

Diffusion of Electrolyte Solutions in Nanoporous Thin-Films

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Abstract:

A number of next generation nano-scale devices require hybrid organic-inorganic nanoporous thin-film glasses for advanced functionality. Though such materials are currently available, the chemically active solutions the films encounter during fabrication can instigate subcritical crack growth which can potentially limit the reliability of a device. It is important to know if reactive aqueous solutions encountered over the lifetime of a product can diffuse into porous methylsilsequioxane (MSSQ), affecting subcritical crack growth. It has been demonstrated that diffusion of the solutions into a porous film can alter the films' stress state, which ultimately affects the rate of crack growth [1]. The MSSQ selected for this study is highly hydrophobic (contact angle with water is $\sim 90^\circ$) and aqueous diffusion into the material is thought to be highly unlikely.

Here we show that various aqueous solution chemistries do in fact diffuse into the films and the rate of diffusion is influenced by salient solution parameters such as pH, ionic strength and organics.

Introduction:

Nanoporous MSSQ is a promising new material being considered in the semiconductor, biosensor, optical and pharmaceutical industries. With porosity levels often approaching ~ 10 -50 vol% the films are incredibly fragile and the Si-O-Si backbone of this glass renders the films susceptible to stress corrosion cracking in reactive environments. These factors have limited integration and long term reliability of the films. Understanding how chemically active solutions effect cracking is essential for these materials to be considered viable candidates in these technologies.

In this study, we examine how aqueous solutions diffuse into nanoporous MSSQ films, a behavior believed to affect the long term reliability of the films [1]. We begin by examining the effects of solution pH and observe that with increasing pH, diffusion rates increase dramatically. The ionic strength of the solutions is also demonstrated to affect the rate of diffusion at a fixed pH. Furthermore, it is shown that the presence of organics dramatically affects the diffusion behavior. This study reveals the complex interplay between solution chemistry and diffusion and identifies the need for further study.

Procedure:

The films used in this study were 400 nm thick, ~ 40 vol% porous MSSQ with pore diameters of ~ 4 nm. We examine the diffusion of aqueous solutions into these films using a previously described technique [2] in which the film is capped with optically transparent silicon nitride using plasma enhanced chemical vapor deposition. A schematic of the Si nitride capped MSSQ can be seen in Figure 1.

The capped MSSQ is then cleaved into wafer sections approximately one-half inch square. The wafer sections are then submerged, exposing the freshly cleaved edges to solution. The diffusion front is observed and recorded using an optical microscope. As the solution diffuses into the MSSQ, the refractive index of the composite changes and the film color changes as seen in the photomicrograph shown in Figure 1. All samples referenced in this paper are LKD-6103 (JSR Corporation, Japan) porous MSSQ. Three samples were run in each test condition. Error bars in all figures are ± 1 standard deviation.

Results and Conclusions:

The MSSQ was initially exposed to a number of buffered solutions with pH values ranging from 1 to 11 and water (pH 6) as shown in Figure 2. These tests demonstrate that aqueous diffusion does indeed take place in MSSQ despite

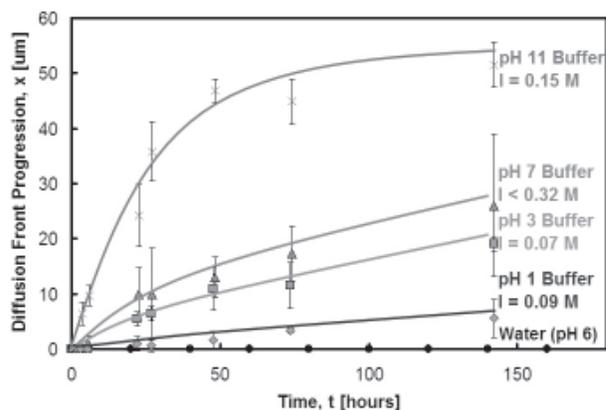


Figure 1: The diagram at the left shows the observation method of capped MSSQ with solution diffusion from the cleaved edge. The photomicrograph at the right is a top down view of the cleaved edge submerged in pH 11 buffer; note the diffusion front that has progressed nearly 100 μm .

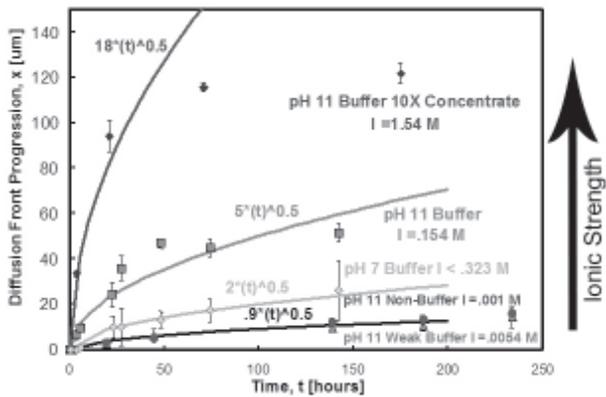


Figure 2: The above diffusion front vs. time graph shows the diffusion behavior of MSSQ in a range of pH buffer solutions and water. In the buffered solutions, higher pH levels increase the rate of diffusion. Note that water does not diffuse.

the inherently hydrophobic nature of the material. With increasing pH in the buffered solutions, the rate of diffusion increases dramatically. The solid lines represent a classic diffusion relationship derived from Fick's laws: diffusion distance goes as the square root of diffusivity multiplied by time. The data is consistent with the model, however, water is an interesting anomaly to this trend as no diffusion is apparent.

To further elucidate the diffusion behavior, we varied the ionic strength (and consequently the activity of the solution) at a fixed pH, as shown in Figure 3. With increasing ionic strength the diffusion rate increases. Note, however, that the pH 7 buffer diffuses faster than some of the lower ionic concentration pH 11 buffers. We believe that this phenomenon is due to the presence of organic species in the buffered solution and as their concentration increased, the solutions diffused faster.

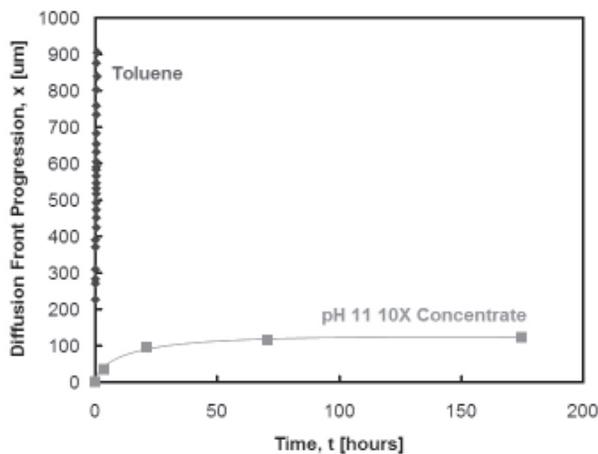


Figure 3: This graph shows the differing diffusion behaviors of pH 11 solutions with different chemistries. Note the deviation from the diffusion behavior predicted by Fick's laws in the pH 11 buffer 10X concentrate.

To investigate the effect of organics, we tested toluene (Figure 4). The startling behavior of toluene confirmed our suspicion. A higher concentration of organics increases the rate of diffusion; in toluene the entire specimen was saturated in under 40 minutes.

Overall, this work has shown that aqueous diffusion does take place in porous MSSQ. Our data reveals a very complex interplay between diffusion and solution chemistry; diffusion behavior is affected interdependently by ionic concentration (solution activity), pH and organic species concentration.

Future Work:

We are currently investigating the diffusion behavior of thin-films with lower porosities. We would like to isolate individual buffer constituents to see if they have an effect on diffusion behavior alone. In order to further investigate the effects of pH and ionic concentration, we would like to formulate our own solutions at specific pH levels and ionic concentrations (solution activity). Lastly, we would like to investigate the apparent deviation from Fick's law behavior at high ionic concentrations.

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References:

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- [2] M. A. Worsley, et. al., Detection of Open or Closed Porosity in Low-k Dielectrics by Solvent Diffusion. To be submitted to the *Journal of Materials Research*. 2004.

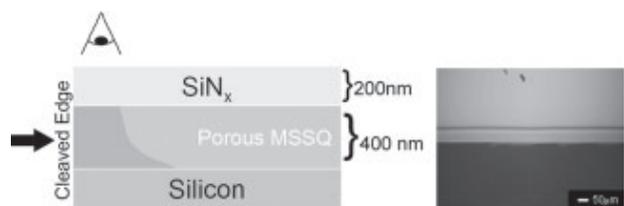


Figure 4: In this graph the diffusion rate of toluene is many orders of magnitude more rapid than pH 11 concentrated buffer solution, saturating the entire sample in less than 40 minutes. Error bars are too small to be visible at this scale.