Water diffusion and fracture in organosilicate glass film stacks

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Abstract

Organosilicate glass (OSG) coatings with low dielectric permittivity are widely used as dielectrics in high-performance integrated circuits. OSG is very brittle and it is susceptible to stress-corrosion cracking in water-containing environments. We have investigated the adhesion degradation of silicon nitride/OSG and silicon carbonitride/OSG interfaces caused by water diffusion. Experimental results are in good quantitative agreement with an analytical model that combines water diffusion with subcritical crack growth. Fracture experiments show that water diffusion in OSG film stacks is remarkably fast and that it has an activation energy of 0.27 eV. The adhesion degradation is completely reversible under mild annealing conditions. Interfacial plasma treatments result in a significant enhancement of the adhesion in the absence of water, but this enhancement is lost almost completely upon exposure of the film stack to water. A diffusion study using deuterium as an isotopic tracer shows that the Si/OSG interface is the main diffusion path.

Keywords: Diffusion; Fracture; Organosilicate glass; Adhesion; Thin films

1. Introduction

Organosilicate glass (OSG) is a hybrid organic–inorganic material that consists of a siloxane network similar to that of amorphous silicon dioxide where some of the bridging oxygen atoms have been replaced by hydrogen (–H) or hydroxyl groups (–OH) and by organic groups such as methyl (–CH 3) or methylene (–CH 2–) [1–3]. OSG has found many applications in the microelectronic [4–6], biomedical [7–12] and environmental fields [13,14] as a result of its excellent electronic, biological, optical and catalytic properties. In the semiconductor industry, OSG is used as the dielectric material between copper interconnects in high-performance integrated circuits because of its low permittivity. But integration of OSG into electronic process flows is challenging, because of the low fracture toughness of OSG and its vulnerability to stress-corrosion cracking [15–20]. It is well established that the presence of water in the environment has a detrimental effect on the resistance of OSG to fracture and on the adhesion of other films to it; even small amounts of water in the atmosphere can significantly accelerate crack velocity as water molecules react with the strained Si–O bonds at the crack tip. The correlation between crack velocity, water partial pressure and applied energy release rate has been extensively characterized for OSG film stacks by means of subcritical crack growth experiments [16,18], in which crack velocity in a controlled environment is measured as a function of applied energy release rate.

The susceptibility of OSG to stress-corrosion cracking has important consequences for the interpretation of adhesion tests in the presence of reactive species such as water, because of the kinetics of the reactive bond-breaking process [21,22]. If, for instance, an interfacial crack is driven at a finite velocity, the applied energy release rate does not correspond to the equilibrium adhesion energy. Rather, it is a kinetic value that depends not only on the materials system under consideration, but also on crack velocity and the availability of reactive species. Without performing extensive subcritical measurements, there is no way of knowing a priori the proximity of this energy release rate to a specific adhesion energy.
to the equilibrium adhesion energy. From a practical point of view, however, these energy release rates can be used for system–system comparisons and they may be referred to as adhesion energies \([21,22]\) with the implicit understanding that they correspond to the energy release rates required to drive a crack at a given velocity in a given environment. This is the approach taken in this study.

If an OSG-containing film stack is exposed to water prior to delamination, diffusion of water into the film stack can severely degrade its adhesion \([23]\), a phenomenon also observed for some other materials systems \([22]\). Even though the fracture process in this case is nearly independent of the testing environment, this adhesion degradation is the result of subcritical crack growth: indeed, if water is already present in the film stack, it will lower the adhesion energy even if the measurement is made in an inert atmosphere; transport of water molecules from the environment to the crack tip is not necessary.

Evidently, adhesion degradation is an issue of concern for OSG film stacks used in integrated circuits because integrated circuits are repeatedly exposed to water during the manufacturing process. In this paper, we present the results of an in-depth study of the adhesion degradation of OSG film stacks as a result of exposure to water prior to fracture. We will show that this phenomenon can be used to measure the diffusion coefficient of water in multi-layered structures and we will explore the effect of interfacial plasma treatments on the degradation process. In Section 2, we briefly discuss a quantitative model that couples diffusion of a reactive species and subcritical crack growth to predict how the adhesion energy varies with exposure time. In the following section, a series of four-point flexure experiments is presented to evaluate the effects of water exposure time and temperature on adhesion. Next, we address the effects of interfacial plasma treatments and we present the results of \(\text{D}_2\text{O}\) diffusion experiments aimed at identifying the main diffusion path. We conclude our discussion with a simple application in the form of adhesion degradation maps.

### 2. Water diffusion-induced adhesion degradation in film stacks

In this section, we describe a model for the degradation of the adhesion energy of a film stack caused by the diffusion of an active species such as water. We apply the model to the four-point flexure geometry, which was used to perform the adhesion measurements in this study, but the model is easily generalized to other geometries. Fig. 1a shows a schematic diagram of the four-point flexure specimen. In the four-point flexure technique, which is commonly used to measure adhesion energies \([24–27]\), the film stack of interest is sandwiched between two substrates and the entire assembly is deformed in bending until delamination occurs. A more detailed description of the technique is given in the experimental section of this paper. One of the main advantages of the technique is that the energy release rate for film delamination can be calculated from macroscopic variables that are readily measured.

When a four-point flexure specimen is exposed to water, water molecules diffuse into the film stack from the edges of the sample and diffusion fronts develop as illustrated schematically in Fig. 1b. In a typical four-point flexure measurement, the crack propagates at or near the film-substrate interface in the direction perpendicular to the direction of diffusion, i.e. the water concentration varies along the crack front. Thus, if the crack travels at constant velocity, the energy release rate must also vary along the crack front. It is well known that the energy release rate to drive a crack at a given velocity in the reaction-controlled regime varies linearly with the chemical potential of water in the environment \([15–18,28,29]\). If the water vapor in the environment can be regarded as an ideal gas, then

\[
G = B - nNRT \ln p_{\text{H}_2\text{O}} = B - A \ln p_{\text{H}_2\text{O}} \quad \text{for } G \leq G_c, \tag{1}
\]

where \(n\) is the number of water molecules reacting with each broken bond, \(N\) is the areal bond density, \(B\) is a constant that depends on crack velocity, \(R\) is the ideal gas constant, \(T\) is the absolute temperature at which the crack propagates and \(G\) is the energy release rate for that crack velocity. \(A\) and \(B\) are readily determined using subcritical fracture measurements \([16,18,23]\). Eq. (1) makes it possible to couple the water diffusion profile in the film stack to the energy release rate required to drive a crack at a constant velocity. Now consider an experiment in which water is allowed to diffuse into a four-point flexure specimen at temperature \(T_D\) and the specimen is tested at a temperature \(T_A\). If water dissolved in OSG follows Henry’s law, the energy release rate needed to fracture a four-point flexure specimen decreases with increasing exposure time \(t\) according to the following expression \([23]\):

![Fig. 1. (a) Schematic view of a four-point flexure specimen. (b) Cross-sectional view of an adhesion sample showing the geometry of the diffusion problem.](image-url)
where
\[
\Phi(\gamma, \tau) = \int_0^1 \ln \left\{ 1 - (1 - \gamma) \left( \frac{4}{\pi} \sum_{k=0}^{\infty} \frac{1}{2k+1} \sin((2k+1)\pi \xi) \right) \right\} d\xi
\]
and
\[
\gamma = \frac{C_s^{T_0} P_l^{T_0}}{C_s^{T_A} p_n^{T_A}} \quad \text{and} \quad \tau = \frac{D_{H_2O}^{T_0}}{b^2} t.
\]
In these expressions, \( C_s^{T_0} \) and \( C_s^{T_A} \) represent the solubility of water at \( T_D \) and \( T_A \), respectively; \( p_l^{T_A} \) is the water vapor pressure at \( T_A \); \( p_n^{T_A} \) is the water partial pressure at \( T_A \) in equilibrium with the initial water content of the film stack. \( D_{H_2O}^{T_0} \) is the diffusion coefficient of water in the film stack and \( b \) is the width of the four-point flexure specimen. The quantities \( \gamma \) and \( \tau \) are non-dimensional measures for the initial water concentration in the film stack and the time the specimen has been exposed to water, respectively. The function \( \Phi(\gamma, \tau) \) determines how the energy release rate changes with exposure time and is readily evaluated numerically (Fig. 2a). Fig. 2b shows the adhesion energy required to delaminate a four-point flexure specimen as a function of exposure time and for different levels of initial water content. It should be noted that Eq. (3) is valid only as long as the initial water content is large enough that the critical energy release rate \( G_c \) is not exceeded anywhere along the crack front. If the initial water concentration is too low, the linear relationship between energy release rate and chemical potential breaks down. The energy release rate is then bounded by the critical energy release rate and Eq. (3) takes on a rather less convenient form.

The geometry analyzed in this section is also appropriate for the double-cantilever-beam specimen, another test geometry often used for thin-film fracture measurements. Eqs. (2)–(4) can be applied directly to double-cantilever-beam experiments, provided the constants \( A \) and \( B \) are obtained under pure mode I conditions. Finally, it should be noted that, with the exception of the diffusion coefficient \( D_{H_2O}^{T_0} \), the solubility ratio, and the constant \( \gamma \), all parameters in Eq. (2) can be measured independently using subcritical fracture measurements. Accordingly, Eq. (2) can be used to determine the water diffusion coefficient in a film stack from a series of fracture experiments.

Instead of exposing a dry film stack to water and measuring the change in adhesion energy as a function of exposure time, it is also possible to first saturate the film stack with water and then drive out the water by annealing in a flowing inert gas. Such an out-gassing experiment has several advantages: using this approach, the diffusion experiments can be performed at temperatures well above the boiling point of water. Consequently, it is possible to obtain diffusion data over a wide range of temperatures and to establish an accurate value of the diffusion activation energy. An out-gassing experiment also provides information on the reversibility of the adhesion degradation. If water diffuses into the OSG and participates in a chemical reaction, a low-temperature anneal is unlikely to reverse the degradation. If, on the other hand, there is no interaction between water and OSG except in the presence of a stress field, the degradation process is expected to be reversible. In the latter case, it is straightforward to show that the change in adhesion energy with annealing time is given by
\[
G(t) = B - A \left[ \ln \left( \frac{p_l^{T_A}}{p_l^{T_0}} \right) + \Phi(\gamma_t, \tau) \right],
\]
where \( \gamma_t \) is now a non-dimensional measure of the water partial pressure \( p_l^{T_0} \) in the annealing environment:
\[
\gamma_t = \frac{C_s^{T_A} P_l^{T_0}}{C_s^{T_0} p_n^{T_0}}.
\]
3. Experimental methods

OSG films with a thickness of 420 nm were deposited onto bare (100)-oriented silicon substrates at 400 °C using an industrial plasma-enhanced chemical vapor deposition (PECVD) process with 1,3,5,7-tetramethylcyclotetrasiloxane (TMCTS) as a precursor, oxygen as an oxidizer and carbon dioxide. The films had a porosity of approximately 7% as determined by X-ray reflectometry, and a relative dielectric constant of approximately 2.8. The OSG films were capped with one of two types of barrier layers, either a 200-nm-thick PECVD silicon nitride (SiNₓ) or a 375-nm-thick PECVD silicon carbonitride (SiCN) coating. The OSG films with the SiCN coatings were treated with an ammonia or a helium plasma immediately prior to the deposition of the OSG film stacks. The OSG film stacks have been bonded to supporting Si substrates using a spin-on epoxy (EPO-TEK 353ND from Epoxy Technology) and cured for 1 h at 120 °C.

Thin-film delamination tests were conducted using the four-point flexure technique under constant displacement rate conditions [24–26]. Such conditions lead to a constant load during crack extension, which is directly related to the adhesion energy of the film stack [21]. The sample preparation technique and testing procedure have been described in detail elsewhere [16–18]. Briefly, the Si substrates with the OSG film stacks were bonded to supporting Si substrates using a spin-on epoxy (EPO-TEK 353ND from Epoxy Technology) and cured for 1 h at 120 °C. The bonded substrates were cut into 60 mm · 6 mm beams using a high-speed dicing saw. Notches were machined across the substrate beams to facilitate crack initiation upon bending. The specimens were baked at 180 °C in a vacuum furnace with a base pressure of 5 × 10⁻⁴ Pa for 14 h, before being submerged in deionized water at 25 or 95 °C for pre-defined periods of time. After submersion, the samples were dried and immediately tested using the four-point flexure technique. Additionally, some specimens were submerged in deionized water at room temperature for 4 weeks to fully saturate them with water. These samples were subsequently baked at 150 °C in flowing argon for specified periods of time and immediately tested using the four-point flexure technique. All four-point flexure tests were performed in dry N₂ at 25 °C at a crosshead speed of 0.3 μm s⁻¹. The corresponding crack velocity was approximately 20 μm s⁻¹. All experimental loading curves displayed well-developed load plateaus during crack extension allowing the determination of the adhesion energies. As stated previously, the adhesion energies thus obtained correspond to the energy release rates required to drive a crack at a given velocity in a given environment.

After the adhesion measurement, the fracture surfaces were analyzed by X-ray photoelectron spectroscopy (XPS) to determine the precise fracture interface. Throughout the measurements, all specimens were fully randomized to eliminate systematic errors caused by substrate-to-substrate variations or subtle variations in sample preparation and testing procedures. Subcritical crack growth measurements in environments with controlled water partial pressure were performed on the OSG/SiCN samples using a load relaxation technique as described in Ref. [18]. Subcritical results for the OSG/SiNₓ film stacks have been reported previously [18].

In order to determine whether water diffuses through the bulk of the OSG film or mainly along the interfaces, a diffusion experiment was carried out with deuterium as an isotopic tracer: three 8 mm × 8 mm Si substrates with the OSG/SiNₓ film stack were exposed to heavy water (D₂O, from Cambridge Isotope Laboratories, Inc.) at room temperature for periods of 1, 7 and 15 days, respectively. The SiNₓ coating is an effective barrier to D₂O diffusion so that D₂O could diffuse into the film stack only from the edges of the samples. The composition at the center of these samples was measured as a function of depth using secondary ion mass spectroscopy (SIMS) with a primary beam of 3 keV Cs⁺ ions. Concentrations were calculated from measured secondary ion counts using relative sensitivity factors determined from the absolute concentrations of carbon and fluorine in a reference sample measured by Rutherford backscattering spectroscopy.

4. Results and discussion

4.1. Adhesion degradation

Fig. 3 shows the adhesion energy of the OSG/SiNₓ interface as a function of the time the film stacks were exposed...
to water at 25 and 95 °C. XPS analysis confirms that the delamination occurred at the OSG/SiN interface. The arrow marks the adhesion energy for film stacks immediately after the vacuum bake at 180 °C. The two curves in the figure are very similar: the adhesion energy is approximately 7 J m⁻² prior to exposure to water, but it drops off quickly after water is allowed to diffuse into the film stack. Eventually, the adhesion energy reaches a plateau value of less than 3 J m⁻², indicating that the film stacks are saturated. The figure clearly demonstrates the detrimental effect of water on the adhesion of the OSG/SiN interface. Two observations are noteworthy. First, the plateau value for the diffusion experiment at 95 °C is lower than for the experiment at 25 °C. The difference is small, but is statistically significant; it is probably associated with an enhanced solubility of water in the OSG coating at elevated temperature. Second, the degradation of the adhesion occurs much faster at elevated temperature. This accelerated degradation is the result of a nearly tenfold increase in the diffusion coefficient at this temperature. The model presented in the previous section can be used to calculate quantitative values for the diffusion coefficient using the procedure described in Ref. [23] along with the subcritical measurements published by Vlassak et al. [18].

The values of A, B, γ and D thus obtained are listed in Table 2. The solid lines in Fig. 3 represent the adhesion energy obtained from the diffusion model – it is evident that the model is in close agreement with the experimental results.

Experiments were also carried out in which OSG/SiN film stacks that were previously saturated with water were annealed in flowing argon at a temperature of 150 °C. Fig. 4 shows the adhesion energy required to delaminate these OSG/SiN film stacks as a function of the annealing time. The arrow marks the value of the adhesion energy prior to exposure to water. After 4 weeks in deionized water, the adhesion energy decreases to less than 3 J m⁻². During the annealing process the adhesion gradually recovers and reaches a value comparable to the pre-exposure adhesion energy. The annealing data can be analyzed using Eqs. (2), (5) and (6) (see Table 2) to obtain the diffusion coefficient; the value of γf was estimated from the water content of the argon and the change in water solubility between 25 and 95 °C. The diffusion coefficient for water into the OSG film stack at 150 °C is 5.5 × 10⁻¹⁰ m² s⁻¹.

<table>
<thead>
<tr>
<th>Table 2</th>
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</thead>
<tbody>
<tr>
<td>Summary of model parameters and diffusivities</td>
</tr>
<tr>
<td>Si/OSG/SiN</td>
</tr>
<tr>
<td>25 °C</td>
</tr>
<tr>
<td>A (J m⁻²)</td>
</tr>
<tr>
<td>B (J m⁻²)</td>
</tr>
<tr>
<td>γ</td>
</tr>
<tr>
<td>D (m² s⁻¹)</td>
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</tbody>
</table>

* Samples for this series were prepared in a separate batch from the other OSG/SiN samples and had a slightly lower adhesion value, hence the lower B value.

b γf Value.

4.2. The effect of interfacial plasma treatments

Fig. 5 shows the subcritical crack growth curves for the OSG/SiCN film stacks where the interface was subjected to a He plasma for 10 s followed by a NH₃ plasma for 90 s. The subcritical crack growth data for film stacks with different plasma treatments were similar and are not reproduced here. All curves show a reaction-controlled regime.
where the crack velocity changes exponentially with energy release rate and where the crack velocity is a sensitive function of the relative humidity, and a transport-controlled regime, where the crack velocity changes much more slowly with energy release rate. Fig. 6 shows the linear relationship between the energy release rate required to drive a crack at a given velocity and the natural logarithm of the water partial pressure in the testing environment as described by Eq. (1). Since the crack velocity of interest is relatively large, the reaction-controlled regimes of the subcritical crack growth curves were extrapolated to the appropriate crack velocity. This was necessary to avoid any transport-control effects. Because water is already present in the film stacks in this study, there is no need to transport water molecules to the crack tip during delamination. The figure demonstrates that the linear relationship between the energy release rate to drive a crack at a given velocity or adhesion energy, and the logarithm of the water partial pressure is valid over a wide range of water partial pressures. The figure also illustrates the rather significant effect water vapor can have on the adhesion of a film stack. As the water partial pressure decreases, the adhesion energy increases until eventually the critical energy release rate is reached (not shown), at which point the linear relationship breaks down and the adhesion energy becomes independent of the environment. It is evident from the figure that the slope of the linear relationship changes for different plasma treatments and that the slope is larger than for the untreated OSG/SiN<sub>x</sub> film stack. According to Eq. (1), the slope is determined by \( A = nNRT \), i.e. the slope scales with the bond density \( N \). Consequently, the data suggest that the bond density increases when the interface is exposed to a plasma treatment. Furthermore, it is evident from Fig. 6 that at a given water partial pressure, the plasma-treated OSG/SiCN film stacks require a larger energy release rate for delamination than untreated film stacks. A closer look further reveals that the precise sequence of the plasma treatments makes a difference: Compared with film stacks treated with a He plasma only, film stacks exposed to both He and NH<sub>3</sub> plasmas show improved adhesion if the NH<sub>3</sub> treatment occurs before the He treatment, and worse adhesion otherwise.

These observations can be rationalized if one assumes that the plasma treatments modify the surface of the OSG to create a thin, dense SiO<sub>2</sub>-like layer that is depleted of organic groups as suggested by some reports in the literature [30–32]. If the OSG is placed in an He plasma, interaction between the OSG and the excited He<sup>*</sup> species in the plasma would leave a surface with a high density of dangling bonds as well as H–Si–O bonds that should form a strong bond with the SiCN capping layer deposited immediately after the He plasma treatment [31]. If the OSG is placed in an NH<sub>3</sub> plasma after the He treatment, however, some of the dangling bonds will react with NH<sub>3</sub> and related species in the plasma to form amine groups. Our results suggest that this produces a net reduction of the bond density across the interface and hence a reduction of the adhesion energy compared with an OSG surface that was exposed to just an He plasma. If the He treatment is performed after the NH<sub>3</sub> treatment, the He<sup>*</sup> species in the plasma strip the amine groups from the OSG surface. The result is an improvement in the adhesion energy to a value that is somewhat larger than for samples with just the He treatment, presumably because of the additional OSG densification that takes place during the NH<sub>3</sub> treatment.

Fig. 7 shows the adhesion energy of the OSG/SiCN interface as a function of water diffusion time, along with the adhesion energy obtained from the diffusion model. Agreement between the experimental measurements and the model is very good over the entire range of diffusion times. The effect of the plasma treatments is clearly reflected in the results; the as-prepared plasma-treated film stacks have adhesion energies that are nearly a factor of two larger than the untreated films. The effect of the
plasma treatments is greatly reduced, however, after allowing water to diffuse into the film stacks; the adhesion energy for a saturated film stack is comparable to that of an untreated film stack that is fully saturated. This large reduction in adhesion energy is a direct consequence of its enhanced dependence on water partial pressure for plasma-treated film stacks as illustrated in Fig. 6. This finding has obvious consequences for the effectiveness of this type of plasma treatments in the presence of water. Moreover, the results show that it is imperative to avoid any exposure to water when comparing plasma treatments with a goal of enhancing the adhesion.

The results in Fig. 7 suggest that the time scale for adhesion degradation is independent of the precise interfacial treatment the film stacks received. Indeed, the diffusion coefficients obtained from the model and which are summarized in Table 2 are the same for each of the plasma treatments. Furthermore, they have the same value as the diffusion constant for untreated film stacks. This observation suggests that the diffusion path is the same for all the film stacks and that it is not the OSG/SiNₓ or OSG/SiCN interface.

4.3. Diffusion coefficient and diffusion path

The question remains what the precise diffusion path of the water molecules in the OSG film stack is. Table 3 provides an overview of water diffusivities available in the open literature for quartz, amorphous silica, and other relevant materials systems. It is evident that the diffusion coefficient for water in most of these materials is many orders of magnitude smaller than the values found in this study. Even the diffusion coefficient for hydrogen silsesquioxane (HSQ), which is probably the dielectric most comparable to OSG in terms of mass density and structure, is three orders of magnitude smaller. Therefore, the value of the diffusion coefficients measured in this study suggests that water diffusion through the OSG is not responsible for the adhesion degradation process. Further insight can be gained if the temperature-dependence of the diffusion coefficient is considered. An Arrhenius graph of the diffusion coefficient yields a diffusion activation energy of \( 26 \text{kJ mol}^{-1} \), or 0.27 eV, and a pre-exponential factor of \( 8.95 \times 10^{-7} \text{m}^2 \text{s}^{-1} \). Hence, the activation energy for water diffusion in the OSG film stacks is at least a factor of two smaller than the activation energies for bulk diffusion listed in Table 3. The activation energy is consistent, however, with interfacial diffusion. For instance, the activation energy for diffusion along the TiN/SiO₂ interface is reported to be 0.21 eV [37]. Since the diffusion coefficient is independent of the precise nature of the OSG/capping layer interface, it seems logical that the fast diffusion path for the OSG film stacks used in this investigation lies along the OSG/Si interface. This is confirmed by the composition profiles obtained from the SIMS analysis of the OSG/SiNₓ film stacks that were exposed to deuterium oxide. Fig. 8 shows the deuterium concentration as a function of depth for four films stacks: one as-deposited reference sample and three samples exposed to D₂O for 1, 7 and 15 days, respectively. The deuterium concentration in the SiNₓ capping layer is very low – it corresponds to the natural abundance of deuterium in the hydrogen present in the SiNₓ film – and it is independent of whether the sample was exposed to D₂O. This confirms that SiNₓ is a good barrier to D₂O diffusion. The deuterium concentration in the OSG, by contrast, shows a significant variation with exposure time: the concentration in the reference sample is equal to what one would expect based on the hydrogen content of the OSG and the natural incidence of deuterium, but the other

Table 3

<table>
<thead>
<tr>
<th>Material</th>
<th>Solute</th>
<th>( D ) at 25 °C (m² s⁻¹)</th>
<th>Activation energy (eV)</th>
<th>Temperature range (°C)</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quartz</td>
<td>D₂O, H₂¹⁸O</td>
<td>( 4.5 \times 10^{-24} )</td>
<td>0.61</td>
<td>125–200</td>
<td>Nuclear reaction</td>
<td>[33,34]</td>
</tr>
<tr>
<td>Silica</td>
<td>D₂O, H₂¹⁸O</td>
<td>( 4.5 \times 10^{-21} )</td>
<td>0.61</td>
<td>125–200</td>
<td>Nuclear reaction</td>
<td>[33,34]</td>
</tr>
<tr>
<td>Silica</td>
<td>D₂O, HTO, H₂O, H₂¹⁸O</td>
<td>( 5.9 \times 10^{-21} )</td>
<td>(extrapolated) 0.74</td>
<td>160–1200</td>
<td>–</td>
<td>[35,36]</td>
</tr>
<tr>
<td>PECVD silica</td>
<td>D₂O, H₂¹⁸O</td>
<td>( 3.61 \times 10^{-14} )</td>
<td>0.74</td>
<td>8–90</td>
<td>SIMS</td>
<td>[37]</td>
</tr>
<tr>
<td>HSQ</td>
<td>H₂O</td>
<td>( 6 \pm 2 \times 10^{-17} )</td>
<td>0.21</td>
<td>8–90</td>
<td>Quartz crystal microbalance</td>
<td>[38]</td>
</tr>
<tr>
<td>TiN/SiO₂ interface</td>
<td>D₂O, H₂¹⁸O</td>
<td>( 6 \pm 2 \times 10^{-17} )</td>
<td>0.21</td>
<td>8–90</td>
<td>SIMS</td>
<td>[37]</td>
</tr>
</tbody>
</table>
three samples show elevated levels of deuterium. Furthermore, the samples that were exposed for 1 and 7 days show distinct concentration gradients through the OSG film thickness, while the sample exposed for 15 days shows a relatively flat profile. This is precisely the profile one expects if the OSG/Si interface is the fast diffusion path. It should be noted that the oscillations in the $D$ concentration are not the result of noise in the measurements, but reflect the fact that the OSG coatings were deposited in six discrete layers. Having demonstrated that the water molecules diffuse primarily along the OSG/Si interface, it is now possible to derive bounds for the diffusion coefficient of water in OSG. In order to degrade the adhesion of the OSG/SiN, or OSG/SiCN interface, water molecules need to diffuse through the film from one interface to the other. Since this step is not rate limiting, we find that

$$D_{\text{OSG/Si}} \gg D_{\text{OSG}} \gg \left( \frac{h}{b} \right)^2 D_{\text{OSG/Si}},$$  \hspace{1cm} (7)

where $h$ is the film thickness and $b$ the sample width. Eq. (7) implies that the diffusion coefficient in OSG at room temperature is larger than $2 \times 10^{-15}$ m$^2$ s$^{-1}$, which is reasonable given the data in Table 3. The equation further implies that if the film thickness is increased sufficiently, diffusion through the OSG may become rate limiting.

The diffusion of water through amorphous silica is understood in terms of a mechanism where water diffuses in molecular form and reacts with the silicon–oxygen network of glass to form SiOH groups [35]:

$$\text{SiO} - \text{Si} + \text{H}_2\text{O} \rightarrow 2\text{SiOH}.$$  \hspace{1cm} (8)

At high temperature, the reaction represented by Eq. (8) proceeds relatively quickly and the mobile water molecules are in equilibrium with the nearly immobile hydroxyl groups; at low temperature the reaction is slow and the water molecules are not necessarily in equilibrium with the hydroxyl groups. The results presented here do not provide information on the precise diffusion mechanism of water along the Si/OSG interface or in the OSG, but they are certainly consistent with a similar mechanism for water diffusion in OSG. The adhesion degradation process is well described by Fick’s law; moreover, the data presented in Fig. 4 demonstrate that the adhesion degradation process is entirely reversible under relatively mild annealing conditions. This result suggests that the diffusion of mobile water molecules dominates over reaction: at the low test-temperatures used in this study, the reaction between water molecules and Si–O bonds is either negligible in the absence of a stress field or fully reversible at the time scales involved in the experiments.

### 4.4. Adhesion degradation maps

The adhesion degradation that occurs as a result of water diffusion can lead to delayed fracture of a film stack. For instance, a flaw that is too small to cause fracture in a dry film stack may be unstable after the film stack is exposed to water for some time and may cause delamination of the film stack. For specific geometries, it is possible to solve the diffusion equation and hence to predict how the adhesion energy varies with exposure time. In this case it is appropriate to use the adhesion energy for zero crack velocity, i.e. the equilibrium interfacial fracture resistance. It is also possible to determine how the crack extension force changes as a function of flaw size by solving the appropriate boundary value problem. By combining both pieces of information, one can devise a map that predicts when a film stack fails as a function of exposure time and initial flaw size. Consider, for instance, the case of film delamination starting at an edge. Fig. 9 shows the corresponding geometry. The energy release rate for an interfacial crack in this geometry has been calculated by Yu et al. [39]: it is zero for a crack of vanishing length and quickly approaches a steady-state value $G_{ss}$:

$$G_{ss} = \frac{(1 - v_f^2)\sigma^2_{res}t_f}{2E_f}$$  \hspace{1cm} (9)

where $v_f$ is the film Poisson’s ratio and $\sigma_{res}$ is the residual stress in the film. The resistance to fracture is given by the model discussed in this paper combined with the expressions for diffusion into a semi-infinite solid to account for the different geometry. Fig. 10a shows the energy release rate as a function of crack length along with the fracture resistance for the special case where the resistance of a dry film stack is large enough to prevent failure, but the resistance of a wet stack is not. Initially, the entire fracture resistance curve lies above the curve for the energy release rate, i.e. flaws of any length are stable. After exposure to water for a period of time, part of the fracture resistance curve drops below the energy release rate curve and cracks with lengths in this range become unstable. This result is summarized in the critical crack length map in Fig. 10b. The solid lines in this figure give as a function of exposure time the critical crack length at which cracks start growing; the dashed lines give the maximum length to which an unstable crack will grow; if the crack length exceeds the dotted lines, the crack will grow indefinitely. The map in Fig. 10b is valid for plane-strain cracks, but is readily extended for more realistic flaw geometries. One limitation of the map in Fig. 10b is that it implicitly assumes that diffusion through the film stack is the main water transport mechanism. If there is an existing crack when the film stack is first exposed to water, transport of water along the crack faces would...
presumably occur much faster than for diffusion through the film or along an interface. Hence the map is strictly valid only for flaws that do not allow water transport or that are introduced right after water exposure.

5. Conclusions

When OSG/SiN and OSG/SiCN film stacks are exposed to water, the adhesion energy decreases with time as a result of the in-diffusion of water. Experimental measurements of adhesion energy as a function of exposure time are in good quantitative agreement with an analytical model that couples water diffusion and subcritical crack growth. When the film stack is saturated with water, the adhesion reduction can be quite large. The degradation is completely reversible under mild annealing conditions. This observation suggests that in the absence of a stress field the reaction between water and the Si–O bonds in the OSG is either negligible or fully and readily reversible. Plasma treatments of the OSG/SiCN interface result in a significant increase in the adhesion energy in the absence of water, but this enhancement is lost almost completely upon exposure of the film stack to water. The kinetics of the degradation process is independent of the plasma treatment suggesting that water does not diffuse preferentially along the OSG/SiCN interface. Diffusion experiments with deuterium oxide suggest that the Si/OSG interface is the main diffusion path for the film stacks in this study. Even though the diffusion paths in actual integrated circuits are likely to be different and much slower than in this study, adhesion degradation is an issue for integrated circuits because length scales in integrated circuits are also much smaller than those considered in this study. The incorporation of porous low- \( k \) dielectrics in integrated circuits in the near future is expected to further increase their susceptibility to diffusion-induced adhesion degradation.

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