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Successive hydrogen-elimination reactions with low activation energies in the *a*-Si:H formation process: An *ab initio* molecular-orbital study

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Successive hydrogen elimination reactions with low activation energies during the formation of *a*-Si:H by silane plasma chemical vapor deposition are proposed on the basis of an *ab initio* molecular-orbital method. The activation energy of the first step, the reaction of a dangling-bond site with an adjacent tetrahedrally coordinated silicon atom, was found to be 25.2 kcal/mol at 0 K when the zero-point vibrational energy was taken into account. The subsequent step was an exothermic process with a lower activation energy. The total process was thermodynamically much more favorable than the molecular processes by which a hydrogen atom or molecule is eliminated.

Properties of *a*-Si:H films depend strongly on the hydrogen content in the films. Thus, it is of primary importance to understand the predominant processes which determine the hydrogen content in the formation of *a*-Si:H films. Itabashi *et al.*,[1] using a gas phase IR diode laser measurement, reported that a major precursor in plasma chemical vapor deposition (CVD) of silane was SiH_3. The hydrogen content of *a*-Si:H films prepared by plasma CVD with heated substrates is much lower than that of the precursor. Hence, hydrogen-elimination processes play an important role in determining the hydrogen content in *a*-Si:H films produced by plasma CVD of silane at relatively high substrate temperatures. Matsuda and Tanaka[2] proposed that the activation energy for a hydrogen elimination process in the growth zone which was some atomic layers under the top surface was very low in plasma CVD of silane, on the basis of the substrate temperature dependence of the hydrogen content of *a*-Si:H films prepared by triode plasma CVD of silane. Hydrogen-elimination reactions from silane[3] and disilane[4] were studied by Gordon and co-workers by using an *ab initio* molecular-orbital method. Activation energies for the reactions (1) and (2) which had the lowest activation energies were 56.9 and 55.5 kcal/mol, respectively.

$$SiH_4 \rightarrow :SiH_2 + H_2 , \tag{1}$$

$$Si_2H_6 \rightarrow :SiHSiH_3 + H_2 . \tag{2}$$

The activation energy of a hydrogen-elimination reaction accompanying the coupling of tetrahedrally coordinated molecular silicon atoms as shown by Eq. (3) was also calculated to be 102 kcal/mol by Tsuda and Oikawa.[5]

$$R_3Si{-}H + H{-}SiR_3 \rightarrow R_3SiSiR_3 + H_2 (R = \text{Si or H}) . \tag{3}$$

As molecular processes such as in Eqs. (1)-(3) have very high activation energies, there should be other hydrogen-elimination processes with low activation energies occurring in the formation process of *a*-Si:H films.

The present paper will describe successive hydrogen-elimination reactions with low activation energies in the formation process of *a*-Si:H films predicted by using an *ab initio* molecular-orbital method.

An *ab initio* molecular-orbital method was used for all the calculations. The Hartree-Fock method was employed for the geometry optimization. Electron correlations were taken into account by the second-order Møller-Plesset perturbation theory.[6] A 3-21G^* basis set[7,8] was employed for the energy calculation of the hydrogen detachment reaction. A 3-21G basis set was used for hydrogen abstraction reactions. The GAUSSIAN 86 program[9] was used for the calculations. All the *ab initio* calculations were conducted on HITAC M880 of Computer Center, University of Tokyo and HITAC M680H of Chiba University.

Vibrational, rotational, translational energies, and entropies were calculated as functions of temperature by Eqs. (4)-(9), respectively.[10]

$$E_{\text{vib}} = E_{0,\text{vib}} + NkT \sum_i \frac{h\nu_i/kT}{\exp(h\nu_i/kT) - 1}, \quad E_{0,\text{vib}} = \sum_i Nh\nu_i/2 , \tag{4}$$

$$S_{\text{vib}} = Nk \sum_i \left[\frac{(h\nu_i/kT)\exp(-h\nu_i/kT)}{1 - \exp(-h\nu_i/kT)} - \ln[1 - \exp(-h\nu_i/kT)] \right] , \tag{5}$$

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$$E_{\mathrm{rot}} = \tfrac{3}{2} RT\,, \tag{6}$$

$$S_{\mathrm{rot}} = R(\tfrac{1}{2}\ln ABC + \tfrac{3}{2}\ln T - \ln\sigma_3 - 2.7106)\,, \tag{7}$$

where A, B, C, are moments of inertia along three rotational axis, and σ_3 is a rotational symmetry number.

$$E_{\mathrm{trans}} = \tfrac{3}{2} RT\,, \tag{8}$$

$$S_{\mathrm{trans}} = R(\tfrac{3}{2}\ln M + \tfrac{5}{2}\ln T - \ln P - 1.1650)\,. \tag{9}$$

The electronic energy (E_{elec}) was directly obtained by the *ab initio* molecular-orbital calculation. The electronic entropy was calculated by Eq. (10).

$$S_{\mathrm{elec}} = R \ln g_0\,, \tag{10}$$

where g_0 is the degree of degeneracy.

Vibrational frequencies (ν_i) for calculating E_{vib} and S_{vib} by Eqs. (4) and (5) were obtained by the normal-mode analysis based on the energy gradients determined by the *ab initio* calculation. Activation energies and entropies were calculated by Eqs. (11) and (12), respectively.

$$\begin{aligned} E_a &= RT + \Delta E^T \\ &= RT + (E^T_{\mathrm{elec}} + E^T_{\mathrm{vib}} + E^T_{\mathrm{rot}} + E^T_{\mathrm{trans}}) \\ &\quad - (E^0_{\mathrm{elec}} + E^0_{\mathrm{vib}} + E^0_{\mathrm{rot}} + E^0_{\mathrm{trans}})\,, \end{aligned} \tag{11}$$

$$\begin{aligned} \Delta S^T &= (S^T_{\mathrm{elec}} + S^T_{\mathrm{vib}} + S^T_{\mathrm{rot}} + S^T_{\mathrm{trans}}) \\ &\quad - (S^0_{\mathrm{elec}} + S^0_{\mathrm{vib}} + S^0_{\mathrm{rot}} + S^0_{\mathrm{trans}})\,, \end{aligned} \tag{12}$$

where T and 0 correspond to the transition state and the initial state, respectively.

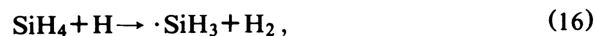
The rate constants for the first-order and second-order reactions were determined on the basis of transition-state theory[11] by using Eqs. (13) and (14), respectively.

$$k_1 = e(kT/h)\exp(\Delta S^T/R)\exp(-E_a/RT)\,, \tag{13}$$

$$k_2 = e^2(kT/h)(RT/P)\exp(\Delta S^T/R)\exp(-E_a/RT)\,. \tag{14}$$

The reactions treated in this study are shown in Eqs. (15)-(19).

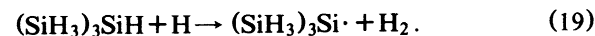
$$SiH_4 + \cdot SiH_2SiH_3 \rightarrow SiH_3SiH_2SiH_3 + H\,, \tag{15}$$



$$SiH_4 + H \rightarrow \cdot SiH_3 + H_2\,, \tag{16}$$

$$SiH_3SiH_3 + H \rightarrow \cdot SiH_2SiH_3 + H_2\,, \tag{17}$$

$$SiH_3SiH_2SiH_3 + H \rightarrow SiH_3\dot{S}iHSiH_3 + H_2\,, \tag{18}$$



$$(SiH_3)_3SiH + H \rightarrow (SiH_3)_3Si\cdot + H_2\,. \tag{19}$$

Equation (15) is a model reaction of hydrogen detachment accompanying the coupling of a dangling bond site with an adjacent tetrahedrally coordinated silicon atom. Equations (16)-(19) are subsequent hydrogen abstraction reactions with a hydrogen atom which is a product of the reaction (15).

The structure of the transition state of the reaction (15) is shown in Fig. 1. Only one Si-H bond is much longer (1.72 Å) than the other Si-H bonds. This bond is collinear with the adjacent Si-Si bond.

The vibrational mode corresponding to the imaginary frequency at the transition state is shown in Fig. 2. Cleavage of an Si-H bond and formation of an Si-Si bond corresponds to this vibrational mode. Thus, the structure obtained is the transition state for the reaction (15).

As the representative of hydrogen abstraction reactions, the structure of the transition state of a hydrogen abstraction reaction (18) in which the reactant is identical with the product of reaction (15) is shown in Fig. 3.

The vibrational mode for the imaginary frequency obtained by normal-mode analysis of this structure, which is

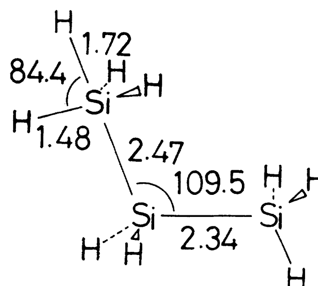


FIG. 1. The structure of the transition state of $SiH_4 + \cdot SiH_2SiH_3 \rightarrow SiH_3SiH_2Si_3 + H$. (Lengths in angstroms, angles in degrees.)

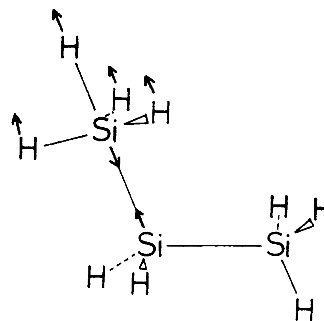


FIG. 2. The vibrational mode corresponding to the imaginary frequency at the transition state.

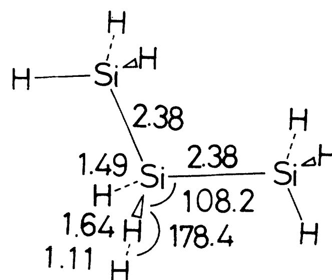


FIG. 3. The structure of the transition state of $SiH_3SiH_2SiH_3 + H \rightarrow SiH_3\dot{S}iHSiH_3 + H_2$. (Lengths in angstroms, angles in degrees.)

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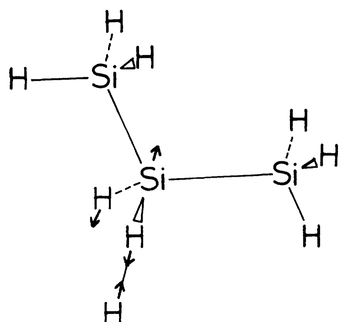

FIG. 4. The vibrational mode corresponding to the imaginary frequency at the transition state.

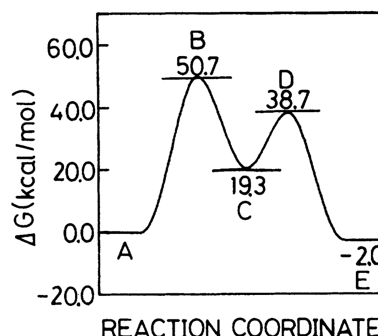

FIG. 5. A Gibbs' free-energy profile. A, $SiH_4+\cdot SiH_2SiH_3$; B, $SiH_4SiH_2SiH_3$ (TS); C, $SiH_3SiH_2SiH_3+H$; D, $SiH_3SiH_2HSiH_3$ (TS); E, $SiH_3\dot{S}iHSiH_3+H_2$.

shown in Fig. 4 assures us that this structure is the desired transition state for the reaction. The transition states of the other hydrogen abstraction reactions were also examined by normal-mode analysis.

Energy and entropy changes accompanying these reactions are listed in Table I. The activation energy for the hydrogen detachment reaction (15) is much lower than those for molecular processes such as reactions (1)–(3). Subsequent hydrogen abstraction reactions are exothermic reactions with small activation energies. As hydrogen atoms are substituted by silicon atoms, the activation energy becomes lower. If this rule also holds for hydrogen detachment reactions, the activation energy of the first step of the successive reactions becomes lower than that of reaction (15).

The Gibbs' free-energy profile of the successive hydrogen-elimination processes at 600 K, which corresponds to the substrate temperature for preparing device-quality a-Si:H films, is shown in Fig. 5. The value for the second step is the value of reaction (18), which is the reaction of the product of reaction (15). The second step is more favorable than the reverse reaction of the first step (15). Thus, the successive processes shown in Fig. 5 are thermodynamically favorable overall. These successive reactions do not change the number of dangling bonds. Therefore, this process catalytically scavenges many hydrogen atoms adjacent to a dangling bond. Yamasaki, Isoya, and Matsuda[12] reported that the distance between a dangling bond and the nearest hydrogen in a-Si:H was longer than 4.2 Å, determined from a pulsed electron spin resonance measurement.[13] The mechanism proposed in this paper is consistent with this observation.

The rate constants of the reactions (15)–(19) at 600 K are listed in Table II. These reactions are fast enough for thermodynamic discussion.

In conclusion, the activation energies of successive hydrogen-elimination processes accompanying the cou-

TABLE I. Activation energies (E_a), activation entropies (ΔS^T), heats of reactions (ΔH), and entropy changes (ΔS).

	T (K)	$\equiv SiH+\cdot Si\equiv$ [a] $\rightarrow \equiv Si-Si\equiv +H$	SiH_4+H [b] $\rightarrow \cdot SiH_3+H_2$	$-SiH_3+H$ [b] $\rightarrow -\dot{S}iH_2+H_2$	$=SiH_2+H$ [b] $\rightarrow =\dot{S}iH+H_2$	$\equiv SiH+H$ [b] $\rightarrow \equiv Si\cdot +H_2$
E_a [c]	0	25.2	9.9	8.8	7.9	7.2
	600	28.1	10.9	9.9	9.1	8.4
ΔS^T [d]	600	−30.8	−20.7	−19.2	−21.2	−22.2
ΔH [c]	0	8.1	−15.2	−16.7	−17.6	−18.0
	600	10.2	−14.4	−16.1	−17.4	−17.6
ΔS [d]	600	−6.8	6.6	8.4	5.1	6.8

[a]By $MP2/3-21G^*$.
[b]By $MP2/3-21G$.
[c]In kcal mol^{-1}.
[d]In cal mol^{-1} K^{-1}.

TABLE II. Rate constants of reactions.

	$\equiv SiH+\cdot Si\equiv$ [a] $\rightarrow \equiv Si-Si\equiv +H$	SiH_4+H [b] $\rightarrow \cdot SiH_3+H_2$	$-SiH_3+H$ [b] $\rightarrow -\dot{S}iH_2+H_2$	$=SiH_2+H$ [b] $\rightarrow =\dot{S}iH+H_2$	$\equiv SiH+H$ [b] $\rightarrow \equiv Si\cdot +H_2$
k_1 [c]	3.5×10^{-4}				
k_2 [d]		2.4×10^{-14}	1.2×10^{-13}	4.5×10^{-14}	9.5×10^{-14}

[a]By $MP2/3-21G^*$.
[b]By $MP2/3-21G$.
[c]In sec^{-1}, at 600 K.
[d]In cm^3 sec^{-1} molecule^{-1}, at 600 K.

pling of the dangling bond site with an adjacent tetrahedrally coordinated silicon atom proposed in this paper are much smaller than those of the molecular processes which were previously studied. The successive process is thermodynamically favorable. This process is also consistent with the structure around the dangling bond of *a*-Si:H films observed by a pulsed electron spin resonance measurement of Yamasaki *et al.* As the concentration of dangling bond sites in the growth zone of silane plasma CVD is expected to be higher than that of the film produced, this process is a potential hydrogen-elimination process in the formation of *a*-Si:H films.

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