

Effects of Nonionic Surfactants on the Fracture of Nanoporous Methylsilsesquioxane Thin-Film Glasses

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Abstract

Fracture of nanoporous methylsilsesquioxane (MSSQ) thin-film glasses by chemical mechanical planarization (CMP) is significant challenge for the integration of these mechanically fragile materials in emerging microelectronic technologies. Here, we demonstrate that the fracture of nanoporous MSSQ can be suppressed by the careful selection of nonionic surfactants in CMP slurry. Crack growth was reduced more in the solutions of nonionic surfactants with a longer alkyl chain. Bridging effects by hydrophobic interaction near the crack tip are proposed.

Introduction

Nanoporous MSSQ thin-film glasses are superior candidates for use as low-k interlayer dielectrics. However, their mechanically fragile nature and susceptibility to environmentally assisted cracking challenge their viability. Of particular concern is the CMP process, which involves subjecting the mechanically fragile structures to applied shear loads in the presence of chemically active solutions that can greatly accelerate cracking [1]. The effects of nonionic surfactants in CMP slurry on the fracture of nanoporous MSSQ are not known, although their effects on the removal rates and selectivity have been studied.

In this study, polyoxyethylene alkyl ethers were studied for their effects on the subcritical crack growth of nanoporous MSSQ. Polyoxyethylene alkyl ethers, C_mE_n , are nonionic surfactants with m being the number of carbon atoms in the hydrophobic alkyl chain and n being the number of hydrophilic oxyethylene (EO) units. The surfactants with various m and n were tested to observe the role of the chain length of the hydrophilic and hydrophobic parts, respectively.

Experimental Procedures

500 nm thick spin-on MSSQ films with a dielectric constant (k) of 2.3 containing pores ~ 2.2 nm in diameter were deposited onto silicon wafers containing a 25 nm thick Ta or TaN barrier layer. Following deposition of the MSSQ films, they were UV cured and then capped with a 25 nm thick TaN layer.

Double cantilever beam (DCB) specimens were fabricated and tested by previous reported techniques [2]. Subcritical crack-growth testing was conducted using the DCB specimens in an aqueous environmental chamber with a constant temperature of 30 °C. Aqueous environments investigated included 0.1 wt% C_mE_n in DI water of pH 10 set by adding ammonium hydroxide. After testing, the specimens were examined using x-ray photoelectron spectroscopy (XPS). In all cases, cohesive failure of the MSSQ was observed.

Results and Discussion

As shown in Fig. 1(a), (b), and (c), alkyl chain length is a dominant factor in controlling the subcritical crack growth behavior. Crack growth in the solutions of surfactants with a longer alkyl chain was slower than with a shorter alkyl chain. Threshold values of the applied strain energy release rates, G_{th} , are plotted in Fig. 1(d). Surprisingly $C_{18}E_{20}$ has G_{th} of 2.1 J/m^2 while $C_{10}E_{20}$ has G_{th} of 1.4 J/m^2 .

The ability for C_mE_n to control the crack propagation is presumably attributed to the hydrophobic interaction. Introducing a non-polar molecule into water strongly disturbs the hydrogen bond network. Therefore, when dissolving non-polar molecules such as the hydrocarbon tails of surfactant molecules, they will try to minimize the damage to the water hydrogen bond network by aggregating [3]. As a crack propagates in the nanoporous MSSQ, hydrophobic surfaces containing non-polar methyl groups inside cracked nanopores are exposed to the solution providing optimal spots for the hydrophobic alkyl tails to aggregate. Cylindrical micelles can be formed bridging the both sides of cracked nanopores near the crack tip and this may cause the hindrance for the crack propagation.

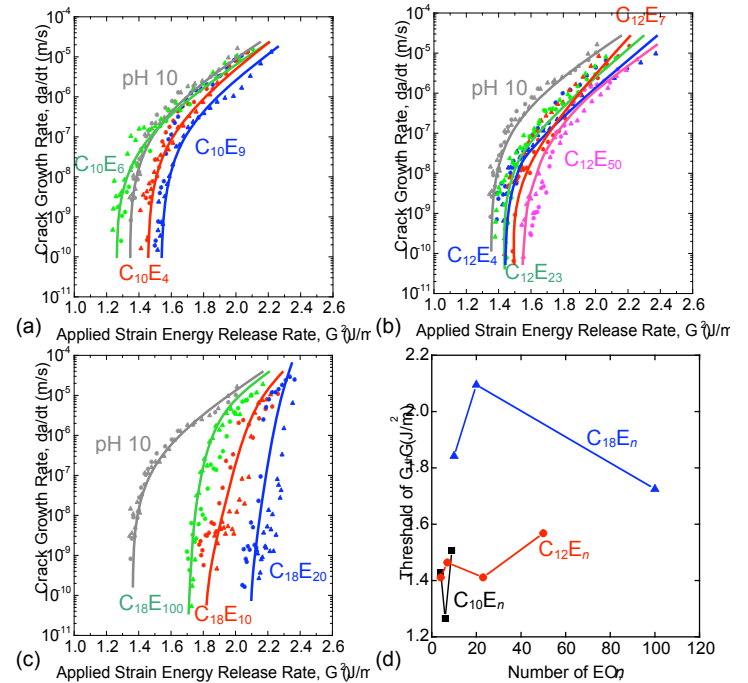


FIG. 1. Subcritical crack growth behavior of nanoporous MSSQ in (a) polyoxyethylene decyl ether ($C_{10}E_n$), (b) polyoxyethylene lauryl ether ($C_{12}E_n$), and (c) polyoxyethylene stearyl ether ($C_{18}E_n$) solutions. Crack growth curves for pH 10 solutions without surfactants are included as fiducials. (d) Thresholds of applied strain energy release rates are plotted in terms of the number of EO.

Conclusion

This research shows that fracture of nanoporous MSSQ in aqueous solutions can be controlled by careful selection of surfactants. Especially hydrophobic interaction involving methyl groups on the cracked MSSQ surfaces and alkyl chains of surfactant molecules is thought to be important for control of crack propagation.

References

- [1] E.P. Guyer and R.H. Dauskardt, "Fracture of nanoporous thin-film glasses," *Nature mater.* 3(1), pp. 53-57, 2004.
- [2] E.P. Guyer, M. Patz, and R.H. Dauskardt, "Fracture of nanoporous methylsilsesquioxane thin-film glasses," *J. Mater. Res.* 21(4), pp. 882-894, 2006.
- [3] K. Holmberg, B. Jönsson, B. Krøngerg, and B. Lindman, "Surfactant and Polymers in Aqueous Solution", Wiley, New York, 2003.