Development of Mesoporous, Ultra Low Dielectric Constant, Patterned Films by 3-D Replication of Structured Organic Templates: A University/Industry/National Laboratory Collaboration

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PIs: James J. Watkins[1], Sandra L. Burkett[2], Dimitrios Maroudas[1], Christopher K. Ober[3] Michelle T. Schulberg[4]

[1]Chemical Engineering Dept., University of Massachusetts, Amherst, MA
[2]Chemistry Department, Amherst College, Amherst, MA
[3]Materials Science and Engineering, Cornell University, Ithaca, NY
[4]Novellus Systems Inc., San Jose, CA

Continuation of the historical trend of reduced device dimensions in integrated circuits requires production-worthy approaches to porous interlayer dielectrics with dielectric constants (k) of less than 2.2 that can survive the structural and mechanical demands of integration. Moreover, at device dimensions less than 45 nm, techniques that offer pore sizes of 2 nm or less, control over long range order and pore orientation, and patterning at multiple length scales may be required for practical integration schemes. New ultra-low dielectric constant and other highly ordered mesoporous silicate materials are being developed through our NIRT program. The synthetic strategy involves the infusion and selective condensation of metal oxide precursors within one domain of highly ordered block copolymer templates using supercritical (SC) carbon dioxide as the reaction medium. The template is then removed to produce the mesoporous oxide. By separating template preparation from oxide condensation, the block copolymer architecture can be manipulated at the local level by domain orientation and alignment using surface and external fields and at the device level by lithographic patterning prior to precursor infusion. Recently we demonstrated the utility of this approach for the rapid and efficient preparation of robust, defect free mesoporous films that exhibit an excellent combination of electrical and mechanical properties (*Science* 2004, 303, 507). Figure 1 shows a SEM image of the cross-section of a highly ordered mesoporous film and provides hardness and dielectric constants for a family of films produced by this approach.

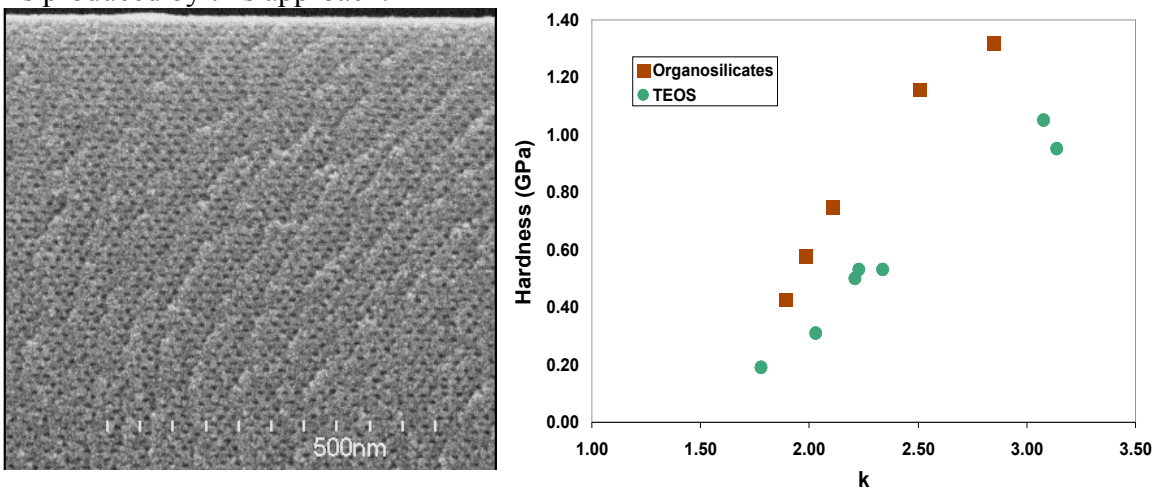

Figure 1. SEM micrograph of a highly ordered silicate film prepared in supercritical carbon dioxide (**left**). The film contains sub-5 nm pores in a cubic lattice and is designed for use as an ultra-low dielectric constant insulator in interconnect structures for next generation integrated circuits. The material exhibits exceptional electrical and mechanical properties (**right**) and is capable of withstanding chemical mechanical planarization, a rigorous test of film acceptability in commercial applications.[2]

Detailed structural characterization of the organosilicate mesoporous films has been undertaken by the NIRT team in a collaboration led by Dr. Eric Lin at the Polymers Division of NIST.[3] The pore structure and pore distribution were probed using contrast variation SANS porosimetry and x-ray porosimetry, while pore wall composition was determined by Rutherford backscattering (RBS) and forward recoil elastic spectroscopy (FRES). The films were prepared by infusion of poly(ethylene oxide-block-propylene oxide-block-ethylene oxide) films doped with p-toluenesulfonic acid (p-TSA) with (2:3) mixtures of methyltriethoxysilane and tetraethylorthosilicate in humidified supercritical carbon dioxide at 60 °C and 123 bar. After template removal by calcination, two distinct populations of pores were present in the films. Spherical mesopores were templated by the hydrophobic domain of the copolymer. Micropores in the pore walls were present due to removal of the hydrophilic poly(ethylene oxide) block, which forms an interpenetrating network (IPN)-like structure with the silicate network during infusion and condensation of the precursor. The wall density was determined to be (1.95 ± 0.05) g cm^{-3} and the overall porosity was found to be 39 % by volume, with good agreement between the SANS and x-ray reflectivity results. A significant fraction of the total porosity, 44 % to 53 %, in these materials is attributed to the micropores in the wall structure. The presence of significant fractions of micropores in the walls enables very low dielectric constants in films with spherical pore morphologies.

Second generation template systems that yield ultra-small pores and broader processing conditions are now in development. While commercially available amphiphilic block copolymers including Brij and Pluronic surfactants are useful templates for mesostructured films, they are not ideal. One limitation of Brij and Pluronic surfactants is the use of poly(ethylene oxide), PEO, as the hydrophilic component. In particular, crystallization of PEO can affect ordering and template stability and the weak interaction of PEO with the native oxide on the substrate surface can result in template de-wetting at elevated infusion temperatures. Amorphous organic templates comprised of homogeneous blends of the PEO-containing block copolymers and amorphous homopolymers including poly(acrylic acid) (PAA) and poly (hydroxystyrene) (PHOST) that exhibit strong interactions with the PEO block resolve these issues. As expected these blends exhibit reduced levels of crystallinity and significantly improved substrate-wetting properties. However, these templates also yield a significant improvement in pore order and permit the stabilization of short chain surfactants for the production of continuous films with very small pores. Figure 2 shows a TEM image of a well ordered film with ~ 2 nm pores. A higher degree of pore-order can translate into better mechanical properties for the same k.

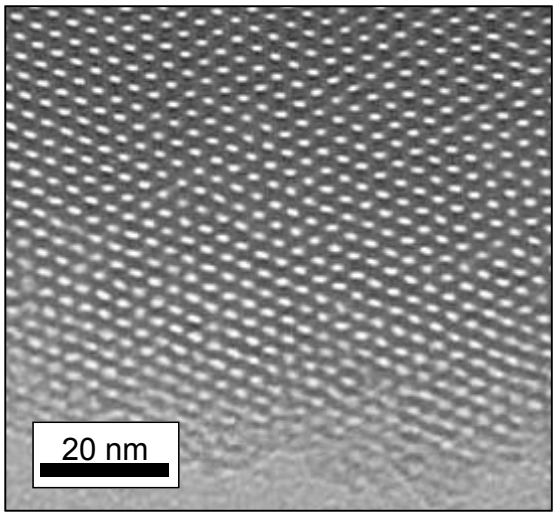

Figure 2. TEM images of a mesoporous silicate film templated by a blend of Brij 78 surfactant and a poly(hydroxystyrene).[4]

The NIRT team is now pursuing the formation of directly patterned dielectrics and mesoporous materials with cylindrical channels oriented normal to the substrate surface. Figure 3 shows a mesoporous silica film with 20 nm channels perpendicular to the surface prepared using a block copolymer template with aligned cylindrical domains.[5] The normal channel geometry in silicates is enabling for applications including magnetic data storage, sensors, separations media and catalytic devices, but efficient methods for direct fabrication at dimensions of this scale have to date remained elusive.

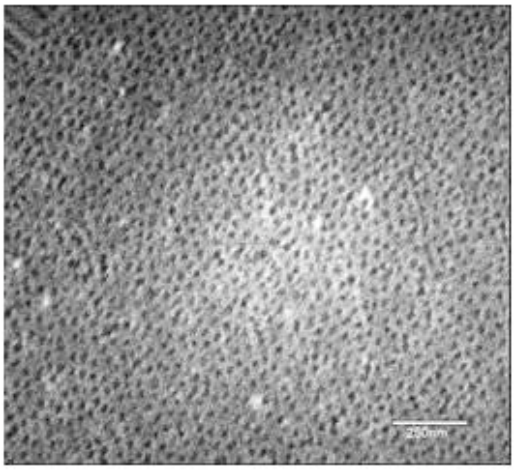

Figure 3. SEM micrograph of a mesoporous silica film with 20 nm channels oriented normal to the substrate surface prepared in supercritical CO_2 using an alligned block copolymer template. Perpendicular channels are enabling for applications in magnetic data storage, sensor and detection arrays, catalysis and separations.[5]

1. For further information about this project link email watkins@ecs.umass.edu
2. Pai, R. A.; Humayun, R.; Schulberg, M. T.; Sengupta, A.; Watkins, J. J. "Preparation of Mesoporous Materials by 3-D Replication of Block Copolymer Templates in Supercritical Fluids" *Science*, **2004**, 303, 507.
3. Vogt, B. D.; Pai, R. A.; Lee H-J.; Hedden, R. C.; Soles, C. L.; Wu, W-L.; Lin, E.K.; Bauer, B. J.; Watkins, J. J. "Characterization of Ordered Mesoporous Silica Films using Small Angle Neutron Scattering and X–ray Porosimetry" submitted to *Chemistry of Materials* August, 2004.
4. Pai, R.A., Testa, J.J.; Watkins, J.J., in preparation.
5. Nagarajan, S.; Li, M.-Q.; Pai, R.A.; Weinman, C.; Ober, C.K.; Russell, T.P.; Watkins, J.J., in preparation.