First-principles study of the effects of halogen dopants on the properties of intergranular films in silicon nitride ceramics

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The nanoscale intergranular films that form in the sintering of ceramics often occur as adherent glassy phases separating the crystalline grains in the ceramic. Consequently, the properties of these films are often equal in importance to those of the constituent grains in determining the ceramic's properties. The measured characteristics of the silica-rich phase separating the crystalline grains in Si_3N_4 and many other ceramics are so reproducible that SiO_2 has become a *model* system for studies of intergranular films (IGF's). Recently, the influence of fluorine and chlorine dopants in SiO_2-rich IGF's in silicon nitride was precisely documented by experiment. Along with the expected similarities between the halogens, some dramatically contrasting effects were found. But the atomic-scale mechanisms distinguishing the effects F and Cl on IGF behavior have not been well understood. First-principles density functional calculations reported here provide a quantum-level description of *how* these dopant-host interactions affect the properties of IGF's, with specific modeling of F and Cl in the silica-rich IGF in silicon nitride. Calculations were carried out for the energetics, structural changes, and forces on the atoms making up a model cluster fragment of an SiO_2 intergranular film segment in silicon nitride with and without dopants. Results show that both anions participate in the breaking of bonds within the IGF, directly reducing the viscosity of the SiO_2-rich film and promoting decohesion. Observed differences in the way fluorine and chlorine affect IGF behavior become understandable in terms of the relative stabilities of the halogens as they interact with Si atoms that have lost one if their oxygen bridges.

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I. INTRODUCTION

Ceramics are heterogeneous multiphase materials containing not only crystalline phases, but also phases lacking long range order. The matrix in which the crystallites are bound is such a phase, and it often appears as an ultrathin (nanoscale) film between counterpoised grains. Intergranular films form in the initial stages of sintering, e.g., in the silicon nitride ceramics, from melting of a native surface oxide on grain surfaces of the starting nitride powder. The viscous intergranular film is subject to capillary forces and thins by flow of the glass from the grain boundary volume into triple pockets, etc. As the vitreous IGF is compressed by mutually attracting grains,[1] repulsive back forces (*steric forces* in the model of Clarke[2]) originating within the film increase and balance the forces exerted on the IGF by the opposing grains. Under conditions that allow equilibrium to be attained, the IGF thickness reaches a characteristic value that is frozen in on cooling. With such factors determining film thickness, it is clearer, though no less remarkable, that the thickness of such films is frequently observed to be constant[3] to a few tenths of a nanometer, and thus uniform between adjacent parallel grain surfaces. Only a few basic SiO_2 tetrahedral units span the thickness of such IGF's—these are inherently *nanoscale* structures. Film properties and behavior are expected to reflect atomic-level interactions, such as the bonding characteristics of the oxygen-bridged tetrahedra, rather directly, and dopant effects should be readily apparent for the same reason.

Intergranular films remain an important issue in ceramic science by virtue of their widespread occurrence and strong influence on mechanical properties (e.g., toughness, strength and creep resistance). For example, the use of ceramics in structural applications is always limited by their lack of ductility and low fracture toughness. The associated failure mechanism by brittle crack propagation[4] clearly depends strongly on bonding properties at the IGF/crystallite interface. Because intergranular films are most often ''weak links'' and show lower softening or melting points than the more refractory reinforcing grains in ceramics, they have traditionally been viewed as a problem whose presence should be minimized. However, recent debonding experiments[5–7] have shown that IGF's can be used to *enhance* fracture toughness, **if** their interfacial chemistry can be controlled and understood. For example, sintering aids can be selected to control the composition and growth of epitaxial phases that directly influence the adherence between intergranular films and reinforcing grains.[8–10] This is a central issue in ''debonding behavior'' and has stimulated research to understand intergranular chemistry and bonding at the IGF/crystallite interface at the atomic level.

Efforts to characterize ceramics at the atomic scale have faced many challenges in the past. However, refinements in processing procedures[11,12] have so advanced sample repro-

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ducibility that experimentation previously found only in basic studies of laboratory specimens is now routine for selected ceramics. With the discovery of the nanometer scale dimensionality and great importance of IGF's in silicon nitride (and other) ceramics, numerous basic experimental[5,13] and theoretical studies[1,14–18] have now appeared.

The mechanism of introducing halogen anions into the IGF sets the basis for the conceptual framework of this study and is briefly described here. Carbon, part of a carrier group along with F (or Cl), drives a reaction in the sintering step, but is not itself incorporated in the glass. In the case of F doping,[19] F-C-F fragments formed in the thermal decomposition of polytetrafluoroethylene are the carrier groups. The reduction of bridging oxygen atoms to form CO proceeds with detachment of the pair of fluorine atoms. Simultaneously, each fluorine atom interacts with the near Si atom neighbor, such that a fluorine pair locate at the position of the former O bridge, consistent with valence rules. A similar mechanism occurs in the introduction of chlorine by the addition of hexachloroethane.[20] This reaction mechanism is then a classic example of simultaneous electrophilic and nucleophilic attack at a bridge site as carbon is oxidized and the fluorine atoms bond with the pair of under-coordinated Si atoms. The reaction is clearly a critical step to all the effects that follow, but it is a separable event and the subject of another study. In this work, modeling begins with the IGF in the stage following CO evolution, when a distribution of bridging-oxygen atoms have been replaced by pairs of halogen ions.

Halogen interactions with silica are both common and important, as illustrated by fluorine-doping for control of the dielectric properties of silica,[21] its use in the elimination of surface hydroxyl ions,[22] and the removal[23] of native oxides. By Pauling's ordering of atoms, fluorine and chlorine are, respectively, first and third most electronegative atoms that can be used in dopant studies (oxygen is second strongest). Consequently, characterization of the effects of F and Cl doping in model Si_3N_4 ceramics[24] has been extensive, including HRTEM (Refs. 19,20,25) and internal friction measurements[26,27] of high-temperature mechanical properties. It is observed that structural changes induced at the subnanometer scale by these anions correlate with changes in mechanical properties at the macroscopic level.[24,28] While both anions induce bond-breaking effects, differences are also found. For example, F doping is found to increase the film thickness uniformly by 0.1 nm over the 1.0 nm thickness of the undoped reference case. However, the effects of Cl doping are nonuniform, with some IGF's expanded to thicknesses of 1.3 nm. Understanding the origin of these effects clearly requires investigation at the atomic level. Since F and Cl display both similar and contrasting effects,[25] they are particularly interesting for first-principles study within a comparative basis.

Principal questions that surround the behavior of simple halogen anions in silicon nitride include the following. (i) What are the changes in bonding within the IGF caused by halogen-dopants, and how do those changes lead to a reduction in viscosity of the IGF? (ii) What is the mechanism leading to increases in IGF thickness in F- and Cl-doped films? (iii) Why are the effects of F and Cl similar in some regards, while they are in marked contrast for others? For example, why is the concentration of F within the doped IGF so high, compared with that of Cl? Why is the F-induced expansion constant, whereas the expansion produced by Cl is variable? The experimental data that raise these questions has been reported in a comprehensive series of recent papers.[19,20,24–28] Those observations will be briefly described later in connection with the first-principles results that answer the specific questions.

II. ATOMIC CLUSTER STRUCTURAL MODELS AND THE PARTIAL-WAVE SELF-CONSISTENT FIELD APPROACH

For vitreous materials, there is no unique unit cell to guide in constructing a cluster model of a fragment of the IGF, in distinction to the case of crystalline solids. However, in silica, the integrity of the basic structural units is maintained (distinguishing the vitreous glass from general amorphous solids). So SiO_4 tetrahedra are taken as building blocks of the cluster models used in this work, however the atoms are *not* constrained to the initial positions in the self-consistent calculations. By reducing symmetry constraints in the calculation, the absence of crystalline symmetry is readily handled—the atoms relax to stable positions according to the calculated force field. The challenge then becomes selection of a particular configuration of SiO_4 tetrahedra that can respond accurately to anisotropic stress fields in the film.

In order to address the expansion effect, first consider an array of basic tetrahedral units of SiO_2 that are joined to make up a segment of the silica network across the intergranular film. A set of possible IGF linkages makes up a nonunique distribution, with members ranging from those parallel to the boundary, to those that are perpendicular to the interface. These latter ''normal'' linkages make up the shorter components of the distribution and are likely the most effective in transmitting structural change at an O-bridge site to a change in film thickness (see IGF-spanning cluster shown in Fig. 1). While the silica tetrahedra can easily bend over a large angular range about an O bridge (subject to the constraints of corner connectivity) bond length changes typically require greater forces (except very close to equilibrium). Compressive forces acting on the low-viscosity glassy IGF should first result in angle bending about vertices of the tetrahedra, as SiO_2 linkages become more aligned by the stress field. Required variational freedom for such distortions is allowed in the low symmetries of the clusters used in the calculations described later (e.g. C_{2v} as in Fig. 1). Bonds in each tetrahedron are free to reorient and change length, consistent with the overall symmetry and the steric constraints of maintaining corner connectivity of the tetrahedra. But the greatest *force response*, either to external pressure or to expansion effects on doping, occurs in the Si-O-Si bonds oriented *normal* to the IGF plane. However, the film thickness in *undoped* systems is observed to be insensitive to adjoining grain boundary structure, suggesting that the factors which determine the thickness do not depend on details of how the SiO_2 linkages terminate at the grain faces. Lastly,

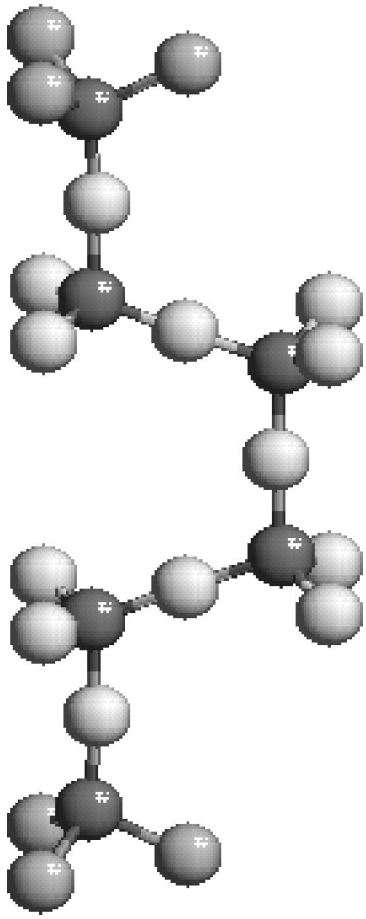

FIG. 1. Cluster model of coupled SiO_4 tetrahedra spanning glassy intergranular film (IGF). Fragment terminates with surface SiN_3 groups of Si_3N_4 grains defining IGF. In grey-scale Si atoms are shaded dark, N medium, and O light.

this invariance to grain surface structure suggests that film thickness is predominantly determined by the *internal* character of the film itself, as well as any modifier of that character.

The undoped fragment cluster links two facing Si_3N_4 grain boundaries. It is made up of coupled basic tetrahedral SiO_4 units, spanning the thickness[29] of the undoped IGF and initially aligned normal to the IGF surfaces, as in Fig. 1. This cluster is expected to be sufficiently realistic to calculate the response of the actual IGF to changes in (a) internal forces of chemical origin and (b) ''external'' pressure from the grains. If the calculated thickness of this host cluster is acceptable, the effects of anion doping will be well represented in this model linkage. This criterion is actually stronger than necessary, since the object of the study concerns a *difference* between the doped and undoped cases.

Beginning with an SiO_4 unit at the silicon nitride boundary, terminal oxygen atoms of the IGF can form O-Si bonds with Si atoms of the grains. An orientation of the O-Si bond *normal* to the grains is preferred on steric grounds (SiO_4 tetrahedral units are not normally observed to share edges or faces). We then complete the linkage by inserting SiO_4 tetrahedra to join these, forming the fragment of the IGF shown in Fig. 1. The outermost oxygen atoms in this fragment bond with Si sites of the Si_3N_4 grains. Nitrogen atoms exposed at the surface of the Si_3N_4 grains bounding the IGF are not favored to bond with the terminal oxygen atoms of the SiO_4 units. However, N atoms are included in the cluster (as part of the nitride grain) in order to complete the chemical coordination of the Si atom in the *grain surface* and provide better boundary conditions for the cluster. The stoichiometry of the IGF-spanning cluster appearing in Fig. 1 is correctly that of SiO_2, allowing a reduction factor for the outer oxygen atoms that are shared by Si atoms outside this *active* cluster. For a fluorine pair in the cluster, the predicted F concentration is also consistent with that measured experimentally [25 atom % F/(F+O) ratio]. The effect of any nitrogen in the IGF film is ignored in this calculation. While the amount may be non-negligible [an N/(N+O) ratio of about 0.30 ± 0.12 is quoted for the undoped case by Yoshiya *et al.*[14]], nitrogen in the IGF can only participate as a next-near neighbor to the O bridges, where its effect is found to be similar to that of oxygen.

Observed properties of silica-rich glassy intergranular films reflect strong localized bonding and the lack of long-range order. A number of different theoretical techniques can be applied in this case, each offering various advantages.[30–35] The formal basis for the calculations in this work is the local density approximation[36] (LDA) in its spin-polarized form, using the exchange-correlation functional of Vosko, Wilk, and Nusair.[37,38] Gradient corrections[39,40] that go beyond the LDA were also calculated to assess their importance for this system. Since these additional terms did not affect any of the initial findings obtained with the simpler LDA, the energies quoted in text were calculated without such corrections.

The partial-wave self-consistent field (PWSCF) atomic cluster method[35] was used to solve the LDA equations. This is a linear variational technique based on partial-wave expansions for charge densities and Coulomb potentials on the atomic sites. Orbital basis sets of unrestricted radial form can be used, such as numerical orbitals, Gaussian functions, etc. Gaussian basis sets of double-zeta plus polarization quality[41] (including supplementary functions of higher atomic l values) were used in these calculations. This method is particularly well suited for low symmetry systems with strongly localized bonding, but requiring completeness and high precision in the self-consistent calculation of the ground state electronic structure and associated quantities (total energy, equilibrium structure, interatomic forces, etc.) Atom positions were allowed to change according to the calculated force field until full relaxation was achieved (or a specific boundary pressure was attained).

Properties exhibit different degrees of localization, and the property of interest dictates the cluster size needed for convergence. In pure and doped silica, the local bond character and equilibrium bond lengths and angles are adequately given by clusters of minimum size[42] (number of active atoms, $N<10$). On the other hand, to accommodate more long-ranged character in the strain field, and to calculate the magnitude of the film expansion directly, the larger interface-

spanning cluster (Fig. 1) was used ($N=25,26$). In this case, the pressure effects of the cluster's environment can be of central importance. *Electronic structure* effects involving distant atoms can be safely omitted for this study; however, an SiN_3 group was included in the active cluster as part of the Si_3N_4 grain interface. The embedding force-field representation of more distant atoms of the crystallite was evaluated for each of the terminal active cluster atoms. The effective force values were obtained from force-separation curves calculated for small Si-(O,N) clusters.

III. FIRST-PRINCIPLES RESULTS

The first structural model for the calculations in this work is geometrically similar to the point ion model introduced by Pezzotti *et al.*[26] As in that work, it is assumed that dopant-anions are incorporated into the SiO_2 network at former bridging oxygen sites, defining an initial configuration for calculation of the relaxed structure. The minimum size host cluster for modeling this bridge-site reaction includes a central O-bridge site and its near and next-nearest neighbors (two Si atoms and the three O atoms bonded to each Si, respectively). While the potential shortcomings of modeling large systems with small cluster fragments are well known,[43] bond localization is so strong in SiO_2 that nearly every aspect of doping is given adequately by these minimal-size clusters, as judged from results for larger cluster models described later. Formula units for the host and F-doped clusters are, respectively, Si_2O_7 and $Si_2F_2O_6$ (structurally, $O_3Si\text{-}O\text{-}SiO_3$ and $O_3Si\text{-}F\cdots F\text{-}SiO_3$).

Beginning with these smaller "primitive" clusters, the local density equations were solved self-consistently, allowing the atoms to relax to the equilibrium structure. Calculation of the *formation energy* of the $Si_2F_2O_6$ fragment cluster from reactants, silica and CF_2, tests the proposed mechanism of anion insertion into the former O-bridge site.[26] The LDA calculation of the formation energy indeed determines a higher stability of the reaction products (in large part due to the highly exothermic carbon oxidation).

A. IGF bonding and viscosity

Anion doping is observed to dramatically affect the high temperature mechanical properties of the silicon nitrides. The most important result of the fluorination (-O- replacement by -F···F-) and chlorination is a local depolymerization of the glass network. This is observed in several ways. A significant reduction in the softening temperature of the vitreous IGF takes place, as evidenced by internal friction data acquired using a torsion pendulum apparatus that measures the internal friction related to grain boundary sliding under stress.[19,26] Mechanical spectroscopy measurements carried out for anion-doped samples and the "clean" reference material at very high temperatures provided quantification of temperature-dependent viscosity changes in the IGF. Specifically, analysis of structure in the internal friction *versus* temperature curves (see Fig. 2) shows grain-boundary relaxation peak shifts that correlate with anion concentration and indicate a general *reduction* in the effective viscosity of the IGF

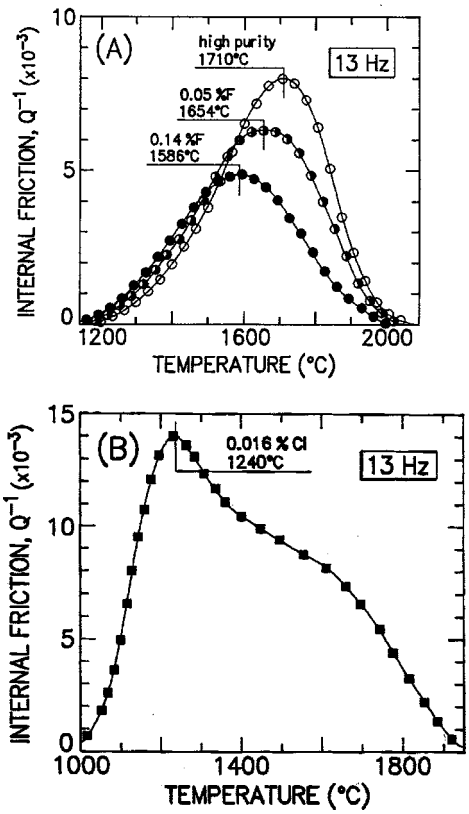

FIG. 2. Comparison of high temperature internal friction measurements for (A) F-doped and (B) Cl-doped samples showing multipeak structure that differentiates viscosity effects produced by intergranular F and Cl in Si_3N_4. Deconvolution indicates three separate peaks in Cl-doped material (B); one peak appears in position of that for *undoped* samples.

with increasing anion concentration. The reduction in viscosity is also associated with markedly higher creep rates.[24] Observed transitions from mainly transgranular to intergranular fracture upon anion doping[26] also indicate a reduction in cohesive strength within the IGF and/or at the IGF/grain boundary interface. These results support earlier work which showed the incorporation of anions significantly decreases a ceramic's resistance to both creep and subcritical (initial stage) crack growth.[28]

How do the model calculations explain these findings? In general terms, breaking oxygen bridge bonds (and reduction of the restoring force between structural units) affects mechanical properties that depend on network connectivity in a straightforward and obvious way. Calculations show that as a result of the anion-doping reaction, local decohesion within the IGF is induced, as previously strong O-bridged fragments of the glassy network become essentially free to move apart, i.e., network bonds are broken. Results show that as a consequence of the strong Si-F bond that forms in F doping, each pair of participating O-bridged tetrahedral units of the glass network are transformed into two stable, but weakly interacting, SiO_3F tetrahedra. Although this structure is more stable than the pair of O-bridged SiO_2 units, chemical displacement of the bridging-oxygen atom is not completed simply by the nucleophilic action of fluorine on Si. The total

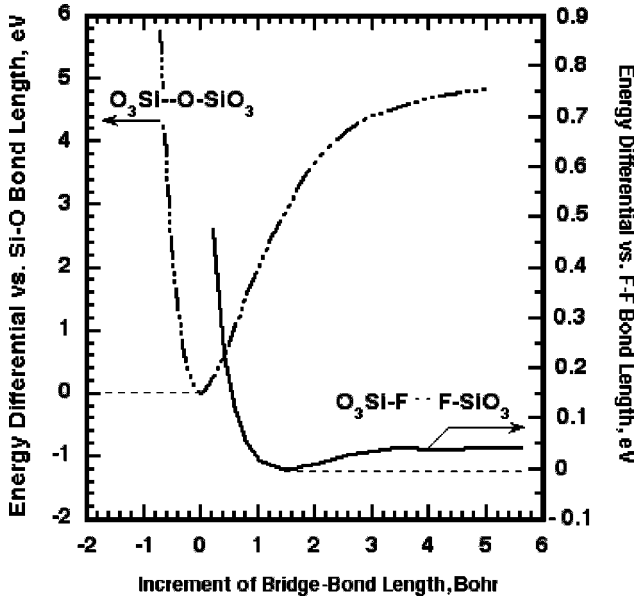

FIG. 3. Binding energy curves calculated for cluster fragments of: (upper) undoped O-bridged SiO_4 units and (lower) doped F···F linked SiO_3F tetdrahedra. Abscissa measures displacement of one tetrahedral unit from the other relative to stable Si-O bridge-bond length (3.014 Bohr). Shallow energy minimum in doped case indicates weak coupling and vanishingly small restoring forces over large region.

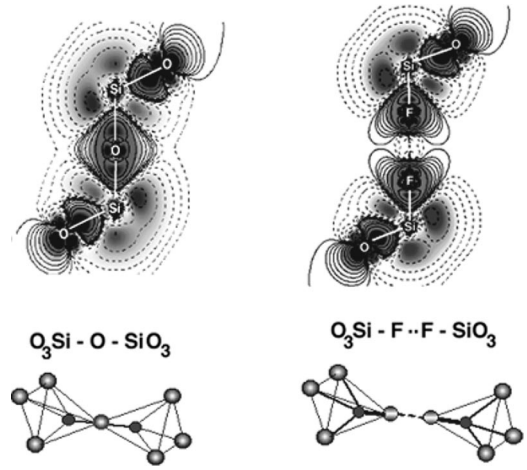

FIG. 4. Charge density difference plots comparing charge redistribution in an O-bridged fragment of SiO_2 (left) and the same cluster with F···F replacement of the bridging O (right). Plot plane includes major symmetry axis and plane of cluster; solid contour lines denote increased density and dashed lines represent decreased density. Adjacent contours differ by a factor of 1.8.

energy calculations show that the mechanism of joint electrophilic-nucleophilic action is needed to break the polymeric linkage, just as in other fluorine reactions with SiO_2-rich interfaces.[23] The simultaneous electrophilic attack of C on the bridging oxygen atom is the driving mechanism that allows the reaction to proceed readily.

How do these alterations of intergranular bonding reduce the viscosity? Consideration of the forces in the IGF fragment reveals the answer. Accurate force fields are calculated within the PWSCF method, however, for this discussion forces are estimated from the slope of the energy curve vs a structural parameter of the system. In Fig. 3, binding energy curves are compared for increasing the distance between (rigid) tetrahedral units that are (a) oxygen-bridged and (b) linked by the -F···F- unit (see bottom Fig. 4 for corresponding ball and stick drawings.) Comparison of the behavior of restoring forces between O-bridged SiO_2 units and F···F linked units shows that local mechanical properties differ markedly at this scale. For purposes of shape comparison, the energy curves are plotted with respect to a common coordinate (measure of displacement of tetrahedral groups relative to the Si-O equilibrium bond length) and referred to their respective energy minima (the zero of energy of the F-doped system has been raised about 1.76 eV to place the curves closer together in Fig. 3; note also the order of magnitude change of scale for energies of the F-doped cluster). As the SiO_3F units are displaced along the dissociation path shown in Fig. 3, there are three principal features of note: (1) a repulsive barrier between the SiO_3F units for $r < 1.0$ Bohr (corresponding to F-F separations < 4.0 Bohr), (2) fragment equilibrium given by a weak energy minimum, corresponding to a separation between fluorine atoms of about 4.4 Bohr, and (3) vanishingly small restoring forces over the broad region for $r > 2.5$ Bohr. Energy minima for the O-bridged and F···F-bridged clusters correspond to an SiO bond length of 3.014 Bohr and an F···F separation of 4.453 Bohr, respectively. While the O-bridged cluster shows a sharp drop in energy to the ground state, the F-doped cluster displays a very shallow minimum for binding of the SiO_3F tetrahedra. Molecules containing silicon and fluorine atoms are characterized by very strong Si-F bonding.[44] Similarly, in the IGF cluster, the strength of the nearest neighbor Si-F bonds corresponds to very stable SiO_3F units (calculations give 1.5 eV greater binding for the fluorinated unit compared with the SiO_4 units). Connections *between* these stable structural units are quite different, however. The O-bridged units of SiO_2 are linked very strongly, as indicated in Fig. 3, by the rapid change in energy with respect to the O-bridge bond connecting the tetrahedra. In contrast, the F···F coupling between fluorine-doped units is extremely weak. This is consistent with observations of a halogen-induced reduction in grain boundary viscosity and decrease in creep resistance.[20] Chlorine-doping also markedly reduces the grain boundary viscosity. However, Cl shows weaker binding than F *within* the IGF, and this leads to more complicated structural effects (discussed later).

The essentially flat binding energy curve in the region of $r > 2.5$ Bohr indicates the very weak restoring force between the units. This force acts weakly to keep the linkage intact, and from Fig. 3 it rapidly vanishes as one SiO_3F unit is displaced from the other. These weakly associated components indicate a local break in the connectivity of the polymeric network and thus a reduction in high temperature viscosity, as observed experimentally. Such disrupted linkages in the solidified intergranular film form (local) regions of reduced cohesion. As a consequence, significant weakening

is expected in F-doped samples, and experiment confirms a shift in behavior from transgranular fracture to a mainly intergranular mode.[20] Similar behavior is obtained for Cl doping, indicating halogen additions, as a class, reduce viscosity of silica melts, and lead to reduced cohesion in solidified IGF's. The introduction of either halogen results in a significant (nearly 20-fold) decrease in viscosity of the IGF at high temperature.[13] The mechanism of reduction is the same in each case; a bridging oxygen atom is chemically displaced, and insertion of a pair of halogen atoms satisfies the bond requirements for the pair of undercoordinated Si sites. In the case of F, the Si-F bond in each SiO_3F tetrahedron is strong, and weakly interacting (but internally strong) SiO_3F units are formed. Fluorine is bound and stable within the IGF units with no driving force for diffusion of F elsewhere, e.g., to the IGF/grain interface. Chlorine additions, as in the case of fluorine, lead to a significant reduction in viscosity and reduce the cohesive strength of the intergranular film.[19] In contrast however, the concentration of Cl^- in the film is found to be much lower than that of F^- (0.86 atom % compared with 25 atom %, respectively), and the expansion effects are not uniform.[25] This shows there is chemical sensitivity within the IGF that distinguishes F and Cl, and this leads to behavior differences and further questions that are addressed in a later section.

While incorporation of the F···F species at the former O-bridge site is calculated to be energetically favorable, calculations show that a single F atom is *not* more stable than O. This result supports the conclusions based on valency arguments within the earlier ionic model.[26] In the latter work, substitution of two F^- ions for the single O^{--}- bridging ion leads to a local expansion driven by the Coulomb repulsion between the anions. The first-principles results support this picture in general, but covalency and other subtleties appear in the results at the quantum level. While the coordination result appears valid, the force between tetrahedral units is far from simple Coulomb repulsion between ions of unit charge. Rather there is a near-vanishing interaction between the counterpoised SiO_3F units for separations beyond the region of core overlap repulsion, as shown in Fig. 3. The interaction between SiO_3F fragments shows much less ionicity than implied by a point ion model. This is found in a Mulliken population analysis of the atomic orbital occupancy in the ground state one-electron orbitals. Rather, the interaction is more typical of that between nearly closed shell or bond-saturated systems. This is in turn consistent with the strong internal bonding of the SiO_3F fragment.

Calculated charge density distributions are also useful for analysis of the IGF bonding, and in Fig. 4 the deformation density $\delta(\mathbf{r})$ is plotted in an plane cutting through the major axis of the cluster. Here the deformation (or difference) density $\delta(\mathbf{r})$ is defined as the *change* in charge density given by subtracting the sum of N overlapping atomic charge densities ρ_j from the total cluster charge density $P(\mathbf{r})$

$$\delta(\mathbf{r}) = P(\mathbf{r}) - \Sigma \sum_{j}^{N} \rho_j(\mathbf{r}), \tag{3.1}$$

where

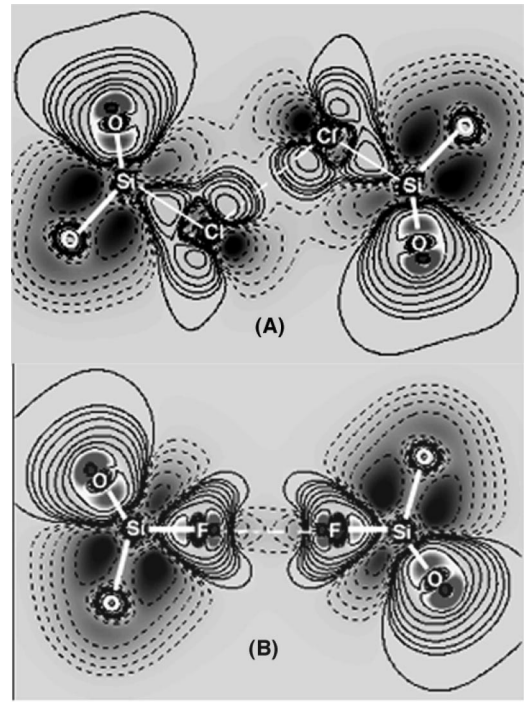

FIG. 5. Calculated structure and local charge density shifts at the displaced O-bridge site of SiO_2 IGF for (A) Cl doping and (B) F doping, taken from Si_2O_7 and $Si_2O_6M_2$ clusters where M = F and Cl. Contour values are same as for Fig. 4.

$$P(\mathbf{r}) = \sum_{i}^{M} f_i |\Psi_i(\mathbf{r})|^2 \tag{3.2}$$

and the M occupied one-electron cluster solutions Ψ_i are each weighted by the occupancy f_i of the state. Charge conservation requires that the integral of $\delta(\mathbf{r})$ over all space is identically zero, so the plots in Fig. 4 show the *rearrangement* in electron density in forming the two clusters. As the rearrangement in electron density in going from free atoms to the cluster, the calculated density shifts of Fig. 4 represent the *bond* densities of the IGF. The solid and dashed lines in the figure denote constant values of increased and decreased density, respectively. It is interesting to note the similar features in the density shifts around the F···F pair and the bridging O in Fig. 4. Although the two cases are not greatly different in energy at equilibrium, one can easily dissociate by bisecting the -F···F- bond to give equivalent neutral species, whereas the other can only stretch (or dissociate asymmetrically). This observation reinforces the idea that the origin of high stability of the F-doped structure has more to do with bonding *internal* to each tetrahedral unit, rather than *between* the units.

The breaking of the connectivity in the silica network is very clear in Fig. 4, and in Fig. 5 we compare difference densities calculated for F and Cl dopants in the Si_2O_7 host clusters. The results for Cl^- are distinctly different from those for F doping. The Cl pair does not remain aligned along the Si-Si axis as the F pair does, but *rotate* oppositely off this axis. In this way each Cl ion maintains a bond with the nearest Si atom while reducing its overlap with the

neighboring Cl ion. This behavior is also seen in molecular and crystalline halides.[45] However, even this energy lowering action cannot achieve a stabilization energy greater than the reference energy of the undoped case, because this off-axis configuration reduces shielding between the Si sites, increasing Si-Si repulsion. As a result, the configuration corresponds to only a *local minimum* in the potential energy surface, i.e., a metastable state, with oxygen able to displace the two Cl^- ions.

B. Intergranular film thickness

The factors that determine the thickness of the (fluid) IGF have been mentioned earlier as leading to a force balance between compression from attracting grains and repulsion from compression of the atomic network within the IGF itself. The resulting thickness of this state is *frozen in* at equilibrium as the temperature decreases. This description far oversimplifies the interactions that determine IGF formation; but details of the phenomenon are described in recent papers by French[46] and Cannon *et al.*[47]

Native silica-rich IGF's (that can form with a variety of impurity-free ceramic starting materials[48,49]) show *uniform* thickness values of 1.0 ± 0.1 nm. Dopants generally lead to an expansion in volume and increase in equilibrium values for the thickness of the IGF. It has been reasoned earlier[25] that anions induce an expansion of the IGF due to: (a) breaking connections between tetrahedral units and (b) the Coulomb repulsion between anions. HRTEM micrographs of F- and Cl-doped samples are shown in Figs. 6 and 7, respectively, illustrating the appearance of characteristic intergranular films at Si_3N_4 grain boundaries. The dilatational effect of F on IGF thickness and the insensitivity of the expansion to the surface structure of the grains bounding the intergranular film are apparent in Fig. 6. The F-doped films show an *expansion* of 0.1 nm, which is uniform over the different grain boundaries. HRTEM micrographs of the *undoped* reference material (not shown) appear the same as those shown in Fig. 6, but with reduced characteristic thickness. These observations indicate that the effect of F doping is homogeneous and perturbative to the principal factors determining the thickness of the undoped IGF, and that these factors remain largely unaltered by the F doping.

Chlorine doping is also associated with an increase in thickness of the IGF. However, in contrast to the uniform expansion found for F, the Cl-doped boundaries, shown in Fig. 7, have thicknesses that are *not* uniform,[19] but are sensitive to the type of adjoining grain boundary. The Cl-induced expansion effect appears to depend upon the structure and/or composition of the crystallite surface forming the boundary with the intergranular layer, such that the magnitude of the expansion varies from one region to another. This variation is large; some boundaries retain a thickness of about 1.0 nm, characteristic of the undoped samples, while others are dilated by 30% (0.3 nm). Therefore, while F-doped films display a thickness characteristic of a homogeneous distribution of F within the SiO_2 structure, the Cl-doped films are suggestive of an inhomogeneous distribution of Cl over the grain boundary films. The HRTEM images are

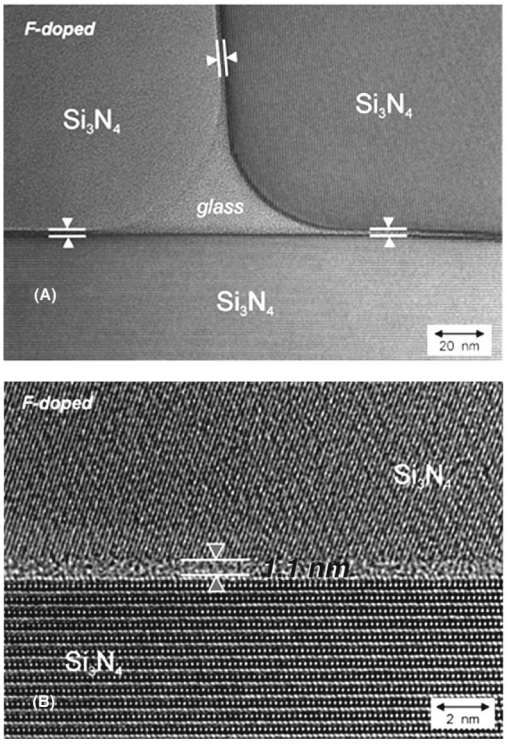

FIG. 6. HRTEM micrographs of silicon nitride with F-doped SiO_2 intergranular films: (A) at triple point junction where the three IGF's each have same 1.1 nm thickness and (B) higher magnification of one of the IGF's. SiO_2-rich IGF's are similar in appearance with characteristic thickness of 1.0 nm.

so indicative of the type anion contained in the IGF, that IGF thickness can be taken as a characteristic of the chemistry of the IGF.[25]

Calculated results for the small clusters give a relaxed structure for the F-doped case for a Si-Si separation of 0.55 nm, compared with 0.32 nm for the O-bridged cluster. This expansion (and the greatly reduced maximum restoring force between SiO_3F units) qualitatively agrees with observations. The expansion originates from the presence of a short-ranged repulsive barrier (see Fig. 3) preventing the F-doped structural units from relaxing in as closely as the undoped (O-bridged) units. Note this expansion mechanism is qualitatively different from that based on simple ionic repulsion, involving instead the overlap repulsion of the almost-fulled F-valence shells. Consistent with this, it is clear from Fig. 3 that the more compact shell of oxygen gives a repulsive barrier in the O-bridged host that is an order of magnitude stronger than that in the F-doped case.

The magnitude of the expansion was also calculated for the larger interface spanning cluster fragment shown in Fig. 1. As discussed earlier, this is not a unique choice, but one that will respond to forces that affect the thickness and/or structure of the IGF, whether the force is expansive (from within) or compressive (originating outside the IGF). The PWSCF calculation of the relaxed structure, electronic structure, total energy and force field determines the lowest energy structure within the C_{2v} symmetry of the IGF cluster. Applying the embedding force boundary condition to the ter-

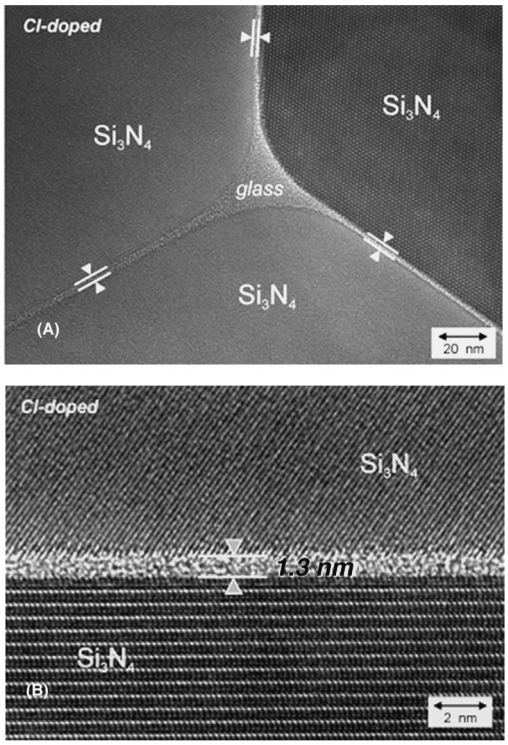

FIG. 7. HRTEM micrographs of silicon nitride with Cl-doped SiO_2-rich intergranular films: (A) at a triple point showing intersecting IGF's of variable thicknesses and (B) example film with 1.3 nm thickness.

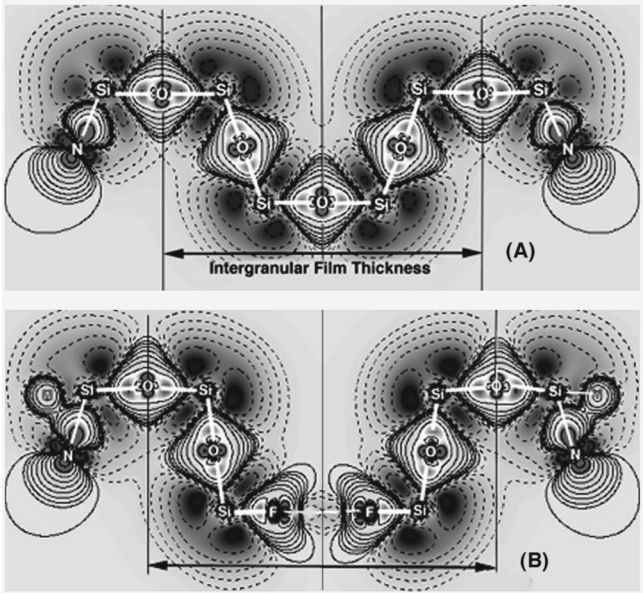

FIG. 8. Plots of calculated charge density difference in major symmetry plane through fragment cluster models of (B) undoped and (B) F-doped IGF's in silicon nitride. In (A) reference $Si_6O_{13}N_6$ cluster links Si_3N_4 grains across the amorphous intergranular film with bridging oxygens (O) connecting SiO_4 tetrahedra (Si at tetrahedra centers). In (B) two F atoms replace O-bridging atom. Vertical lines in the two panels designate the chemical thickness of the film. Contour values are described in caption of Fig. 4.

minal O atoms of the cluster, equilibrium conditions require that these atoms assume positions such that they experience an outward force that balances the compressive inward force[50] exerted on them by the adjacent nitride grains[28] (estimated to be 1.35 eV/Bohr as an upper bound). Relaxing positions such that the calculated force on each of the remaining (nonterminal) atoms is zero determines the reference binding energy and dimensions of the interface-spanning host cluster shown in a bond density representation in Fig. 8(A). Calculated relaxations of atom positions gives a thickness, indicated by vertical lines through the boundary oxygen atoms, of 0.85 nm, which is 15% smaller than the thickness[51] measured in HRTEM. Using the same embedding force on the terminal O atoms and substituting an F pair for the oxygen connecting the tetrahedra at the cluster center gives the IGF fragment shown in Fig. 8(B). The ground state of this fully relaxed fragment is about 2.1 eV more stable than that of the reference system. Figure 8 shows that the change in thickness is strongly localized between the two doped structural units. The chemical thickness, defined by the vertical lines in Fig. 8(B) is 0.95 nm, an expansion over the reference fragment thickness by 0.10 nm, in very good agreement with the HRTEM results. As anticipated, the cluster model is most accurate for the *change* in thickness, whereas the absolute values of the thickness are less accurate (15% too small for each case). This indicates the choice of embedding force used here is probably too large, but as discussed earlier, the *relative* values of main interest are not very sensitive to the absolute force value.

C. Contrasting effects: The F/Cl puzzle

Similarities in the effects of F and Cl are at least qualitatively understood in terms of halogen chemistry and earlier discussion in terms of the point-ion model[25] of the F effect. But explanation of the *contrasting* behavior and identifying the mechanisms that differentiate F and Cl are more challenging. However, the calculated electronic structure results give a plausible, if inconclusive, explanation of the observations.

Characterization has shown distinct differences between F and Cl, even at the qualitative level. This is particularly interesting given the similarities in electronic structure of these ions. Measurement of dopant concentration levels in the IGF using electron energy loss spectroscopy (EELS) and other TEM-based techniques (AEM, EDX) showed a high level of F in the doped silica film[25] [F/(F+O) ratio of about 25%]. On the other hand, the level of Cl was *below* the detection limit for all of the analytical TEM-based techniques. An ICP analysis[25] determined a Cl concentration (0.86 atom %) an order of magnitude *smaller* than that for F in the respective samples. Both ion chromatography (IC) and x-ray fluorescence[19,25] confirm that Cl is indeed introduced into the samples, but the measured concentration of Cl is very low.

Yet, internal friction measurements[19,25] summarized in Fig. 2 show that Cl-doping effects a shift in the internal friction vs temperature curve that is even *greater* than that for F doping. A high-temperature peak is also present for the Cl-doped system that coincides with that of the *undoped* reference material. This puzzling and apparently contradictory result indicates quite different behaviors for these halogen

dopants in silica-rich intergranular films. Such behaviors are certainly not within scope of a simple point ion model. The presence of multiple peak positions in the internal friction data can arise from *nonuniformity* in the distribution of Cl at the grain boundary/IGF interfaces. Support for this explanation comes from HRTEM results[19] for Cl that directly show nonuniform changes in thickness of the IGF, suggesting that chlorine appears *inhomogeneously* across the distribution of crystallite grain boundaries, in contrast with the behavior of fluorine. These distinctions show that the behavior of F and Cl as intergranular species are fundamentally different and beyond the scope of simple ionic models, which would not distinguish F and Cl at all.

Results from calculations for the 26 atom IGF fragment cluster containing chlorine do not change the conclusions reached concerning Cl effects in the smaller clusters. The Cl-doped cluster achieves a local minimum energy with a cluster expansion, but the energetics are not favorable for the reaction kinetics. Calculations yield a *positive* formation energy[52] of 1.43 eV, indicating the Cl pair can be displaced if oxygen is available. The limiting step in the reaction is the energy of binding for Cl ions at the bridge site, which is only slightly greater (by 0.1 eV) than oxygen's. It might be possible for this Cl-doped structure to persist as a long-lived metastable state in an environment of limited oxygen, however, experimental data do not provide strong support, considering the nearly vanishing amount of Cl detected in the IGF. Also, if this metastable configuration were long-lived, the calculations indicate the resulting expansion of the IGF would only be slightly greater than that for F. But experimental observations finding IGF's in Cl-doped samples ranging from 1.0 to 1.3 ± 0.1 nm thick (Fig. 7), strongly suggests that Cl and F do not follow identical reaction paths in the film.

From these results, the conclusion is compelling that the Cl-induced expansion mechanism, in those boundaries where it is observed, must differ from that of fluorine. The low concentration of Cl measured in the IGF suggests that the distribution of stable Cl-binding sites within the IGF must be very small. Indeed, first-principles calculations carried out for a number of other possible structures for bonding of the $Cl\cdots Cl$ pair have identified none of greater stability. Considering other possibilities, with oxygen displaced by carbon, Cl termination of one Si dangling bond could occur, leaving a dangling bond on the other Si atom. But calculations show such a configuration is less stable (by about 3.2 eV) than the O-bridged reference case, suggesting it may not be long-lived either. Calculations also show that a single Cl atom that is bridge bound in place of an oxygen is considerably less stable (by about 4.5 eV). Similar to singly-bound fluorine, this low binding is a result of valency mismatch (more precisely, an extra electron from the near neighbor Si atoms populates a cluster orbital with low binding contribution.)

So how is the observation of reduced viscosity and enhanced fracture tendency consistent with such a low concentration of Cl in the film? The calculations suggest F and Cl doping is effected only because carbon oxidation is a strong driving force for the reaction in the sintering stage. While Si-F bonds are relatively strong, those of Si-Cl are weak, such that Cl pairs remain only temporarily bound as the nucleophilic reagent in the removal of O bridges. In this picture Cl reduces the viscosity and leaves a weaker IGF, in agreement with observations. But the metastability of Cl means that any increase in pressure on the IGF (through dispersion forces[1] and stresses in cooling and solidification) reduces the binding of the Cl, enhancing its diffusion rate to regions of more ''open'' volume.

Where then is the Cl? There is no measurable Cl *within* the Si_3N_4 crystallites, and theory predicts that none is expected in view of the absence of a chemical driving force. But if there is open volume at the IGF/Si_3N_4 grain boundary interface, Cl could segregate and trap there as it diffuses out of the SiO_2-rich IGF. The HRTEM measurements of IGF thickness in the Cl-doped systems suggest this possibility as well, since as discussed earlier, Cl-doped films are not of uniform thickness, but differ from one crystallite boundary to another. There is no obvious physical basis for an *internal* expansion effect (such as that of fluorine) to be sensitive to boundary structure. But surface structure sensitivity *is* suggestive of another operative mechanism, such as segregation with its dependence on available volume and degree of atom match at the film-crystallite interface. Conversely, it is difficult to envision *structure sensitivity* of the equilibrium film thickness being dependent on bonding effects localized *within* the IGF, but interfacial segregation is often structure sensitive and its occurrence is well understood to affect film growth. Segregation to internal interfaces would affect the equilibrium film thickness[53] through the ion contribution to the electric double layer field strength.

Certainly, other factors play a role in the occurrence of different concentrations of F and Cl. For example, F and Cl have different carrier fragments, C_2F_4 and C_2Cl_6, respectively, that initiate the reaction sequence with oxygen. The carbon-carbon bond in the F carrier is a double bond (C=C), but the C-C bond in C_2Cl_6 is a weaker single bond. In addressing the dopant incorporation stage of the reaction, it can be expected that these differences will affect the release rate of the halogen, as well as the quantity released. Also, in the Cl case, the role of an extra Cl ion released with the breakup of C_2Cl_6 at the reaction site is at present unknown. It can be safely assumed that it can not be accommodated with the other two Cl ions, which are themselves unstable as a pair at the former O-bridge site. The Cl released from the carbon-based carrier (C_2Cl_6 or CCl_3) during the attachment of the carrier to the O bridge in the initial stages of the CO formation very likely form Cl_2 and diffuses out of the system. Of course, if the ''extra'' Cl is released in the high-temperature sintering before reaching the O-bridge reaction site, the carriers are on an equal footing (CF_2 and CCl_2). Entirely different mechanisms related to possible electric double layers[53] also warrant further study.

IV. SUMMARY AND CONCLUSION

The first-principles studies of silica intergranular fragments and the effects of F and Cl doping give results supporting and clarifying the principal findings from compre-

hensive experimental investigations. At the qualitative level, calculated results give a vivid description of broken connectivity and altered bond density that lead to a reduction in viscosity and cohesion of halogen-doped IGF's in silicon nitride. Both F and Cl are alike in this action, because both participate in removal of O bridges in the high-temperature melt. But other properties of the IGF (thickness) depend upon stabilities of the respective ions in the vacated O-bridge sites as cooling occurs. In F doping, where stability is high, the increase in film thickness is calculated with rather good quantitative agreement with HRTEM data. The contrasting and puzzling observations from comparative experimental studies of Cl-doping reflect its relatively low stability. Calculated energetics show Cl is at best metastable over numerous possible sites within the IGF, including the O-bridge site preferred by F. The fundamental reason behind the different behaviors of Cl and F is that the Si-Cl bond is much weaker than the Si-F bond. This basic property determines how the anion will behave as a nucleophilic species, as it is carried to the O-bridge site by the strong carbon-oxygen association. And it governs the stability of anions within the IGF, providing a plausible explanation for the observations. Although grain sites for increased binding of Cl have not been identified, the calculations make it clear that fluorine and chlorine follow very different reaction pathways in the IGF. The significance of this result is its indication of the marked sensitivity of IGF properties to details of the interfacial bonding.

In order to extend this study, it may be feasible to prepare well-characterized interfaces using single crystal β-Si_3N_4 on which doped SiO_2 films could be grown. The distribution of possible binding sites for Cl could then be better characterized and controlled with this idealized arrangement, and calculations could check experimental results more directly. Certainly energy band[16] and molecular dynamics[30] methods that scale the dimensionality of the system could provide very useful extensions and checks on results of the cluster model in this regard.

The agreement with experiment reported here implies that first-principles studies should be useful in screening for sintering additions to give desired results. The systems discussed in this paper entail the most strongly interacting species for reaction with the silica network. Less aggressive reagents are known in the class of network modifiers, and reagents that could yield small cluster fragments (A_mB_n) that can bond at the Si-O-Si bridge site are worth exploring. Intergranular film additions that could modify local elastic response of the O bridges, without removing them, would yield an interesting new path to the control of IGF properties.

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[1] R. H. French, H. Müllejans, D. J. Jones, G. Duscher, R. M. Cannon, and M. Rühle, Acta Mater. **46**, 2271 (1998).

[2] D. R. Clarke, J. Am. Ceram. Soc. **70**, 15 (1987).

[3] I. Tanaka, H.-J. Kleebe, M. K. Cinibulk, J. Bruley, D. R. Clarke, and M. Rühle, J. Am. Ceram. Soc. **77**, 911 (1994).

[4] B. Lawn, *Fracture of Brittle Solids* (Cambridge University Press, Cambridge, 1993).

[5] G. Pezzotti, I. Tanaka, and T. Nishida, Philos. Mag. Lett. **67**, 95 (1993).

[6] P. F. Becher, E. Y. Sun, C.-H. Hsueh, K. B. Alexander, S.-L. Hwang, S. B. Waters, and C. G. Westmoreland, Acta Mater. **44**, 3881 (1996).

[7] E. Y. Sun, P. F. Becher, C.-H. Hsueh, G. S. Painter, S. B. Waters, S. L. Hwang, and M. J. Hoffmann, Acta Mater. **47**, 2777 (1999).

[8] E. Y. Sun, P. F. Becher, C.-H. Hsueh, S. B. Waters, K. P. Plucknett, K. Hirao, and M. Brito, J. Am. Ceram. Soc. **81**, 2831 (1998).

[9] P. F. Becher, E. Y. Sun, K. P. Plucknett, K. B. Alexander, C.-H. Hsueh, H.-T. Lin, S. B. Waters, C. G. Westmoreland, E.-S. Kang, K. Hirao, and M. Brito, J. Am. Ceram. Soc. **81**, 2821 (1998).

[10] P. F. Becher, G. S. Painter, E. Y. Sun, C.-H. Hsueh, and M. J. Lance, Acta Mater. **48**, 4493 (2000).

[11] M. J. Hoffmann, in *Tailoring of Mechanical Properties of Si_3N_4 Ceramics*, edited by M. J. Hoffmann and G. Petzow (Kluwer Academic Publishers, Dordrecht, Netherlands, 1994), pp. 59–72.

[12] F. Ernst, O. Kienzle, M. Rühle, J. Eur. Ceram. Soc. **19**, 665 (1999).

[13] For a review of basic experimental work see H.-J. Kleebe, J. Ceram. Soc. Jpn. **105**, 453 (1997).

[14] M. Yoshiya, I. Tanaka, and H. Adachi, in *Key Engineering Materials, Vol. 175-176 Engineering Ceramics-Multifunction Properties-New Perspectives*, edited by P. Sajgalik and Z. Lences (Trans. Tech. Publications, Zürich, Switzerland, 1999), p. 107.

[15] I. Tanaka, H. Adachi, T. Nakayasu, and T. Yamada, in *Ceramic Microstructure: Control at the Atomic Level*, edited by A. P. Tomsia and A. Glaeser (Plenum Press, New York, 1998), p. 23.

[16] W.-Y. Ching, M.-Z. Huang, and S.-D. Mo, J. Am. Ceram. Soc. **83**, 78 (2000).

[17] Theoretical work in related systems is reviewed by M. W. Finnis, J. Phys.: Condens. Matter **8**, 5811 (1996).

[18] L. L. Hench and J. K. West, in *Annual Review of Material Science*, edited by B. W. Wessels, E. N. Kaufmann, J. A. Giordmaine, and J. B. Wachtman, Jr. (Annual Reviews, Palo Alto, 1995), Vol. 25, p. 37.

[19] G. Pezzotti, K. Ota, and H.-J. Kleebe, J. Am. Ceram. Soc. **80**, 2341 (1997).

[20] G. Pezzotti, H.-J. Kleebe, K. Ota, T. Nishida, and M. Sakai, J. Ceram. Soc. Jpn. **104**, 19 (1996).

[21] K.-L. Yeh, M.-J. Jeng, and J.-G. Hwu, Surf. Sci. Spectra **43**, 671 (1999).

[22] S. Hayakawa and L. L. Hench, J. Non-Cryst. Solids **242**, 1 (1998).

[23] P. P. Apte, H. Park, K. C. Saraswat, and C. R. Helms, in *Interface Control of Electrical, Chemical, and Mechanical Properties*, MRS Symposia Proceedings, No. 318, edited by S. P. Murarka, K. Rose, T. Ohmi and T. Seidel (Materials Research Society, Pittsburgh, 1994), p. 281.

[24] H.-J. Kleebe, G. Pezzotti, T. Nishida, and M. Rühle, J. Ceram. Soc. Jpn. **106**, 17 (1998).

[25] H.-J. Kleebe and G. Pezzotti, in *Ceramic Microstructure: Control at the Atomic Level*, edited by A. P. Tomsia and A. Glaeser (Plenum Press, New York, 1998), p. 107.

[26] G. Pezzotti, K. Ota, H.-J. Kleebe, Y. Okamoto, and T. Nishida, Acta Metall. Mater. **43**, 4357 (1995).

[27] G. Pezzotti and K. Ota, J. Am. Ceram. Soc. **80**, 599 (1997).

[28] G. Pezzotti, T. Nishida, H.-J. Kleebe, K. Ota, N. Muraki, and V. Sergo, J. Mater. Sci. **34**, 1667 (1999).

[29] The *number* of SiO_2 units must be specified to define the system and initiate calculations. This choice effectively sets the initial dimensions of the IGF so that the *approximate* film thickness is consistent with experimental observations. Structural relaxation of the atoms and the changes that occur on doping are then calculated from first principles.

[30] S. Blonski and S. H. Garofalini, J. Am. Ceram. Soc. **80**, 1997 (1997).

[31] D. A. Litton and S. H. Garofalini, J. Mater. Res. **14**, 1418 (1999).

[32] J. Koplik and J. R. Banavar, Phys. Rev. Lett. **84**, 4401 (2000).

[33] K. Raghavachari and J. Eng, Jr., Phys. Rev. Lett. **84**, 935 (2000).

[34] C. M. Fang, G. A. de Wijs, R. A. de Groot, R. Metselaar, H. T. Hintzen, and G. de With, Chem. Mater. **12**, 1071 (2000).

[35] F. W. Averill and G. S. Painter, Phys. Rev. B **50**, 7262 (1994).

[36] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules, International Series of Monographs in Chemistry,* Vol. 16 (Oxford University Press, New York, 1989).

[37] S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).

[38] G. S. Painter, Phys. Rev. B **24**, 4264 (1981).

[39] J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Foilhais, Phys. Rev. B **46**, 6671 (1992).

[40] F. W. Kutzler and G. S. Painter, Phys. Rev. Lett. **59**, 1285 (1987).

[41] H. F. Schaefer III, *The Electronic Structure of Atoms and Molecules* (Addison-Wesley, Reading, MA, 1972), pp. 67–78.

[42] G. V. Gibbs, E. P. Meagher, M. D. Newton and D. K. Swanson in *Structure and Bonding in Crystals*, edited by M. O'Keeffe, and A. Navrotsky (Academic Press, New York, 1981), Vol. 1, p. 195.

[43] K. C. Hass, W. F. Schneider, A. Curioni, and W. Andreoni, J. Phys. Chem. B **104**, 5527 (2000).

[44] R. T. Sanderson, *Chemical Bonds and Bond Energy, Physical Chemistry Series,* Vol. 21, edited by E. M. Loebl (Academic Press, New York, 1971).

[45] F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry* (Interscience Publishers, New York, 1972), p. 467.

[46] R. H. French, J. Am. Ceram. Soc. **83**, 2117 (2000).

[47] R. M. Cannon, M. Rühle, M. J. Hoffmann, R. H. French, H. Gu, A. P. Tomsia, and E. Saiz in *Grain Boundary Engineering in Ceramics*, proceedings of JFCC International Workshop on Fine Ceramics 2000, edited by T. Sakuma and Y. Ikuhara (Ceramics Transactions, American Ceramic Society, 2000).

[48] The importance of IGF's in practical applications is well illustrated in this case. The presence of a lower softening-temperature SiO_2-rich phase surrounding the highly refractory Si_3N_4 grains sets an inherent limit to high-temperature applications of silicon nitride ceramics.

[49] H. Gu, R. M. Cannon, and M. Rühle, J. Mater. Res. **13**, 376 (1998).

[50] The value of this force is unknown, but an estimate can be obtained from the force-separation dependence of the Si-O bond in clusters. The magnitude of the compressive force on the film and the density of SiO_2 linkages terminating on the crystallite surface also affect estimates for the embedding force. The important point is that the *same* force boundary condition applies to both host and doped system to a good approximation, with the result that comparative results will not be very sensitive to uncertainties in each case.

[51] A recent discussion of the relation between *chemical width* and HRTEM measurements is given by Yoshiya *et al.* (Ref. 14 of this paper).

[52] For calculation of the energy of formation, CCl_2 fragments of C_2Cl_6 were used for consistency with the CF_2 units used in computing the formation energy of the F-doped system, where the energy balance favored the reaction. This method gives a lower bound to the energy as a more stable reactant would raise the energy of formation.

[53] D. R. Clarke, T. M. Shaw, A. P. Philipse, and R. G. Horn, J. Am. Ceram. Soc. **76**, 1201 (1993).