

## Molecular Orbital Theory Examination into the Improvement of Gate Oxide Integrity with the Incorporation of Nitrogen and Fluorine

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### 1. Introduction

The scaling of thin oxides used in metal-oxide-semiconductor (MOS) devices to thicknesses below 10 nm requires improved film resistance against both the hot-carrier effect and time-dependent dielectric breakdown (TDDB). The incorporation of nitrogen atoms along with rapid thermal processing has been found to alleviate these reliability problems[1]. Also, it has been recently reported that fluorine incorporation in ultrathin gate oxides and oxynitrides ( $\sim 40 \text{ \AA}$ ) has beneficial effects[2]. Although the improved oxide quality brought about by the incorporation of nitrogen or fluorine atoms is usually thought to stem from both the reduction of interfacial mechanical stress between Si and  $\text{SiO}_2$  and the inhibition of atomic hydrogen transport in the oxide[3], these mechanisms have not been clearly demonstrated in experiments. To obtain more robust gate oxides, we really need to clarify the beneficial effects brought about by the incorporation of foreign atoms from an atomistic point of view. In this study, we sought to elucidate these mechanisms explicitly by employing molecular orbital theory. We focused our calculation on the change of chemical bond strength in the oxide before and after hole trapping since the hole transport across ultrathin thermal oxides and oxynitrides is directly correlated to dielectric breakdown[4].

### 2. Analysis

#### Cluster Models

For nitrogen-atom incorporation, we prepared three kinds of cluster models that have different chemical environments around the nitrogen —  $\text{N} \equiv \text{Si}_3$ ,  $\text{O}=\text{N}=\text{Si}_2$ , and  $\text{O}_2=\text{N}-\text{Si}$  — as nitrogen atoms replace oxygen in the oxide upon incorporation. Subsequent incorporation of monovalent fluorine atoms should bring about the replacement of hydrogen atoms that terminate imperfect bonds distributed in the oxide and the interfacial region between Si and  $\text{SiO}_2$ . In this study, Si-F, Si-OF, and  $\text{Si}_2=\text{N}-\text{F}$  were assumed as the resultant structures of the fluorine incorporation. The Si-F bonds may exist mainly at the interfacial region since a *Pb* center, that is, a Si dangling bond, is the major imperfect bond at the interface. On the other hand, Si-OF, and  $\text{Si}_2=\text{N}-\text{F}$  bonds may exist both in the oxide and at the interface. Two cluster models corresponding to nitrogen and fluorine incorporation are shown in Fig.1.

#### Molecular Orbital Program Package

We used a semiempirical program package, MOPAC (Ver. 6.02)[5], to predict the change in the chemical bond properties that accompanied hole trapping. The atomic parameter set "PM3" was specified for the MOPAC calculations. The applicability of MOPAC to the hole trapped state was confirmed

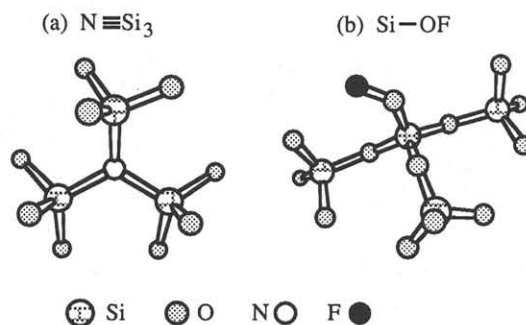


Fig. 1 Examples of model structures thought to be created by the incorporation of N and F into an oxide. Terminating H atoms bonded to the oxygen atoms are omitted for clarity.

by comparing the chemical properties predicted by MOPAC for the hole trapped state of a  $\text{Si}_5\text{O}_{16}\text{H}_{12}$  cluster with those obtained by first-principle calculation[6].

### 3. Results and Discussion

#### Electronic and Structural Change

The electronic structure for neutral and hole trapped states for the nitrogen-incorporated oxide whose structure is shown in Fig. 1(a) is as follows. The valence top orbital of the neutral state is an N 2p non-bonding orbital, which is a lone pair orbital. The band gap energy is almost 9 eV, which is 5 eV higher than that calculated for an  $\alpha\text{-Si}_3\text{N}_4$  crystal by means of first-principle local density calculations[7]. As it is usual for cluster calculations to yield larger band-gap energies compared with those calculated for a periodic system, these electronic energy levels should be considered a qualitative property. After hole trapping, a new energy level appears in the middle of the band gap. Its orbital character is mainly the 2p atomic orbital of nitrogen. This means that the hole positive charge tends to localize on the nitrogen atom rather than on oxygen, while the hole localizes on an oxygen atom in the case of a native oxide. Most of the positive charge around the nitrogen extends only to the neighboring atoms. We observed the same charge localization scheme for all other model clusters containing nitrogen examined in this study. As to the geometrical structure, bond elongation was observed for both the Si-O and the Si-N bonds upon hole trapping as has been reported for native oxide[6]. Although hole trapping usually weakens the chemical bonds near a localization site by removing the bonding electrons and bond elongation is to be expected, the N-O bond actually shrink by about  $0.1 \text{ \AA}$  after hole trapping. This shrinkage of the bond length can be attributed to a decreased electrostatic repulsion exerted by non-bonding electrons of the di-

rectly bonded nitrogen and oxygen. This bond shrinkage suggests that the dissociation energy of the N-O bond should be increased by hole trapping. This increase of dissociation energy will be discussed in the following section.

#### Bond Durability against Hot-hole Injection

The change in the bond dissociation energy that accompanies hole trapping is considered a relevant measure of bond durability against hot-hole injection because the excess energy transferred by a hot hole into an oxide will be dissipated through the excitation of lattice motion and its accumulation will eventually cause bond breakage. (The change in the bond dissociation energy that accompanies hole trapping is summarized in Table 1 for oxide and oxynitride structures.) While the Si-O bond is the most durable structure in the neutral state, it will be greatly weakened by hole trapping. The decrease in its bond dissociation energy is about 2.3 eV. On the other hand, the N-Si bond contained in the  $N \equiv Si_3$  structure exceeds the Si-O bond of the oxide in terms of durability in the hole trapped state, although it is slightly weaker than the oxide in the neutral state. All other bonds contained in the  $O-N=Si_2$  and  $O_2=N-Si$  structures showed an increase in their dissociation energy upon hole trapping and their bond strength exceeded that of the oxide in the hole trapped state. Unfortunately, their bond strengths in the neutral state are much smaller than that of the Si-O bond in oxide and the N-Si bond in the  $N \equiv Si_3$  structures. These results imply that the incorporation of nitrogen into an oxide improves film integrity by increasing the bond resistance to hot hole injection compared to that of native oxide. It follows that the Si-N bond configuration in the  $N \equiv Si_3$  structure should be increased to attain a more robust insulating film in both the neutral and hole trapped states.

The effects of fluorine incorporation following nitrogen incorporation into an oxide are tabulated in Table 2. These results show that the replacement of hydrogen terminating Si dangling bonds with F in the interfacial region significantly improves bond durability in both the neutral and hole trapped states. Thus, a pile-up of fluorine in the interfacial region is desirable to provide interfacial robustness. The weakest bond except for the Si-H bond in both the neutral and hole trapped states is the O-F bond in the Si-O-F structure. Its bond dissociation energy is 0.7 eV lower than that of native oxide in the neutral state and it provides a rather low bond energy, 1.9 eV, in the hole trapped state. It is well known that excessive incorporation of F tends to produce non-bridging oxygen defects in oxides, such as a Si-Si bond[8], which would seem to result in lower robustness due to the increase in the occurrence of the weaker Si-O-F structure and the increased number of conductive Si-Si bonds. The synergetic effect of nitrogen and fluorine incorporation can be seen by comparing the N-H bond in the  $Si_2=N-H$  structure with the N-F bond in the  $Si_2=N-F$  structure. The  $Si_2=N-F$  structure has extremely high durability against holes and sufficient durability in the neutral state. So it is desirable to increase the occurrence of the  $Si_2=N-F$  structure both in oxide and in the interfacial region.

#### 4. Conclusion

The mechanism for the improvement of gate oxide integrity

Table 1 . The dissociation energy change in representative bonds in oxide and oxynitride films that accompanies hole trapping.

Model structure*	Bond	Dissociation energy (eV)		
		Neutral	Hole trapped	Change
Si — O — Si	Si — O	4.9	2.6	- 2.3
Si — N — Si   Si	N — Si	4.0	3.3	- 0.7
Si — N — O — Si   Si	N — Si	2.9	3.0	+ 0.1
	N — O	1.8	3.8	+ 2.0
Si — N — O — Si   O — Si	N — Si	1.8	2.5	+ 0.7
	N — O	1.4	2.4	+ 1.0

\* Oxygen atoms bonded to Si are omitted for clarity.

Table 2 . The dissociation energy change in terminal bonds at the interface between Si and  $SiO_2$  modified with different atoms.

Model structure*	Bond	Dissociation energy (eV)		
		Neutral	Hole trapped	Change
$\equiv Si - H$	Si — H	2.8	0.4	- 2.4
$\equiv Si - F$	Si — F	6.1	2.8	- 3.3
$\equiv Si - O - F$	O — F	2.1	1.9	- 0.2
Si — N — H   Si	N — H	3.6	2.9	- 0.7
Si — N — F   Si	N — F	2.5	3.6	+ 1.1

\* For the top three models, the O-[Si(OH)3] fragments bonded to the terminal Si are omitted for clarity.

through the incorporation of nitrogen and fluorine atoms was extensively examined in terms of molecular orbital theory by considering the chemical bond changes that accompany hole trapping and which cause degradation of the oxide. We found that the robustness against hot-hole injection was significantly improved by the formation of the  $N \equiv Si_3$  structure in the oxide and the Si-F structure in the interfacial region. Also, the synergetic effect of N and F incorporation was due to the formation of the  $Si_2=N-F$  structure in both the oxide and the interfacial region.

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