

## Environmental Effects on Crack Characteristics for OSG Materials

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### ABSTRACT

To improve capacitance delay performance of the advanced back-end-of-line (BEOL) structures, low dielectric constant organosilicate glass (OSG) has emerged as the predominant choice for intermetal insulator. The material has a characteristic tensile residual stress and low fracture toughness. A potential failure mechanism for this class of low-k dielectric films is catastrophic fracture due to channel cracking. During fabrication, channel cracks can also form in a time-dependent manner due to exposure to a particular environmental condition, commonly known as stress-corrosion cracking. Within this work, the environmental impacts of pressure, ambient, temperature, solution pH, and solvents upon the channel cracking of OSG thin films are characterized. Storage under high vacuum conditions and exposure to flowing dry nitrogen gas can significantly lower crack propagation rates. Cracking rates experience little fluctuation as a function of solution pH; however, exposure to aqueous solutions can increase the growth rate by three orders of magnitude.

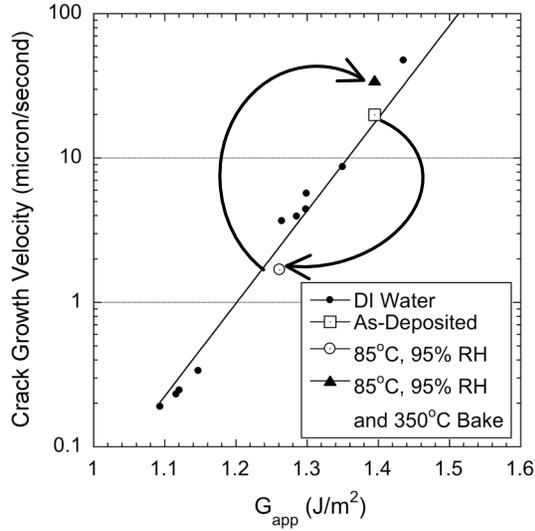
### INTRODUCTION

The integration of low-k dielectric films is required to maintain and improve device performance in future technologies. For intermetal dielectrics, the class of materials known as organosilicate glass (OSG) has emerged as the principal candidate. During the manufacturing process, catastrophic fracture due to channel cracking is a potential failure mechanism.<sup>1</sup> The driving force for channel cracking is dependent on several material properties, with the film modulus, density, and residual tensile stress serving as key factors.<sup>2-3</sup> Channel cracks can also form in a time-dependent fashion due to exposure to specific environmental conditions.<sup>2</sup> These mechanisms are commonly known as environmentally-assisted or stress-corrosion cracking.

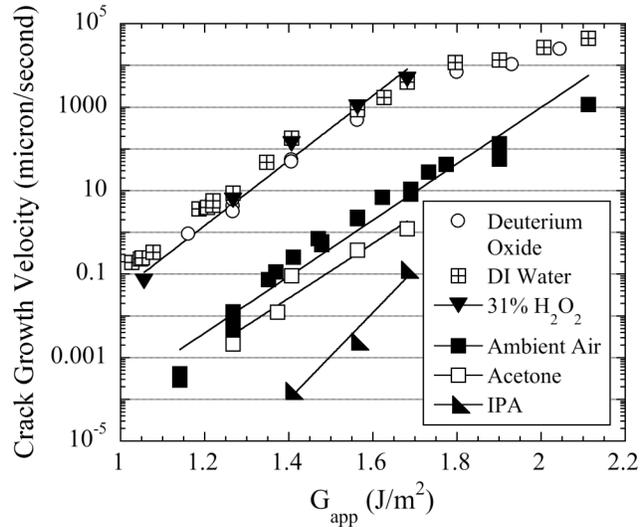
A typical cohesive failure mode for thin films under stress is channel cracking. Channel cracks are defined as extending through the film thickness and propagating perpendicular to the substrate-film interface.<sup>2</sup> Studies by Cook et al.<sup>3,4</sup> showed that the crack propagation rate  $V$  in the reaction-limited regime can be expressed by Equation 1. Where  $\sigma$  represents the residual film stress,  $h$  the film thickness, and  $E$  the elastic modulus. The variable  $k$  is Boltzmann's constant,  $T$  is temperature, and  $n$  denotes the area density of bonds fractured at the crack tip during crack propagation.  $Z$  is a constant defined by crack geometry and  $V_o$  is a fitting constant. The density of bonds fractured during crack separation  $n$  is analogous to the average film density  $\rho$ .<sup>5</sup>

$$V = V_o e^{\frac{Z}{2nkT} \left( \frac{\sigma^2 h}{E} \right)} \quad (1)$$

The majority of studies<sup>6-13</sup> regarding the cracking and failure of silicon-based structures have employed double cantilever beam geometries and cleavage techniques. Limited studies<sup>2-3</sup> have utilized channel crack propagation as a means of assessing mechanical stability. Many authors stress the importance of molecular structure in determining solution corrosivity.<sup>2, 7-13</sup> A siloxane



**Figure 1:** Crack Growth Velocity versus Applied Strain Energy Release Rate for samples under different processing conditions.



**Figure 2:** Crack Growth Velocity versus Applied Strain Energy Release Rate for OSG samples.

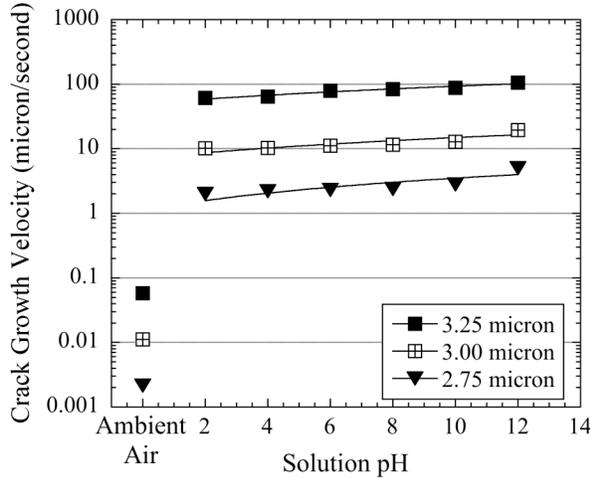
backbone (Si-O-Si) renders silicon-based materials susceptible to stress-corrosion cracking.<sup>2</sup> Solution molecules must fit between Si-O bonds at the crack tip in order to effectively break silical bonds and promote crack propagation.<sup>13</sup> It has been suggested<sup>14-16</sup> that water may have a greater impact on crack growth than temperature, demonstrating the importance of understanding the behaviors of low-k dielectrics during exposure to common manufacturing conditions. In this study, the responses of OSG films were characterized for a range of environmental conditions. The impacts of ambient, solution composition, solution pH, temperature, and pressure on channel crack propagation rates in blanket, low-k dielectric films are discussed at length. The results demonstrate that the well-established fracture theories and relationships pertaining to structured silicate glasses can be extended to channel cracks formed in novel dielectric materials.

## EXPERIMENTAL CONDITIONS

OSG films were deposited onto 200 mm silicon wafers via plasma enhanced chemical vapor deposition (PECVD), using a tetramethylcyclotetrasiloxane (TMCTS) precursor. Temperature and % relative humidity (RH) measurements were recorded by a Traceable Hygrometer/Thermometer Unit. A diamond scribe was used to initiate channel cracks in blanket OSG films. Scratches exceeded 2 cm in length and completely penetrated the films. Crack growth was monitored and measured using electronic digital calipers and optical microscopy. All recorded crack lengths exceeded a minimum length/thickness ratio of 30. Channel crack length was determined to be independent of crack proximity for the materials studied. Certified Fisher Chemicals buffer solutions were used to investigate pH effects on channel crack growth rates. Environmental pressure controlled experiments were conducted in an ultra low pressure XPS chamber with base pressure capabilities of less than  $10^{-8}$  T.

## RESULTS AND DISCUSSION

Throughout these studies, we make direct comparisons between channel crack growth behaviors for a variety of environmental conditions. The intrinsic cohesive strength of our materials was not impacted during testing by these diverse treatments. In Figure 1, the cracking



**Figure 3:** Crack Growth Velocity as a function of Solution pH for OSG films of Variable Thickness.

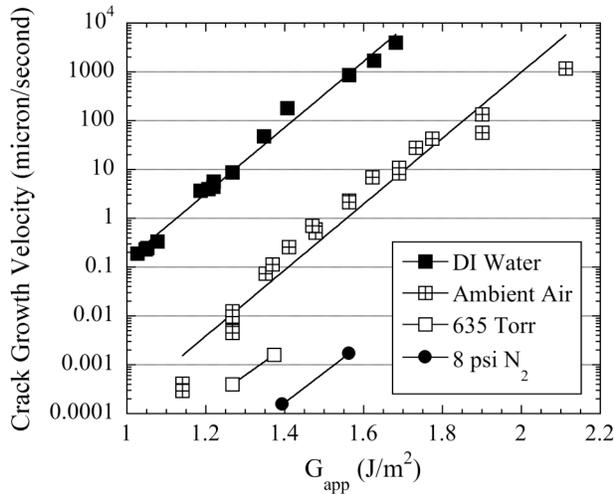
Thickness (microns)	Pressure (Torr)	Crack Growth Velocity ( $\mu\text{m}/\text{sec}$ )
3.25	760	0.060
3.25	635	0.0016
3.25	$1 \times 10^{-9}$	0.0010
3.25	$1 \times 10^{-6}$	0.0003
3.0	760	0.0100
3.0	635	0.0004
3.0	$1 \times 10^{-9}$	$< 1 \times 10^{-6}$

**Table I:** Crack Growth Velocity of OSG films as a function of exposure pressure and film thickness.

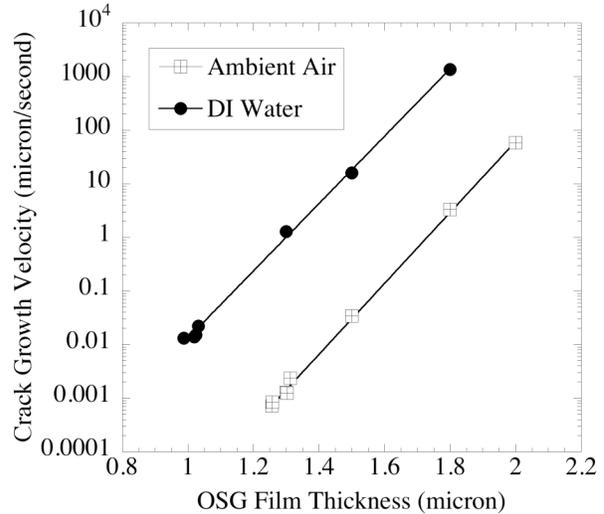
behavior of OSG films in DI water are illustrated for three different types of processing conditions: (1) as-deposited, (2) 85°C/95% RH, and (3) 85°C/95% RH followed by 350°C N<sub>2</sub> bake. The as-deposited film represents material that was tested immediately after deposition. Additional processing occurred directly after film deposition, whereby films were exposed to a temperature of 85°C and 95% RH for two hours. The baking process followed for some samples, proceeding at 350°C for 15 minutes under an inert dry nitrogen ambient. Samples depicted in Figure 1 received some or all of these processing steps prior to testing in DI water. Moisture absorption at elevated temperatures relaxes the films to lower stress states and water undergoes complete desorption at high exposure temperatures. A complete cycle is apparent as we move from an as-deposited state, to 85°C/95% RH, and then 85°C/95% RH and 350°C Bake, where we return to the as-deposited conditions. All three of these processing conditions follow the same trend line as OSG samples of variable thickness tested after a limited period of post-deposition storage, suggesting comparable fracture strengths. The empirical stress and elastic modulus values used throughout our  $G_{\text{app}}$  calculations for as-deposited films are 65 MPa and 10 GPa, respectively. The data in Figure 1 illustrate that the OSG intrinsic fracture toughness is not altered by moisture absorption or exposure to elevated temperatures, as defined by the post-deposition processes.

Channel crack propagation characteristics depend strongly on the environmental testing conditions. Ambient testing was conducted at a temperature of 22°C, 44% RH, and pressure of 760 T. Figure 2 illustrates the crack growth velocities of OSG films versus the applied strain energy release rate. The data follow exponential relationships, in agreement with past works focusing on the reaction rate controlled regime.<sup>2, 7, 9, 15, 16</sup> Exposure to aqueous solutions raised the crack rates by approximately 1000X, as compared to ambient testing conditions. Crack growth velocities were lowest for samples exposed to organic solvents, such as acetone and isopropyl alcohol (IPA). In previous experiments, Guyer et al.<sup>10-12</sup> observed delamination cracking rates to be up to three orders of magnitude higher in lower concentration hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) solutions (< 3 wt%), as compared to water. However, we did not observe a measurable difference between channel cracking rates for samples submerged in DI water and 31 wt% H<sub>2</sub>O<sub>2</sub>.

Cracking rates appear to be primarily a function of environmental water content, as water was the main constituent in our DI water and H<sub>2</sub>O<sub>2</sub> solutions. However, the acetone used in these



**Figure 4:** Crack Growth Velocity versus Applied Strain Energy Release Rate for OSG samples.



**Figure 5:** Crack Growth Velocity as a function of deposited OSG Film Thickness.

studies had a moisture content of 6260 ppm and IPA had only 4480 ppm water, as verified through titration techniques. Once exposure conditions become dominated by the presence of water, no measurable changes in the cracking rates are observed. It is interesting to note that the diffusivity of water molecules in solution is double that of  $H_2O_2$  molecules, inferring a greater reactivity.<sup>10</sup> Our results support the early work of Weiderhorn et al.<sup>9</sup> which states that crack motion is governed by the rate of reaction between water and the silicon-based glass and that the reaction mechanism at the channel crack tip is not altered by changing the moisture content.

The channel cracking rates for OSG films during exposure to deuterium oxide and DI water are also included in Figure 2. Deuterium oxide is an isotopic form of water, commonly referred to as heavy or deuterated water. It is more viscous than water and has greater molecular weight. The self diffusivity of deuterium oxide molecules is 12% lower than that of water.<sup>17</sup> Throughout the  $G_{app}$  range studied, OSG samples immersed in  $D_2O$  and DI water behave similarly, with cracks exposed to  $D_2O$  propagating at a slightly slower velocity than in DI water. This is in agreement with prior studies<sup>13</sup>, whereby double cantilever beam bulk glass specimens produced rates consistently lower within  $D_2O$  than in water. The separation of two distinct regimes can be observed at a crack growth velocity of roughly  $1 \times 10^4$  micron/second – a transition between reaction rate controlled and diffusion rate controlled regimes.

Previous adhesion studies by Guyer et al.<sup>10-12</sup> demonstrated a distinct correlation between solution pH and crack propagation characteristics. Cracking rates were generally higher for basic solutions, decreasing with increasing solution acidity. Rates were reported to drop by as much as 100X over the full range of pH values.<sup>10-12</sup> During the course of our experiments, however, only a minimal dependence on pH was demonstrated. As seen in Figure 3, the crack propagation velocity for OSG films increases by a factor of less than 3X as the solution pH is increased from 2 to 12. A distinct linear relationship exists between the crack rate and solution pH. Samples exhibit roughly one order of magnitude increase in the growth velocity for each  $0.25 \mu m$  increase in film thickness. The pH buffer solutions did not impact the films, as verified through FTIR and XPS analysis. Collectively, our results demonstrate that crack propagation characteristics may depend strongly on the testing geometry, as channel cracks do not always react similarly to cracks monitored in cantilever beam structures under identical environments stimuli.

Testing Environment	ppH <sub>2</sub> O (Torr)
DI Water	19.46
Ambient Air, 760 Torr	8.56
Pressure of 635 Torr	7.15
Flowing Dry N <sub>2</sub>	< 7.15

**Table II:** Partial Pressure of Water (ppH<sub>2</sub>O) at 22°C

The effects of environmental pressure on OSG channel cracking were also investigated. For an exposure temperature of 22°C, the cracking rates of 3.25 and 3.00 micron OSG samples are shown in Table I. It is important to note that as the environmental pressure decreases, the partial pressure of water (ppH<sub>2</sub>O) is also effectively lowered. By decreasing the pressure from 760 to 635 T, cracking rates drop by more than 95%. Under high vacuum conditions of  $1 \times 10^{-6}$  and  $1 \times 10^{-9}$  T, crack growth is greatly retarded; measurable rates are lowered by more than 99% compared to atmospheric pressures. Figure 4 shows the effects of dry N<sub>2</sub> gas flow rate upon the crack growth velocity of OSG films at 22°C. For reference, data for DI water, ambient air, and pressure conditions of 635 T are also included. By raising the N<sub>2</sub> flow rate from 0 psi (i.e. Ambient Air) to 8 psi, cracking rates are lowered by more than 100X. The increase in N<sub>2</sub> flow pressure also serves to further reduce the environmental partial pressure of water. The ppH<sub>2</sub>O for each of the environmental conditions shown in Figure 4 are given in Table II. These results are in agreement with prior studies that have shown moisture content to be a governing factor for crack growth.<sup>9, 14-16</sup> Under low pressure conditions, the entire energy of the bridging structural bond must be overcome for crack propagation to occur.<sup>13</sup> On the other hand, when water is present a charge transfer mechanism offers a lower energy reaction path for growth<sup>13</sup> and lowers the stress required for crack extension.<sup>18</sup> All things being equal, as the environmental water content increases, so does the propensity for channel cracking.

Temperature is another factor governing crack growth in silicon-based dielectric glasses. The temperature response of OSG channel cracks was examined at 635 T for temperatures of 22°C and 72°C. The crack growth velocity  $V$  can be described as follows<sup>7</sup> where  $K_{IC}$  is the stress intensity factor,  $R$  is the universal gas constant, and  $T$  is the exposure temperature. The variables  $V_o$ ,  $E_a$ , and  $b$  are experimental constants obtained by fitting data via the least squares method.

$$V = V_o e^{\frac{-E_a + bK_{IC}}{RT}} \quad (2)$$

Figure 5 shows the impact of exposure temperature on channel cracking in OSG. As temperature increases for a set  $G_{app}$ , the crack rate also increases. The activation energy for OSG channel crack propagation was determined to be 116.8 kJ/mol. A 50°C shift in temperature can alter the measured crack growth velocity by 1.5 orders of magnitude at 635 T. Weiderhorn et al. observed a similar shift for various glasses.<sup>7, 8</sup>

## CONCLUSIONS

The results presented throughout our studies emphasize the key environmental parameters governing channel crack propagation in OSG materials. Many of the well-

established sub-critical fracture theories and empirical relationships formulated for bulk, structured silicate glasses have been shown to apply directly to thin OSG films. In general, channel cracks behave similarly to cracks formed and monitored under more conventional testing techniques.<sup>6-8, 10-13, 15, 16</sup> Thus illustrating that channel crack analysis is a viable method for evaluating and characterizing the sub-critical fracture properties of silica-based thin film glasses. Environmental water content appears to be the most important factor in determining sub-critical channel cracking rates. Moisture levels can be influenced by additional exposure parameters such as solution type, pressure, and dry ambient flow rate. Immersion within aqueous solutions raises crack growth velocities by three orders of magnitude; while solution pH imparts only a minimal influence upon channel crack behavior, adjusting rates by less than 3X.

## ACKNOWLEDGEMENTS

One of the authors, Jeannette Jacques, would like to thank Judy Shaw and Dr. Ben McKee of Texas Instruments Inc. for providing the opportunity to participate in novel research projects as a graduate intern. These works would not have been possible without the materials analysis support of Richard Kuan and Lucyna Carrasco, as well as the processing assistance of Chris Brainard, Jim Burris, Rhida Dalmaico, and Darrell Ingram.

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