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Ab initio molecular-orbital study on successive hydrogen-elimination reactions with low activation energies in the *a*-Si:H formation process: Cluster-size dependence of activation energies

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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 proposed by us were studied by using a larger cluster model 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, was found to be 18.2 kcal/mol (0.79 eV) by employing a larger cluster model. The total process was also shown to be thermodynamically more favorable by using larger cluster models. Thus, the successive process is considered to play an important role in *a*-Si:H formation processes.

Hydrogen-elimination processes play an important role in determining the hydrogen content in *a*-Si:H films produced by plasma chemical vapor deposition (CVD) of silane at relatively high substrate temperatures. Matsuda and Tanaka[1] reported that the activation energy for a hydrogen-elimination process in the growth zone which was some atomic layers below the top surface was 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. As properties of *a*-Si:H films depend strongly on the hydrogen content in the films, it is of primary importance to determine the hydrogen-elimination mechanism. We[2] proposed successive hydrogen-elimination reactions with low activation energies from a theoretical calculation based on an *ab initio* molecular-orbital method. This mechanism is composed of two steps. The first step is a coupling reaction of a dangling-bond site with an adjacent tetrahedrally coordinated silicon atom, as shown in Eq. (1):

$$\cdot\mathrm{Si}\equiv + \equiv\mathrm{SiH} \rightarrow \equiv\mathrm{Si}\text{—}\mathrm{Si}\equiv + \mathrm{H}\ . \tag{1}$$

The second step is a hydrogen abstraction reaction by a hydrogen radical which is produced by the step (1) from an adjacent Si—H bond. This step shown in Eq. (2) reproduces a dangling-bond site:

$$\equiv\mathrm{SiH} + \mathrm{H} \rightarrow \equiv\mathrm{Si}\cdot + \mathrm{H_2}\ . \tag{2}$$

These steps can repeat as a chain reaction and scavenge many hydrogen atoms which are adjacent to a dangling bond consistent with experimental results.[3,4] A multiquantum nuclear magnetic measurement[5] also suggested an inhomogeneous distribution of hydrogen atoms in *a*-Si:H films.

In the previous paper, a small cluster model was used for the first step as shown in Eq. (3):

$$\mathrm{SiH_4} + \cdot\mathrm{SiH_2SiH_3} \rightarrow \mathrm{SiH_3SiH_2SiH_3} + \mathrm{H}\ . \tag{3}$$

In this paper, an *ab initio* molecular-orbital calculation is performed by using larger cluster models such as shown in Eqs. (4) and (5):

$$\mathrm{SiH_3SiH_3} + \cdot\mathrm{SiH_2SiH_3} \rightarrow \mathrm{SiH_3SiH_2SiH_2SiH_3} + \mathrm{H}\ , \tag{4}$$

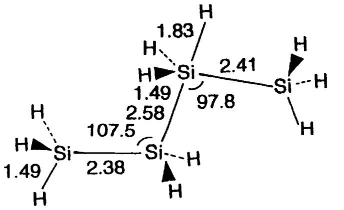

FIG. 1. The structure of the transition state of $\mathrm{SiH_3SiH_3} + \cdot\mathrm{SiH_2SiH_3} \rightarrow \mathrm{SiH_3SiH_2SiH_2SiH_3} + \mathrm{H}$ (lengths in angstroms, angles in degrees).

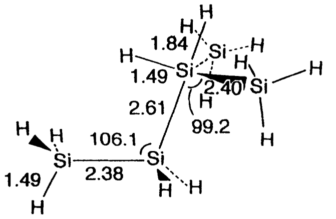

FIG. 2. The structure of the transition state of $\mathrm{SiH_3SiH_2SiH_3} + \cdot\mathrm{SiH_2SiH_3} \rightarrow \mathrm{SiH_3SiH_2SiH(SiH_3)_2} + \mathrm{H}$ (lengths in angstroms, angles in degrees).

$$SiH_3SiH_2SiH_3+\cdot SiH_2SiH_3 \rightarrow SiH_3SiH_2SiH(SiH_3)_2+H \ . \tag{5}$$

The cluster-size dependence of the activation energy of the first step, which is the rate determining step, is examined by comparing the activation energies of reactions (3)–(5).

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

Vibrational, rotational, and translational energies and entropies were calculated as functions of temperature.[10] The equations were given in a previous paper.[2] Vibrational frequencies (ν_i) for calculating vibrational energies and entropies were obtained by the nomal mode analysis based on the energy gradients determined by the *ab initio* calculation. Activation energies and entropies were calculated by Eqs. (6) and (7), respectively:

$$\begin{aligned} E_a &= RT+\Delta E^T \\ &= RT+(E^T_{\text{elec}}+E^T_{\text{vib}}+E^T_{\text{rot}}+E^T_{\text{trans}}) \\ &\quad -(E^0_{\text{elec}}+E^0_{\text{vib}}+E^0_{\text{rot}}+E^0_{\text{trans}}) \ , \end{aligned} \tag{6}$$

$$\begin{aligned} \Delta S^T &= (S^T_{\text{elec}}+S^T_{\text{vib}}+S^T_{\text{rot}}+S^T_{\text{trans}}) \\ &\quad -(S^0_{\text{elec}}+S^0_{\text{vib}}+S^0_{\text{rot}}+S^0_{\text{trans}}) \ , \end{aligned} \tag{7}$$

where T and 0 correspond to transition and initial states, respectively. The Gibbs' free energy was calculated by Eq. (8):

$$\Delta G=\Delta H-T\Delta S \ . \tag{8}$$

The structures of the transition states of reactions (4) and (5) are shown in Figs. 1 and 2, respectively. One of the Si-H bonds (1.83 and 1.84 Å for Figs. 1 and 2, respectively) which is connected with the pentacoordinated silicon atom is much longer than the other Si-H bonds (1.49 Å). This bond is also longer than the long Si-H bond (1.74 Å) of reaction (3), which was previously reported by us.[2] This bond is collinear with the adjacent Si-Si bond.

The vibrational mode corresponding to the imaginary frequency at the transition state of reaction (4) is shown in Fig. 3. Cleavage of a Si-H bond and formation of a Si-Si bond correspond to this vibrational mode. Hence the structure obtained is the transition state of reaction (4).

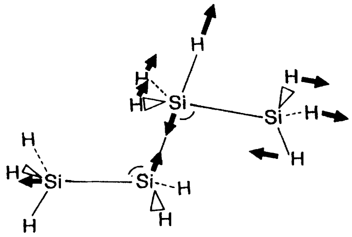

FIG. 3. The vibrational mode corresponding to the imaginary frequency at the transition state.

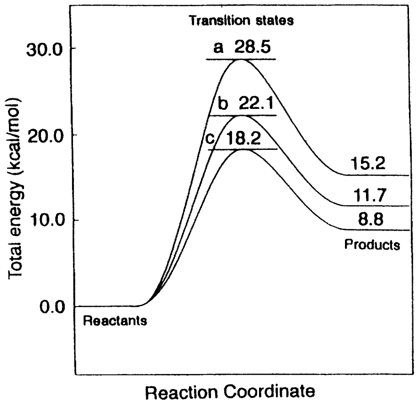

FIG. 4. The electronic-energy diagrams of the first step of the hydrogen-elimination mechanism. (*a*) $SiH_4+\cdot SiH_2SiH_3 \rightarrow SiH_3SiH_2SiH_3+H$. (*b*) $SiH_3SiH_3+\cdot SiH_2SiH_3 \rightarrow SiH_3SiH_2SiH_2SiH_3+H$. (*c*) $SiH_3SiH_2SiH_3+\cdot SiH_2SiH_3 \rightarrow SiH_3SiH_2SiH(SiH_3)_2+H$ (MP2/3-21 G//HF3-21 G.)

The electronic energy diagrams of the first step of the proposed hydrogen-elimination mechanism with different cluster-size models are compared in Fig. 4. As the model cluster size becomes larger and closer to the real system, the activation energy becomes smaller, and the reaction becomes more thermodynamically favorable.

The electronic energy, zero-point vibrational energy, and entropy changes on reactions (3)–(5) are listed in Table I. The activation energy becomes lower by taking the zero-point vibrational energy into account. Although nomal mode analysis could not be performed on reaction (5) due to the large cluster size, the activation energy of reaction (5), which is the similar reaction to reactions (3) and (4), is also expected to become lower than 18.2 kcal/mol (0.79 eV) when the zero-point vibrational energy is included. As the more positive entropy change corresponds to the more favorable reaction, the reaction of

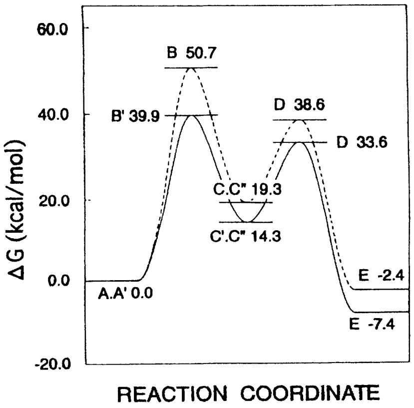

FIG. 5. A Gibbs' free-energy profile at 600 K. (*A*) $SiH_4+\cdot SiH_2SiH_3$. (*A'*) $SiH_3SiH_3+\cdot SiH_2SiH_3$. (*B*) $SiH_4SiH_2SiH_3$ (TS). (*B'*) $SiH_3SiH_3SiH_2SiH_3$ (TS). (*C*) $SiH_3SiH_2SiH_3+H$. (*C'*) $SiH_3SiH_2SiH_2SiH_3+H$. (*C''*) $(SiH_3)_3SiH+H$. (*D*) $(SiH_3)_3SiHH$ (TS). (*E*) $(SiH_3)_3Si\cdot+H_2$.

the larger cluster is also entropically more favorable than that of the smaller cluster.

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 for two cluster sizes [reactions (3) and (4) for the first step] in Fig. 5. As the population of a monohydride site is considered to be largest, $(SiH_3)_3SiH + H \rightarrow (SiH_3)_3Si\cdot + H_2$ is adopted as the second step. The successive process becomes thermodynamically more favorable as the cluster size becomes larger. As the actual system is closer to the larger cluster model, the successive process in which a dangling-bond site is involved is predicted to be thermodynamically favorable.

In total, the hydrogen-elimination mechanism which we proposed was proven to be both kinetically and thermodynamically more favorable by employing larger cluster models. This mechanism is expected to play an important role in *a*-Si:H film formation by plasma chemical vapor deposition processes.

TABLE I. Activation energies (E_a)[a,b] and activation entropies (ΔS^T)[a,c].

	E_a at 0 K	with $E_{0,\mathrm{vib}}$	ΔS^T at 600 K
$SiH_4 + \cdot SiH_2SiH_3 \rightarrow SiH_3SiH_2SiH_3 + H$	28.5	26.8	−30.3
$SiH_3SiH_3 + \cdot SiH_2SiH_3 \rightarrow SiH_3SiH_2SiH_2SiH_3 + H$	22.1	20.4	−29.3
$SiH_3SiH_2SiH_3 + \cdot SiH_2SiH_3 \rightarrow SiH_3SiH_2SiH(SiH_3)_2 + H$	18.2		

[a] By MP2/3-21 G.

[b] In kcal mol^{-1}, 1 kcal mol^{-1} corresponds to 4.34×10^{-2} eV.

[c] In cal mol^{-1} K^{-1}.

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