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Theoretical Studies of Chemical Reactivity:
Some Approaches and Applications

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2000
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General Introduction

The birth of quantum mechanics in physics at the beginning of the 20th century makes it possible to understand how the electrons and atomic nuclei form the chemical bonds that bind the atomic nuclei in molecules and solids. At the same time, the new field called quantum chemistry which meant applications of quantum mechanics to chemical problems was born. Although the application was mainly of qualitative nature in early days, it has been developed rapidly since the 1960s with the appearance of powerful computers. Now quantum chemistry is indispensable to studies in various fields of chemistry.

The methods to describe the electronic structure of atoms and molecules are classified into two different theories: the molecular orbital (MO) theory and the density functional theory (DFT). The MO theory that is based on the one-electron approximation has been a conventional idea for both the calculational method and the theories of reactivities of molecules. The Hartree-Fock approximation established by Roothaan and Hall, for instance, is known to be used widely as the first step in many electronic structure calculations, and the theory of orbital-symmetry conservation by Woodward and Hoffmann and the frontier orbital theory by Fukui are based on the Hückel MO theory. Moreover, there are excellent methods, such as the configuration interaction, the cluster expansion, and the perturbation theory, that estimate the electron correlation energy beyond the Hartree-Fock approximation. The growth of the MO theory has led to prosperity of quantum chemistry.

On the other hand, the DFT in which an electronic system is described by the electron density $\rho(\mathbf{r})$ instead of the wave function $\Psi(\mathbf{r})$ has also been developed recently. Although the original idea of this theory was initiated by Thomas and Fermi in 1920s, this theory was established by Hohenberg and Kohn in 1964. Hohenberg and Kohn proved that an external potential $v(\mathbf{r})$ is a unique functional of $\rho(\mathbf{r})$. That is, they showed that the ground state of many-particle system is a unique functional of $\rho(\mathbf{r})$. They also showed that the energy functional $E[\rho(\mathbf{r})]$ equals the ground-state energy $E$ for the correct $\rho(\mathbf{r})$. 
Furthermore, in 1965, Kohn and Sham introduced the idea of non-interactive reference system in which the electron density is resolved into $N$ orbital components. This enables us to regard the many-particle problem as the one-particle problem. Although there remains a problem that the form of the exact functional is unknown, this Kohn-Sham formalism has been used widely for the electronic structure calculations of the solid-state systems, and also for the molecular systems recently.

Although the DFT is noted as a very useful method for calculations of large molecular systems, it has another possibility of describing the chemical reactivity. In the DFT, the important concept like the chemical potential $\mu$, that is the derivative of the energy $E$ with respect to the electron number $N$, is introduced. The chemical potential $\mu$ is connected with the electronegativity $\chi$ by inverting its sign. Moreover, Parr and his co-workers defined the absolute hardness and the Fukui function of the system. These terms are easy to understand intuitively for chemists, therefore the DFT may provide an intuitive picture to help understanding of chemical reactions.

The main theme of this thesis is to study the chemical reactivity of molecules along the reaction coordinate and the surface reactions in manufacturing the silicon semiconductor device by using the MO theory and the DFT. It is composed of eight chapters. In the first two chapters, the author studied the chemical reactivity of molecules along the reaction path. The next six chapters present the applications of quantum chemistry to the silicon chemistry.

In Chapter 1, the orbitals participating in electron delocalization have been investigated by taking the aromatic substitution reaction as an example. The interacting orbitals have been localized around the reaction sites. It was observed that the chemical bonds were generated and broken transiently along the reaction path. Next, the reactive orbitals that were very similar to the interacting orbital were obtained by projecting the reference orbital function to specify the bond being formed onto the MO spaces of the reactant molecules. The local potential of the reaction site for electron donation estimated for substituted benzene molecules by using these projected orbitals has been compared with the experimental scale of electron-donating and electron-withdrawing strength of substituent groups.

In Chapter 2, the population analysis along the intrinsic reaction coordinate (IRC) has been performed in order to reveal the variation of the electronic structure along the reaction coordinate. The derivatives of the gross atomic charge by Mulliken, the bond orders and the atom valence by Mayer with respect to the nuclear motion along the IRC have been calculated analytically. This method has been applied to the 1,3-dipole cycloaddition reaction between fulminic acid and acetylene.

In Chapter 3, the gas phase reaction between singlet oxygen (1D) and silane has been studied. A low energy reaction path has been found in addition to the excited-state reaction path.

In Chapter 4, a cluster model reaction of the oxidation sites in hydrogen- and water-terminated Si dimers has been investigated by means of $ab$-initio molecular orbital calculations in order to obtain a chemical insight into the bond in the Si surface network which the oxidant prefers to attack.

In Chapter 5, the oxidation mechanism of hydrogen-terminated Si(111) surface by oxygen anions has been studied using the $ab$ initio molecular orbital method. The author studied a silicon cluster model, which was a local model of the hydrogen-terminated Si(111) surface. The author clarified that oxygen anions were stable in a cage of silicon cluster. To ensure the result of the cluster model the author has also studied an extended model with the periodic boundary condition. The author has proposed that an oxygen anion attacks Si atoms to form a penta-coordinated complex and inserts into a Si–Si bond to form a local Si–O–Si structure.

In Chapter 6, the reaction mechanism of the aluminum deposition over the hydrogen-terminated Si surface by dimethyl aluminum hydride has been discussed. This study provides a new insight into the aluminum selective chemical vapor deposition (CVD) on the silicon surface which has received much attention as a promising technology of ULSI metallization.
In Chapter 7, the deposition of SiH$_4$ on the fluorine-terminated Si surface and the p-doping effect have been studied. The author clarified that in the case of p-doped system the fluorine atom immersed in the bulk inserted into a pair of Si atoms to form chemical bonds.

In Chapter 8, the gas-phase reaction mechanism of the low-temperature thermal chemical vapor deposition between GeF$_4$ and Si$_2$H$_6$ has been studied.

Chapter 1:

Transient Bonds and Chemical Reactivity of Molecules
1. Introduction

Reactions are essentially a series of formations and breakings of bonds between atoms. The development of the precise picture of atoms and chemical bonds has affected, therefore, the outlook of chemists. The mechanisms of reactions that they propose must be in harmony with the theoretical concept of bonds. The formation of new bonds between the reagent and the reactant is brought about by mutual electron delocalization. In this interaction, the highest occupied (HO) MO and the lowest unoccupied (LU) MO play usually the dominant roles. The energy levels of the HOMO and the LUMO have been connected with some important quantities of molecules, e.g., the "electronegativity" by Mulliken, the "absolute hardness" and "chemical potential" by Parr et al. The concept of "hard and soft acids and bases" (HSAB) proposed by Pearson is related also to the frontier orbital energy levels. These are all molecular quantities, representing the chemical and physical properties that apply to the whole system, a molecule, an ion, or a radical. However, the reactivity of molecules should be related essentially to the power of an atom or a functional group in a molecule to attract or release electrons. Thus, in the frontier orbital approach, the amplitude on an atom and the nodal property between atoms in the HOMO and the LUMO are of crucial importance. As the systems that we study become more and more complicated, we need a way of connecting the abilities of a molecule for electron donation and acceptance in reactions to some local quantities. In evaluating those, it is important to take the effects of the molecular periphery appropriately into account. We report here that analysis of the bonds that are being formed and broken with the progress of chemical reactions leads to a reactive scale that will be applicable to large molecular species.

2. Results and Discussion

2.1. Transient Bonds in Chemical Reactions

Electron delocalization between two molecular species is represented by a combination of the occupied MOs of one part and the unoccupied MOs of the other
part. Though the HOMO of the electron donor part and the LUMO of the electron acceptor part play the dominant roles, the MOs relevant for the orbital interactions tend to increase in number as the interacting species becomes larger in size. To evaluate the participation of other MOs in chemical interactions, it may be helpful to utilize a concept of hybridized MOs. The situation is similar to molecules in which chemical bonds are represented compactly in terms of hybrid atomic orbitals. The hybridized MO should have a large amplitude in a particular region of the reactant molecule to specify the active site and should have an appropriate nodal property to indicate the bonds that are broken or strengthened in the course of the reaction.

First, we want to see the orbitals that participate in electron delocalization. Then, we carry out simultaneous transformations of the occupied MOs $\psi_1 (i = 1, 2, ..., m)$ of the donor part and the unoccupied MOs $\psi_{n+1} (i = 1, 2, ..., N-n)$ of the acceptor part within each of the two fragment species so as to represent the intermolecular elements of the bond-order matrix for the composite reacting system in terms of the pairs of hybridized fragment MOs, ($\phi_i, \psi_j$), $j$ being the smaller of $m$ and $N-n$. The simplest example to apply the method, with abundant experimental data, may be electrophilic substitution of aromatic molecules. Figure 1 sketches the benzene molecule interacting with an attacking NO$_2^+$ to cause an electrophilic aromatic substitution. The transition-state structure for the system in the presence of a methyl alcohol molecule has been determined. The calculated C1–N distance was reported to be 2.48 Å. This C–N length may be too long to form a covalent bond. To make simpler our arguments here, we have fixed the C1–N bond at 2.5 Å and at 2.0 Å and determined the other geometrical variables disregarding the solvent molecule. The MOs of the interacting system and of the two fragment species were calculated by applying the Gaussian 92 program with the simplest STO-6G minimal basis set. The pair of orbitals that plays the principal role in electron delocalization from the benzene part to the NO$_2^+$ part is presented in Figure 1.

At the stage shown by $R_{C1-N} = 2.5$ Å, the orbital of the benzene part looks similar to its HOMO, but the orbital was amplified on C1, C2, and C6 and was attenuated on C3 and C5. This distortion of the orbital becomes clearer at $R_{C1-N} = 2.0$ Å. The interaction

![Figure 1](image_url). A sketch of the reaction model for nitration of benzene and the pair of orbitals taking part in electron delocalization from the benzene part to the NO$_2^+$ part. The orbital of benzene is shown on the left and that of NO$_2^+$ on the right. The orbitals are illustrated arbitrarily in the plane parallel to and 2.0 Å above (for $R_{C1-N} = 2.5$ Å) and 1.0 Å above (for $R_{C1-N} = 2.0$ Å) the plane defined by C2, C3, C5, and C6.
is three-centered in the benzene part, the carbons C2 and C6 adjacent to the reaction site C1 taking part in the electron delocalization to NO$_2^+$. The HOMO is the dominant component of the interacting orbital $\phi_1$ of the benzene part, but another $\pi$-type MO, $\pi_1$, participates significantly in the orbital $\phi_1$ to mix in-phase with the HOMO on the reaction site, C1. The resulting orbital is strongly bonding between C1 and C2 and between C1 and C6. This indicates that the $\pi$ conjugation is weakened between the reaction site and the adjacent carbons upon electron donation to the attacking cation. This is obviously in harmony with the chemists' view of bond interchange in this reaction process that the C1-C2 and C2-C6 bonds are converted into single bonds, while the conjugation is retained in the remaining part to give a $\sigma$-complex.

Theoretically, an old reactivity index, "localization energy", was proposed by assuming intuitively such a change in conjugation in the reaction course. A part of the electrons donated from the orbital $\phi_1$ of the benzene part is not transferred to the paired counterpart $\psi_1$ of the NO$_2^+$ part, but is retained in the region between the two species through the overlap between $\psi_1$ and $\phi_1$ to form a loose bond between the C2-C1-C6 region of the benzene part and the nitrogen center of the electrophile. As the interaction proceeds, electrons are promoted to the unoccupied MOs in the benzene part induced by electron delocalization and they participate in bonding interactions with the electrophile unoccupied orbital. Then, the (C1, C2, C6)-N transient bond is converted into the C1-N bond of the sigma complex. The mixing in of the $\sigma$-type MOs of benzene is not important at the early stages of the reaction.

2.2. Projected Reactive Orbitals

An important aspect of electron delocalization disclosed above is that it determines the active structural units of the reagent and reactant molecules for a given reaction. It tells us what bonds are formed and what bonds are broken. The next step for us is to find a way of obtaining such orbitals without carrying out time-consuming MO calculations on the composite reacting system. In the reaction model studied above, the benzene is supposed to produce the orbital that has the maximum amplitude on the reaction center, C1, by combining the occupied MOs. In the occupied MO space, however, the orbital cannot be localized completely on the reaction site, but is delocalized over other carbons.

Now, projection of a certain orbital function, $\delta_i$, onto the occupied MO subspace of a molecule should give the occupied orbital, $\phi_i$, that has the maximum amplitude on the function, $\delta_i$. The projected reactive occupied orbital, $\phi_{n\sigma} (\delta_i)$, of an isolated reactant molecule is given by

$$\phi_{n\sigma} (\delta_i) = \left( \sum_{j=1}^{m} d_{i,j} \phi_j \right) \left/ \left( \sum_{m+1}^{M} d_{i,m+1} \phi_j \right) \right. \right)^{1/2}, \quad (1)$$

where $d_{i,j}$ is the coefficient of the occupied MO $\phi_j$ in the linear expansion of $\delta_i$ in terms of the occupied canonical MOs $\phi_j (i = 1, \ldots, m)$ and the unoccupied canonical MOs $\phi_j (j = m+1, \ldots, M)$:

$$\delta_i = \sum_{j=1}^{m} d_{i,j} \phi_j + \sum_{j=m+1}^{M} d_{i,m+1} \phi_j. \quad (2)$$

To discuss the reactivity of a carbon in benzene against an electrophile, it is simplest to take the 2p$\pi$ AO of the reaction site as the reference orbital, $\delta_i$. One may find easily that the intermixing of the one of the HOMOs, $\pi_1$, with the $\pi_1$ MO of benzene gives rise to the orbital that has the largest amplitude on C1, but is delocalized on the adjacent carbons, C2 and C6. The orbital is bonding between C1 and C2 and between C1 and C6. Actually, the orbital obtained in this manner bears a close resemblance to the interacting orbital $\phi_1$ derived from an analysis of electron delocalization in the reacting system, though the projected reactive orbital is slightly more localized. Inclusion of the 2p$\pi$ AO of C4 in $\delta_i$ makes the projected orbital closer to the interacting orbital, but we may take simply the 2p$\pi$ AO of C1 as $\delta_i$ in the present study. Application of the same procedure to substituted benzenes should lead naturally to the occupied projected orbitals that are very similar in shape to the orbital of benzene. Incidentally, the reference function $\delta_i$ is not necessarily an AO, but may be an atomic hybrid orbital or a combination of several AOs spanning a functional group, depending on the type of reaction to be studied.
Now, the local electron-donating potential of the structural unit associated with $\delta_i$ is given by

$$\lambda_{loc} (\delta_i) = \left( \sum_{i=1}^{\infty} d_{ij}^2 \varepsilon_i \right) / \left( \sum_{j=1}^{\infty} d_{ij}^2 \right),$$

(3)

where $\varepsilon_i$ signifies the energy of the MO $\phi_i$. Note that the quantity defined by eq. (3) does not apply to the whole molecule, but represents a local property of an atom or a group. Abundant experimental results to see relative reactivities of substituted benzenes in an aromatic substitution reaction have been interpreted very compactly in terms of the Hammett $\sigma$ parameter and its modified versions.\textsuperscript{23-27} Figure 2 plots the calculated $\lambda_{loc}$ values against the $\sigma$ parameters for various substituent groups. One sees a good correlation between the theoretical scale and the experimental one for various electron-releasing and withdrawing groups at different positions, $meta$ and $para$. In contrast, $\sigma^+$ parameters deviate significantly from the theoretical scale for $-NH_2$, $-OH$, and $-OCH_3$ groups in the $para$-position, as illustrated in Figure 3. It has been suggested that these groups have an additional stabilizing effect: The resonance between the benzene ring and the substituent group that intervenes when an electronic charge is removed. Then, the deviation from the theoretically estimated values will make it possible to trace the effects involved in the experimental parameters into different origins. The parameters $\sigma^0$ that have been proposed so as to lift the direct resonance effect are seen to agree well with the theoretical scales for $p$-$NH_2$, $p$-$OH$, and $p$-$OCH_3$ groups, as shown in Figure 4. Unfortunately, the correlation between the theoretical scale and the $\sigma^0$ parameters is worse as a whole, relative to the original $\sigma$ parameters. Adjustments within these parameters may be necessary. Now, the theoretically estimated electron-donating potential may be utilized as a reliable measure of discussing the reactivity of atoms and groups in any other type of reaction.

Projection of the reference orbital function $\delta_i$ onto the unoccupied MO subspace gives rise to the unoccupied reactive orbital that has the maximum amplitude on $\delta_i$.\textsuperscript{22}

![Figure 2](image1.png)

**Figure 2.** Correlation between the local electron-donating potential of reaction sites and the Hammett $\sigma$ parameters for substituted benzenes.

![Figure 3](image2.png)

**Figure 3.** Correlation between the local electron-donating potential of reaction sites and the Hammett $\sigma^+$ parameters for substituted benzenes.
The electron-accepting capacitance of the structural unit is evaluated then by

$$\lambda_{\text{win}}(\delta_r) = \left( \sum_{j=m+1}^{M} d_{j,r} \gamma_j \right) + \left( \sum_{j=m+1}^{M} d_{j,r} \gamma_j \right)$$

Now, the reference function is rewritten in terms of $\phi_{\alpha}$ and $\phi_{\mu\alpha}$ as

$$\delta_r = \left( \sum_{i=1}^{m} d_{i,r} \frac{1}{2} \phi_{\alpha}(\delta_r) \right) + \left( \sum_{i=1}^{m} d_{i,r} \frac{1}{2} \phi_{\mu\alpha}(\delta_r) \right)$$

$$= u \phi_{\alpha}(\delta_r) + (1-u) \phi_{\mu\alpha}(\delta_r) \quad (|u| \leq 1).$$

It follows then that we can evaluate the power of the reaction site to attract electrons by

$$- \lambda(\delta_r) = - \left( \sum_{j=m+1}^{M} d_{j,r} \gamma_j \right) - \left( \sum_{j=m+1}^{M} d_{j,r} \gamma_j \right)$$

$$= -a^2 \lambda_{\alpha}(\delta_r) - (1-a^2) \lambda_{\mu\alpha}(\delta_r).$$

The coefficient $a^2$ varies in the range between 0 and 1, depending on the reaction site or the functional group of a reactant molecule used for the reaction. If $a^2$ is 1, the reaction site serves only as an electron donor, whereas the reaction site serves only as an electron acceptor when $a^2$ is 0. Thus, $a^2$ and $(1-a^2)$ measure the efficiency of a reaction site as an electron donor and as an electron acceptor, respectively. The efficiency is related obviously to the localizability of the occupied and unoccupied orbitals, $\phi_{\alpha}$ and $\phi_{\mu\alpha}$ on $\delta_r$ and, hence, to the localizability of interaction on the reaction site, i.e., $a^2$ and $(1-a^2)$ represent, respectively, the active part of $\phi_{\alpha}$ and of $\phi_{\mu\alpha}$. In the case $a^2 = 1/2$, eq. (7) is formally equivalent to the Mulliken electronegativity of a molecule.\(^5\)

Thus, we can regard $- \lambda$ as giving the local electronegativity of the reaction site. This may be quite natural, remembering that the electronegativity indicates the power of an atom to attract electrons in a molecule after the original definition by Pauling.\(^2\)

The electron-donating and -accepting abilities of the functional unit are defined, respectively, by\(^2\)
in which
\[
\eta(\delta) = \frac{1}{2} (\lambda_{\text{noc}}(\delta) - \lambda_{\text{oc}}(\delta)).
\] (10)

The orbital function, \(\delta\), has the electron-releasing or -attracting potential \(\lambda(\delta)\). The electron-donating and accepting potentials of the reaction site are reduced, however, by \(2(1 - a^2)\eta(\delta)\) and \(2a^2\eta(\delta)\) from that of \(\delta\), respectively. The reaction site will be a good electron acceptor when both the inactive fraction \((1 - a^2)\) of the orbital \(\phi_{\text{oc}}\) and \(\eta\) are small. The reaction site will be a good donor when both the inactive fraction \(a^2\) of the orbital \(\phi_{\text{noc}}\) and \(\eta\) are small. Thus, \(2(1 - a^2)\eta(\delta)\) and \(2a^2\eta(\delta)\) are regarded as indicating the basic hardness and acidic hardness of a reaction site or a functional group specified by \(\delta\) in a reactant molecule, respectively. Note that eq. (10) will give the chemical hardness of a molecule, when \(\lambda_{\text{oc}}\) and \(\lambda_{\text{noc}}\) are replaced by \(\phi_{\text{HOMO}}\) and \(\phi_{\text{UMO}}\), respectively.\(^7\)

\[
\lambda_{\text{noc}}(\delta) \quad \lambda(\delta) \quad (1 - a^2)\eta(\delta) \quad \lambda_{\text{oc}}(\delta)
\]

Figure 5 shows the relation between the basic hardness and the Hammett \(\sigma\) parameters for substituted benzenes. Though a linear correlation is found for the para-substituted benzenes, the meta-substituted benzenes show a different trend. This indicates clearly that the reactivity of atoms in a molecule is determined by a balance between its electronegativity and chemical hardness. It is natural that substituent groups affect both of them. The change in the sigma-electronic part is reflected in the reactivity by raising or lowering the value of \(\lambda\).

The function \(\delta\) may be chosen as the orbital that is likely to be utilized in the formation of new bonds with the reagent. It may be an AO or a hybrid AO in a single-centered reaction and a linear combination of several AOs in multicentered reactions. In contrast, the orbitals \(\phi_{\text{oc}}(\delta)\) and \(\phi_{\text{noc}}(\delta)\) have the largest amplitude on \(\delta\), but are delocalized over a bond or over a few atoms. The mode and extent of delocalization of these orbitals provide us a clue to reveal the molecular mechanism of a reaction. An analysis of transient bonds in terms of paired interacting orbitals for the smallest reaction model and the evaluation of local electron-donating and -accepting potentials of atoms and groups in large molecules by projecting a reference orbital will be of use in discussing the reactivity of complicated molecules treated in modern chemistry. The reference orbital should be chosen to be appropriate for representing those bonds, since the transient bonds guide the reacting system to the transition state and to the product. To make this approach more general and practical, we may adopt the frontier MO of the smallest molecule or its principal component as the reference orbital function for larger reactant molecules that undergo the same type of reaction.

Finally, Politzer and collaborators proposed a few years ago a reactivity scale: "the average local ionization potential".\(^31\) If we assume here that a reactant molecule provides the occupied orbital that has the maximum electron density on a point \(r\) in the molecular space when it donates an electronic charge to an electrophilic reagent, such an orbital \(\phi\) is given by

\[
\phi = \left[ \sum_{i=1}^{n} \phi_i(r) \phi_i \right] / \left[ \sum_{i=1}^{n} \phi_i(r)^2 \right]^{1/2}.
\] (11)

The electron-donating potential of this orbital in terms of orthonormal MOs should be

\[
\epsilon_j = \left[ \sum_{i=1}^{n} \rho_i(r) \epsilon_i \right] / \rho(r).
\] (12)

This is nothing but the definition of the average local ionization potential (the sign inverted). It is clear, therefore, that they are concerned with a point in the space around the reactant molecule, whereas we focus our attention on the orbitals of reaction sites. This makes a big difference, however, when we try to discuss multicentered reactions, e.g., cycloadditions, in which orbital symmetry plays a crucial role.\(^32\)
3. Conclusion

Electron delocalization is the major driving force of chemical reactions. An analysis of electron delocalization has disclosed an attracting behavior of molecules in reactions that they recombine their MOs to give the orbitals that are localized specifically around the reaction site. They tell us what bonds are formed and what bonds are loosened in the course of reactions. By taking the interaction between benzene and NO₂⁺ as an example, it has been illustrated that these interacting orbitals are reproduced approximately by projecting a certain reference function onto the MO subspaces. This finding is connected intimately with the fact that chemical interactions are local by nature: Various reactants different in size and structure undergo the same type of reaction if they have the same functional group, while a compound undergoes a variety of reactions against different kinds of reagents, as has been observed in experiments. We can thus estimate local electron-donating and -accepting abilities of an atom or a functional group in large molecules by MO calculations and interpret them in terms of local electronegativity and chemical hardness of reaction sites.

References

Chapter 2:

Population Analysis along the Intrinsic Reaction Coordinate:
Application to 1,3-Dipole Cycloaddition

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Quantum chemistry has developed remarkably and has become a useful method in various areas of chemistry. Not only the energies and structures of various molecular species but also the reaction paths such as the transition states can easily be calculated with high accuracy, using recent powerful computers and many excellent methods of calculation. Here, we should point out some problems that remain to be solved. The first point is that we have not established yet the method for a qualitative understanding of the wave function with high accuracy. The second point is that we do not know how to connect the change in wave function along the reaction coordinate with the enhancement or depression of chemical reactivity. To clarify these subjects, some attractive attempts, such as the valence bond (VB) type approach, the density functional approach, and the atoms in molecules (AIM), have been made.

One of these attempts is the population analysis. This concept was originally proposed by Mulliken and has been generalized and developed. Wiberg introduced the bond order and Giambiagi et al. and Mayer have generalized this idea. The multi-center bond indices have recently been proposed and their physical meanings and the relations between those quantities have also been discussed.

The population analysis has the advantage of its easy treatment. Therefore, it is often used to describe the formation or cleavage of chemical bonds and the change in the atomic charges along the reaction coordinate. When a linear combination of atomic orbitals for the molecular orbital (LCAO-MO) is used, both the gross atomic charge defined by Mulliken and the bond order defined by Mayer are generally made up of the electron density matrix and the overlap matrix. The question we have to ask here is what is the cause of the change in these quantities along the reaction coordinate. The change originates from two different contributions: the change in the electron density matrix with keeping the overlap matrix unaltered and the change in the overlap matrix with keeping the electron density matrix unaltered. The change in the density matrix arises from the electron redistribution caused by the nuclear motions. On the other hand, the change in
the overlap matrix arises from the LCAO formalism. In usual quantum chemical calculations, each AO is centered on the nucleus of an atom, except for the case with the floating orbital or the plane-wave basis set. These two contributions must be classified. This kind of division has already been introduced in the force theory. Nakatsuji et al. investigated the analytical second derivative of the potential energy satisfying the Hellmann-Feynman theorem and discussed the role of each term in the second derivative of the Hartree-Fock energy.26

In the present study, the derivatives of the gross atomic charge, the bond order, and the atom valence with respect to the nuclear positions are calculated analytically along the intrinsic reaction coordinate (IRC). This method is applied to a simple 1,3-dipole cycloaddition reaction between fulminic acid and acetylene. The 1,3-dipole cycloaddition reactions are important not only from a synthetic viewpoint but also from theoretical interests with respect to the reactivity and the regioselectivity. Some interesting studies have recently been done using the density functional theory (DFT) and a hard and soft acids and bases principle (HSAB) model for 1,3-dipole cycloaddition reactions.27,28 Chandra et al.27 investigated the cycloaddition reactions between 1,3-dipoles and dipolarophiles and observed that the hardness went through a minimum along the reaction coordinate. Méndez et al.28 have used the formalism of interaction energy and suggested that the electrophilic nature of 1,3-dipole and the nucleophilic nature of dipolarophiles were important. Furthermore, they indicated that reshuffling of the charge distribution should be more important than charge-transfer processes. On the other hand, Karadakov et al. studied the mechanism of 1,3-dipole cycloaddition in terms of the valence-bond theory.29 They examined the spin-coupled wave function along the reaction coordinate around the transition state and concluded that the following description (I) should be more plausible than (II), by which the mechanism of 1,3-dipole cycloaddition was usually represented.

\[
\text{(I)} \quad \begin{array}{c}
\text{CH} \\
\text{N}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{N} \\
\text{C}
\end{array}
\]

\[
\text{(II)} \quad \begin{array}{c}
\text{N} \\
\text{N}
\end{array} \quad \rightarrow \quad \begin{array}{c}
\text{N} \\
\text{C}
\end{array}
\]

Having their discussion in mind, the reaction mechanism is investigated here by means of the population analysis using the Hartree-Fock electron density.

2. Methods of Calculation

In this study, the LCAO-MO approximation for the Roothaan-Hall equation30 is used:

\[
\phi_i(r) = \sum \alpha_{ij} \chi_j(r),
\]

where \( \alpha_{ij} \) is the coefficient of the AO \( \chi_j(r) \) in the \( i \)th MO \( \phi_i(r) \). Within this formalism, the density matrix \( P \) consists of the elements \( P_{\alpha\beta} \) with respect to the atomic orbital:

\[
P_{\alpha\beta} = \sum \alpha_{\alpha\beta}^2 c_{\alpha \beta} c_{\beta \alpha}.
\]

According to the Mulliken's population analysis, the gross atomic charge of the atom \( A \), \( q_A \), is

\[
q_A = \sum P_{\alpha A} S_{\alpha A},
\]

where \( S \) is the overlap matrix composed with the elements \( S_{\alpha\beta} \):

\[
S_{\alpha\beta} = \int \chi_\alpha(r) \chi_\beta(r) dr.
\]

Therefore, the Mulliken gross atomic charge naturally corresponds to the partitioning of electron density \( \rho(r) \) with respect to AO.22
\[ N = \int \rho(r) \, dr = \int \sum_{\mu} \sum_{\nu} p_{\mu} \chi_{\mu}(r) \chi_{\nu}(r) \, dr = \sum_{\mu} \sum_{\nu} p_{\mu} s_{\mu} = \sum_{\mu} q_{\mu}. \]  

(5)

Another type of analysis was originally introduced by Wiberg and generalized by Giambiagi et al.\(^\text{12}\) and Mayer\(^\text{13-17}\). Mayer defined the bond-order index between the atom A and the atom B:

\[ I_{AB} = \sum_{\mu \in A, \nu \in B} (p S)_{\mu \nu} \left( \frac{p S}{p S_N} \right)_{\mu \nu}. \]  

(6)

and the total valence of the atom A:

\[ V_A = \sum_{\mu \in A} I_{AB}. \]  

(7)

This corresponds to the partitioning of the exchange part of the second-order density matrix:

\[ N = \frac{1}{2} \int \rho_{\mu}(r_{\mu}, r_{\nu}) \rho_{\nu}(r_{\nu}, r_{\mu}) \, dr_{\mu} \, dr_{\nu}. \]  

(8)

Therefore, the relation between Mayer's atom valence and Mulliken's gross atomic charge is given by

\[ 2q_A = V_A + \sum_{\mu \in A} \sum_{\nu \in A} (p S)_{\mu \nu} \left( \frac{p S}{p S_N} \right)_{\mu \nu}. \]  

(9)

Although the population analysis by the partitioning of higher-order density matrices has been proposed\(^\text{18-23}\), it is beyond the scope of this paper.

Now, the derivatives of the Mulliken gross atomic charge, the Mayer bond order and the atom valence with respect to the Cartesian coordinates of nucleus \((X_i, Y_i, Z_i)\) \((i = 1, 2, \ldots, N)\) are given by

\[ \frac{\partial q_A}{\partial X_i} = \frac{\partial}{\partial X_i} \left[ \sum_{\mu \in A} \sum_{\nu \in A} (p S)_{\mu \nu} \left( \frac{p S}{p S_N} \right)_{\mu \nu} \right]. \]  

(10)

\[ \frac{\partial I_{AB}}{\partial X_i} = \sum_{\mu \in A, \nu \in B} \left( \frac{\partial p S}{\partial X_i} \right)_{\mu \nu} + \left( \frac{\partial p S}{\partial X_i} \right)_{\mu \nu} \left( \frac{\partial p S}{\partial X_i} \right)_{\mu \nu}. \]  

(11)

The term which contains the derivative \(\frac{\partial p S}{\partial X_i}\) is called the density derivative term, while the contribution from \(\frac{\partial p S}{\partial X_i}\) is called the overlap derivative term. Moreover, we have

\[ \frac{\partial V_A}{\partial X_i} = \sum_{\mu \in A, \nu \in A} \frac{\partial L_I_{\mu \nu}}{\partial X_i}. \]  

(12)

The derivative of the overlap matrix \(\frac{\partial S}{\partial X_i}\) consists of the elements \(\frac{\partial S}{\partial X_i}\):

\[ \frac{\partial S_{\mu \nu}}{\partial X_i} = \frac{\partial}{\partial X_i} \left( \chi_{\mu}(r) \chi_{\nu}(r) \right) \, dr. \]  

(13)

and the derivative of the density matrix \(\frac{\partial P}{\partial X_i}\) consists of the elements \(\frac{\partial p S}{\partial X_i}\), which can be solved analytically:

\[ \frac{\partial p S}{\partial X_i} = -2 \sum_{\nu \in A} c_{\nu} e_{\nu} S_{\nu \nu}^{(i)} + 2 \sum_{\nu \in A} u_{\nu}^{(i)} \left( e_{\nu} e_{\nu} + 2 e_{\nu} e_{\nu} v_{\nu} \right), \]  

(14)

where \(S_{\nu \nu}^{(i)}\) is the derivative of the MO overlap integral between the MOs \(\phi_{\nu}\) and \(\phi_{\nu}\), and \(u_{\nu}^{(i)}\) is a mixing coefficient between the occupied and unoccupied MOs. The value \(u_{\nu}^{(i)}\) is solved by the coupled-perturbed Hartree-Fock (CPHF) equation.\(^\text{31-33}\) Nakatsuji et al. interpreted the physical meanings of each term in eq.(14) as the renormalization term and the relaxation term in their force theory.\(^\text{26}\) The first term on the right-hand side in eq.(14) which is called the renormalization term works to keep the total wave function normalized. The second term which is called the relaxation term shows the rearrangement of the charge distribution in the reaction system by mixing the occupied and unoccupied orbitals.

It should be noted that the total of Mulliken gross atomic charges must be conserved,

\[ \sum_{\mu \in A} \frac{\partial q_A}{\partial X_i} = 0. \]  

(15)
As shown in eq. (10), the derivative of the Mulliken gross atomic charge is given by two different contributions. The first term on the right-hand side represents the contribution from the change in the density matrix without the change in the overlap matrix, that is to say, the redistribution of electrons due to the nuclear motion. This term is called the density derivative term. What is more, this term is able to be divided into two terms: the renormalization term and the relaxation term. On the other hand, the second term represents the contribution from the change in the overlap without the change in AO coefficients, and hence, this is called the overlap derivative term.

By transforming the derivatives with respect to the $3N$ Cartesian coordinates into those with respect to the $3N$ mass-weighted Cartesian coordinates $\mathbf{x}_i (i = 1, 2, ..., 3N)$, the derivative of the Mulliken gross atomic charge with respect to the intrinsic reaction coordinate (IRC) is given by

$$
\frac{dq_i}{ds} = \sum_i \frac{\partial q_i}{\partial x_i} \frac{dx_i}{ds} = \sum_i \frac{\partial q_i}{\partial x_i} \frac{dx_i}{dV} \frac{dV}{ds},
$$

where $V$ is the adiabatic potential of the reaction system and where the IRC-equation is

$$
\frac{dx_i}{ds} = \frac{\partial V}{\partial x_i} (i = 1, 2, ..., 3N)
$$

has also been used. In the same way, the derivative of the bond order is given by

$$
\frac{dJ_{AB}}{ds} = \sum_{ji} \frac{\partial J_{AB}}{\partial x_{ij}} \frac{dx_{ij}}{ds} = \sum_{ji} \frac{\partial J_{AB}}{\partial x_{ij}} \frac{dx_{ij}}{\partial V} \frac{dV}{ds}
$$

The derivatives of the atom valences are also defined in a similar fashion. These derivatives are divided into the redistribution part of the electron density $\rho(r)$ and the exchange part of the second-order density matrix along the IRC.

The restricted Hartree-Fock scheme with Pople's 6-31G** basis set was used for calculations. The 6-31G** basis set is known to give reliable results for the population analysis. The geometry optimization and analytical frequency analysis with CPHF calculations were performed with the Gaussian94 program package. The IRC calculations by the Gonzalez-Schlegel algorithm with the step size $0.01$ au and $1/2$ bohr were done with the GAMESS program.

### 3. Results and Discussion

Concerning the 1,3-dipole cycloaddition reaction, Huisgen proposed the concerted single step reaction mechanism, while Firestone proposed that this reaction should take place in two steps via a biradical intermediate. Schlegel et al. performed the MC–SCF study of three different 1,3-dipole cycloaddition reactions and concluded that the concerted single step pathway was preferred to the biradical path. Therefore, the concerted single step reaction is considered here in our study.

#### 3.1. Energy and Geometries

The optimized structures of the reactants, which are fulminic acid 1 and acetylene 2, the transition state TS, and the product, isoxazole 3, are shown in Figure 1. The total energies are presented in Table 1. The activation energy of this reaction is 35.50 kcal/mol and the reaction energy is exothermic by 81.65 kcal/mol (including zero-point energy correction). In literature, it has been reported that the activation energy is 26.0 kcal/mol and the reaction energy is 66.9 kcal/mol (exothermic) at the MRCI //MCSCF/4-31G level. Another study has shown that the activation energy is 11.0 kcal/mol and the reaction energy is 77.7 kcal/mol (exothermic) at the MP4(SDTQ)/6-31G(d,p)//HF/6-31G(d,p) level. More recently, it has been reported that the activation energy is 12.2 kcal/mol at the CASPT2/CAS(6,6)/6-31G* level.

Figure 2 shows the potential energy profile along the IRC. At the point $s = 5.9$, the IRC connects practically to the product. The changes in bond lengths and bond angles along the IRC are shown in Figures 3 (a) and (b), respectively. Here, the numbering of the
Figure 1. Optimized geometries. Bond lengths and bond angles are given in angstroms and degrees, respectively. The bond orders are represented in gothic and the gross atomic charges in italic.
Table 1: Total Energies at the HF/6-31G** Level

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<td>3 isoxazole</td>
<td>-244.59419</td>
<td>35.20</td>
</tr>
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</table>

* Zero-point energy (ZPE) scaled by a factor of 0.89.

Figure 2. The potential energy curve along the IRC.

Figure 3. The geometrical changes along the IRC. The numbering of the atoms corresponds to those in Figure 1. The bond lengths are given in angstroms and the bond angles in degrees.
atoms is the same as in Figure 1. Although the bond length of O1–C4 is shorter than that of C3–C5 in the initial reaction coordinate (s < −1.5), the bond length of C3–C5 is shortened rapidly, while the O1–C4 bond length does not become shorter rapidly until the coordinate reaches the transition state (s > 2.0). These different shapes reflect non-synchronous bond formations. The bond angles of ∠C3C5C4 and ∠O1C4C5 do not change much along the IRC. Therefore, O1 and C3 atoms of fulminic acid attack the carbon atoms of the acetylene from the same directions, bending the ∠O1N2C3 angle of the fulminic acid along the IRC, as shown in Figure 3(b). On the other hand, the C4–C5 bond in acetylene and the O1–N2 and N2–C3 bonds in fulminic acid are lengthened slightly after the transition state is reached.

3.2. Mulliken Charges

Figure 4 shows the gross atomic charges calculated along the IRC. The gross charge of the O1 atom, qO1, does not change so much except for the final stage on the reaction coordinate (s > 5.0). The gross charge of the C3 atom does not change much either. The largest change in the gross charge in the fulminic acid part is seen on the N2 atom. The charge qN2 of the N2 atom is 6.795 in fulminic acid and becomes 7.141 in the product. The C4 and C5 atoms of acetylene show different charge profiles. The charge qC4 of the C4 atom decreases monotonically. In contrast, the charge qC5 of the C5 atom increases both at the initial stage and at the final stage on the reaction coordinate.

In order to investigate the change in the gross charges of each atom in detail, the derivatives of these gross charges, qO1, qN2, qC3, qC4, and qC5, with respect to the IRC are shown in Figures 5(a)-e), respectively. In case of the Mulliken gross charge, it is shown that the total derivative values behave in a similar way to the density derivative term. Moreover, it is seen that the two components of the density derivative term in the atomic charges exhibit different patterns. In the density derivative term of the N2 atomic charge, both the relaxation term and the renormalization term make the N2 atomic charge increase. On the other hand, the decrease in the density derivative term of the O1 atom is dominated by the renormalization term. In case of the density derivative term of the C4 atomic
Figure 5. The derivatives of gross atomic charges (a)\( q_{O1} \), (b)\( q_{N2} \), (c)\( q_{C3} \), (d)\( q_{C4} \), and (e)\( q_{C5} \) with respect to the IRC, respectively. The density derivative term, which consists of the renormalization term \( (dP_{renorm}) \) and the relaxation term \( (dP_{relax}) \), is plotted in the symbol (■). The overlap derivative term is plotted in the symbol (●), and the total derivative values in (▲).
charge, the renormalization term and the relaxation term have different effects from each other. That is to say, the relaxation term reduces the atomic charge, while the renormalization term increases slightly the atomic charge around the transition state. In addition, it should be noted that the trend of the charge redistribution in the final coordinate region is different from that around the transition state.

3.3. Bond Orders and Atom Valences

Figure 6 shows the bond order profile along the IRC. In the fulminic acid part, the bond order between the O1 atom and the N2 atom, \( I_{O1N2} \), is 1.366 and the bond order between the N2 atom and the C3 atom, \( I_{N2C3} \), is 2.447. These values decrease gradually as the reaction proceeds and the bond orders \( I_{O1N2} \) and \( I_{N2C3} \) become 0.955 and 1.642 in the product, respectively. The bond order \( I_{C4C5} \), which represents the triple bond in acetylene, is 3.190 initially and is 1.698 in the product. On the other hand, the bond orders \( I_{O1C4} \) and \( I_{C3C5} \), which show the formation of new chemical bonds, increase along the IRC. It is found that \( I_{C3C5} \) increases more steeply than \( I_{O1C4} \). As a result, the bond order \( I_{C3C5} \) is larger than \( I_{O1C4} \) in the product.

The derivatives of the bond orders, \( I_{O1N2} \), \( I_{N2C3} \), \( I_{C4C5} \), \( I_{O1C4} \), and \( I_{C3C5} \), with respect to the IRC are shown in Figures 7(a)-(e), respectively. First, we examine the derivatives of bond orders \( I_{O1N2} \), \( I_{N2C3} \), and \( I_{C4C5} \), all of which decrease along the IRC. In these, the overlap derivative term \( dS \) contributes to the decrease in bond orders, while the density derivative term \( dP \) contributes to the increase, although the two terms, \( dP_{\text{renorm}} \) and \( dP_{\text{relax}} \), show different contributions. The renormalization term increases the bond orders slightly, while the relaxation term contributes intensely to a decrease in the bond orders. The derivative value of \( I_{O1N2} \) decreases and reaches the minimum at \( s = 1.0 \). On the other hand, the derivative of \( I_{N2C3} \) decreases more steeply than that of \( I_{O1N2} \) till the reacting system comes to the transition state and reaches the minimum at \( s = 0.5 \), since the large negative contribution of the relaxation term dominates the density derivative term. Consequently, the N2–C3 bond is more sensitive to the nuclear motion than the O1–N2 bond is around the transition state. This is connected with the \( \pi \)-electron
Figure 6. The bond order profile along the IRC.

Figure 7. The derivatives of bond orders (a) $I_{ON2}$, (b) $I_{N2C}$, (c) $I_{C4C5}$, (d) $I_{O1C4}$, and (e) $I_{C3C5}$ with respect to the IRC, respectively.
Figure 7. (Continued from the previous page.)
state of the fulminic acid in the initial reaction coordinate. Namely, a part of electrons utilized to form the N2-C3 triple bond in the initial state should be converted to the lone pair of electrons on the N2 atom in the product. After passing the minimum point, the derivative of $\text{I}_0\text{N}_2$ comes close to zero in the product region, while that of $\text{N}_2\text{C}_3$ comes close to zero at $s = 3.0$ and decreases again by the effect of the relaxation term $dP_{\text{relax}}$. The derivative of $\text{IC}_4\text{C}_5$ does not become zero in the final stage on the reaction coordinate either.

We compare next the derivatives of $\text{IC}_3\text{C}_5$ and $\text{I}_0\text{C}_4$. In both of the two terms, the overlap derivative term $dS$ contributes to the increase in bond orders. As to the density derivative term, the relaxation term $dP_{\text{relax}}$ increases these bond orders, while the renormalization term $dP_{\text{renorm}}$ decreases these bond orders. As a result, the density derivative term $dP$ causes these bond orders to increase. Before the transition state, the derivative of $\text{IC}_3\text{C}_5$ is larger than that of $\text{I}_0\text{C}_4$ and $\text{IC}_3\text{C}_5$ increases more steeply than $\text{I}_0\text{C}_4$ as noted above. Moreover, it is found that the maximum points in each derivative value differ from each other, though not large in extent. In the final stage, both of the derivatives also increase. It is interesting to note that the trend is different from that around the transition state. That is, although the density derivative term is a main component till the reacting system reaches the transition state, showing that the electron redistribution forms new bonds, the overlap derivative term is found to be the main part at the final stage. This shows that the nuclear motion is forced to complete the bond formation at the final stage.

We have analyzed the derivatives of the bond order by dividing them into the overlap derivative term and the density derivative term as mentioned above. We can discuss the bond formation also from another point of view. For the derivatives of bond orders presented in Figure 7, the overlap derivative term $dS$ and the renormalization term $dP_{\text{relax}}$ of the density derivative term exhibit the opposite behaviors and they are nearly counterbalanced with each other along the IRC. Therefore, the total derivative value depends on the relaxation term of the density derivative term. That is, the change in bond orders originates from the relaxation of electron density.

The atom valences are shown in Figure 8. While the gross charge of the N2 atom increases gradually with the progress of the reaction as shown in Figure 4, the atom valence, $V_{N2}$, decreases around the transition state. This indicates that the second term of the right-hand side in eq. (9) changes dynamically to break the N2-C3 triple bond and place a lone pair of electrons on N2. The decrease in $V_{N2}$ is caused both by the density derivative term and by the overlap derivative term, as shown in Figure 9(b). The O1 atom valence, $V_{O1}$, increases gradually along the IRC. Because the gross charge of this atom changes little, the electron population of the lone-pair orbital decreases only slightly. This gives rise to the electronic mechanism as described by (II) of the transition state, within the Hartree-Fock scheme of electron density.

The derivative of the O1 atom valence is dominated by the density derivative term around the transition state. On the contrary, the overlap derivative term becomes the main contributor at the final stage. The density derivative term is counterbalanced by the renormalization term and the relaxation term. Thus, the change in the O1 atom valence $V_{O1}$ in the final stage is not positive owing to the electron redistribution. In Figures 10 (a) and (b), the contour maps of the density differential with respect to the IRC at TS and at $s = 5.5$ are shown, respectively. In the final stage around $s = 5.5$, the density changes represent the formation of the a-bonds.

Finally we refer to the other relevant study and mention a limitation of the method used in this study. Balawender et al.43 have studied the derivatives of the molecular valence in order to measure the aromaticity of five-membered heterocycles recently. They treated the derivatives of the molecular valence, which consists of the sum of each atom valences, with respect to the electron number N. The derivatives with respect to the IRC are investigated in the present study. We believed that analysis of the variation in the electronic structure along the reaction coordinate is also important.44,45 It is known well that Mulliken's population analysis gives strange results when diffuse functions are applied in the calculation of the wave function. Some useful localization methods have been introduced to overcome this problem.46-48 These localization methods may describe the variation of bonds along the reaction coordinate suitably. Our calculation was
Figure 8. The atom valence profile along the IRC.

Figure 9. The derivatives of (a) $O_1$ atom valence and (b) $N_2$ atom valence with respect to the IRC, respectively.
performed within the Hartree-Fock formalism. It is possible to extend this study, by using wave functions of higher accuracy.\textsuperscript{16}

4. Conclusion

The population analysis along the IRC has been investigated. The derivatives of the Mulliken atomic gross charge and the Mayer's bond order with respect to the nuclear motion along the IRC have been calculated analytically. These derivatives have been divided into two components: the derivative term of the density matrix and the derivative term of the overlap matrix. Furthermore, the density derivative term has been shown to be divided into two parts, namely, the renormalization term and the relaxation term. The method has been applied to the 1,3-dipole cycloaddition reaction between fulminic acid and acetylene using the Hartree-Fock electron density. Concerted but non-synchronous bond formation has been described clearly in this analysis.

References


Chapter 3:

Quantum Chemical Study on Low Energy Reaction Path for
SiH₄ + O(¹D) → SiO + 2H₂
1. Introduction

One of the methods to produce SiO$_2$ layer over the Si surface is the chemical vapor deposition (CVD) by using oxygen gas and silane gas.\(^1\) A number of relevant reactions have been examined\(^{2-12}\) and some interesting studies have been published recently\(^{13-16}\). But little is known about the mechanism of this oxidation reaction not only on the surface but also in the gas phase. Therefore, we have been applying quantum chemical methods to study these problems. At the first step of a series of these studies, we take up the gas phase reaction between singlet oxygen (\(1^D\)) and silane (SiH$_4$).\(^{17-24}\) This is because excited oxygen species are considered to be important in the CVD reaction, especially plasma CVD reaction, while the detailed reaction mechanism is not well established. For this reaction, Koda et al. observed SiH$_3$ and OH as the reaction products by means of infrared diode laser kinetic spectroscopy.\(^{25}\) Recently, Tezaki et al. have studied this reaction in more detail by laser-induced fluorescence (LIF);\(^{26}\)

(1) The overall observed rate constant is \(3 \times 10^{-10} \text{cm}^3\text{molecule}^{-1}\text{s}^{-1}\), which is three times faster than that of methane.

(2) A H atom was detected as one of the products.

(3) A vibrationally excited (to \(v=11\)) SiO molecule was detected as a product species, and the rate constant agrees with the pseudo-first order rate constant of O atom decay.

Moreover, vibrational distribution of product SiO in low \(v\) regime is distinct from that in high \(v\) regime as compared with prior distribution of surprisal analysis.\(^{26}\) This suggests that a low energy reaction path does exists and plays an important role in addition to the excited state reaction path. We have therefore examined this interesting reaction system SiH$_4$ + O\(^{(1)D}\) $\rightarrow$ SiO + 2H$_2$ using MP2(fc)/6-31G** level \textit{ab initio} molecular orbital calculations.
2. Methods of Calculation

The calculations were performed with the GAUSSIAN-92\textsuperscript{27}, -94\textsuperscript{28} program packages. Geometries of minima and saddle points have been optimized at the Hartree-Fock level and the second-order Møller-Plesset level (frozen core)\textsuperscript{29-30} with 6-31G** basis set (denoted as HF/6-31G** and MP2(fc)/6-31G**). For all species except for triplet and singlet oxygen atoms, restricted Hartree-Fock (RHF) calculations were performed. And for triplet oxygen atoms, unrestricted Hartree-Fock (UHF) calculations were performed.

For the calculation for singlet oxygen atoms, complex orbitals were used in order to describe a closed-shell singlet atom. Electron correlation calculations were also carried out at the MP2 level.

Harmonic vibrational frequencies and zero-point energies were obtained at the MP2 level for each stationary point. Zero-point energies were scaled by the factor 0.94\textsuperscript{31,32}.

3. Results and Discussion

Total energies of all species are listed in Table 1. TS denotes transition state of the reaction path as defined in Figure 1. Reaction energies are summarized in Table 2 and the energy diagram in Figure 1. Vibrational frequencies are listed in Table 3.

3.1. $\text{SiH}_4 + O(1D) \rightarrow \text{SiH}_2\text{OH}$

The title species O(1D) is well known to insert into X–H bonds, such as H–H, C–H, and N–H. Theoretically, the following insertion reactions have been studied: H$_2$ + O (1D)$^{33,34}$, CH$_4$ + O(1D).\textsuperscript{34,35} In the present reaction system also, we assume that the insertion reaction of O(1D) into Si–H bond occurs and the potential surface for SiH$_4$ + O (1D) connects to the most stable species silanol (SiH$_3$OH) with no reaction barrier. Indeed, the reaction is extremely exothermic with reaction energy -175.79 kcal/mol, as shown in Figure 1. To check the accuracy of our estimation of reaction energy, we

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<td>-365.78281</td>
<td>17.73</td>
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<td>SiH$_4$ (C$_d$)</td>
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<td>-365.19933</td>
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<td>17.73</td>
</tr>
</tbody>
</table>

\textsuperscript{57}Total energies are in au, and zero-point energies are in kcal/mol. Zero-point energies are computed at the MP2/6-31G** level and scaled by 0.94.

\textsuperscript{a} Using complex orbitals.

\textsuperscript{b} C$_1$ symmetry at HF/6-31G**, C$_s$ at MP2/6-31G**.
Table 3: Vibrational Frequencies

<table>
<thead>
<tr>
<th>species</th>
<th>harmonic vibrational frequencies</th>
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<tr>
<td>H2O</td>
<td>916 cm⁻¹, 1680 cm⁻¹, 3482 cm⁻¹</td>
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<tr>
<td>SiO</td>
<td>1176 cm⁻¹, 1314 cm⁻¹, 1332 cm⁻¹, 1563 cm⁻¹, 3101 cm⁻¹</td>
</tr>
<tr>
<td>OH</td>
<td>1844 cm⁻¹, 2729 cm⁻¹, 3347 cm⁻¹</td>
</tr>
<tr>
<td>H2O</td>
<td>1602(3.1), 1802(3.1), 3020(3.1)</td>
</tr>
<tr>
<td>SiH3</td>
<td>1078(2.1), 1216(2.1), 2169(2.1)</td>
</tr>
<tr>
<td>SiH4</td>
<td>2168(2.1), 2164(2.1), 2174(2.1)</td>
</tr>
<tr>
<td>SiH3OH</td>
<td>2252(2.1), 2561(2.1), 2579(2.1)</td>
</tr>
<tr>
<td>SiH3O2</td>
<td>2168(2.1), 2169(2.1), 2171(2.1)</td>
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<tr>
<td>SiO2OH</td>
<td>2274(2.1), 2359(2.1), 2357(2.1)</td>
</tr>
<tr>
<td>SiH2O</td>
<td>230(1.5), 231(1.5), 232(1.5)</td>
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<td>H2SiO2</td>
<td>234(1.5), 235(1.5), 236(1.5)</td>
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<tr>
<td>csc-HSOH</td>
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</tr>
<tr>
<td>trans-HSOH</td>
<td>238(1.5), 239(1.5), 240(1.5)</td>
</tr>
</tbody>
</table>

Note: All frequencies in cm⁻¹.

Table 2: Reaction Energies and Analysis

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Reaction Energy</th>
<th>Structure Energy</th>
<th>Heat of Reaction</th>
</tr>
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<tbody>
<tr>
<td>SiF + H2 → SiH + HF</td>
<td>-135 kcal/mol</td>
<td>-120 kcal/mol</td>
<td>-135 kcal/mol</td>
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<tr>
<td>SiF + H2O → SiOH + HF</td>
<td>-120 kcal/mol</td>
<td>-115 kcal/mol</td>
<td>-120 kcal/mol</td>
</tr>
<tr>
<td>SiF + O3 → SiOF + O2</td>
<td>-130 kcal/mol</td>
<td>-125 kcal/mol</td>
<td>-130 kcal/mol</td>
</tr>
</tbody>
</table>

Note: All energies in kcal/mol.

At the MP2/6-31G** level including ZPE (scaled) corrections.
examined the $\text{O}^{(3P)} \leftrightarrow \text{O}^{(1D)}$ splitting energy: our estimate is 49.76 kcal/mol at the MP2 level, and the experimental value is 45.37 kcal/mol, both being in good agreement.

We further assume that this silanol is decomposed into many species, as described below.

### 3.2. $\text{SiH}_4\text{OH}$ Decomposition

Thermal decomposition reaction paths of $\text{SiH}_4\text{OH}$ are considered as follows:

1. $\text{SiH}_4\text{OH} \rightarrow \text{SiH}_3 + \text{OH}$
2. $\text{SiH}_4\text{OH} \rightarrow \text{SiH}_2\text{O} + \text{H}$
3. $\text{SiH}_4\text{OH} \rightarrow \text{SiH}_3\text{O} + \text{H}_2$
4. $\text{SiH}_4\text{OH} \rightarrow \text{TS-1} \rightarrow \text{SiH}_2\text{H}_2\text{O}$ complex
5. $\text{SiH}_4\text{OH} \rightarrow \text{TS-2} \rightarrow \text{trans-HSiOH} + \text{H}_2$
6. $\text{SiH}_4\text{OH} \rightarrow \text{TS-3} \rightarrow \text{H}_2\text{SiO} + \text{H}_2$

$\text{SiH}_3$ and OH were detected by Koda and Suga by the time-resolved infrared-diode laser absorption technique. H atoms were detected by Tezaki et al. by laser-induced fluorescence. These species are considered to be decomposed from $\text{SiH}_4\text{OH}$ as in reactions (1), (2), and (3). Energy diagrams of Figure 1 show that the reactions of $\text{SiH}_4 + \text{O}^{(1D)}$ leading to these products are exothermic, so that these homolytic reaction paths are considered main reaction channels. The barrier height of the reactions (4), (5), and (6) is 79.91 kcal/mol (TS-1), 71.10 kcal/mol (TS-2), and 68.88 kcal/mol (TS-3), respectively, in agreement with higher level calculations by MP4/MC-311G(d,p)\(//\)MP2/6-31G(d,p).

### 3.3. $\text{H}_2\text{SiO} \rightarrow \text{SiO} + 2\text{H}_2$

The unimolecular decomposition of silanone $\text{H}_2\text{SiO}$ has been investigated by Kudo and Nagase and our group. A series of reaction pathways are as follows:

1. $\text{H}_2\text{SiO} \rightarrow \text{TS-4} \rightarrow \text{SiO} + \text{H}_2$
2. $\text{H}_2\text{SiO} \rightarrow \text{TS-5} \rightarrow \text{trans-HSiOH} + \text{H}_2$
3. $\text{trans-HSiOH} \rightarrow \text{TS-6} \rightarrow \text{cis-HSiOH}$
4. $\text{cis-HSiOH} \rightarrow \text{TS-7} \rightarrow \text{SiO} + \text{H}_2$
One channel is direct decomposition (7) through TS-4 and another channel is via rearrangement channel (8)→(9)→(10) through TS-5, TS-6 and TS-7. Reaction (7) has high energy barrier of 88.78 kcal/mol and hence is of little importance. While the rearrangement channel (8)→(9)→(10) proceeds easily as found in Figure 1. In reaction (9), TS-6 was found to have C1 symmetry at the HF/6-31G** level, while C5 symmetry at the MP2/6-31G** level.17

3.4. H2Si-H2O Complex→cis- or trans- HSiOH

Although the favorable reaction path of SiH3OH is H2 elimination leading to trans- HSiOH or H2SiO, yet we propose the path to the SiH2-H2O complex is considerably important. The H2Si-H2O complex has been considered a precursor of the reaction of SiH2 + H2O leading to SiH3OH so far.8-10 Zachariah and Thang considered that in the SiH2 + H2O reaction this CT complex forms at first, and then rearrangement of H atom to silanol occurs.16 In case of singlet carben, this kind of CT complex is not on the reaction coordinate of CH2 + H2O38-41, so it is considered important in case of silicon compounds. Indeed, in our present study, it is confirmed to stay on the reaction surface by HF/6-31G** level calculations of the intrinsic reaction coordinate (IRC) starting from TS-1, as shown in Figure 1.

We propose a new reaction path of this CT complex leading directly to cis- or trans- HSiOH, not via formation of H2SiO:

\[
H_2Si-H_2O \text{ complex} \rightarrow \text{TS-8} \rightarrow \text{trans- HSiOH} + H_2 \quad (11)
\]

\[
H_2Si-H_2O \text{ complex} \rightarrow \text{TS-9} \rightarrow \text{cis- HSiOH} + H_2 \quad (12)
\]

The products trans- HSiOH + H2 or cis- HSiOH + H2 are 41.57, 42.03 kcal/mol higher in energy than silanol, but the barriers of these reactions are considerably lower: 21.59 kcal/mol for TS-8, 22.22 kcal/mol for TS-9. As shown in Figure 1, these reactions are likely to occur. Figure 2 shows the structure of TS-9 for the transition state of the reaction (12). The imaginary frequency of this transition state is 1443i cm\(^{-1}\) as shown in Table 3. The imaginary vibrational mode corresponds to H2 elimination. The reaction paths are interpreted in terms of classical valence bond theory as follows.
The $\text{H}_2\text{Si-H}_2\text{O}$ complex forms through a donor-acceptor CT interaction between a lone-pair orbital in $\text{H}_2\text{O}$ and an empty p orbital in $\text{SiH}_2$. In this complex, the H atom bonded to the Si atom has a hydride-ion-like character (whose atomic charge is calculated to be -0.215 on the average), while a H atom bonded to the O atom has a proton-like character (whose atomic charge is calculated to be +0.39). Here, if the proton-like H moves over to the silylene lone-pair orbital, then new sp$^3$ bond is formed. This is the 1,2-hydrogen shift reaction like the reaction path of silylene derivatives, such as dimethyl silylene. On the other hand, if the proton-like H attacks the hydride-ion-like H, then a $\text{H}_2$ molecule is formed. The resulting new sp$^2$ type vacant orbital of Si is stabilized by hyperconjugation of the oxygen lone-pair orbital.42 It is interesting to observe that the barrier heights for these two reaction paths are comparable.

The additional reaction path that directly leads to $\text{cis-HSiOH}$ is found as follows:

$$\text{SiH}_3\text{OH} \rightarrow \text{TS-10} \rightarrow \text{cis-HSiOH} + \text{H}_2 \quad (13)$$

Figure 3 shows the structure of $\text{TS-10}$ for transition state of the reaction (13).

### 3.5. General View

The low energy reaction paths examined in this paper are here summarized. Silanol proceeds to $\text{SiO} + 2\text{H}_2$ through the following reaction channels:

- (6) $\text{TS-3} \rightarrow (8) \text{TS-5} \rightarrow (9) \text{TS-6} \rightarrow (10) \text{TS-7}$ (Channel 1)
- (5) $\text{TS-2} \rightarrow (9) \text{TS-6} \rightarrow (10) \text{TS-7}$ (Channel 2)
- (4) $\text{TS-1} \rightarrow (12) \text{TS-9} \rightarrow (10) \text{TS-7}$ (Channel 3)
- (13) $\text{TS-10} \rightarrow (10) \text{TS-7}$ (Channel 4)

All channels are possible candidates as low energy processes as shown in Figure 1. Channel 4 is probably the easiest to occur. Elimination reaction of two $\text{H}_2$ molecules can occur through these low energy processes.

### 4. Conclusion

We studied the reaction mechanism of $\text{SiH}_4 + \text{O}(^1\text{D})$. Applying a quantum chemical method, a low energy reaction path is found in addition to the excited state reaction path. This agrees well with the experimental observation on the vibrational energy distribution of product $\text{SiO}$ by laser-induced fluorescence (LIF).

### References


Tezaki, A. et al., private communication.

Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian 92; Gaussian, Inc.: Pittsburgh, PA, 1992.


Møller, C.; Plesset, M. S. Phys. Rev. 1934, 46, 618.
Chapter 4:

Quantum Chemical Study of the Oxidation Sites in Hydrogen- and Water- Terminated Si Dimers:
Attempt to Understand the Si–Si Back-Bond Oxidation on the Si Surface
1. Introduction

A thorough understanding of the silicon surface oxidation processes both scientifically and technologically is significant because of the necessity to control the formation of atomic-scale structures at the Si/SiO\textsubscript{2} interface for application to ultralarge-scale integrated circuits. As a matter of fact, fine control of Si/SiO\textsubscript{2} interface electronic characteristics has become a crucial problem since the oxide layer thickness must be reduced due to the demand of further reduction of the device size. The attempt to have an appropriate understanding of silicon surface oxidation in order to control atomic-scale structures at the interface has just begun.

From a historical point of view, not only experimental studies\textsuperscript{1,2} but also many interesting theoretical studies were made.\textsuperscript{3-14} For example, Goddard III \textit{et al.} studied the chemisorption of an oxygen molecule on a silicon surface using the generalized valence bond (GVB) method.\textsuperscript{3} They treated a Si\textsubscript{3}H\textsubscript{6}O\textsubscript{2} complex, which was used to describe the O\textsubscript{2} molecule chemisorbed on a Si\textsubscript{3}H\textsubscript{6} surface cluster model. They concluded that the chemisorbed O\textsubscript{2} in the initial stage is a peroxy radical. Moreover, they postulated that a local electronic excitation would lead to the subsequent formation of normal SiO\textsubscript{2}-like structure.

Schubert \textit{et al.} studied the initial stages of oxidation of the Si(111)-7×7 surface using extended Hückel tight-binding calculations.\textsuperscript{4,5} They noted that the most reactive site was the adatom in the Takayanagi model, or dimer adatom stacking fault (DAS) model of a Si(111)-7×7 surface when O\textsubscript{2} molecule interacts with a silicon surface.\textsuperscript{4} As a result, they found that the major stable precursors were of the chemisorbed peroxy radical type attached to one Si adatom (which Goddard III \textit{et al.} studied).

Next,\textsuperscript{5} they studied the pathways involved in converting the initial precursors into SiO\textsubscript{4} units and compared the calculated density of states (DOS) with the X-ray photoemission spectroscopy (XPS) and ultraviolet photoemission spectroscopy (UPS) experimental data. Once the initial precursors are inserted into the Si–S back bond, an
O₂ molecule can be inserted into the adjacent Si–Si back bonds to form a normal SiO₄ unit.

On the other hand, Uchiyama and Tsukada investigated the stable structures of oxygen-adsorbed Si(001) surfaces by first principles molecular dynamics and found that back-bond site adsorption was more stable than dimer bond adsorption energetically and that the band structures of surfaces were different because the electronegativity of oxygen enhanced the ionicity of the dimer bond. Recently Kato et al. studied the oxidation of the Si(001) surface and clarified that the back-bond oxidation of the Si surface by O₂ proceeds with no barrier height. In this study, we investigate the stabilities of both Si–O–Si and Si–O–H bonds in molecules. First, we examine the reactions of disilane Si₂H₆ with O₂:

$$\text{SiH}_3\text{SiH}_3 + O_2(3\Sigma_g) \rightarrow \text{SiH}_3\text{SiH(OH)}_2$$  \hspace{1cm} (1)
$$\text{SiH}_3\text{SiH}_3 + O_2(3\Sigma_g) \rightarrow \text{SiH}_3\text{-O-SiH}_2(\text{OH})$$ \hspace{1cm} (2)

We show that the Si–O–Si bond is more stable than the Si–O–H bonds in a small molecule. Next, we note the reaction of SiH₃SiH₂(OH) with H as one of the reactions involved in forming a Si–O–Si bond or a Si–O–H bond. This reaction starts with hydrogen abstraction by exposing a hydrogen atom to make an oxygen radical center:

$$\text{SiH}_3\text{SiH}_2\text{OH} + \text{H} \rightarrow \text{SiH}_3\text{SiH}_2\text{O} + \text{H}_2.$$ \hspace{1cm} (3)

Then oxygen is inserted into a Si–Si back bond:

$$\text{SiH}_3\text{SiH}_2\text{O} \rightarrow \text{SiH}_3\text{-O-SiH}_2.$$ \hspace{1cm} (4)

Moreover, another reaction is considered:

$$\text{SiH}_3\text{SiH}_2\text{O} \rightarrow \text{SiH}_3\text{SiH(OH)}.$$ \hspace{1cm} (5)

On the basis of these results, we discuss the surface oxidation mechanisms in relation to local reaction site character.

2. Methods of Calculation

MO calculations were performed using the GAUSSIAN94 program packages. The geometries were optimized by the analytical energy gradient method at the Hartree-Fock (HF) level and the second-order Möller-Plesset (MP) perturbation theory that includes correlation for all electrons, using the standard 6-31G** basis set (denoted as HF/6-31G** and MP2(full)/6-31G**). In HF calculations, the spin-restricted HF (RHF) method was used for closed-shell singlet states, and the spin-unrestricted HF (UHF) method was used for open-shell doublet states. Theoretical harmonic vibrational frequencies were obtained from analytical second derivatives calculated at the MP2(full)/6-31G** level. Zero-point vibrational energies (ZPE) were then scaled by a factor of 0.94. To obtain higher correlation energies, single point calculations were made by the third-order Möller-Plesset perturbation theory (MP3) and the single and double substituted configuration interaction (CISD) method. In CISD calculations, an unlinked cluster quadruple correction (QC) was added for size-consistency correction [denoted as CISD(full)+QC]. The Mulliken atomic charge was calculated using the self-consistent field (SCF) density at the MP2(full)/6-31G** level optimized geometry.

3. Results and Discussion

The total energies of the species are listed in Table 1 and the vibrational frequencies of these, in Table 2. Figure 1 shows some of the species. TSn denotes the transition state of reaction(n) (n = 3, 4, 5). Reaction energies are summarized in Tables 3 and 4 and the energy diagrams in Figures 2 and 3.

3.1. Reactions of Si₂H₆ with O₂

3.1.1. Optimized Structures Before we studied SiH₃SiH(OH)₂, we investigated the simple dihydroxy molecule SiH₂(OH)₂ because dihydroxy silane SiH₂(OH)₂ has been studied by many researchers due to its anomeric effects and simplicity for use as a model for silicone polymers and for silicates. It was reported that there are less anomeric effects in silicon compounds than in carbon compounds. As demonstrated in Figure 1, we considered two structures for SiH₂(OH)₂. One of them, 4, maintains C₂ symmetry and the other, 5, has C₃ symmetry. Reed et al. reported that the C₃ symmetry
Table 2: Vibrational Frequencies at the MP2(full)/6-31G** Level

<table>
<thead>
<tr>
<th>species</th>
<th>harmonic vibrational frequency (cm⁻¹)</th>
<th>ZPE²</th>
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<tbody>
<tr>
<td>1</td>
<td>4609(ε2)</td>
<td>6.21</td>
</tr>
<tr>
<td>2</td>
<td>1412(ε2)</td>
<td>1.90</td>
</tr>
<tr>
<td>3</td>
<td>974(e2), 1018(e), 2347(a1), 2360(e2)</td>
<td>19.39</td>
</tr>
<tr>
<td>4</td>
<td>257(a1), 314(b1), 391(a1), 638(b1), 787(a1), 837(a2), 902(b1), 920(c1), 958(b1), 1020(a1), 1023(b1), 2379(a1), 2383(b1), 3955(b1), 3957(a1)</td>
<td>27.92</td>
</tr>
<tr>
<td>5</td>
<td>91(ε2), 285(a1), 349(a2), 624(a1), 762(a1), 830(a1), 894(a1), 937(a1), 945(a1), 1012(a1), 1030(a1), 2318(a1), 2429(a1), 3971(a1), 3972(a1)</td>
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<tr>
<td>6</td>
<td>1466(a1), 384(a2), 460(a1), 667(e1), 901(e1), 980(e1), 985(e2), 1002(e2), 2318(e2), 2327(e1), 2333(e2), 2341(e1)</td>
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<tr>
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<td>102(a1), 110(a1), 172(a1), 199(a1), 279(a1), 361(a1), 455(a1), 566(a1), 560(a1), 761(a1), 798(a1), 814(a1), 900(a1), 926(a1), 977(a1), 994(a2), 999(a1), 1000(a1), 2284(a1), 2325(a1), 2343(a1), 2373(a1), 2394(a1), 2397(a1)</td>
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<td>8</td>
<td>35, 69, 97, 269, 363, 616, 670, 760, 766, 816, 869, 930, 987, 1011, 1019, 1031, 1070, 1111, 2344, 2350, 2365, 2370, 2391, 3958</td>
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<td>9</td>
<td>1176(a1), 1644(a1), 228(a1), 393(a1), 450(a1), 549(a1), 659(a1), 772(a1), 825(a1), 856(a1), 924(a1), 988(a1), 990(a1), 1014(a1), 1041(a1), 2302(a1), 2304(a1), 2322(a1), 2335(a1), 2360(a1), 3943(a1)</td>
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<td>10</td>
<td>1127(a1), 1444(a1), 377(a1), 441(a1), 515(a1), 631(a1), 680(a1), 817(a1), 847(a1), 931(a1), 989(a1), 999(a1), 1045(a1), 2325(a1), 2337(a1), 2341(a1), 2349(a1), 2359(a1)</td>
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<td>11</td>
<td>1134(a1), 1634(a1), 378(a1), 444(a1), 545(a1), 662(a1), 798(a1), 841(a1), 891(a1), 912(a1), 983(a1), 989(a1), 991(a1), 2315(a1), 2327(a1), 2330(a1), 2338(a1), 2344(a1)</td>
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<td>1013(a1), 1017(a1), 1060(a1), 1135(a1), 2303(a1), 2323(a1), 2343(a1), 2359(a1)</td>
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<td>26.96</td>
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<td>TS3</td>
<td>1747(a1), 84, 179, 359, 436, 545, 577, 703, 866, 916, 948, 985, 989, 2033, 2310, 2328, 2341, 2360</td>
<td>25.55</td>
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</table>

²ZPE (kcal/mol) scaled by 0.94.
Figure 1. Optimized geometries of some species at the MP2(full)/6-31G** level. Bond lengths are in angstroms and bond angles and dihedral angles are in degrees. HF level optimized data are in parentheses. The Mulliken atomic charges are in italics. The spin densities are in gothic. Arrows in TSn show movement of nuclei along the imaginary vibrational mode.

(Continued from the previous page.)
Table 3: Reaction Energies

<table>
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<tr>
<th>reaction</th>
<th>MP2(full)</th>
<th>MP3(full)</th>
<th>CISD(full)+QC</th>
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</thead>
<tbody>
<tr>
<td>SiH₂SiH₃ + O₂(3Πg) → SiH₂SiH(OH)₂</td>
<td>-143.19 (-6.21)</td>
<td>-143.48 (-6.22)</td>
<td>-135.65 (-5.88)</td>
</tr>
<tr>
<td>SiH₂SiH₃ + O₂(3Πg) → SiH₂OSiH₃(OH)</td>
<td>-171.87 (-7.45)</td>
<td>-170.31 (-7.39)</td>
<td>-163.08 (-7.07)</td>
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Including ZPE(scaled) at the MP2(full)/6-31G** level.

Table 4: Reaction Energies in kcal/mol (eV in parentheses)

<table>
<thead>
<tr>
<th>reaction</th>
<th>activation energy</th>
<th>heat of reaction</th>
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<tbody>
<tr>
<td>SiH₂SiHOH + H₂ → SiH₂SiH₂O(2A)' + H₂</td>
<td>28.23 (1.22)</td>
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<td>/17.72 (0.77)</td>
<td>/9.72 (0.42)</td>
</tr>
<tr>
<td>SiH₂SiO(2A) → SiH₂OSiH₂(C₁)</td>
<td>2.27 (0.10)</td>
<td>2.01 (0.09)</td>
</tr>
<tr>
<td></td>
<td>/5.42 (-1.96)</td>
<td>/4.55 (-1.69)</td>
</tr>
<tr>
<td>SiH₂SiO(2A) → SiH₂Si(OH)(C₁)</td>
<td>24.16 (1.05)</td>
<td>26.54 (1.16)</td>
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<tr>
<td></td>
<td>/29.45 (-1.28)</td>
<td>/22.77 (-0.99)</td>
</tr>
</tbody>
</table>

Including ZPE(scaled) at the MP2(full)/6-31G** level.

Figure 2. Energy diagram (in eV) at the CISD(full)/6-31G** level including ZPE (scaled by 0.94).

Figure 3. Energy diagram (in eV) at the CISD(full)/6-31G** level including ZPE (scaled by 0.94).
structure is 2.16 kcal/mol more stable than the C$_2$ symmetry structure in MP2/6-31G*//HF/3-21G(*) level calculation. However, 4 is 1.29 kcal/mol more stable than 5 in our CISD/6-31G**//MP2/6-31G** level(+ZPE) calculation. This energy difference is so small that the H atom of the hydroxy group is easy to move.

SiH$_3$SiH(OH)$_2$ 7 has C$_3$ symmetry as depicted in Figure 1. It corresponds to 5 in SiH$_2$(OH)$_2$ with respect to the hydroxyl combination. Another structure corresponding to 4 could not be optimized at the HF/6-31G** level, although it was optimized at the HF/STO-3G level. Comparing SiH$_3$SiH(OH)$_2$ 7 with SiH$_3$SiH$_3$, the Si-Si bond length is shorter in 7 due to hydroxyl groups, whereas the Si-H bond length is longer.

SiH$_3$O-SiH$_2$(OH) 8 has C$_1$ symmetry as shown in Figure 1, due to the repulsive O-O interaction induced by polarization effects. It was reported that the Si-O-Si bond is very flexible and has a shallow potential surface in SiH$_3$O-SiH$_3$. Moreover, 4 and 7 show that their Si-O-H bonds have the same character. In the same manner, 8 has a very shallow potential surface, which is proved by the low vibrational frequencies listed in Table 2.

3.1.2. Reaction Energies We consider the reaction energies of (1) and (2). From Table 3, we find that these reactions are highly exothermic. The oxidized layer on the silicon surface is strongly stabilized if lattice strain is fully relaxed. Moreover, we compare the reaction energy of (1) with that of (2). The difference is 27.43 kcal/mol and is very large. It shows that the Si-O-Si bond is more stable than the Si-O-H bond.

3.2. Mechanism Involved in the Reaction between SiH$_3$SiH$_2$(OH) and Hydrogen Atom

3.2.1. SiH$_3$SiH$_2$OH + H → SiH$_3$SiH$_2$O + H$_2$ Figure 1 shows that the reactant SiH$_3$SiH$_2$(OH) 9 has C$_4$ symmetry and its structural character is the same as 7 found in previous section. The Si-Si bond length is larger than that of SiH$_3$SiH$_3$ while the Si-H bond length is smaller, although the effect of the hydroxyl group is weaker.

The transition state of this reaction is TS3, as shown in Figure 1. The structure of TS3 and the vector of its imaginary frequency vibrational mode show hydrogen abstraction by a hydrogen atom from the hydroxyl group. The activation energy is 19.24 kcal/mol at the CISD//MP2(+ZPE) level and is almost the same as that for the reaction SiH$_3$OH + H → SiH$_3$O + H$_2$ by Zachariah and Tsang. They studied the reaction using the bond additivity correction (BAC) procedure and estimated an activation energy of about 18 kcal/mol.

The reaction energy is 6.95 kcal/mol (endothermic) at the CISD+QC//MP2(+ZPE) level, which is a small value. Thus, this reaction is not markedly inhibited, and leads to the second stage as found in subsection 3.2.2.

3.2.2. SiH$_3$SiH$_2$O → SiH$_3$O-SiH$_2$ The reactant SiH$_3$SiH$_3$O has C$_3$ symmetry; therefore, two electronic states, 10 for 2A$'$ and 11 for 2A$''$, are considered as depicted in Figure 1. There are few differences in these optimized structures except for the Si-O bonds. Optimized structure 10 is more stable than 11 by 3.56 kcal/mol (CISD(full)//MP2(full)+ZPE level). Spin densities of oxygen are +1.01 for 10 and +1.02 for 11, and the singly occupied molecular orbital (SOMO) of each structure is localized at the oxygen atom.

As shown in Figure 1, the product SiH$_3$O-SiH$_2$ has C$_1$ symmetry. In 12, which has C$_1$ symmetry, low imaginary frequency (52i cm$^{-1}$($a''$)) exists. Indeed, 13, which is an optimized structure with C$_1$ symmetry, exhibits a tendency of excluding the oxygen atom from the symmetry plane. However, the energy difference is very small and the Si-O-Si bond has a very flexible structure. The SOMO is localized at the Si atom (the spin densities are +0.93 for 12 and +0.92 for 13).

The reaction path CH$_3$O → CH$_2$(OH) was studied by many researchers. In particular, this reaction path is considered to be a bifurcating one. Considering an intrinsic reaction coordinate (IRC) path, the bifurcating point that breaks the symmetry retention of the reaction path exists in the reaction path from the transition state to the product CH$_2$OH. Reaction (4) has the same character as this reaction. Therefore, we consider the reaction path of (4) with 2A$'$ potential surface of C$_3$ symmetry. The structure of the transition state TS4 shows an early transition trend, as demonstrated in Figure 1. The activation barrier is 2.01 kcal/mol at the CISD(full)//MP2(full)+ZPE level, which is a very small value. Moreover, the reaction energy is 44.34 kcal/mol (endothermic).
Therefore, although structure 10 is a local minimum structure (having all real vibrational frequencies), 10 reacts to 12 and 13 with almost no barrier and the product is much more stable than the reactant.

The SOMO of SiH₃SiH₂O is localized at oxygen 2p orbital as shown in Figure 4. On the other hand, the highest occupied molecular orbital (HOMO) is the Si-Si σ-bond (Figure 4). These HOMO-SOMO interactions result in a low activation energy of the reaction because SOMO energy level is lower than HOMO energy level in alpha space.

3.2.3. \( \text{SiH}_3\text{SiH}_2\text{O} \rightarrow \text{SiH}_3\text{SiH}_2\text{OH} \)  
Reaction (5) is an alternative to reaction (4) except for the difference of oxygen insertion into Si-H bond. The transition state structure is shown in Figure 1. Its imaginary frequency is 1747 cm⁻¹; thus, the potential energy surface is very sharp along this reaction path. The activation energy is 26.54 kcal/mol, which is higher by 24.53 kcal/mol than that of reaction (4). The reaction energy is 21.40 kcal/mol (exothermic). Comparing reaction (4) with reaction (5), it is found that the Si-Si bond is more easily broken than the Si-H bond and the Si-O-Si bond is definitely more stable than the Si-O-H bond.

3.3. Local Oxidation Character of Hydrogen-Terminated Si Surface

In section 3.1, it is shown that the Si-O-Si bond is more stable than the Si-O-H bond in molecular structure. This corresponds to the preference of back-bond oxidation of H-Si(111), which was observed experimentally by Hattori et al.⁴²-⁴⁶. Recently, Hattori investigated the oxidation of a hydrogen-terminated Si(111) surface, that is, the H-Si(111)-1x1 surface⁴² at 300 °C in dry O₂ under a pressure of 1 Torr up to a thickness of 0.5 nm. Oxidation-induced changes in Si 2p and Si 2p/3 photoelectron spectra and infrared absorption spectra were observed. As a result, he concluded that no desorption of H occurs and no Si-OH bonds are formed, but oxygen is inserted into the Si-Si back bonds. Similar results were reported for the oxidation of a hydrogen-terminated Si(100) surface by Nagasawa et al.⁴⁷ They prepared a hydrogen-terminated Si(100) surface and investigated the change in FT-IR-ATR (Fourier-transform infrared attenuated total reflectance) spectra.
reflection) spectra of the surface exposed to air at room temperature. As a result, they observed a new peak at 2215 cm$^{-1}$ after 12 days, which was attributed to the SiH$_2$ stretching mode where two oxygen atoms combine with Si. They also indicated that oxygen breaks the Si-Si back bond first rather than the Si-H bond in the initial oxidation stage. If indeed chemical bond character affects the reaction site of the Si surface, then their results are completely consistent with ours.

3.4. Mechanisms Involved in the Reaction of H$_2$O-Terminated Si Surface

Here we discuss the oxygen insertion reaction pertinent to the experiment conducted by Ikeda et al.,$^{48}$ on the basis of our results regarding molecular reactions. They studied the reaction between a H$_2$O-terminated Si(100) surface and a hydrogen atom by high-resolution electron energy loss spectroscopy (HREELS) for the purpose of understanding the initial oxidation process. H$_2$O molecules adsorb dissociatively on dangling bonds of Si dimers on Si(100) and form Si-H and Si-OH bonds that have the 2x1 structure.$^{49-56}$ While this H$_2$O-adsorbed Si(100) surface was exposed to hydrogen atoms at room temperature, they investigated the intensity changes of the energy loss peaks for Si-O-Si, Si-OH and Si-H species. It was conjectured that the following reactions are involved in the oxygen uptake into the Si-Si back bond, upon observing that the intensity of Si-OH peaks decreases and that of Si-O-Si and Si-H peaks increases with increasing amount of hydrogen exposure:

\[
\begin{align*}
&\text{H}_2\text{O}^+ + \text{H} \rightarrow \text{H}_2\text{O} + \text{H}^+ \\
&\text{SiH}^+ + \text{H}_2 \rightarrow \text{SiH}_2 + \text{H}_2^+ \\
&\text{SiH}_2 + \text{H}_2 \rightarrow \text{SiH}_4 + \text{H}_2 \\
&\text{SiH}_4 + \text{H}_2 \rightarrow \text{SiH}_6 + \text{H}_2
\end{align*}
\]

Analysis of the LEED pattern revealed that surface structure changed from a monohydride layer that has the 2x1 structure to a dihydride layer that has the 1x1 structure, depending on the amount of hydrogen exposure. This leads to the following reaction:

\[
\begin{align*}
&\text{H}_2\text{O} + \text{H} \rightarrow \text{H}_2\text{O}^+ + \text{H}^+ \\
&\text{SiH}^+ + \text{H}_2 \rightarrow \text{SiH}_2 + \text{H}_2^+ \\
&\text{SiH}_2 + \text{H}_2 \rightarrow \text{SiH}_4 + \text{H}_2 \\
&\text{SiH}_4 + \text{H}_2 \rightarrow \text{SiH}_6 + \text{H}_2
\end{align*}
\]

On the basis of these results, at small amounts of hydrogen exposure, reactions (i)-(v) were considered to occur simultaneously, while at large amounts, (i) and (ii) were dominant over (iii) and (iv). This result indicates that external atomic hydrogen can control the oxidation of Si surfaces. Moreover, of note is that the oxygen atom insertion into the Si-Si back bond (i) occurred on both monohydride and dihydride Si surfaces.

We discuss the oxygen insertion reaction pertinent to this experiment. In this experiment, H$_2$O-terminated Si(100) surface that was terminated by a hydrogen or a hydroxyl group was exposed to hydrogen atoms. As a starting point, reaction (3) was considered to be the cluster model of hydrogen abstraction from the OH group by hydrogen atom. An oxygen atom radical center was found to remain after abstraction of the hydrogen atom by reaction with a hydrogen atom. We need to find out how the oxygen atom radical penetrates into the Si-Si back bond.

The possibilities of the reactions that lead to the insertion of oxygen are shown in Figure 5. In the 2x1 structure, oxygen atom has two possibilities of inserting either into the Si–Si back bond (I) or the Si–Si dimer bond (II). We assume reaction (4) to be the cluster model of both (I) and (II). From the character of reaction (4), which has a smaller activation energy than reaction (3) with high exothermicity, both (I) and (II) are considered to occur. However, only (I) was observed experimentally. Although this experimental result is not resolved at the present stage of calculation, it is considered that
the study by Uchiyama and Tsukada gave a way of explanation.\textsuperscript{12,13} Further work should be done in order to fully understand the selectivity of (I) over (II).

In the 1×1 structure, two reactions, oxygen insertion into the Si–Si back bond (III) and oxygen insertion into the Si–H bond (IV), are considered. Assuming reaction (4) as the model of (III) and reaction (5) as the model of (IV), the former is much more favorable than the latter from the viewpoint of both activation energy and reaction energy. Therefore, only (III) can occur.

If we interpret the local electronic character of the cluster reactions to the surface reactions, HOMO of 10 is regarded as the Si–Si valence band. The oxygen radical is more stable than the Si–Si valence band because it is localized in the oxygen 2p orbital, so it easily inserts into the Si bond and has a strong interaction with the Si valence band.

Consequently, in either the 2×1 or the 1×1 surface structure of H2O-terminated Si(100), the oxygen atom inserts into the Si–Si bond rapidly after an oxygen atom radical center is formed by the reaction of hydrogen atom with the hydroxyl group.

The attacking hydrogen atoms are considered to react in many other ways. For example, Ikeda \textit{et al.}\textsuperscript{43} considered that reaction (iii) is the reason for the inconsistency between the increase in Si–O–H peak and the decrease in Si–O–Si peak at small amounts of hydrogen exposure. They suggested that this reaction did not occur in the 1×1 structure because of steric hindrance. Other experiments\textsuperscript{49} indicated that oxygen species were lost from the silicon surface. Therefore, we must consider the various possibilities of reactions in further experimental and theoretical studies.

4. Conclusion

We studied the local electronic property of Si–Si bond oxidation using \textit{ab initio} molecular orbital calculation and discussed Si–Si back-bond oxidation in the hydrogen-terminated silicon surface.

First, we investigated Si–O–H bond and Si–O–Si bond stability. The cluster model SiH3-O-SiH2(OH) is 27.43kcal/mol more stable than SiH3SiH(OH)2 at the CISD(full)/6-31G**/MP2(full)/6-31G** level(+ZPE). Therefore, the Si–O–Si bond is more stable than the Si–O–H bond. Adapting this result to the local electronic property of the hydrogen-terminated Si surface, we found that the oxygen atom prefers Si–Si back-bond insertion rather than terminating Si–H bond insertion when oxygen molecules oxidize the silicon surface. This result agrees with that from the experimental study by Hattori \textit{et al.}\textsuperscript{42} that not the Si–O–H bond but the Si–O–Si bond is formed upon oxidation of the hydrogen-terminated Si(111) surface.

Second, we investigated oxygen insertion reaction in terms of radical reaction by considering the molecular reaction SiH3SiH2O → SiH3-O-SiH2 (4). The reaction barrier height is 2.01kcal/mol and the reaction energy is 44.34kcal/mol (exothermic) at the CISD(full)/6-31G**/MP2(full)/6-31G** (+ZPE) level. Therefore, this reaction easily occurs. Another reaction, which is insertion of oxygen into the Si–H bond, has a possibility but its corresponding reaction SiH3SiH2O → SiH3SiH(OH) (5) has higher activation energy and lower reaction energy than reaction (4). Therefore, once a hydrogen atom attacks the hydrogen of the OH group and makes an oxygen atom radical center, as assumed in the model reaction (3), reaction (4) should occur rapidly. This agrees well with the results of an experimental study on surface reaction processes of hydrogen atoms with H2O-terminated Si(100) by Ikeda \textit{et al.}\textsuperscript{48}

References

Chapter 5:

Quantum Chemical Study on the Oxidation of Hydrogen-Terminated Silicon Surface by Oxygen Anions
1. Introduction

The crucial demand for reduction in the design rule of ultralarge-scale integrated circuit (ULSI) technology will soon lead us to a new era of future metal-oxide-semiconductor (MOS) devices with minimum feature sizes below 0.1 μm. The electrical properties of MOS devices are strongly correlated with structural characteristics at the SiO₂/Si interface. It now appears that atomic-scale control of ultrathin SiO₂ film formation to only 5-6 atomic layers should play an important role in order to obtain an SiO₂/Si interface of the highest-quality.

Surface cleaning is the primordial process of preparing a tailor-made surface of a Si single crystal clean enough to enable fabrication of a well-designed SiO₂ film on it. Hydrocarbon contamination or native oxide that covers the surface of pristine Si single crystal can be removed by hydrogen fluoride (HF) etching whereby an atomically flat hydrogen-terminated Si surface (abbreviated as H-Si surface hereafter) is obtained. A novel method of preparing the atomically flat H-Si(111) surface was found via 40% NH₄F solution or boiling water treatment. The H-Si surface is chemically passivated against oxidation even if it is exposed to air at room temperature. Hattori performed the oxidation of the H-Si(111) surface at 300°C in dry O₂ under a pressure of 1 torr up to a thickness of 0.5 nm, whereby further heating resulted in layer-by-layer oxidation at the SiO₂/Si interface. The oxidation process and the role of hydrogen atoms in the surface reaction remain to be clarified.

In the present paper, the chemical reactivity of an oxygen anion O⁻ with the H-Si(111) surface is studied using ab initio molecular orbital method of quantum chemistry. The oxygen anion O⁻ has milder reactivity with Si than the oxygen atom O; moreover, if it were included in the Si bulk, it would become a major diffusing species. However, the formation of O⁻ from O₂ gas is inhibited on the H-Si(111) surface since the route of charge transfer from the surface to O₂ is blocked by hydrogen termination. Our idea is to supply O⁻ efficiently. This can be done by carefully choosing plasma processes, such as a variation of the remote plasma method, although we do not intend to restrict
ourselves to a particular technique of O⁻ supply. Instead, we would like to demonstrate the hypervalency of Si that stabilizes five (penta)-coordinated anionic species.

Theoretical studies have proved that the penta-coordinated Si plays an important role in the hydroxide-containing reactions of Si.12-16 Gordon et al.15 studied the penta-coordinated silicon anionic species H₃(CH₃)SiOH⁻ and (CH₃)Si(OH)₄⁻ in the experiments by DePuy et al.12 on the reactions of OH⁻ with methylsilane or tetramethyilsilane. They identified the penta-coordinated intermediates in a series of pseudo-rotation reaction pathways. Gordon et al. noted the formation of the penta-coordinated intermediate Si(OH)₅⁻ along the reaction pathway:

\[
\text{Si(OH)₄ + OH⁻ → penta-coordinated Si(OH)₅⁻ → Si(OH)₃O⁻ + H₂O}
\]

for polymerization and sol-gel processes.16 In the case of O⁻ with Si, the hypervalency of Si works in a similar manner to stabilize the penta-coordinated complex.

2. Methods of Calculation

Molecular orbital calculations were performed using the GAUSSIAN 94 program package.17 The geometry of the cage model Si₁₀H₁₆ was optimized by the analytical energy gradient method using the spin-restricted Hartree-Fock (RHF) procedure with 6-31G* basis sets.18 Vibrational frequencies were then obtained analytically. The geometry of this cage model was reoptimized with O⁻ in it under the constraint of C₃v symmetry and Si-O bond length of 2.3 Å, where we added a diffuse orbital for O⁻ (6-31+G*) using the spin-unrestricted HF (UHF) method. Electron correlation energies were estimated by the second-order Möller-Plesset perturbation theory that includes correlation for valence electrons (MP2(fc)).19,20

The geometries of all other cluster models were optimized using the HF procedure with 6-31+G** basis set (denoted as HF/6-31+G**). In HF calculations, the RHF method was used for closed-shell singlet states, and the UHF method for open-shell doublet and triplet states. Vibrational frequencies were then obtained analytically at the HF/6-31+G** level. Electron correlation energies were estimated by the second-order and third-order Möller-Plesset perturbation theory (MP2 and MP3) and single and double substituted configuration interaction (CISD)21 that includes correlation for all electrons with 6-31+G** basis sets at the HF/6-31+G** optimized geometries (denoted as MPn(full)/6-31+G**//HF/6-31+G** (n=2,3) or CISD(full)/6-31+G**//HF/6-31+G**). In CISD calculations, unlinked cluster quadruple correction (QC) was added to enable size-consistency correction (denoted as CISD(full)+QC).22 To estimate the effects of higher spin contaminations, spin-projected MP2 calculations were also made.23 The Mulliken atomic charge24 and spin densities were calculated using SCF density.

Surface model calculations discussed in section 3.6 were performed in CASTEP code. We used LSDA as parameterized by Perdew and Zunger26 and non-local pseudopotentials with the plane wave basis set of the Kleinman-Bylander type.27,28

3. Results and Discussion

3.1. Reaction Pathways

The possible reaction pathways (I), (II), and (III) of O⁻ on H-Si(111) surface are schematically shown in Figure 1. The energy diagrams along the reaction coordinates are shown in Figure 2, where the local cluster models 1-12 adopted are shown in Figure 3. Total energies of 1-12 are shown in Table 1 and vibrational frequencies, in Table 2. Relative energies of reaction pathways (I)-(III) are given in Tables 3 and 4. The presence of the penta-coordinated anionic species 7 at the beginning of all the reaction pathways strongly supports the hypervalency of Si that initiates the reactions, where the stabilization energy of 7 is 41.31 kcal/mol at CISD(full)+QC/6-31+G**. An oxygen anion can therefore be inserted into a Si-Si bond to form a local Si-O-Si structure. The stabilization energy is enhanced if the deformation energy in the local Si-O-Si structure is released from 10 to 9 via 11 or 5 to 4 via 6, as shown in Figure 2. At the final stage of each reaction pathway, the escaping tendency of an excess electron is estimated as follows.
Figure 1. Reaction pathways (I), (II), and (III) of O' on H-Si(111) surface.

Figure 2. Relative energy diagrams at the CISD(full)+QC//HF level (kcal/mol) for the reaction pathways of (a) (I) and (II), and (b) (III).
Figure 3. Optimized geometries of the species 1-12 at the HF/6-31+G** level. Bond lengths are in Å and bond angles in degrees. The Mulliken atomic charges are in italics. The spin densities are in parentheses.
Table 2: Vibrational Frequencies at the HF/6-31+G** Level

<table>
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<th>species</th>
<th>harmonic vibrational frequencies (cm⁻¹)</th>
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<td>SiH₃</td>
<td>874(α), 1018(ε), 2343(α), 236(ε)</td>
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<td>2SiH₃O⁻</td>
<td>804(ε), 1058(ε), 1099(α), 1180(ε), 2043(α), 2154(α)</td>
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<td>3SiH₃SiH₃</td>
<td>36(α), 418(ε), 461(α), 696(ε), 948(α), 1026(ε)</td>
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<td>1031(ε), 1044(ε), 2383(α), 2388(ε), 2347(α), 2354(α)</td>
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<td>4SiH₃SiH₅(OH)</td>
<td>95(α), 181(α), 397(α), 438(α), 563(α), 670(α), 714(α), 800(α), 902(α), 944(α), 1029(α), 1036(α), 1044(α), 1048(α), 2253(α), 2270(α), 2290(α), 2325(α), 2399(α), 3917(α)</td>
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<td>5SiH₃SiH₅(OH)⁺</td>
<td>53(α), 124(α), 175(α), 248(α), 300(α), 497(α), 543(α), 686(α), 845(α), 907(α), 955(α), 970(α), 1015(α), 1052(α), 1061(α), 1961(α), 2128(α), 2152(α), 2181(α), 2194(α), 4139(α)</td>
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<td>7SiH₃SiH₅(O²⁻)²⁺</td>
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Table 3: Relative Energies of Reaction Pathways (I) and (II) (kcal/mol)

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<th>MP2(full)(^{a})</th>
<th>PMP2(full)(^{a})</th>
<th>MP3(full)(^{a})</th>
<th>CISD(full)+QCh(^{b})</th>
<th>CISD(full)+QCh(^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{SiH}_2\text{SiH}_3 + \text{O})</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>(\rightarrow \text{SiH}_2\text{SiH}_3\text{O}^-) 7</td>
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<td>-42.14</td>
<td>-41.10</td>
<td>-41.31</td>
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<td>-61.95</td>
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<td>(\rightarrow \text{SiH}_2\text{O}^- + \text{SiH}_3\text{O}^-) 10</td>
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<td>-99.29</td>
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</tr>
<tr>
<td>(\rightarrow \text{SiH}_2\text{O}^- + \text{SiH}_3\text{O}^-) 11</td>
<td>-99.22</td>
<td>-97.84</td>
<td>-91.18</td>
<td>-88.79</td>
<td>-85.36</td>
</tr>
<tr>
<td>(\rightarrow \text{SiH}_2\text{O}^- + \text{SiH}_3) 9</td>
<td>-133.79</td>
<td>-132.38</td>
<td>-125.90</td>
<td>-123.05</td>
<td>-119.00</td>
</tr>
</tbody>
</table>

\(^{a}\)Without ZPE correction.
\(^{b}\)With ZPE correction.

Table 4: Relative Energies of Reaction Pathway (III) (kcal/mol)

<table>
<thead>
<tr>
<th>reactions</th>
<th>MP2(full)(^{a})</th>
<th>PMP2(full)(^{a})</th>
<th>MP3(full)(^{a})</th>
<th>CISD(full)+QCh(^{b})</th>
<th>CISD(full)+QCh(^{b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{SiH}_2\text{SiH}_3 + \text{O})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\rightarrow \text{SiH}_2\text{SiH}_3\text{O}^-) 7</td>
<td>-41.80</td>
<td>-41.73</td>
<td>-42.14</td>
<td>-41.10</td>
<td>-41.31</td>
</tr>
<tr>
<td>(\rightarrow \text{SiH}_2\text{SiH}_3\text{O}^- + \text{H}) 12</td>
<td>-61.64</td>
<td>-60.23</td>
<td>-48.78</td>
<td>-47.69</td>
<td>-51.65</td>
</tr>
<tr>
<td>(\rightarrow \text{SiH}_2\text{SiH}_2\text{OH}^-) 5</td>
<td>-82.42</td>
<td>-82.33</td>
<td>-76.12</td>
<td>-73.53</td>
<td>-71.90</td>
</tr>
<tr>
<td>(\rightarrow \text{SiH}_2\text{SiH}_2\text{OH}^-) 6</td>
<td>-83.94</td>
<td>-82.57</td>
<td>-77.16</td>
<td>-74.45</td>
<td>-70.51</td>
</tr>
<tr>
<td>(\rightarrow \text{SiH}_2\text{SiH}_2\text{OH}^-) 4</td>
<td>-106.82</td>
<td>-105.42</td>
<td>-100.60</td>
<td>-94.50</td>
<td>-89.99</td>
</tr>
</tbody>
</table>

\(^{a}\)Without ZPE correction.
\(^{b}\)With ZPE correction.

3.2. Electronic Structure

We have investigated the electronic structure of the penta-coordinated complex \(\text{SiH}_2\text{SiH}_3\text{O}^-\) using Gaussian-1 (G1) and Gaussian-2 (G2) procedures. The optimized geometry using the G2(MP2) procedure gives a bond length of 1.579 Å for the Si-O bond, which is similar to the experimental value of 1.563 Å. In our case, the Si-O bond length is 1.56 Å. This is because all degenerate Si-O orbitals are occupied in SiOH: Similar propensity is expected for SiOH. The penta-coordinated complex \(\text{SiH}_2\text{SiH}_3\text{O}^-\) has \(C_4v\) symmetry in the \(\text{SiH}_2\text{SiH}_3\text{H}_2\) phase. Curtiss et al. studied it using Gaussian-1 (G1) and Gaussian-2 (G2) procedures and reported. Their optimized results for the penta-coordinated complex \(\text{SiH}_2\text{SiH}_3\text{O}^-\) is 366.0 kcal/mol at the G1 and 364 kcal/mol at G2 levels. Their optimized results for the penta-coordinated complex \(\text{SiH}_2\text{SiH}_3\text{O}^-\) in the gas phase are 357.9 kcal/mol at the G1 and 356 kcal/mol at G2 levels. The optimized results for the penta-coordinated complex \(\text{SiH}_2\text{SiH}_3\text{O}^-\) in the gas phase are 357.9 kcal/mol at the G1 and 356 kcal/mol at G2 levels.

The optimized results for the penta-coordinated complex \(\text{SiH}_2\text{SiH}_3\text{O}^-\) is 366.0 kcal/mol at the G1 and 364 kcal/mol at G2 levels. Their optimized results for the penta-coordinated complex \(\text{SiH}_2\text{SiH}_3\text{O}^-\) in the gas phase are 357.9 kcal/mol at the G1 and 356 kcal/mol at G2 levels.

In Figure 2, m denotes the relative energy in the case where the neutral species \(m\) gets the excess electron at the same geometry of \(m\) (vertical electron attachment). The excess electron releases an excess energy in the case where the neutral species \(m\) gets the excess electron.
coordination at Si. Equatorial Si–Si and Si–H bonds are slightly longer than those of normal coordination. On the other hand, axial Si–H and Si–O bonds are very long, exhibiting the typical 3-centers 4-electrons bonding. The spin density of O in 7 is +0.97 as its singly occupied molecular orbital (SOMO) is localized on it.

### 3.3. Reaction Mechanism

We discuss the microscopic mechanism of O\(^{-}\) insertion into an Si–Si bond at the early stage of oxidation. We consider that O\(^{-}\), which is in the gas phase or diffusing into Si crystal, attacks Si atom on the silicon surface to form the penta-coordinated complex. O\(^{-}\) has three possible ways of attacking Si atom, as shown in Figure 1. The initial way (I) is that the gas-phase O\(^{-}\) attacks the second-most Si atom of the surface. The second way (II) is that diffusing O\(^{-}\) attacks from the back of the topmost Si atom on the surface. The third one (III) is that the gas-phase O\(^{-}\) attacks from skewed-front of the topmost Si atom on the surface. All of these are supported by the hypervalency of Si that leads to the penta-coordinated structure.\(^{35}\) At the early stage of the reaction, the lone-pair electrons of O\(^{-}\) attack the lowest unoccupied molecular orbital (LUMO) of Si that spreads to the backside of the apical bond. The unpaired electron of O\(^{-}\) remains intact and is situated in the radical SOMO of O\(^{-}\) that spreads orthogonal to the apical bond. The occupied orbital energy diagram of SiH\(_3\)SiH\(_3\)O\(^{-}\) at HF/6-31+G** level is shown in Figure 4(b). The 8a' highest occupied molecular orbital (HOMO) and the 5a' orbital are for 3c-4e bonding of apical O–Si–H bond. The 4a' orbital SOMO is localized in the oxygen atom because of the difference in electronegativity between Si and O, which stabilizes the orbital significantly. It is characteristic of the Si–O radical system that the energy of SOMO be stabilized. The 7a' orbital is for Si–Si σ bond.

The Si–Si bond in 7 is easily cleaved through the electron transfer from 7a' to 4a', which leads to the formation of SiH\(_3\)O\(^{-}\) 2 and SiH\(_3\) 1. This is supported by a large stabilization energy of 4a' even after accepting an additional electron, as shown in Figure 5. In Figure 5 is also shown the residual SOMO-LUMO interaction remaining in 7. In the separation limit, SiH\(_3\) 1 + SiH\(_3\)O\(^{-}\) 2 is more stable than 7 by 21.79 kcal/mol at

![Figure 4](image_url)

**Figure 4.** (a) Classical bond image of penta-coordinated Si with O\(^{-}\) and (b) Occupied orbital energy diagram of SiH\(_3\)SiH\(_3\)O\(^{-}\) 7 at the UHF/6-31+G** level for both α and β spin spaces.
The separated SiH$_3$ and SiH$_2$O$^-$ are again bound to form SiH$_3$SiH$_2$O$^-$ or SiH$_3$O$^-$. From an energetic view, 10 or 11 is more stable by about 27.43 kcal/mol than SiH$_3$ + SiH$_2$O$^-$. As discussed above, the structure 10 may have a very short lifetime or be excluded from the reaction pathway. However, an important point is that there exists a local level that affects the local electronic character of a reaction series when a lattice collapses locally. Analogously, the separated SiH$_3$SiH$_2$O$^-$ and H are recombined to form SiH$_3$SiH$_2$O$^-$ 5 or 6, the stabilization energy of which is about 25.84 kcal/mol. After releasing the excess electron, neutral species SiH$_3$SiH$_2$O in reaction pathways (I) and (II) or SiH$_3$SiH$_2$OH 7 in (III) are obtained as demonstrated in Figure 2.

It should be noted from Tables 3 and 4 as well as Figure 2 that SiH$_3$SiH$_2$O 9 is more stable than its structural isomer SiH$_3$SiH$_2$OH 4 by 28.55 kcal/mol. This proves the preference for Si–Si bond oxidation. Moreover, after all the back bonds are oxidized, the reaction pathway (III) is opened when the terminating H is removed en route to the recombination of SiH$_3$SiH$_2$O$^-$ 12 and H.

The discussions given above are all based on the assumption of a localized electron in the domain of a model cluster that is cast in a defect of crystal surface acting as a transient center of electron trap. This picture works well in 7 where the unpaired electron is exclusively localized in O using the 4a' orbital, as shown in Figure 4(b); indeed, (1) the spin density is +0.97 for O as shown in Figure 3, which dictates a completely localized spin, (2) the value of $\langle s^2 \rangle$ is 0.761 in the UHF calculation, which is very close to the exact value of 0.75 and hence supports the relevance of the electron configuration shown in Figure 4(b), and (3) the weight of the electron configuration is 0.936 in the CISD calculation with which the argument of Figure 4(b) is clearly reinforced. Moreover, the 7a' orbital in Figure 4(b) has the character of Si–Si σ bond with an orbital energy of -6.499 eV and therefore represents that of the conduction band in n-doped Si. However, the electron transfer from this 7a' orbital to the 4a' orbital with an orbital energy of -11.54 eV will result in the formation of the doubly negatively charged ion O$^{2-}$, which is strictly

**Figure 5.** SOMO-LUMO interaction between SiH$_3$O$^-$ 2 and SiH$_3$ 1 in SiH$_3$SiH$_2$O$^-$ 7.
inhibited by the experimental fact that the second electron affinity of O should be negative because of the resultant large electron-electron repulsion. On the other hand, no matter how transient the lifetime of the species \( \textbf{10} \) or \( \textbf{5} \) is, the excess electron in these species has strong interaction with the conduction band of Si as demonstrated by the distribution of charge and spin density in Figure 3. Thus, we can further assume that with the lapse of sufficient time, the excess electron should be released even from \( \textbf{10} \) or \( \textbf{5} \).

### 3.4. Reactivity of Oxidized Si with Oxygen Anion

We have investigated the reactivity of \( \text{O}^- \) with Si that is partially oxidized on the surface using the following consecutive reactions:

\[
\begin{align*}
\text{SiH}_3\text{Si(OH)O}^- & \rightarrow \text{SiH}_3\text{Si(OH)O}^- \\
\rightarrow & \text{SiH}_3\text{Si(OH)O}^- \\
\rightarrow & \text{SiH}_3\text{Si(OH)O}^- \\
\end{align*}
\]

The reaction energies are summarized in Table 5 and energy diagrams and geometries are shown in Figure 6. In all cases, the stable penta-coordinated complexes are found. The stabilization energy increases as the number of \( n \) (\( n=0-4 \)) increases. This tendency may serve as the driving force for layer-by-layer oxidation of H-Si(111) using \( \text{O}^- \) as a reactive species. The stabilization energy is enhanced if it releases the excess electron, which is a natural extension from the situation in preceding subsections. The most stable products up to \( n=3 \) is the neutral species \( \text{SiH}_3\text{Si(OH)O}^- \). The reaction energy increases as the number of \( n \) (\( n=0-3 \)) increases.

Further investigation including the effects of surface strain in H-Si(111) is necessary in order to study a real material under oxidation. A preliminary attempt toward this investigation may be found in section 3.5.

### 3.5. Cage Model

For the H-Si(111) surface we have adopted a local cage model \( \text{Si}_{10}\text{H}_{16} \) whose optimized geometry in \( Td \) symmetry at HF/6-31+G* level is shown in Figure 7. The total energy is shown in Table 6 and vibrational frequencies are shown in Table 7. The Si-Si

---

**Table 5: Reaction Energies in SiH_4-n(OH)_n^- + O^- System (First Row : CISD(full)/6-31+G**/HF/6-31+G**; Second Row : HF/6-31+G** (kcal/mol))**

<table>
<thead>
<tr>
<th>( n=0 )</th>
<th>( n=1 )</th>
<th>( n=2 )</th>
<th>( n=3 )</th>
<th>( n=4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{SiH}_4\text{Si(OH)O}^- )</td>
<td>-74.728</td>
<td>-85.384</td>
<td>-91.011</td>
<td>-92.380</td>
</tr>
<tr>
<td>(axial)</td>
<td>-31.266</td>
<td>-39.837</td>
<td>-44.470</td>
<td>-45.141</td>
</tr>
<tr>
<td>( \text{SiH}_4\text{Si(OH)O}^- )</td>
<td>-75.954</td>
<td>-88.209</td>
<td>-95.058</td>
<td>-96.608</td>
</tr>
<tr>
<td>(equatorial)</td>
<td>-31.044</td>
<td>-41.397</td>
<td>-47.380</td>
<td>-48.158</td>
</tr>
<tr>
<td>( \text{SiH}_3\text{Si(OH)O}^- )</td>
<td>-112.889</td>
<td>-123.472</td>
<td>-132.260</td>
<td>-132.553</td>
</tr>
<tr>
<td>(axial)</td>
<td>-57.958</td>
<td>-68.500</td>
<td>-77.390</td>
<td>-78.194</td>
</tr>
<tr>
<td>( \text{SiH}_3\text{Si(OH)O}^- )</td>
<td>-141.347</td>
<td>-148.800</td>
<td>-150.549</td>
<td>-151.131</td>
</tr>
<tr>
<td>(equatorial)</td>
<td>-93.121</td>
<td>-100.276</td>
<td>-102.759</td>
<td>-103.743</td>
</tr>
</tbody>
</table>
Figure 6. Energy diagrams in SiH₄(3OH)n + O⁻ systems at the CISD(full)+QC/6-31+G** level [the HF/6-31+G** level] in kcal/mol: (a)-(e) corresponds to n=0-4, respectively.
Table 6: Total Energies at the Hartree-Fock and MP2(fc) Levels in au

<table>
<thead>
<tr>
<th>systems</th>
<th>HF</th>
<th>MP2(fc)/HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cage model Si(1)H16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(T_d)</td>
<td>-2898.53000</td>
<td>-2899.33663</td>
</tr>
<tr>
<td>O⁻ in Cage (Si-O 2.3Å fixed)</td>
<td>(C₃ᵥ)</td>
<td>-2973.32690</td>
</tr>
<tr>
<td>aUsing 6-31G* basis set.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| bUsing the 6-31G* basis set for Si and H atoms and the 6-31+G* basis set for O atom.

Table 7: Vibrational Frequencies of Cage Model at the HF/6-31G* Level

<table>
<thead>
<tr>
<th>harmonic vibrations (cm⁻¹)</th>
<th>ZPE⁻⁻⁻</th>
<th>ZPE⁻⁻⁻⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>80(θ₁), 111(ε₁), 123(ε₂), 202(ε₂), 329(a₁), 347(a₁), 367(ε₁), 417(τ₁), 437(ε₁), 456(ε₂), 511(τ₁), 533(ε₂), 626(τ₁), 636(ε₂), 698(τ₁), 713(ε₁), 747(τ₂), 756(ε₁), 798(ε₁), 847(τ₁), 1006(α), 1012(τ₂), 1026(α), 2326(α), 2327(τ₂), 2341(ε₁), 2345(τ₂), 2345(τ₂), 2352(τ₂), 2359(α)</td>
<td>86.60</td>
<td></td>
</tr>
<tr>
<td>aZPE scaled by 0.89.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 7. Optimized geometry of a local cage model $\text{Si}_{10}\text{H}_{16}$ of H-Si(111) surface. Bond length is given in Å and bond angle in degree. Mulliken atomic charges are given in italics.

Figure 8. Stabilization of $\text{O}^-$ in the cage model. (a) Optimized geometry of the cage model with Si-O bond length fixed at 2.3 Å along the $C_3$ axis of the cage model. Bond length is given in Å and bond angle in degree. Mulliken atomic charges are given in italics. The spin densities are in parentheses. (b) Energy diagram at the MP2(fc)/HF level (kcal/mol).

3.6. Extended Model of Periodic Boundary Condition

For an extended model of the oxidation of H-Si(111) surface by $\text{O}^-$, we adopted the supercell geometry system shown in Figure 9(a), (b). In the 2x2 surface unit cell, 4 layers of Si are contained and the vacuum region is 13.04 Å in size. An $\text{O}^-$ anion approaches the H-Si(111) surface via reaction pathway (I) in Figure 1. The stabilization of the penta-coordinated reaction complex is unambiguously proven, as shown in Figure 9(c).
4. Conclusion

We have investigated the oxidation mechanism of the H-Si(111) surface by O\textsuperscript{−} using \textit{ab initio} molecular orbital method of quantum chemistry. We have found that the hypervalency of Si is fundamentally important to initiate and promote the oxidation. O\textsuperscript{−} can attack surface Si atoms to form penta-coordinated complexes, which should further lower the diffusion barrier for O\textsuperscript{−} transfer into the Si bulk. This has been proven using a local cage model of the H-Si(111) surface augmented by an extended model of periodic boundary condition. O\textsuperscript{−} should then be inserted into an Si−Si bond to form a local Si−O−Si structure. The reactivity of insertion arises from the unpaired radical electron in O\textsuperscript{−}. The stabilization energy is enhanced if the deformation energy in the local Si−O−Si structure is released. That the oxidized Si has a strong tendency to accept additional O\textsuperscript{−} is concluded using a series of cluster model calculations. Since the active species is a charged one, the external electric field will play an important role in controlling its reactivity, \textit{e.g.}, charge-up of the material or the thickness of SiO\textsubscript{2} film.

References


Chapter 6:

Quantum Chemical Study on Aluminum Selective CVD Reaction Mechanism
1. Introduction

Aluminum (Al) selective chemical vapor deposition (CVD) on the silicon (Si) surface has received much attention as promising technology for ultralarge-scale integration (ULSI) metallization. Clever choice of the molecular precursor of Al as well as the substrate surface should play an important role in initiating selective nucleation of Al. One of the recent key issues in this field of research has shown that the best possible selectivity is achieved by the combination of dimethylaluminum hydride (DMAIH) as the Al precursor and hydrogen (H)-terminated Si as the substrate surface.

The reaction kinetics of the Al-selective CVD on the H-terminated Si has been studied as a function of temperature using the \textit{in-situ} Fourier transform infrared (FTIR) attenuated total reflection (ATR) technique. Then, the variations in the FTIR-ATR desorption intensity of Al–H, Si–H and CH$_3$–Al bands have concluded the following facts:

(1) DMAIH gas is physisorbed on the H-terminated Si surface at 10 min, 1 Torr and room temperature. No desorption of any kind is observed in this low temperature regime.

(2) As temperature is raised, H atom exclusively from DMAIH is desorbed below 150 °C.

(3) If the temperature is raised further, H atom from the H-terminated Si surface and CH$_3$ group from DMAIH are desorbed simultaneously over around 150 °C.

In this paper, we have devised model reaction species and reaction paths and studied this interesting temperature-dependent reaction mechanism in terms of \textit{ab initio} molecular orbital (MO) theory of quantum chemistry.

2. Methods of Calculation

MO calculations were performed with the GAUSSIAN94 program package. The geometries were optimized by the analytical energy gradient method at Hartree-Fock (HF)
self consistent field (SCF) level and second-order Möller-Plesset (MP) perturbation theory,^{8,9} which includes correlation for all electrons, using the standard 6-31G** basis set (denoted as HF/6-31G** and MP2(full)/6-31G**).^{10} Theoretical harmonic vibrational frequencies were obtained from analytical second derivatives calculated at MP2(full)/6-31G** level to verify each equilibrium structure as a true energy minimum or a saddle point. Zero-point vibrational energies (ZPE) were then scaled by a factor of 0.94.^{11} To obtain higher correlation energies, single point calculations of single and double substituted configuration interaction (CISD)\(^12\) including unlinked cluster quadruple corrections (QC)\(^13\) were carried out on the MP2(full)/6-31G** geometries (denoted as CISD+QC(full)/6-31G**//MP2(full)/6-31G**).^{11} The Mulliken atomic charge\(^{14}\) was calculated using SCF density at MP2(full)/6-31G** level optimized geometry.

### 3. Results and Discussion

Model reaction paths and total energies of reactant and product species are listed in Tables 1 and 2. The transition state (TS) of the \(r\)th reaction path is denoted as \(TSr\). For the first and second reaction paths, the \(TS1\) and \(TS2\) are shown in Figure 1. The reaction energies are summarized in Table 1. The MO energy levels of the selected molecular species are shown in Figure 2 and the MO patterns in Figure 3. The energy diagrams are collected in Figure 4.

#### 3.1. Optimized Structures

According to our calculation for alane (Al\(_3\)H\(_3\)), Al–H bond length is 1.582Å at HF level and 1.577Å at MP2 level. Electron correlation tends to shorten the Al–H bond. Aggregates of Al\(_3\)H\(_3\) and its alkyl substitution products will polymerize at low temperature making strong charge transfer complexes\(^{15}\) in a similar way borane (BH\(_3\)) does.\(^{16-22}\) Theoretically, Al\(_3\)H\(_3\) is also predicted to form Al–Al bond leaving hydrogen (H\(_2\)).\(^{19-25}\) The resultant Al\(_3\)H\(_4\) has several geometrical isomers\(^{26,27}\), and we use a conventional \(D_{2h}\)

### Table 1: Reaction Energies (kcal/mol)\(^a\)

<table>
<thead>
<tr>
<th>reaction</th>
<th>activation energy</th>
<th>heat of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlH(_3) + AlH(_3) –&gt; H(_2)AlAIH(_2) + H(_2)</td>
<td>25.29(27.16)</td>
<td>-0.08(1.39)</td>
</tr>
<tr>
<td>AlH(_3) + SiH(_4) –&gt; AlH(_2)SiH(_3) + H(_2)</td>
<td>30.89(31.07)</td>
<td>0.80(1.14)</td>
</tr>
<tr>
<td>AlH(_3) + AlH(_2)(CH(_3)) –&gt; H(_2)AlAIH(_2) + CH(_4)</td>
<td>34.91(34.32)</td>
<td>-4.26(-1.70)</td>
</tr>
<tr>
<td>AlH(_2)(CH(_3)) + SiH(_4) –&gt; AlH(_2)SiH(_3) + CH(_4)</td>
<td>38.49(36.47)</td>
<td>-3.38(-1.94)</td>
</tr>
<tr>
<td>AlH(_2)(CH(_3)) + AlH(_2)(CH(_3)) –&gt; H(_2)AlAIH(_2) + CH(_3)CH(_3)</td>
<td>84.18(83.79)</td>
<td>7.19(9.96)</td>
</tr>
<tr>
<td>AlH(_2)(CH(_3)) + H(_2) –&gt; AlH(_3) + CH(_4)</td>
<td>34.25(33.62)</td>
<td>-4.18(-3.08)</td>
</tr>
</tbody>
</table>

\(^a\)At the CISD(full)+QC/6-31G**//MP2(full)/6-31G** level including ZPE(scaled) corrections.

### Table 2: Total Energies(au)

<table>
<thead>
<tr>
<th>species</th>
<th>HF/6-31G**(^a)</th>
<th>MP2(full)/6-31G**(^b)</th>
<th>CISD+QC(full)/6-31G**(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)</td>
<td>-1.13133</td>
<td>-1.15766</td>
<td>-1.16514</td>
</tr>
<tr>
<td>2CH(_4)</td>
<td>-40.20170</td>
<td>-40.36986</td>
<td>-40.39258</td>
</tr>
<tr>
<td>3SiH(_4)</td>
<td>-291.23084</td>
<td>-291.34986</td>
<td>-291.37821</td>
</tr>
<tr>
<td>4CH(_3)CH(_3)</td>
<td>-79.23824</td>
<td>-79.53371</td>
<td>-79.59025</td>
</tr>
<tr>
<td>5AlH(_3)</td>
<td>-243.61899</td>
<td>-243.69917</td>
<td>-243.72073</td>
</tr>
<tr>
<td>6Al(_2)H(_4)</td>
<td>-486.09547</td>
<td>-486.23750</td>
<td>-486.27548</td>
</tr>
<tr>
<td>7AlH(_2)(CH(_3))</td>
<td>-282.67013</td>
<td>-282.90120</td>
<td>-282.93625</td>
</tr>
<tr>
<td>8AlH(_2)(SiH(_3))</td>
<td>-533.70499</td>
<td>-533.88689</td>
<td>-533.92987</td>
</tr>
<tr>
<td>TS1</td>
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<td>-487.40335</td>
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<td>TS2</td>
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<td>-535.05117</td>
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<td>TS3</td>
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<td>TS4</td>
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<td>TS6</td>
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</table>

\(^a\)At HF/6-31G** optimized geometries. \(^b\)At MP2(full)/6-31G** optimized geometries.
\(^c\)Optimized in \(C\(_1\)\) symmetry. \(^d\)Optimized in another \(C\(_2\)\) symmetry.
Figure 1. Optimized geometries at MP2(full)/6-31G** level. Bond lengths are in angstroms and bond angles and dihedral angles are in degrees. HF/6-31G** level optimized data are in parentheses.

Figure 2. MO energy diagrams of AlH₃, AlH₂(CH₃), and AlH₂(SiH₃) at HF/6-31G** level on the MP2(full)/6-31G** level geometries.

Figure 3. MO patterns of each energy levels.
Figure 4. Energy diagrams of each reaction in kcal/mol. Relative energies are calculated by using total energies at CISD(full)+QC/6-31G**//MP2(full)/6-31G** level corrected with ZPEs.

3.2. Reactivity of DMAIHF on the H-Terminated Si Surface

The Al in AlH3 is calculated to be highly positively charged (+0.60) and the H on the terminated Si surface is assumed to be highly negatively charged, judging from the electronegativity difference. Actually, using silane (SiH4) as a local model of the H-terminated Si in this case provides the value of -0.17 for the charge of H attached to Si. Because of the electrostatic effect, we may then assume that AlH3 can easily be physisorbed on the H-terminated Si surface at room temperature. On the surface, the physisorbed AlH3 may first react with another AlH3 to form the Al-Al bond prior to Al-Si bond formation. We assume reaction (1) in Table 1 as the model of this elementary process (i), while reaction (2) in Table 1 is the model of the elementary process (ii) to form the Al-Si bond.
For reaction (1), the symmetry of the TS1 is optimized to be C1 at HF/6-31G** level, but C3 at MP2/6-31G** level, as shown in Figure 1. The activation energy of this reaction is 25.29 kcal/mol at CISD+QC level including ZPE and heat of reaction nearly zero. This reaction is a combination of the elimination of H2 and the succeeding internal rotation of Al–Al bond.

For reaction (2), the symmetry of the TS2 is optimized to be Cs as shown in Figure 1. The barrier height is 45.93 kcal/mol at HF/6-31G** level, 31.07 kcal/mol at MP2/6-31G** level including ZPE, 30.89 kcal/mol at CISD+QC/6-31G** level including ZPE. The LUMO of AlH3 has very low orbital energy as shown in Figure 2. This means that AlH3 works as a good electron acceptor in a similar manner BH3 does. According to the orbital patterns shown in Figure 3, the orbital interaction scheme below guides the course of this chemical reaction. Subsidiary back donation of charge is less active in this path.

The barrier height of reaction (1) is lower than that of reaction (2) by 5.60 kcal/mol at CISD level. It follows that the elementary process (i) can more easily occur than the elementary process (ii) at sufficiently low temperature regime. This qualitatively agrees quite well with the experimental fact that is observed below 150 °C.6

But in high temperature regime, the reactivity for the Al–Al bond formation is comparable with the Al–Si bond formation, so that both processes (i) and (ii) can occur competitively. Moreover, the Al as deposited on Si is terminated by H. Therefore, the following elementary process (i)' can also occur.

Evidently, the elementary process (i)' provides bump of nucleation. This may be a stumbling block for getting excellent morphology of the Al surface. If we can inhibit the elementary process (i)', then we may acquire perfect layer-by-layer nucleation, a defect-free Al surface as deposited. This may be achieved partly by using DMAIH in place of AlH3, as will be shown below.

Now, in the reaction system composed of DMAIH and H-terminated Si, two new elementary processes (iii) and (iv) should occur.

For the elementary process (iii), we assume reaction (3). The barrier height is 34.91 kcal/mol at CISD+ZPE level, which is 9.62 kcal/mol higher than reaction (1).

For the elementary process (iv), we assume reaction (4). The barrier height is 38.49 kcal/mol at CISD+QC+ZPE level, which is 7.6 kcal/mol higher than reaction (2). Additionally, the formation of C2H6 is examined by assuming reaction (5). The
activation energy is 84.18 kcal/mol at CISD + ZPE level, so it rarely occurs actually. Namely, methyl group reacts only with H.

These higher activation energies for the elementary processes (iii) and (iv) tell us that the elementary processes (i) and (ii) are still dominant over and above (iii) and (iv) in this reaction system. But in high temperature regime, all the elementary processes (i)-(iv) are likely to occur. This corresponds to the experimental fact that is observed over around 150 °C.6

Moreover, the Al as deposited on Si is protected by methyl group and then the elementary process (i)' is rather inhibited. Therefore, a good morphology of the Al surface will result in this reaction system.

Furthermore, we can consider the following elementary processes.

\[
\text{Me} \quad \text{Me} \quad \text{Al} \quad \text{Al} \quad \text{Me} \quad \text{Me}
\]

(vi) \quad (vii) \quad (viii)

Each process has correspondence with the model reaction discussed above: that is, (v) with reaction (3), (vi) with reaction (3), (vii) with reaction (5), and (viii) with reaction (4). Clearly, the most probable processes are (v) and (vi) followed by (viii).

3.3. The Role of H₂ Carrier Gas

Finally, we discuss the role of H₂ carrier gas. What we have found so far is that the Al as deposited on Si is terminated by methyl group using DMAIH as the molecular precursor. Then, the H₂ carrier gas can play an active role to transform the methyl-terminated Al surface into the H-terminated Al surface that is more reactive. This will be shown as follows, using model reaction (6).

The activation energy of reaction (6) is 51.67 kcal/mol at HF level, 33.62 kcal/mol at MP2 level including ZPE, 34.25 kcal/mol at CISD+QC level including ZPE. The LUMO of AlH₂CH₃ has very low orbital energy as shown in Figure 2. According to the orbital patterns shown in Figure 3, the orbital interaction scheme below guides the course of this chemical reaction.

There occurs charge transfer from HOMO of H₂ to LUMO of AlH₂CH₃. Also, back-donation of charge from AlH₂CH₃ to H₂ may occur through interaction between HOMO of AlH₂CH₃ and LUMO of H₂. The latter interaction makes cleavage of Al–C bond and formation of Al–H bond. This completes the transformation of the methyl-terminated Al surface into the H-terminated Al surface. This function of H₂ also acts against intact DMAIH molecule. The whole idea of the active role of H₂ is shown below.

4. Conclusion

We have studied the reaction mechanism of the Al selective CVD processes in the system of DMAIH over H-terminated Si in terms of ab initio MO theory of quantum chemistry. Various elementary chemical reaction processes have been identified to account for the temperature-dependent reaction mechanism. We have also revealed that
methyl group suppresses the reactivity of DMAIH with the substrate surface. This reactivity suppression has been recovered by H₂ carrier gas. These results are qualitatively in good agreement with the experimental observations.⁶

In a real CVD system, the situation should be more complex. For example, even in a gas phase, a reaction intermediate may collide with an intact DMAIH molecule or stick to the surface. Defects and impurities on the substrate surface may also change the reactivity. Much work should be done in order to fully understand these new and extremely exciting phenomena.

References

(27) Lammertsma, K.; Günter, O. F.; Drewes, R. M.; Reed, A. E.; Schleyer, P. v. R. 


Chapter 7:

Quantum Chemical Study on p-Doping Effect of F-Terminated Silicon Surface Reaction with Silane
1. Introduction

The atomic-scale control of various silicon (Si) interface structures has been the most fundamentally important subject in the present and future ultralarge-scale integration (ULSI) technology.\textsuperscript{1-3} In particular, the thermal chemical vapor deposition (CVD) processes have played an important role for the basic technology toward fabrication of new Si semiconductor devices. However, the elementary reaction mechanism has not been completely clarified so far in various CVD processes of the variety of source gases with the variety of reaction surfaces.

Thus, Ohmi et al. have devised ultra clean gas supplying system and applied it to the very basic study of the deposition of SiH\textsubscript{4} and Si\textsubscript{2}H\textsubscript{6} gases on the surface of fluorine (F)-terminated Si (F-Si)\textsuperscript{4} together with its p-doping effects as well as on the variety of Si surfaces.\textsuperscript{6} Then, the following experimental facts have been concluded:\textsuperscript{5,6}

1. For the deposition of SiH\textsubscript{4} on F-Si surface, the catalytic activity of the F-Si surface is maintained even after the deposition of SiH\textsubscript{4}. Namely, the F atom is situated on top of the Si surface during the deposition process.

2. On the other hand, for p-doped F-Si surface, the F atom is immersed under the Si polymer as deposited.

In this paper, we have devised model reaction species and reaction paths and studied the local electronic property pertaining to this interesting reaction mechanism in terms of \textit{ab initio} molecular orbital (MO) theory of quantum chemistry.

2. Methods of Calculation

MO calculations were performed with the GAUSSIAN94 program package.\textsuperscript{7} The geometries were optimized by the analytical energy gradient method at Hartree–Fock (HF) level and second-order Møller–Plesset (MP) perturbation theory\textsuperscript{8,9} which includes correlation for all electrons, using the standard 6-31G** basis set (denoted as HF/6-31G** and MP2(full)/6-31G**).\textsuperscript{10} In HF calculation, the spin-restricted HF (RHF)
method was used for closed-shell singlet states, the spin-unrestricted HF (UHF) method was used for open-shell doublet states. Theoretical harmonic vibrational frequencies were obtained from analytical second derivatives calculated at MP2(full)/6-31G** level. Zero-point vibrational energies (ZPE) were then scaled by a factor of 0.94. To obtain higher correlation energies, single point calculations of single and double substituted configuration interaction (CISD) including unlinked cluster quadruple corrections (QC) were carried out on the MP2(full)/6-31G** geometries (denoted as CISD+QC(full)/6-31G**/MP2(full)/6-31G**).

3. Results and Discussion

Following our preceding works, we use molecular cationic species for local models of p-doped Si. Model reaction paths and total energies of reactant and product species are listed in Tables 1 and 2. The transition state (TS) of the nth reaction path is denoted as $T_{Sn}$. The $T_{S1}$ and $T_{S2}$ are shown in Figure 1. Reaction energies are summarized in Table 1. The energy diagrams and the stability of the local structure are demonstrated in Figure 2.

3.1. Optimized Structures

Some of the model species are found in our preceding works. SiH$_4^+$ has several geometrical isomers due to Jahn-Teller distortions. We use a conventional $C_{3v}$ structure of SiH$_4^+$ here in this paper. SiH$_3$SiH$_3^+$ is thought to be a reaction complex between SiH$_3$ and SiH$_4^+$, and is optimized to have symmetry of $D_{3d}$, the same as the neutral SiH$_3$SiH$_3$.

For the optimized geometry of SiH$_3$SiH$_3^+$, the Si–Si bond length is 2.658 Å at MP2/6-31G** level, which is longer than that of neutral SiH$_3$SiH$_3$ by 0.32 Å, showing the Si–Si bond in the p-doped Si is weakened. These data are in accord with the theoretical results published by Curtiss et al. Moreover, the energy barrier of internal rotation around the Si–Si bond in SiH$_3$SiH$_3^+$ is only 1 kcal/mol at the MP2/631G* level. Judging from the data presented above, the local structure is considered

| Table 1: Reaction Energies (kcal/mol) | reaction | heat of reaction
<table>
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<td>$\rightarrow$eclipsed-SiH$_3$F-SiH$_3^+$ + SiH$_3$</td>
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<tr>
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<tr>
<td>$\rightarrow$eclipsed-SiH$_3$F-SiH$_3^+$ + H</td>
<td>$\Delta H$ (-44.99(-46.72))</td>
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</table>

At CISD(full)+QC/6-31G**//MP2(full)/6-31G** level including ZPE(scaled).
At MP2(full)/6-31G** level including ZPE(scaled) in parentheses.
Table 2: Total Energies (au)

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Figure 1. Optimized geometries at MP2(full)/6-31G** level: (a) TS1 and (b) TS2. Bond lengths and bond angles are given in angstroms and degrees, respectively. HF/6-31G** level values are in parentheses.

Figure 2. Relative energy diagrams at CISD(full)+QC/6-31G**/MP2(full)/6-31G** level including ZPE(scaled).
rather flexible in the p-doped Si. The tendency is valid also for the p-doped F-Si. Indeed, for the optimized geometry of SiF\(_3\)SiH\(_3^+\), the Si-Si bond length is 2.312Å, which is longer than that of the neutral SiF\(_3\)SiH\(_3\) by 0.29Å.

3.2. Reaction of Two Neutral Silicon Compounds

We consider the following neutral molecule reactions (1) and (2):

\[
\text{staggered-SiH}_3\text{SiH}_3 + \text{SiH}_3\text{F} \rightarrow \text{staggered-SiH}_3\text{SiH}_3 + \text{SiH}_3\text{F} \quad (1)
\]

\[
\text{staggered-SiH}_3\text{SiH}_3 + \text{SiH}_3\text{F} \rightarrow \text{staggered-SiH}_3\text{SiH}_3 + \text{SiH}_2\text{F}_2 \quad (2)
\]

The optimized geometries of TS\(_1\) and TS\(_2\) have symmetry of C\(_1\), as shown in Figure 1. There were no marked differences between the HF optimized geometries and the MP2 optimized geometries, except slight difference in bond length between Si and F.

In reaction (1), the activation energy is 65.34kcal/mol at CISD+QC level including ZPE. The heat of the reaction is zero. In reaction (2), the activation energy is 63.58kcal/mol and the heat of reaction is -9.73kcal/mol at CISD+QC level.

We observe no tendency for F atoms to be immersed into the bulk of Si. This is confirmed also for the models of larger systems.\(^{16}\) Namely, for the F-Si surface, the most probable position where an F atom can be situated is on top of the surface, trapped by the dangling bond of Si.

![Diagram](image)

This "floating" reaction mechanism of F will be proved from a different viewpoint in the following discussions.

3.3. Reaction of Cation and Neutral Silicon Compounds

We consider the following reaction (3):

\[
\text{SiH}_3\text{SiH}_3^+ + \text{SiH}_3\text{F} \rightarrow \text{eclipsed-SiH}_3\text{F-SiH}_3^+ + \text{SiH}_3 \quad (3)
\]

In reaction (3), the product SiH\(_3\)F-SiH\(_3^+\) is optimized in either staggered or eclipsed form both at linear configuration of Si–F–Si. Examining the normal vibrational modes of SiH\(_3\)F-SiH\(_3^+\), the staggered form has three imaginary frequencies (2 \times 58i, 20cm\(^{-1}\)) and eclipsed form has two (2 \times 57cm\(^{-1}\)). These results agree with the theoretical work of Palafox.\(^{23}\) There is no significant energy difference between these two alternative forms, which shows that the SiH\(_3\) group is nearly free for rotation. Indeed, for the staggered form, one of the imaginary frequency mode whose symmetry species is \(A_1u\) corresponds to SiH\(_3\) group internal rotation. For the residual imaginary frequency modes, the \(E_u\) mode in staggered form and \(E'\) mode in eclipsed form correspond to degenerate Si-F-Si rocking mode.\(^{24}\) Aside from these imaginary frequency vibrational modes, what is most important here is that the (Si–F–Si)+ configuration is stable against the Si–F–Si configuration decomposition mode whose symmetry species is \(A_2^-\). Namely, the F-bridged structure (Si–F–Si)+ is considerably stabilized in the bulk of Si. This observation has also been found in our preceding study on the p-doping effect on chemical etching of Si.\(^{14,15}\)

We have further optimized SiH\(_3\).H\(_3\)Si-F-SiH\(_3^+\) complex in C\(_3v\) symmetry, which keeps linearity of Si\(_1\)–F–Si\(_2\)–Si\(_3\) configuration. For the optimized complex, the staggered form has three imaginary frequencies and the eclipsed form has two imaginary frequencies, which have the same trends in the case of H\(_3\)Si-F-SiH\(_3^+\). The Si\(_2\)-Si\(_3\) bond length is 2.755Å at HF/6-31G** level and 3.14Å at MP2/6-31G** level. From the viewpoint of the Sn2 type reaction, the relative energy is -17.99kcal/mol for SiH\(_3\).H\(_3\)Si-F-SiH\(_3^+\) complex and -12.56kcal/mol for SiH\(_3^+\) + SiH\(_3\)-F-SiH\(_3^+\) at CISD+QC level. As is apparent, this reaction has no activation energy and is exothermic.

Then, we have examined the stability of the F-bridged structure (Si–F–Si)+ for various model reactions as follows.

The reaction (4):
SiF₂SiH₇⁺ + SiH₃F → *eclipsed*-SiH₃-F-SiH₇⁺ + SiF₃

As compared with the reaction (3), the relative energy is more exothermic by 15.83 kcal/mol because the SiH₃ group is here substituted by the SiF₃ group.

The reactions (5) and (6):

\[
\begin{align*}
\text{SiH}_4^+ + \text{SiH}_3 & \rightarrow *eclipsed*-\text{SiH}_3-F-\text{SiH}_3^+ + \text{H} \\
\text{SiH}_3\text{F}^+ + \text{SiH}_4 & \rightarrow *eclipsed*-\text{SiH}_3-F-\text{SiH}_3^+ + \text{H}
\end{align*}
\]

The relative energy is -42.05 kcal/mol for the reaction (5) and -44.99 kcal/mol for the reaction (6) at CISD+QC level.

In Figure 2 are collected the reaction energy diagrams. The reaction (6) is just corresponding to the situation when SiH₄ is decomposed on the p-doped F-Si, which shows maximum exothermicity.

To conclude, upon SiH₄ decomposition, the terminating F atoms are immersed into the bulk by making (Si−F−Si)⁺ bonds because the reactions are exothermic and bonds are stable.

3.5. Stability of (Si−F−Si)⁺ Bond

In this section, we study the stability of SiH₃-F-SiH₃⁺ in terms of the Bader-Pearson's theory of the second-order Jahn-Teller effect.²⁵-²⁷

We assume that the electronic ground state is nondegenerate. When a molecule is distorted from local maximum or minimum along the \( Q_i \) normal coordinate, then using second-order perturbation theory, the electronic energy \( E \) for the ground state becomes

\[
E = \sum E_i + \sum b_{ij} Q_i Q_j.
\]

**Figure 3.** MO energy level diagram of eclipsed H₃Si-F-SiH₃⁺ and eclipsed H₃Si-F-SiH₃ at HF/6-31G** level and \( A_2'' \) vibrational mode.
\[ E = E_0 + \frac{1}{2} f Q_i^2 \]

with the force constant

\[ f_i = \left( \psi_i \frac{\partial^2 H}{\partial Q_i^2} \psi_0 \right) + 2 \sum_{k \neq 0} \left( \frac{\psi_i \frac{\partial H}{\partial Q_i} \psi_k}{E_k - E_0} \right)^2 \]

where \( \psi_0 \) is the ground state wave function and \( E_k \) is the kth excited state energy of the Hamiltonian \( H \).

For the force constant \( f_i \), the second term gives negative contribution, which is brought about by mixing an excited state wave function \( \psi_k \) into the ground state wave function \( \psi_0 \). Because of the denominator \( E_0 - E_k \), lowest excited state contributes most for \( f_i \). The matrix element \( \left( \psi_i \frac{\partial H}{\partial Q_i} \psi_k \right) \) will be nonzero only if the symmetry rule is fulfilled:

\[ \Gamma_{\psi_i} \times \Gamma_{\psi_k} \subset \Gamma_{\psi_0} \]

In Figure 3 are shown the MO energy level diagrams of eclipsed \( \text{H}_3\text{Si-F-SiH}_3 \) and \( \text{H}_3\text{Si-F-SiH}_3^+ \) at HF/6-31G** level. The lowest energy excitation in neutral \( \text{H}_3\text{Si-F-SiH}_3 \) is from singly occupied MO (SOMO) \( 3a_1 \) to lowest unoccupied MO (LUMO) \( 3a_2 \). It gives the transition density of the \( A_2^* \) symmetry, which corresponds to decomposition into \( \text{SiH}_4 \) and \( \text{FSiH}_3 \). The results of frequency analysis at MP2(full)/6-31G** level actually give an imaginary frequency for the \( A_2^* \) mode (150cm\(^{-1}\)). On the other hand, for \( \text{H}_3\text{Si-F-SiH}_3^+ \), the \( A_2^* \) transition corresponds to a much larger excitation energy, which fails to bring about the imaginary frequency. Indeed, the corresponding \( A_2^* \) mode has positive frequency (629cm\(^{-1}\)) from our numerical frequency analysis.

Thus the stability of the F-bridged structure (Si–F–Si)+ is proved for the p-doped Si in contrast with the F-floating reaction mechanism for the undoped Si.

### 4. Conclusion

In this study, we have studied the deposition of SiH\(_4\) on the surface of Si with p-doping effect using \textit{ab initio} molecular orbital calculations. We have calculated the local model of reaction sites and proved that (Si–F–Si)+ bond formation is exothermic with no barrier of activation energy. The stability of the (Si–F–Si)+ bond structure in contrast with the unstable neutral Si–F–Si structure is proved in terms of the second-order Jahn-Teller effect.

We have thus clarified the tendency of F that is immersed into the bulk for chemical bonding in between a pair of Si for the p-doped case. This high stability of the F-bridged structure (Si–F–Si)+ in constant with the neutral F-floating reaction mechanism agrees qualitatively well with the experimental observation.

### References


5. Ohmi, T., private communication.


Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.;
Peng, C. Y.; Ayala, P. A.; Chen, W.; Wong, M. W.; Andres, J. L.; Repogle, E. S.;
Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defreces, D. J.; Baker, J.; Stewart,
J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian 94, Revision B.3; Gaussian,


(10) Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. Ab initio Molecular

(11) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. Israel J. Chem. 1993, 33,
345.


(13) Pople, J. A.; Binkley, J. S.; Krishnan, R. Int. J. Quantum Chem. Symp. 1977, 11,
149.


(15) Tachibana, A.; Kawauchi, S.; Yamabe, T.; Fukui, K. Molecules in Natural
Science and Medicine; Maksić, Z. B., Maksić, M. E., Eds.; Ellis Horwood: New York,
1991; pp 375-393.

1993, 3, 553.


1991, 95, 2433.


(27) Pearson, R. G. Symmetry Rules for Chemical Reactions; Wiley: New York,
1976.
Chapter 8:

Quantum Chemical Study on the Reaction between GeF₄ and Si₂H₆
1. Introduction

Recently low-pressure chemical vapor deposition (LPCVD) for low-temperature growth of group IV (Si, Ge) semiconductor films attracts much attention because of the feasibility of depositing a uniform large-area film. Fabrication of high-quality poly-Si or poly-SiGe becomes indispensable for the application of LPCVD to thin film transistors (TFTs) and solar cells.

Hanna et al. have proposed a novel technique for low-temperature film growth in thermal CVD, called 'reactive thermal CVD'.1-5 In this technique, germanium tetrafluoride GeF₄ as a Ge source and disilane Si₂H₆ as an activator for germanium tetrafluoride were used. They applied this technique to fabrication of the hetero-epitaxial and polycrystalline Ge thin films at temperature lower than 400°C1,2 and high crystallinity poly-Si₀₉₅Ge₀₀₅ thin films at 450°C.5 This technique appears to be useful to produce high-quality large-area thin films, but little is known about this reaction mechanism. Their experiments showed that the film deposition proceeded in the case of the combination of GeF₄ and SbH₆ at the temperature 300-450°C, although it did not proceed in the case of the combination of GeF₄ and SiH₄ at the same temperature.1 They also suggested that these reactions proceed in two parts, namely, in the gas near the surface and on the surface of the hot substrate. Therefore, both the gas phase reaction and the surface reaction must be investigated for a proper understanding of the deposition mechanism. Unfortunately the deposition mechanism seems subtle and is poorly understood yet; the quality of various depositing film depends sensitively on the experimental conditions, namely, the gas flow ratio, temperature, and substrates.

In this study we concentrate on the gas-phase reaction mechanism and make an effort to clarify why Si₂H₆ is more effective as an activator than SiH₄. We investigate the reactions of GeF₄ with two species of silane (Si₂H₆ and SiH₄) and compare the reactivities of Si₂H₆ and SiH₄. Although GeH₄, which is popularly used for the Ge film growth, is unstable, GeF₄ is stable thermally up to 1000°C in the moisture-free atmosphere. Therefore, the reaction between GeF₄ and silane should produce the Ge
active species of GeF$_2$ and GeF$_3$. Thus we examine reaction channels which produce GeF$_2$ and GeF$_3$ from GeF$_4$ activated by Si$_2$H$_6$ or SiH$_4$ in the following.

We assume that the reaction between Si$_2$H$_6$ and GeF$_4$ begins with formation of Si–Ge bond:

$$\text{SiH}_3\text{SiH}_3 + \text{GeF}_4 \rightarrow \text{SiH}_3\text{GeF}_3 + \text{SiH}_3\text{F}. \quad (1)$$

In the case of SiH$_4$, the corresponding reaction is

$$\text{SiH}_4 + \text{GeF}_4 \rightarrow \text{SiH}_3\text{GeF}_3 + \text{HF}. \quad (2)$$

From the result of our calculation, it has been found that the reaction (2) has a higher activation energy than the reaction (1) and the reaction is endothermic. On the other hand, the reaction (1) proceeds with exothermic reaction energy.

Next, we investigate the succeeding reactions to decompose the Si–Ge bond:

$$\text{SiH}_3\text{GeF}_3 \rightarrow \text{SiH}_3\text{F} + \text{GeF}_2 \quad (3)$$
$$\text{SiH}_3\text{GeF}_3 \rightarrow \text{SiH}_2 + \text{GeF}_3\text{H} \quad (4)$$
$$\text{SiH}_3\text{GeF}_3 \rightarrow \text{SiH}_3 + \text{GeF}_3. \quad (5)$$

We show that GeF$_2$ is easy to be produced through the reaction channel (1) $\rightarrow$ (3). On the other hand, the reaction channel (2) $\rightarrow$ (3) needs high activation energy.

2. Methods of Calculation

The quantum chemical calculations were carried out with the Gaussian98 program package. Geometry optimization and vibrational analysis were performed by the density functional theory (DFT) using Becke’s three-parameter hybrid method with the Lee, Yang, and Parr correlation functional (B3LYP). The electron correlation energy for each geometry was estimated with the coupled cluster calculation including single and double excitations with non-iterative inclusion of triple excitations (CCSD(t)). Pople’s 6-31G(d) basis sets for Si, F, and H atoms and the 6-41(d) basis set for Ge atom proposed by Binning and Curtiss were used. Zero-point energies obtained by the B3LYP level calculations were included in the activation energies and reaction energies. These methods are denoted by CCSD(t)//B3LYP(+ZPE).

3. Results and Discussion

The transition state (TS) and the complex of the nth reaction path are denoted by T$_{Sn}$ and C$_{Xn}$, respectively. The optimized geometries of the reactant and product molecules are shown in Table 1. The structures of all the transition states and complexes are represented in Figure 1. The activation energies and the heat of reactions are summarized in Table 2. Energy diagram of the reaction between GeF$_4$ and Si$_2$H$_6$ and that of the reaction between GeF$_4$ and SiH$_4$ are shown in Figures 2(a) and (b), respectively.

3.1. Reaction 1

One of the reactants, GeF$_4$, has been studied theoretically from the interests in the edge inversion process, vibrational frequencies, and so on. The Ge–F bond length is found to be 1.710 Å in our study and it agrees well with the previous studies: the length reported by Dixon et al. is 1.672 Å, which was obtained by a Hartree-Fock calculation using the basis sets of (14s11p6d)/[10s8p3d] for Ge and (9s5pld)/[3s2pld] for F while the length reported by Shulz et al. is 1.727 Å, which was obtained with the MP2(fc) level calculation using the ECP for Ge and the 6-31+G* basis set for F.

The transition state T$_{S1}$ of this reaction is shown in Figure 1. The activation energy is 36.77 kcal/mol and the reaction is exothermic by 17.67 kcal/mol at the CCSD(t)//B3LYP(+ZPE) level. The comparison with the reaction (2) is made later. In the product SiH$_3$GeF$_3$, the Si–Ge bond length is 2.379 Å. Some theoretical investigations have already been done for SiH$_3$GeH$_3$. Some theoretical investigations have already been done for SiH$_3$GeH$_3$. The Si–Ge bond length in SiH$_3$GeH$_3$ was reported to be 2.415 Å by Grev et al. and 2.374 Å by Windus et al. With a more precise calculation, Leszczynski et al. reported 2.372 Å at the CISD/TZP level. Our calculation shows that the Si–Ge bond length in SiH$_3$GeH$_3$ is 2.376 Å, which is not so different from the length in SiH$_3$GeF$_3$. Thus, we conclude that the Si–Ge bond length is not affected substantially by the substitution of H by F.
Table 1: Optimized Geometriesa

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<tr>
<th>species</th>
<th>symmetry</th>
<th>geometrical parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>$C_{nv}$</td>
<td>$r$(HF)=0.934</td>
</tr>
<tr>
<td>F$_2$</td>
<td>$D_{vdh}$</td>
<td>$r$(FF)=1.404</td>
</tr>
<tr>
<td>$^{1}$SiH$_2$</td>
<td>$C_{2v}$</td>
<td>$r$(SiH)=1.530, $\theta$ (HSiH)=91.18</td>
</tr>
<tr>
<td>SiH$_3$</td>
<td>$C_{3v}$</td>
<td>$r$(SiH)=1.489, $\theta$ (HSiH)=108.06</td>
</tr>
<tr>
<td>SiH$_4$</td>
<td>$T_d$</td>
<td>$r$(SiH)=1.486</td>
</tr>
<tr>
<td>SiH$_3$F</td>
<td>$C_{3v}$</td>
<td>$r$(SiF)=1.613, $r$(SiH)=1.485, $\theta$ (HSiF)=110.60</td>
</tr>
<tr>
<td>SiH$_3$SiH$_3$</td>
<td>$D_{3h}$</td>
<td>$r$(SiSi)=2.350, $r$(SiH)=1.489, $\theta$ (SiSiH)=110.60</td>
</tr>
<tr>
<td>$^{1}$GeF$_2$</td>
<td>$C_{2v}$</td>
<td>$r$(GeF)=1.757, $\theta$(FGeF)=97.24</td>
</tr>
<tr>
<td>GeF$_3$</td>
<td>$C_{3v}$</td>
<td>$r$(GeF)=1.739, $\theta$(FGeF)=112.82</td>
</tr>
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<td>GeF$_3$H</td>
<td>$C_{3v}$</td>
<td>$r$(GeH)=1.524, $r$(GeF)=1.723, $\theta$(HGeF)=112.70</td>
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<tr>
<td>GeF$_4$</td>
<td>$T_d$</td>
<td>$r$(GeF)=1.710</td>
</tr>
<tr>
<td>SiH$_3$GeF$_3$</td>
<td>$C_{3v}$</td>
<td>$r$(GeSi)=2.379, $r$(GeF)=1.735, $r$(SiH)=1.481</td>
</tr>
</tbody>
</table>

$^{a}$Bond length ($r$) in Å, bond angle ($\theta$) in degree.

Table 2: Reaction Energies at the CCSD(t)/B3LYP(+ZPE) Level in kcal/mol (B3LYP(+ZPE) Level in Parentheses)

<table>
<thead>
<tr>
<th>reaction</th>
<th>activation energy</th>
<th>heat of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH$_3$SiH$_3$ + GeF$_4$ $\rightarrow$ SiH$_3$GeF$_3$ + SiH$_3$F</td>
<td>(1) 36.77 (33.84)</td>
<td>-17.67 (-21.53)</td>
</tr>
<tr>
<td>SiH$_4$ + GeF$_4$ $\rightarrow$ SiH$_3$GeF$_3$ + HF</td>
<td>(2) 54.68 (48.64)</td>
<td>5.71 (3.29)$^a$</td>
</tr>
<tr>
<td>SiH$_3$GeF$_3$ $\rightarrow$ SiH$_3$F + GeF$_2$</td>
<td>(3) 31.86 (29.99)</td>
<td>1.79 (-3.42)$^a$</td>
</tr>
<tr>
<td>SiH$_3$GeF$_3$ $\rightarrow$ SiH$_2$ + GeF$_3$H</td>
<td>(4) —</td>
<td>14.59 (7.41)</td>
</tr>
<tr>
<td>SiH$_3$GeF$_3$ $\rightarrow$ SiH$_3$ + GeF$_3$</td>
<td>(5) —</td>
<td>78.44 (75.66)</td>
</tr>
</tbody>
</table>

$^{a}$Complex.

Figure 1. Optimized structures of transition states and complexes. Bond lengths are in Å, bond angles are in degrees.
3.2. Reaction 2

The transition state of the reaction (2), TS2, is shown in Figure 1. Compared with TS1, they have different structures although the Ge atom has the penta-coordinate structure in both of the two structures. The Si atom in Si2H6 approaches the Ge atom along the C3 axis from the bottom of GeF4 and the fluorine atom is located on equatorial site in TS1 as shown in Figure 1. On the contrary, the Si atom in SiH4 approaches the Ge atom along the C2 axis of GeF4 and the fluorine atom which is released from GeF4 is located at the axial site in TS2. In Figure 3(a), the orbital energy diagram of the reactants calculated by the Hartree-Fock method is shown. It is clear that the energy levels of the occupied orbitals of GeF4 are lower than those of silane. If Koopman's theorem is taken into account, this is the reason why the Ge-F bond is strong as explained later. One of the unoccupied triply degenerate orbitals 3t2z can be expressed equivalently as linear combinations of three 3t2 orbitals as shown in Figure 3(b). These orbitals play an important role for electron delocalization from SiH4 or Si2H6 to GeF4. The 2a1 LUMO and the 3t2 next-LUMO are responsible for the reaction with Si2H6, while the LUMO and the 3t2 orbital play dominant roles in the reaction with SiH4. Certainly the orbital energies of the HOMOs and the next-HOMOs of Si2H6 are higher than those of the triply degenerate HOMOs of SiH4, so electron delocalization from Si2H6 occurs more easily than that in the case of SiH4. In Figures 4 (a) and (b), the HOMOs of TS1 and TS2 are shown. They share a similar feature in which the Ge atom orbital overlaps in-phase with the Si atom orbital. These orbitals are formed from the interaction between the occupied orbitals of silanes and the unoccupied orbitals of GeF4.

The activation energy of the reaction (2) is 54.68 kcal/mol and the reaction energy is 18.43 kcal/mol endothermic at the CCSD(t)//B3LYP(+ZPE) level. The energetic difference between the reactions (1) and (2) is brought about by the orbital interactions as discussed above. Moreover, this tendency can be understood from a general fact that the Si–Si bond is weaker than the Si–H bond and that the Si–F bond is stronger than the H–F bond.

Figure 2. Energy diagrams (in kcal/mol) of the reactions of (a) Si2H6 + GeF4 and (b) SiH4 + GeF4 at the CCSD(t)//B3LYP(+ZPE) level (B3LYP(+ZPE) level in parentheses).
Figure 3. (a) Orbital energy diagrams of GeF₄, SiH₄, and Si₂H₆ at the Hartree-Fock level. Geometries optimized by B3LYP calculations were used. (b) 3t₂, 3t₂ orbitals of the next-LUMO and the LUMO (2a₁).

Figure 4. The contours of HOMO of (a) TS₁ and (b) TS₂ on the C₃ mirror plane obtained by the Hartree-Fock calculations. For the geometries, see Figure 1.
The complex formed by SiH₃GeF₃ and hydrogen fluoride, CX₂, is shown in Figure 1. The hydrogen- and fluorine-atomic charges are evaluated by the natural population analysis to be +0.565, -0.562, respectively, while these are ±0.535 in hydrogen fluoride molecule. The stronger polarization of the H–F bond in CX₂ was also confirmed by the calculation with the Hartree-Fock wave function (+0.604, -0.605 for H and F atom in the CX₂, respectively, and ±0.560 in hydrogen fluoride molecule). Thus we see the hydrogen fluoride in CX₂ is highly polarized.

3.3. Reaction 3–5

The reaction (3) is the decomposition process of SiH₃GeF₃ into GeF₂ and SiH₃F. The B3LYP calculation unveils that TS₃ does not have any symmetry as shown in Figure 1. The activation energy is 31.86 kcal/mol. This reaction proceeds to form the complex CX₃ and to decompose into SiH₃F + GeF₂ as shown in Figure 2(a). A recent density functional study showed that the Ge–F bond length of GeF₂ was about 1.747–1.794 Å. Our result (1.757 Å) is consistent with that result. The other CASSCF and MRCI calculations showed that the ground state is singlet.

The reaction (4) represents the decomposition of SiH₃GeF₃ into SiH₂ and GeF₃H. The reaction is endothermic by 61.04 kcal/mol. The transition state of this reaction was found at the Hartree-Fock level calculation, but was not found at the B3LYP level. We may conclude that no energy barrier seems to exist on the way of the reaction.

The homolytic decomposition of the Si–Ge bond into SiH₃ + GeF₃ has the reaction energy of 78.44 kcal/mol. In SiH₃GeH₃, the bond dissociation energy is estimated to be 67.0 kcal/mol by the CCSD level calculation. Although the B3LYP level calculations show that the Si–Ge bond lengths are almost the same in SiH₃GeH₃ and SiH₃GeF₃ as noted above, the Ge–Si bond is strengthened by the substitution of H by F.

3.4. Comparison of Si₂H₆ and SiH₄ on the Reactions with GeF₄

Before we discuss the reaction between GeF₄ and silanes, we examine the stability of GeF₄, SiH₄, and Si₂H₆ in an isolated state. To find plausible mechanisms for the decomposition of GeF₄, we examine two reactions:

\[
\text{GeF}_4 \rightarrow \text{GeF}_3 + F \quad (6)
\]

\[
\text{GeF}_4 \rightarrow \text{GeF}_2 + F_2 \ . \quad (7)
\]

For comparison we also investigate the stability of GeH₄. The reaction energies of these decomposition processes are summarized in Table 3. The reaction energies of (6) and (7) are 130.16 kcal/mol and 172.71 kcal/mol, respectively, in our calculations at the CCSD(t) //B3LYP(+ZPE) level. In GeH₄, the Ge–H bond dissociation energy was estimated to be 84.0 kcal/mol by CCSD//SCF calculations. The other theoretical study by CCSD(t) level calculation showed that the activation energy of the decomposition reaction of GeH₄ into GeH₂ + H₂ is 59.0 kcal/mol and that its reaction energy is 42.5 kcal/mol. The Dirac–Hartree–Fock calculation showed the similar reaction energy, 42.4 kcal/mol. Compared to GeH₄, the decomposition of GeF₄ needs a higher activation energy. Therefore, it is found that GeF₄ is more stable than GeH₄. Actually, it is known that GeF₄ is stable thermally up to 1000°C. On the other hand, the decomposition reactions of SiH₄ and Si₂H₆ have been studied precisely and the reported results are summarized in Table 4. It is important to note that the decomposition energies exceed 50 kcal/mol in both molecules.

Then we discuss the reaction channels of (a) GeF₄ and Si₂H₆ and of (b) GeF₄ and SiH₄ by connecting the reactions (1) with (3), and (2) with (3) as illustrated in Figures 2 (a) and (b). In the case of (b) GeF₄ and SiH₄, the initial reaction process (2) needs a high activation energy. The decomposition of silane into SiH₂ and H₂ has almost the same activation energy as shown in Table 4. Moreover, SiH₃GeF₃ + HF is less stable than SiH₄ and GeF₄ because the reaction (2) has the endothermic reaction energy. Therefore, the entire reaction to produce GeF₂ + SiHF₃ + HF needs a large amount of energy.

On the other hand, in the case of (a), the initial reaction (1) needs a lower activation energy than those of disilane decomposition reactions as shown in Table 4 and the
Table 3: Decomposition Energies of GeF4 and GeH4 (kcal/mol)

<table>
<thead>
<tr>
<th>reaction</th>
<th>activation energy</th>
<th>heat of reaction</th>
<th>references</th>
</tr>
</thead>
<tbody>
<tr>
<td>GeF4 → GeF3 + F (6)</td>
<td>–</td>
<td>130.16</td>
<td>present study$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(126.22)</td>
<td></td>
</tr>
<tr>
<td>GeF4 → GeF2 + F2 (7)</td>
<td>–</td>
<td>172.71</td>
<td>present study$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(159.36)</td>
<td></td>
</tr>
<tr>
<td>GeH4 → GeH3 + H</td>
<td>–</td>
<td>84.0</td>
<td>Ref. 15$^b$</td>
</tr>
<tr>
<td>GeH4 → GeH2 + H2</td>
<td>59.0</td>
<td>42.5</td>
<td>Ref. 21$^c$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ref. 22$^d$</td>
</tr>
</tbody>
</table>

$^a$CCSD(0/B3LYP+ZPE) level. (B3LYP+ZPE) level in parentheses.
$^b$CCSD calculation with DZP basis set.
$^c$CCSD(1) calculation with Hay-Wadt ECP.
$^d$Dirac-Hartree-Fock calculation.

Table 4: Decomposition Energies of Si2H6 and SiH4 (kcal/mol)

<table>
<thead>
<tr>
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<th>heat of reaction</th>
<th>references</th>
</tr>
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<tr>
<td>SiH3SiH3 → SiH4 + SiH2</td>
<td>–</td>
<td>50.0</td>
<td>Ref. 24$^d$</td>
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<tr>
<td></td>
<td>56</td>
<td>56</td>
<td>Ref. 25$^b$</td>
</tr>
<tr>
<td>SiH3SiH3 → SiH3SiH+ H2</td>
<td>55.5</td>
<td>53.4</td>
<td>Ref. 24$^d$</td>
</tr>
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<td></td>
<td>55</td>
<td>55</td>
<td>Ref. 25$^b$</td>
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<tr>
<td>SiH3SiH3 → SiH2SiH2+ H2</td>
<td>86.1</td>
<td>47.0</td>
<td>Ref. 24$^d$</td>
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<tr>
<td></td>
<td>86</td>
<td>47</td>
<td>Ref. 25$^b$</td>
</tr>
<tr>
<td>SiH3SiH3 → SiH3 + SiH3</td>
<td>–</td>
<td>70.0</td>
<td>Ref. 24$^d$</td>
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<td></td>
<td>76</td>
<td>76</td>
<td>Ref. 25$^b$</td>
</tr>
<tr>
<td>SiH4 → SiH3 + H</td>
<td>92</td>
<td>92</td>
<td>Ref. 26$^c$</td>
</tr>
<tr>
<td>SiH4 → SiH2 + H2</td>
<td>60</td>
<td>57</td>
<td>Ref. 26$^c$</td>
</tr>
<tr>
<td></td>
<td>56.9</td>
<td>55.2</td>
<td>Ref. 27$^d$</td>
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</tbody>
</table>

$^a$MP4(SDTQ)/MC-311G**//MP2/6-31G** for heat of reaction and MP4(SDTQ)/MP-311G**//MP2/6-31G** for activation energy.
$^b$MP4(SDTQ)/6-31G**//HF/6-31G** for activation energy.
$^c$Gaussian-2 theory.
$^d$MP4/MC-311++G(3df,3pd)//MP2/MC-311G(2d,2p)(+ZPE).

reaction (1) is exothermic. Therefore this reaction is considered to be an important path. Furthermore, the most likely products of decomposition of SiH3GeF3 are SiH3F and GeF2. The products of this reaction have almost the same stability as Si2H6 + GeF4. Hanna et al. observed epitaxial growth of Ge film on Si(100) substrate from GeF4 and Si2H6 at 370°C. In the case of Si epitaxial growth by SiCl4 deposition, SiCl2 is known to be the key molecule. If Ge compounds have an analogous character, GeF2 is also considered to be an important species for surface epitaxial growth. A more important fact is that the GeF2 was detected in gas phase although its origin is not yet clear.

Moreover, our results suggest that other reaction processes in Figure 2(a) to produce SiH2 and GeF3H will be forwarded at high temperature. It is expected that these products influence the surface reaction. In fact, experiments also show the polycrystalline growth in higher temperature region (>400°C).

4. Conclusion
To understand the reaction mechanism of low-temperature thermal chemical vapor deposition between GeF4 and Si2H6, we investigated the gas-phase reaction between GeF4 and Si2H6 and the reaction between GeF4 and SiH4 by ab initio quantum chemical techniques and compared those reactions. For the Si-Ge bond formation between GeF4 and Si2H6, the activation energy is 36.77kcal/mol and the reaction is exothermic by 17.67kcal/mol at the CCSD(t)//B3LYP(+ZPE) level, while the activation energy is 54.68kcal/mol and the reaction is endothermic by 17.35kcal/mol in the case of SiH4 and GeF4. A study of orbital interactions also supported that the formation of the Si-Ge bond was easier in the case of Si2H6 than in that of SiH4. One of the products of these reactions, SiH3GeF3, is easily decomposed into SiH3F and GeF2, which is considered to be one of key molecules for Ge film growth. This result gives us a clue to understand the experimental observation reported by Hanna et al.
References

(29) Hanna, J., private communication.
General Conclusion

The development of quantum chemistry and the spread of its applications have provided us with clear understanding of complicated chemical phenomena abundantly. On the other hand, attempts to understand a variety of chemical phenomena give new insights into theoretical chemistry. Intimate connection of the two aspects is now indispensable to the development of chemistry.

In the field of quantum chemistry, there remains many subjects to be solved. One of these subjects is the establishment of more precise theory of chemical reactivity. Now, we can calculate easily the accurate wave function and its eigenvalue for a variety of reaction models and its reaction paths. However, it seems that these calculations do not make the most of the results to clarify chemical reactivity of molecules. We must construct a new view of chemical reactivity which is adapted to the present conditions.

The another subject to be solved is the establishment of a new view of chemical reactions under the macroscopic environment, such as surface reactions and the chemical reactions in solution. Toward these problems, especially in solution chemical reactions, some interesting methods, such as a hybrid between the quantum mechanical method and the molecular mechanical method or a combination of ab initio electronic structure theory and the statistical mechanics of molecular liquids, have to be explored. In material science which includes solid-state science and surface science, we must also develop a mesoscopic view which comprehends both the macroscopic and the microscopic regions. Fortunately, an application of the first-principle calculations using the Car–Parrinello’s method to surface reactions is already attempted. The author assumes that its development gives closer connections between physics and chemistry, between which there is yet a gap.

This thesis summarizes the studies of chemical reactivity of molecules and some surface reactions which appear in manufacturing the silicon semiconductor devices by utilizing the molecular orbital theory and the density functional theory.

In Chapter 1, electron delocalization between NO$_2^+$ and substituted benzenes has been examined by the molecular orbital theory. It has been shown that the interacting
orbitals were localized around the reaction site. By projecting a reference orbital function that has been chosen to specify the bond to be formed onto the MOs of the substituted benzenes, the local potential of the reaction site for electron donation has been estimated. The results were consistent with the experimental scale of the electron-donating and withdrawing strength of substituent groups. It has been shown that the reactivity was governed by the local electronegativity and the local chemical hardness and also by the localizability of interaction on the reaction site.

In Chapter 2, the population analysis along the intrinsic reaction coordinate has been performed, taking the 1,3-dipole cycloaddition as an example. By calculating the derivatives of the Mulliken atomic charge and the Mayer's bond order with respect to the nuclear motion analytically, the decomposition of the derivatives into two components, the density derivative term and the overlap derivative term, was demonstrated. The density derivative term represents the effect of redistribution of electrons due to the nuclear motion. By using this method, the electronic character of asynchronous bond formation was revealed clearly.

In Chapter 3, the author has taken up the gas-phase reaction between singlet oxygen \((1D)\) and silane. One of the methods to produce \(\text{SiO}_2\) layer over the Si surface is the chemical vapor deposition (CVD) using oxygen gas and silane gas. Applying a quantum chemical method, a low energy reaction path has been found in addition to the excited-state reaction path. This agrees well with the experimental observation on the vibrational energy distribution of the product SiO found by laser-induced fluorescence.

In Chapter 4, cluster model reactions of the oxidation sites in hydrogen- and water-terminated Si dimers have been examined using \textit{ab initio} molecular orbital calculations, to obtain a chemical insight into the bond in the Si surface network which the oxidant prefers to attack. First, the author focused on the basic reaction enthalpies of \(\text{Si}_2\text{H}_6\) with \(\text{O}_2\) and found that the Si–Si bond in the cluster was more easily oxidized than the terminal Si–H bond. A similar oxidation tendency was also found in the reaction of \(\text{SiH}_3\text{SiH}_2(\text{OH})\) with H. The transient reaction intermediate that possessed a terminal oxygen radical was fully transferred with low activation energy to the Si–Si bond, but with much higher activation energy to the adjacent Si–H bond. These results demonstrated a facile Si–Si back-bond oxidation, which should provide a key to understand the microscopic character of the oxidation site on the Si surface.

In Chapter 5, the oxidation mechanism of the hydrogen-terminated \(\text{Si}(111)\) surface by an oxygen anion has been studied using \textit{ab initio} molecular orbital method. The author has clarified the stability of an oxygen anion in a cage of silicon cluster. The oxygen anion attacks the Si atom to form a penta-coordinated complex, which should lower the diffusion barrier for the oxygen anion transfer in the Si bulk. The oxygen anion inserts then into the Si–Si bond to form a local Si–O–Si structure. The stabilization energy is enhanced if the deformation energy in the local Si–O–Si structure is released. The oxidized Si has a tendency to accept additional oxygens. This has been concluded using a series of cluster model calculations, assuming that the crystallographic strain is completely relaxed.

In Chapter 6, the author has discussed the reaction mechanism between dimethyl aluminum hydride and the Si surface terminated by hydrogen. The author has clarified that the Al–Al bond formation occurs prior to the Al–Si bond formation and that the methyl group has an effect to suppress the reactivity of Al and Si. Moreover, the \(\text{H}_2\) carrier gas has been found to enhance the reactivity.

In Chapter 7, the author has performed a quantum chemical study of the deposition of \(\text{SiH}_4\) on the surface of F-terminated Si to see the p-doping effect. It has been clarified that the fluorine atom immersed into the bulk had a tendency to insert into a pair of Si atoms and to form chemical bonds in the p-doped case. The high stability of the (Si–F–Si)+ bonding structure makes a clear contrast to the unstable Si–F–Si antibonding structure and this conclusion agrees qualitatively well with the experimental observation.

In Chapter 8, the gas-phase reaction mechanism of the low-temperature thermal chemical vapor deposition between \(\text{GeF}_4\) and \(\text{Si}_2\text{H}_6\) has been studied by quantum chemical techniques. For the Si–Ge bond formation reaction between \(\text{GeF}_4\) and \(\text{Si}_2\text{H}_6\), the activation energy has been found to be 36.77 kcal/mol and the reaction is exothermic by 17.67 kcal/mol, while the activation energy is 54.68 kcal/mol and the reaction is
endothermic by 18.43 kcal/mol in the case of the reaction between GeF$_4$ and SiH$_4$ at the CCSD(t)/B3LYP/ZPE level. One of products in these reactions, SiH$_3$GeF$_3$, has been shown to be easily decomposed into SiH$_3$F and GeF$_2$.

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List of Publications

Chapter 1. Hiroshi Fujimoto, Ken Sakata, and Kenichi Fukui
"Transient Bonds and Chemical Reactivity of Molecules,"

Chapter 2. Ken Sakata
"Population Analysis along the Intrinsic Reaction Coordinate: Application to 1,3-Dipole Cycloaddition,"
to be published.

Chapter 3. Akitomo Tachibana and Ken Sakata
"Quantum Chemical Study on Low Energy Reaction Path for SiH₄ + O(1D) → SiO + 2H₂,"

Chapter 4. Ken Sakata, Akitomo Tachibana, Shigeaki Zaima, and Yukio Yasuda
"Quantum Chemical Study of the Oxidation Sites in Hydrogen- and Water-Terminated Si Dimers: Attempt to Understand the Si–Si Back-Bond Oxidation on the Si Surface,"

Chapter 5. Akitomo Tachibana, Ken Sakata, and Takahiro Sato
"Quantum Chemical Study on the Oxidation of Hydrogen-Terminated Silicon Surface by Oxygen Anions,"

Chapter 6. Akitomo Tachibana, Ken Sakata, and Kiyoyuki Omoto
"Quantum Chemical Study on Aluminum Selective CVD Reaction Mechanism,"

Chapter 7. Akitomo Tachibana and Ken Sakata
"Quantum Chemical Study on p-Doping Effect of F-Terminated Silicon Surface Reaction with Silane,"

Chapter 8. Ken Sakata and Akitomo Tachibana
"Quantum Chemical Study on the Reaction between GeF₄ and Si₂H₆,"
submitted.