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Theoretical Investigation on the Reactions of Dichlorosilane with Ammonia

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SiH_2Cl_2 decomposition into $SiCl_2$ and H_2, $SiCl_2$ insertions into NH_3 and SiH_4, and 1,1-HCl elimination from $SiHCl_2NH_2$, which seem to occur in chemical vapor deposition processes of the silicon-nitride film growth, were theoretically investigated using second-order Moller–Plesset perturbation theory based on ab initio restricted Hartree–Fock method. The calculated results suggest that the Cl atoms create an energy barrier larger in Si–Si bond formation and facilitate the growth of stoichiometrically better films.

It is necessary to grow extremely thin silicon-nitride (SiN) films by chemical vapor deposition (CVD) processes in order to develop denser dynamic random access memory (DRAM) cells for the next generation of ultra-large scale integrated circuits (ULSIs).1) For this purpose, stoichimetrically better SiN films need to be produced with appropriate source gases under conventional CVD conditions. It has been proved experimentally2–4) that a mixture of SiH_2Cl_2 and NH_3 is more efficient than that of SiH_4 and NH_3 as a source gas for film growth. To our knowledge, the difference in the growth mechanism between these two cases has not been theoretically or experimentally researched in detail.

The film-growth processes from SiH_4 and NH_3 were examined using the experimental results and theoretical studies concerning reactions of SiH_4 and NH_3.5) In the present study, we investigate the film-growth mechanism from SiH_2Cl_2 and NH_3. Based on an analogy with the reactions of SiH_4 and NH_3, the following four reactions seem to occur in a mixture of SiH_2Cl_2 and NH_3 at the CVD temperature:

$$SiH_2Cl_2 \longrightarrow SiCl_2 + H_2, \qquad (R1)$$

$$SiCl_2 + NH_3 \longrightarrow SiHCl_2NH_2, \qquad (R2)$$

$$SiCl_2 + SiH_4 \longrightarrow SiHCl_2SiH_3, \qquad (R3)$$

$$SiHCl_2NH_2 \longrightarrow Cl\text{–}Si\text{–}NH_2 + HCl. \qquad (R4)$$

Therefore, we carried out ab initio molecular orbital calculations on these four reactions; we discuss the effects of Cl atoms in comparison with the analogous reactions of SiH_4 and NH_3. On the basis of the calculated results for these vapor-phase reaction, we also make some suggestions concerning the growth mechanism of SiN films when a mixture of SiH_2Cl_2 and NH_3 is adopted.

Methods of Calculation

MC-311G(d,p)6) and 6-311G(d,p)7) basis sets were employed for the second-row atoms (Si and Cl) and for N and H atoms, respectively. The geometrical structres at stationary points were optimized within the restricted Hartree–Fock (RHF) approximation8) using the analytic gradient method.9) Vibrational analyses were also performed for all geometries. The relative energies of the geometries were recalculated using second-order Moller–Plessett perturbation theory (MP2)10) with an RHF zero-point energy correction. All of the calculations were made on an NEC SX2 machine using the quantum chemistry program code GAMESS developed by Schmidt et al.11)

Results and Discussion

Decomposition: Reaction (R1) had been predicted to be the most favorable path of SiH_2Cl_2 decomposition.12) The transition-stete geometry **1** for (R1) is illustrated in Fig. 1; the energy barrier was calculated to be 80 kcal mol^{-1} (see Fig. 2). Regarding an analogous decomposition of SiH_4, MP2 calculations yielded an energy barrier of 62 kcal mol^{-1}; the energy barrier had been predicted to be 57 kcal mol^{-1} in more reliable calculations.13) Therefore, since the MP2 calculations tend to slightly overestimate the energy barriers, the energy barrier of (R1) could be smaller than 80 kcal mol^{-1}

Gosavi et al.14) reported 36 kcal mol^{-1} for the energy gap between the ground state ($^1A_1$) and the lowest triplet state ($^3B_1$) of $SiCl_2$ using self-consistent-field methods; an energy gap in SiH_2 had been predicted to be about 17 kcal mol^{-1}.15) Since the large energy gap for $SiCl_2$ is explained by the effect of electronegative Cl atoms, $SiCl_2$ has been predicted to be less reactive than SiH_2.15) This prediction is consistent with the calculated results concerning the reversereaction of (R1) (a relatively large energy barrier of 46 kcal mol^{-1}); a larger barrier may exist in $SiCl_2$ insertions into NH_3 and SiH_4 (R2 and R3).

Insertions: The calculated results show that the energy barriers of (R2 and R3) are 21 and 25 kcal mol^{-1}, respectively (Fig. 2). Raghavachari et al.16) and Gordon et al.17) reported an energy barrier of 13 kcal mol^{-1} for

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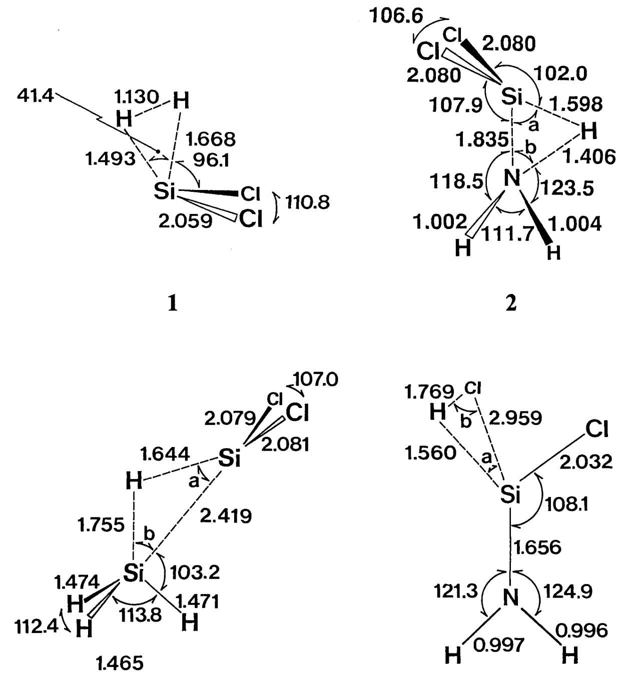
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Fig. 1. Transition-state geometries of the thermal decomposition of SiH_2Cl_2 **1**, the $SiCl_2$ insertion **2** into NH_3 (a=47.7, b=52.3), the $SiCl_2$ insertion **3** into SiH_4 (a=46.5, b=42.8), and the 1,1-HCl elimination **4** (a=29.2, b=25.5, and Cl–Si–Cl=116.5). The bond lengths and bond angles are in angstroms and degrees.

SiH_2 insertion into NH_3 and no energy barrier for SiH_2 insertion into SiH_4. It was thus confirmed that $SiCl_2$ is less reactive than SiH_2, as suggested above. The transition-state geometries (**2** and **3** in Fig. 1) of (R2 and R3) have no symmetry since their C_s geometries have 2 imaginary frequencies. An additional complex (**5** in Fig. 3) having no negative force constant was found for (R2). The huge stabilization (22 kcal mol^{-1}) of **5** would be caused by a strong interaction between the empty 3pπ orbital of $SiCl_2$ and the lone-pair orbital of NH_3.[18] The formation of Si–N bonds needs to be facilitated for the growth of SiN films, while Si–Si bonds cause the films to have some electric deficiencies.[19] If the above discussion can be applied in a straight-forward way to reactions on the film surface, Si–Si bonds would be created much more easily than the Si–N bond when a mixture of SiH_4 and NH_3 is adopted. Then, the films tend to have a composition which deviated from the stoichiometrically correct one (Si_3N_4) and easily becomes Si-rich.[3] On the other hand, the formation of Si–N bonds can be accelerated by a large NH_3 ratio in the mixture of SiH_2Cl_2 and NH_3,[2,3] since both (R2 and R3) have similar energy barriers. Therefore, stoichiometrically better films are expected to be produced more efficiently using the latter mixture. This theoretical interpretation thus seems to reasonably explain the experimental results.[2,3]

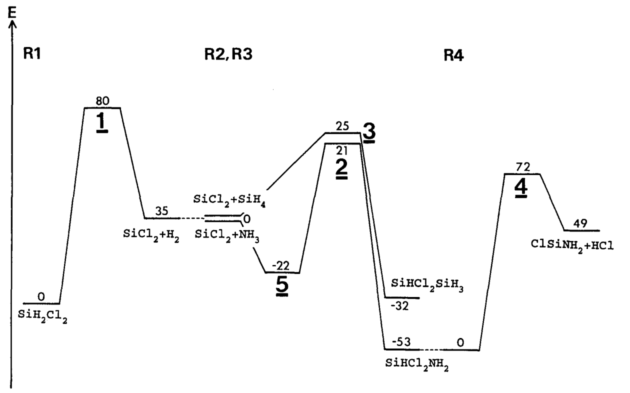

Fig. 2. Reaction profile for R1, R2, R3, and R4. The reactions proceed from left to right. Bold numbers correspond to those in Figs. 1 and 3. The relative energies are in kcal mol^{-1}.

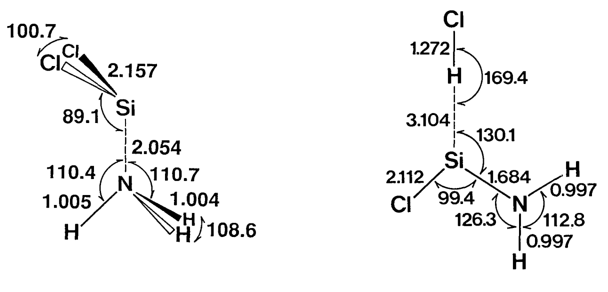
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Fig. 3. Geometries of additional complexes for the $SiCl_2$ insertion **5** into NH_3 and the 1,1-HCl elimination **6**. The bond lengths and bond angles are in angstroms and degrees.

Elimination: The reaction energy (49 kcal mol^{-1}) of the 1,1-HCl elimination (R4) from $SiHCl_2NH_2$ is much smaller than that (129 kcal mol^{-1}) of 1,1-Cl_2 elimination and some kinds of 1,2-eliminations (75–78 kcal mol^{-1}). The energy barrier for R4 was calculated to be 72 kcal mol^{-1} (Fig. 2); its transition-state geometry **4** is depicted in Fig. 1. This barrier is somewhat larger than that (67 kcal mol^{-1})[20] of the 1,1-H_2 elimination from SiH_3NH_2. Then, the product Cl–Si–NH_2 may react with another NH_3 to create a new Si–N bond. Accordingly, the repeat of $SiCl_2$ insertion into an N–H bond and HCl elimination could produce various SiN particles.

An additional complex (**6** in Fig. 3), whose force constant matrix is positive definite, is predicted to be formed before (R4) is completed. Although highly polarizes HCl seems to strongly interact with the lone-pair of the Si atom in Cl–Si–NH_2, **6** is only about 1 kcal mol^{-1} lower than the dissociation limit, in contrast with that of **5**. This small stabilization energy might be explained in the following manner: More electronegative groups (Cl and NH_2) in Cl–Si–NH_2 derive a large positive charge (+0.7 e) on the Si atom, so that the attractive interaction between the H atom and the lone-pair of the Si atom is weakened by the charge–charge repulsion between the H atom and the entire Si atom. This fact would also explain an energy barrier of 23 kcal mol^{-1} for the reverse reaction of (R4).

Conclusion

The present work involved four vapor-phase reactions (R1—R4) using ab initio molecular orbital methods. It is preliminarily concluded that Cl atoms create an energy barrier that is larger in Si–Si bond formation, which seems to facilitate the growth of stoichiometrically better films. We plan to investigate fundamental reactions on the film surface based on the calculated results for these vapor-phase reactions.21)

References

1) J. Yugami, T. Mine, S. Iijima, and A. Hiraiwa, Ext. Abstr. 20th (1988 Int.) Conf. Solid state Devices and Materials, Tokyo, 1988, Abstr., p. 173.

2) K. Ando, A. Ishitani, and K. Hamano, *Appl. Phys. Lett.*, **59**, 1081 (1991).

3) R. S. Bailey and V. J. Kapoor, *J. Vac. Sci. Technol.*, **20**, 484 (1982).

4) A. Lekholm, *J. Electrochem. Soc.*, **119**, 1122 (1972).

5) A. Ishitani and S. Koseki, *Jpn. J. Appl. Phys.*, **29**, L2322 (1990).

6) A. D. McLean and G. S. Chandler, *J. Chem. Phys.*, **72**, 5639 (1980).

7) R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, *J. Chem. Phys.*, **72**, 650 (1980).

8) C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

9) a) J. Baker, *J. Comput. Chem.*, **7**, 385 (1986); b) S. Bell and J. S. Crighton, *J. Chem. Phys.*, **80**, 2464 (1984); c) H. B. Schlegel, "Ab Initio Methods in Quantum Chemistry, Part I, " ed by K. P. Lawley, John Wiley & Sons, New York (1987).

10) P. Carsky, B. A. Hess, Jr., and L. J. Schaad, *J. Comput. Chem.*, **5**, 280 (1984).

11) a) M. Dupuis, D. Spangler, and J. J. Wendoloski, "Program QG10, National Resource for Computation in Chemistry Software Catalog," Lawrence Berkeley Laboratory, Berkeley, CA (1980), p. 60; b) M. W. Schmidt, K. K. Baldridge, J. A. Boatz, J. H. Jensen, S. Koseki, M. S. Gordon, K. A. Nguyen, T. L. Windus, and S. T. Elbert, *Quantum Chem. Program Exchange Bull.*, **10**, 52 (1991).

12) A. Ishitani, T. Takada, and Y. Ohshita, *J. Appl. Phys.*, **63**, 390 (1988). The reaction energies of H_2, HCl, and Cl_2 eliminations from SiH_2Cl_2 were reported to be 39, 63, and 138 kcal mol^{-1}.

13) a) A. Sax and G. Olbrich, *J. Am. Chem. Soc.*, **107**, 4868 (1985); b) M. S. Gordon, D. R. Gano, J. S. Binkley, and M. J. Frisch, *J. Am. Chem. Soc.*, **108**, 2191 (1986); See also: c) J. M. Jasinski, *J. Phys. Chem.*, **90**, 555 (1986); d) H. M. Frey, R. Walsh, and I. M. Watts, *J. Chem. Soc., Chem. Commun.*, **1986**, 1189; e) S. K. Shin and J. L. Beanchamp, *J. Phys. Chem.*, **90**, 1507 (1986).

14) R. K. Gosavi and O. P. Strausz, *Chem. Phys. Lett.*, **123**, 65 (1986).

15) K. K. Baldridge, J. A. Boatz, S. Koseki, and M. S. Gordon, *Annu. Rev. Phys. Chem.*, **38**, 211 (1987).

16) K. Raghavachari, J. Chandrasekhar, M. S. Gordon, and K. J. Dykema, *J. Am. Chem. Soc.*, **106**, 5835 (1984).

17) M. S. Gordon, T. N. Truong, and E. K. Bonderson, *J. Am. Chem. Soc.*, **108**, 1421 (1986).

18) $SiHCl_2NH_2$ has C_s and C_1 symmetric structures. The RHF/MC-311G(d, p) calculations show that the C_1 structure is lower than the C_s structure by only 1 kcal mol^{-1}.

19) a) H. J. Stein, *J. Appl. Phys.*, **57**, 2040(1985); b) S. Fujita and A. Sasaki, *J. Electrochem. Soc.*, **132**, 398(1985).

20) T. N. Truong and M. S. Gordon, *J. Am. Chem. Soc.*, **108**, 1775 (1986).

21) S. Koseki and A. Ishitani, *J. Appl. Phys.*, in press.