Effects of Absorption of Water and Other Reactive Species on the Fracture Properties of Organosilicate Glass Thin Films
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Abstract
This paper investigates the effects of the absorption of water and several other reactive species on the adhesion energy between organosilicate glass (OSG) thin films and various capping layers. The adhesion energy of these interfaces was measured by four-point bending tests conducted at room temperature in an ambient environment. The amount of absorbed reactant in the organosilicate glass films was controlled by exposing the capped organosilicate films to aqueous solutions for various periods of time. Results show that the initial degradation of the critical adhesion energy of the interfaces between OSG and tantalum, tantalum nitride (TaNx), silicon nitride (SiNx), and silicon dioxide (SiO2) capping layers is very fast, but that the adhesion energy reaches a saturation value thereafter. The reduced adhesion energy can be fully recovered to the “dry” value by baking the samples. A quantitative model based on Henry’s law is used to predict the adhesion degradation rate as a function of moisture exposure time. This model leads to a new and simple method for measuring the diffusion coefficient of water in OSG coatings or their interfaces.

Introduction
Silica-based dielectrics are often doped with carbon atoms and other organic molecules in order to reduce the permittivity of back-end-of-line (BEOL) inter-layer dielectrics. The resulting organosilicate glass (OSG) has a dielectric constant value less than 3.0 with approximately one half the density of fused silica. The open network structure makes it easy for reactive molecules to diffuse and absorb into the OSG. Vlassak et al. [1-3] and Dauskardt et al. [4-6] have used the four-point-bend and double-cantilever beam techniques to demonstrate that the cohesive and adhesive fracture of OSG is strongly dependent on the chemical reactivity of the testing environment as measured by pH or relative humidity (% R.H.). However, there are very few, if any, studies to elucidate the effects of the absorption of water and other reactive species on the fracture behavior of OSG. The objective of this work is to quantitatively characterize this effect. The adhesion strength between OSG low-k films was measured as a function of exposure time to various aqueous solutions. The results demonstrate that the interfacial strength can be reduced by as much as 50% after a 2-week exposure. A diffusion model is used to extract the water diffusion coefficient in OSG from the time-dependent adhesion data.

Experimental Procedure
Organosilicate glass thin films (OSG) with a thickness of 400 nm were deposited on 200 mm diameter bare silicon wafers at 400°C by using the plasma-enhanced chemical vapor deposition (PECVD) techniques. The precursor gases used in the deposition were 1, 3, 5, 7-tetramethylcyclo-tetrasiloxane (TMCTS), carbon dioxide, and oxygen. The OSG density measured by using X-Ray Reflectivity (XRR) is approximately 1.4 g/cm³; the relative dielectric constant of the OSG was 3.0. The precise chemical composition and mechanical properties of the OSG have been reported in previous studies by Vlassak and coworkers [1-3, 7]. Here, the effect of water
diffusion on the adhesion between 400 nm thick OSG and four different capping materials is investigated – tantalum, tantalum nitride (TaN), silicon nitride (SiNₓ), and silicon dioxide (TEOS - SiO₂). The last three capping layers are identical to those studied by Vlassak et al [1-3]. The TaNₓ coatings were deposited using reactive sputtering, followed by an in-situ sputter deposition of ~100 nm thick copper. The Ta coatings were sputter-deposited. The thickness of the barrier metal coatings is in the range of 10 to 20 nm. The 200 nm thick SiO₂ and SiNₓ coatings were deposited at 400°C using PECVD.

The adhesion energy of all samples was measured using the four-point bend technique [3, 8-9] conducted under ambient conditions with a temperature and relative humidity of 24 ± 2°C and 45 ± 5 %, respectively. Adhesion samples were prepared by cleaving 200 mm silicon substrates into 12 mm x 60 mm strips. These strips were then bonded face-to-face using epoxy and cured for one hour in an air convection oven at 120°C and a water partial pressure of (1.3 ± 0.1) x 10³ Pa. After curing the epoxy, notches were made in the samples by using a diamond saw. If \( P \) is the load at which the crack propagates along the interface, the corresponding energy release rate \( G \) is [3, 8-9]

\[
G = \frac{21P^2l^2}{16Eb^2h^3} (1 - \nu^2),
\]

where \( E \) and \( \nu \) are the elastic modulus and Poisson’s ratio of the Si substrate, \( l \) the distance between the inner and outer loading pins in the four-point bending set-up, \( b \) the width of the specimen, and \( h \) the substrate thickness. The crack velocity was approximately 60 µm/s for all measurements. For each capping material, one group of samples was tested immediately after the epoxy was set. The rest of the specimens were submerged in de-ionized water at a temperature of 24 ± 2°C and tested after exposing them for specific periods of time (t).

**Results and Discussions**

**The effect of water diffusion on fracture toughness**

Figure 1 shows the adhesion energy between the OSG and the various capping layers as a function of water exposure time at 24°C.

![Fig 1. Adhesion energy between OSG and various capping layers as a function of water exposure time at 24°C.](image)

![Fig 2. Adhesion energy of OSG/ SiO₂ inter-faces with different film thickness values after soaking in DI water.](image)
function of submersion time in de-ionized water at 24°C. Each data point represents the average of at least five measurements and the error bars correspond to one standard deviation. X-ray photoelectron spectroscopy (XPS) of the fractures surfaces reveals that the SiNₓ, Ta, and TaNₓ-capped samples fractured cohesively. The adhesion energy of TaN/OSG interface is the largest. This can be explained by the pre-deposition plasma clean of the OSG surface, which removes surface contaminants and densifies the OSG surface. The crack path is located inside the OSG at a distance of approximately 5-10 nm from the interface. For the OSG/ SiO₂ samples, by contrast, the XPS results show that the delamination occurred at the interface. This is consistent with observations reported by Vlassak et al. [3]. It is evident from Fig. 1 that the adhesion of each of the four film stacks degrades with increasing exposure time. The figure also reveals that the degradation of samples with SiO₂ and SiNₓ caps can be recovered by baking the samples at 120°C for 16 hours.

In order to eliminate the possibility that the time-dependent adhesion degradation is caused by changes in the mechanical properties of the epoxy as a result of the absorption of water, OSG/SiO₂ samples with different bi-layer thicknesses were tested: 200 nm SiO₂/420 nm OSG, 1600 nm SiO₂/420 nm OSG, and 1600 nm SiO₂/3000 nm OSG. If energy dissipation in the epoxy contributes significantly to the experimental adhesion values, the different film stacks should yield different adhesion values, because the stress distribution at the crack tip depends on the thicknesses of the films in the stack [10]. As illustrated in Fig. 2, this is clearly not the case: The initial adhesion values and the rates of degradation are indistinguishable within experimental scatter for the different film stacks. This indicates that the adhesion degradation is related to real changes that take place at the delaminating interface.

Model and discussion

The solution of a one-dimensional diffusion problem that results in a water concentration profile in the OSG strip can be found in reference [11]. The adhesion strength (Gₐ) of the interface can be related to the moisture concentration by the following expression based on the assumption that water dissolves into the OSG film and follows Henry’s Law.

\[ G_a(t) = B - A \left( \ln p_{H_2O}^\gamma + \Phi(\gamma, \tau) \right) \]  

(2)

where \( \Phi(\gamma, \tau) \) is a complicated function of the normalized time \( \tau = \frac{Dt}{a^2} \) and of the initial water content \( \gamma = \frac{p_i}{p_{H_2O}^\gamma} \). A more detailed description of the diffusion model is given in reference [12].

The parameters \( A \) and \( B \) are material constants that describe the dependence of \( G \) at a given crack

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<td>A</td>
<td>0.46</td>
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<td>B</td>
<td>6.27</td>
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<td>( \gamma )</td>
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velocity on the natural logarithm of the water partial pressure. This dependence is well established [13-14] and the values of these parameters were obtained from independent subcritical crack growth measurements for OSG coatings that are similar to the coatings used in this investigation [3]. The numerical values are listed in Table 1. The initial water content was determined from adhesion measurements of as-fabricated specimens in an N₂ environment and is also given in Table 1. Equation (1) shows that the adhesion is a function of initial moisture partial pressure \(p_i\), saturated partial pressure \(p_{v_{H_2O}}\), moisture exposure time \(t\), sample width \(a\), and moisture diffusivity in OSG film. Figure 3 shows the experimental data for the OSG/SiO₂ system along with the results obtained from Eq. (1), in which the diffusion coefficient was used as a fitting parameter. Agreement between the experimental data and the model calculations is very good and is shown in Fig. 3. The diffusion coefficient obtained from the model is \(D = 1.6 \times 10^{-7} \text{ cm}^2/\text{s}\).

**Effects of other reactive species**

In the previous sections, we have demonstrated that the adhesion energy of the OSG interfaces is reduced by exposure to water in the environment before the adhesion test. Recent work by Jacques et al. [15] and Vlassak et al. [3] shows that the fracture behavior of organosilicate glass (OSG) is also affected by the chemical reactivity of the environment as measured by pH. Similar results were also reported by Wiederhorn et al. [13-14] for bulk glasses. However, the effect of the absorbed reactants into the OSG film or the interface on the cohesive and adhesion properties has not been characterized. In this part of the study, 420 nm thick OSG samples were capped with 1600 nm thick SiO₂ films. The samples were submerged in a 3% hydrogen peroxide solution (H₂O₂) or a 29% weight ammonium hydroxide solution (NH₄OH) for various periods of time. The solutions have pH values of 5 ± 1 and 13 ± 1, respectively. The
critical adhesion energy of the samples was measured by the four-point bend test in the ambient condition described above. For safety, samples were rinsed in DI water for 20 minutes after removing from the chemical solution. Figure 4 shows the OSG/SiO₂ interfacial strength degrades with the exposure time in H₂O₂, NH₄OH, and DI water. Interestingly, the results show that the rate of degradation is unchanged by the presence of H₂O₂ or NH₄OH in the aqueous solution. This should be contrasted with results reported by Jacques et al. [15] and Vlassak et al. [3], who showed that the fracture energy of interfaces or the cohesive energy of silicate-based materials degrades with the pH value of the environment during testing. A large effect of H₂O₂ has also been demonstrated [4]. XPS analysis shows that the failure occurs at the OSG/SiO₂ interfaces regardless of the reactive species. Since the H₂O₂ or NH₄OH in the solutions do not make the adhesion degradation worse - as one would expect based on the subcritical measurements in references [3] and [4] - the experimental data suggest that diffusion of these reactive species in OSG is much slower than that of water, possibly as a result of steric hinder. The adhesion degradation in this study is clearly caused by water. Figure 4 shows further that degradation can be recovered partially by a post-exposure bake at 120 °C for 24 hours. It is evident from the figure that the amount of recovery is the same for samples soaked in DI water or in NH₄OH solutions. Both samples have a post-bake value of approximately 80% of the original “dry” value. This suggests that there is little or no permanent damage to the interface as a result of water absorption and that the degradation in the adhesion can indeed be attributed to the diffusion of water.

Conclusions
1. It has been demonstrated that the four-point-bend adhesion energy of the OSG films with dielectric and metal capping layers can be degraded by exposure to water in the environment prior to fracture. The amount of degradation can be as much as 50% after 2 weeks of exposure. The interfacial adhesion energy can be recovered by removing the absorbed water molecules using thermal treatments.
2. A quantitative diffusion model was used to describe the effect of water absorption on the adhesion degradation and to extract the diffusivity of water in the OSG coatings.
3. The amount of adhesion degradation as a result of exposure to H$_2$O$_2$ (pH~5) and NH$_4$OH (pH~14) containing solutions is comparable to that for DI water.

References