Stability of Si-O-F low-K dielectrics: Attack by water molecules as function of near-neighbor Si-F bonding arrangements

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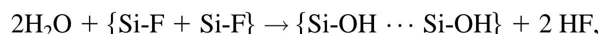
Ab initio configuration interaction calculations have been previously used to account for the relatively large decreases in the static dielectric constant of Si-O-F alloys with low alloy concentrations of F atoms, ~22% for F concentrations of ~10 at. %. The present study addresses the stability of these alloy films with respect to attack of Si-F bonds by water molecules. The present calculations show that the reaction: $H_2O+2Si\text{-}F \rightarrow 2HF+Si\text{-}O\text{-}Si$ is exothermic by about 0.7 eV. Our calculations focus on the reaction energetics and geometries as a function of the distance between the F atoms of the Si-F groups and water molecules. Combining these calculations for interactions with H_2O with a statistical model of bonding in the alloy films as presented in our previous article, an upper limit for chemically stable F corporation has been determined to be ~10–12 at. % F, which corresponds to static dielectric constant of 3.2–3.4. © *1998 American Institute of Physics.* [S0734-2101(98)58303-0]

I. INTRODUCTION

There is considerable interest in insulating films with static dielectric constants, ϵ_s, lower than SiO_2. One alloy system that has attracted considerable attention is Si-O-F or fluorinated silicon oxide, SiO_2:F. Previously we have studied and discussed the reduction of the static dielectric constants of Si-O-F alloy films deposited by chemical vapor deposition with respect to those of similarly prepared SiO_2 films in terms of infrared (IR) absorption spectra and contributions of electronic and vibrational transitions to ϵ_s.[1] *Ab initio* configuration interaction calculations were then used to identify inductive effects of Si-F bonds on the properties of Si-O-Si groups that are back bonded to the Si atom of that Si-F group.[1] Our *ab initio* calculations provide a theoretical framework for understanding why relatively small additions of F atoms to SiO_2, ~10–12 at. %, produce significant decreases in ϵ_s, ~22%, from approximately 4.1±0.1 in SiO_2 deposited by low pressure chemical vapor deposition (LPCVD) to ~3.2–3.4.

The present study addresses the stability of the Si-O-F alloy films with respect to attack of Si-F bonds by water molecules. IR data have shown that the Si-O-F films are hydroscopic.[2,3] Spectra presented in Ref. 3 indicate two features in the OH absorption regime: (i) one with a spectral peak at ~3650 cm^{-1} and an asymmetric line shape that has been assigned to Si-OH groups with H-bonding interactions with a random distribution of O neighbors, and (ii) a second with a spectral peak at ~3300 cm^{-1} and a symmetric line shape that is due to near-neighbor pairs of Si-OH groups.[4] The 3300 cm^{-1} band is assigned to postfilm formation water absorption via the reaction pathway given as:



$$2H_2O + \{Si\text{-}F + Si\text{-}F\} \rightarrow \{Si\text{-}OH \cdots Si\text{-}OH\} + 2\,HF,$$

where the "{ }" notation indicates nearest neighbors and the "···" notation indicates a paired H-bonding interaction, i.e., the H atom of each OH group interacts via a H bond with the O atom of the neighboring OH group. This pairing of OH bonds has also been attributed as H-OH bonding in Ref. 3.

The near-neighbor {Si-OH····Si-OH} configurations can be removed by relatively low temperature thermal annealing as in Ref. 4 via the following reaction:

$$\{Si\text{-}OH \cdots\cdot Si\text{-}OH\} \rightarrow Si\text{-}O\text{-}Si+H_2O$$

so that combined effect of atmospheric exposure and annealing is to reduce the bonded F content. The reaction pathway attack of the Si-O-F film by water was through near-neighbor F atom bonding sites, e.g., those with paired Si-F atom bonding arrangements. Since these dominate when the fraction of Si-F bonding sites occupied exceeds 0.2 of those available, we can expect hydroscopic behavior to become increasingly important when the F atom concentration begins to exceed ~7 at. % (note that for a structural model that assumes only Si-F bonding arrangement complete occupancy of available F atom bonding sites corresponds to ~28.6 at. % F). This restricted bonding model has been assumed for the low F-content alloys of this study.

The present article studies the stability of the Si-O-F alloy films with respect to attack of Si-F bonds by water molecules. Our calculations focus on the reaction energetics and geometries as a function of the distance between the F atoms of the Si-F groups.

II. THEORY AND CALCULATIONS

Total energy calculations are performed using a many-electron embedding theory that permits the accurate compu-

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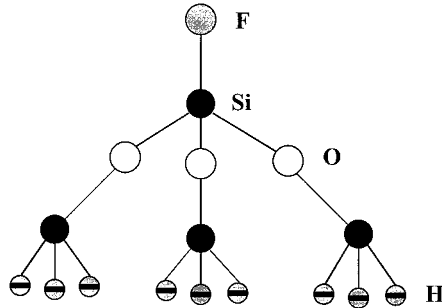

FIG. 1. Cluster geometry used to model the Si-O-F alloy film.

tation of molecule-solid surface interactions. Calculations are carried out at an *ab initio* configuration interaction (CI) level, i.e., all electron-electron interactions are explicitly calculated and there are no exchange approximations or empirical parameters. The details of the method are extensively discussed in Refs. 5–7.

Calculations are performed by first obtaining self-consistent-field (SCF) solutions for the Si-O-F cluster plus water molecule. The occupied and virtual orbitals of the SCF solution are then transformed separately to obtain orbitals spatially localized within the Si-F bonds and H_2O molecule. This unitary transformation of orbitals which is based upon exchange maximization with atomic valence orbitals enhances convergence of the configuration interaction expansion.[5–7]

The dominant SCF configuration with several other configurations, selected with a coefficient >0.05 in the initial expansion, defines the multiconfiguration expansion of ψ_0. Configuration interaction expansions, ψ, are generated from ψ_0, by single and double excitations, to give excited configurations, ψ_k, $\psi=\psi_0+\Sigma_k c_k \psi_k$.

Configurations are retained if an interaction threshold

$$\langle \psi_k | H | \psi_0 \rangle |^2/(E_k-E_0) > 1.0\times 10^{-5} \text{ hartree}$$

is satisfied. In the present work CI expansions contain approximately 5000–7000 configurations. Contributions of excluded configurations are estimated using second-order perturbation theory. The inclusion of several other configurations as reference states besides the SCF dominant configuration increases the correlation energy by increasing variational degrees of freedom.

The Si-O-F cluster used in the present study is shown in Fig. 1. The silicon atom bonded to the F atom is described at an all electron level by Dunning's [6s4p] basis sets contracted from [11s7p] primitive sets of Huzinaga,[8] augmented by a set of d polarization functions with an exponent of 0.4. Other silicon atoms are described at the 3s, 3p valence electron level by a set of double-zeta five term 3s and four term 3p basis functions used by Chattopadhyay *et al.*[9] and a [1s-2p] effective core potential. The double-zeta s and p basis for oxygen and fluorine are taken from Whitten[10] and augmented with a set of *d* functions with the same exponent of 0.8. For the hydrogen atoms saturating the secondary silicon atoms, a double-zeta s basis is used. The hydrogen atoms of the water

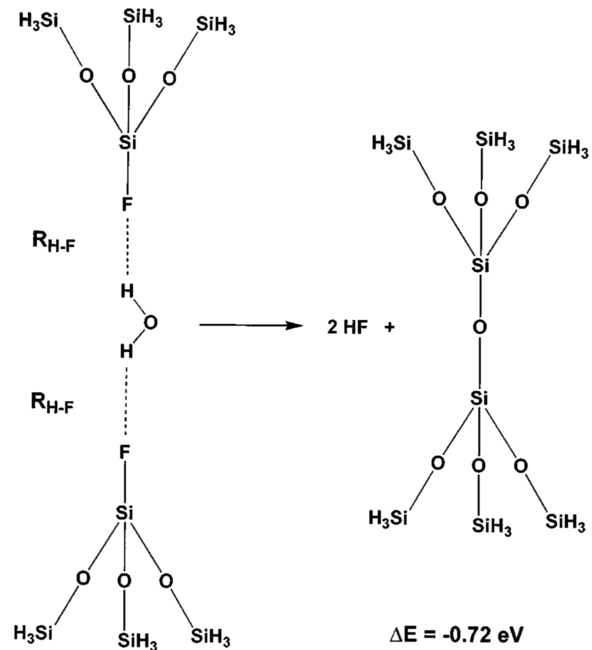

FIG. 2. Reaction energetics and geometries of 2Si-F+H_2O→Si-O-Si+2HF, as calculated by *ab initio* configuration interaction theory.

molecule are described by the same double-zeta basis with an additional set of 2p functions with an exponent of 0.6. All of the basis sets accurately describe the atomic and molecular properties and have been widely used in electronic calculations.[11–13]

III. RESULTS

Figure 2 shows the interaction between H_2O and two neighboring Si-F bonds. The reaction of 2Si-F +H_2O→Si-O-Si+2HF is exothermic by 0.72 eV, as calcu-

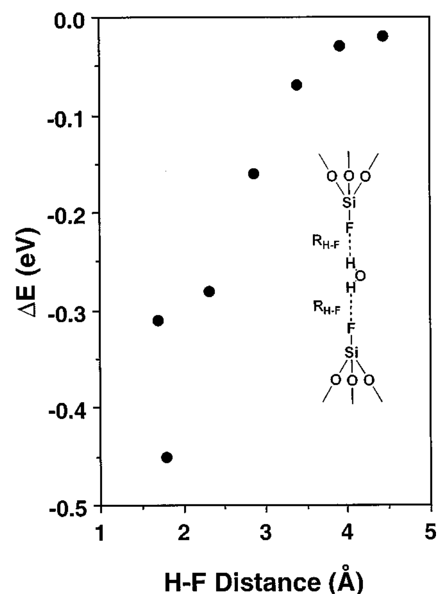

FIG. 3. Interaction energy ΔE vs the H-F distances. ΔE is relative to 2Si-F and H_2O at infinite separation.

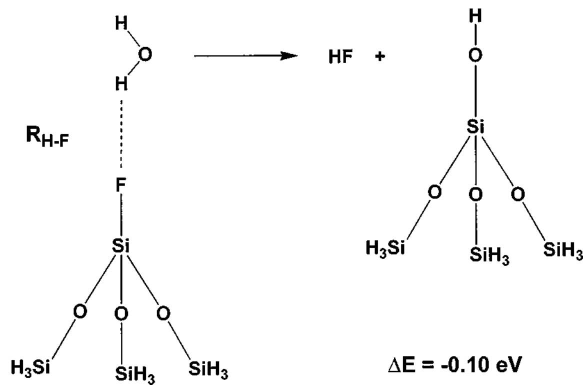

FIG. 4. Reaction energetics and geometries of Si-F+H_2O→Si-OH+HF, as calculated by *ab initio* configuration interaction theory.

lated at the configuration interaction level. Figure 3 shows the reaction energetics of 2Si-F+H_2O as a function of the H-F distances. The energy minimum occurs at R_{H-F}~1.8Å, with the total energy of the system about 0.45 eV lower than 2Si-F and H_2O at infinite separation. The insertion of H_2O into the Si-F bonds is due to the strong hydrogen bonding between F and H atoms.

Figure 4 depicts the interaction between H_2O and one neighboring Si-F bond. The reaction of 2Si-F +H_2O→Si-O-Si+2HF is exothermic only by 0.10 eV. Figure 5 shows the reaction energetics of Si-F+H_2O as a function of the H-F distances. The energy minimum occurs at R_{H-F}~2.2 Å, with the total energy of the system about 0.07 eV lower than Si-F and H_2O at infinite separation.

Our calculations indicated that a water molecule is much more stable when two Si-F bonds are nearby, and that atmospheric exposure is to reduce the bonded F content. The reaction pathway of the interaction of the Si-O-F film and water was via near-neighbor F atom bonding sites, e.g., those

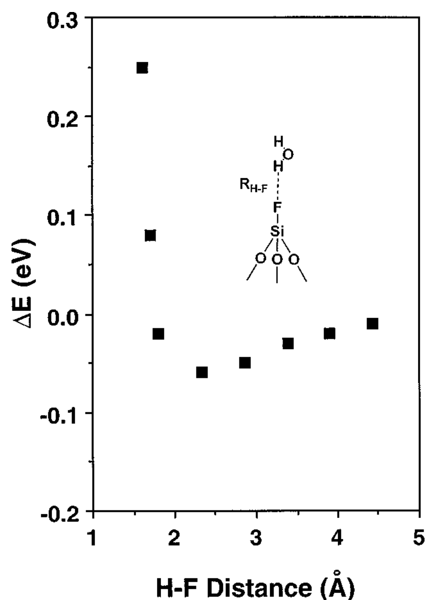

FIG. 5. Interaction energy ΔE vs the H-F distances. ΔE is relative to Si-F and H_2O at infinite separation.

TABLE I. Calculated total energies for molecules and clusters.

Molecule or cluster	Total energies (hartree)	
	SCF	CI
H_2O	−76.0258	−76.1332
HF	−100.0322	−100.1733
F-Si(-$OSiH_3$)$_3$	−629.1628	−629.3298
HO-Si(-$OSiH_3$)$_3$	−605.1321	−605.3192
O-[Si(-$OSiH_3$)$_3$]$_2$	−563.9278	−564.0647

with paired Si-F bonding arrangements. As reported in Ref. 4, since the interaction of 2Si-F + H_2O and thermal annealing dominate when the fraction of Si-F bonding sites occupied exceeds 0.2 of those available, one would expect hydroscopic behavior to become increasingly important when the F atom concentration begins to exceed ~7 at. % (note that complete occupancy of available F atom bonding sites corresponds to ~28.6 at. % F). If the film has been exposed to water vapor resulting in the reduction of the bonded F contents and incorporating nearest-neighbor Si-OH groups, then annealing will always result in an increase in dielectric constant as has been reported in Ref. 3.

Table I lists the total energies as calculated at both self-consistent-field and configuration interaction levels for H_2O and HF molecules and other Si-O and Si-O-F clusters using basis sets discussed in Sec. II.

IV. CONCLUSIONS

In summary, *ab initio* configuration interaction calculations have been used to study the stability of Si-O-F alloy films with respect to attack of Si-F bonds by water molecules. The present calculations show that the reaction: H_2O +2Si-F→2HF+Si-O-Si is exothermic by about 0.7 eV. The reaction energetics is a function of the distance between the F atoms of the Si-F groups and the H atoms of H_2O molecule. Strong hydrogen bonding between H and F atoms is found. Combining these calculations for interactions with H_2O with a statistical model of bonding in the alloy films as presented in our previous article,[1] an upper limit for chemically stable F corporation has been determined to be ~10–12 at. % F, which corresponds to static dielectric constant of 3.2–3.4.

ACKNOWLEDGMENTS

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