Functionalization of semiconductor surfaces by organic layers: Concerted cycloaddition versus stepwise free-radical reaction mechanisms

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Abstract

In the age when the miniaturization trend that has driven the semiconductor industry is reaching its limits, organic modification of semiconductors is emerging as a field that could give much-needed impetus. We review the current state of understanding of the functionalization of C(100), Si(100), and Ge(100) surfaces through chemisorption of alkenes and alkynes, focussing on adsorbate structural control. While reactions on C(100) show most of the properties expected for concerted cycloaddition reactions such as [2+2] and [4+2] (Diels-Alder) processes, reactions on Si(100) present a wide range of variant behaviour, including in some cases the prominence of non-cycloaddition products. More general stepwise free-radical addition processes are seen to provide a better description of reactions on Si(100), their prominence being attributed to either the non-existence or ineffectiveness of π bonding within surface silicon dimers. The investigations of these systems provide not only insight into driving mechanisms for chemisorption but also motivation for the development of new techniques of organic functionalization on semiconductors.

1. Introduction

Over the decades there has been a great interest in the Group IV semiconductors because of their widespread use as the building blocks for microelectronic devices. Silicon is at present the most technologically important material and closely related germanium, diamond, and gallium arsenide also play important roles in the microelectronics industry. The rapid miniaturization trend that has driven and revolutionized the technology, however, is facing challenges. As the size of active elements in a device approaches nanometer dimensions, it follows that the functionality of the device will increasingly rely on the processes that take place on the scale of just a few atomic layers in an interface. Therefore, the interfacial chemistry research on semiconductor surfaces is certain to become an increasingly important field.

A particularly promising line of research seems to be the organic functionalization of semiconductors, that is, the modification of semiconductor surface via the deposition of layers of organic molecules. The motivation for the incorporation of organic material at a semiconductor surface is to endow the semiconductor device with desirable properties of the organic material. Given the wealth of structures, sizes, and composition of organic molecules, the combination of organic materials with conventional semiconductors provides an opportunity to create hybrid devices that offer new possibilities for electronic, optical, and mechanical functions. Such hybrid materials are being investigated for use in molecular electronics, computing, nonlinear optics, thin-film displays, lithography and for device implantation.

In recent years much progress has been made in the development of new methodologies for the generation of organic/semiconductor interfaces and in understanding of the mechanisms that govern the attachment reactions at the surface. The majority of the studies have focussed on the basic principles of attachment and bonding at the surface. This, and the great deal of knowledge acquired regarding the nature of the semiconductor surface, is providing the foundation for the development of future applications.

The focus of this Chapter is on understanding and controlling molecular adsorption of alkenes and alkynes on semiconductor surfaces. The goal is to provide a microscopic insight into the structure and bonding of the organic/semiconductor interface. Selected examples are used to illustrate general principles of the chemistry at semiconductor surface in an effort to suggest ways that will allow the hybrid properties of organic/semiconductor interfaces to be utilized. Control of surface adsorbate structure is a central issue. In particular, the usefulness of the picture of these reactions as being concerted cycloaddition reactions, say of the classic [2+2] or [4+2] (Diels-Alder) type, as opposed to stepwise free-radical reactions, is analysed. These two views of the reaction mechanisms are similar but differ fundamentally in terms of the way the reconstructed surface dimers are viewed: are they or are they not effectively π bonded? They lead to different, experimentally testable, predictions for reaction kinetics and reaction products. In order to perform our analysis, we review in detail the nature of the semiconductor surfaces, and the detailed experimental and computational evidence that illuminates the chemisorption kinetics and products.

2. The semiconductor surfaces

Silicon is the predominant semiconductor material in the microelectronics industry. It is commercially available in the form of silicon wafers of high purity. The Si(100) and Si(111) surfaces are the most common orientations and most important for industrial applications and therefore, for understanding the chemistry of these surfaces, has particular importance. Both the surfaces undergo reconstruction, producing surface atomic geometries that differ markedly from that of the bulk [1,2]. The (100) crystal faces of silicon, germanium, and diamond share a common bonding motif in which neighboring atoms pair up to form the so-called dimers along the [110] crystal direction and dimer rows along [1$\underline{1}$0], which are separated by troughs. Such a surface is illustrated in Fig. 1a. The new structure is referred to as Si(100)-(2x1), where (2x1) designates the doubled size of the unit cell relative to the unreconstructed surface. The Si(111) surface exhibits a complex (7x7) reconstruction which contains 49 surface atoms per unit cell.

a)   b)   c)

Figure 1: Models of the silicon (100) surface. (a) The clean reconstructed Si(100)-(2x1) surface lined with rows of symmetric dimers. (b) The tilted-dimer model of the surface. Note that the actual periodicity is c(4x2). (c) The monohydride-passivated Si(001)-(2x1)-H surface, Dimers are symmetrized upon hydrogen adsorption.

The Si(100)-(2x1) dimers are often thought of as being connected via a double bond, i.e. a σ and a π bond [2]. Scanning tunnelling microscopy (STM) images of the surface reveal occupied and empty electronic states having the symmetry properties that correspond to π orbitals as the highest-occupied and lowest-unoccupied electronic states [3]. The advantage of this picture is that analogies between the dimer bond and molecule double bonds, such as C=C in alkenes, can be drawn; as their reactivity is very well categorized in terms of symmetry-controlled concerted cycloaddition reactions [4], it is tantalizing to consider whether such simple correlations also hold for surface chemistry [5]. In general, it is known that π bonding in silicon compounds is weak [6-8], and the STM results can also be interpreted in terms of independent isolated silicon free radicals rather than as π bonds. If this is indeed the case, then cycloaddition reaction mechanisms would be thwarted, as discussed in detail later in Section 4.

An additional complication affecting silicon surface chemistry is the well-established fact that dimers tilt away from the symmetric position (c.f. Fig. 1b). Associated with dimer tilting is a charge transfer from the "down" atom to the "up" atom. Hence, the dimers exhibit somewhat zwitterionic character, with one electron-poor atom and one electron-rich atom. Such a property of the Si(100)-(2x1) surface makes it possible to use nucleophilic and electrophilic attachment reactions. At temperatures less than 120 K, dimer tilting on Si(100)-(2x1) can be observed in STM experiments [3,9], while at higher temperatures the direction of the tilt oscillates on a time scale faster than the order milliseconds sampling times of the STM.

Upon reconstruction, both Si(100)-(2x1) and Si(111)-(7x7) are still very reactive and, if exposed to air, quickly oxidize by forming a native SiO_2 layer. In order to stabilize the

surface and prevent oxidation it is hydrogenated by exposure to atomic hydrogen. At Si(100)-(2x1) a modest exposure to hydrogen results in the formation of the Si(100)-(2x1)-H monohydride phase. The hydrogen atoms react with Si surface bonds leaving the dimers still bonded and the (2x1) reconstruction still present, as illustrated in Fig. 1c. At higher exposures a dihydride phase is formed in which each surface silicon atom bonds with two hydrogen atoms, causing the disappearance of the dimer bonds and the restoration of a (1x1) periodicity. On the Si(111) surface, because of certain weak Si-Si bonds that are replaced by strong Si-H bonds, hydrogenation results in a structure that does not reconstruct, but rather exhibits a bulk-like periodicity.

Functionalization studies have been carried out at both clean and hydrogen-passivated surfaces. The vast majority of studies on clean silicon substrates are performed under "dry" ultra-high vacuum conditions (UHV). On the other hand, reactions at hydride-terminated silicon commonly rely on "wet" chemical methods performed in solution. Regardless of the different environment and surface structure, common principles of the functionalization at semiconductor surfaces are emerging from these studies.

3. Prototype examples: the chemisorption of ethylene and acetylene to the silicon (100) surface

The investigations of organic/semiconductor interfaces were initially driven by the need to generate silicon-carbide, which is a promising wide-gap semiconductor material, and diamond-like films on the silicon substrate. For this purpose small unsaturated hydrocarbons have been adsorbed on the Si(100) surface via chemical vapor deposition. In the late 80's most studies involved ethylene C_2H_4 and acetylene C_2H_2 (see ref. [1] for a review of this

work) and, more recently, other simple alkenes. These were found to adsorb readily on the surface at room temperature, in a geometry known as the "di-σ" configuration [10], depicted for ethylene in Fig. 2a. This case is of particular significance because it turns out that analogous adsorption structures have been observed for many other alkenes. The bonding is termed di-σ because it takes place through the formation of two new σ bonds between Si and C atoms. While the reaction breaks the π bonds of the hydrocarbons and, if actually present, the Si-Si dimer, the original σ bonds remain preserved [11-13]. For ethylene a barrier to desorption of 1.65 eV (38 kcal mol^{-1}) was evaluated from thermal desorption [14], which represents an upper bound to the binding energy. Density functional theory (DFT) based calculations predict slightly higher adsorption energies 1.81-1.89 eV [13,15], however these do not include zero-point energy corrections to the computed values which should improve the agreement between the calculated and observed quantities.
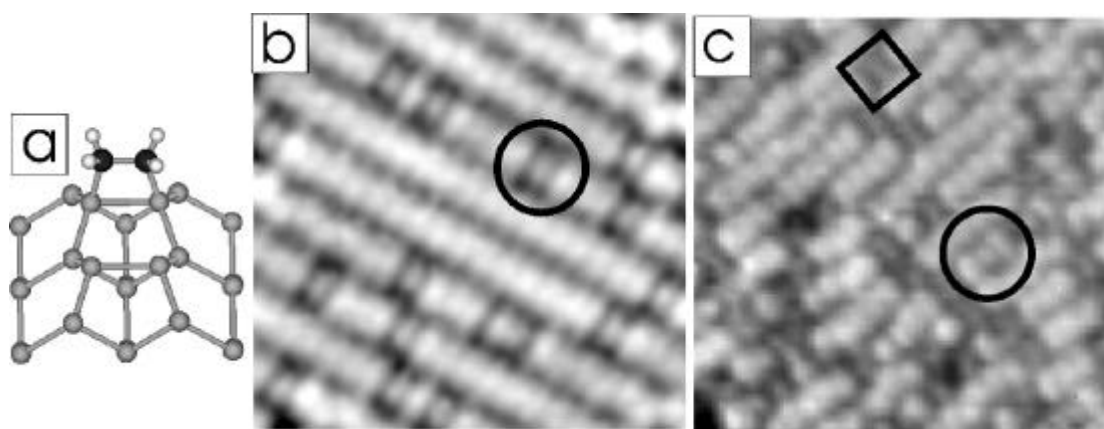
Figure 2: (a) Ethylene adsorbed on Si(100) in the di-σ conformation. (b) STM image of ethylene/Si(100), filled-state scan. Circle shows one adsorbed molecule. (c) Filled state scan of acetylene/Si(100). (Square) One molecule in the bridge configuration. Reprinted from Ref. [16] with permission from Annual Reviews.

Initial investigations of acetylene on Si(100)-(2x1), that used electron-energy loss spectroscopy (EELS), low energy electron diffraction (LEED) and temperature programmed

desorption (TPD) concluded that the adsorption geometry also corresponds to a di-σ model [17]. The molecules were found to be adsorbed undissociated, but at elevated temperatures they largely decomposed, with less than 5% desorbed intact [18]. An estimate of 46 kcal mol^{-1} for the adsorption energy was obtained from these. Even though the energy could not be accurately measured by thermal desorption, it is certain to be higher than that of ethylene, because it is more costly to turn a double bond into a single one than to turn a triple into a double bond. Interestingly, it was argued in a number of studies that the Si dimer bond was completely cleaved upon adsorption [18-20]. The reason for this is that on a post-hydrogenation, hydrogen attaches to the Si dangling bonds. Since both the Si-C and Si-H coexist on the surface, as well as two Si-Si bonds to the subsurface layer, the Si dimer bonds could not be preserved. The picture did not agree with computational predictions [5,21] that clearly favour the structural model with Si dimers intact. Eventually, the cleaved-dimer model has been ruled out by theoretical work [12,22] that suggests that the dimer bond is indeed broken in the presence of co-adsorbed atomic hydrogen and C_2H_2, but the bond cleavage occurs as a consequence of the post-hydrogenation rather than of the initial attachment of the hydrocarbon.

Surfaces exposed to ethylene and acetylene have been investigated by STM [23,24]. For ethylene the results at low coverage clearly demonstrate symmetrical adsorption atop of a dimer, as shown in Fig. 2b, consistent with the di-σ model. The STM scans indicate that adsorbates tend to attach to the surface so as to avoid nearest-neighbour interactions. At around 50% of full coverage the molecules adsorb preferably on alternate dimer sites, exhibiting either (2x2) or c(4x2) local periodicity. However, these are only local domains and there is no long-range order. Once the alternate dimers are populated, the adsorption continues to fill in the remaining adjacent sites [14,23,25]. For acetylene more recent STM

images [26] confirmed the observation of the di-σ model, but at low coverages they adopt instead the so-called bridge structure involving bridging the ends of two adjacent dimers in the same row by bonding to just one atom of each dimer. Both configurations are visible in Fig. 2c. Since most calculations favour the di-σ model as energetically favourable, it is rather unusual that the bridge structures are so evidently dominant. Wolkow has speculated [16] that the bridge configuration, while not as strongly bound, is more accessible kinetically to arriving molecules than is the di-σ. According to a recent DFT study [27], the bridge structure is only 0.05 eV higher in energy at a coverage of 0.5 monolayers [ML] (one ML corresponds to one molecule per each Si dimer). The thermal stability of the bridge-bonded molecules indicates the existence of a large barrier that separates it from the energetic minimum. It has been suggested that at a high coverage the di-σ adsorption structure takes place at every other dimer [26], but an alternative interpretation [16] is that these are actually bridge adsorbed molecules. Studies based on high-resolution photoemission spectroscopy [28] and photoelectron holographic imaging technique [29] have also challenged the di-σ model of C_2H_2 on Si(100). They have instead proposed a pedestal configuration in which the molecule is symmetrically bonded to four Si atoms between two adjacent silicon dimers. A recent STM-based investigation [30] has identified three distinct bonding configurations being the di-σ, bridge, and fourfold-bonded configurations. DFT calculations [31] have again confirmed that the di-σ adduct is the ground state at an adsorption energy of 69 kcal mol^{-1}, the bridge is next with a binding energy of 66 kcal mol^{-1}, while the fourfold bonded configuration at 46 kcal mol^{-1} is much less stable. The simulated STM images [31] corroborate the experimental assignment [30].

4. Interpretation of the chemisorption in terms of either concerted cycloaddition or stepwise free-radical addition reactions.

While originally the reactions of ethylene and acetylene with Si(100)-(2x1) were not recognized as such, it is intriguing that they are analogous to an important class of reactions, in organic chemistry known as "cycloadditions" [4,5]. The covalent nature of the surface suggests that its reactivity can be described through analogies with molecules: the dimers of the Si(100)-(2x1) surface are reminiscent of organic reactants bonded by a strong σ and weak π bond. In a cycloaddition reaction, two molecules combine to form a cyclic molecule via the synchronous scission of π bonds and the creation of new σ bonds. The reaction is designated by the number of electrons on each independent moiety that participates in the process. Some classic examples including [2+2] and [4+2] (Diels-Alder) reactions, as they could be applied to chemisorption on silicon(100), are depicted in Figure 3; in these cases the independent moieties are the adsorbate, contributing either 2 or 4 π electrons, and the silicon dimer, contributing 2 π electrons in each case.
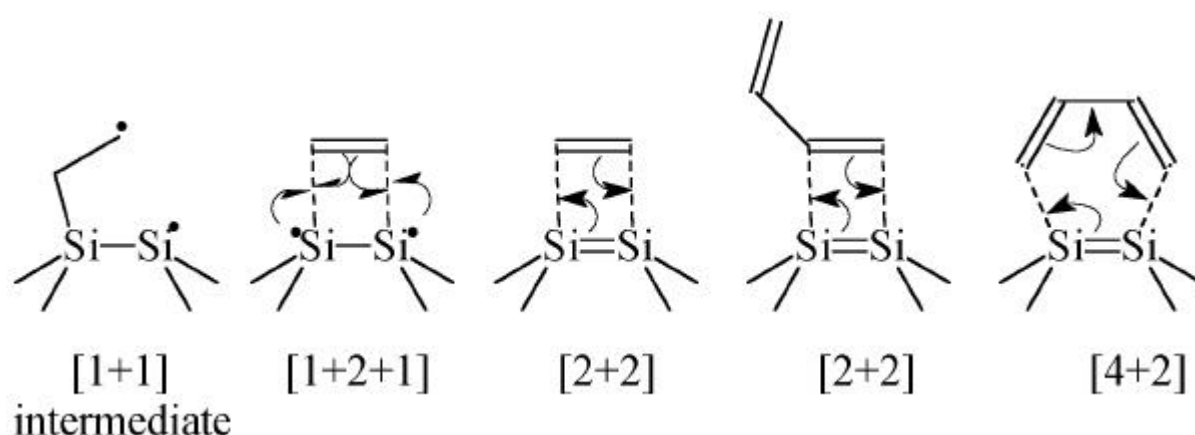
Figure 3: Some examples of postulated concerted [2+2] and [4+2] cycloaddition reactions of alkenes with silicon double bonds, as well as alternate descriptions in terms of a [1+2+1] reaction with silicon free radicals that would be expected to proceed in a non-concerted fashion through the intermediate [1+1] adduct shown.

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The description of the chemisorption in terms of cycloaddition reactions is useful if it leads to reliable predictions of the reaction products: for most reactions, a variety of products are possible, yet only one will result from a particular cycloaddition mechanism. Central to the applicability of such schemes is the notion that the silicon dimers contain a weak π bond responsible for the enforced concerted motion of the two electrons involved. However, in reality there is little evidence to support the presence of even a weak π bond within the dimers. While DFT calculations that enforce spin pairing depict the bond as a singlet biradical [32], spin-polarized calculations predict a triplet ground state for the unbuckled dimer [33] with no π character whatsoever. The decoupling of the two silicon electrons means that their motion is not likely to be concerted so that a [2+2] cycloaddition reaction becomes better represented as an independent [1+2+1] process, a notation that recognizes the independence of the silicon free radicals. This mechanism is also illustrated in Fig. 3. In practice, such a reaction is unlikely to proceed in a concerted fashion and a key signature for it would be the detection of an unstable intermediate formed by a simple [1+1] radical reaction, requiring a second independent [1+1] reaction to complete the chemisorption; such an intermediate is also indicated in the figure.

The reactions of ethylene and acetylene with Si(100)-(2x1) were initially described as being [2+2] cycloadditions, with the di-σ configuration predicted by this mechanism believed to provide the dominate reaction products. A variety of alternate reaction products could actually be formed as a result of the chemisorption, with, eg., the organic molecule spanning silicon atoms in different dimer rows, adhering above a row oriented perpendicular to the silicon dimers, or adhering above a row and parallel to the dimers. As reviewed in Section 3, a variety of alternate structures have now indeed been found for chemisorbed acetylene.

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Hence, while the [2+2] cycloaddition mechanism appears apt for ethylene chemisorption, its applicability to similar processes in acetylene is questionable.

A characteristic feature of [2+2] cycloaddition reactions is that the symmetry properties of the frontier orbitals of the reactants make them formally symmetry forbidden [4] through a symmetric pathway. As a result, the reactants must overcome an activation barrier which makes the process very slow for homogeneous reactants. In organic chemistry, photoexcitation can be used to change the nature of the frontier orbital occupation, breaking the π bond and hence facilitating the reaction, but otherwise high heat and other extreme conditions are required in order to make this type of reaction proceed. For reactions with silicon(100), chemisorption is observed to be facile for most alkenes even at the room temperature [16], contrary to naive expectations based on the cycloaddition model.

The symmetry rules can be relaxed due to the dynamic dimer tilting observed for the surface silicon dimers. Liu and Hoffmann [5] investigated the mechanism of acetylene attachment at several levels of theory. They proposed that the reaction takes place through an asymmetric pathway that reduces the symmetry and leads to an almost zero-energy barrier. In effect, this mechanism assumes that the silicon dimers form a weak π bond when parallel to the surface that is broken by the reorganizational process (electron-phonon coupling) that drives symmetry breaking via dimer tilting. After tilting, the silicon atoms become independent moieties and so the [2+2] mechanism in fact degenerates to the more primitive [1+2+1] one, and [1+1] intermediates may be observed. Liu and Hamers studied the adsorption of cis- and trans−1,2-dideuterioethylene by Fourier transformed infrared (FTIR) spectroscopy and were able to interpret their results in terms of the anticipated intermediate [34].

While the question of whether silicon dimers can be considered as having either a weak π bond or no π bond at all [32,33] is of significance, in this case a more important feature is the ratio of the π bond strength to the strength of the tilting reorganizational process [35]. The π bond is clearly too weak to prevent tilting, a process that localizes the bonding electrons into atom-based free radicals that affects all of the chemical and spectroscopic properties of the dimer. Processes of this nature dominate chemical reactivity and structure [36] and form the core of the Marcus-Hush theory [37,38] that describes electron transport through molecular and biomolecular systems [39].

5. The chemisorption of other alkenes to Si(100)

Cis- and Trans- Butene. Lopinski et al. [40] have studied the chemisorption of cis-butene and trans-butene on Si(100), investigating the stereospecificity of the chemisorption. Molecules chemisorbed in the cis and trans configurations give rise to distinct STM images, allowing the fraction of each type of adsorbate to be determined for each type of reactant. They found that 2-3 % of adsorbate molecules underwent cis-trans isomerization *during* the chemisorption process. Concerted [2+2] cycloaddition reactions occur by electron rearrangements at a single critical transition-state geometry, with the barrier crossing being too fast to allow for isomerization and other nuclear motions. Alternatively, stepwise reactions proceed via two distinct transition states, and following the first reaction the system has time to allow for nuclear rearrangements before the second reaction locks the structure. Loss of stereospecificity is thus clear evidence that at least part of the reaction products arise from a stepwise mechanism: the degree of isomerization is controlled by the relative rate constants for the isomerization process and the second chemisorption reaction, with the later

determined to be of order a few ps. This rate is in good agreement with calculated stepsise reaction processes for [4+2] cycloaddition [41].

Cyclopentene. Among a number of simple alkenes reacting with Si(100)-(2x1) one system is interesting as it provides a particularly well ordered monolayer. Using the STM and FTIR Hamers and coworkers have investigated the adsorption of cyclopentene (a five-member ring molecule, C_5H_8, sketched in Fig. 4a) on the surface [42-44]. It has been established that cyclopentene bonds with silicon to give again the products predicted by the [2+2] cycloaddition mechanism, making a well-ordered monolayer on the surface as shown in Fig. 4b. Each bright oval-shaped object represents a cyclopentene molecule. The molecules are clearly aligned in rows, suggesting that the adducts spontaneously order with very specific bonding sites. In addition, individual molecules are elongated along a direction that appears common for all, with the elongation corresponding to the direction of the ring. Therefore, the layer exhibits both translational and rotational order. The presence of some vacant sites can be attributed to steric intermolecular repulsions or missing dimer defects on the substrate. Figure 4c shows an STM image of cyclopentene monolayer on a vicinal Si(100) surface, oriented by few degrees away from the (100) face so as to exhibit double-height steps. It is worth noting that across the steps the molecules preserve a uniform rotational orientation, thus maintaining the orientational anisotropy. The film is even slightly better ordered on the vicinal surface, indicating that the presence of steps relaxes sterical interactions between adjacent adsorbates.
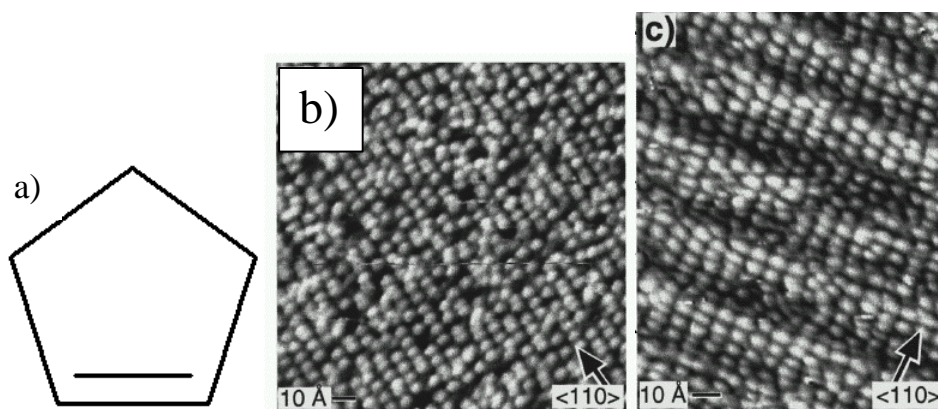
Figure 4: (a) The cyclopentene molecule. (b) STM image of cyclopentene adsorbed on Si(100). (c) STM image of cyclopentene on a vicinal (100) surface obtained by a miscut of 4°. The molecules remain ordered across double-height steps. Reprinted from Ref. [42] with permission from American Chemical Society.

Such success in fabricating an ordered overlayer is quite unusual and remarkable considering the nature of the system. Firstly, the sticking coefficient of cyclopentene, like that of ethylene, is nearly unity, which means that each molecule impinging on the surface has the probability of ~1 of attaching to it. Secondly, given the strength of the bonds and large kinetic barriers, molecular diffusion on the surface is expected to be highly restricted [16,32] indicating that once the molecule is chemically bound to the surface, it will stay at that particular site. Such a frustrated surface mobility is expected to prevent or greatly reduce the ability of the adsorbates to conform in a well-ordered way. Hence, the growth of the cyclopentene layer seems to be controlled solely by the strong directional interactions at the interface that steer molecules towards Si dimers, with the substrate acting as a template for molecule attachment. However, the range of the steering effects is presumably quite short and given the observed fact that molecules do not necessarily stick at their point of impact [16], it is likely that a particular character of the short-lived physisorbed precursor states plays some part in the process.

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In conclusion, the regular dimer spacing on the surface produces the translational order in the cyclopentene film and the directional character of the interacting π bonds imparts the rotational order of the dimers to the overlayer. Cyclopentene thus stands out as a prototypical example of the use of the alkene chemisorption reactions as a general strategy for fabricating well-defined anisotropic organic films. Its binding is in accord with predictions of the cycloaddition reaction mechanism.

Maleic anhydride. One of the key challenges in the organic functionalization of semiconductor surfaces is the ability to grow multiple layers in a controllable manner. To date much of the work has focussed on the first monolayer. It has been speculated [42] that the translational and rotational order of the initial overlayer could be propagated further to successive layers through the directional character of the bonding and steric interactions at the surface as a way of controlled linking of various organic substituents to the Si(100) surface. Bitzer and Richardson [45] have demonstrated the formation of organic multilayers of polyimide on Si(100) via a Si-NH-C linkage. In a subsequent work [46] the surface was functionalized by a layer of maleic anhydride prior to the deposition of phenylene diamine, as a route of growing the polyimide film with the Si-C linkage to the substrate. Maleic anhydride was chosen because, like cyclopentene, it consists of a five-membered, albeit heterocyclic, ring (C_2H_2-C_2O_3, sketched in Fig. 5a).
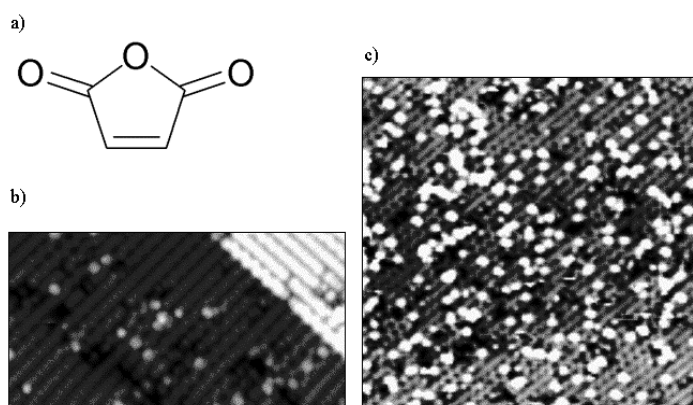

Figure 5: (a) The maleic anhydride molecule. (b) Occupied-state STM image of maleic anhydride on Si(100) at a coverage of 0.03 ML. (c) STM image taken at a coverage of 0.12 ML. Reprinted from Ref. [47] with permission from the American Chemical Society.

The nature of the binding of maleic anhydride to silicon has been investigated using a range of analytical techniques [46-49]. STM images have revealed that maleic anhydride binds preferentially above the dimer troughs, i.e. by straddling two dimers in adjacent rows. This product is not in accord with the predictions of a concerted [2+2] cycloaddition mechanism but does provide another example of a radical [1+2+1] addition. In effect, the two dimers are broken and a new one is formed across the trough.

The STM image in Fig. 5b taken at a coverage of 0.03 ML suggests that the above-row attached molecules make about 20% of all adducts, while the rest is above-trough. At an increased coverage of 0.12 ML, shown in Fig. 5c, 98% of the species are adsorbed above trough. DFT calculations [15], on the other hand, show energetic preference for the above-row conformation at all coverages. Even though they suggest the above-trough structures become relatively more favoured with the coverage, this effect could not account for the observed strong preference for above-trough binding.

It has been speculated [47] that the strong electrophilic character of the molecule contributes to the anomalous binding. The charge transfer from C to O atoms, experienced through the large dipole moment, leaves the C atoms electron-poor. This could bias the reaction with silicon to proceed via the bonding to nucleophilic buckled-up atoms of two Si dimers in adjacent rows. The effect has been calculated to be energetically minor [15], however, and such a surface would not lie at the energetic minimum. On the other hand, when growth is kinetically controlled, this effect could contribute the enhanced above-trough attachment by stabilizing the associated physisorptive precursor species and by lowering (or completely removing) the barrier to chemisorption.

Norbornadiene. Hamers and coworkers first studied the adsorption of norbornadiene (bicyclo[2.2.1]hepta-2,5-diene) [43] on Si(100); this molecule and a sample STM image are shown in Figure 6 along with a functionally modified norbornadiene analogue [50] containing a silyl molecular rotor that we have also investigated. Norbornadiene was in fact the first hydrocarbon containing multiple C=C bonds to be studied in this fashion. Its two double bonds are separated by 2.4 Å and are chemically independent moieties and hence this molecule could react twice with silicon via a double [2+2] cycloaddition-type reaction to bridge two adjacent dimers, separated by 3.85 Å, along a dimer row. Such a binding would guarantee the azimuthal orientation and vertical placement of the apex atom relative to the surface. Functionalization of norbornadiene, at say the 7-position like the example shown in Fig. 6, would then lead to controlled architectures on the silicon surface. Abeln et al. [51,52] have also utilized norbornadiene for a selective attachment to exposed dangling bonds on the otherwise hydrogen passivated Si(100)-(2x1)-H surface. This approach has been envisaged as a route to nanopatterned functionalization of the surface and has subsequently been refined [53,54] so as to make possible the fabrication of templates of individual dangling bonds.
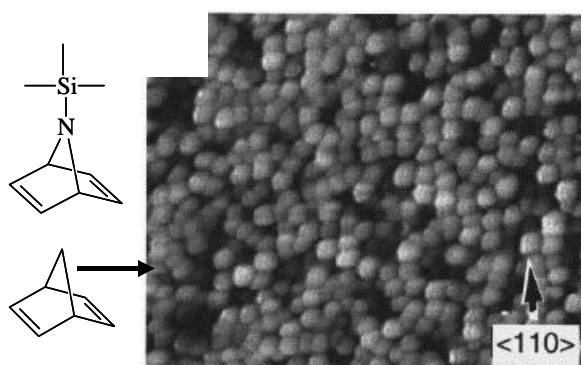

Figure 6: Norbornadiene, its functionalized analogue *N*-trimethylsilyl-7-azanorbornadiene, and the occupied-state STM image of Si(100) upon an exposure of 30 ML of norbornadiene reprinted from J. Vac. Sci. Technol B (Ref. [43]. Copyright 1997 AIP).

Most noticeable in Fig. 6, however, is the complete lack of ordering in the STM scan, taken at a high coverage, indicating that there must be more that one type of binding site at

the substrate. Four different modes of attachment were originally proposed [43]: both C=C bonded to adjacent dimers along a row; one C=C bonded to a single dimer; both C=C bonded to two dimers in adjacent rows (that is, above a trough); and one C=C bonded above a trough. A recent DFT investigation [32] has addressed the issue of the optimum bonding geometry, considering these and a number of variants. In summary, four strongly bound norbornadiene configurations have been found, with the C-C bonds situated either above a Si-Si dimer row or trough, and oriented either parallel or perpendicular to the Si-Si bonds. When norbornadiene is adsorbed above a row with C-C parallel to Si-Si, it corresponds to the product of a double [2+2] cycloaddition; all other products require more general mechanisms such as the [1+2+1] free-radical process. The calculated binding energies are 96, 85, 81, and 72 kcal mol^{-1} for the perpendicular above-row and above-trough, and parallel above-row and above-trough conformations, respectively, at a moderate coverage; these results thus lead to the conclusion that the [2+2] mechanism does not provide proper insight into the chemisorption process.

It has also been suggested [55] that the disorder in norbornadiene films is due to the steric hindrance the adsorbate experiences when approaching the surface. Consistent with this hypothesis, DFT calculations [32] suggest that in general the observed [43] structural disorder in the norbornadiene overlayer arises from kinetic rather than thermodynamic control of the reaction products. This control is shown [32] to be associated with large barriers in excess of 40 kcal mol^{-1} for surface diffusion and annealing. At high coverage, enhanced disorder is also predicted owing to the strong partial binding of norbornadiene via a single alkene linkage only, with the analogous four structural motifs being calculated to be very similar in energy to each other.

With reference to general mechanisms for alkene chemisorption, we note that the optimum calculated [32] single-alkene-bonded configuration, with an adsorption energy of 47 kcal mol^{-1}, corresponds to the anticipated [2+2] cycloaddition product, consistent with the structure for most mono-alkene adducts. The second most favourable single-alkene-bonded structure, with an energy of 45 kcal mol^{-1}, corresponds to the "bridge" (c.f. acetylene), i.e. above-row placement with C-C perpendicular to the Si dimers. These two reactions thus lead to similar binding energies. However, as the corresponding total norbornadiene double-binding energies are 81 vs. 96 kcal mol^{-1}, respectively, it is clear that addition of the second double bond when oriented parallel to the silicon dimers is far less exothermic than when oriented perpendicular. Thus the preference of the uncommon, perpendicular azimuthal orientation of norbornadiene on the surface is interpreted as arising from a cooperative effect associated with the silicon-lattice relaxation required to accommodate two adjacent chemisorbed moieties. It is indeed this same effect that causes the tendency for adsorbed ethylene to avoid nearest-neighbour sites along a row [22,23]. Hence, in summary, we see that concerns such as this appear to be more important in determining the structure of chemisorbed alkenes to the silicon(100) surface than the symmetry constraints that are manifest in concerted cycloaddition reaction mechanisms.

1,5-Cyclooctadiene. Following the work on norbornadiene, Hovis and Hamers [55] utilized another diene, 1,5-cyclooctadiene; representative images are shown in Figure 7 whilst molecular and adsorbate structures are shown in Figure 8. Like norbornadiene, this molecule contains two chemically independent C=C groups held rigidly separated at a specific geometry. The STM images show that at high coverage the adsorbates interact with the surface to form a highly ordered monolayer of uniformly oriented molecules aligned in rows. The separation between the adsorbates is 7.7 Å, twice the separation between adjacent dimers

in a row. Such a spacing can lead to local regions of (2x2) or c(4x2) periodicity, depending on whether the molecules in neighbouring rows are aligned or staggered. The observation of both types of ordering suggests that there are little direct or substrate-mediated interactions.
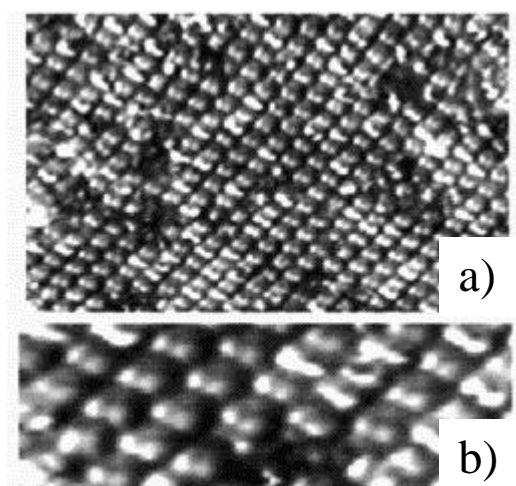

Figure 7: (a) STM image of COD adsorbed on Si(100) at the saturation coverage. (b) Magnified view of a smaller area of the surface. Reprinted from Ref. [55] with permission from American Chemical Society.

A most significant feature of the chemisorption is that, as is clear from the FTIR spectra [55], only *one* of the two bonds actually binds to the substrate. Since no dissociation could be observed, it follows that each molecule identified in the scans is the product of a single alkene chemisorption. The significance of this finding is that the modified surface thus presents an array of ordered and exposed C=C bonds which can be exploited for a further functionalization.

The ability to bond via one of the two equivalent C=C groups has been ascribed to the particular molecular shape of 1,5-cyclooctadiene [55]. The lowest energy configuration of the molecule is a twisted-boat geometry, illustrated in Fig. 8a, in which the two C=C bonds,

$^{\circ}$ with respect to one another; this arrangement is quite different from that in norbornadiene, for which the two C=C bonds are parallel. Fig. 8b and 8c schematically show two possible ways of interaction with Si dimers, termed "endo" and "exo", respectively. In order to bond to two adjacent dimers 1,5-cyclooctadiene makes the

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endo approach. In this scenario there is a relatively weak overlap between the π orbitals, in part due to an imperfect match in the separation of the bonds in the two subsystems (3.85 vs. 3.20 Å) and also because the C=C bonds are not coplanar. On the other hand, in the exo approach a good overlap is possible without steric obstacles. In addition, the rigidity of the molecule provided by the ring structure supports the selective attachment. Therefore, steric constraints seem to be responsible for the easily controllable growth of the COD monolayer.
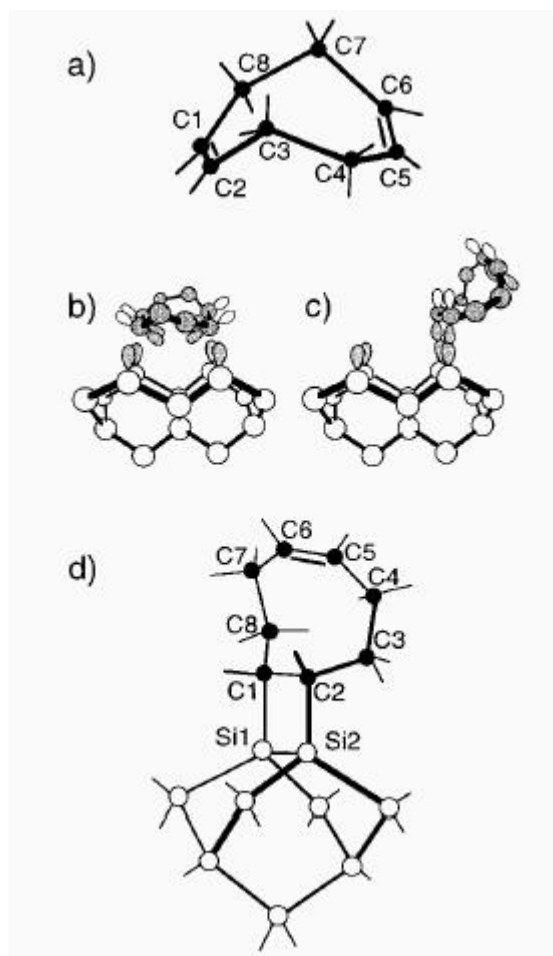
Figure 8: Geometry of gas-phase and adsorbed COD. (a) Minimum-energy structure ("twisted boat") of the free COD molecule. (b) "Endo" interaction of COD with Si(100). (c) "Exo" interaction of COD with Si(100). (d) Optimized structure of COD on a Si(100) cluster. Reprinted from Ref. [55] with permission from American Chemical Society.

1,3,5,7-Cyclooctatetrene. To investigate the hypothesis that stereochemistry governs the ordered growth of 1,5-cyclooctadiene, Hovis and Hamers [56] studied the structure of 1,3,5,7-cyclooctatetrene on Si(100). This molecule, shown in Fig. 9, is symmetric and conjugated, with two sets of coplanar C=C bonds. STM images taken on a high exposure are
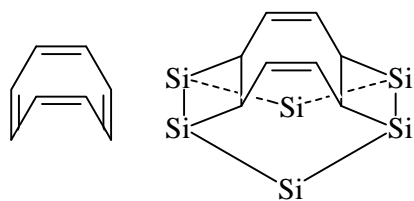
Figure 8: 1,3,5,7-cyclooctatetrene and its adsorption geometry on Si(100) for majority species comprising two C=C bonds reacting each in the di-σ configuration with adjacent silicon dimers.

shown in Fig. 10. The single height step from the clean surface still visible in Fig. 10a demonstrates that the molecules are aligned along dimer rows (the upper terrace is rotated by 90° with respect to the lower terrace) making a well-ordered overlayer. Again, the separation between most of them is 7.7 Å. A closer look (Fig. 10b) shows that the majority species are elongated along the rows and appear identical (a few white protrusions are attributed to contaminants). At even higher resolution (Fig. 10c) a minority species, labeled "D", can be seen. STM scans at low coverage [56] elucidate the nature of the majority type. The common features are placement above a dimer row, with the centre of each molecule being midway between two dimers, and the direction of elongation along a dimer row. FTIR indicates that 1,3,5,7-cyclooctatetrene has at least two C=C bonds preserved on adsorption. Hovis and
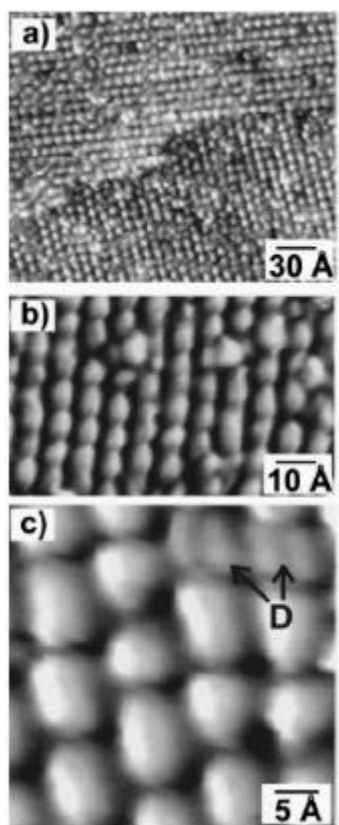
Hamers considered possible bonding geometries that are consistent with these findings and, with the help of DFT calculations [56], the geometry illustrated in Fig. 9 was identified as the most likely configuration of the majority species. This structure leaves two C=C bonds exposed and amenable to further functionalization.

Figure 9: STM images of 1,3,5,7-cyclooctatetrene on Si(100) taken at a saturation coverage. (a) Molecules aligned themselves in rows on the two terraces that are separated by a single-height step. (b) Magnified view showing the adsorption pattern. (c) High-resolution scan indicating the presence of a minority species, labelled "D". Reprinted from Ref. [56] with permission from American Chemical Society.

As in the case of norbornadiene and 1,5-cyclooctadiene, the particular reactivity of 1,3,5,7-cyclooctatetrene with Si(100) has been attributed to the molecular shape [56]. While the separation between terminal C=C bonds is slightly shorter than in 1,5-cyclooctadiene (3.1 vs. 3.2 Å) and thus a poorer match for a pair of adjacent Si dimers, the C=C groups are now parallel to one another and, therefore, a better overlap of the π bonds is expected at both ends. In addition, the intermediate CH_2 groups in 1,5-cyclooctadiene that could produce steric repulsions and prevent this molecule from taking up the shape needed for the attachment via both C=C bonds are replaced with CH ones and pushed away from the surface. It is the "antiaromatic" nature of 1,3,5,7-cyclooctatetrene (i.e. energy lower in a lower symmetry geometry than in a planar delocalized π system of 8 electrons) that provides the rigidity that prevents alternate reactions from proceeding. Compared to norbornadiene, the C=C bonds are much further spaced (3.1 vs. 2.4 Å) and hence different steric constraints are placed on the binding from the underlying silicon lattice. It would appear that these constraints result in the dramatic difference in binding topology observed for the two molecules.

1,3-butadiene, 2,3-dimethyl-1,3-butadiene, and 1,3-cyclohexediene These molecules are dienes with one single bond separating the two double bonds. In terms of cycloaddition chemistry, two reactions with single double bonds are expected; the forbidden [2+2] cycloaddition reaction on a single double bond discussed previously at length, and an alternate allowed [4+2] cycloaddition, known as the Diels-Alder reaction, in which both double bonds react synchronously [4]; both mechanisms are illustrated in Fig. 3. As this approach predicts that the allowed process should have a much lower reaction barrier and hence should dominate, only one reactant product is expected and hence these molecules form another test of the appropriateness of the concerted cycloaddition mechanism for alkene chemisorption.

The surface equivalent of the Diels-Alder reaction was first predicted to be the most important reaction by Konecny and Doren [57,58] who used DFT calculations to investigate the adsorption of 1,3-cyclohexadiene on Si(100). They obtained binding energies of 54 kcal mol^{-1} for the [4+2] product and 39 kcal mol^{-1} for the [2+2] product, and also a negligible barrier for the [4+2] process. Concomitantly to this study, Bent and coworkers [59] carried out an infrared spectroscopic investigation of 1,3-butadiene and 2,3-dimethyl−1,3-butadiene films which provided experimental evidence for the formation of the [4+2] reaction product on the surface. Subsequent results by Hovis et al. [60,61] shown in Figure 11 support the observation of a Diels-Alder product as the majority species, which makes about 80% of the adducts. However, a minority (20%) species is also observed and is attributed to the [2+2] cycloaddition. Finally, experimental studies for 1,3-cyclohexadiene itself [44] were performed with the observation that only 55% products arise from the [4+2] cycloaddition, 35% from [2+2], while 10% an unknown product. Thus, the selectivity of 1,3-cyclohexadiene towards the Diels-Alder product is even poorer than that of 2,3-dimethyl-1,3-butadiene. For both molecules subsequent annealing of the surface at high temperature failed to convert the product distribution to the thermodynamically more stable [4+2] products. Hence, it has been suggested [44] that the reaction is controlled by adsorption kinetics.
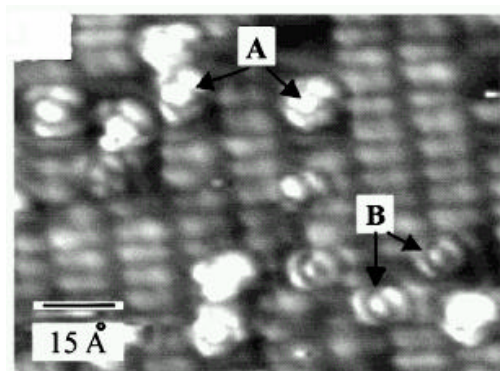

Figure 10: STM image of 2,3-dimethyl-1,3-butadiene on Si(100), with visible two reaction products, labelled "A" and "B" attributed to [4+2] and [2+2] cycloaddition products, respectively. Reprinted from Ref. [61] with permission from American Chemical Society.

Viewing the reactions of these molecules with silicon(100) as occurring through concerted cycloaddition reactions is useful in that likely products are predicted, but the failure to observe almost exclusively the symmetry-allowed product again indicates that this approach does not recognize the most important features governing the surface adsorption of alkenes. Simplistic ideas based on free-radical reaction mechanisms also give rise to the prediction that the [4+2]-like process should be energetically favoured in preference to the [2+2]-like one, as in the second case a highly strained 4-membered ring is produced. Once again, however, kinetic concerns and possibly also surface relaxation effects appear to be of greatest importance. Ab initio molecular dynamics calculations have recently been performed that model the time dependence of the reaction [41]. These clearly indicate the [4+2] products forms via a stepwise mechanism

Benzene In the context of conjugated addition reactions, one needs to consider the adsorption of aromatic systems. It was observed by Taguchi et al. [62] that benzene (C_6H_6) chemisorbs on Si(100) at room temperature. Particularly interesting features of benzene are it's ability to adsorb and desorb reversibly [62], unlike simple alkenes and dienes, and to migrate from one bonding configuration to another [63]. The TPD spectra indicate the existence of two species with binding energies of 28 and 32 kcal mol^{-1}, respectively, and the EELS spectra are consistent with a di-σ bonded structure. Based on these findings, models of binding structures were proposed that correspond to [4+2] and [2+2] cycloaddition products to a single silicon dimer as well as non-cycloaddition products involving two silicon dimers [62]. Since it was not possible to distinguish between the two possibilities, the system has been investigated by STM, FTIR, and semiempirical calculations [16,63].

An STM image of benzene on silicon(100) is shown in Figure 12 and contains three distinct bonding configurations labelled "S", "B1, and "B2". The S-configuration images are the largest ones and centred above one dimer; these are preferentially occupied upon adsorption but are unstable with respect to relaxation to form B1 sites.
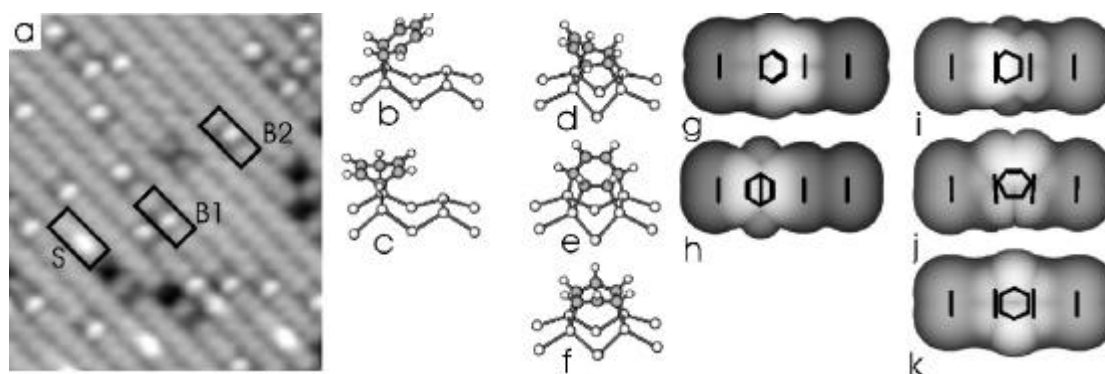

Figure 11: (a) Filled-state STM image of benzene on Si(100). Single-dimer bonded molecules, and molecules in two other distinct bridging configurations are labelled "S, B1, and B2, respectively. (b-f) describe various adsorption configurations considered while (g-k) are simulated STM images of the adsorption geometries. Reprinted from Ref. [16] with permission from Ann. Rev. Phys. Chem..

Both chemisorption to a single silicon dimer and two adjacent silicon dimers in the same dimer row have been considered in the calculations, as illustrated in Fig.12 b-f. The 1,2-single-dimer structure in Fig. 12b that corresponds to a single [2+2] reaction product is predicted to be only weakly bonded with an evaluated energy of 9 kcal mol^{-1}. This species is thus expected to be only transient on the surface. On the other hand, for the 1,4-single-dimer configuration in Fig. 12c a binding energy of 24 kcal mol^{-1} is predicted and is assigned to the observed feature labelled S [16]. This corresponds to the product of a [4+2] cycloaddition reaction. The adsorption of benzene can be considered as being analogous to that of 1,3-butadiene [57,58], with the relatively weaker binding of benzene by ~30 kcal mol^{-1} being simply the consequence of the loss of aromaticity of benzene upon adsorption [64].

As for the non-cycloaddition conformations in which benzene reacts with two adjacent silicon dimers within the one dimer row, the structure in Fig. 12f was predicted to be very unfavourable, with an energy of only 5 kcal mol^{-1}, owing to the creation of radicals on both of the two central C atoms [16]. However, the structure in Fig. 12d, with an adsorption energy of 26 kcal mol^{-1}, was predicted to be the most stable of all the examined structures and was assigned to the observed structure labelled B1 in the STM images. The configuration shown in Fig. 12e was also predicted to be quite stable, with a binding energy of 21 kcal mol^{-1} and has been assigned to the B2 feature, a feature found exclusively in conjunction with the type-C defects [16,65] that occur on Si(100). These assignments have been verified by STM-simulated images shown in Fig.12 g-k. The symmetric nature of Fig. 12h confirms that the S features are indeed due to the 1,4-single-dimer bonded structure of Fig. 12c. Also, the brighter contrast above one of the two affected dimers in Fig. 12i agrees with that observed for the B1-type product while a similar character is observed in Fig. 12j rotated by 90°, corresponding to B2-type products. More recent studies of benzene and chlorobenzenes have focused also chemisorbed species in which H or Cl atoms detach from the adsorbate, and on non-cycloaddition products in which the adsorbates span dimer troughs [66]. In summary, non-cycloaddition products are again seen to dominate the chemisorption.

6. Cycloaddition chemistry at Ge and diamond (100) surfaces

Both Ge(100) [2] and diamond(100) [67] surfaces undergo the same (2x1) reconstruction as does Si to form rows of dimers. However, there are some obvious differences in the strength and associated geometry of the dimer bonds. While on silicon, tilting on the ms STM timescale is observed only at temperatures < 120 K, on germanium such structures persist to much higher temperatures [2]. While this could be attributed to

slightly weaker π bonding in Ge than on Si resulting in a higher and sharper tilting interchange barrier, it is more likely due to an increased reorganization energy favouring more metallic configurations in Ge. Significant π bonding is expected in dimerized diamond surfaces, while the reorganization energy driving localized structures with near 90° bond angles produced by tilting would also be greatly reduced [68,69]. These forces most likely account for the observation of symmetric dimers on the diamond surface [70].

Adsorption of ethylene [71], cyclopentene and cyclohexane [72], and cyclohexadiene [73] on Ge(100)-(2x1) has been observed, but the resulting monolayers are disordered. FTIR spectra of adsorbed cyclopentene [72] imply the formation of what would be the [2+2] cycloaddition product, but while on Si the sticking coefficient of cyclopentene is close to unity, on Ge it is only about 0.1. Conjugated polyenes react with Ge(100) to form predominantly what appear to be [4+2] cycloaddition products [73,74], but, in contrast to reactions on Si(100), the chemisorption is weak and reversible [74]. All of these observations of much weaker chemisorption can be rationalized by noting that the Ge-C bond is less stable than the Si-C bond by ~10 kcal mol^{-1} [75].

In contrast to Si and Ge, on the diamond C(100) surface the [2+2] cycloaddition of alkenes is rather slow and more in accord with what is expected for a forbidden reaction of this type. The sticking coefficient of cyclopentene on C(100) is very small, of the order of 0.001 [76], also consistent with naive expectations for a [2+2] cycloaddition process. 1,3-butadiene has been shown to react prominently via the conjugated [4+2] addition [77] mechanism. While the reaction probability for this reaction is again found to be lower than that on Si or Ge, presumably owing to the presence of π bonds in diamond dimers, the effect is not as large as for [2+2] addition of cyclopentene, so once again the symmetry properties

of the reaction correlate with observed phenomena. Experimentally, it remains unknown whether the observed symmetric carbon dimers are composed of independent free radicals or form a π bond, but the applicability of cycloaddition selection rules for carbon(100) compared to their inapplicability for silicon(100) suggests the presence of significant π-bonding character.

7. Conclusions

Organic functionalization of semiconductors has become an area of increasing importance, principally owing to its prospective use in the fabrication of devices that incorporate properties of organic and inorganic matter. However, there are a number of difficulties that need to be overcome before it becomes a useful technology. As examples presented in this Chapter suggest, a particular weakness is the preparation process that commonly results in several competing products. Consequently, monolayers so formed are usually not well-defined. A number of studies have indicated that, more often than not, the reaction system is kinetically rather than thermodynamically controlled. In order to control and manipulate reaction products a better understanding of driving mechanisms and experimental variables that govern the adsorption process is needed.

Concepts of cycloaddition reactions from organic chemistry provide a useful framework for describing certain classes of reactions of hydrocarbons with Group IV surfaces. For reactions with carbon surfaces, the observed products and kinetics may readily be predicted and interpreted using this approach, suggesting that the surface dimers display a significant amount of π character. Silicon surfaces, however, are characterized by either no π character whatsoever, or by π bonding interactions that are too weak to prevent symmetry

breaking via dimer tilting with its subsequent loss of π character. In this case, concerted cycloaddition reactions are not expected to occur, being replaced by simpler multi-step free-radical processes that are not subject to the symmetry selection rules of cycloaddition chemistry. The cycloaddition concept remains useful in that it readily allows significant reaction products to be predicted and identified, but it fails to predict the alternate products that dominate many reactions. It now appears that aspects such as kinetic effects as well as steric strain, both across the surface-molecule junction and within the top surface layers, are more important than symmetry selection rules in determining chemisorption products.

Acknowledgements

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