

## A Model for SiN<sub>x</sub> CVD Film Growth Mechanism by Using SiH<sub>4</sub> and NH<sub>3</sub> Source Gases

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This paper theoretically explores the SiN<sub>x</sub> CVD film growth mechanism by means of the ab initio molecular orbital method. In a chemical vapor deposition (CVD) reactor, an SiH<sub>4</sub> and NH<sub>3</sub> gas mixture produces silylenes (X-Si-Y: X and Y are substituents). Insertion of silylene into a surface Si-H or N-H bond is the important part of the CVD film growth mechanism. Following the insertion, H<sub>2</sub>-elimination reaction occurs from the surface. To obtain the reaction energies of these insertion and H<sub>2</sub>-elimination reactions, ab initio molecular orbital calculations are carried out. The proposed SiN<sub>x</sub> CVD film growth mechanism explains Si-H and N-H bonds remaining in an SiN<sub>x</sub> film and the stoichiometry deviation. Based on the mechanism, it is predicted that new source gas (SiNH<sub>5</sub>) deposits a stoichiometric SiN<sub>x</sub> film.

### 1. Introduction

Because of the rapid advances in ULSI fabrication technology, a very thin film SiN<sub>x</sub>, e.g., approximately 70 Å thick CVD film for stacked capacitor of a 16 Mbit DRAM, is needed for next generation ULSIs. Low pressure CVD method with SiH<sub>4</sub> and NH<sub>3</sub> gas mixture is usually adopted for preparing an SiN<sub>x</sub> film on a stacked polycrystalline silicon (poly-Si) film. After SiN<sub>x</sub> film deposition, the SiN<sub>x</sub> film surface is thermally oxidized to decrease leakage current. This stacked capacitor fabrication process forms an SiO<sub>2</sub>/SiN<sub>x</sub>/SiO<sub>2</sub>(native oxide)/poly-Si layered structure.

Electrical characteristics and chemical properties of the layered structure are very sensitive to the thin SiN<sub>x</sub> CVD film quality. Actually, the thermally oxidized SiO<sub>2</sub> (top layer) thickness depends on the oxidation resistance of the thin SiN<sub>x</sub> film. The current vs voltage characteristics also depends on the SiN<sub>x</sub> CVD condition. These experimental observations are attributed to the remaining Si-H and N-H bonds in an SiN<sub>x</sub> CVD film or the film composition. It is well known that an SiN<sub>x</sub> film, deposited from SiH<sub>4</sub> and NH<sub>3</sub> source gases, contains many Si-H and N-H bonds, and is Si-rich [1]. However, to our knowledge, no microscopic SiN<sub>x</sub> CVD film growth mechanism has been proposed that explains the remaining Si-H and N-H bonds and film composition. Therefore, in this work, the SiN<sub>x</sub> CVD film growth mechanism is theoretically studied in an attempt to understand these imperfections.

### 2. Computational method

The geometries for all the stationary points in the vapor phase reactions are optimized at the restricted Hartree-Fock (RHF) level with an MC-311G(d,p) basis set. This level of theory is denoted by RHF/MC-311G(d,p). The complete set of harmonic force constants is also evaluated for each stationary point. These can then be used to characterize the nature of the stationary point, a minimum being characterized by all positive eigenvalues of the force constant matrix and a transition state being characterized by only one negative eigenvalue. The force constants are also used to compute zero-point vibrational energies. Electron correlation effects are included by means of MCSCF/MC-311G(d,p)//RHF/MC-311G(d,p).

As for the surface reactions, the reaction energies are calculated at RHF level with an MC-311G(d,p) basis set. The geometries of clusters are not optimized, because the clusters simulate a solid surface. Electron correlation energies are evaluated by GVB-PP(3)/MC-311G(d,p)//RHF/MC-311G(d,p), because accurate MCSCF calculation is impractical for such a large system at the present stage. Consequently, the computational results give us qualitative explanation about the surface reactions. However, it is possible to obtain a model for the SiN<sub>x</sub> CVD film growth mechanism based on our computational results coupled with experimental results in the literature. All the calculations in the present work are performed by using the quantum chemistry code GAMESS [2].

### 3. Vapor phase reactions

Before discussing the  $\text{SiN}_x$  CVD film growth mechanism, it is useful to summarize the vapor phase reactions of  $\text{NH}_3$ ,  $\text{SiH}_4$ , and their products. In an  $\text{SiN}_x$  CVD reactor, many kinds of species can be produced from an  $\text{SiH}_4$  and  $\text{NH}_3$  gas mixture by thermal decomposition. The dissociation energies of  $\text{NH}_3$  and  $\text{SiH}_4$  are listed in Table 1. The values include zero-point-energy correction.  $\text{NH}_3$  molecule decomposition can be neglected in a conventional  $\text{SiN}_x$  CVD reactor at around an  $800^\circ\text{C}$  deposition temperature, since the lowest dissociation energy is 91.5 kcal/mol (3.8 eV). On the other hand,  $\text{SiH}_4$  easily produces  $\text{SiH}_2$  and  $\text{H}_2$  due to the dissociation energy of 48.8 kcal/mol. But, the other decomposition reaction can be neglected.

It has been reported that the insertion of  $\text{SiH}_2$  into an N-H bond of  $\text{NH}_3$  produces  $\text{SiNH}_5$ , and that the stabilization energy is 60 kcal/mol [3].  $\text{H}_2$ -elimination from  $\text{SiNH}_5$  occurs with the endothermic reaction energy of 35 kcal/mol, and the product is  $\text{SiNH}_3$ .  $\text{SiNH}_3$  has  $\text{HSi-NH}_2$  structure through 1,1-elimination reaction, and  $\text{H}_2\text{Si-NH}$  structure through the 1,2-elimination reaction. According to the RHF/MC-311G(d,p)//RHF/MC-311G(d,p) calculation,  $\text{HSi-NH}_2$  is lower in energy than  $\text{H}_2\text{Si-NH}$  by 13 kcal/mol. Due to the subsequent insertions of silylenes with silanes and  $\text{NH}_3$ , homogeneous nucleation in the vapor phase occurs. Namely, particles are generated in a CVD reactor through high temperature insertion reactions, since higher order reactions need sufficient thermal excitation.

However, at relatively low deposition temperature, i.e., around  $800^\circ\text{C}$ , the main species are source gas molecules and lower order products. Therefore,  $\text{SiH}_4$ ,  $\text{NH}_3$ ,  $\text{SiH}_2$ ,  $\text{SiNH}_5$ , and  $\text{SiNH}_3$  seem to play an important role in the  $\text{SiN}_x$  CVD film growth.

Table 1. The dissociation energies of  $\text{NH}_3$  and  $\text{SiH}_4$ .

Product	Dissociation energy (kcal/mol)
( $\text{NH}_3$ )	----
$\text{NH}_2 + \text{H}$	91.5
$\text{NH} + \text{H}_2$	122.1
$\text{N} + \text{H} + \text{H}_2$	200.7
( $\text{SiH}_4$ )	----
$\text{SiH}_3 + \text{H}$	78.9
$\text{SiH}_2 + \text{H}_2$	48.8
$\text{SiH} + \text{H} + \text{H}_2$	113.8
$\text{Si} + 2\text{H}_2$	86.1

### 4. $\text{SiN}_x$ film surface

In order to simulate surface reactions between gas phase species and an  $\text{SiN}_x$  film surface by means of quantum chemistry calculations, cluster models have to be prepared for surface Si and N atoms. Figure 1 shows the  $\alpha$ - $\text{Si}_3\text{N}_4$  structure. The  $\alpha$  form crystallizes in the space group P31c with unit-cell dimensions  $a=7.818 \text{ \AA}$  and  $c=5.591 \text{ \AA}$  [4]. The  $\beta$  form unit-cell dimensions are  $a=7.606 \text{ \AA}$  and  $c=2.909 \text{ \AA}$  in the space group P6<sub>3</sub>/m [4]. Amorphous  $\text{Si}_3\text{N}_4$  is considered to be structured by mainly 6-membered ( $\alpha$  form) and 8-membered ( $\beta$  form) rings and by partly other membered rings, since Si-N bond length and  $\angle \text{SiNSi}$  bond angle of the  $\beta$  form are flexible in the vicinity ( $1.69\text{-}1.73 \text{ \AA}$ ,  $128\text{-}135^\circ$ ) of the energy minimum [5]. In any membered ring, tetrahedral coordination for Si atoms and trigonal coordination for N atoms are conserved. Therefore, in the present work, N-centered  $\text{Si}_2\text{NH}_6$  and Si-centered  $\text{SiN}_3\text{H}_6$  cluster models are used for simulating trigonally coordinated surface N atoms and tetrahedrally co-ordinated surface Si atoms, respectively. In the cluster models, the third neighbour Si or N atoms are replaced by H atoms.

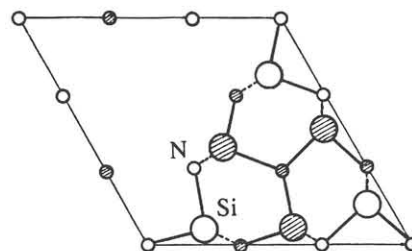


Fig.1. Top view of  $\alpha$  form  $\text{Si}_3\text{N}_4$ . Open and shaded circles indicate the first and the second layer atoms, respectively. Large and small circles show Si and N atoms, respectively. Lines mean chemical bonds except for the unit-cell rhombi.

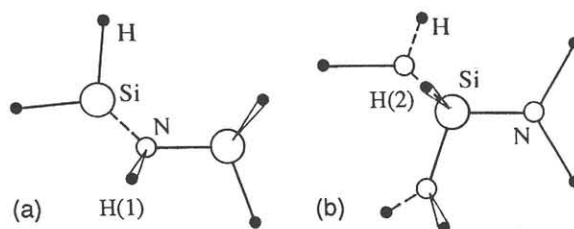


Fig.2. Top views of (a) the  $\text{Si}_2\text{NH}_7$  cluster for a surface N atom, and (b) the  $\text{SiN}_3\text{H}_7$  cluster for a surface Si atom.

In the present work, dangling bonds of surface Si and N atoms in  $\text{Si}_2\text{NH}_6$  and  $\text{SiN}_3\text{H}_6$  cluster models are terminated by H(1) and H(2) atoms as shown in Fig.2, since an H-terminated  $\text{SiN}_x$  CVD film surface model is adopted here. As discussed in the

following sections, surface Si and N atoms unterminated by an H atom cannot react with SiH<sub>4</sub>, NH<sub>3</sub>, SiH<sub>2</sub>, SiNH<sub>5</sub>, and SiNH<sub>3</sub>. Moreover, the chemisorbed Si and N atoms of these species, which become new surface atoms, should be H-terminated, because these species are all H-terminated. Therefore, an Si<sub>3</sub>N<sub>4</sub> film surface is simulated by an N-centered Si<sub>2</sub>NH<sub>7</sub> cluster model and an Si-centered SiN<sub>3</sub>H<sub>7</sub> cluster model as illustrated in Fig.2.

In the total energy calculations, the cluster geometries are fixed at an 1.743 Å Si-N bond length and 109° ∠NSiN bond angle, corresponding to the α form. It is desirable to know the adsorption potential curve depending on the locally optimized Si and N atom positions of clusters. However, the local geometry optimization calculation is not feasible at the present stage of computational ability. Instead of this calculation, other cluster models with C<sub>3v</sub> and C<sub>s</sub> symmetry are examined for the total energy calculation to confirm the computational results.

### 5. Surface reaction

First, by using an N-centered Si<sub>2</sub>NH<sub>7</sub> cluster model, insertion of silylenes into the surface N-H bond are analyzed. Due to the similar insertion mechanism of SiH<sub>2</sub> into NH<sub>3</sub> [3], SiH<sub>2</sub> inserts into an N-H bond of the H-terminated surface N atom, and the Si-N bond is formed as illustrated in Figs.3(a) and (b). This insertion reaction is represented by the following equation in the present work.

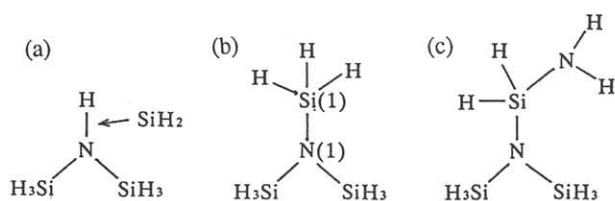
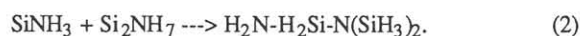


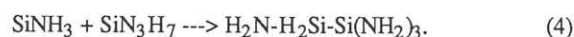
Fig.3. (a) Insertion of SiH<sub>2</sub> into the N-H bond of Si<sub>2</sub>NH<sub>7</sub> cluster, (b) chemisorbed SiH<sub>2</sub> and Si<sub>2</sub>NH<sub>7</sub> cluster, and (c) chemisorbed SiNH<sub>3</sub> and Si<sub>2</sub>NH<sub>7</sub> cluster.

The exothermic reaction energy for this insertion is calculated to be 64 kcal/mol by the RHF/MC-311G(d,p)//RHF/MC-311G(d,p) method. SiNH<sub>3</sub> also attacks the surface N-H bond, and Si-N bond is formed as illustrated in Fig.3(c) with the exothermic reaction energy of 41 kcal/mol.



To estimate the reliability of these reaction energy values, the dependence of the reaction energy on the computational method and the cluster symmetry are investigated. When electron correlation energy for the insertion reaction of Eq.(1) is included by GVB-PP(3)/MC-311G(d,p)//RHF/MC-311G(d,p) calculation, the reaction energy is 61 kcal/mol. If the cluster symmetry in Fig.2(a) is modified to C<sub>3v</sub> by rotating the terminated H atoms around the Si-N bond axis, the reaction energy is 63 kcal/mol. The large exothermic reaction energy for Eq.(1) is almost independent on the computational method and cluster symmetry.

Next, by using an Si-centered SiN<sub>3</sub>H<sub>7</sub> cluster model, insertions of silylenes into the surface Si-H bond are analyzed. SiH<sub>2</sub> and SiNH<sub>3</sub> insert into the surface Si-H bond with the exothermic reaction energies of 47 and 22 kcal/mol, respectively.



Due to these insertion reactions, Si-Si bonds are formed. When electron correlation energy is included by GVB-PP(3)/MC-311G(d,p)//RHF/MC-311G(d,p) calculation, the reaction energies are 41 and 17 kcal/mol for Eqs.(3) and (4), respectively. In addition to the cluster model in Fig.2(b), which corresponds to α-form Si<sub>3</sub>N<sub>4</sub>, the cluster models with C<sub>3v</sub> and C<sub>s</sub> symmetries are prepared by rotating the terminated H atoms around the Si-N bond axis and used for the reaction energy calculations. The obtained values are 46 and 47 kcal/mol. The exothermic reaction energies for Eq.(3) are not so much affected by the computational method and cluster symmetries.

After the insertion reaction of Eq.(1), H<sub>2</sub>-elimination from the cluster occurs as illustrated in Fig.4(a) with the endothermic reaction energies of 54 kcal/mol.



After the insertion reaction of Eq.(3), another H<sub>2</sub>-elimination reaction occurs with the endothermic reaction energy of 65 kcal/mol,



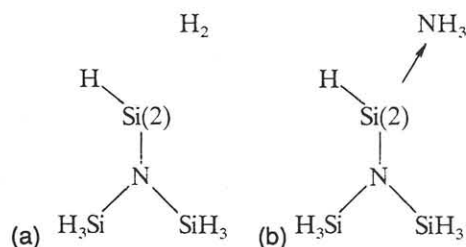
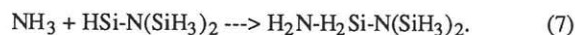


Fig.4. (a) H<sub>2</sub>-elimination from the chemisorbed SiH<sub>2</sub>, and (b) insertion of Si(2) into NH<sub>3</sub>.

H- and H<sub>3</sub>-elimination reactions need very large endothermic reaction energies, and seem not to occur in a conventional SiN<sub>x</sub> CVD reactor. H<sub>2</sub>-elimination from the SiNH<sub>3</sub>-chemisorbed Si<sub>2</sub>NH<sub>7</sub> and SiN<sub>3</sub>H<sub>7</sub> clusters also occur. After these H<sub>2</sub>-elimination reactions, the Si atom has an sp<sup>2</sup>-like molecular orbital. Therefore, the H<sub>2</sub>-eliminated system corresponds to a silylene, and intervenes into an N-H bond of NH<sub>3</sub>. For instance, following the H<sub>2</sub>-elimination reaction of Eq.(5), the chemisorbed Si(2) atom intervenes into NH<sub>3</sub> as illustrated in Fig.4(b).



The reaction energy for this insertion is 60 kcal/mol. The H<sub>2</sub>-eliminated systems are able to intervene not only NH<sub>3</sub> but also silanes.

## 6. Discussion

As described in the previous section, the H-terminated SiN<sub>x</sub> surface model explains the CVD film growth mechanism on an SiN<sub>x</sub> surface in consistency with the insertion and H<sub>2</sub>-elimination reactions. The experimental observations, that many Si-H and N-H bonds are contained in an SiN<sub>x</sub> CVD film, also support the H-terminated surface model. This is because the Si-H and N-H bonds remaining seem to result from missing the insertion and H<sub>2</sub>-elimination reactions of these bonds during the growth.

The CVD film growth mechanism proposed here also explains that the SiN<sub>x</sub> film composition deposited by using SiH<sub>4</sub> and NH<sub>3</sub> is Si-rich. According to the mechanism, Si atoms are incorporated by the SiH<sub>2</sub> and SiNH<sub>3</sub> insertion reactions into the surface Si-H and N-H bonds, while N atoms are incorporated only by the SiNH<sub>3</sub> and Eq.(7) insertion reactions. Therefore, the film composition is inevitably Si-rich. Consequently, in a conventional SiN<sub>x</sub> CVD reactor, NH<sub>3</sub> flow rate has to be much

higher than SiH<sub>4</sub> flow rate to minimize the stoichiometry deviation.

Last, to improve the very thin SiN<sub>x</sub> film quality for a stacked capacitor, we can obtain two predictions from the model for the SiN<sub>x</sub> CVD film growth mechanism. First, if SiNH<sub>5</sub> is used as a source gas instead of SiH<sub>4</sub> and NH<sub>3</sub>, the film composition approaches being stoichiometric. Since the main species produced from SiNH<sub>5</sub> is SiNH<sub>3</sub>, Si and N atoms are mostly incorporated into the film in pairs. Second, a transition layer exists in the SiN<sub>x</sub> film. As mentioned in the introduction of this article, an SiN<sub>x</sub> film is deposited on a native oxide film by using SiH<sub>4</sub> and NH<sub>3</sub>. Since there is no surface Si-H and N-H bonds on the native oxide, heterogeneous three dimensional nucleation of silicon must happen before the subsequent SiN<sub>x</sub> film growth. Therefore, there seems to exist an Si-rich transition layer between the native oxide and the bulk SiN<sub>x</sub> film. The electrical characteristics of stacked capacitor will be much improved, if we can prepare an SiN<sub>x</sub> film without the transition layer.

## 7. Conclusion

The SiN<sub>x</sub> CVD film growth mechanism is explained by the insertions of silylenes into the surface Si-H and N-H bonds and the H<sub>2</sub>-eliminations from the surface, and the H-terminated SiN<sub>x</sub> surface model is successfully adopted to simulate the surface reactions. The proposed CVD mechanism accounts for not only Si-H and N-H bonds remaining in the SiN<sub>x</sub> CVD film but also the stoichiometry deviation. It is predicted that new source gas (SiNH<sub>5</sub>) deposits a stoichiometric SiN<sub>x</sub> film, and that an Si-rich transition layer exists between the native oxide and the bulk SiN<sub>x</sub> film.

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