DESIGN OF NANOPOROUS ULTRA LOW-DIELECTRIC CONSTANT ORGANOSILICATES BY SELF-ASSEMBLY

Shu Yang1, Peter Mirau2, C.-S. Pai3, Om Namalasu1, Elsa Reichmann1, Eric K. Lin4, Hae-jeong Lee3, David Gidley1, W. E. Frieze3, T. L. Dull4, J. Sun4 and A. F. Yee4

1Bell Laboratories, Lucent Technologies, 600 Mountain Ave., Murray Hill, NJ
2National Institute of Standards and Technology, Polymer Division, 100 Bureau Drive, Gaithersburg, MD
3Department of Physics, University of Michigan, Ann Arbor, MI
4Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI

Introduction
As nanoscience and nanotechnology have attracted great attention in many fields in recent years, the device features in integrated circuits (IC) continue to shrink also to less than 100 nm. However, when more wires are needed to connect tightly packed individual devices, low-dielectric constant materials, with k less than 3.0, will be preferred to avoid the RC delay, power consumption and wire cross-talk. Although several promising materials have achieved k<3, ultra low-k (k<2.2) materials are nearly impossible to create without introducing porosity into the film by taking advantage of the low dielectric constant of air, k=1.

Nanoporous or mesoporous materials have been studied as membranes, sensors, waveguides, photonic materials and zeolites, etc. Controlling and understanding the structure and property of the mesopores are of great challenge to the material scientists. Ordered cubic, hexagonal and lamellar structures can be prepared using ionic surfactants by sol-gel process1-2. Block copolymers, as nonionic surfactants, have controlled molecular weights and polydispersities. They will microphase into different morphologies and direct the self-assembly of organic/inorganic composites3-4.

Porous silica with ordered structures has been fabricated through sol-gel process as ultra low-k materials5. Although small pores are obtained (<10 nm), more than 50% porosity is required to extend the k value to less than 2.0, which is achieved from the low dielectric constant of air, k=1. Nanoporous or mesoporous materials have been studied as membranes, sensors, waveguides, photonic materials and zeolites, etc. A promising approach is to add sacrificial materials, such as polymers6, high boiling point solvents7 in an organic/inorganic hybrid silicate, such as poly(methyl silsesquioxane) (MSQ), MeSiO1.5. Only 30% porosity is required to reach the ultra low-k region through these organosilicates as matrices, which have a relatively low dielectric constant, k ~ 2.6-2.8. Because the dielectric layers are thin, less than 1 µm, the pore size and structure, which depend on the chain length and composition of the polymer templates, play an important role on the material properties. Low-k materials with closed, nanopores will have the advantage of good electrical properties, strong mechanical strength and high resistant to metal diffusion.

Here we report a new class of materials that can reach ultra low- dielectric constants while maintaining good mechanical properties. In this approach, amphiphilic triblock copolymers, poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) (PEO-b-PPO-b-PEO) are used as sacrificial templates in poly(methyl silsesquioxane) (MSQ), to generate pores. The structure and dynamics of triblock copolymers were studied by solid-state proton NMR. The organization of the polymer domains in the composite can be probed with proton spin diffusion. On a very short length scale (0.2-0.5 nm), the spatial correlation length of polymer blocks (the correlation length of the polymer domains) can be measured by 2D spin exchange experiments which was used to identify spin pairs in close proximity. On a longer length scale (1-20 nm), proton spin diffusion can be used to measure the domain sizes and average distances between the domains. Cross sections through the propylene oxide methyl peak show large cross peaks to both the methylene/methylene peak and the methyl silsesquioxane peak. Intramolecular spin diffusion in the propylene oxide is expected to quickly lead to magnetization exchange between the propylene oxide methyl protons and the other main chain protons. The large cross peaks from the propylene oxide methyl protons to the methyl silsesquioxane peak shows that they must be in close proximity, with the propylene oxide block near the methyl silsesquioxane interface in the composites.

Experimental
Preparation of Nanocomposite and Nanoporous Materials
Triblock copolymers, poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) (PEO-b-PPO-b-PEO), and poly(methyl silsesquioxane) (MSQ) precursor (see Scheme 1) were dissolved in n-butanol and passed though 0.45 µm PTFE filters. The block copolymers have an average molecular weight of 11,400 with 80 wt% of PEO. The solutions were cast as thin films and annealed at 120°C overnight under vacuum. These MSQ nanocomposites were then used for solid state NMR measurement. The nanoporous materials were first spun on Si wafers followed by baking at 100°C for 30 minutes. The films were then placed in a tube furnace purged under N2 and heated slowly to 400 or 500°C. They were held at the temperature for 1-2 hours to remove the triblock copolymer templates to generate pores.

Characterization
Structure and Dynamics of the Nanocomposites
The solid-state proton NMR experiments were performed at 400 MHz using a Varian Unity NMR spectrometer with a 4 mm magic-angle spinning probe and spinning speed regulation at 12 kHz. The proton pulse widths were 3.5 µs and the dipolar filter pulse sequence8 was used to measure the chemical shift and for the spin diffusion experiments. Hypercomplex pure-phase two-dimensional spin exchange spectra were measured using the (90°-t1-90°-t2) pulse sequence. Density and Pore size. Spectral X-ray reflectivity (SRX) was measured using a 0-2θ configuration with a fine focus copper X-ray tube as the radiation source. The data was collected at grazing incident angles, ranging from 0.01 to 0.6 degree to determine the density of the overall dielectric film9. The wall density of the pores and pore sizes were measured by SANS, which was conducted on the NG1 and NG3 instruments at the Center for Neutron Research at the National Institute of Standards and Technology (NIST)10. In addition, the pores sizes were measured by PALS for comparison11. The spectra were acquired at varied beam energy, 1.1-5.0 KeV, with an 8000 channel time-to-digital converter over a time range of 1.25 µs. Further, samples were capped with 80nm silica to compare the posireronium (Ps) intensity and lifetime to those of uncapped.

Electrical Properties. The capacitance of the film was measured between electrodes, Al and TiN, at room temperature in air by a 4284A precision LCR meter with a frequency of 1 kHz. The capacitance measurement was averaged on 4 dots. The dielectric breakdown strength was measured on a 4145B Hewlett-Packard (HP) semiconductor parameter analyzer with the same sample setups.

Results and Discussion
Block copolymers have unique amphiphilic characteristics and have been used as directing templates or surfactants14-15. Due to the strong incompatibility between each block, they tend to microphase separate into different domains. When block copolymers are blended with the matrix, the block copolymer may aggregate to form micelles or self-assemble into a spherical structure with the miscible block as the shell and the immiscible block buried inside to minimize the interfacial energy. Given the ability to precisely control their functionalities and properties, block copolymers are used in our approach as sacrificial templates to mix with the MSQ prepolymer to generate pores.

In triblock copolymers of PEO-b-PPO-b-PEO, PEO is relatively more hydrophilic than PPO, which is more hydrophobic. After curing, Si-OH/Si-0Et groups in the MSQ precursors were polycondensed to Si-O-Si linkages. The cured MSQ films became hydrophobic due to the methyl groups in the crosslinked network. It was found from solid-sate 1HNMR that after curing, the PPO block preferred to stay at the interface with the MSQ matrix, while the PEO block was buried inside away from the polymer-MSQ interface (see Scheme 2). The organization of the polymer domains in the composite can be probed with proton spin diffusion. On a very short length scale (0.2-0.5 nm), the 2D spin exchange experiments can be used to identify spin pairs in close proximity. On a longer length scale (1-20 nm), proton spin diffusion can be used to measure the domain sizes and average distances between the domains. Cross sections through the propylene oxide methyl peak show large cross peaks to both the methylene/methylene peak and the methyl silsesquioxane peak. Intramolecular spin diffusion in the propylene oxide is expected to quickly lead to magnetization exchange between the propylene oxide methyl protons and the other main chain protons. The large cross peaks from the propylene oxide methyl protons to the methyl silsesquioxane peak shows that they must be in close proximity, with the propylene oxide block near the methyl silsesquioxane interface in the composites.
Dipolar filter pulse sequence has been used to probe the molecular dynamics of the triblock copolymer and methyl silsesquioxane in the composites, and to measure the length scale of phase separation using proton spin diffusion. The delay times for the composites are chosen such that the block copolymer signals remain while the signals from the MSQ are saturated. The two parameters, the distance \( d \) across the minor phase and the overall repeat distance, or long period \( d_L \), have been extracted, 2.2 nm and 3.6 nm, respectively. For a three-dimensional morphology, \( d \) is the sphere diameter and \( d_L \) is the center-to-center spacing of the spheres. Compared to the size of the bulk block copolymer, which has a domain size of 6.1 nm and a long period of 8.8 nm, the block copolymers seem to collapse in the MSQ matrices and form dense micelles. Further studies are required to determine how the pore sizes in the composites compares with the final material where the polymer is removed, and how the domain size and spacing vary with the polymer loading.

When the nanocomposites were heated to above 400°C, the dielectric constants (\( f = 1 \) KHz) decreased from 2.6-2.8 to 2.0 with 30 wt% loadings of MV/cm. At 0.5 MV/cm, the leakage current density is on the order of 10–8 to 10–9 A/cm2 for porous MSQ films with a k value of 2.0.

Conclusions

A new class of nanoporous organosilicate has been developed to attain an ultra low-dielectric constant, \( k \) of less than 2.0. Triblock polymers, poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) (PEO-b-PPO-b-PEO), are self-assembled into poly(methyl silsesquioxane) (MSQ) matrices and used as templates to generate pores. It is found from solid-state proton NMR that the triblock copolymers are microphase separated from the MSQ, while the PPO block is at the interface with the MSQ. The polymers in MSQ, have domain sizes on the order of 2-3 nm, smaller than those of the bulk polymers. After decompose the polymer templates, both SANS and PALS revealed that extremely small pores, 2-4 nm, are generated.