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A Theoretical Study of the Structure and Thermochemistry of 1,3-Butadiene on the Ge/Si(100)-2 × 1 Surface

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We present an ab initio investigation of the structure and thermochemistry of the products of the chemisorption of 1,3-butadiene on the Ge/Si(100)-2 × 1 surface. The surface was modeled using a Si cluster with one dimer and Ge substitution for surface Si to study the effects of Ge on the cycloaddition. Calculations were performed using the Becke3LYP hybrid density functional theory method. Both the [4 + 2] Diels−Alder and the [2 + 2] cycloaddition products are energetically stable on all the Ge/Si(100)-2 × 1 surfaces investigated. The [4 + 2] Diels−Alder products on the Si−Si, Si−Ge, and Ge−Ge dimers are more stable than the corresponding [2 + 2] cycloaddition product due to ring strain. The binding energies of all cycloaddition reaction products decrease with increasing Ge composition on dimers, which can be explained by differences in bond strength. The structures and energetics will be explained and discussed.

Introduction

The growing interest in silicon−germanium ($Si_{1-x}Ge_x$) devices reflects their potential for extending traditional silicon technology, allowing faster field-effect transistors,[1,2] CMOS, and bipolar chips for next-generation wireless telecommunications,[3] infrared photodetection,[4] and quantum nanostructures.[5] A major advantage of $Si_{1-x}Ge_x$ over III−V materials is that $Si_{1-x}Ge_x$ technology can be integrated with existing silicon CMOS processes, resulting in lower development costs.

Because of the technological interest in $Si_{1-x}Ge_x$ heteroepitaxy, the growth of Ge on Si(100)-2 × 1 and the structure of the Ge/Si(100)-2 × 1 surface have been studied previously, and both Ge−Si heterodimers and Ge−Ge homodimers were observed experimentally.[6−11] During the initial stages of Ge growth on Si(100), when the Ge coverage is below 0.2 ML, Ge−Si heterodimers were observed by both MIR−FTIR[6] and photoemission measurements[7] to form on the surface. STM studies observed buckled Ge−Ge homodimers to appear on the Ge/Si(100)−2 × 1 surface when the Ge coverage was 0.2 ML.[8,9] At intermediate Ge coverages between 0.2 and 0.8 ML, both Ge−Si heterodimers and Ge−Ge homodimers were observed to form on the Si(100)−2 × 1 surface. After a critical concentration of 0.8 ML, the 2 × *N* reconstruction pattern, which consists of Ge−Ge dimer rows of length *N* separated by missing dimers, was observed on the Ge/Si(100)−2 × 1 surface.[10] The 2 × *N* reconstruction of the Ge/Si(100)−2 × 1 surface was attributed to surface strain effects.[11]

Different results have been reported for the geometry of the dimers on the Ge/Si(100)-2 × 1 surface. Theory predicted the Ge−Ge homodimer bond lengths between 2.38 and 2.51 Å and buckling angles from 12.7° to 20.4°.[12−19] On the other hand, experiments using various techniques obtained Ge−Ge bond lengths of 2.40−2.60 Å and buckling angles from 0° to 17.8°.[20−30] In general, theoretical calculations predict shorter Ge−Ge bond lengths than experimental measurements. There are fewer studies on the geometry of the Ge−Si heterodimer on the Ge/Si(100)-2 × 1 surface. Recent density functional theory calculations[16−19] predict the Ge−Si heterodimer bond length to be 2.34 Å with a buckling angle of 19.3°, while core level photoelectron diffraction (CLPD) measurements[31] obtain a Ge−Si bond length and buckling angle of 2.43 Å and 31.0°, respectively.

Although the demand for $Si_{1-x}Ge_x$ based microelectronics is increasing, the surface chemistry of the alloys remains mostly unexplored. The focus of this work is to study the reactivity of the $Si_{1-x}Ge_x$ alloy surface toward adsorption of organic compounds. We are interested in the Ge-covered Si(100) surface because it acts as a good model system to investigate the effect of Ge on the reactivity of the $Si_{1-x}Ge_x$ alloy surface. One of the few reactive studies of the Ge-covered Si(100) surface investigated hydrogen desorption and found that the presence of Ge enhances the rate of H_2 desorption.[32−35] This result explains the enhancement in Si film growth rate when Ge-containing species are present in the reactant gas mixture because H_2 desorption is the rate-limiting step in Si epitaxial growth.

The formation of organic monolayers on semiconductor surfaces is an attractive technique to integrate into existing $Si_{1-x}Ge_x$ technology. For example, an organic monolayer could serve as a gate dielectric on the surface with subnanometer thickness. Cycloaddition reactions can covalently attach a monolayer of organic molecules to the surface. The [2 + 2] cycloaddition involves a reaction between the Si=Si π-bond of the surface dimer with a C=C double bond of an unsaturated hydrocarbon, forming two new Si−C σ-bonds to the surface to generate a four-membered ring. Reactions of some unsaturated

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hydrocarbons by [2 + 2] cycloaddition to the Si(100)-2 × 1 surface result in the formation of well-ordered organic monolayers.[36−38] Potential applications including lithography, optical devices, and biosensors have been proposed for ordered organic monolayers on semiconductor surfaces. Surface cycloaddition reactions on Si(100)-2 × 1 also demonstrate the close relationship between the π-bonding character resulting from dimer reconstruction on the Si(100)-2 × 1 surface and its reactivity toward unsaturated hydrocarbons.

The [4 + 2] cycloaddition or Diels−Alder reaction occurs between a 1,3-diene and the Si(100)-2 × 1 surface when the surface Si═Si dimer π-bond reacts with both C═C double bonds of the 1,3-diene, resulting in two new Si−C σ-bonds and a new C═C double bond between the 2 and 3 carbon atoms. The Diels−Alder reaction between 1,3-cyclohexadiene and the Si(100)-2 × 1 surface was theoretically predicted to be energetically favored over the [2 + 2] reaction with a low activation barrier.[39,40] Multiple internal reflection Fourier transform infrared (MIR−FTIR) spectroscopy under ultrahigh vacuum (UHV) conditions confirmed the theoretical predictions, demonstrating that 1,3-butadiene chemisorbed on the Si(100)-2 × 1 surface by the Diels−Alder [4 + 2] cycloaddition reaction.[41] The thermochemistry and the geometry of Diels−Alder products was studied by temperature-programmed desorption (TPD) and near-edge X-ray absorption fine structure (NEXAFS) measurements, respectively.[42] It was found that both chemisorbed 1,3-butadiene and 2,3-dimethyl-1,3-butadiene decompose on the Si(100)-2 × 1 surface upon heating. The angle between the π orbitals of chemisorbed 2,3-dimethyl-1,3-butadiene and the Si(100)-2 × 1 surface was also determined to be about 40°. More recent studies by scanning tunneling microscopy (STM) and MIR-FTIR observed both [4 + 2] and [2 + 2] cycloaddition products for the reactions of 1,3-cyclohexadiene and 1,3-butadiene on the Si(100)-2 × 1 surface, with the [4 + 2] product as the major product in each case.[43,44]

Diels−Alder reactions on group-IV single-crystalline semiconductor surfaces have also been demonstrated on the Ge(100)-2 × 1 surface, indicating the generality of cycloaddition to dienophile surfaces. Both 1,3-butadiene and 2,3-dimethyl-1,3-butadiene were observed to chemisorb on the Ge(100)-2 × 1 surface by the Diels−Alder reaction and desorb by the retro-Diels−Alder reaction.[45] In particular, 1,3-butadiene was observed to desorb completely from the Ge(100)-2 × 1 surface at 570 K. Because of the difference in surface reactivity of group-IV semiconductor surfaces toward unsaturated hydrocarbons, it may be possible to tune the properties of the semiconductor−organic interface by alloying and using different organic molecules.

The surface reactivity of group IV semiconductors is closely coupled to their surface electronic structure, particularly the dimer reconstruction of the (100) surface. Because the Ge/Si(100)-2 × 1 surface consists of dimers as well, we expect the surface to act as a dienophile and to be reactive toward unsaturated hydrocarbons such as the clean Si(100)-2 × 1 and Ge(100)-2 × 1 surfaces. Here, we present a theoretical study of [4 + 2] and [2 + 2] cycloaddition reactions of 1,3-butadiene on the Ge/Si(100)-2 × 1 surface to determine the possibility of organic monolayer formation on the alloy surface. We choose to use the Ge/Si(100)-2 × 1 surface as a model system to study the effect of Ge on the reactivity of a $Si_{1-x}Ge_x$ alloy surface toward [4 + 2] and [2 + 2] cycloaddition reactions. Our results show that both [4 + 2] and [2 + 2] cycloaddition products of 1,3-butadiene on the Ge/Si(100)-2 × 1 surface are thermodynamically stable on the Si−Si, Ge−Si, and Ge−Ge dimers. The thermochemistry of these cycloaddition reactions and the geometry of the reaction products will be discussed and explained using physical arguments.

Computational Details

All calculations were done using the Gaussian 94 computational chemistry software package.[46] Density functional theory[47,48] (DFT) employing the Becke3−Lee−Yang−Parr exchange correlation functional[49,50] (B3LYP) was used to predict the energies and geometries of all the reactants and products in this study. The hybrid B3LYP functional includes exact exchange and correctly predicts the reaction energy and activation barrier of the Diels−Alder reaction between 1,3-butadiene and ethylene.[51] B3LYP-DFT has also been shown to predict accurate geometries and frequencies for similar cycloaddition reactions on the Si(100)-2 × 1 surface.[39,40] In this investigation, we used dimer clusters consisting of 2 surface dimer atoms, 7 subsurface Si atoms, and 12 terminating H atoms to maintain the sp^3 hybridization of the bulk Si atoms. To study the effect of surface Ge, three types of dimer clusters were used, including Si−Si, Ge−Si, and Ge−Ge dimer clusters. Although Ge atoms can substitute into any position of the cluster as in the actual $Si_{1-x}Ge_x$ alloy, we choose to only consider Ge atoms in the dimer positions to focus directly on the effect of Ge atoms on the alloy surface chemistry. We use a split basis set scheme in order to maximize the accuracy on the chemically active electrons of the reactions while minimizing computational time. A triple-ζ basis with polarization and diffuse functions was used to describe reacting surface Si or Ge atoms and the 1,3-butadiene molecule so that the orbitals active in the bond breaking and bond forming processes would be accurately described during the surface reaction. In the split basis set scheme, the 6-31G* basis set was used for the terminating H atoms and the bulk Si atoms, and 6-311+G** was used for surface Si or Ge dimer atoms and for all atoms of 1,3-butadiene. The accuracy of this split basis scheme has been tested and found to produce absolute errors in relative energies for similar surface reactions of less than 2 kcal/mol.[52] All geometry optimizations were performed without constraints or symmetry restrictions imposed on the clusters. Our calculations testing the effects of imposing constraints have shown that they do not have a significant effect on the calculated energetics of surface adsorption reactions.[52] The more stable conformation of 1,3-butadiene, which has a "trans" configuration and a C_{2h} symmetry, is used as the reactant in the calculations. A diagram of the split basis set scheme and the surface cycloaddition products involved in this study is shown in Figure 1.

Results and Discussion

From our calculations, both the [4 + 2] and the [2 + 2] cycloaddition reaction products are energetically stable on Si−Si, Ge−Si, and Ge−Ge dimers of the Ge/Si(100)-2 × 1 surface. On the Si−Si dimer cluster, the [2 + 2] cycloaddition product is more stable than the reactants by 37.0 kcal/mol, while the [4 + 2] (Diels−Alder) product has an overall binding energy of 61.8 kcal/mol. Thus, the [4 + 2] product is found to be more stable than the [2 + 2] product by 24.8 kcal/mol. These energies are in good agreement with those calculated by Konecny and Doren.[40] The difference in energies between the two products is attributed to ring strain. For the [4 + 2] reaction, a six-membered ring is formed, while a strained four-membered ring is formed in the [2 + 2] reaction. The difference in strain energy is mainly due to the bond-angle bending. The C−Si−Si bond angles of the [2 + 2] product are only about 78°, while

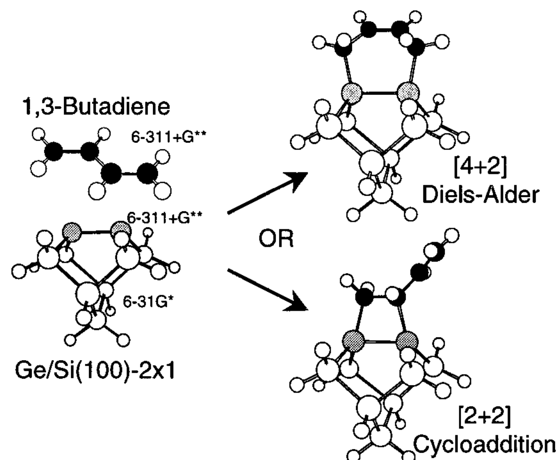

Figure 1. Possible [4 + 2] and [2 + 2] cycloaddition reaction product on a dimer cluster representing the Ge/Si(100)-2 × 1 surface. The split basis set scheme is also shown. The 6-31G* basis set was used for the terminating H atoms and the bulk Si atoms and 6-311+G** was used for surface Si or Ge dimer atoms and for all atoms of 1,3-butadiene.

the same angles are about 100° for the [4 + 2] product, which is more similar to the ideal sp^3 hybridization angle of 109.47°. Selected structural parameters of the two cycloaddition products on a Si−Si dimer cluster are shown in Figure 2a. The angle between the plane of the C=C π-orbital of the [4 + 2] and the [2 + 2] products and the surface plane (not shown Figure 2a) is found to be 31.4° and 48.5°, respectively.

Lower binding energies are found for the reaction products on the Ge−Si heterodimer. In this case, there are two possible [2 + 2] cycloaddition products. One product has the Ge atom of the dimer closer to the C=C double bond of adsorbed 1,3-butadiene. These two [2 + 2] products have similar adsorption energies, with values of 29.9 and 29.1 kcal/mol, respectively. The [4 + 2] product has an overall binding energy of 53.7 kcal/mol. Because of ring strain effects similar to the case of the Si−Si dimer, the [4 + 2] product is more stable than the two [2 + 2] products by 23.8 and 24.7 kcal/mol, respectively. The products have similar geometries to those formed on the Si−Si dimer, except that the bonds involving Ge are longer and the angles with Ge centers are smaller (Figure 2b).

Our results show a similar trend for reactions on the Ge−Ge dimer. The [2 + 2] cycloaddition product is 22.1 kcal/mol lower in energy than the reactants, while the [4 + 2] Diels−Alder product is more stable than the [2 + 2] product by 23.7 kcal/mol, which is equivalent to an overall binding energy of 45.7 kcal/mol. As in the case of Ge−Si, bonds involving Ge are longer and angles with Ge centers are smaller than the corresponding product on the Si−Si and Si−Ge dimers in general, as shown in Figure 2c.

The reaction energetics show two general trends. First, the differences in energies between the [4 + 2] and the [2 + 2] cycloaddition products are similar (~24 kcal/mol) for reactions on Si−Si, Ge−Si, and Ge−Ge dimers. This result shows that the difference in energy between the six-membered ring formed in a [4 + 2] addition and the four-membered ring formed in a [2 + 2] addition is largely independent of the presence of Ge atoms. Comparison of structural parameters provides further evidence for this trend, where bond lengths and angles are similar in the corresponding products on different dimers. The second trend is the decrease in binding energies from Si−Si to Ge−Si to Ge−Ge. For the same reaction on the three dimers, the binding energy is reduced by the same amount for each

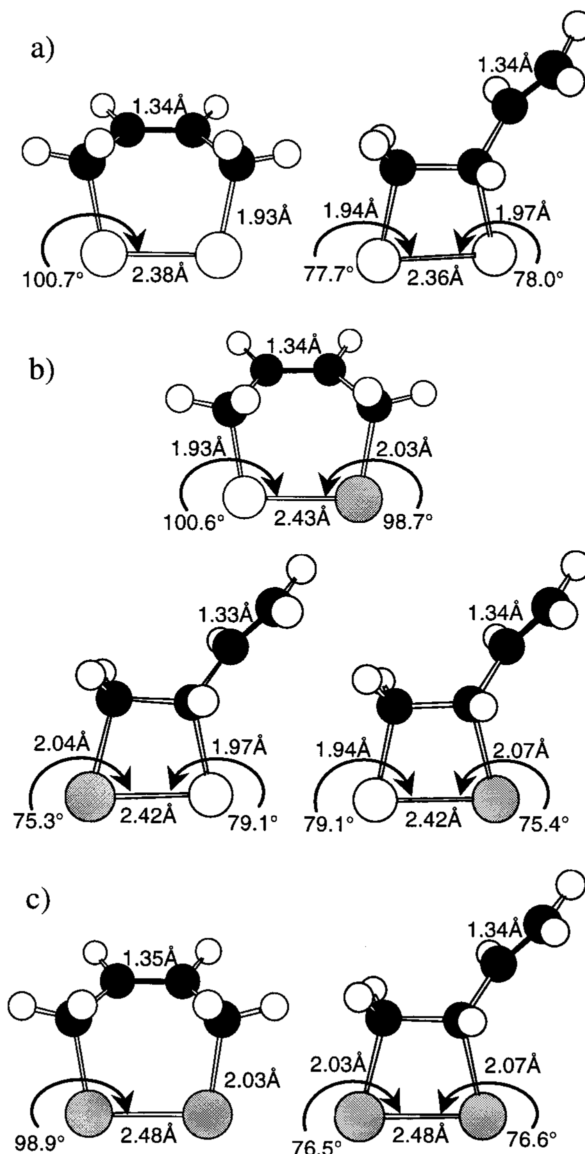

Figure 2. (a) Geometry of the [4 + 2] (left) and [2 + 2] (right) cycloaddition products on the Si−Si dimer. The [4 + 2] product is symmetric, but the [2 + 2] ring is puckered, consistent with the results of Konecny and Doren.[40] (b) Geometries of the [4 + 2] product (top) and [2 + 2] products (bottom) on the Ge−Si dimer cluster. The [2 + 2] rings are puckered. The right [2 + 2] product has lower energy than the left product. (c) Geometries of cycloaddition products on the Ge−Ge dimer. The [4 + 2] product is symmetric but the [2 + 2] ring is puckered. The large white atoms are Si, and the large gray atoms are Ge. The small black atoms are C, and the small white atoms are H.

additional Ge atom added to the dimer. For instance, the difference in binding energy for the [4 + 2] Diels−Alder reaction product on the Si−Si dimer and the Ge−Si dimer is 8.1 kcal/mol, and the difference between the [4 + 2] products on the Ge−Si dimer and the Ge−Ge dimer is 8.0 kcal/mol. Similar differences in adsorption energy (~8 kcal/mol) are found for the [2 + 2] products on the three dimers. The difference in adsorption energies can be explained by the fact that the Ge−C bond is weaker than the Si−C bond, resulting in lower binding energies for products on dimers with more Ge atoms. A diagram summarizing the energies calculated in this study is shown in Figure 3.

Analysis of our results clearly shows the effect of Ge on the reactivity of the Si(100)-2 × 1 surface toward unsaturated hydrocarbons. The presence of Ge on the surface decreases the

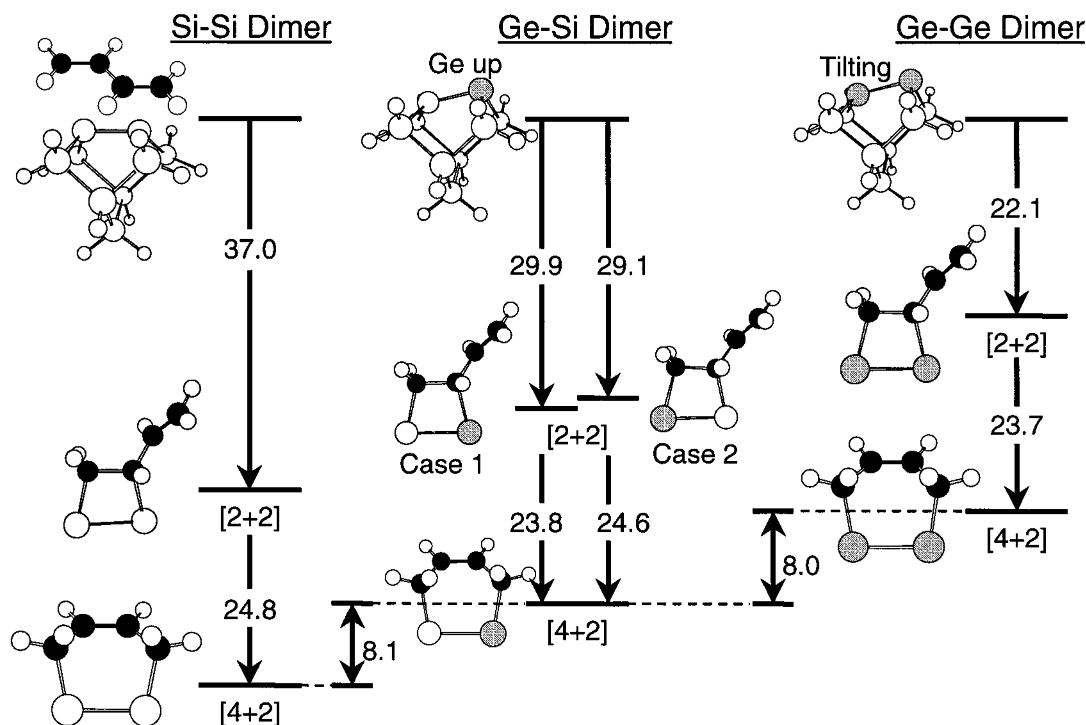

Figure 3. Summary of the energetics of cycloaddition reactions on different dimer clusters representing Ge/Si(100)-2 × 1 surfaces with different surface Ge concentrations. All energies are in kcal/mol. The trends in binding energies and ring strain effects are also shown.

adsorption energy of unsaturated hydrocarbons. This trend can explain the difference in thermal desorption behavior of 1,3-butadiene on Si(100)-2 × 1[41] and Ge(100)-2 × 1.[45] On Si(100)-2 × 1, chemisorbed 1,3-butadiene dissociates on the surface because the desorption barrier is larger than the energy needed to dissociate the product on the surface. In contrast, on Ge(100)-2 × 1, 1,3-butadiene desorbs reversibly because the weaker surface Ge−C bonds break and 1,3-butadiene desorbs before the product dissociates on the surface during thermal desorption.

The exothermicity of cycloaddition reactions originates from the difference in bonding of the reactants and products. For example, when 1,3-butadiene chemisorbs on a Si(100)-2 × 1 surface via the Diels−Alder reaction, there is a net loss of one C═C π-bond and a Si═Si dimer π-bond, while two new Si−C σ-bonds within a six-membered ring are formed on the surface. Thus, the binding energy of the cycloaddition products on the Ge/Si(100)-2 × 1 surface can be estimated by the following general equation:

$$\Delta E = \sigma_1 + \sigma_2 - \pi_{c=c} - \pi_d - \gamma - \Delta\delta \qquad (1)$$

where σ_1 and σ_2 are the energies of the new Si−C or Ge−C σ-bonds formed on the surface, $\pi_{C=C}$ is the energy required to break a C═C π-bond of the diene, π_d is the energy required to break the dimer π-bond on the surface, γ is the resonance energy of the conjugated diene system, and $\Delta\delta$ is the difference in ring strain energies between the reactants and the products.

A hypothetical isomerization between the [4 + 2] and the [2 + 2] product on a particular dimer is an isodesmic reaction. That is, the total number of each type of bond is identical in the reactants and the products. The energy of such an isomerization reaction on a dimer gives the difference in adsorption energies between the [4 + 2] and the [2 + 2] products on a dimer, which, according to the above equation, is estimated to be only the ring strain energy difference $\Delta\delta$ between the two products on the surface. Therefore, the result that the energy difference between the two cycloaddition products on a particular dimer is independent of the type of dimer on which the reaction takes place can be explained by similar ring strain energy effects on different dimers. In other words, the difference in ring strain between the six-membered ring of a [4 + 2] product and the four-membered ring of a [2 + 2] product is independent of the presence of Si or Ge atom in the dimer. The main contribution of ring strain energy comes from the distortion of bond angles. For instance, the ∠C−Si−Si of the [4 + 2] product on the Si−Si dimer is ~101°, while the angle is only ~78° for the [2 + 2] product. One might argue that Ge−Ge bonds are longer than Si−Si bonds, thus ∠C−Si−Si should be larger than ∠C−Ge−Ge in a [2 + 2] product, resulting in more ring strain for the [2 + 2] product on a Ge−Ge dimer. However, as ∠C−Ge−Ge decreases, the opposite ∠C−C−Ge increases simultaneously, compensating this effect and resulting in a strain energy difference similar to the case of the Si−Si dimer.

The difference in the stiffness between Si-centered angles and Ge-centered angles has only a minor contribution to the hypothetical [4 + 2]−[2 + 2] isomerization energetics on the dimers. From gas-phase frequency calculations at the B3LYP/6-311G** level, it was found that the bending motion of the GeH_2 radical has a lower frequency (955.8 cm^{-1}) than the same mode in the SiH_2 radical (1025.7 cm^{-1}). A lower bending frequency of the GeH_2 radical means that less energy is required to distort the H−Ge−H angle than to bend the H−Si−H angle. Thus, it requires less energy to convert a six-membered [4 + 2] product to a four-membered [2 + 2] product if Si atoms in the ring are substituted by Ge atoms. This explains the slight difference in the [4 + 2]−[2 + 2] isomerization energy on Si−Si and Ge−Ge dimers, which is the largest on the Si−Si dimer (24.8 kcal/mol) and the smallest on the Ge−Ge dimer (23.7 kcal/mol).

Comparison of adsorption energies of the same cycloaddition products on different dimers revealed that the same product on a dimer with one Si atom replaced by Ge is lower by 8 kcal/mol. From the above exothermicity analysis in eq 1, the

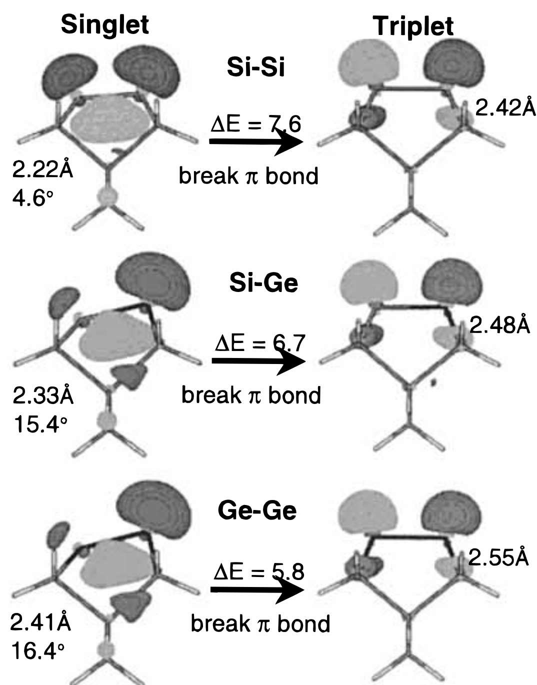

Figure 4. HOMO diagrams, geometries, and π-bond energies of the Si−Si, Ge−Si, and Ge−Ge dimers in this theoretical study. The Si−Si dimer has the highest π-bond energy, while the Ge−Ge dimer has the lowest. Triplet dimers are symmetric.

difference in adsorption energies for the same product on different dimers arises mainly from a difference in σ-bond formation energies and dimer π-bond energies. To determine the strengths of Si−C and Ge−C bonds, we calculated the dissociation energy of the Si−C bond in methylsilane H_3C-SiH_3 and the Ge−C bond in methylgermane H_3C-GeH_3, using the B3LYP/6-311G** level of theory with zero-point corrections. It was found that the Si−C and the Ge−C bond energies are 81.7 and 72.7 kcal/mol, respectively. From the above-calculated gas-phase dissociation energetics, a Si−C bond is stronger than a Ge−C bond in GeH_3 by 8.9 kcal/mol. Hence, bond strength differences have the major contribution on the thermodynamics of reactions on different dimers.

A less important contribution is the difference in π-bond energies between different dimer systems. One can approximately determine the π-bond energy of a dimer by calculating the energy difference between the singlet and triplet state of the same dimer, because the π-bond is broken in the triplet state due to the Pauli exclusion principle. We performed such calculations for the Si−Si, Ge−Si, and Ge−Ge dimers. The highest occupied molecular orbitals (HOMO's) of each dimer, together with dimer geometries and dimer π-bond energy, are shown in Figure 4. We can see from the figure that weak π-bonds are formed between the two atoms of the dimer, and charge transfer from the down atom to the up atom of the dimer is evident in the larger electron density above the up dimer atom, especially in the cases of Si−Ge and Ge−Ge dimer. The dimer π-bond energy is 7.6 kcal/mol for the Si−Si dimer, 6.7 kcal/mol for the Ge−Si dimer, and 5.8 kcal/mol for the Ge−Ge dimer. Thus, when one Si atom on the Si−Si dimer is replaced by a Ge atom, the π-bond energy decreases by 0.9 kcal/mol, and this π-bond difference has a minor contribution to the difference in adsorption energies between the same product on different dimers.

The rates of these cycloaddition reactions on the surface depend on the activation barriers of the adsorption process. Experimental studies have shown that kinetic factors may control the pathways of cycloaddition reactions at the surface.[43,44,53] Konecny and Doren have shown theoretically that the [4 + 2] surface reaction between 1,3-cyclohexadiene and the Si(100)-2 × 1 surface has a very low activation barrier.[39,40] We have begun further calculations to investigate the mechanisms and activation barriers of cycloaddition reactions on the Ge/Si(100)-2 × 1 surface, and in particular, the effect of Ge on the kinetics of these reactions.

Conclusions

To explore the possibility of cycloaddition reactions and the formation of an organic monolayer on the surface of an $Si_{1-x}Ge_x$ alloy, we performed quantum chemical calculations of 1,3-butadiene adsorption on the Ge/Si(100)-2 × 1 surface. With dimer cluster models, we conclude that both the [4 + 2] Diels−Alder and [2 + 2] cycloaddition reaction products are energetically stable on Si−Si, Ge−Si, and Ge−Ge dimers representing the Ge/Si(100)-2 × 1 surface. We observed two general trends for the energetics of cycloaddition reactions on the Ge/Si(100)-2 × 1 surface. First, the difference in binding energies between the [4 + 2] and the [2 + 2] product are similar for reactions on all three types of dimer. This can be explained by the fact that the difference in ring strain energy between the six-membered ring formed in a [4 + 2] reaction and the four-membered ring formed in a [2 + 2] reaction is independent of the presence of Ge atoms on the dimer. Second, the adsorption energy for the same cycloaddition product decreases as the number of surface Ge dimer atoms increases. This can be explained by the bond strength differences between the Si−C and the Ge−C bond.

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