possibly due to the deposition of impurities from a contaminated tip and noise caused by the real-time scanning. In addition, bright spots on top of either side of buckled dimers are attributed to \( \text{H} \) adsorption, which are marked with arrows in Fig. 3(a). For the study of atomic hydrogen adsorption both on \( \text{Si}(100)^{39} \) and \( \text{Ge}(100)^{40} \) at low exposures, hydrogen atoms reside singly on top of the dimerized Si and Ge atoms, and bare Si and Ge atoms without \( \text{H} \) adsorption are imaged brightly. The STM images are the same as those of bright spots in Fig. 3(a). Therefore, we assume that the bright images marked with arrows are attributed to the atomic hydrogen originated mostly from partial decomposition of exposed \( \text{C}_2\text{H}_2 \) molecules. As \( \text{C}_2\text{H}_2 \) coverage increases, the buckling of the unreacted Ge dimers disappears due to an elastic strain field induced by \( \text{C}_2\text{H}_2 \)-filled dimers, which constrain neighboring bare Ge dimer bonds.

Figure 4 shows the dependence of the population of each configuration on the \( \text{C}_2\text{H}_2 \) coverage, which was measured by directly counting the number of each configuration in the STM images. The numbers of each configuration counted from the STM images taken of three different surface regions were averaged and normalized by the coverage of adsorbed \( \text{C}_2\text{H}_2 \) molecules. The STM images recorded for coverages higher than 0.22 ML were not used for counting since the poor tip condition at high exposures of \( \text{C}_2\text{H}_2 \) made it difficult to distinguish between unreacted dimer and the on-top configuration. To confirm the stability of each configuration, the transition between the two configurations was checked by monitoring the same area of the STM images as a function of \( \text{C}_2\text{H}_2 \) coverage. No conversion between the configurations was observed at room temperature, suggesting that chemisorbed \( \text{C}_2\text{H}_2 \) does not diffuse on the \( \text{Ge}(100) \) surface. Figure 4 shows that the population of each configuration increases linearly with increasing coverage and the \( p \)-bridge configuration is normalized by the coverage of adsorbed \( \text{C}_2\text{H}_2 \).
Adsorption of acetylene on the Ge(100) surface

evaluate the preference of C2H2 adsorption configurations on studied. Further theoretical study of this system is needed to C2H2 on the Ge ever, this surface state is removed by the chemisorption of like the on-top C2H2 molecules, the resonant tunneling through the surface state and results in between ~

Figure 5 shows STM images of C2H2 adsorbed on the Ge(100) surface recorded at different sample bias voltages. Two types of C2H2 adsorption features are observed in these images, denoted as circles (on-top) and squares (p-bridge). The insets in Fig. 5 show enlarged images of the p-bridge (left) and on-top (right) configurations. As shown in Fig. 5, the images of the on-top configuration, but not those of the p-bridge configuration, show a strong dependence on the bias voltage. At the bias of −1.8 V, both configurations appear as protrusions, brighter for the on-top configuration, since the tunneling current through molecules is enhanced. It is difficult to distinguish the on-top configuration from the bare Ge dimer at this bias. However, at lower values of the bias, the molecules are imaged darker and narrower due to the reduced tunneling current. At biases of −1.4 and −1.0 V, molecules in the on-top configuration are imaged as depressions similar to a missing dimer because there are neither accessible molecular states nor surface states of the Ge dimer π bond. The clean Ge surface is imaged by means of the surface state of the dimer π bond at sample biases between −1.0 and −1.3 eV below the Fermi level.41,42 However, this surface state is removed by the chemisorption of C2H2 on the Ge(100) surface, which leads to an absence of resonant tunneling through the surface state and results in depressions in the STM image at the chemisorbed sites. Unlike the on-top C2H2 molecules, the p-bridged C2H2 mol-
ecules are imaged as protrusions in the range of sample biases used for effective imaging. However, even for the p-bridge configuration, the C2H2 molecules are imaged darker and narrower at low biases. The voltage-dependent STM images give information about the position of the highest occupied surface states. For the on-top configuration, the highest occupied molecular orbital (HOMO) state induced by the chemisorption of C2H2 is below the energy level corresponding to the sample bias of −1.4 V; thus the C2H2 molecule is imaged as a depression at this sample bias. For C2H2 molecules in the p-bridge configuration, on the other hand, it is noted that the highest occupied surface state is localized closer to the Fermi level.

B. Thermal desorption study of C2H2 molecules chemisorbed on the Ge(100) surface

TPD experiments over the mass range 2–80 amu were performed to investigate the thermal behavior of C2H2 on Ge(100). TPD spectra of C2H2 (m/e = 26) taken at different initial coverages are presented in Fig. 6(a). The spectra show distinctive desorption features at 520 K (α state) and 560 K (β state). These two features are observed even at very low coverage, which indicates that two types of adsorption sites are present at the initial stage of adsorption. The adsorption configurations corresponding to these two TPD peaks will be discussed in detail in the following section. As the C2H2 exposure increases, the desorption maxima of the β state remain constant at 560 K while the α state shifts to lower temperature. This shift of the peak maximum to lower temperature is attributed to the repulsive interaction between chemisorbed C2H2 molecules. Figure 6(b) shows the integrated TPD peak areas for the two desorption states plotted as a function of exposure (solid curve, α state; dotted curve, β state). Both states reach saturation at 100 L and the β state is dominant at all coverages. The TPD peak areas cited in Fig. 6(b) are normalized by the peak area obtained at an exposure of 100 L.

In addition to the parent mass, C2H2+ (m/e = 26), other fragments including C+ , CH+, C2+, and C2H+ were also monitored during the TPD experiment. The ratio of these mass intensities was in good agreement with that reported previously for the fragmentation pattern of acetylene.43 Therefore, the detected species are attributed to the fragments of C2H2 molecules cracked by the QMS ionizer. These results imply that C2H2 desorbs nondissociatively from the Ge(100) surface. This behavior is distinctly different from the behavior reported for the C2H2/Si(100) system, in which more than 95% of chemisorbed C2H2 was found to dissociate on the Si(100) surface and then the resulting surface carbon diffused into the bulk of the silicon crystal on the time scale of seconds above 800 K.44 The difference in the thermal behavior of the Ge and Si systems is attributed to the difference in the bond strength between adsorbate and substrate, Si–C and Ge–C, which is revealed by the different desorption temperatures observed for the two systems. The desorption temperature of C2H2 from the Ge(100) surface ranges from 510 to 580 K, whereas the intact desorption of C2H2 molecules from Si(100) along the minor pathway (5%) occurs at close to 800 K with an activation energy of 2.0

FIG. 5. Bias-dependent STM images taken of the same area (23 × 23 nm2) after C2H2 adsorption to 0.1 ML; (circle) on-top configuration, (square) p-bridge configuration. The sample bias voltages are (a) −1.8 V, (b) −1.6 V, (c) −1.4 V, and (d) −1.0 V. Insets show enlarged images for the p-bridge (left) and on-top (right) configurations.
Desorption temperatures of molecules on surfaces depend on desorption activation energies. We determined the desorption energy of C\textsubscript{2}H\textsubscript{2} from Ge(100) using the method of Parker, Jones, and Koel (PJK).\textsuperscript{45} In this method, the desorption order (n) and energy are determined by plotting [ln(rate) – n ln(θ)] versus 1/T at the limit of zero coverage, in which rate, θ, and T represent the desorption rate, C\textsubscript{2}H\textsubscript{2} coverage, and Ge surface temperature, respectively. Pre-exponential factors, ν(θ), can be also determined from the intercept of the plotted straight line. In addition, the method is applicable in the limit of zero since severe deviations occur at higher coverages.

Quantitative analysis of the TPD spectrum of C\textsubscript{2}H\textsubscript{2} on Ge(100) reveals that the desorption follows first-order kinetics for both desorption states (α and β) and the desorption energies for the two states are 1.3 and 1.4 eV, respectively. These values are about 0.6 eV lower than those reported for the C\textsubscript{2}H\textsubscript{2}/Si(100) system.\textsuperscript{34} In addition, the pre-exponential factors are estimated to \(10^{13.4±0.5}\) s\(^{-1}\) (α state) and \(10^{13.6±0.6}\) s\(^{-1}\) (β state).

In Table I, the desorption temperatures and energies with pre-exponential factors for four different systems—C\textsubscript{2}H\textsubscript{2}/Si, C\textsubscript{2}H\textsubscript{4}/Si, C\textsubscript{2}H\textsubscript{2}/Ge, and C\textsubscript{2}H\textsubscript{4}/Ge—are summarized. For both the Si and Ge surfaces, the desorption energy of C\textsubscript{2}H\textsubscript{2} is about 0.2 eV larger than that of C\textsubscript{2}H\textsubscript{4}. For ethylene–Ge(100), the C atoms rehybridize from sp\(^2\) to sp\(^3\) as they become forming σ bonds with the Ge dimer dangling bonds. On the other hand, acetylene is di-σ bonded to the Ge dangling bonds with the C–C rehybridization state of sp\(^2\) for the on-top configurations. As the s character of the orbitals binding carbon to Ge atoms increases, the electrons in those orbitals are closer to the carbon nucleus, and the pair of electrons is more strongly held. Therefore, it requires more energy for dissociation of the C–Ge bond in the case of C\textsubscript{2}H\textsubscript{2} on Ge(100). In the case of the p-bridge configurations for the C\textsubscript{2}H\textsubscript{2}/Ge(100) system, the desorption activation energy of C\textsubscript{2}H\textsubscript{2} is larger than that of C\textsubscript{2}H\textsubscript{4} because two pi orbitals of C\textsubscript{2}H\textsubscript{2} are involved in covalent bonding with the Ge dangling bonds.

Additionally, the Si–C interaction between the dangling bond of silicon and the carbon of C\textsubscript{2}H\textsubscript{2} or C\textsubscript{2}H\textsubscript{4} is approximately 0.6–0.7 eV stronger than the Ge–C interaction. Similar differences in the thermal behavior of hydrocarbons on Si and Ge surfaces have been observed in studies of 1,3-butadiene on the two surfaces.\textsuperscript{13,22} These studies showed that the 1,3-butadiene molecule reacted with the dimers of both Si(100)\textsuperscript{22} and Ge(100)\textsuperscript{13} surfaces to form products of the [4+2] or Diels–Alder reaction. On increasing the substrate temperature, the Diels–Alder product was found to decompose on the Si(100) surface,\textsuperscript{22,23} whereas it desorbed nondissociatively from the Ge surface via a retro Diels–Alder reaction.\textsuperscript{13} As for the case of C\textsubscript{2}H\textsubscript{2}, the difference in the reactions on the Si and Ge surfaces can be attributed to the

![Image](https://example.com/image1.png)

**FIG. 6.** (a) Thermal desorption spectra for different initial C\textsubscript{2}H\textsubscript{2} (m/e = 26) exposures (0.5, 3, 5, 10, 30, 50, 100, and 250 L) on the Ge(100) surface adsorbed at room temperature and (b) relative probabilities for different C\textsubscript{2}H\textsubscript{2} desorption features.

<table>
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<th>Systems</th>
<th>Desorption energy (eV)</th>
<th>Pre-exponential factor (s(^{-1}))</th>
<th>Desorption temperature (K)</th>
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<tr>
<td>C\textsubscript{2}H\textsubscript{2}/Si(100)\textsuperscript{a}</td>
<td>2.0 (10^{3.3±1})</td>
<td>800</td>
<td></td>
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<tr>
<td>C\textsubscript{2}H\textsubscript{2}/Ge(100)</td>
<td>1.3 (α), 1.4 (β) (10^{3.4±0.5}) (α), (10^{13.2±0.6}) (β)</td>
<td>520 (α), 560 (β)</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{4}/Si(100)\textsuperscript{b}</td>
<td>1.8 (10^{14.4})</td>
<td>620</td>
<td></td>
</tr>
<tr>
<td>C\textsubscript{2}H\textsubscript{4}/Ge(100)\textsuperscript{b}</td>
<td>1.1 (10^{13.3})</td>
<td>400</td>
<td></td>
</tr>
</tbody>
</table>

\(^a_{\text{Reference 34.}}\)

\(^b_{\text{Reference 44.}}\)

| TABLE I. Desorption energies and temperatures with pre-exponential factors of C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} chemisorbed on Si(100)–2 × 1 and Ge(100)–2 × 1. |
Two additional features indicated by arrows in Fig. 7(c), which differ from the on-top and p-bridge configurations, are observed. These features, which were mentioned above in the discussion of the STM images in Fig. 3, are a bright spot on top of either side of buckled dimers and a feature that resembles a missing dimer defect. We propose that the former feature is attributed to hydrogen atoms adsorbed on one of the dangling bonds in the Ge dimer and the latter monohydride species. These hydrogen atoms are considered to originate from the partial decomposition of C₂H₂ molecules (<4%). Another product of the decomposition of C₂H₂ gas, carbon, is imaged as bright spots. After annealing at 650 K, a temperature well above the desorption temperature of monohydride species chemisorbed on Ge(100), the STM image in Fig. 7(d) shows that both adsorbed C₂H₂ molecules and monohydride species desorb completely leaving a clean Ge(100) surface.

**IV. CONCLUSIONS**

We have investigated the adsorption geometries and thermal desorption behavior of C₂H₂ on the Ge(100) surface. On the basis of measured STM images, we conclude that acetylene chemisorbs on the Ge(100) surface in two distinctive configurations (the so-called on-top di-σ and p-bridge tetra-σ configurations) even at initial coverage. By direct inspection of the STM images, we showed that the p-bridge configuration dominates at all C₂H₂ coverages and that chemisorbed C₂H₂ does not diffuse on the Ge(100) surface at room temperature. The on-top configuration, but not the p-bridge configuration, shows a strong dependence on the bias voltage. Below a sample bias of −1.4 V, the on-top di-σ molecules are imaged as depressions, whereas the p-bridged C₂H₂ molecules are imaged as protrusions. This voltage-dependent STM result indicates that the highest occupied surface state of the p-bridge configuration is localized closer to the Fermi level than that of the on-top configuration. The thermal desorption spectra show that most C₂H₂ molecules desorb from Ge(100) nondissociatively with two different desorption features, located at 520 K (α) and 560 K (β), which are attributed to the on-top di-σ and p-bridge tetra-σ configurations, respectively. The ratio of on-top configurations to p-bridge C₂H₂ configurations at saturation coverage is 0.38:0.62. The desorption peak for the on-top configuration shifts to lower temperature with increasing C₂H₂ coverage. We note that at higher C₂H₂ coverage, the on-top di-σ configuration is more affected by the repulsive interaction between chemisorbed C₂H₂ molecules. Quantitative analysis of the TPD spectra indicated that the desorption of C₂H₂ follows first order kinetics for both states and the desorption energies for the α (520 K) and β (560 K) states are 1.3 and 1.4 eV, respectively. In addition, the pre-exponential factors are estimated to 10^{13.4±0.5} s^{-1} (α state) and 10^{13.6±0.6} s^{-1} (β state). The thermal behavior of C₂H₂ on Ge(100) differed from that reported for C₂H₂ on Si(100), in which more than 95% of chemisorbed C₂H₂ was found to dissociate on the Si(100) surface; this difference was attributed to the difference in the strength of the Si–C and Ge–C bonds (the Ge–C interaction is approximately 0.6–0.7 eV weaker than the Si–C interaction).

**C. Thermal stability of C₂H₂ chemisorbed on the Ge(100) surface**

For this study, a clean Ge(100)–2×1 surface was exposed to 0.2 ML of C₂H₂ at room temperature and then the system was annealed at various surface temperatures. The surface was cooled down to room temperature for STM imaging. Figure 7 shows the filled-state STM images of C₂H₂ on Ge(100) obtained after annealing at various temperatures. Annealing at temperatures above the desorption temperature leads to molecular desorption of C₂H₂ molecules, resulting in the disclosure of the bare Ge dimers on the surface. The ratio of on-top (circle) to p-bridge (square) configurations on the unannealed surface [Fig. 7(a)] is approximately 35:65. As shown in Fig. 7(b), the STM image taken after annealing at 560 K indicates that the on-top configuration is considerably reduced, and the dominance of the p-bridge structure is increased to approximately greater than 80%. After annealing at 580 K, only p-bridge configurations are present as shown in Fig. 7(c). This annealing temperature coincides with the temperature at which the α state desorbed completely in the TPD spectra shown in Fig. 6(a). Therefore, the α and β states observed in the TPD spectra are attributed to the on-top (di-σ) and p-bridge configurations (tetra-σ), respectively. Furthermore, the desorption temperature of each configuration monitored in the STM experiments is consistent with that of the TPD measurement.
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43. NIST Mass Spectrometry Data Center; http://webbook.nist.gov/chemistry/