Adhesion degradation and water diffusion in nanoporous organosilicate glass thin film stacks

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Abstract

The diffusion of water in nanoporous organosilicate glass (NPOSG) film stacks causes significant adhesion degradation of the capping layer on top of the NPOSG. We have used this adhesion degradation to estimate the diffusivity of water in a NPOSG film stack. The effective diffusivity is $1.0 \times 10^{-9}$ m$^2$/s, nearly two orders of magnitude larger than in previous generations of dense organosilicate glass film stacks. This result is consistent with the diffusion coefficient measured using secondary ion mass spectroscopy and a deuterium oxide tracer. An optical microscopy study yields similar results for the diffusion of toluene in NPOSG film stacks, but the optical technique is not suitable for measuring the diffusion coefficient of water.

Keywords: Water diffusion; Ultra low-k; Nanoporous organosilicate glass; Adhesion degradation; Thin films

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Introduction

Nanoporous organosilicate glass (NPOSG) with a relative dielectric constant \( k \) of less than 2.7 is used as inter-metal dielectric in high-performance integrated circuits, including microprocessors and memory chips.\(^1\) NPOSG is similar to the organosilicate glass used in previous generations of integrated circuits, but contains nano-scale pores that reduce the permittivity of the material and thus improve the signal transmission characteristics of the dense copper interconnection wires used in advanced integrated circuits. Even though NPOSG is nominally hydrophobic due to the presence of organic groups such as –CH\(_3\), film stacks containing NPOSG are known to absorb water.\(^2,3\) The methyl groups in NPOSG are easily damaged during subsequent plasma processing, making NPOSG film stacks even more susceptible to moisture uptake.\(^4,6\) Water uptake is detrimental to both the performance and the reliability of integrated circuits because water increases the NPOSG dielectric permittivity, accelerates fracture in NPOSG, and degrades the adhesion between the NPOSG and the capping layer. Hence, successful integration of NPOSG films into a microelectronics process flow requires a thorough characterization of water transport in these coatings.

Recently, we demonstrated that adhesion degradation in a wet environment could be used to measure the diffusivity of water in dense organosilicate glass (OSG) film stacks.\(^7,8\) OSG is very sensitive to stress corrosion fracture in the presence of water. The energy release rate required to drive an interfacial crack at a given velocity is directly correlated with the concentration of water in the OSG.\(^9\) Using this approach we have measured the effective diffusion coefficient of water in OSG film stacks.\(^7,8\) In this study, we report a significant reduction of the adhesion energy (more than 50%) for NPOSG film stacks caused by the absorption and diffusion of water, and we estimate the corresponding diffusion coefficient. Specifically, the adhesion between the NPOSG
coating and a SiO$_2$ capping layer is measured after exposing the film stacks to water for different lengths of time. The diffusion coefficient of water in the film stacks is then determined from the change in adhesion over exposure time. This result is compared with results obtained by means of secondary ion mass spectroscopy (SIMS) and optical microscopy (OM).

**Experimental**

The adhesion energy of the NPOSG films stacks is measured by means of the four-point bend test.$^{10-13}$ Detailed sample preparation and testing procedures have been described elsewhere.$^{14-16}$ Briefly, NPOSG films with a thickness of 260 nm were deposited on 200 mm (100) silicon wafers using a commercial plasma-enhanced chemical vapor deposition (PECVD) process and a diethoxymethylsilane precursor. The NPOSG had a dielectric constant of 2.5 and a porosity of 25%. Immediately after deposition of the NPOSG, the films were capped with 2.6 µm layers of PECVD SiO$_2$. The wafers with the NPOSG/SiO$_2$ film stacks were then bonded to bare silicon wafers with epoxy. The inset in Figure 1 shows the final film stack. The bonded wafers were diced into 12 mm-wide beams. In each of these specimens, a notch was machined to initiate a pre-cracks for the adhesion test. The specimens were then baked out for 14 hours at 180°C in a vacuum furnace with flowing argon to remove any moisture absorbed during sample preparation. For the adhesion degradation experiments, the specimens were submerged in distilled water at 24 ± 2°C immediately after bake-out. After a preset period of time, at least five specimens were taken out, superficially dried with a paper towel, and loaded in a four-point bending configuration inside an environmental cell with a dry N$_2$ atmosphere. The experimental load-displacement curves displayed well-defined load plateaus during crack propagation, indicating steady-state crack growth. The crack velocity during these measurements was approximately 60 µm/s. The adhesion energy $G$ was then calculated from$^{10-12}$
\[ G = \frac{21(1 - \nu^2)M^2}{16Eb^2t^3}, \]  

(1)

where \( M \) was the plateau value of the applied bending moment, \( b \) was the width of the specimen, \( t \) was the substrate thickness, \( E \) was Young’s modulus of the Si substrate, and \( \nu \) was its Poisson’s ratio. This procedure was repeated until the adhesion energy did not change anymore with additional submersion time. Subcritical crack velocity curves were obtained for the NPOSAG/SiO\(_2\) interface using the four-point bend test in a load-relaxation scheme. These measurements were performed inside an environmental cell with controlled water partial pressure.\(^{14-16}\) In a typical subcritical measurement, a specimen was first loaded at a constant displacement rate until fracture initiated. At that point, the crosshead was stopped and the load was recorded as the crack continued to grow under subcritical conditions. The crack velocity and corresponding energy release rate were calculated from the load-relaxation data as described by Vlassak, Lin and Tsui.\(^{16}\) In all adhesion measurements, fracture occurred at the interface between the NPOSAG and the SiO\(_2\) capping layer as identified by X-ray photoelectron spectroscopy (spectra not shown).

Diffusion of water in the NPOSAG/SiO\(_2\) film stacks was studied using dynamic SIMS and deuterium oxide (D\(_2\)O) as a tracer. A 16 mm \( \times \) 16 mm sample was soaked for 30 minutes in D\(_2\)O at room temperature. The sample was then dried and loaded in a SIMS system (Physical Electronics 6650 instrument; Chanhassen, MN). Tracer concentration profiles were measured at several locations along the centerline of the sample. During the measurements, the sample was cooled to liquid nitrogen temperatures to minimize diffusion of water. Note that the SIMS sample was not baked out immediately prior to soaking because there was no vacuum furnace at the SIMS facility.
Results and Discussion

Figure 1 shows a typical set of subcritical crack velocity curves as a function of applied energy release rate for different levels of ambient relative humidity. The subcritical curves demonstrate the susceptibility of this materials system to stress-corrosion fracture in the presence of water. Both reaction- and transport-controlled regimes are clearly visible: In the reaction-controlled regime, there exists an exponential relationship between crack velocity and energy release rate, marked by the straight-line fits in the figure. In the transport-controlled regime, the dependence of crack velocity on driving force decreases and the crack velocity saturates. In the reaction-controlled regime, the energy release rate $G$ to drive a crack at a given velocity changes linearly with the chemical potential of water in the ambient:

$$G = B - nNRT \ln p_{H_2O} = B - A \ln p_{H_2O},$$

(2)

where $n$ is the number of water molecules reacting with each broken siloxane bond, $N$ is the areal bond density, $R$ is the ideal gas constant, $T$ is the absolute temperature, $p_{H_2O}$ is the partial pressure of water in the ambient, and $B$ is a constant that depends on crack velocity. Equation (2) provides a direct correlation between the energy release rate and the local water concentration as expressed by the partial pressure and will be used to analyze the adhesion degradation data. The constants $A$ and $B$ are readily determined from the subcritical crack velocity data in Fig. 1: The dashed line in the figure relates the energy release rate at a given crack velocity (60 $\mu$m/s in this study) to the corresponding water partial pressure as defined by the relative humidity. The energy release rate is shown as a function of the water partial pressure in Fig. 2 and a simple linear fit yields $A$ and $B$. Note that Eq. (2) is valid only in the reaction-controlled regime so that for large crack velocities it may be necessary to extrapolate the reaction-controlled regimes.
When samples are submerged in adhesion degradation experiments, water diffuses into the film stacks from the edges of the specimens, as illustrated in the inset in Fig. 3, forming a water concentration profile perpendicular to the direction of crack propagation. Through integration of Eq. (2) over the concentration profile, the adhesion energy can be expressed as a function of the diffusion time \( t \): \(^7,\,^8\)

\[
G(t) = B - A \left[ \ln(p_v) + \Phi(\gamma, \tau) \right],
\]

where

\[
\Phi(\gamma, \tau) = \int_0^1 \ln \left( 1 - (1 - \gamma) \left( \frac{4}{\pi} \sum_{k=0}^{\infty} \frac{1}{2k+1} \sin \left( \left( 2k + 1 \right) \pi \xi \right) \exp \left( -\left( 2k + 1 \right)^2 \pi^2 \tau \right) \right) \right) d\xi
\]

and

\[
\gamma = \frac{p_i}{p_v}, \text{ and } \tau = \frac{D_{H_2O}}{b^2} t.
\]

In Eq. (5), \( p_v \) is the water vapor pressure, \( p_i \) is the water partial pressure in equilibrium with the initial water content in the film stacks, \( D_{H_2O} \) is the diffusivity of water in the film stacks, and \( b \) is the width of the specimens. The results in Fig. 3 show that the adhesion energy for the NPOSG/SiO2 interface starts at a value of approximately 5 J/m\(^2\) and drops to a saturation value of 2.2 J/m\(^2\) in the span of approximately 24 hours. The figure clearly demonstrates the sensitivity of the adhesion energy to the water content in the NPOSG film stacks and it highlights the risk of exposing a NPOSG film stack to water: a simple wet rinse of an integrated circuit during the manufacturing process may lead to fracture and delamination later on in the process. The adhesion degradation experiment provides a means for determining the water diffusivity in the film stack by fitting the data with Eq. 3. With constants \( A \) and \( B \) determined from the data in Fig.
2, the water diffusivity and the initial water content are the sole fitting parameters. The curve fit is shown in Fig. 3 as a solid line for an effective diffusivity of $1.0 \times 10^{-9} \text{ m}^2/\text{s}$. For comparison, the dashed line shows the adhesion degradation for a Si/OSG/SiO$_2$ film stack with an effective diffusivity of $1.4 \times 10^{-11} \text{ m}^2/\text{s}$. The nearly two orders of magnitude difference in diffusivity between water in the NPOSG and OSG film stacks is evident in the timescale of the adhesion degradation process.

Deuterium concentration profiles obtained by SIMS for a sample that was submerged in D$_2$O for 30 minutes are shown for several locations along the sample centerline in Figure 4. Also shown is the concentration profile for a reference sample that was not exposed to D$_2$O. The low and flat deuterium count in the SiO$_2$ layer indicates that the SiO$_2$ coating is an effective barrier to D$_2$O diffusion and that D$_2$O diffused into the film stack only from the edges of the sample. The bell-shaped appearance of the deuterium peaks associated with the NPOSG layer is caused by non-uniform sputtering of the SiO$_2$ barrier layer across the measurement area. The deuterium count for the reference sample represents the natural abundance of deuterium in NPOSG. The deuterium count in the exposed NPOSG sample is much larger than in the reference sample and decreases with increasing distance from the edge of the specimen, i.e., there exists a concentration gradient from which the D$_2$O diffusivity can be estimated. Excess integrated deuterium counts are plotted as a function of distance from the sample edge in Figure 5. As evident in the figure, the experimental data is well fitted by the traditional error function concentration profile with a diffusivity of $2.4 \times 10^{-10} \text{ m}^2/\text{s}$. The diffusivity obtained from the SIMS analysis is approximately four times smaller than the value obtained from the adhesion experiments – well within the experimental error for both techniques. The diffusivity derived from the adhesion measurements has a relatively large uncertainty given the scatter in the data.
and the assumptions in the model. A parameter that has a relatively large effect in this regard is the initial water content of the samples, which was used as a fitting parameter in the data analysis. The SIMS results, on the other hand, probably underestimate the water diffusivity somewhat because of the water already present in the sample. Considering the difference between the two measurement techniques, the experimental values are in reasonable agreement.

In the microelectronics industry, diffusivities in low-k dielectrics are sometimes evaluated by means of optical microscopy (OM). In this technique an organic solvent such as toluene or methanol diffuses into the dielectric coating from the edge of a freshly cleaved sample and the diffusion front is tracked using an optical microscope. The OM technique works well for these solvents since a well-defined diffusion front can be observed as illustrated in Fig. 6a for the diffusion of toluene into an NPOSG/SiO$_2$ film stack. The diffusivity of toluene in the NPOSG/SiO$_2$ film stack is readily determined from a graph of diffusion distance squared versus time (Fig. 7) and is equal to $1.7 \times 10^{-10}$ m$^2$/s. In the case of water diffusion, the OM technique does not result in a visible diffusion front as shown in Fig. 6b. This observation has been taken as evidence that water does not diffuse into hydrophobic nanoporous glasses such as NPOSG, unless it contains a volatile organic solute that adsorbs on the interior surface of the porous glass ahead of the diffusion front. Both the deuterium tracer and the adhesion degradation experiments suggest, however, that water can indeed diffuse into film stacks containing hydrophobic nanoporous materials. It is possible that the change in refractive index associated with water diffusion is not large enough for the diffusion front to be optically visible. This may be so because water diffuses mainly in the vapor phase without condensing inside the pores of the hydrophobic coating. The Kelvin equation indeed predicts that water condensation in very small hydrophobic pores requires a pressure larger than the normal saturation vapor pressure.
Alternately, it is likely that water does not diffuse through the NPOSG, but along the NPOSG/SiO₂ interface. The current SIMS data do not allow us to distinguish between both possibilities, but the results of a recent study strongly suggest that the interface is indeed the main diffusion path.²⁴ The preference of water for interfacial diffusion is attributed to the hydrophilic character of the interface; demethylation of the OSG surface during plasma processing makes the NPOSG/SiO₂ interface an attractive diffusion path for water. Toluene, by contrast, readily wets OSG and diffuses through the NPOSG layer. Evidently, the agreement between the water diffusivity measured in this study and the toluene diffusivity must be regarded as fortuitous. The diffusion of toluene is not a good measure for water transport into NPOSG film stacks.

**Conclusions**

In summary, water absorption and diffusion causes significant adhesion degradation in NPOSG/SiO₂ film stacks. The sensitivity of the adhesion energy to the presence of water makes it possible to estimate the diffusivity of water in the NPOSG/SiO₂ film stack, yielding a value of \(1.0 \times 10^{-9} \text{ m}^2/\text{s}\), significantly larger than for similar film stacks containing dense OSG. This result is consistent with the value of the diffusivity measured with a deuterium oxide tracer. Optical microscopy provided meaningful results for the diffusion of toluene in NPOSG, but was found not useful for the study of water transport in the film stacks.

**Acknowledgements**

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References


Figure Captions

Figure 1. Subcritical crack growth curves for NPOSG/SiO₂ films at different levels of relative humidity at room temperature. The inset shows the film stacks of the adhesion specimens.

Figure 2. Linear relation between the energy release rate to drive an interfacial crack at a given velocity and the natural logarithm of the water partial pressure in the environment for NPOSG/SiO₂ film stacks.

Figure 3. Adhesion energy of the NPOSG/SiO₂ interface as a function of water-exposure time. Discrete points represent experimental measurements; the solid line is the model fit with an effective diffusivity of $1.0 \times 10^{-9}$ m²/s and an initial water partial pressure of 3.95 Pa, the dashed line shows data for an OSG/SiO₂ film stack with an effective diffusivity of $1.4 \times 10^{-11}$ m²/s (adapted from reference [7]). The inset shows the geometry of a four-point bend specimen and a cross-sectional view of the diffusion problem.

Figure 4. Depth profiles of deuterium concentration in NPOSG/SiO₂ film stacks; the lines represent the depth profiles at various distances from the edge of the specimen after exposure to D₂O for 30 minutes.

Figure 5. Deuterium concentration profile in NPOSG/SiO₂ film stacks after exposure to D₂O for 30 minutes, normalized with the concentration at the edge; the discrete points were measured by SIMS, the lines were calculated profiles for various diffusivities.

Figure 6. Optical images of two NPOSG/SiO₂ film stacks showing (a) a clear diffusion front for toluene and (b) no visible diffusion front for water.

Figure 7. Diffusion distance of toluene in NPOSG/SiO₂ film stacks as a function of time, with a fitted diffusivity of $1.7 \times 10^{-10}$ m²/s.
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Figure 2. Linear relation between the energy release rate to drive an interfacial crack at a given velocity and the natural logarithm of the water partial pressure in the environment for NPOS/SG/SiO$_2$ film stacks.

\[ G = B - A \ln(p_{H_2O}) \]
\[ = 5.62 - 0.44 \ln(p_{H_2O}) \]
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