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Design of New Ultra Low-dielectric Materials and Characterization

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1. Introduction

For next-generation semiconductors the interlevel dielectric (ILD) materials must have an ultra low dielectric constant ($k < 2.2$) while being compatible with patterning processes where the minimum features will be smaller than 40 nm.[1-6] These structures, owing to their size and dielectric requirements, can only be realized by introducing large quantities of nanoscale porosity. Unfortunately, large quantities of nanoscale porosity will significantly deteriorate the mechanical properties of glasses such as modulus or hardness. This is especially a problem for spin-on type materials that, even in their non-porous forms, typically have an elastic modulus less than (5 to 10) GPa. Unfortunately, these materials also tend to be mechanically fragile and inducing the porosity significantly worsens the problem. Chemical vapor or plasma enhanced chemical vapor deposition techniques can also be used to produce nanoporous glasses, typically with enhanced mechanical properties, but these materials typically offer less control in terms of porosity and the dielectric constant. Therefore, the spin-on ILD materials may have certain advantages over the CVD materials for the ultra low-dielectric (ULK) applications.

2. Results and Discussion

For the development of successful spin-on ULK materials, it is essential to significantly improve the mechanical properties of spin-on matrix materials. We have achieved this goal by systematically modifying the molecular architecture of polymethylsilsesquioxane (PMSQ) organosilicate glass and inserting organic bridging units between the reactive trifunctional silane monomers, as shown in Figure 1. As a result, we both improved the mechanical and thermal properties. The elastic modulus increases from (4.5 ± 0.3) GPa to (28.8 ± 0.6) GPa (see Figure 1) and the thermal expansion coefficient decreases from $(104.4 \pm 8.4) \text{ } ^\circ\text{C}^{-1}$ to $(4.3 \pm 2.0) \text{ } ^\circ\text{C}^{-1}$ (see Figure 2).

Characterization of the microstructure, density, and porosity indicates that the bridging units bias the initial reaction to form small strained cyclic and cage type precursors and it is crucial to ensure that these become covalently connected to the final network.

In order to introduce controlled nanoporosity, novel organosilicate polymers have been prepared which contain thermally degradable groups (porogens) grafted to the polymer backbone. Upon optimizing the backbone polymer

structure and the grafted porogen, the fully cured films exhibit nanoporous structures with excellent mechanical properties significantly improved over those of conventional blended porogen systems, together with closed-pore morphology up to the porosity of 15 %. However, as the porosity increases over 20 %, the pores become highly interconnected although the average pore diameter remains smaller than ca. 2 nm, as determined by the positronium annihilation lifetime spectroscopy (PALS).

For the purpose of increasing the threshold porosity of pore interconnectivity, a dual porogen system containing another immiscible porogen polymer component has been investigated. As a result, nanoporous films of ultra low-dielectric constant (< 2.2), with the porosity of ca. 30%, have been obtained, which also exhibit excellent mechanical properties, including a high modulus (> 6 GPa) and nearly closed-pore morphology.

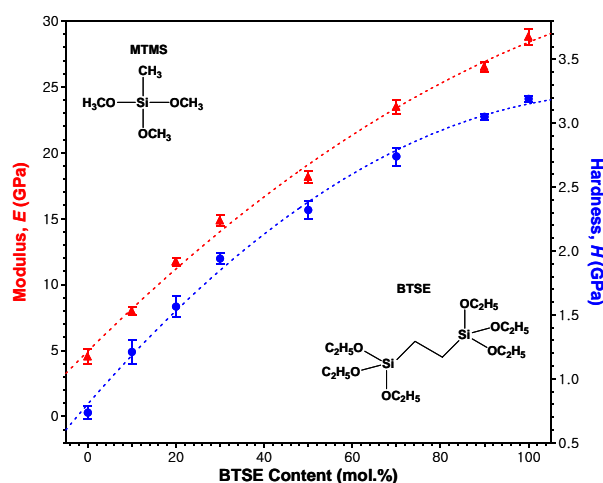


Figure 1. The modulus (E_r) (triangles) and hardness (H) (squares) of the films, as characterized by nanoindentation, show a marked increase with the bridging monomer BTSE content.

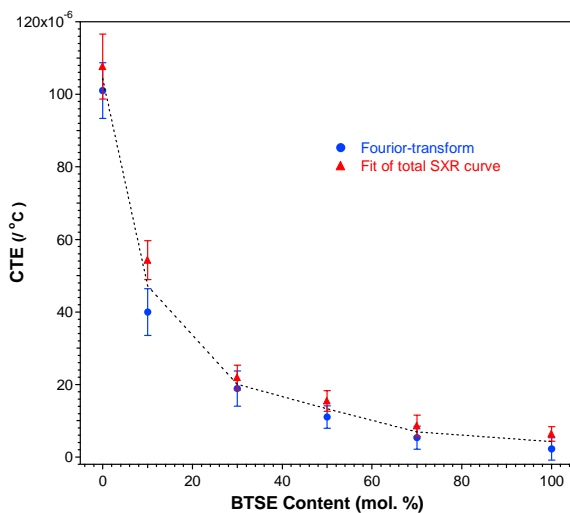


Figure 2. A drastic decrease in the coefficient of thermal expansion (CTE) with increasing BTSE content is observed with specular X-ray reflectivity.

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