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

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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, photonics materials and zeolites, etc.[1-2] 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 process[1-2]. 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 composites[3, 4].

Porous silica with ordered structures has been fabricated through sol-gel process as ultra low-k materials[5]. Although small pores are obtained (<10 nm), more than 50% porosity is required to extend the k value to less than 2.0, which makes the mechanical properties questionable to withstand chemical mechanical polishing (CMP) processing steps during circuit fabrication. Another promising approach is to add sacrificial materials, such as polymers[6], high boiling point solvents[7] in an organic/inorganic hybrid silicate, such as poly(methyl silsesquioxane) (MSQ), $MeSiO_{1.5}$. Only 30% porosity is required to reach the ultra low-k region using 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 nanopores. The structure and dynamics of triblock copolymers were studied by solid-state proton NMR. The domain size of polymer in MSQ is 2.2 nm with PPO at the interface between the MSQ matrices. When the composite was heated to above 400°C, the MSQ matrix is cured, followed by the calcinations of block polymers to generate pores. The porous materials have dielectric constants equal to or less than 2 and exhibit low I-V leakage, less than 10^{-8} A/cm² at 0.5 MV/cm. Small angle neutron scattering (SANS) and positronium annihilation lifetime spectroscopy (PALS) revealed that these materials had extremely small pores, of the order of 2-3 nm.

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 N_2 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 sequence[8] was used to measure the chain dynamic and for the spin diffusion experiments. Hypercomplex pure-phase two-dimensional spin exchange spectra were measured using the $(90^o-t_1-90^o-\tau_m-90^o-t_2)$ pulse sequence[9].

Density and Pore size. Specular X-ray reflectivity (SXR) was measured using a θ-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 film[10]. 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 comparision[11]. 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 positronium (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 surfactants[1-4]. 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 either 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-OEt 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/methine 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_{lp} have been extracted, 2.2 nm and 3.6 nm, respectively. For a three-dimensional morphology, d is the sphere diameter and d_{lp} 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 block copolymers. Compared to more than 50 % porosity required in SiO_2 by sol-gel process, the porous MSQ has an advantage to achieve stronger mechanical strength. Although a low dielectric constant can be achieved by adding pores, some low-k materials are not useable due to their poor electrical properties. In a thin dielectrics layer, even applying a small voltage could result in a high electric field on the device. The current-voltage (I-V) curves were measured for porous MSQ with different polymer loadings and compared to MSQ. The applied voltage was ramped from 0 to 100 V at a step of 5 V/s. It was demonstrated that all the porous MSQ films had very high breakdown filed, >2 MV/cm. At 0.5 MV/cm, the leakage current density is on the order of 10^{-8} to 10^{-9} A/cm^2 for porous MSQ films with a k value of 2.0.
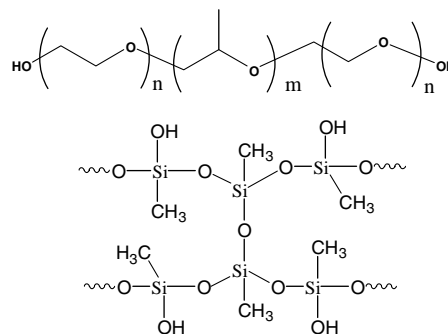
The superior electrical properties have indicated small pore sizes in the dielectric films. SANS and PALS are very unique techniques to measure small voids at a length scale of nm size in thin films. Depending on the morphologies and configurations of the triblock copolymers, they may interact with matrices differently, which strongly affects the pore structures and mechanical properties of the low-k materials.

High-resolution specular X-ray reflectivity has been used to monitor the thin film density directly on Si wafer after the film processing. SANS has the distinct advantage of measuring the pore structures in thin films spun on the Si wafers, since single crystal silicon wafers are essentially transparent to neutrons. By fitting the SANS data with Debye model, the pore size, porosity (P) and pore wall density (ρ_w) are deduced, 1.159 ± 0.174 g/cm^3, given the mass density of thin film measured from SXR, 0.877 ± 0.024 g/cm^3. The pore size was found extremely small, 1.4 ± 0.326 nm, with $24.3 \pm 11.2\%$ porosity.

Such a small pore size is close to the limit of SANS probing capability, however it is in the probing range of PALS. When collide with pore surface, the positronium will annihilate and stay in the pore. The reduced lifetime associates with the intrinsic average pore size. The pore interconnectivity can be demonstrated by the intensity of Ps vacuum component of the uncapped samples. For interconnected pores, a 2-dimensional tubular pore model is used, while for isolated pores a 3-dimensional cubic pore model is used for fitting. It was found that the porous MSQ, with k of 2.0, have completely interconnected pores, with an average size of 2.7 nm. This data correlates well with pore size obtained from SANS. In addition, it confirms that the self-organization of triblock copolymers in MSQ matrices contributes to the final pore size when the triblock copolymers are removed by heat.

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.

References

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Scheme 1. The structures of PEO-b-PPO-b-PEO triblock copolymer and MSQ precursor.
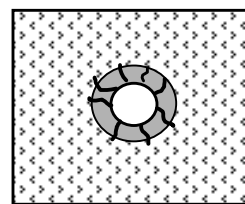
Scheme 2. Schematic structure of PEO-b-PPO-b-PEO triblock copolymer in MSQ Matrix.