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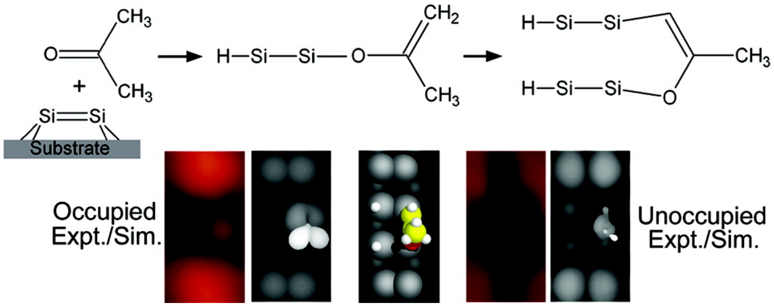

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Organic Bonding to Silicon via a Carbonyl Group: New Insights from Atomic-Scale Images

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Abstract: The ability to covalently attach organic molecules to semiconductor surfaces in a controllable and selective manner is currently receiving much attention due to the potential for creating hybrid silicon−organic molecular-electronic devices. Here we use scanning tunneling microscopy (STM) and density functional theory calculations to study the adsorption of a simple ketone [acetone; $(CH_3)_2CO$] to the silicon (001) surface. We show both bias and time-dependent STM images and their agreement with total energy DFT calculations, simulated STM images, and published spectroscopic data. We investigate the stability of the resulting adsorbate structures with respect to temperature and applied STM tip bias and current. We demonstrate the ability to convert from the kinetically favored single-dimer α-H cleavage adsorbate structure to thermodynamically favored bridge-bonded adsorbate structures. This can be performed for the entire surface using a thermal anneal or, for individual molecules, using the highly confined electron beam of the STM tip. We propose the use of the carbonyl functional group to tether organic molecules to silicon may lead to increased stability of the adsorbates with respect to current−voltage characterization. This has important implications for the creation of robust single-molecule devices.

1. Introduction

There are currently several proposals to create molecular electronic devices[1,2] using individual organic molecules adsorbed to semiconductor surfaces.[3−5] This endeavor requires a detailed understanding of the nature of the organic/semiconductor interface and the ability to produce adsorbates that are stable during their characterization by current−voltage ($I-V$) measurements.[4,6] Over the past decade, a variety of organic molecules have been investigated on semiconductor surfaces. However, as yet there have been extremely few reports utilizing scanning tunneling microscopy (STM) to produce real-space images of ketones, even though this is expected to provide chemically insightful information for the organic/semiconductor interface.[7] For this reason we have chosen to study the adsorption of acetone to the (001) surface of silicon using the powerful combination of atomic-resolution STM and density functional theory (DFT). Our results challenge the accepted interpretation of this interaction. In addition, our results suggest that bonding of organic molecules to silicon via a carbonyl functional group may be utilized to produce organic adsorbates with increased stability under $I-V$ characterization. Such molecules are therefore expected to be useful for molecular electronic applications.

Acetone on Si(001) has been studied using X-ray photoelectron spectroscopy (XPS),[8,9] Fourier transform infrared spectroscopy (FTIR),[9] high-resolution electron energy loss spectroscopy, (HREELS)[8] and temperature programmed desorption (TPD),[8,10] as well as DFT[9,11−13] and STM.[9] It has been suggested[8,9] that acetone adsorbs in a [2 + 2] cycloaddition configuration where the π components of the carbonyl C=O, and Si dimer double bonds have reacted to form Si−C and Si−O σ-bonds (Figure 1a). A possible intermediate structure for this adsorption is shown in Figure 1b, where the O atom has formed a dative bond to the electrophilic down-atom of a Si dimer (the Si(001) ground state comprises alternatively buckled dimers that appear symmetric in room temperature STM images due to the dynamic flipping between orientations.[14]) An alternative intermediate structure (not shown) is one where the π electrons of the carbonyl bond interact with the Si down-atom, such as is thought to occur for some alkenes.[15] It has also been suggested that the dative bonded structure might relax via a proton shift reaction[16] to form the α-H cleavage structure shown in Figure 1c.

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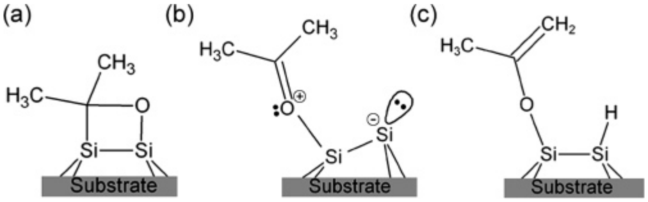

Figure 1. Possible bonding configurations of acetone to Si(001) as suggested in the literature: (a) [2 + 2] cycloaddition, (b) dative bonded, (c) α-H cleavage.

Our atomic-resolution STM images reveal three separate acetone-derived adsorbate structures on Si(001). One of these is a single-dimer feature that we attribute to the α-H cleavage structure, Figure 1c. The other two observed structures both involve neighboring Si dimers and so cannot be attributed to any of the structures that have been previously proposed in the literature. We will show that these are two bridge-bonded structures involving neighboring Si dimers. Moreover, we show that the kinetically favored single-dimer structure is unstable with respect to the formation of the thermodynamically favored bridge-bonded structures. We will show that we can promote this conversion both on a single-molecule level (using the highly confined electron beam of the STM tip) and for the entire surface (using a moderate thermal anneal).

2. Methods

Experiments were performed using a commercial ultrahigh vacuum STM (Omicron variable-temperature STM with Matrix control electronics) with base pressure $<5 \times 10^{-11}$ mbar. Silicon wafers were [001] orientated, 0.1−0.01 Ωcm, p-type (B-doped) from Virginia Semiconductor Inc. Samples were prepared by radiatively heating to ∼850 K overnight followed by direct current heating to ∼1400 K for 15 s and a 3 K/s cool down from 700 K to room temperature. During dosing, acetone (99.9% pure; Sigma-Aldrich) was admitted to the UHV system via a high-precision leak valve after first being purified by freeze−pump−thaw cycles. Acetone purity was confirmed using an in situ Stanford Research Systems 300 amu residual gas analyzer. Acetone doses were calibrated by monitoring the total chamber pressure, although the actual dose may be many times higher due to acetone being directed at the sample by a 3-mm stainless steel capillary approximately 1 cm from the sample surface. All images were acquired at room temperature. The sample temperature was estimated by monitoring the sample heating current and comparing to a calibration performed subsequently where a thermocouple was held to the sample in vacuo during annealing. We estimate an error in the temperature calibration of ±50 °C.

DFT calculations were performed using the Vienna Ab initio Simulation Package (VASP).[17] The unit cell was a 4 × 4 periodic slab containing four atomic layers (bottom layer fixed and H-terminated) and a vacuum region of approximately 10 Å. The electron−ion and electron−electron exchange and correlation interactions were accounted for using ultrasoft pseudopotentials of the Vanderbilt type[18] and the Perdew and Wang (PW91) functional,[19] respectively. A 275 eV energy cutoff was used in the plane-wave expansions and Brillouin zone integration was performed on a Monkhorst−Pack 2 × 2 × 1 k-point mesh.[20] Binding energies were calculated as $E_{\text{binding}} = E_{\text{total}} - E_{\text{substrate}} - E_{\text{free molecule}}$. Simulated STM images were obtained using the Tersoff−Hamann approximation[21] where it is assumed that the tunneling current is proportional to the surface local density of states (LDOS). To match the experimental conditions, the simulated STM images were generated by integrating the LDOS over an energy range from the Fermi level including all the electronic surface states that are important for imaging (±2 eV). Simulated images are generated for both buckling orientations of the substrate dimers; the brightest pixels of the two images are selected to produce the final image. This effectively reproduces the dynamic dimer flipping observed in room-temperature STM images of Si(001).

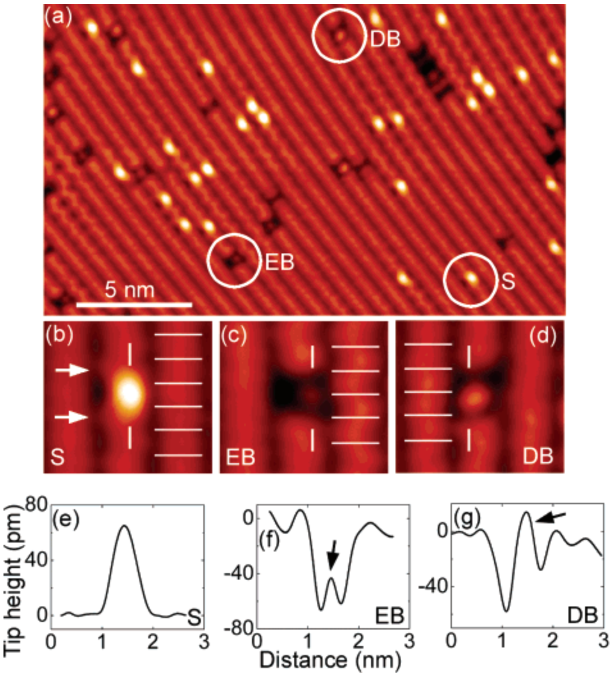

Figure 2. Filled-state STM images of acetone on Si(001) (−2 V sample bias, 0.5 nA tunneling current). (a) Acetone adsorbates are labeled S (single-dimer), EB, and DB (bridging structures), with enlargements shown in panels (b−d). Tip height line profiles shown in (e−g) are from the images in (b−d), respectively, and are along the directions indicated by the vertical white lines (taken top to bottom). Horizontal lines in (b), (c), and (d) indicate the position between dimers along the adjacent dimer row. Arrows in (b) indicate the up-buckled end of the Si dimers on either side of the adsorbate, confirming these two dimers to be unaffected by the adsorbate. Arrows in (f) and (g) indicate the position of the adsorbate protrusion.

3. Results

3.1. Identification of Adsorbate Structures. A filled-state STM image of a Si(001) surface after a light exposure to acetone (5 s at 5×10^{-11} mbar acetone partial pressure) is shown in Figure 2a. The features seen in this image are representative of those seen in many such acetone dosing experiments performed in our laboratory. By carefully comparing these features to those of the clean Si(001) surface (including intrinsic surface defects[22,23]) we have identified three distinct acetone-derived features, labeled S, EB, and DB, denoting single-dimer, end-bridge, and dimer-bridge structures, respectively. Enlargements of each of the features are shown in panels b−d of Figure 2. The uniqueness of each of these features was confirmed by performing a tip-height line profile analysis over several data sets. Representative line profiles of each feature are shown in Figure 2e−g. We have also performed counting statistics for the relative abundance of each feature after dosing at low coverage. The bridging structures EB and DB occur with

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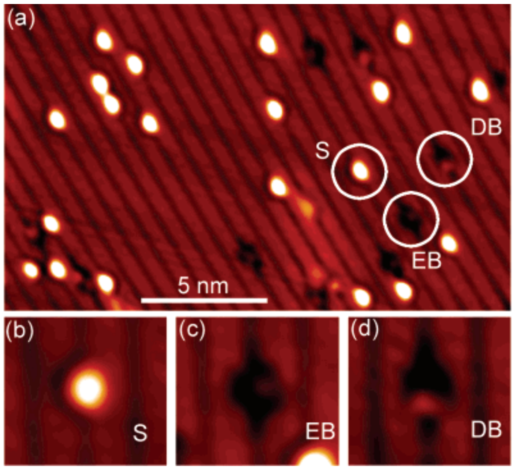

Figure 3. Empty-state STM images of acetone on Si(001) (2 V sample bias, 0.5 nA tunneling current). Acetone adsorbates are labeled S (single-dimer), EB, and DB (bridging structures). (Note that at this tunneling bias the dimer rows appear as depressions and the troughs between rows appear as protrusions.[27])

approximately equal abundance, while the single-dimer feature S is 4 times as abundant as EB and DB combined (i.e., S:EB: DB = 8:1:1).

The single-dimer feature S, shown in Figure 2b, is the brightest of the three acetone-derived adsorbates. It can be confirmed that this feature presents a protrusion located above a single silicon dimer by observing the periodicity of the surrounding surface dimers in Figure 2a,b. In Figure 2b this dimer periodicity is highlighted by white horizontal lines, which show the S feature to be centered on a single dimer. The feature appears slightly broader that a single-dimer width. We attribute this to the combination of the finite radius of curvature of the STM tip and/or the effect of vibrational and rotational motion of the adsorbate about the C−O−Si bond that holds it to the surface (Figure 4a; discussed further below). There is an intrinsic asymmetry of the S feature about the dimer row; e.g., the feature shown in Figure 2b is brightest on the right side of the dimer row. In Figure 2a it can be observed that there are equal numbers of left- and right-orientated S features.

The other two acetone-related adsorbates (EB and DB, shown in panels c and d of Figure 2) present features that span the width of two neighboring dimers. This indicates that the molecules either bridge across or have dissociated over two dimers. We will show below that both bridging and dissociation are present for these two features. Both features EB and DB present a two-dimer wide depression and have a small protrusion located within this depression. In both cases, the protrusion is in an asymmetric position about the dimer row. This can be seen in Figure 2a by observing the position of the protrusions with respect to the dimer row periodicity and also in the enlargements in panels c and d of Figure 2. If we now consider the direction parallel to the dimer rows, the protrusion in feature EB (Figure 2c) is located at the midpoint of the two dimers. This is illustrated in the line profile in Figure 2f. In contrast, the protrusion in feature DB (Figure 2d) is more localized at one of the missing dimer positions, as is evident by the asymmetry in the line profile in Figure 2g.

An empty-state image of the surface after acetone dosing, in which we have labeled the features S, EB, and DB, is shown in Figure 3. Enlargements of each of these features are shown in panels b−d of Figure 3. The qualitative appearance of each of the features is similar to their corresponding filled-state appearances: The S feature presents a slightly asymmetric, single-dimer protrusion, and features EB and DB present two-dimer wide depressions with a small protrusion located within this depression. The only qualitative difference between the filled- and empty-state images of the three features occurs for feature DB (Figure 3d). In this case, the small protrusion is symmetric about the dimer row, not asymmetric as it was in the filled-state image of this feature (Figure 2d).

Table 1. Binding Energies (eV) for Acetone-Derived Adsorbate Structures[a] on Si(001) Calculated in the Present Paper (First Column) and Refs 9, 11, 12, and 13

	present	ref 9	ref 13	ref 11	ref 12
dative	−1.03	−	−0.59	−0.11	−
cycloaddition	−1.83	−1.50	−1.54	−1.05	−1.7
S (α-H)	−1.90	−1.87	−1.94	−	−
EB	−3.14	−	−	−	−
DB	−3.49	−	−	−	−

[a] The dative and [2 + 2] cycloaddition structures are shown in Figure 1b and a, respectively. The α-H cleavage structure is shown in both Figure 1c and Figure 4a. The bridging structures EB and DB are shown in Figure 4b and c, respectively.

We have employed total energy DFT calculations to identify the structure of these three acetone-derived adsorbate features. In our calculations we have explored more than 30 different possible configurations of acetone in various states of dissociation and bonding on the Si(001) surface, including bridging configurations, which have not been previously considered (full details will be published elsewhere[24]). Table 1 presents the binding energy values that we have calculated for the structures that are important for discussion in this paper, as well as comparisons to other values reported in the literature. The relative energetic ordering of the structures agrees across all of the reported studies. We see very good agreement for the α-H cleavage structure.[9,13] The variation in calculated energies for the [2 + 2] cycloaddition structure reflects the surface strain induced by this ring-structure, and hence the sensitivity of its binding energy to surface relaxation. The calculated binding energy is therefore highly sensitive to constraints such as unit cell size and number of relaxed substrate atoms, which have varied among the reports in the literature. The binding energies for the EB and DB bridging structures were the overall lowest values found in our systematic search.[24] These structures are lower in energy by more than 1.2 eV over the α-H cleavage structure, which can be attributed to the saturation of two additional surface dangling bonds.

In Table 1, we label the α-H cleavage structure S, and the two bridging structures EB and DB to indicate our preference for assigning these to the S, EB, and DB features observed in our experiments. The chemical structures and geometry-optimized ball models for each of these features are shown in panels a−c and panels d−f of Figure 4, respectively. Structure EB involves an acetone molecule bridge-bonding across the ends of two neighboring dimers with a corresponding dissociation of H atoms to the opposite ends of these dimers. Structure DB is qualitatively similar to structure EB; however, in this case the bridge bonding is across a single dimer with the dissociation of two H atoms to the neighboring dimer (effectively a 90°

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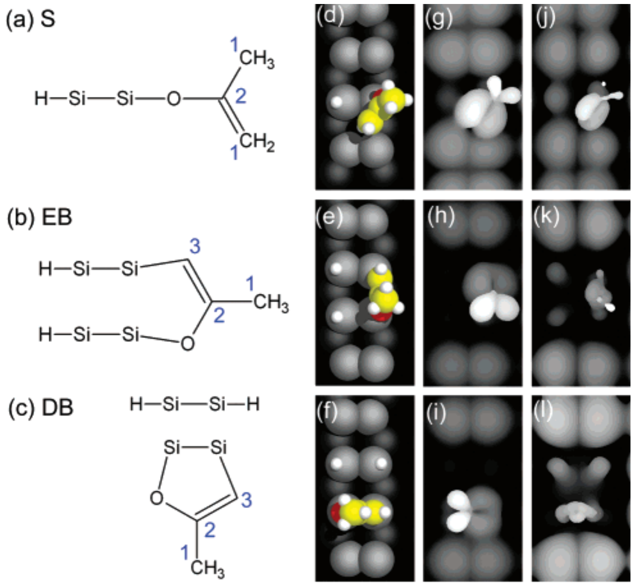

Figure 4. (a−c) Chemical structures for the three acetone-derived adsorbate structures S, EB, and DB. The numbers adjacent to the C atoms denote the group to which these are assigned for XPS analysis (see text). (d−f) Geometry-optimized atom-model representations of the three structures. (g−i) Simulated filled-state STM images (compare with Figure 2b−d). (j−l) Simulated empty-state STM images (compare with Figure 3b−d).

rotation of the adsorbate structure within a 2 × 2 unit cell). The fact that these are the lowest-energy structures and that EB and DB involve two neighboring Si dimers lends strong support to our assigning these to the adsorbate features we observe in experiment.

To further confirm the assignments shown in panels a−c of Figure 4, we have computed the simulated filled- and empty-state STM images for each, shown in panels g−i and panels j−l of Figure 4, respectively. These reproduce the features seen in the STM images remarkably well (compare to panels b−d of Figure 2 and panels b−d of Figure 3, respectively). (Note that the finite size of the STM tip results in the fine detail of the molecular density of states not being resolved in the experimental STM images.) Structure S presents a slightly asymmetric single-dimer protrusion in filled- and empty-states, while features EB and DB present two-dimer wide depressions with small protrusions within, in agreement with experiment. The protrusion for EB is located in between the position of two dimers, while the DB protrusion is above a dimer position. In addition, we see in Figure 4l that the DB protrusion becomes symmetric about the dimer row in empty-state, in excellent agreement with experiment (Figure 3d).

3.2. Agreement with Spectroscopic Data. Our results are in excellent agreement with published spectroscopic data.[8,9] XPS studies have reported two O(1*s*) peaks and three C(1*s*) peaks, with very good agreement among the binding energy values, if not the relative intensities of the peaks.[8,9] Our analysis of the XPS data follows that of ref 9. The two O(1*s*) peaks are shifted downward in energy from the intact carbonyl value due to the formation of Si−O bonds. Analysis of the geometries of our S, EB, and DB structures shows that the oxygen environment is very similar for S and EB, with Si−O bond lengths of 1.68 and 1.69 Å, and bond angles of 132.1° and 133.2°, respectively. The DB structure, on the other hand, has a substantially longer Si−O bond length of 1.72 Å, and a significantly smaller bond angle of 117.9°. These differences provide an explanation for the observation of two peaks in the O(1*s*) spectrum.

The three C(1*s*) lines can be explained by considering the local chemical environments of each C atom in our three adsorbate configurations. We divide these into three groups. Group 1 consists of C atoms that are only bonded to one other C atom (either C−C or C═C); group 2 consists of C atoms that have one neighboring O atom (C−O) and two C atoms (one C−C and one C═C); group 3 consists of C atoms that have one neighboring Si atom (C−Si) and one neighboring C atom (C═C). We have labeled each C atom in Figure 4a−c according to the group to which it belongs. Since there are three distinct local chemical environments for all of the carbon atoms, we expect three peaks in the C(1*s*) spectrum, in agreement with experiment.[8,9]

Our results are also in excellent agreement with vibrational spectroscopy measurements (FT-IR and HREELS[8,9]). These measurements found an absence of carbonyl (C═O) stretching modes, indicating that this bond is reduced upon adsorption to Si(001), in agreement with our results. Hamai et al.[9] reported various FT-IR peaks that were assigned to C−H stretching modes of alkene and alkane fragments. These peaks can be similarly attributed to the C−H stretching modes of the α-H cleavage CH_2 group, and the methyl groups of the three structures, respectively (panels a, b, c of Figure 4).

Furthermore, Hamai et al.[9] found a splitting of the Si−H stretching mode in their FT-IR data that until now has remained unexplained. We attribute this splitting to the formation of the monohydride (H−Si−Si−H) dimer of the DB bridging structure (Figure 4c). The magnitude of the splitting is greater than that observed for monohydride dimers on the monolayer H-terminated Si(001) surface. We attribute this increase in splitting energy for the acetone-dosed surface to the increased local strain induced on the monohydride dimer by the adjacent bridge-bonded acetone fragment (Figure 4c).

3.3. Adsorbate Stability. We now turn our attention to the stability of the acetone-derived adsorbates on the Si(001) surface, and in particular, we note that the α-H cleavage structures (S) become unstable when the STM tip bias is increased to ∼3 V or higher. Figure 5a shows a filled-state STM image, acquired at −2 V sample bias, where two α-H cleavage structures can be seen. Panels b and c in Figure 5 show the two subsequent images of the same area of the surface, imaged at −3 V sample bias. The adsorbate indicated by an arrow undergoes a transition to a bridge-bonded EB structure while being imaged in Figure 5b and remains that way in Figure 5c and all subsequent images. (Note that the protrusion in this EB feature appears slightly brighter than those in Figure 3 due to the higher bias at which the image was acquired.) We have observed many such adsorbate changes from the single-dimer α-H cleavage structure to the bridging structures, EB and DB. However, we have never observed the reverse process (i.e., EB or DB → S), and we have never observed transitions between the two bridging structures (i.e., EB ↔ DB). This indicates that the bridging structures EB and DB are thermodynamically more stable than the α-H cleavage structure, in agreement with our calculations (Table 1).

The random adsorbate conversions discussed above can also be selectively induced to occur on a molecule-by-molecule basis. Panels d and f of Figure 5 show filled- and empty-state images,

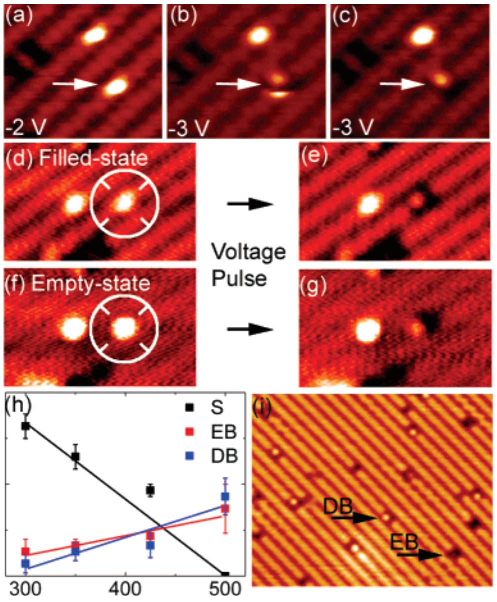

Figure 5. (a) Two single-dimer α-H cleavage adsorbates on Si(001) imaged at −2 V sample bias (filled-state). (b,c) The bottom adsorbate changes to a bridging EB structure when the bias is increased to −3 V. (d,f) Two α-H cleavage adsorbates imaged at −2 and +2 V sample bias, respectively. (e,g) The right-hand adsorbate has been induced to dissociate to the bridging DB configuration by applying a swept voltage pulse (−4 to +4 V) directly above the adsorbate (images are −2 and +2 V sample bias, respectively). (h) Plot of the relative coverage of the three adsorbates as a function of temperature (Kelvin). (i) Filled-state STM image of the surface after annealing to 500 K showing the complete disappearance of α-H cleavage adsorbates.

respectively, where two single-dimer α-H cleavage structures can be observed. After acquiring this image, the STM tip was positioned above the right-hand adsorbate and a tunneling spectra was recorded; i.e., the feedback loop of the STM tip was switched off and the voltage swept from −4 V to +4 V while simultaneously recording the tunneling current. Panels e and g of Figure 5 show the filled- and empty-state images of the same area subsequent to this process. It can be seen that the adsorbate on which the tunneling spectra was recorded has undergone a chemical change and now exhibits the characteristic signature of a DB bridging structure (compare the filled- and empty-state images to Figure 2d and Figure 3d). This process has been performed repeatedly in our laboratory. Inspection of the tunneling spectra revealed that the change in the adsorbate structure was usually accompanied by a discontinuous drop in the tunneling current between 3 and 4 V sample bias. This drop probably indicates the moment of the conformation change of the adsorbate, similar to that reported in ref 6 for styrene molecules (where, however, the resulting adsorbate structures were not identified to the level of detail we have done here).

To investigate the thermodynamic stability of the adsorbates further, we performed a series of experiments where the room-temperature dosed surface was annealed to the successively higher temperatures of 350, 425, and 500 K. The surface coverage density of each type of adsorbate was determined by averaging over several images taken after each annealing stage, and the results are plotted in Figure 5h. This plot clearly shows that the number of α-H cleavage adsorbates decreases with increasing anneal temperature, while the number of both of the bridging structures EB and DB increases. The decrease in the density of α-H cleavage adsorbates is equal to the increase in the density of the bridging structures EB and DB to within the accuracy of the experiment, indicating that very little (if any) desorption of the adsorbates occurs within this temperature range in agreement with previous TPD studies.[8,10] Annealing to 500 K was sufficient to completely convert all of α-H cleavage adsorbates to bridging EB and DB structures, as can be seen in Figure 5i.

4. Discussion and Conclusion

Our results indicate that acetone molecules adsorb to the Si(001) surface in the α-H cleavage configuration (Figure 4a). This is almost certainly facilitated by an initial formation of the dative bonded structure (Figure 1b) followed by a proton shift reaction. The majority of surface adsorbates (∼80%) remain in the single-dimer α-H cleavage configuration; however, a fraction (∼20%) convert to the thermodynamically more stable bridge-bonding structures EB and DB (Figure 4b,c). In the case of the EB structure, this conversion is facilitated by an interaction of the C═C double bond of the α-H cleavage structure (Figure 4a) with a neighboring Si dimer, and a simultaneous (i.e., within the time frame of the interaction) proton transfer to the other end of this Si dimer. In the case of the DB structure, it is likely that the large fragment of the α-H cleavage structure first shifts to a neighboring Si dimer, facilitated by the formation of a transition bond between an O lone pair orbital and the neighboring Si dimer (similar to the process by which PH_2 is thought to diffuse on Si(001)[25]).

We make a brief comment on our reasons for preferring to assign the single-dimer feature to the α-H dissociation structure, rather than to the [2 + 2] cycloaddition structure, due to the prevalence of the latter structure in the literature.[8,9] Our atomic-resolution STM data clearly show that there is only *one* single-dimer adsorbate. In other words, the experimental data allow for the formation of *either* the α-H cleavage structure *or* the [2 + 2] cycloaddition structure, but not both. Neither structure can be ruled out based on the inspection of their simulated STM images. Of the two structures, the α-H cleavage structure is the most energetically favorable (Table 1). We have shown that the observed single-dimer adsorbate can be easily converted to either of the two bridging structures EB and DB, and we have presented a plausible route for this conversion. The [2 + 2] cycloaddition structure would need to follow the same steps as the α-H cleavage structure to convert to the bridging structures. However, the [2 + 2] cycloaddition would also need to undergo an additional preceding step in that its Si−C bond would first need to be broken (see Figure 1a), which would likely increase the activation barrier for the process. We found no competing two-dimer structures that can be more easily reached from the [2 + 2] cycloaddition structure. In addition, it has been shown that the α-H cleavage structure, and not the [2 + 2] cycloaddition structure, forms when acetone is adsorbed to the Ge(001) surface,[13] which is chemically similar to Si(001). For these reasons we believe the data suggests that the single-dimer feature is more likely to be the α-H cleavage structure than [2 + 2] cycloaddition. It is interesting that even with the combination of atomic-resolution STM, energy minimization DFT, photoemission, and vibrational spectroscopy experiments, this seem-

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ingly fundamental bonding assignment cannot be made with certainty. However, we believe the addition of transition-state barrier energy DFT calculations will finalize this issue. We are currently performing such calculations.

A crucial factor governing the success or failure of any molecular electronic device is the ability of the molecule in question to sustain an electronic current. This issue has been explored in some detail by the Wolkow group,[6,26] who have cautioned that inelastic electron-scattering processes can lead to bond breaking and adsorbate desorption. This has been found to occur for both cyclopentane and styrene on the Si(001) surface, making these adsorbates unsuitable for molecular electronic applications.[4,6] This instability has been attributed to the existence of unsaturated C═C double bonds in the molecules. Our results for the α-H cleavage structure are in agreement with these earlier observations. However, we have observed the bridge-bonded configurations of acetone on Si(001) to be stable up to a tunneling bias of ±4 V. We attribute this increased stability to the existence of two molecule−surface bonds (Si−C and Si−O) and the saturation of nearby reactive Si dangling bonds with H. The molecules themselves nevertheless still contain unsaturated C═C double bonds and so may be expected to exhibit improved conductance properties over saturated molecules (e.g., TEMPO used in ref 4). We therefore propose bonding more complicated organic molecules to Si(001) through the carbonyl group (e.g., benzaldehyde). We believe this may lead to adsorbates of interest for molecular electronic applications that exhibit high conductivity and are stable under *I*−*V* characterization. Such measurements are underway in our laboratory.

In summary, we have performed a detailed experimental/theoretical study of the interaction of a simple ketone (acetone) with the technologically important silicon (001) surface. Our atomic-resolution scanning tunneling microscopy images unambiguously reveal for the first time that acetone molecules bond to the Si(001) surface in three unique configurations at room temperature, two of which involve the bridge bonding of the molecule to two neighboring silicon dimers. The two bridge-bonding structures are greater than 1.2 eV thermodynamically more stable than the kinetically favored single-dimer α-H cleavage structure. We demonstrate that conversion to the more thermodynamically stable state can be achieved on a molecule-by-molecule basis using the highly confined electron beam of the STM tip or, for the entire surface, using a moderate thermal anneal. These results have important implications for the interaction of molecules containing carbonyl functional groups with semiconductor surfaces and suggest that the interpretation of data for some similar ketone/silicon interactions in the literature may need to be revisited. In addition, we propose that the use of the carbonyl functional group to tether organic molecules to the Si(001) surface in a bridge-bonded configuration through both the O and C atoms may lead to greater stability for molecular electronic devices.

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