

The Role of Surfactants in Aqueous Solution Diffusion in Hydrophobic Nanoporous Thin-Film Glasses

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Abstract

Nanoporous organosilicate thin-film glasses are superior candidates for use as ultra-low- κ interlayer dielectrics in advanced microelectronic devices. However, it has been recently reported that aqueous solutions containing organic species can readily diffuse in the film, despite the hydrophobic nature of the film, and increase the κ value during processing [1,2]. Of particular concern is the chemical mechanical planarization (CMP) process in which these extremely brittle materials are subjected to applied down force and shear load in the presence of chemically active aqueous solutions. This harsh process not only increases the κ value but also mechanically damages the thin-films. In this study, we demonstrate the role of surfactants, which are essential components of the CMP slurry, on the solution diffusion in nanoporous organosilicate thin-films. Surfactants were found to enhance the diffusion significantly depending on hydrophobic/hydrophilic group lengths and the structure of the surfactant molecule. Direct evidence of surfactant penetration was obtained using x-ray photoelectron spectroscopy after ion etching.

We propose a possible diffusion mechanism using the polymer reptation model to explain surfactant penetration in the nanoporous glass network. Finally, the implication of surfactant diffusion on an optimized CMP process in terms of κ value requirements is presented.

Introduction

Organosilicate ultra-low- κ dielectric glasses are incorporated into interconnect structures of advanced microelectronics to prevent parasitic transmittance. While these glasses are very effective insulators, they are also extremely vulnerable to the diffusion of solution that yields the undesirable result of an increased κ constant. Chemical mechanical planarization (CMP) is an essential process in interconnect fabrication as it results in a flat surface on which the next layer of the structure can be deposited. Now we consider the role of surfactants, which are necessary components of the CMP solution, in diffusion.

Procedure

Two types of surfactants were considered in this study: monomeric (C_mE_n) and Gemini (Surfynol[®]) surfactants. Various surfactant molecular weights and hydrophobic/ hydrophilic group lengths of both types were considered. Initially, solutions made with each surfactant were used, but pure surfactants in liquid phase were also considered. All surfactant solutions were 0.1 weight percent surfactant concentration in deionized water.

The ultra-low- κ dielectric thin-film considered in our study was methylsilsesquioxane (MSSQ), which is a hydrophobic, structurally modified form of silicon oxide that has the approximate atomic composition of $SiO_{1.5}CH_3$ [3]. A porous MSSQ was used that had an average pore diameter of 2.2 nm and a κ constant of 2.3.

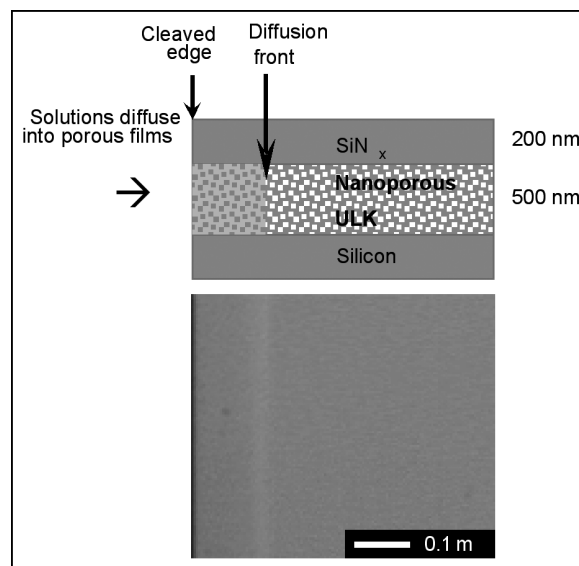


Figure 1: Solution diffusion in MSSQ.

For our study, 500 nm of MSSQ was deposited on a silicon substrate and was capped with an optically transparent silicon nitride layer (200 nm) using the plasma-enhanced chemical vapor deposition system (PECVD). The wafer was then cleaved into 1.5×1.5 cm specimens that were placed in Pyrex[®] petri dishes and submerged in either solution or liquid phase surfactant. The diffusion front was then observed and measurements were taken using an optical microscope at 50x magnification (Figure 1).

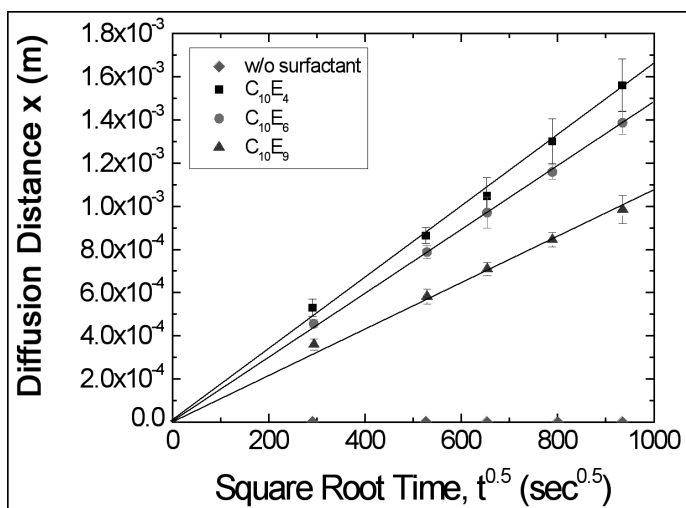


Figure 2: Fick's Law dependent diffusion of linear surfactant solutions.

These techniques were modified from previous studies used to observe the diffusion of aqueous solution [2].

Results and Conclusions

The diffusion distances of both surfactant solutions and pure surfactants showed a square-root time dependence that is characteristic of Fick's first law: $x = \sqrt{Dt}$, where x is the diffusion distance, D is the diffusion coefficient, and t is time (Figure 2). The diffusion coefficient D was observed to be a function of molecular weight, the hydrophobic/ hydrophilic group lengths, and the molecular geometry of the surfactant. For both the monomeric and Gemini pure surfactants as well as the solutions, the diffusion coefficient increased as the surfactant molecular weight decreased.

It was also observed that as the size of the hydrophilic group length of the surfactants (in both pure surfactant and solution) the diffusion coefficient decreased. The diffusion coefficients of the same surfactant at different concentrations (pure vs. 0.1 % wt) were remarkably similar. So it was determined that the surfactant is the determining factor in diffusion. However, the diffusion coefficients of the linear monomeric surfactants were significantly greater than the diffusion coefficients of the non-linear Gemini surfactants.

Despite the assumption that surfactant molecules are too large to penetrate the nanoporous network, we observed diffusion of pure surfactants. To verify this observation, we used x-ray photoelectron spectroscopy (XPS) and found that there was a significant increase in carbon content (from surfactant molecules) within the diffusion front.

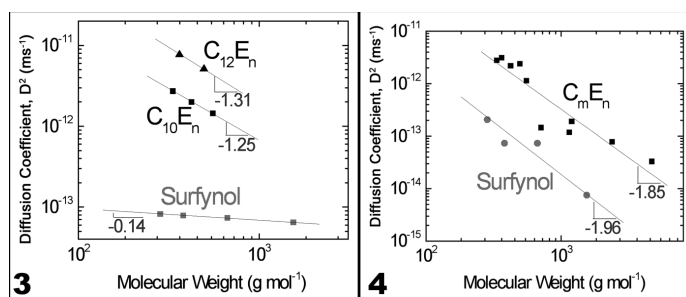


Figure 3: Pure, liquid-phase surfactant D vs. M .

Figure 4: Surfactant solution D vs. M .

Figures 3 and 4 show each calculated diffusion coefficient D of all surfactant solutions and pure liquid-phase surfactants plotted against the molecular weight (M) of the molecules. It can be noted that the slope of each regression for the surfactant solutions is approximately -2. The polymer reptation model describes the relationship between a polymer's molecular weight and the diffusion coefficient of a polymer melt so that $D:M^{-2}$. The polymer reptation model describes the self-diffusion of polymers [4]. Due to the close correlation between this model and the experimental data, we proposed that the surfactant molecules reptate through the nanoscopic pores in MSSQ.

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