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Cycloaddition Chemistry of Organic Molecules with Semiconductor Surfaces

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ABSTRACT

Recent investigations have shown that cycloaddition reactions, widely used in organic chemistry to form ring compounds, can also be applied to link organic molecules to the (001) surfaces of crystalline silicon, germanium, and diamond. While these surfaces are comprised of Si═Si, Ge═Ge, and C═C structural units that resemble the C═C bonds of organic alkenes, the rates and mechanisms of the surface reactions show some distinct differences from those of their organic counterparts This article reviews recent studies of [2 + 2], [4 + 2] Diels−Alder, and other cycloaddition reactions of organic molecules with semiconductor surfaces and summarizes the current understanding of the reaction pathways.

Introduction

The Group IV semiconductors Si, Ge, and C (diamond) are of great interest because of their widespread use as the starting point for microelectronic devices. Additionally, new fields of science and engineering are emerging which seek to leverage the knowledge obtained from microelectronics processing, while pushing into new directions. Examples include molecular electronics and the "bio chip", in which biological molecules attached to surfaces of silicon or other materials serve as a means of sequencing DNA and/or identifying other biological species. Because the (001) crystal face of silicon is the starting point for almost all integrated circuits used for microprocessors and memory chips, understanding the chemistry of this surface has particular importance.

The (001) crystal faces of Si, Ge, and C (diamond) all share a common bonding motif in which adjacent atoms pair together into dimers, as illustrated in Figure 1a (top view) and b (side view). Formally, at least, the bonding within these dimers can be described in terms of a strong σ bond and a weak π bond. In this picture, there are some obvious analogies that, in principle, can be drawn between the double bonds of the surface atoms and the C═C double bonds of alkenes. In reality, however, the picture is more complex. While the covalent bonding at the surface is most easily described using the concept of Si═Si, Ge═Ge, or C═C double bonds (Figure 1c),[1] the π bonds of Si(001) and Ge(001) are quite weak, suggesting that these dimers might be better thought of as a diradical with each Si atom having a single unpaired electron (Figure 1d).[2] To further complicate the issue, we note that it is widely recognized that the dimers of the Si(001) and Ge(001) surfaces can tilt; associated with the dimer tilting is a charge transfer from the "down" atom to the "up" atom, thereby adding zwitterionic character to the dimers (Figure 1e).[3] Electron correlation effects can also play an

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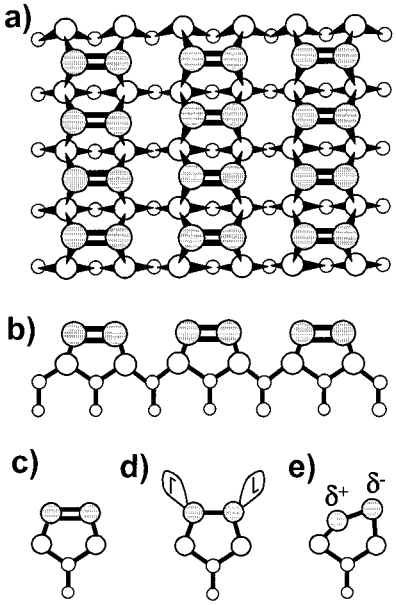

FIGURE 1. Schematic illustration of the Si(001) surfaces. (a) Top view. Gray atoms represent Si═Si dimers in the topmost layers. Deeper layers are depicted with smaller circles. (b) Side view. Surface dimers are depicted in gray. (c) Covalent bonding picture of Si═Si dimer. (d) Singlet diradical picture of Si═Si dimer. (e) Zwitterionic character of tilted Si═Si dimer.

important role in controlling dimer tilting.[4,5] It is likely that none of the above models are perfect descriptions of the bonding at these surfaces, but rather that the bonding has characteristics of all three models. Despite their oversimplified nature, these models have provided a great deal of insight into how the atomic structure of the Si(001) surface controls the rates and pathways of chemical reactions of importance in microelectronics manufacturing.[6]

A great deal of interest has developed recently in understanding the reactions of *unsaturated organic* compounds with Group IV semiconductor surfaces. Early studies by a number of groups showed that ethylene and acetylene can bond to the Si(001) surface in a geometry known as the "di-σ" configuration, as depicted for ethylene in Figure 2a.[7−15] This adsorption process can be viewed as utilizing two electrons from the π bond of one Si═Si dimer and two electrons from the π bond of the ethylene molecule to form two new strong Si−C bonds. There were several intriguing aspects of such a reaction that caught our attention. First and foremost is that this reaction is analogous to a concerted [2 + 2] cycloaddition reaction. In organic chemistry, such reactions are symmetry-forbidden because the nodal character of the molecular orbitals formed in the highest-symmetry suprafacial−suprafacial approach geometry corresponds to an excited electronic state of the product.[16] Consequently, simple [2 + 2] reactions (such as the reaction of two ethylene molecules to form cyclobutane) are extremely slow at room temperature. Surprisingly, however, the analogous reaction of ethylene with the Si═Si dimers of the Si(001) surface was known to be facile at room temperature.[7,17]

By exploring to what extent reactions known from organic chemistry could serve as guides in understanding

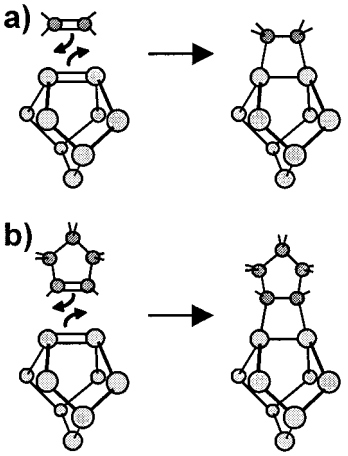

FIGURE 2. (a) Adsorption of ethylene onto Si(001) to form "di-σ"-bonded product, analogous to a [2 + 2] cycloaddition reaction. (b) Adsorption of cyclopentene onto Si(001) via a [2 + 2] pathway.

reactions of organic molecules with Si, Ge, and diamond surfaces, we hoped to gain new insight into a wide class of surface reactions. We were further intrigued by the fact that, while reactions of most saturated organic molecules with Si, Ge, and C surfaces involve large thermal activation barriers associated with cleavage of C−C or C−H bonds, cycloaddition reactions of unsaturated organic molecules do not require any bond cleavage. This suggests that they may be more facile at room temperature and may minimize fragmentation and side reactions, possibly resulting in new strategies for chemical functionalization of silicon, germanium, and diamond surfaces suitable for attachment of complex or unusually sensitive molecules.

During the last several years our research has centered on understanding the interaction of unsaturated organic molecules with the silicon(001) surface and testing our understanding with comparative studies on Ge(001) and C(001) (diamond). From a fundamental standpoint, we desire to understand the nature of cycloaddition reactions on semiconductor surfaces and to understand to what extent the reactions are analogous to those in organic chemistry. From a more practical standpoint, we are interested in developing new strategies for forming well-defined interfaces between silicon and a wide range of organic materials. Here we review some of the latest research aimed at understanding cycloaddition reactions at surfaces and the implications for controlled functionalization of semiconductor surfaces. Experimental results presented here utilize scanning tunneling microscopy (STM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS).[18]

[2 + 2] Cycloaddition Reactions of Simple Alkenes

Our initial investigations of [2 + 2] cycloaddition reactions focused on the molecule cyclopentene as a model system.[18] Figure 3a shows a scanning tunneling microscopy (STM) image obtained at a low surface coverage, where the individual cyclopentene molecules and the underlying Si═Si dimers can both be observed. STM images such as

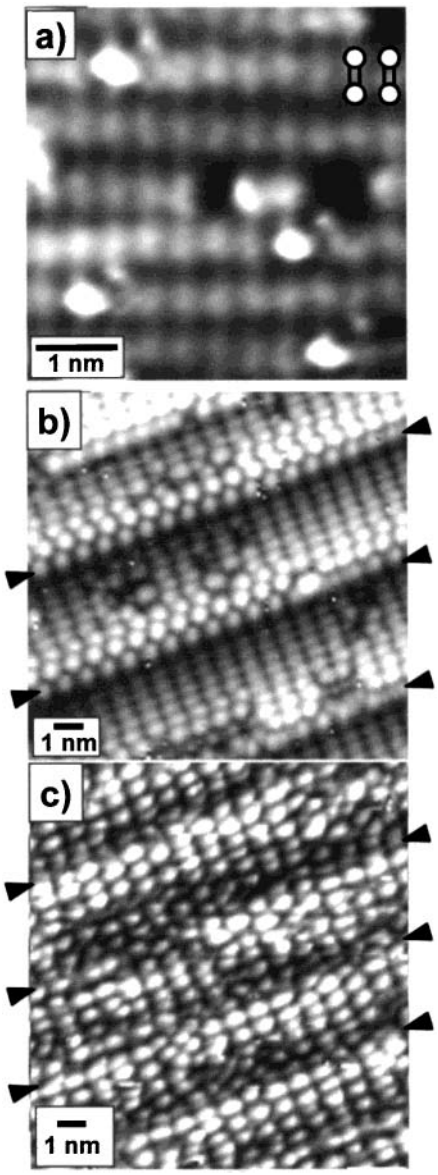

FIGURE 3. (a) High-resolution STM image showing individual cyclopentene molecules (bright spots) and Si═Si dimers (gray ovals). (b) "Vicinal" Si(001) surface showing several terraces separated by steps. Arrows indicate positions of step edges. Each oval structure is a Si═Si dimer. (c) STM image of vicinal Si(001) surface after exposure to cyclopentene. Each oval protrusion is a single cyclopentene molecule.

this reveal important information about the symmetry of molecular bonding sites. Figure 3a, for example, shows that each cyclopentene molecule appears as a protrusion occupying the space of approximately one dimer, located along the center of the dimer rows. More detailed confirmation of the bonding geometry has been obtained from surface infrared spectroscopy.[18] For cyclopentene on Si(001), FTIR spectra reveal that the high-frequency alkene C−H stretching mode is eliminated upon surface adsorption, and no evidence for C−H bond cleavage is observed. Combined with other evidence from STM and XPS, the experiments confirm the geometry of Figure 2b.

One of the unique aspects of the [2 + 2] cycloaddition chemistry is that it involves the interaction of *two* directional bonds. Consequently, the Si(001) surface acts as a template both for the translational order of the molecules and also for their *orientation*. We are interested in controlling molecular orientation at interfaces because oriented molecular ensembles often have unusual optical and electronic properties. To control the molecular orientation on *macroscopic* length scales, it is necessary to use "vicinal" silicon surfaces in which the surface is oriented a few degrees away from the (001) crystal axis. Figure 3b shows a clean, vicinal Si(001) surface; the STM image reveals terraces containing oval-shaped Si═Si dimers, with steps (each two atomic layers high) at the locations of the arrows. Figure 3c shows a complete monolayer of cyclopentene molecules after bonding to the surface. In this image, each molecule appears as a protrusion, elongated parallel to the direction of the underlying Si═Si dimer bonds. The molecules are clearly observed to form a highly ordered, two-dimensional array, in which the ordering and orientation are controlled by the Si═Si dimers of the underlying Si(001) substrate.

The [2 + 2] cycloaddition chemistry also can be used to attach more complicated molecules. The molecule 1,5-cyclooctadiene (COD),[20] shown in Figure 4a, for example, has two C═C groups separated by 3.2 Å. STM images (Figure 4b) show that the molecules attach to the surface, forming a highly ordered monolayer film of oriented molecules. At the highest resolution (Figure 4c), one can even resolve internal structure within each molecule. Infrared spectroscopy (Figure 4d) clearly shows a strong alkene C−H stretching vibration near 3020 cm^{-1}, demonstrating that only one of the two C═C double bonds is used in attaching to the surface. Thus, the surface imaged in Figure 4b and c is essentially an ordered array of C═C double bonds! The well-defined orientation of the attached molecules leads to large anisotropy in optical properties. In Figure 4d, the optical anisotropy can be observed as rather pronounced differences between infrared spectra obtained with the electric field of the light parallel to the Si═Si dimer bonds and those obtained with the electric field vector perpendicular to the Si═Si dimer bonds of the underlying substrate.

In subsequent studies, we found that other alkenes could attach to Si(001) surfaces in an analogous manner. In general, molecules with high symmetry such as cyclopentene,[18] 1,5-cyclooctadiene,[20] and 1,3,5,7-cyclooctatetraene[21] (an antiaromatic molecule) bonded in a unique geometry, forming ordered arrays of oriented molecules. In these cases, STM and FTIR experiments indicated that most or all of the molecules bonded in a [2 + 2] geometry. In some more complex molecules such as norbornadiene[22] and 3-pyrroline,[22,23] multiple bonding geometries were detected. In these cases, attempts to control the distribution of products by heating the sample led to molecular fragmentation before significant interconversion was achieved. We conclude from this that the great strength of the Si−C bonds makes the overlayers quite stable, even though they involve formation of a four-member ring at the Si−C interface. The stability of Si−C bonds also has

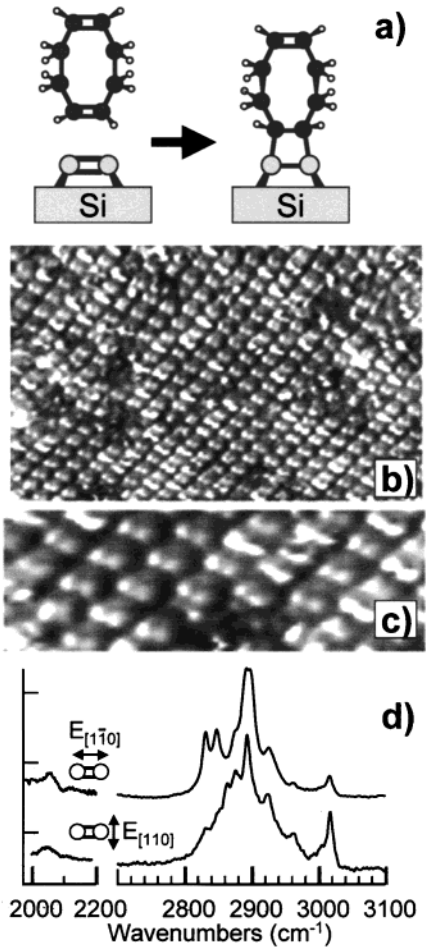

FIGURE 4. (a) 1,4-Cyclooctadiene (COD) adsorption onto Si(001) surface. (b) STM image of COD bonded to Si(001) surface, showing adsorption into ordered rows. (c) High-resolution image of COD bonded to Si(001), showing internal structure of each molecule. (d) FTIR spectra of COD adsorbed on vicinal Si(001) surface, showing s-polarized spectra obtained with the electric field parallel to and perpendicular to the Si═Si dimer bond.

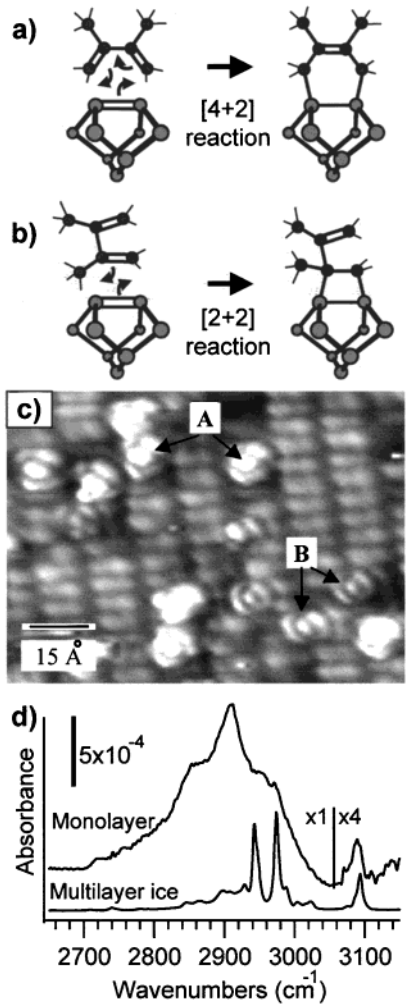

FIGURE 5. (a) [4 + 2] reaction of 2,3-dimethyl-1,3-butadiene (DMBD) with Si(001) surface. (b) [2 + 2] reaction of DMBD with Si(001) surface. (c) STM image of DMBD on Si(001) showing multiple reaction products. (d) FTIR spectrum of DMBD chemosrbed on Si-(001) and DMBD condensed "ice". Note the residual alkene C−H stretch due to [2 + 2] side product in the spectrum of chemisorbed DMBD.

implications for controlling selectivity in surface cycloaddition reactions, as will be discussed below.

Virtually all studies of simple alkenes have found that their interaction with the Si(001) surface is quite facile,[7−15,17−25] despite the fact that the analogous reaction of two organic alkenes is forbidden in the high-symmetry suprafacial−suprafacial approach.[16] Furthermore, experiments have shown that the molecular stereochemistry is preserved throughout the reaction, thereby ruling out the suprafacial−antarafacial and radical mechanisms.[16,25] To understand why the analogous surface reactions occur so readily, we investigated other types of cycloaddition reactions and also extended our studies to other Group IV semiconductors.

[4 + 2] Diels−Alder Reactions at Silicon Surfaces

One of the most common types of cycloaddition reaction in organic chemistry is a [4 + 2], or "Diels−Alder" reaction, in which a molecule containing two conjugated double bonds (a "conjugated diene") reacts with a simple alkene (a "dienophile") as depicted in Figure 5a, to form a six-member ring. Figure 5 depicts the interaction of a prototypical alkene, 2,3-dimethyl-1,3-butadiene (DMBD), with a Si═Si dimer via a [4 + 2] process (Figure 5a) and also via a [2 + 2] process involving only one C═C bond (Figure 5b). Because [4 + 2] reactions are symmetry-allowed while [2 + 2] reactions are symmetry-forbidden, most organic molecules in solution show a high degree of selectivity for the [4 + 2] reaction. Additionally, the [4 + 2] product is expected to be more stable thermodynamically because it forms a six-member ring at the interface, while the [2 + 2] reaction is predicted to form a more highly strained four-member ring.[26−28] The product of a Diels−Alder reaction of DMBD with Si(001) was detected in infrared spectroscopy studies by Teplyakov, Kong, and Bent.[29] However, our FTIR and STM studies of DMBD and a related molecule, 1,3-cyclohexadiene (CHD), showed that, while in both cases the [4 + 2] process was

indeed the predominant pathway, very substantial quantities of the [2 + 2] adduct were *also* formed. For example, Figure 5c shows an STM image of DMBD in which the Si═Si dimers and the two distinguishable surface products are visible. Additionally, infrared spectra showed a clear high-frequency alkene-like C−H stretching vibration that should not be observed for the [4 + 2] reaction (Figure 5a) but is expected for the [2 + 2] reaction (Figure 5b). Counting the number of different types of molecular adsorption features observed in STM showed that for DMBD ~80% of the molecules reacted via a [4 + 2] mechanism ("A" features in Figure 5c), while ~20% reacted via a [2 + 2] process ("B" features in Figure 5c). Since the Diels−Alder reaction requires the double bond to be in a cis configuration, we attempted to improve the selectivity by using 1,3-cyclohexadiene. Even though the ring structure of this molecule keeps it in the cis configuration, selectivity toward the Diels−Alder product was even poorer than that for DMBD.[19] For both DMBD and CHD, attempts to convert the product distribution to the most thermodynamically stable product by annealing to higher temperatures failed. Heating DMBD to 420 K yielded no significant change in the product distribution, and heating to higher temperatures led to obvious C−H bond cleavage. Given that for more typical reactions of organic compounds the symmetry-allowed [4 + 2] reactions take place much more quickly than [2 + 2] reactions, the *absence* of comparable selectivity for the analogous surface reactions is somewhat surprising.

Several conclusions can be drawn from these studies of conjugated dienes. First, they show that the product distributions are not controlled by the overall thermodynamics but are controlled by the adsorption *dynamics*. Second, they show that the high strength of the Si−C bond effectively prevents the molecules from sampling the entire potential energy surface; this in turn inhibits the ability to find the thermodynamically most stable bonding configuration. Finally, they show that the high selectivity favoring [4 + 2] over [2 + 2] that is predicted by Woodward−Hoffmann symmetry rules for a high-symmetry reaction pathway does not hold for the analogous reactions on silicon (001) surfaces.

Cycloaddition Reactions on Ge and Diamond Surfaces and Mechanistic Implications

Experimental measurements on Si(001) surfaces show that cycloaddition reactions occur in a surprisingly facile way. The "reactive sticking probability" (the probability that a gas-phase molecule undergoing a single collision with the surface will react) of cyclopentene, for example, is nearly unity on Si(001). Since Ge(001) and diamond(001) surfaces likewise consist of Ge═Ge and C═C dimers,[30,31] a comparison of the reactions on all three surfaces may provide some useful insights into the mechanistic pathways. The diamond(001) surface provides a particularly important connection between the surface studies and reactions of more conventional organic alkenes. Figure 6a shows the FTIR spectra of cyclopentene adsorbed onto Si(001), Ge-(001), and diamond(001) surfaces.[18,31,32] On all three surfaces, the absence of high-frequency stretching vibrations at >3000 cm^{-1} indicates that cyclopentene reacts using its alkene group to bond in a [2 + 2] configuration. By measuring the increase in vibrational intensity with increasing exposure, it was determined that the sticking probability for cyclopentene is approximately unity on Si, ~0.1 on Ge, and on the order of 10^{-3} on the diamond-(001) surface.[32]

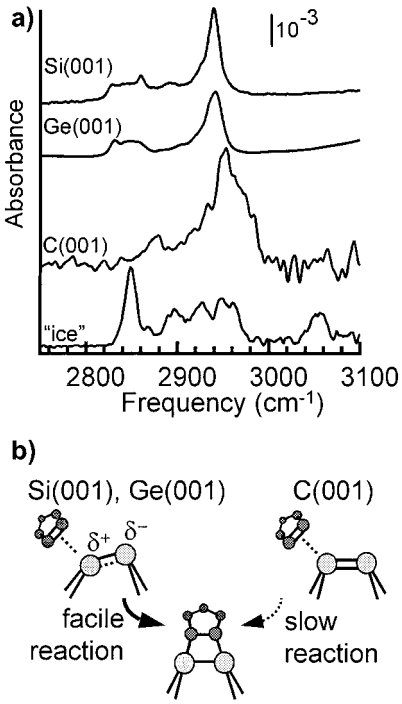

FIGURE 6. (a) FTIR spectra of cyclopentene on (001) surfaces of diamond, germanium, and silicon. Note the absence of alkene C−H stretching modes on all three surfaces. (b) Schematic illustration of how the low-symmetry pathway for adsorption on Si(001) and Ge-(001) surfaces is facilitated by dimer tilting, while the absence of dimer tilting on diamond(001) leads to a much lower reaction probability.

Germanium(001) surfaces also undergo [4 + 2] reactions with conjugated dienes.[32−34] While the potential presence of [2 + 2] side products has not been quantitatively evaluated on Ge, the Diels−Alder reaction on Ge-(001) is partially reversible, as evidenced by the fact that intact diene molecules can be desorbed from the surface at elevated temperature.[33] Similarly, ethylene will desorb intact from Ge(001).[31,35] Both of these studies are consistent with the idea that Ge−C bonds are weaker than Si−C bonds. Overall, the studies show that Ge(001) and Si(001) show similar reactivities in [2 + 2] reactions, with Ge interacting more weakly than Si(001); in contrast, C(001) shows substantially lower reactivity in [2 + 2] reactions.

The kinetic barrier associated with "forbidden" [2 + 2] cycloaddition reactions is normally expected to depend strongly on the $\pi-\pi^*$ splitting of reactants.[16] The relative reaction rates of diamond ≪ Ge < Si correlates (negatively) with the ordering of $\pi-\pi^*$ surface-state band gaps of 350 kJ/mol for diamond(001),[36] 140 kJ/mol for Ge(001),[37] and ~110 kJ/mol for Si(001) [38] However, ab initio calculations

show that the high-symmetry approach is repulsive on all three surfaces.[32] We believe that the unique *geometry* of the surface dimers plays a critical role in controlling reactivity. The bonds between the dimers and the underlying bulk are bent away from planarity, causing the empty π^* orbital at the dimer ends to be accessible to nucleophilic reactants. Ab initio calculations show that cyclopentene can bond to Si(001) and Ge(001) surfaces with little or no barrier through a low-symmetry pathway, as depicted in Figure 6b.[28,32,39] On Si and Ge the low-symmetry pathway is facilitated by the ability of Si═Si and Ge═Ge dimers to tilt out of the surface plane, transferring electron density from the "down" atom to the "up" atom of the dimer. On C(001), however, no dimer tilting is present initially,[32] and none is induced by nearby alkenes. We believe that the absence of dimer tilting on C(001) is largely responsible for its lower reaction probability in [2 + 2] reactions.

The most important conclusion from these studies is that the surface [2 + 2] cycloaddition reactions do *not* take place via a concerted, high-symmetry pathway. Instead, the reactions are better described as nucleophilic addition reactions between the electron-rich C═C alkene bond and the electron-deficient ends of the dimers, further facilitated on Si and Ge by the substantial dimer tilting on these surfaces. Because the [2 + 2] reactions are so facile, there is little preference for [4 + 2] over [2 + 2] mechanisms, leading to poor selectivity with conjugated dienes. Recent calculations confirm this very picture for the [2 + 2] and [4 + 2] reactions of 1,3-cyclohexadiene at a high level of theory.[28]

[2 + 2] Cycloadditions on Si(001) Involving Other Unsaturated Groups

In principle, coupling of organic molecules to Si(001) can take place using a variety of other unsaturated functional groups such as azo (N═N), isothiocyanate (N═C═S), and carbonyl (C═O) groups. FTIR and XPS studies of azo-*tert*-butane showed that this molecule bonds almost exclusively via a [2 + 2] reaction through the N═N bond, forming a four-member Si_2N_2 ring at the interface (Figure 7a).[40]

The [2 + 2] cycloaddition chemistry of oxygen-containing compounds such as isocyanate groups is complicated due to the propensity of oxygen to insert into Si—Si bonds. In biacetyl the carbonyl (C═O) group bonds to silicon(001) by forming a four-member Si_2CO ring, but adsorption is accompanied by decomposition.[41] Likewise, we have found that oxygen-containing species such as phenyl isocyanate and furan commonly fragment upon bonding to the Si(001) surface. In contrast, however, the corresponding *iso*thiocyanate groups, in which S replaces O, give rise to well-defined attachment chemistry. For example, methyl isothiocyanate and phenyl isothiocyanate both attach almost exclusively through the N═C═S group.[42] XPS measurements confirm that the bonding occurs through the N═C bond as depicted in Figure 7b. The differences in behavior between oxygen and sulfur can be

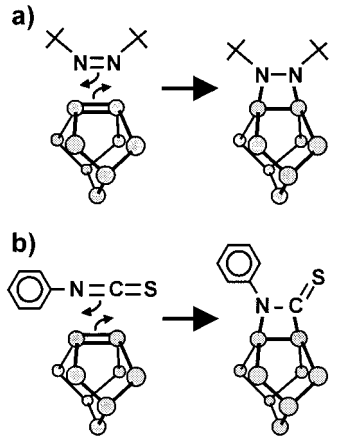

FIGURE 7. Schematic of [2 + 2] cycloaddition reactions of azo-*tert*-butane and phenyl isothiocyanate.

rationalized on the basis of the smaller Si—S vs Si—O electronegativity differences, as well as physical size: oxygen is small enough that it can insert readily into Si—Si bonds, while the much larger sulfur atom cannot be physically accommodated within the Si lattice. This, in turn, leads to greater selectivity in the attachment chemistry for the isothiocyanate functionality.

Selectivity in Surface Attachment: The Role of Aromaticity

Ideally, one would like to be able to use cycloaddition reactions to attach a wide variety of more complex organic molecules to surfaces of Si, Ge, and diamond. The molecule 3-pyrroline, for example, has a C═C double bond and an amine group, and bonding to Si(001) occurs both via the C═C group and via direct nucleophilic attack of the nitrogen atom to the Si═Si dimer.[22] Controlling the selectivity in attachment of molecules having multiple functional groups to Si(001) surfaces is inherently difficult because the kinetic rates are very fast and the high strength of Si—C, Si—O, and Si—N bonds makes the reactions essentially irreversible.

Most unsaturated molecules containing more than one functional group tend to react via multiple pathways. However, functionalized *aromatic* systems present one potentially important exception to this rule. While adsorption of simple alkenes and dienes on Si(001) is essentially irreversible, benzene has been shown to adsorb and desorb *reversibly*[43] and is even able to migrate from one bonding configuration to another at 300 K.[44−49] The remarkable stability of benzene arises from its ability to delocalize its electrons. When benzene is adsorbed onto the Si(001) surface, however, the aromaticity is lost.[44−50] This loss of aromaticity can be observed very clearly through infrared spectroscopy.[49] Figure 8 shows FTIR spectra for liquid benzene and for benzene, toluene-d_3, *p*-xylene-d_6, and styrene-d_3 adsorbed on the Si(001) surface.[49,50] While the spectrum of liquid benzene has C—H vibrational modes only above 3000 cm^{-1}, the spectra for benzene, toluene-d_3, and *p*-xylene-d_6 on Si(001) all show new, low-frequency modes near 2850−2950 cm^{-1}. These

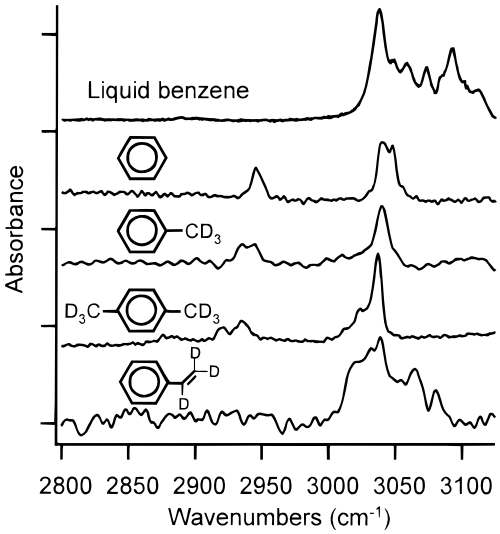

FIGURE 8. Infrared spectra of liquid benzene, and of benzene, toluene-d_3, *p*-xylene-d_6, and styrene-d_3 chemisorbed onto the Si-(001) surface. In each case the side groups are deuterium labeled, so the FTIR spectra represent C−H vibrational modes of the ring only. Note the appearance of low-frequency alkane-like C−H vibrations for benzene, toluene, and *p*-xylene, but not for styrene.

new modes arise from direct bonding of the aromatic ring to Si(001), which creates new alkane-like stretches due to loss of aromaticity and donation of electron density from Si to C, lowering the C−H vibrational force constant. Additionally, the FTIR spectra show that bonding of benzene, toluene, and *p*-xylene to the surface eliminates the high-frequency vibrational modes above 3060 cm^{-1} that are present in the intact benzene molecule. While the exact bonding geometry of these aromatic molecules remains uncertain,[44−49] polarization-dependent infrared spectra of these molecules on vicinal Si(001) surfaces showed that the molecules are strongly oriented with respect to the crystallographic axes.[49] The infrared spectra of *o*-, *m*-, and *p*-xylene (with methyl groups deuterated in all cases) also showed characteristic differences that might be expected if the methyl groups are able to "steer" the benzene molecules toward particular bonding configurations. However, they may also simply reflect differences in the intrinsic symmetry of the molecules. Understanding the role of steric blocking groups and other "substituent effects" in controlling cycloaddition reactions on surfaces is an area of continuing interest.

Finally, Figure 8 also shows the spectrum of styrene-d_3.[50] Notably, this molecule does not show any evidence for low-frequency modes in the 2800−3000 cm^{-1} region, but it does show very high-frequency vibrational modes above 3050 cm^{-1} that are similar to those observed for the intact benzene molecule. Both of these pieces of evidence indicate that adsorption occurs almost exclusively through the vinyl group and not through the aromatic ring; more extensive studies using various isotopic derivatives further support this conclusion.[50] The ability of functionalized aromatic molecules such as styrene and phenyl isothiocyanate to bind selectively through the external substituent can be attributed in part to the unusual stability of free aromatic ring systems. Surprisingly, however, ab initio calculations predict that the energy differences between bonding through the aromatic ring and bonding through the external substituent group are small, largely because bonding of the aromatic system in the "tight-bridge" configuration can form four Si−C bonds at the surface,[45] while bonding through the vinyl or N=C=S groups forms only two bonds to the surface. We believe that the observed selectivity arises in large part from the dynamics of the molecule-surface interaction. Specifically, our calculations suggest that interactions between the dimers and the external substituents (vinyl groups, isothiocyanate group, etc.) can be attractive at relatively large molecule−surface separations, thereby preferentially "steering" these substituent groups toward the Si=Si dimers. Understanding selectivity in these systems will likely require a more detailed understanding of the dynamics of the molecule−surface interactions.

Summary

Concepts from organic chemistry provide a useful starting point for understanding the chemistry of Si(001), Ge(001), and diamond(001) surfaces. However, these surfaces also show reactivies that are significantly different from those of more conventional alkenes and disilenes, due largely to the unique geometric deformations at the surface. We anticipate that further studies aimed at understanding how other concepts from organic chemistry can be applied to reactions at semiconductor surfaces will continue to be a fruitful area of research.

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