

Local Atomic Bonding in Fluorinated Silicon Oxides: Static Dielectric Constant and Chemical Stability

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There is considerable interest in insulating films with static dielectric constants lower than that of SiO₂. One alloy system that has attracted much recent attention is Si-O-F. This paper i) discusses the bonding configuration of F atoms in the SiO₂ network structure and develops a procedure for characterizing composition of these materials in a pseudo-binary alloy notation, ii) explains the reductions in the dielectric constant induced by F atoms in terms of bond-ionicity-controlled contributions from electronic and vibrational dipole transitions, and iii) addresses briefly the chemical stability of the films.

1. INTRODUCTION

There is considerable interest in insulating films with static dielectric constants, ϵ_s , lower than SiO₂.^{1,2)} An alloy system that has attracted considerable attention is Si-O-F: fluorinated silicon oxide, SiO₂:F. This paper i) focuses on the bonding of F atoms in SiO₂, ii) shows that Si-O-F can be described as a pseudo-binary alloy, iii) explains reductions in ϵ_s in terms of bond-ionicity-controlled contributions from electronic and vibrational dipole transitions, and iv) addresses chemical stability. The paper is restricted to alloys with less than ~10 atomic percent (at.%) fluorine since these compositions have a sufficient degree of chemical stability to be used in device applications. The paper draws heavily on published infrared (IR) data,^{1,2)} and on papers presented at the Spring 1996 Electrochemical Society Meeting in Los Angeles, California.³⁾

The important points are i) for incorporation of F to about 10 at.% there are two significant changes in the IR absorption with respect to SiO₂: (a) development of a weak Si-F bond-stretching absorption at ~950 cm⁻¹, and (b) changes in the shape of the Si-O bond-stretching band at ~1070 cm⁻¹, ii) reductions in ϵ_s to values of 3.3±0.1 from 3.8 for F concentrations of 7-10 at.%, and iii) changes in film properties upon exposure to atmospheric water and low-temperature annealing.

2. BONDING OF FLUORINE IN Si-O-F ALLOYS

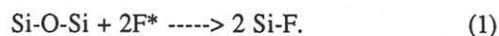
The atomic bonding of univalent atoms or groups in SiO₂ has been previously addressed with emphasis on hydrogen (H) atoms and hydroxyl (OH) groups. In SiO₂:F alloys, F atoms replace the H atoms or OH groups of the hydrogenated SiO₂. The Si-F bond is isoelectronic with the double-bonded P=O group in P₂O₅ glasses, and the Si-F bond-order is also greater than one due to back-donation from filled lone pair-p-orbitals of the F atom into empty anti-bonding states of Si with a d³s symmetry; i.e., $\pi\pi$ - $d\pi$ bonding. The hydroscopic nature of the Si-O-F alloys derives from the terminal Si-F bond, paralleling the behavior of P=O in P₂O₅.

The bonding model is restricted to an alloy regime in which

each Si atom of the host SiO₂ network is bonded to at most one F atom. For compositions to 10 at.% F there is no persuasive spectroscopic evidence for multiple attachment of F atoms as in Si-F₂ arrangements. If monofluoride bonding is taken to the limit of one F atom/Si atom of the Si-O network, then the resulting composition is Si₂O₃F₂. These fluorinated oxides can then be described as a homogeneous mixture of SiO₂ and Si₂O₃F₂, so that a pseudo-binary alloy notation can be used: (SiO₂)_x(Si₂O₃F₂)_{1-x}. The alloys lie on the join-line between SiO₂ and Si₂O₃F₂ in a ternary composition diagram. Once the at.% F is fixed, the ratio of Si to O is also fixed. The number of Si-O bonds/Si atom = $N_{Si-O} = (6-2x)/(2-x)$, and the number of Si-F bonds/Si atom = $N_{Si-F} = (2-2x)/(2-x)$. Figure 1(a) contains N_{Si-O} and N_{Si-F} and Fig. 1(b) contains the alloy fractions, [Si], [O] and [F], both as functions of x.

The proximity of near-neighbor F atoms can have an effect on alloy stability with respect to interaction with atmospheric water vapor. For the alloys with one F atom per Si atom, the statistical probability of F atoms being on nearest neighbor Si atoms is given by $\{[F]/[Si]\}^2$, so that the fraction of neighboring Si-F groups is approximately 10% for an alloy with 7 at.% F.

The changes in the line shape of the dominant Si-O bond-stretching vibration of the Si-O-F alloys are similar to those induced by the post-film formation addition of OH groups through interactions with atmospheric H₂O,⁴⁾ suggesting that incorporation takes place during deposition via a reaction in which the most strained Si-O bonds are removed; i.e.,



This suggests that near-neighbor Si-F bonding arrangements may not be completely random as in the calculation discussed above. Structure in the Si-F bond-stretching band is also consistent with near-neighbor Si-F bonding groups.⁵⁾

3. DIPOLE CONTRIBUTIONS TO ϵ_s

ϵ_s can be expressed as a sum of i) the optical frequency dielectric, ϵ_0 , which includes the integrated contributions of

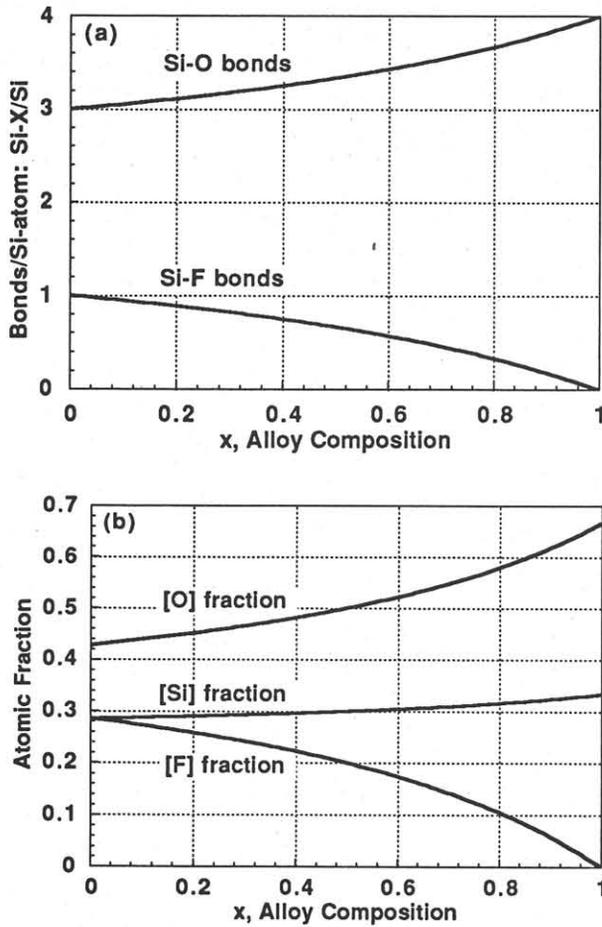


Figure 1. (a) Si-F and Si-O bonds/Si atom as a function of x . (b) Atomic fractions of Si, O and F as a function of x .

all of the electronic transitions, and ii) a sum over the contributions from specific types of IR-active vibrations.² IR studies indicate significant reductions in absorption associated with Si-O-Si bond-stretching modes as F is added to the alloy,^{1,2} as well as a weak IR response for the Si-F bond-stretching mode, so that the substitution of F for O leads to a significant reduction in the contribution of the vibrational modes to ϵ_s . ϵ_s can be written as a three-band Penn model,⁶ as in Eqn. (2)

$$\epsilon_s = 1 + \left\{ \frac{E_p^E}{E_g^E} \right\}^2 + \left\{ \frac{E_p^{VSiO}}{E_g^{VSiO}} \right\}^2 + \left\{ \frac{E_p^{VSiF}}{E_g^{VSiF}} \right\}^2 \quad (2)$$

where i) E_p^E is an effective electronic plasma frequency, ii) E_g^E is an effective optical band-gap, and iii) E_p^{VX} and E_g^{VX} are vibrational frequency analogs of E_p^E and E_g^E , reflecting the separate contributions from $X = \text{Si-O}$ and Si-F vibrations. The first two terms are ϵ_0 :

$$\epsilon_0 = 1 + \left\{ \frac{E_p^E}{E_g^E} \right\}^2 \quad (3)$$

Relations between the vibrational and plasma terms in Eqn. (2) and vibrational frequencies and IR effective charges can be obtained from i) the macroscopic equations that relate transverse optical (TO) and longitudinal optical (LO) frequencies to IR oscillator strengths, and ii) the Lydanne-Sachs-Teller relationship.

4. BOND-IONICITY REDUCTIONS IN ϵ_s

To illustrate how increasing bond-ionicity reduces ϵ_s , the contributions from electronic and vibrational excitations are discussed for a series of Si-based materials in which bond-ionicity increases: crystalline Si, crystalline Si-C, amorphous SiO_2 and Si_3N_4 , and amorphous Si-O-F alloys. The ionicity of each of these materials is characterized by a partial charge obtained from the electronegativities of their constituent atoms. Using the Sanderson approach,⁷ an effective electronegativity (X'_A) is calculated for each of the materials (A_nB_m) according to the relationship in Eqn. (4):

$$X'_A = X'_B = \{(X_A)^n(X_B)^m\}^{1/(n+m)} \quad (4)$$

Using the values of X'_{Si} for Si from Eqn. (4), the Si-atom partial charge, e_{Si} , is calculated from Eqn. (5):

$$e_{Si} = \frac{X'_{Si} - X_{Si}}{2.08\sqrt{X_{Si}}} \quad (5)$$

where X_{Si} is the electronegativity of a Si atom in a purely covalent bond, as in crystalline Si. Figure 2(a) contains plots of ϵ_0 and ϵ_s as functions of the Si partial charge. The difference between ϵ_s and ϵ_0 is the contribution from the vibrational modes and is shown in Fig. 2(b). As the partial charge of the Si atom increases (always positive), the contribution of the vibrational modes decreases. The contribution of the vibrational modes to ϵ_s depends on the ratio of a plasma frequency to a vibrational bandgap or average TO frequency. Two factors contribute the trend in Fig. 2(b): i) decreases in the IR effective charge with increasing bond ionicity, and ii) increases in the effective TO frequency with increasing ionicity.

The microscopic mechanisms that underpins the reductions in ϵ_s is based on two contributions to the IR effective charges, e^* : i) a static contribution that is determined by the bond-ionicity, and ii) a dynamic contribution that derives from charge redistribution during the atom motion of the IR active vibrations. The signs of these two contributions are always opposite. For example for the bond-stretching vibrations which make the dominant contributions to ϵ_s , the dynamic contribution is always in a direction which promotes neutral atom bonding, and hence is always of the opposite sign as the static contribution. Therefore the addition of F to SiO_2 has two effects on the bond-stretching vibrations: i) it replaces Si-O bonds with Si-F bonds that have a weaker IR e^* , and ii) by increasing the partial charge on the Si atoms, also decreases the e^* 's of the remaining three Si-O vibrations. Similar arguments apply to bond-bending modes (Fig. 2 of Ref. 2).

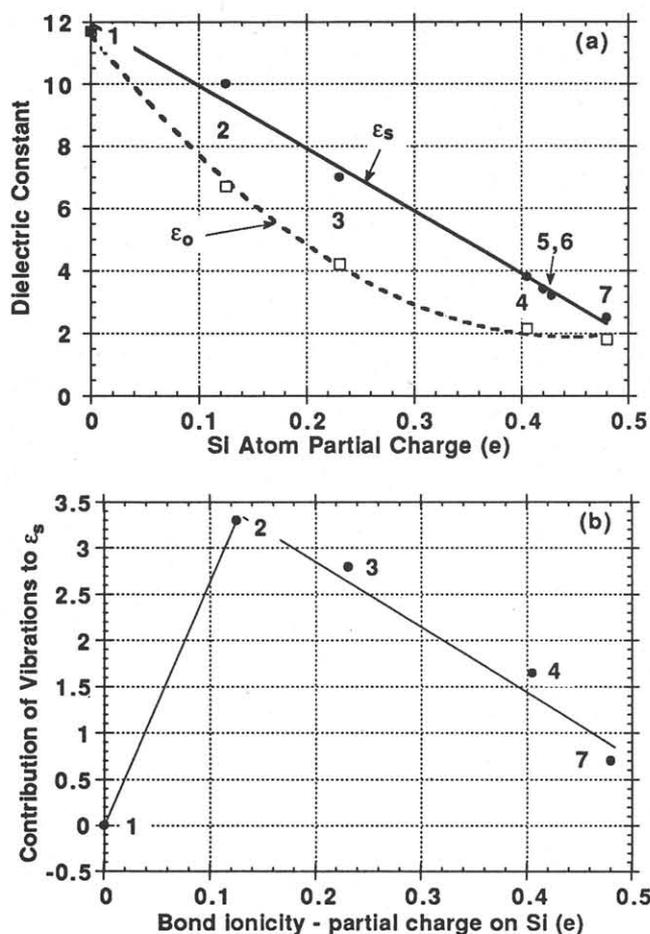
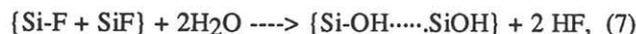


Figure 2. (a) Static and optical frequency dielectric constants versus Si atom partial charge. (b) Contribution of vibrational modes to the static dielectric constant. Legend: 1 = crystalline Si; 2 = crystalline SiC; 3: amorphous SiO₂; 4 = amorphous Si₃N₄; 5 and 6 = Si-O-F alloys with 7 and 10 at.% F respectively; and 7 = extrapolated values for the compound composition Si₂O₃F₂.

5. CHEMICAL STABILITY

Experiments have shown that the Si-O-F films are hydroscopic. Spectra presented in Ref. 2 indicate two features in the OH absorption regime: i) one spectral peak at about 3650 cm⁻¹ and an asymmetric lineshape that is assigned to Si-OH groups with H-bonding interactions with a random distribution of O neighbors, and ii) a second spectral peak at ~3300 cm⁻¹ and symmetric lineshape due to near-neighbor pairs of Si-OH groups.⁴⁾ The 3300 cm⁻¹ band is assigned to post deposition H₂O absorption by the reaction:



where the { } notation indicates nearest-neighbors and the "...." notation indicates a paired H-bonding interaction; i.e., the H atom of each OH groups interacts via a H-bond with the O

atom of the neighboring OH group. This pairing of OH bonds has been designated as H-OH bonding (see Ref. 2).

The near-neighbor {Si-OH.....SiOH} configurations can be removed by relatively low temperature (<300°C) thermal annealing via the following reaction:



so that combined effect of atmospheric exposure and annealing is to reduce the bonded F content.

6. CONCLUSIONS

The main points are: i) for relatively small additions of F to SiO₂, up to 10 at.%, there is one terminal F/Si; ii) the statistical probability of nearest-neighbor Si atoms having F atom neighbors is small, at most 10%, however, IR spectra suggest significantly more pairing; iii) alloy compositions with small additions of F can be described in terms of a pseudo-binary notation, (SiO₂)_x(Si₂O₃F₂)_{1-x}, from which alloy atom and bonding configurations can be computed; iv) the primary factor contributing to decreases in ε_s in these alloys is a decrease in the contributions from the vibrational modes; v) the replacement of O with F has two effects on the IR effective charges which determine the absorption strengths: a) Si-F vibrations have lower e*^s than Si-O vibrations, and b) the increased partial charge on the Si reduces the e*^s of the three remaining Si-O vibrations; vi) the hydroscopic nature of the Si-O-F alloys is related to Si-F bonding, predominantly near-neighbor Si-F groups; and vii) there are no other inorganic dielectrics based on alloy formation with SiO₂ that can yield lower values of ε_s, so that the alloy approach to the so-called low-k dielectrics is limited to reductions of ε_s to values between 3.2 and 3.4. Finally, the chemical stability of with respect to atmospheric H₂O is determined by reactions in which OH groups from ambient water replace F bonded to Si to form HF. Thermal annealing then releases H₂O with a reduction in the number Si-F bonding arrangements.

7. ACKNOWLEDGMENTS

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8. REFERENCES

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