Ab initio molecular-orbital study on the surface reactions of methane and silane plasma chemical vapor deposition

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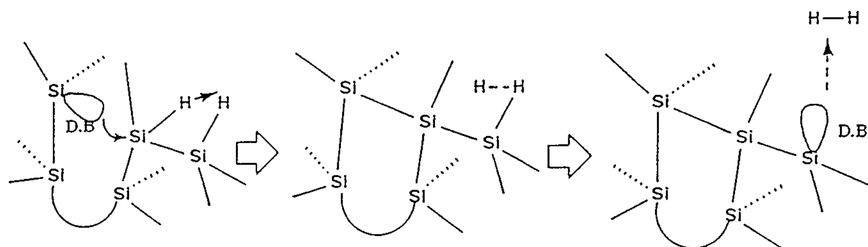
(Received 25 November 1996)

Hydrogen-elimination reactions on the substrate surface of methane plasma are studied on the basis of an *ab initio* molecular-orbital method. The activation energy of the reaction of the rate determining step (by MP2/3-21G//HF/3-21G) is much higher than the analogous reaction in silane plasma. In the case of carbon surface reactions, the activation energy becomes larger as the model cluster size becomes larger, while in the case of silicon surface reactions, the activation energy becomes lower as the model cluster size becomes larger. Thermodynamically, the relative stability of the reactant and the product of the hydrogen elimination reaction on the substrate surface of methane plasma are similar to that of silane plasma. Thus the methane plasma surface reactions are expected to be qualitatively different from silane plasma surface reactions at low substrate temperatures, while they are expected to be similar at high substrate temperatures. [S0163-1829(97)04324-5]

Surface processes are important in plasma chemical vapor deposition (plasma CVD), because they are the final process by which the structure of the film is controlled. Sato *et al.*[1] already proposed a network formation mechanism accompanying hydrogen-elimination reactions in *a*-Si:H formation process by silane plasma CVD on the basis of an *ab initio* molecular-orbital study. This mechanism consists of two steps. The first step is a coupling reaction of a dangling bond site with an adjacent tetrahedrally coordinated silicon. In this step, a hydrogen atom is displaced. The second step is a hydrogen abstraction reaction from the adjacent silicon atoms by the hydrogen atom created. These two steps are schematically shown in the diagram below.



The repetition of these two steps eliminates hydrogen atoms around dangling bonds and forms a network. Thus if the proposed mechanism is predominant the hydrogen distribution in *a*-Si:H films is expected to be inhomogeneous. This mechanism is consistent with experimental observations of the hydrogen distribution in *a*-Si:H films. An inhomogeneous hydrogen distribution was reported on the basis of NMR measurement,[2] and the distance between a dangling bond and the closest hydrogen atom was reported to be farther than 4 Å based on a pulsed electron spin resonance (ESR) measurement.[3]

When surface processes are treated by a model cluster in *ab initio* calculations, the dependence of the result on the cluster size is important. In the case of the mechanism treated, the activation energy of the rate determining step of the proposed mechanism becomes smaller as the cluster size becomes larger.[4] This tendency contributes to the plausibility of the proposed mechanism because the real surface is infinitely large. Whether or not a similar mechanism occurs in other group-IV compounds is a basic and interesting problem. Methane plasma is practically important because this is utilized for diamond film formation.

In this paper, a carbon analog of the silane plasma surface reaction, the methane plasma surface reaction, is studied by using an *ab initio* molecular-orbital method. The results will be compared with those of the silane plasma surface reaction.

An *ab initio* molecular-orbital method was employed in this study. The geometry was optimized for all the geometrical parameters by using an energy gradient method[5] on the basis of electronic structure obtained by the Hartree-Fock method.[6] The total energy at the optimized geometry was calculated by taking electron correlation into account by using the Møller-Plesset second-order perturbation theory[7] (MP2) level. A 3-21G basis set[8], in which 3 is the number of Gaussian-type orbitals for inner shells, 2 and 1 are the numbers of Gaussian-type orbitals for a valence shell (split valence), was employed for all the calculations. Since the basis set employed in this work does not contain polarization functions, and since polarization functions are known to be important for quantitatively reliable results on hydrogen atom

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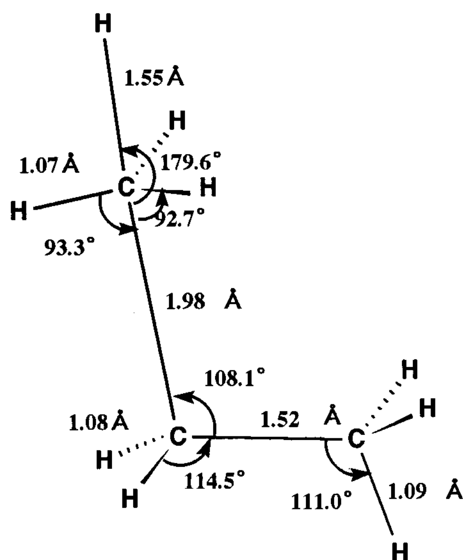


FIG. 1. The geometrical structure of the transition state of $CH_4 + \cdot CH_2CH_3 \rightarrow CH_3CH_2CH_3 + H$.

abstraction reactions,[9] the results presented in this paper should be considered for the qualitative insights they provide and for trends in transition state properties, but the calculated geometries and energies should not be construed as quantitatively reliable. The GAUSSIAN 86 program[10] was used for the calculations. All the calculations were conducted on the HITAC M-880 of the Computer Center, University of Tokyo.

The surface reaction processes of group-IV compounds treated in our studies are schematically represented by Eqs. (1) and (2).

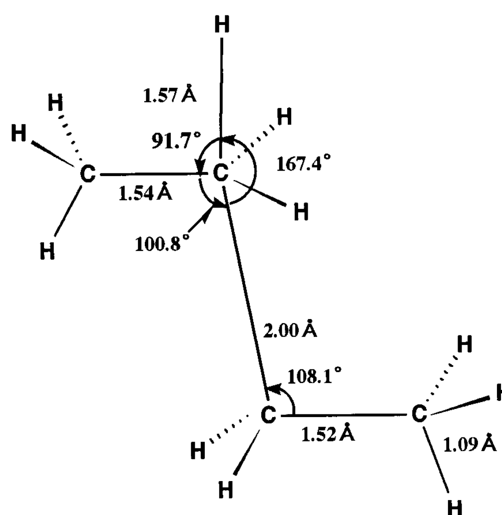
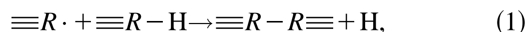
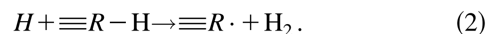


FIG. 3. The geometrical structure of the transition state of $CH_3CH_3 + \cdot CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_3 + H$.



$$\equiv R\cdot + \equiv R-\mathrm{H} \rightarrow \equiv R-R\equiv + \mathrm{H}, \quad (1)$$



$$H + \equiv R-\mathrm{H} \rightarrow \equiv R\cdot + \mathrm{H}_2. \quad (2)$$

In this study, the infinitely large surface is modeled by a cluster of a limited size, and the cluster size dependence of the results was examined. Three cluster models with different sizes [Eqs. (3)–(5)] were employed for the reaction (1), and the results were compared in this study.

$$CH_4 + \cdot CH_2CH_3 \rightarrow CH_3CH_2CH_3 + H, \quad (3)$$

$$CH_3CH_3 + \cdot CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_3 + H, \quad (4)$$

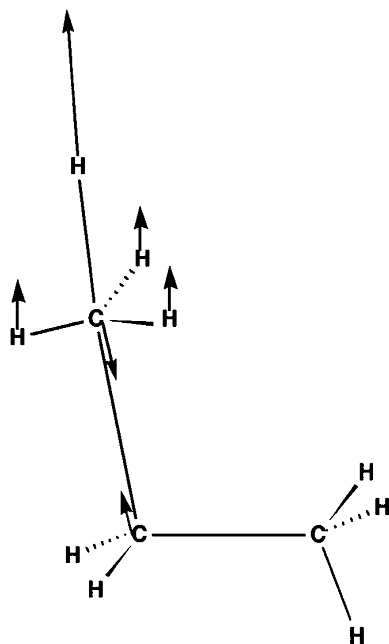


FIG. 2. The vibrational mode corresponding to the imaginary frequency at the transition state of $CH_4 + \cdot CH_2CH_3 \rightarrow CH_3CH_2CH_3 + H$.

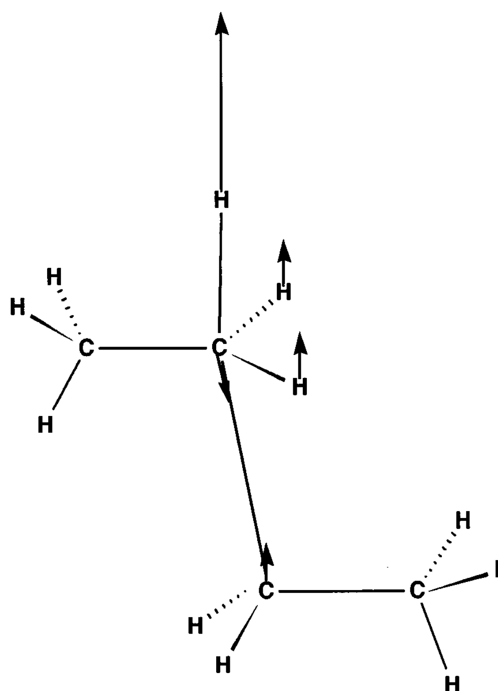


FIG. 4. The vibrational mode corresponding to the imaginary frequency at the transition state of $CH_3CH_3 + \cdot CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_3 + H$.

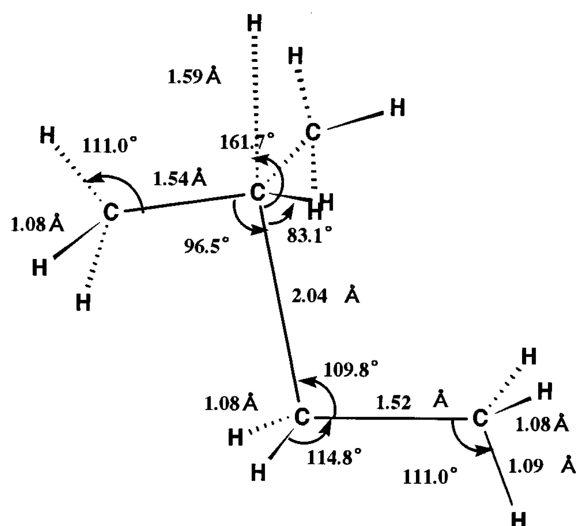
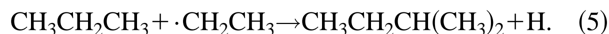


FIG. 5. The geometrical structure of the transition state of $CH_3CH_2CH_3 + \cdot CH_2CH_3 \rightarrow CH_3CH_2CH(CH_3)_2 + H$.



$$CH_3CH_2CH_3 + \cdot CH_2CH_3 \rightarrow CH_3CH_2CH(CH_3)_2 + H. \quad (5)$$

Figure 1 shows the geometrical structure of the transition state of the reaction (3). A C—H bond which is bound to be cleaved is longer (1.55 Å) than the other C—H bonds (1.07 Å). This bond is almost collinear with the adjacent C—C bond, as the long Si—H bond is collinear with the adjacent Si—Si bond at the transition state of $SiH_4 + SiH_2SiH_3$.[1]

Only one vibration is in an imaginary frequency at the transition state. This vibration reflects the direction of the reaction coordinate. The vibrational mode corresponding to the imaginary frequency at the transition state of reaction (3) is shown in Fig. 2. The strong component of stretching C—H vibration in the reaction coordinate indicates that this is the transition state of a hydrogen-displacement reaction.

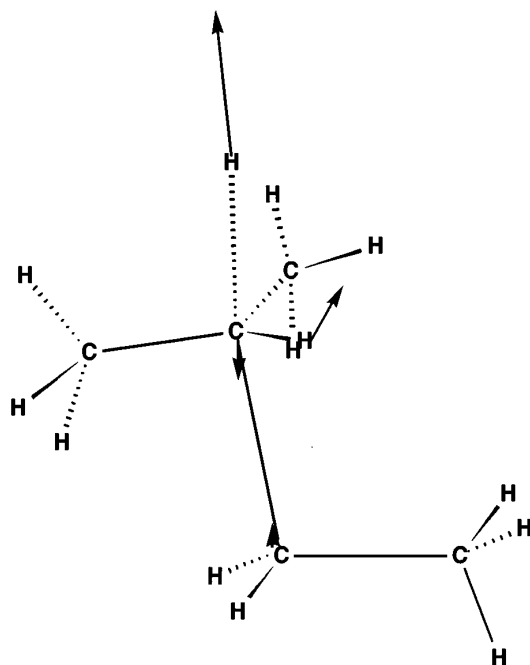


FIG. 6. The vibrational mode corresponding to the imaginary frequency at the transition state of $CH_3CH_2CH_3 + \cdot CH_2CH_3 \rightarrow CH_3CH_2CH(CH_3)_2 + H$.

TABLE I. The imaginary frequency at the transition state of the first step of the hydrogen elimination mechanism (cm^{-1})

	$R = C$	$R = Si$
$RH_4 + RH_2RH_3$	1682*i*	1031*i*
$RH_3RH_3 + RH_2RH_3$	1642*i*	938*i*
$RH_3RH_2RH_3 + RH_2RH_3$	1586*i*	

Figure 3 shows the geometrical structure of the transition state of reaction (4). The C—H bond that will be cleaved in proceeding to products is slightly longer (1.57 Å) than the corresponding bond of reaction (3). The difference is, however, smaller than for the case of the topologically similar silicon system. In addition, the C—H bond is not collinear with the adjacent C—H bond [θ(C—C—H) = 167.4°], while the Si—H bond is collinear with the adjacent Si—Si bond for all sizes of model cluster.

Figure 4 shows the vibrational mode corresponding to the imaginary frequency at the transition state of reaction (4). The vibration is similar to that of the transition state of reaction (3). Hence this is also considered to be the transition state of a hydrogen-displacement reaction.

Figure 5 shows the geometrical structure of the transition state of reaction (5). One of the C—H bonds is slightly longer (1.59 Å) than the corresponding bond in reaction (4). The angle between the C—H bond and the adjacent C—C bond is 161.7°. The deviation from collinear is larger than for reaction (4).

The vibrational mode corresponding to the imaginary frequency at the transition state of reaction (5) is shown in Fig. 6. A stretching vibration similar to that of the transition state of reactions (3) and (4) is dominant in this mode. Thus this is also considered to be the transition state of a hydrogen-displacement reaction.

The imaginary frequencies at the transition states of hydrogen-displacement reactions in the carbon and silicon systems are compared in Table I. The frequency is much higher in the carbon system than the silicon system. The

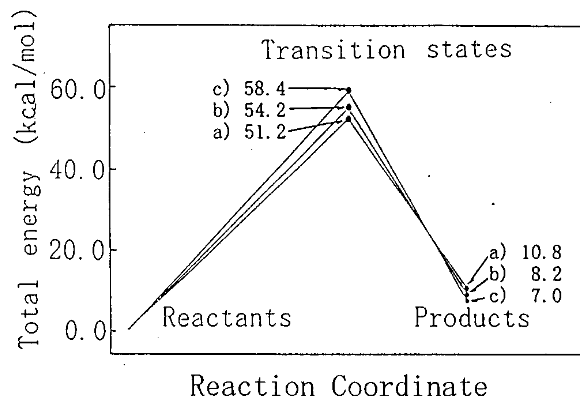


FIG. 7. The energy diagram of the first step of the hydrogen-elimination reaction.

TABLE II. The activation energies (kcal/mol) in the surface model reactions of methane and silane plasma by using MP2/3-21G.

	R=C	R=Si
$RH_4+RH_2RH_3$	51.2	28.5
$RH_3RH_3+RH_2RH_3$	54.2	22.1
$RH_3RH_2RH_3+RH_2RH_3$	58.4	18.2

frequency in the larger model has a lower frequency in both the carbon and the silicon system.

The energy diagram of the first step of the hydrogen-displacement reaction is shown in Fig. 7. For every cluster size, the activation energy in the carbon system is more than twice as high as for the silicon system. Thus kinetically the reaction of this type is much slower in the carbon system. As the model cluster size becomes larger, the activation energy becomes larger. This is opposite to the cluster size dependence observed in the silicon system. As for the relative stability of the reactant and the product, it is similar for the carbon and silicon systems. Thus the opposite tendency at the transition state seems to be related to its crowded structure. Thermodynamically, these two systems are similar.

The activation energies of the first step of the hydrogen-displacement reaction in the carbon and silicon systems are compared in Table II.

The energy differences between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the surface model clusters are shown in Fig. 8. As the cluster size increases, the different between HOMO and LUMO becomes smaller in both carbon and silicon systems. The difference is, however, much smaller for the silicon system. Hence the stabilization of the transition state by the electronic delocalization effect is expected to be large when the cluster becomes larger. On the other hand, the steric effect is expected to be larger at the transition state of the carbon system when the cluster becomes larger. This is considered to be an origin of the opposite cluster size dependence of the activation energy in the carbon and the silicon system.

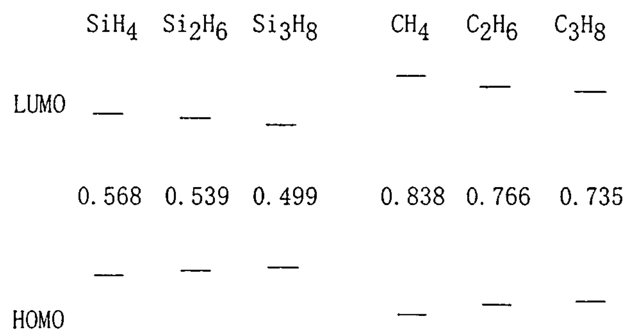


FIG. 8. The energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the surface model clusters (in atomic units).

As for the second step [Eq. (2)], Sato *et al.*[11] already calculated the activation energies of $SiH_4+H\rightarrow\cdot SiH_3+H_2$ and $CH_4+H\rightarrow\cdot CH_3+H_2$. The former and the latter are 16.4 and 24.9 kcal/mol, respectively, by *ab initio* HF/3-21G level. The heat of reaction (the relative stability of the product and the reactant) of these reactions at 0 K is -12.7 and 4.7 kcal/mol, respectively at the HF/3-21G level. Both of them have a low-energy barrier. Thus the first step is the rate determining step.

In conclusion, we note that although the two systems are thermodynamically similar, the activation energy of the reaction as shown by Eq. (1) in the carbon system is much higher than that in the silicon system. Thus the hydrogen-displacement mechanism just below the surface of methane plasma is expected to be different from that just below the surface of silane plasma at low substrate temperatures, while they are expected to be similar at high substrate temperatures. Hence the hydrogen-displacement mechanism on the surface of methane plasma is expected to be similar at high substrate temperatures, while it is expected to be different at low substrate temperatures. This is considered to be one reason a diamondlike sp^3 network can be formed only at high (>600 °C) substrate temperatures in CH_4/H_2 plasma CVD. At lower temperatures, the fraction of sp^2 structures was reported to be larger than sp^3 structure in the film.[12] In this case, a different mechanism is considered to be predominant.

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