Example of a Thermodynamically Controlled Reaction on a Semiconductor Surface: Acetone on Ge(100)-2 × 1

George T. Wang,[†] Collin Mui,[†] Charles B. Musgrave,[†,‡] and Stacey F. Bent*,[†]

Department of Chemical Engineering, Stanford University, Stanford, California 94305, and
Department of Materials Science and Engineering, Stanford University, Stanford, California 94305

Received: August 7, 2001; In Final Form: October 12, 2001

The adsorption of acetone on the Ge(100)-2 × 1 surface has been investigated using multiple internal reflection infrared spectroscopy and density functional theory quantum chemistry calculations and was found to be under thermodynamic control at room temperature. Acetone undergoes attachment at the carbonyl oxygen with loss of an α hydrogen at room temperature on the Ge(100)-2 × 1 surface to form an enol-like adduct. This so-called ene reaction has not been seen on the Si(100) surface, on which the reaction of acetone is under kinetic control and instead a less thermodynamically favored [2 + 2] addition across the carbonyl bond is observed. At low temperature, acetone adsorbs via dative-bond formation with the surface, which we find to be too weak to remain at room temperature in contrast to the stronger dative bonds formed by amines on the Si(100) and Ge(100) surfaces. There is evidence that the acetone ene product may undergo oxygen migration and insertion into Ge−Ge bonds, especially at elevated surface temperatures. Whereas the reactions of organics on Si(100)-2 × 1 are typically under kinetic control, thermodynamic control on the Ge(100)-2 × 1 surface is made possible by the reversibility of weak surface adsorption. The strategic use of thermodynamically controlled reactions on the Ge(100)-2 × 1 surface represents a new and potentially powerful approach for the selective formation of organic-functionalized semiconductor surfaces.

I. Introduction

The body of work, both experimental and theoretical, examining the reactions of organic molecules on semiconductor surfaces has grown considerably over the past several years in the expectation that coupling the vast array of organic material properties with modern and mature semiconductor technologies will lead to new device applications, including molecular electronics,[1] sensors,[2] and nanotechnology.[3] Studies in this field have focused primarily on the covalent attachment of organics to the silicon(100)-2 × 1 surface, although reactions on the germanium(100)-2 × 1 and diamond(100)-2 × 1 surfaces have also been examined. Some of the representative attachment chemistries used to functionalize clean semiconductor surfaces in vacuum include cycloaddition and N−H dissociation.[4−7]

The creation of organic−semiconductor surface structures with custom-designed properties will likely necessitate the use of multifunctional compounds and the ability to attach them to the surface in a controlled, selective manner. One of the major obstacles to this approach is that it appears, upon the basis of the body of work in the literature, that organic reactions on Si(100) are under kinetic control rather than thermodynamic control. This means that the products with the most favorable kinetics (i.e., lowest barriers) and not necessarily the most favorable thermodynamics (i.e., greatest binding energies) are formed on Si(100).[8] We believe that kinetic versus thermodynamic control is a useful concept that can apply to semiconductor surface reactions, even though these are not always strict equilibrium processes. Kinetic control is problematic because many reactions on clean semiconductor surfaces proceed with little or no activation barrier, making it difficult to selectively form the desired structure over competing side products. For example, dienes such as butadiene and cyclohexadiene have been shown to form varying amounts of a [2 + 2] side product in addition to the principal Diels−Alder [4 + 2] product on Si(100)-2 × 1, even though the [4 + 2] product is significantly more stable.[9,10] Moreover, annealing of covalently bound organics on Si(100)-2 × 1 or exposure of organics to a heated Si surface typically leads to decomposition rather than conversion to the more thermodynamically stable product.[5,7] Hence, heating, which is a common method in organic chemistry for changing reactions from kinetic to thermodynamic control, is not usually a viable option on the Si(100) surface. Inevitably, it is the relative kinetics of the competing pathways rather than the thermodynamics of the products that determine the final product distribution on Si(100).

There is another problem inherent with the kinetic control of Si(100) surface reactions. The indiscriminate nature of the clean Si(100) surface, which reacts with most functional groups regardless of type, all but guarantees that the most reactive functionalities (i.e., those with the fastest kinetics) will bind preferentially to the surface, leaving the less reactive ones for further functionalization. This presents challenges for second layer growth, where the remaining functional group from the first layer must be highly reactive toward attachment of the next organic layer, particularly if the reactions are to continue under vacuum conditions. For example, attempts at attaching a second layer at the C=C double bond remaining from [4 + 2] and [2 + 2] reactions of dienes have so far been unsuccessful by our group and others. If thermodynamic control could be achieved, it may be possible to leave the more reactive functional group intact if the less reactive one leads to a more stable surface product.

---

* To whom correspondence should be addressed. E-mail: sbent@stanford.edu. Fax: 650-723-9780.
† Department of Chemical Engineering.
‡ Department of Materials Science and Engineering.

While organic reactions on Si(100)-2 × 1 are likely to be under kinetic control, thermodynamically controlled reactions may be possible on Ge(100)-2 × 1 because of the weaker bonds that organics form with Ge compared to Si or C. For example, surface Ge−C bonds are approximately 7−9 kcal/mol weaker than Si−C bonds as calculated for 1,3-butadiene on the Si(100)-2 × 1 and Ge(100)-2 × 1 surfaces.[11] In contrast to the Si(100) surface, on Ge(100) 1,3-butadiene[12,13] and cyclopentene[14] are known to undergo reversible desorption upon thermal annealing most likely because of the weak Ge−C bonds. This is relevant because reversibility is a necessary condition for thermodynamic control, in that interconversion between products must be able to occur (i.e., from the kinetically favored to the thermodynamically favored product).

In this paper, we present evidence for a reaction of an organic compound on a clean semiconductor surface under thermodynamic control at room temperature—that of acetone on Ge(100)-2 × 1. We show, using multiple internal reflection infrared spectroscopy and density functional theory quantum chemistry calculations, that acetone undergoes attachment at the carbonyl oxygen with loss of an α hydrogen at room temperature on the Ge(100)-2 × 1 surface to form an enol-like "ene" adduct. This ene reaction has not been seen for the reaction of acetone on the Si(100) surface, in which a [2 + 2] addition across the carbonyl bond is observed instead.[15] We will show that on both Si(100)-2 × 1 and Ge(100)-2 × 1 surfaces, the [2 + 2] C=O addition reaction is kinetically favored while the ene reaction is thermodynamically favored. Thus, the formation of the more stable ene product at the expense of the kinetically favored [2 + 2] C=O product indicates that the reaction of acetone on the Ge(100)-2 × 1 surface is under thermodynamic control at room temperature. The strategic use of thermodynamically controlled reactions on the Ge(100)-2 × 1 surface to create new organic−semiconductor interfaces that are kinetically uncompetitive on the Si(100)-2 × 1 surface represents a new and potentially powerful approach for the selective formation of organic-functionalized semiconductor surfaces.

II. Experimental and Computational Details

The experiments were performed in an ultrahigh vacuum (UHV) chamber, which has previously been described in detail.[16] Infrared data were collected in multiple internal reflection (MIR) mode using a Fourier transform infrared (FTIR) spectrometer with a narrow-band HgCdTe detector. For each experiment, a background IR emissivity spectrum for the clean sample was recorded, and subsequent scans after adsorption were ratioed to this background spectrum and transformed to absorption spectra. Spectra have been corrected for baseline instabilities. The sample, a Ge(100) crystal of trapezoidal geometry (1 mm × 20 mm × 50 mm, 45° beveled edges), can be conductively heated by a resistive tungsten heater and cooled by heat exchange with a liquid nitrogen coldfinger. The sample surface was cleaned by sputtering with Ar$^+$ ions at room temperature followed by annealing to 875 K for 4 min. The back face of the crystal, which is not cleaned by sputtering, was covered with a thin molybdenum plate to prevent adsorption. Acetone (99.5% purity) was transferred to a sample vial in a nitrogen-purged glovebag and further purified by repeated freeze−pump−thaw cycles before introduction into the chamber through a variable leak valve. All exposures were performed by filling the chamber with the compound for a given pressure and time and are reported in units of langmuir (1 L = 1 × 10^{-6} Torr sec). The pressures have not been corrected for ion gauge sensitivity.

All calculations in this work were done using the B3LYP hybrid density functional theory (DFT) method with the Gaussian 98 software package.[17] B3LYP has been used extensively to calculate binding and activation energies of organic reactions on group IV(100)-2 × 1 surfaces using the cluster approximation. Calculated binding energies using this method are generally in good agreement with experimental results, when available.[18] Additionally, B3LYP has been used to correctly predict that the [4 + 2] reaction of dienes on Si(100)-2 × 1,[19,20] Ge(100)-2 × 1[11] and C(100)-2 × 1[21] is kinetically and thermodynamically favored over the [2 + 2] reaction and that *N*-methyl dissociation for amines on Si(100)-2 × 1 has a prohibitive barrier to dissociation at room temperature while N−H dissociation does not.[18,22] The geometries of all minima and transition states in the potential energy surfaces in this work are calculated at the B3LYP/6-31G(d) level of theory without application of geometry constraints. Geometry optimization is followed by a single-point energy calculation at the more rigorous B3LYP/6-311++G(d,p) level of theory because single-point energy calculations are typically more sensitive to basis set size than geometry optimizations. The energies reported have not been zero-point corrected.

The Si(100)-2 × 1 surface is modeled by a Si$_9$H$_{12}$ one-dimer cluster consisting of four layers of silicon atoms, with the two Si atoms in the top layer comprising the surface dimer. The seven subsurface Si atoms are terminated with twelve hydrogen atoms to maintain the sp^3 hybridization of the bulk Si atoms. To model the Ge(100)-2 × 1 surface, the top two Si atoms of the Si one-dimer cluster were replaced with Ge atoms (Ge$_2$-Si$_7$H$_{12}$). A full nine-atom Ge cluster was not used due to the computational expense required. Previous calculations of the [4 + 2] and [2 + 2] cycloaddition reactions of 1,3-butadiene on Ge(100)-2 × 1 using B3LYP have found that using a Ge$_2$-Si$_7$H$_{12}$ cluster to model the Ge surface rather than the full Ge$_9$H$_{12}$ cluster results in less than a 2 kcal/mol difference in the calculated binding energies (which are weaker on Ge$_2$Si$_7$H$_{12}$).[23] Hence, we expect this approach to be acceptable for modeling the present system.

III. Results and Discussion

A. Ene Reaction. The infrared spectrum of the Ge(100)-2 × 1 surface after a saturation dose (2000 L) of acetone at room temperature is shown in Figure 1a. Notable is the growth of a Ge−H stretch mode at 1967 cm^{-1}, indicating C−H dissociation upon adsorption. Also of interest is the presence of modes at approximately 1638 and 1672 cm^{-1}, which are indicative of alkene C=C stretching modes, and the loss of the strong carbonyl modes above 1700 cm^{-1} that are seen in the physisorbed multilayer spectrum (Figure 1c). The growth of the Ge−H peak upon chemisorption concurrent with the appearance of C=C stretching modes and the loss of C=O stretching modes is consistent with the formation of an enol-like product, as shown in Scheme 1.

This "enolization" reaction involves the surface attachment of acetone at the carbonyl oxygen and transfer of an α hydrogen from a methyl group to the surface and is analogous to the pericyclic "ene" reaction in organic chemistry. No other obvious reaction products are consistent with the infrared data. While a [2 + 2] addition reaction across the carbonyl, as shown in Scheme 2, would also result in the loss of the C=O stretching mode, it is inconsistent with the growth of the Ge−H and C=C modes.

To our knowledge, the ene reaction has not been previously observed on a semiconductor surface, including in a previous
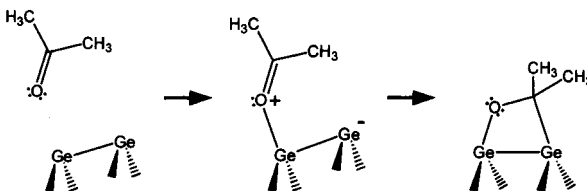
Controlled Reaction on a Semiconductor Surface

J. Phys. Chem. B, Vol. 105, No. 50, 2001 **12561**
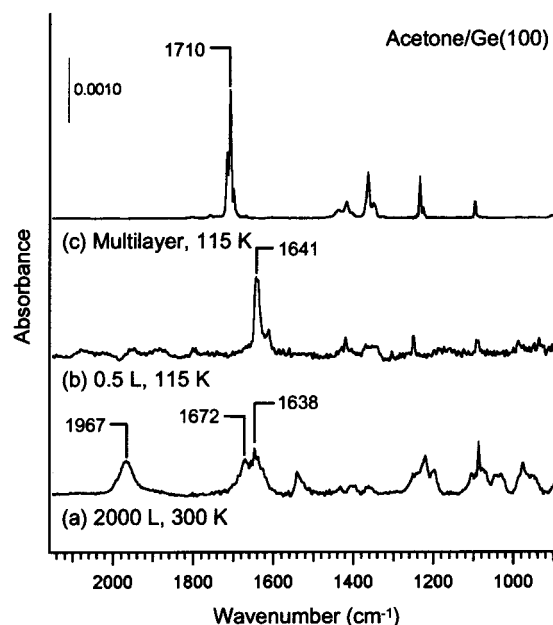
Figure 1. Infrared spectra of acetone on the Ge(100)-2 × 1 surface: (a) 2000 L at 300 K; (b) 0.5 L at 115 K; (c) multilayers (scaled) at 115 K.

SCHEME 1
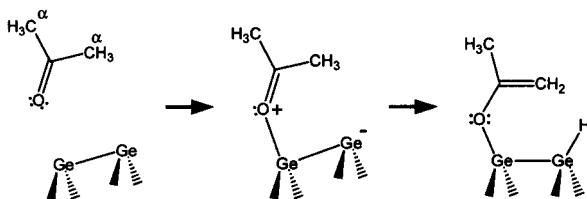
SCHEME 2

study of the adsorption of acetone on the Si(100)-2 × 1 surface.[15] Instead, on the Si(100) surface, Armstrong et al. observed a [2 + 2] addition product across the carbonyl bond as well as some product with the carbonyl bond totally cleaved, most likely from subsequent O insertion reactions from the [2 + 2] state.[15] We estimate that, at saturation, roughly two-thirds of the Ge(100)-2 × 1 surface dimers have reacted to form the ene adduct. This estimate is based on comparison of the integrated intensity of the ν(Ge−H) peak in Figure 1a with that of a water-saturated Ge(100) surface at room temperature, which has been reported to have one Ge−H and one Ge−OH bond per surface dimer due to dissociative adsorption.[24]

The binding energies of the ene and [2 + 2] C=O addition reaction products have been computed on the Ge(100) and Si(100) surfaces and are reported in Table 1. It can be seen from the respective binding energies that the ene product is thermodynamically preferred (more stable) over the [2 + 2] C=O product on both surfaces by approximately 10 kcal/mol. Of special note is the binding energy of the [2 + 2] C=O addition product on the Ge(100) surface, which at 12−13 kcal/mol, is quite weak for an organic species covalently bound to a semiconductor surface. The weakness in large part is due

TABLE 1: Calculated Energies, in kcal/mol, of the Bonding and Transition States of Acetone on the Ge(100)-2 × 1 and Si(100)-2 × 1 Surfaces, Relative to the Vacuum Level[a]

	Ge(100)	Si(100)
dative-bonded	−12.3	−13.7
ene product	−22.8	−44.7
ene transition state	1.9	−8.8
ene O insertion	−28.5	−75.2
[2 + 2] C=O product	−12.5	−35.5
[2 + 2] C=O transition state	−1.8	−8.6

[a] Energies were calculated using the 6-311++G(d,p) basis set.
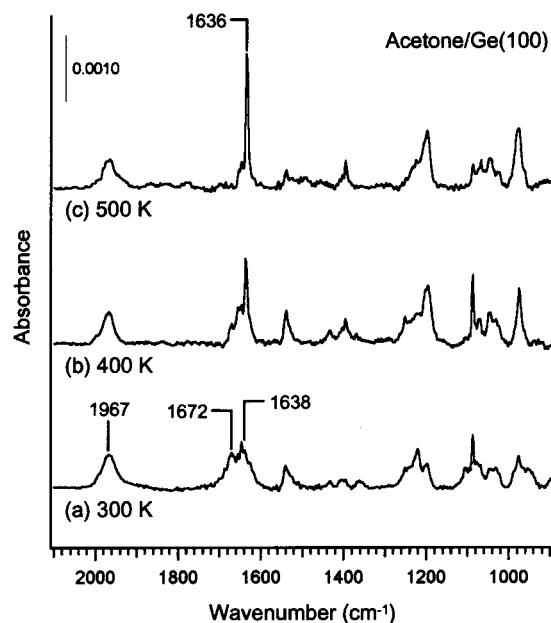
SCHEME 3
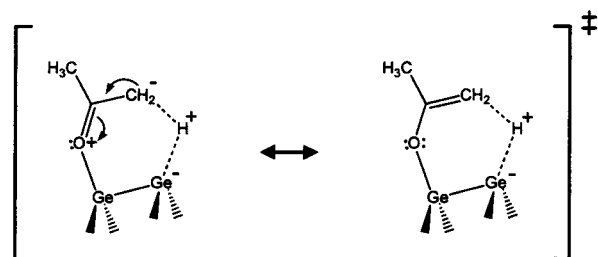
to the surface Ge−O bond strength, which we estimate from our calculations to be 14−16 kcal/mol weaker than a surface Si−O bond. A kinetic analysis employing a first-order Arrhenius form and a range of preexponential factors reveals that this [2 + 2] C=O adsorption energy is insufficient for the product to remain kinetically stable at room temperature. Thus, we conclude that at room temperature on the Ge(100) surface, the [2 + 2] C=O product is reversibly desorbed and the ene product is allowed to form instead. In contrast, on the Si(100) surface, the [2 + 2] C=O binding energy of 36 kcal/mol is more than adequate for room temperature stability, and this product appears to be preferentially formed on the Si(100) surface[15] rather than the more stable ene product. It follows logically that the reaction of acetone on Si(100) must be under kinetic control, because the less thermodynamically favored product is formed.

The observation of dissociation of the α-C−H bond upon adsorption of acetone is initially unexpected, considering that C−H bonds are quite strong and typically remain intact during organic reactions on semiconductor surfaces. However, a well-known characteristic of carbonyl compounds is the high acidity of the α hydrogens. For example, the pK_a values of α hydrogens in simple ketones such as acetone are approximately 19−20, compared to 38 and 50 for the hydrogen atoms in ammonia and ethane, respectively. In fact, while C−H dissociation occurs for acetone on Ge(100), N−H dissociation is not observed for ammonia[25,26] and methylamines[27] on Ge(100), which is consistent with the trend in acidity. Thus it appears that acidity measures such as pK_a may be a useful guide for predicting the reactivity of surface reactions involving proton transfer (i.e., from the molecule to the surface) of which the ene and N−H dissociation[27] reactions are two examples. The acidity of the α hydrogens in the acetone molecule can be explained by the resonance stabilization of the anion after loss of a proton, which is made possible by the carbonyl bond. A similar mechanism may take place for the surface ene reaction of acetone in which the transition state is resonance stabilized, as shown in Scheme 3. Note that the pictured reaction scheme is not intended to accurately represent the actual atom charge densities of the surface states but to show instead how resonance stabilization of the transition state is possible.
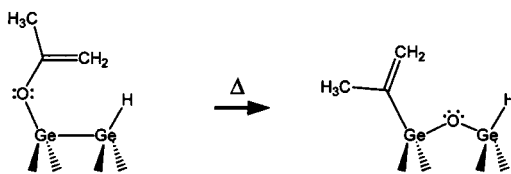
To probe the thermal stability of the ene product, annealing IR studies were performed after a saturation dose of acetone

12562 *J. Phys. Chem. B, Vol. 105, No. 50, 2001*

Wang et al.

Figure 2. Infrared spectra of an annealing series of acetone on the Ge(100)-2 × 1 surface: (a) 2000 L at 300 K; (b) followed by annealing at 400 K; (c) followed by annealing at 500 K.

SCHEME 4

on Ge(100)-2 × 1 at room temperature. Figure 2 shows the infrared spectra of acetone on Ge(100) at room temperature and after successive anneals to 400 and 500 K. It can be seen that upon annealing to 400 K and continuing to 500 K some peaks lose intensity while others grow stronger. Additionally, the Ge−H mode is essentially unaltered and the overall integrated intensity of all surface modes combined is roughly the same after annealing, indicating that little or no decomposition or desorption is taking place. At 500 K, the ν(C=C) mode at ∼1638 cm^{-1} has gained sharply in intensity at the expense of the 1672 cm^{-1} mode, which has disappeared. The data suggest that two products may be present at room temperature, one of which is converted to the other upon annealing. It is possible that the two products represent the ene adduct bonded in different local environments, for example, at step vs terrace sites or in islands vs isolated sites. However, we believe a more likely explanation is that the oxygen atom of the ene product can undergo migration and insertion into Ge−Ge bonds, as shown in Scheme 4.

This hypothesis is supported by previous studies of carbonyl compounds, including acetone, on the Si(100) surface. These studies have found evidence of products with the carbonyl bond completely cleaved, consistent with [2 + 2] C=O addition products that have undergone oxygen insertion.[15,28] Experimental and theoretical work studying the thermal oxidation of H$_2$O on Si(100) has found that oxygen inserts into the Si−Si dimer and Si−Si back-bonds upon annealing.[29−32] Furthermore, frequency calculations on Ge(100) predict a red shift (∼17 cm^{-1}) of the ν(C=C) mode following oxygen insertion of the ene product into the dimer bond, which compares favorably with the experimentally observed red shift (∼34 cm^{-1}) following annealing and lends support to the insertion hypothesis. We have

calculated the energies of the ene product following oxygen insertion (shown in Scheme 4) into the Ge(100) and Si(100) dimer bonds, which are reported in Table 1. A thermodynamic driving force for the insertion process does indeed exist and is calculated to be ∼6 and 31 kcal/mol on the Ge(100) and Si(100) surfaces, respectively. The significantly greater stabilization of the ene product on Si(100) compared to Ge(100) after insertion reflects the greater strength of Si−O versus Ge−O bonds. We have not yet calculated the products for oxygen insertion from the ene state into Ge−Ge back-bonds, which may also be possible. Barriocanal and Doren have recently calculated structures for oxygen insertion into Si−Si back-bonds for acetone initially bonded in the [2 + 2] C=O addition state on Si(100), finding that insertion process thermodynamically favorable as well.[33]

B. Dative-Bond Formation. Because of the lone pairs on the oxygen atom, it may be possible for acetone to form a dative bond with the surface by donating charge from the lone pair to the electrophilic "down" atom of a surface dimer. On both the Si(100)-2 × 1 and Ge(100)-2 × 1 surfaces, the dimers are known to be tilted rather than symmetric. This tilting gives the dimers a zwitterion-like diradical character in which the down atom is slightly positive relative to the up atom. Dative-bonded structures on the Si(100)-2 × 1 surface have been previously observed for tertiary amines such as *N*-methylpyrrolidine[22] and trimethylamine[18] at temperatures as high as 300 K. Recently, we have observed that, on the Ge(100)-2 × 1 surface, primary and secondary amines in addition to tertiary amines form dative-bonded adducts at room temperature through the nitrogen lone pair. [27] For the present system, we have calculated stable dative-bonded states for acetone on the Ge(100) and Si(100) surfaces with energies of approximately −12 and −14 kcal/mol, as reported in Table 1. It is interesting to note that the surface Ge−O and Si−O dative bonds are nearly the same strength while, as previously mentioned, surface Ge−O and Si−O covalent bonds differ by a substantial 14−16 kcal/mol. The existence of the dative-bonded state is significant because it is the likely precursor state for both the ene and the [2 + 2] C=O addition reactions, as shown in Schemes 1 and 2.

The dative-bonded or [2 + 2] C=O products may be preferred over the ene product on the Ge(100) surface at temperatures low enough for them to be stabilized. To explore this possibility, the adsorption of acetone was carried out at low temperature. Figure 1b shows the infrared spectrum of a 0.5 L dose of acetone chemisorbed at 115 K on the clean Ge(100)-2 × 1 surface. It is apparent that the low-temperature chemisorbed spectrum in Figure 1b closely resembles the physisorbed multilayer dose in Figure 1c, with the exception that the strong carbonyl peaks in the low-temperature chemisorbed spectrum have red-shifted approximately 70−90 cm^{-1} relative to the multilayer spectrum. Our frequency calculations predict a large red shift of the C=O stretching frequency to the low-1600's region for acetone dative-bonded to the Ge(100) surface. The observed shift of the carbonyl stretch to this region, together with the strong resemblance to the physisorbed multilayer spectrum, indicates the presence of dative-bonded acetone at low temperature. No significant Ge−H, and hence ene product, is seen in Figure 1b, indicating that the barrier for the ene reaction is inaccessible at low temperature. Thus the low-temperature peaks around 1640 cm^{-1} attributed to dative-bonded carbonyl can be ruled out as arising from a C=C bond, which would only exist if the ene product were present. No evidence is seen for a significant [2 + 2] C=O addition product in the low-temperature spectrum either, which indicates that a barrier exists for this reaction on

Controlled Reaction on a Semiconductor Surface

J. Phys. Chem. B, Vol. 105, No. 50, 2001 **12563**
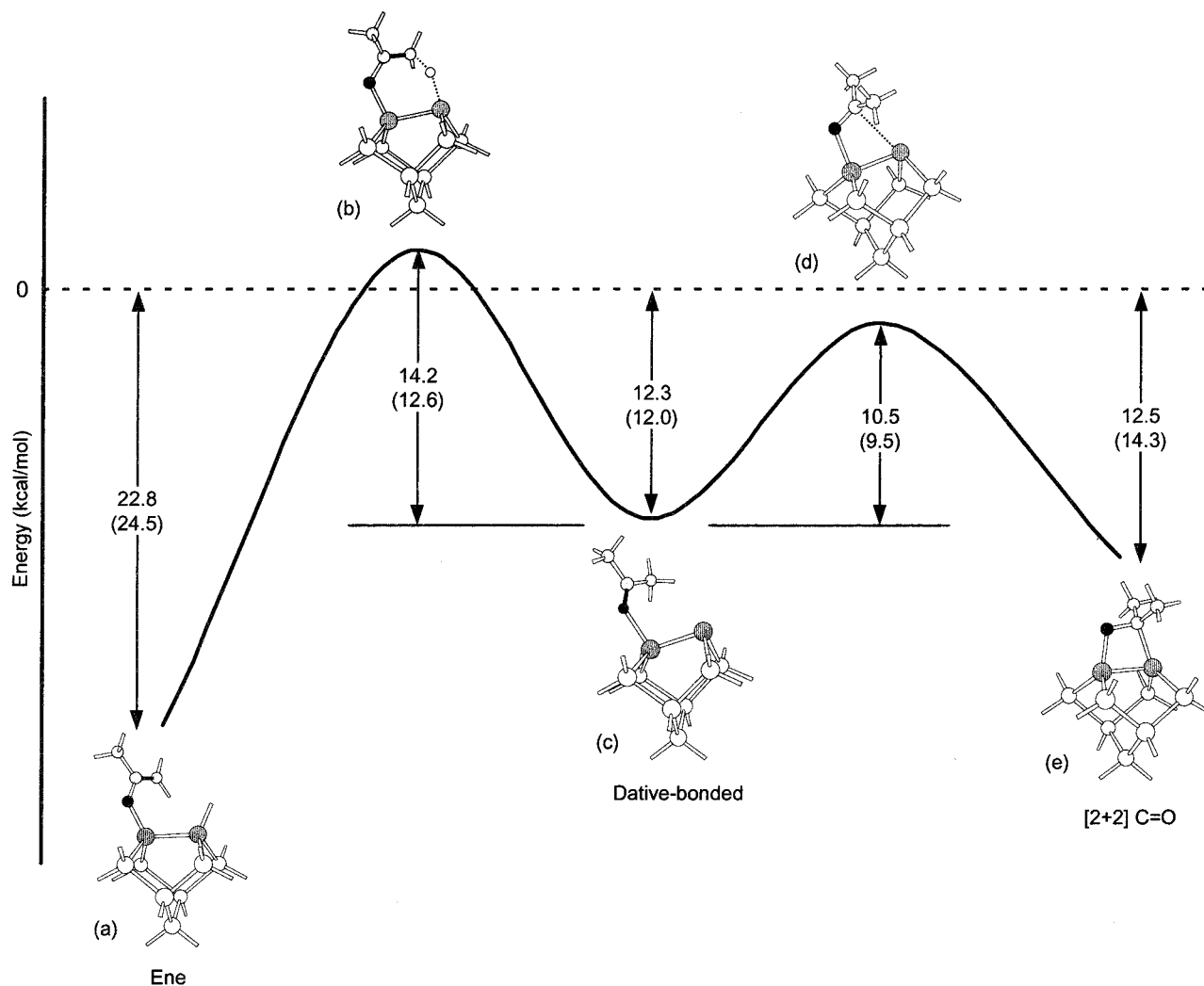
Figure 3. Reaction pathways for acetone on Ge(100)-2 × 1: (a) ene product; (b) ene transition state; (c) dative-bonded precursor state; (d) [2 + 2] C=O addition transition state; (e) [2 + 2] C=O addition product. Energies are reported in kcal/mol and were calculated using the 6-311++G(d,p) basis set, followed in parentheses by values calculated with the 6-311+G(2df,pd) basis set for comparison. The structures shown are the calculated energy-minimized geometries. The larger white and gray atoms represent Si and Ge, respectively, while the smaller black and gray atoms represent O and C, respectively. Double bonds are filled-in black.

Ge(100). There are only two small peaks at approximately 938 and 989 cm^{-1} in the low-temperature spectrum in Figure 1b that are not present in the physisorbed multilayer spectrum in Figure 1c, which could indicate a minor side product such as the [2 + 2] C=O adduct. Additionally, the intensity of the shifted C=O mode relative to the other modes in Figure 1b is similar to that in the multilayer spectrum, indicating that most if not all of the low-temperature chemisorbed product contains a perturbed C=O bond (i.e., is dative-bonded), which would not be present in the [2 + 2] C=O addition product.

While one or both of the peaks at 1638 and 1672 cm^{-1} in the room-temperature chemisorbed spectrum (Figure 1a) might also be attributed to red-shifted carbonyl stretches from a dative-bonded state, the calculated binding energy of 12 kcal/mol indicates that the dative-bonded state would not be present at this temperature. To verify experimentally that the dative-bonded state is not kinetically stable at room temperature, we tested the adsorption of a simple ether, tetrahydrofuran, on the Ge(100)-2 × 1 surface. Tetrahydrofuran was chosen because it has no obvious reaction pathways with the surface other than dative-bond formation, which we calculated to have a similar binding energy to acetone of 12 kcal/mol on Ge(100). We found

no significant adsorption of tetrahydrofuran at room temperature. Additionally, relatively high exposures (250 L) are required before adsorption of acetone on Ge(100) is observed in a significant amount at room temperature, even though dative-bond formation is a barrierless process and should be observed at low exposures, as seen in our work with amines on Si(100) and Ge(100).[18,22,27] Thus, the experimental and theoretical evidence shows that oxygen dative-bond formation is too weak to persist at room temperature on the Ge and presumably Si surfaces as well. This is in contrast to nitrogen dative bonds to Ge(100) and Si(100), which are stable at room temperature and have been calculated to have binding energies of approximately 20−27 kcal/mol.[18,22,27,34] The substantial difference in oxygen versus nitrogen dative-bond strengths can be understood from electronegativity arguments. Oxygen is more electronegative than nitrogen and thus is less willing to share its lone pair electrons. This can be seen, for example, in the stronger Lewis basicity of amines compared to alcohols and ketones.

C. Reaction Pathways. To compare the kinetics and thermodynamics of the ene and [2 + 2] C=O addition reactions, the pathways of both processes on the Ge(100)-2 × 1 surface were calculated and are shown in Figure 3. The pathways on

the Si(100) surface were also calculated and are reported along with the Ge(100) results in Table 1. Energies of the pathways on the Ge(100) surface were also calculated using the larger 6-311+G(2df,pd) basis set (shown in parentheses in Figure 3) but did not differ significantly from the reference 6-311++G(d,p) energies. The pathways are shown starting from the dative-bonded state (Figure 3c), which is the precursor for both calculated pathways and forms without barrier.

We begin with a discussion of the kinetically favored pathway, the [2 + 2] C=O addition reaction, which proceeds to the right in Figure 3. As noted earlier, the adsorption behavior of acetone on Ge(100) at low temperature indicates the existence of a finite barrier for the [2 + 2] C=O reaction. We have found a transition state for the [2 + 2] C=O addition reaction, shown in Figure 3d, which is calculated to lie approximately 2 kcal/mol *below* the vacuum level and 10 kcal/mol above the dative-bonded precursor state. A smaller barrier of 5 kcal/mol from a dative-bonded state was found on the Si(100) surface, in which the transition state is calculated to be 9 kcal/mol below the vacuum level. This is interesting because Barriocanal and Doren have recently found a barrierless pathway for [2 + 2] C=O addition that passes through a dative-bonded state for glyoxal adsorption on the Si(100) surface also using DFT cluster-model calculations.[33] We have been unable to locate pathways for acetone that proceed to the [2 + 2] C=O product without a barrier. The difference suggests that steric considerations may play a role in determining the barrier for [2 + 2] C=O addition reactions. Whereas in glyoxal the atoms are all planar, acetone contains methyl groups on both sides of the carbonyl carbon, which could sterically hinder the approach to form the [2 + 2] C=O product. Another possibility for the difference is that the C=O bonds in glyoxal are conjugated whereas in acetone the carbonyl bond is not. Conjugation may have the effect of weakening the C=O bond strength and allowing the [2 + 2] C=O addition reaction to proceed with a reduced barrier or no barrier at all.

The reaction pathway for the ene reaction on Ge(100) is shown starting with the dative-bonded state and proceeding to the left in Figure 3. After formation of a dative bond with the surface, acetone goes through a transition state (Figure 3b) which is calculated to be 2 kcal/mol *above* the vacuum level. Thus, the barrier from the precursor state is ∼14 kcal/mol, which is approximately 4 kcal/mol greater than the barrier for the [2 + 2] C=O addition reaction on the Ge(100) surface. The relatively high exposures that were needed for acetone to form the ene product provide support for the computational result that the transition states lies slightly above the vacuum level. We have noticed that the N−H dissociation reaction of amines on Si(100) is much more facile (∼5 L needed for near-saturation) compared to the ene reaction of acetone on Ge(100) (∼1000 L for near-saturation), even though the overall barrier heights for both reactions relative to their precursor states are calculated to be approximately the same (14 kcal/mol for acetone on Ge(100)-2 × 1 versus 13−15 kcal/mol for amines on Si(100)-2 × 1).[18,22] The difference is that for N−H dissociation of amines on Si(100) the transition state lies well below the vacuum level[18,22] while for the ene reaction of acetone on Ge(100), the transition state is slightly above the vacuum level. This results in the unfavorable competition of the ene reaction against reversible desorption from the dative-bonded precursor state (with a barrier of only 12 kcal/mol), which may explain the low sticking probability observed for acetone on Ge(100) at room temperature. These results indicate that the transition state energy relative to the vacuum level plays an important

role in the adsorption behavior in addition to the absolute barrier height from the precursor state.

Interestingly, the calculated transition state for the ene reaction on the Si(100) surface is almost 11 kcal/mol below that on Ge(100), as reported in Table 1. The lower energy of the transition state on Si(100) is most likely due the stronger bonds being formed with the surface relative to the Ge(100) surface. Because the dative-bonded precursor states are similar in energy on both surfaces (<2 kcal/mol apart), the ene reaction (as well as the [2 + 2] C=O addition reaction) possesses an overall lower activation barrier on Si(100) than that on Ge(100) from the precursor state (about 5 kcal/mol vs 14 kcal/mol, respectively). In general, we expect that reactions that proceed from a dative-bonded precursor state will have a lower reaction barrier on Si(100) than that on Ge(100) because the precursor states will be similar in energy on both surfaces while the transition state energy will be higher (less stable) on Ge(100) due to the weaker bonds being formed. We have recently verified this for N−H dissociation reactions of methylamines on Si(100) and Ge-(100).[27]

Another point concerning the low energy of the ene transition state on Si(100) is that it is calculated to be similar in energy to that of the [2 + 2] C=O addition transition state, as seen in Table 1, implying a similar activation barrier. This apparent discrepancy with the experiments on Si(100) by Armstrong et al.,[15] in which the ene product is not observed and is thus kinetically unfavored, could have several explanations. The simplest is that the calculated values fall within the expected error of the theory. It is also possible that the [2 + 2] C=O addition of acetone on Si(100) and even Ge(100) follows a lower barrier pathway that we have not yet located, such as the barrierless pathway calculated for glyoxal on the Si(100) surface.[33] Regardless of the calculated barriers, the adsorption of acetone on Si(100) is still a kinetically controlled process in which the ene reaction may compete kinetically to some degree. The previous data[15] on Si(100) do not show any experimental evidence of the ene product, although it is possible that it exists as a side product unobserved above the noise level.

IV. Conclusions

From the combined experimental and theoretical results, the following picture emerges that shows the reasons that the reaction of acetone on Ge(100) at room temperature is under thermodynamic control. At room temperature, the large majority of acetone molecules may proceed from the dative-bonded precursor state and undergo [2 + 2] C=O addition, which has a lower barrier than the ene reaction. However, at room temperature the [2 + 2] C=O adduct would be too weak to remain stable and will quickly undergo reversible desorption. Even though the ene reaction is kinetically unfavored compared to [2 + 2] C=O addition, the ene reaction product is stable at room temperature and is eventually the observed product after sufficient exposure of the Ge(100) surface to acetone. Because the product distribution is determined by the equilibrium position rather than the reaction kinetics, the adsorption of acetone on Ge(100) at room temperature is under thermodynamic control. In contrast, the [2 + 2] C=O reaction is preferred over the thermodynamically favored ene reaction on the Si(100) surface and hence is under kinetic control.

The results also show that the adsorption behavior of acetone on Ge(100)-2 × 1 is strongly dependent on temperature. There is evidence that the acetone ene product may undergo oxygen migration and insertion into Ge−Ge bonds, especially at elevated surface temperatures. At low temperature (∼115 K),

Controlled Reaction on a Semiconductor Surface

J. Phys. Chem. B, Vol. 105, No. 50, 2001 **12565**

there is insufficient energy to cross the barrier for either the ene reaction or the [2 + 2] C=O addition, leaving acetone in a weak but stable dative-bonded precursor state on Ge(100). Indeed, the [2 + 2] C=O product may be difficult to observe experimentally, as there is likely to be only a narrow temperature range on Ge(100) in which acetone has enough energy to cross over the [2 + 2] C=O reaction barrier and is also sufficiently stable to remain bonded in that state. In this temperature range at which the [2 + 2] C=O product is predicted to be observed, the reaction of acetone on Ge(100) would be considered to be under kinetic control.

In conclusion, we have shown that acetone undergoes a thermodynamically preferred ene reaction rather than the kinetically preferred [2 + 2] C=O addition reaction on the Ge(100)-2 × 1 surface at room temperature. To our knowledge, this is the first clear demonstration for thermodynamic control of a reaction of an organic molecule on a clean semiconductor surface that has competing pathways available to it. Thermodynamic control on the Ge(100)-2 × 1 surface is made possible by the reversibility of weak surface adsorption. On the Si(100)-2 × 1 and (most probably) diamond(100)-2 × 1 surfaces, reversibility is typically not possible because of the strong bonds formed with organic molecules, and hence, organic reactions on these surfaces will generally be under kinetic control. While not all or even most reactions will necessarily be thermodynamically controlled on the Ge(100) surface, judicious selection of the reactant molecules and careful consideration of the possible reaction pathways will allow the growth of thermally stable surface structures that are kinetically unfavorable against competing reactions. Additional control over the product distribution may be possible by the use of thermal annealing to convert surface adducts to even more thermally favored products and to eliminate weakly bound side products that are kinetically competitive. We believe that the design and realization of thermodynamically controlled reactions represent a new and potentially powerful strategy for the selective functionalization of semiconductor surfaces.

References and Notes

(1) Lopinski, G. P.; Wayner, D. D. M.; Wolkow, R. A. *Nature* **2000**, *406*, 48.

(2) Strother, T.; Hamers, R. J.; Smith, L. M. *Nucleic Acids Res.* **2000**, *28*, 3535.

(3) Hersam, M. C.; Guisinger, N. P.; Lyding, J. W. *Nanotechnology* **2000**, *11*, 70.

(4) Wolkow, R. A. *Annu. Rev. Phys. Chem.* **1999**, *50*, 413.

(5) Hamers, R. J.; Coulter, S. K.; Ellison, M. D.; Hovis, J. S.; Padowitz, D. F.; Schwartz, M. P.; Greenlief, C. M.; Russell, J. N. *Acc. Chem. Res.* **2000**, *33*, 617.

(6) Buriak, J. M. *Angew. Chem., Int. Ed.* **2001**, *40*, 532.

(7) Bent, S. F. *J. Phys. Chem. B*, submitted for publication, 2001.

(8) For a brief discussion of kinetic versus thermodynamic control, see: Solomons, T. W. G. *Organic Chemistry*, 6th ed.; John Wiley & Sons: New York, 1996; Chapter 12.

(9) Hovis, J. S.; Liu, H. B.; Hamers, R. J. *J. Phys. Chem. B* **1998**, *102*, 6873.

(10) Kong, M. J.; Teplyakov, A. V.; Jagmohan, J.; Lyubovitsky, J. G.; Mui, C.; Bent, S. F. *J. Phys. Chem. B* **2000**, *104*, 3000.

(11) Mui, C.; Bent, S. F.; Musgrave, C. B. *J. Phys. Chem. A* **2000**, *104*, 2457.

(12) Teplyakov, A. V.; Lal, P.; Noah, Y. A.; Bent, S. F. *J. Am. Chem. Soc.* **1998**, *120*, 7377.

(13) Teplyakov, A. V.; Kong, M. J.; Bent, S. F. *J. Chem. Phys.* **1998**, *108*, 4599.

(14) Lee, S. W.; Hovis, J. S.; Coulter, S. K.; Hamers, R. J.; Greenlief, C. M. *Surf. Sci.* **2000**, *462*, 6.

(15) Armstrong, J. L.; White, J. M.; Langell, M. *J. Vac. Sci. Technol., A* **1997**, *15*, 1146.

(16) Kong, M. J.; Lee, K. S.; Lyubovitsky, J.; Bent, S. F. *Chem. Phys. Lett.* **1996**, *263*, 1.

(17) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.5; Gaussian, Inc.: Pittsburgh, PA, 1998.

(18) Mui, C.; Wang, G. T.; Bent, S. F.; Musgrave, C. B. *J. Chem. Phys.* **2001**, *114*, 10170.

(19) Konecny, R.; Doren, D. J. *Surf. Sci.* **1998**, *417*, 169.

(20) Choi, C. H.; Gordon, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 11311.

(21) Fitzgerald, D. R.; Doren, D. J. *J. Am. Chem. Soc.* **2000**, *122*, 12334.

(22) Wang, G. T.; Mui, C.; Musgrave, C. B.; Bent, S. F. *J. Phys. Chem. B* **2001**, *105*, 3295.

(23) Mui, C.; Musgrave, C. B. Unpublished results.

(24) Kuhr, H. J.; Ranke, W. *Surf. Sci.* **1987**, *189*, 420.

(25) Ranke, W. *Surf. Sci.* **1995**, *342*, 281.

(26) Ranke, W.; Platen, J. *Phys. Rev. B* **1996**, *54*, 2873.

(27) Mui, C.; Han, J. H.; Wang, G. T.; Musgrave, C. B.; Bent, S. F., Manuscript in preparation.

(28) Armstrong, J. L.; Pylant, E. D.; White, J. M. *J. Vac. Sci. Technol., A* **1998**, *16*, 123.

(29) Weldon, M. K.; Stefanov, B. B.; Raghavachari, K.; Chabal, Y. J. *Phys. Rev. Lett.* **1997**, *79*, 2851.

(30) Stefanov, B. B.; Raghavachari, K. *Appl. Phys. Lett.* **1998**, *73*, 824.

(31) Queeney, K. T.; Chabal, Y. J.; Weldon, M. K.; Raghavachari, K. *Phys. Status Solidi A* **1999**, *175*, 77.

(32) Weldon, M. K.; Queeney, K. T.; Gurevich, A. B.; Stefanov, B. B.; Chabal, Y. J.; Raghavachari, K. *J. Chem. Phys.* **2000**, *113*, 2440.

(33) Barriocanal, J. A.; Doren, D. J. *J. Am. Chem. Soc.* **2001**, *123*, 7340.

(34) Widjaja, Y.; Mysinger, M. M.; Musgrave, C. B. *J. Phys. Chem. B* **2000**, *104*, 2527.