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# 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.
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## 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of a siloxane network similar to that of amorphous silicon dioxide where some of the bridging oxygen atoms have been replaced by hydrogen (–H) or hydroxyl groups (–OH) and by organic groups such as methyl ($–CH_3$) or methylene ($–CH_2–$) [1–3].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 microelectronic 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

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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 $D_2O$ 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

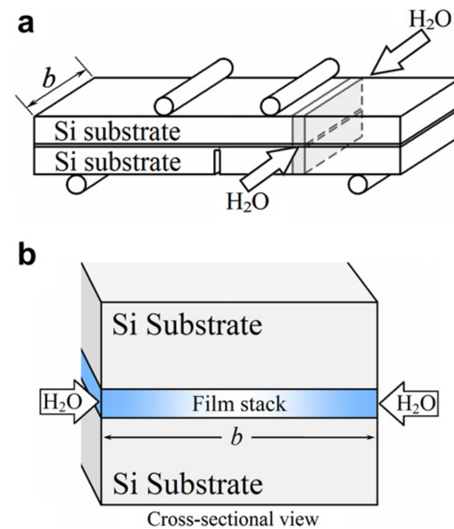


Fig. 1. (a) Schematic view of a four-point flexure specimen. (b) Cross-sectional view of an adhesion sample showing the geometry of the diffusion problem.

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

$$G = B - nNRT \ln p_{H_2O} = B - A \ln p_{H_2O} \quad \text{for } G \leqslant G_c, \qquad (1)$$

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]:

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