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Mesoporous Silicates Prepared Using Preorganized Templates in Supercritical Fluids

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Well-ordered mesoporous silicate films were prepared by infusion and selective condensation of silicon alkoxides within microphase-separated block copolymer templates dilated with supercritical carbon dioxide. Confinement of metal oxide deposition to specific subdomains of the preorganized template yields high-fidelity, three-dimensional replication of the copolymer morphology, enabling the preparation of structures with multiscale order in a process that closely resembles biomineralization. Ordered mesoporous silicate films were synthesized with dielectric constants as low as 1.8 and excellent mechanical properties. The films survive the chemical-mechanical polishing step required for device manufacturing.

Well-defined mesoporous metal oxide films offer great promise for applications including sensor and detection arrays, separations, optoelectronics, and microelectronics. To date, these materials have been prepared from solution through the surfactant-directed assembly of polymerizing metal alkoxide sols in which specific interactions between the surfactant and precursor species produce micellar phases that ultimately yield the corresponding mesostructures (*1–5*). Cooperative assembly yields well-defined local pore structures, but the production of hierarchical films with long-range order, oriented pores, or domain patterning at the local or device level requires manipulation by external fields during alkoxide polymerization. Recent effort has led to advances in pore orientation and film patterning through shear alignment during dip coating, guided growth (*6*), magnetic field alignment (*7*), and substrate surface modifications (*8*). However, because structure evolution is coincident with precursor condensation, film morphology cannot be fully prescribed by preorganization of the template before network formation. This presents an inherent obstacle to the rapid fabrication of arbitrarily chosen, well-ordered, multiscale architectures in thick films or monoliths.

A more robust model for the preparation of templated materials is provided by biomineralization processes in nature (*9–12*). Hierarchical structures such as abalone nacre and bone evolve through spatial delimitation of the incipient inorganic phase within subunits of preorganized macromolecular template that preserve the template morphology. Here, we demonstrate an analogous laboratory mimic: the rapid and efficient preparation of mesostructured metal oxides by the in situ condensation of metal oxides within preformed block copolymer (BCP) templates. BCPs consist of two or more homopolymer segments tethered through covalent bonds. Upon microphase separation, these materials can self-assemble to yield nanoperiodic (~5 to 100 nm) spherical, cylindrical, lamellar, and bicontinuous structures (*13*). In thin films, the copolymer domains can exhibit long-range order and can be oriented with respect to a substrate through surface interactions (*14–16*), external fields (*17*), or controlled solvent evaporation (*18*). Moreover, BCP films can be patterned by photolithography to yield 100-nm device features (*19*). Although conceptually straightforward, the three-dimensional (3D) replication of ordered BCP morphologies by selective deposition of an inorganic phase within one domain of the template has not previously been realized. The principal challenge has been to achieve efficient transport and reaction within the polymer film under conditions at which the precursor partitions favorably into the template and at which the use and removal of process solvents to facilitate transport does not degrade template order. In our approach, these conditions are satisfied by using a supercritical fluid (SCF) as the process medium.

Our procedure for the preparation of mesoporous metal oxides is shown in Fig. 1A (*20*). A BCP template containing hydrophobic and hydrophilic segments is prepared by spin-coating from a solution containing a suitable acid catalyst. Upon drying and annealing to induce micro-

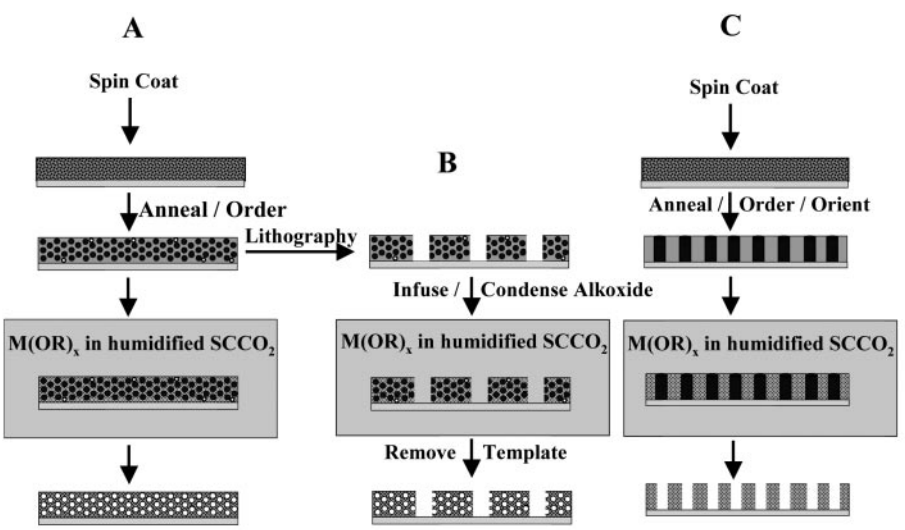

Fig. 1. Schematic drawing of the synthesis of mesoporous metal oxides in $scCO_2$. (**A**) The template is prepared by spin-coating a BCP containing hydrophilic and hydrophobic domains from a solution containing an organic acid. Upon annealing, the BCP orders into a periodic morphology and the acid partitions selectively into the hydrophilic domain. Next, the template is slightly dilated by a dilute solution of metal alkoxide in humidified $scCO_2$, whereupon the alkoxide condenses selectively in the hydrophilic domain of the copolymer (M, metal; R, alkyl group). After depressurization, the template is removed by calcination or reactive plasmas. Confinement of the reaction within one domain of the copolymer results in 3D replication of the template. Because template formation and metal oxide infusion occur in discrete steps, templates patterned at the device level by lithography (**B**) or with cylindrical domains oriented normal to the substrate surface (**C**) offer a means to control architecture at multiple length scales.

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phase separation and enhance order, the acid partitions into the hydrophilic domain of the template. The template is then exposed to a solution of metal alkoxide in humidified supercritical CO_2 ($scCO_2$). The precursor diffuses into the template, which is dilated slightly by the SCF solution, and condenses selectively within the acidic hydrophilic domain of the copolymer to form the incipient metal oxide network. Because the catalyst is localized in the hydrophilic block, no reaction occurs in the bulk fluid phase or in the hydrophobic domains. Moreover, the alcohol by-product of alkoxide condensation is extracted rapidly from the film into the CO_2 phase, which promotes rapid and extensive network condensation. After decompression, the template can be removed by calcination or by degradation in reactive plasmas to yield a mesoporous structure. Alternatively, the template can be retained for materials that rely on its mechanical properties for direct application or for postprocessing. Because the template and the metal oxide network form in discrete steps, it is possible to pattern the template via lithography or to orient the copolymer domains before the formation of the metal oxide network (Fig. 1, B and C). This creates future opportunities for complete specification of the mesoporous oxide architecture in the polymer film.

To validate our approach, we prepared mesoporous silicate films using two families of templates, poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock (PEO-b-PPO-b-PEO) copolymers (Pluronic surfactants, BASF) and polyethylene-b-PEO (PE-b-PEO) copolymers (Brij surfactants, Aldrich). Cross sections of a film prepared using PEO_{127}-b-PPO_{48}-b-PEO_{127} (Pluronic F108) infused in $scCO_2$ show that it is ~1 μm thick, uniform, and free of cracks (Fig. 2, A and B). The template for the film was prepared by spin-coating from an alcohol solution containing *p*-toluene sulfonic acid (pTSA) onto a 50-mm silicon wafer. After annealing at 60°C, the film was exposed to a solution of tetraethylorthosilicate (TEOS) in $scCO_2$ at 60°C and 123 bar for 2 hours in an opposed flange reactor, which led to precursor infusion and pTSA-catalyzed condensation within the template (*20*). X-ray diffraction (XRD) patterns (Fig. 2C) acquired before and after removal of the template by calcination at 400°C in air for 6 hours exhibit multiple reflections indicative of well-ordered cubic morphologies in both cases. The infusion and template removal process times can be substantially shortened for device applications.

Cylindrical pores are accessible through the appropriate choice of template and alkoxide loading. A scanning electron microscopy (SEM) cross-section image (Fig. 2D) of a mesoporous silica film prepared by infusion of a PEO_{106}-b-PPO_{70}-b-PEO_{106} (Pluronic F127) template with TEOS in $scCO_2$ solution at 60°C and 125 bar for 10 min reveals numerous grains of ordered cylinders, typical of unoriented BCP systems. Because TEOS sorption is selective for the hydrophilic domain, transitions between cylindrical and spherical morphologies, consistent with solvent-induced order-order transitions in the BCP template (*21*), can occur in these systems at high precursor loadings (fig. S1). If desired, such transitions can be suppressed by lightly cross-linking the template before silicate network formation or can be facilitated by choosing template compositions near order-order transitions.

Low–molecular weight PE-b-PEO templates also yield ordered films. Figure 3 shows XRD patterns and transmission elec-

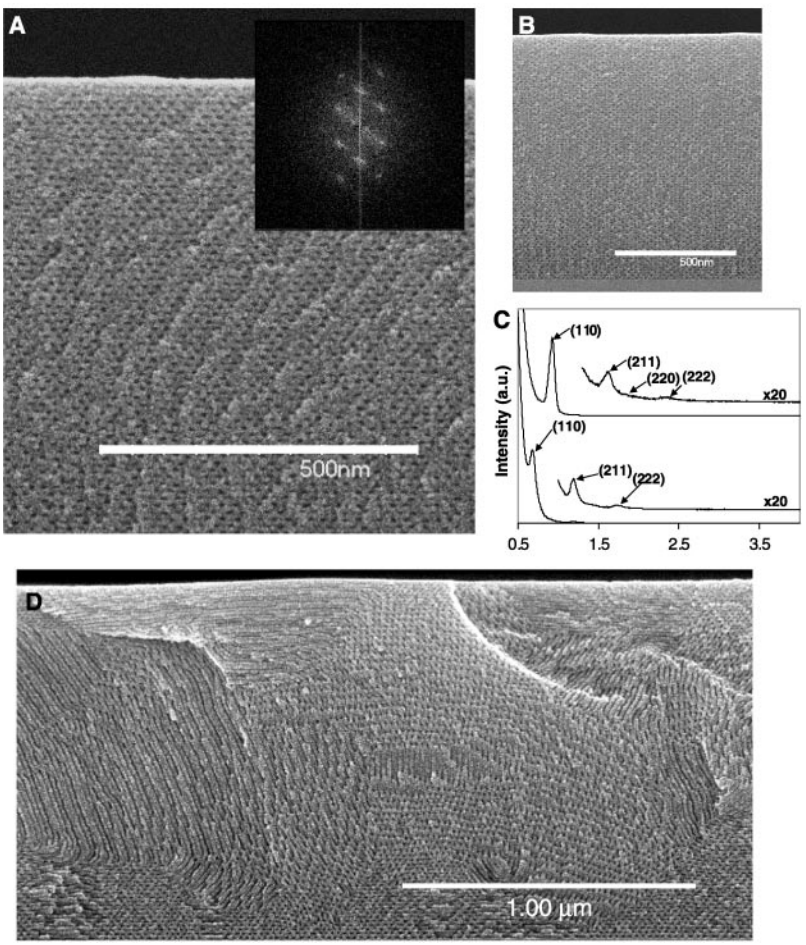

Fig. 2. (**A** and **B**) SEM micrographs showing the cross section of a highly ordered mesoporous silicate film prepared on a Si wafer in $scCO_2$. The film was prepared by infusion and condensation of TEOS within a preorganized PEO_{127}-b-PPO_{48}-b-PEO_{127} BCP film dilated with $scCO_2$ at 60°C and a pressure of 123 bar followed by removal of the template by calcination. The images and their Fourier transform [(A), inset] suggest a cubic structure, which is confirmed by XRD data. (**C**) XRD patterns for the mesostructured silicate film, before (bottom) and after (top) removal of the template by calcination at 400°C in air. The XRD pattern of the as-infused film shows three sharp Bragg peaks, corresponding to *d* spacings of 125.3 Å, 72.4 Å, and 50.9 Å, that are attributed to the (110), (211), and (222) planes of a 3D cubic mesostructure with a cell parameter $a = 177$ Å. For the calcined film, the Bragg peaks for *d* spacings of 93.5 Å, 53.7 Å, and 37.9 Å are indexed as the (110), (211), and (222) reflections of a 3D cubic mesostructure (cell parameter $a = 132.5$ Å). The diffraction patterns were collected with a Philips X'Pert PW3040 diffractometer using Cu Kα radiation ($\lambda = 0.15418$ nm) in the Bragg-Brentano geometry. (**D**) SEM micrograph showing the cross section of a highly ordered mesoporous silicate film exhibiting a cylindrical pore morphology. The film was prepared by infusion and condensation of TEOS within a preorganized PEO_{106}-b-PPO_{70}-b-PEO_{106} BCP film dilated with $scCO_2$ at 60°C and a pressure of 123 bar, followed by removal of the template by calcination at 400°C in air. The image reveals a preferential alignment of cylinders at the interfaces and grains of random orientation within the bulk of the film.

tron microscopy (TEM) images of a film prepared by exposing a pTSA-doped PE_9-b-PEO_{10} (Brij 76) film to a solution of TEOS in humidified $scCO_2$ at 40°C and 123 bar for 2 hours. The x-ray data can be indexed to a 3D hexagonal array of spherical domains with cell parameter ratios, *c*/*a*, close to the ideal ratio of 1.633 for the hexagonal close-packed (hcp) phase.

Although a number of SCFs could be used for the process, $scCO_2$ is particularly attractive, in part because it is a good solvent at elevated pressure for many small organic and organometallic compounds, including metal alkoxides, but is normally a poor solvent for polymers. Thus, in heterogeneous polymer-SCF systems, solvent sorption is equilibrium limited and can be controlled by pressure-mediated adjustments in density. CO_2 loadings of 5 to 15% in the template are typical for our modification reactions. At these modest dilations, CO_2 sorption can increase the diffusivity of penetrant species in polymer films by several orders of magnitude (*22*), but it does not disrupt template order in strongly segregated BCP melts (*23*). Moreover, manipulation of solvent quality by pressure-mediated adjustments in density provides a means to control solute distribution between polymer substrates and supercritical solutions. Decreasing the solvent quality of the fluid drives efficient partitioning of the reagents into polymer substrates. Johnston and coworkers (*24*) demonstrated this phenomenon quantitatively by using SCF chromatography to measure the distribution of small molecules between CO_2 and CO_2-dilated polymers. Finally, once the template modification is complete, CO_2 desorbs during depressurization without disrupting the composite morphology.

SCF-based synthesis of well-ordered mesoporous silicates has numerous applications. Here, we focus on the preparation of ultralow–dielectric constant (*k*) films, an unresolved technological challenge in microelectronics that requires strict morphological control at both the local and device levels (*25*). As semiconductor device dimensions decrease in accordance with Moore's Law, the capacitance of the interlayer dielectric (ILD) layers must be reduced to shorten the time required for a signal to propagate between transistors. At device nodes below 65 nm, porosity must be introduced into the insulator to achieve a sufficiently low *k*; however, the mechanical and thermal stability of the ILD cannot be sacrificed. To date, methodologies to prepare these materials have led to an unsatisfactory compromise in properties or have not been amenable to scale-up and manufacturing.

The electrical and mechanical properties of low-*k* films are dictated by the nature of the framework material, the degree of porosity, and pore structure and order. The bulk *k* of carbon-substituted silicates (k = 2.7 to 3.2) is considerably less than that of dense silica (k = 4.0). Thus, alkyl-substituted and alkyl-bridged Si alkoxides including methyltriethoxysilane (MTES) and bis(triethoxysilylethane) are attractive candidates for framework precursors. Alkyl substitution, however, decreases the number of available Si-O-Si network linkages, which can have an adverse impact on mechanical properties. In the SCF route to mesoporous materials, these factors can be balanced by using mixed-precursor systems and by controlling precursor loading. Moreover, replication of the spherical BCP template morphologies enables the formation of highly ordered structures that impart mechanical stability to the porous metal oxide. For spherical pores, cubic structures are more mechanically robust than hexagonally packed structures, whereas disordered structures are considerably more fragile.

Figure 4A shows a SEM micrograph of a mesoporous organosilicate prepared from a mixture of TEOS (60%) and MTES (40%) and a PEO_{106}-b-PPO_{70}-b-PEO_{106} template processed at 60°C and 123 bar for 2 hours. The film was detemplated and the silanol groups in the film were capped using a sequence of hydrogen-nitrogen plasma (8 min) and vapor-phase reaction with hexamethyldisilazane (HMDS). The HMDS treatment to cap the silanols renders the silicate surface hydrophobic, lowering the effective dielectric constant. Fourier transform infrared (FTIR) spectroscopy indicated that the template had been completely removed and confirmed the elimination of silanol functionality in the films (fig. S2). After posttreatment, the film *k* value and hardness were 2.1 and 0.75 GPa, respectively. A dielectric constant of 2.1 meets the requirements for the 65-nm technology node expected to be in production in 2007. Figure 4B provides representative dielectric constant and hardness data for additional mesoporous films prepared using TEOS and TEOS/MTES mixtures.

Because the template is preorganized, precursor loading can be varied over broad ranges without loss of order by manipulating the alkoxide concentrations in the fluid phase. Therefore, in addition to controlling template morphology and precursor composition, it is possible to further tune the properties of the mesoporous film by manipulating pore wall density and structure. Figure 4C shows dielectric constant as a function of mass uptake after infusion for an expanded set of the 60/40 TEOS/MTES family of films. The degree of mass uptake was controlled by varying the precursor loadings in the fluid phase. The ability to tailor film properties is critical for extending this approach to low-*k* films through multiple generations of devices.

The outlook for using our approach at the production scale is promising. Recent advances in CO_2 processing for semiconductor applications, including photoresist spin-coating, drying, stripping, and devel-

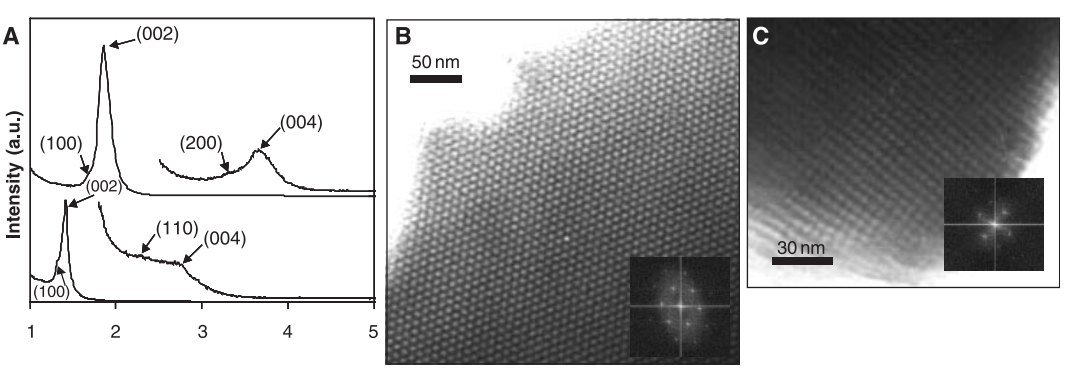

Fig. 3. XRD patterns and TEM micrographs of a mesostructured silicate film. (**A**) Lower traces are XRD patterns for the as-infused film, consistent with a 3-dH mesostructure with lattice constants a = 76.2 Å and c = 126 Å (c/a = 1.653). Upper traces are XRD patterns for the calcined film, consistent with a 3-dH mesostructure with a = 59.7 Å and c = 95.5 Å (c/a = 1.6). (**B**) Lattice image of a 3-dH mesostructure of the calcined film recorded along the [001] axis. (**C**) Lattice image consistent with the [211] zone axis. Insets in (B) and (C) show the Fourier transforms of the images, which indicate a high degree of order. The images were recorded with a JEOL 100CX electron microscope operated at 100 kV.

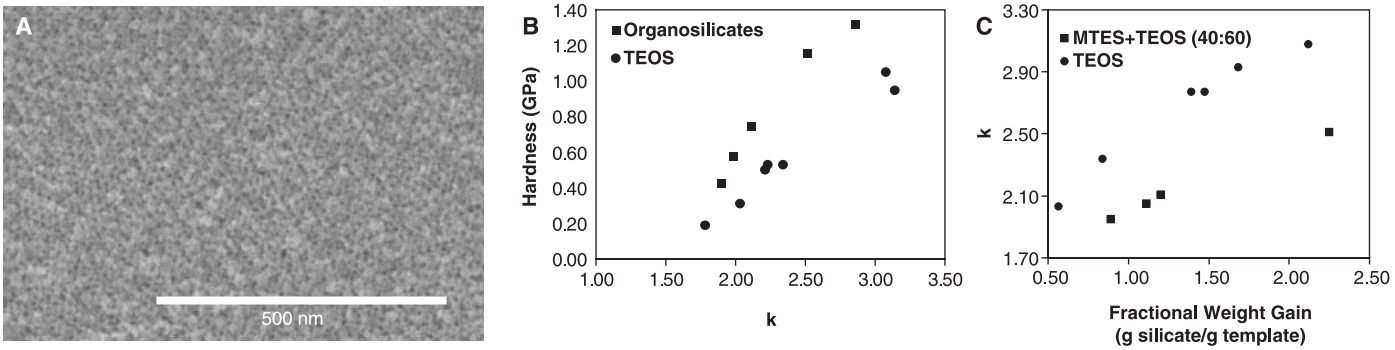

Fig. 4. (**A**) SEM image of the cross section of an ordered, mesoporous organosilicate film exhibiting a dielectric constant of 2.1 and a hardness of 0.75 GPa. The film was prepared by infusion and condensation of a solution of 60% TEOS and 40% MTES within a PEO_{106}-b-PPO_{70}-b-PEO_{106} BCP film in $scCO_2$ at 60°C and a pressure of 123 bar. The template was removed with a reactive plasma; the residual silanol groups were then capped by vapor phase reaction with HMDS. (**B** and **C**) Electrical and mechanical properties of a family of silicate and organosilicate mesoporous films prepared in $scCO_2$ with Pluronic F127 as the template. (B) Hardness versus dielectric constant for films prepared using TEOS, a 60/40 mixture of TEOS/MTES, and a 75/25 mixture of TEOS/MTES as precursor. (C) Dielectric constant versus fractional mass uptake of the silicate within the template during infusion for an expanded family of films prepared using 60/40 TEOS/MTES mixtures.

opment (*26–29*) and conformal metal deposition (*30*), have spurred the development of full wafer (200 and 300 mm diameter) demonstration tools for integration into process streams, providing a technology platform for implementation. The difficulties associated with simultaneous reaction and evolution of film morphology are effectively eliminated, especially the need for the aging periods typical of traditional sol-gel processes. In unoptimized experiments, highly ordered mesostructured films could be prepared in CO_2 with compression-infusion-decompression cycles of less than 30 min. The resulting films exhibit sufficient mechanical integrity to withstand the stresses of chemical-mechanical planarization (CMP), a polishing process that removes excess copper during fabrication of interconnect structures.

To assess performance during CMP, we prepared planar test structures on 200-mm wafers. Mesoporous films were deposited using an F108 template spin-cast on a SiC underlayer. The template was then infused with a 75/25 TEOS/MTES precursor solution in CO_2 at 60°C and 125 bar with the use of a 22-min pressurization-infusion-decompression cycle. After detemplating in H_2-N_2 plasma for 8 min and capping residual silanol functionality by reaction with HMDS, the films exhibited a k value of 2.2. The remainder of the test stack was constructed by sequential deposition of a SiO_2 cap (50 nm) by plasma-enhanced chemical vapor deposition (PECVD), a 250-nm TaN-Ta barrier layer by physical vapor deposition (PVD), a PVD copper seed layer, and finally 800 nm of electroplated copper (fig. S3A). The stack was then polished under standard conditions for dense SiO_2 and carbon-doped oxide dielectric films currently in production. SEM images acquired after polishing through the stack to the TaN-Ta layer and after polishing through to the mesoporous film (fig. S3, B and C) indicated that the mesoporous films were not damaged by CMP. We note that CMP polishing of planar test stacks is a more rigorous test than polishing of integrated structures, in which metal lines provide mechanical reinforcement of the dielectric.

The strategies shown in Fig. 1 will also enable the fabrication of oriented arrays of cylindrical pores and of patterned mesoporous films. The former is enabled by advances in domain alignment in BCPs, including the work of Russell and co-workers, who demonstrated vertical alignment of cylindrical domains in poly(styrene)-b-PEO copolymers, which can be stabilized by lightly cross-linking with ultraviolet radiation (*18*). The latter can be realized by the infusion of lithographically patterned templates (such as BCP photoresists for 193-nm lithography) that contain acidic hydrophilic and hydrophobic domains. Such an approach could eliminate the need for oxide etching of device features.

Looking forward, there are additional advantages to a processing scheme that separates template preparation from metal oxide network formation in nonaqueous media. The templates and precursors can be selected independently, without regard to compatibility in solution, coordinated assembly, or hydrolytic instability common to precursors for technologically important metal oxides such as titania. Relaxation of these constraints will enable the preparation and patterning of hierarchical mesoporous metal oxide films for a broad range of device applications including sensing and detection, catalysis, separations, and photonics.

References and Notes

1. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **359**, 710 (1992).
2. D. Y. Zhao *et al*., *Science* **279**, 548 (1998).
3. Y. F. Lu *et al*., *Nature* **389**, 364 (1997).
4. P. T. Tanev, T. J. Pinnavaia, *Science* **267**, 865 (1995).
5. N. A. Melosh *et al*., *Macromolecules* **32**, 4332 (1999).
6. M. Trau *et al*., *Nature* **390**, 674 (1997).
7. S. H. Tolbert, A. Firouzi, G. D. Stucky, B. F. Chmelka, *Science* **278**, 264 (1997).
8. H. Y. Fan *et al*., *Nature* **405**, 56 (2000).
9. G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **254**, 1312 (1991).
10. S. I. Stupp, P. V. Braun, *Science* **277**, 1242 (1997).
11. I. A. Aksay *et al*., *Science* **273**, 892 (1996).
12. S. Mann, *Nature* **365**, 499 (1993).
13. F. S. Bates *et al*., *Faraday Discuss.* **98**, 7 (1994).
14. T. Thurn-Albrecht *et al*., *Adv. Mater.* **12**, 787 (2000).
15. E. Huang, L. Rockford, T. P. Russell, C. J. Hawker, *Nature* **395**, 757 (1998).
16. R. A. Segalman, H. Yokoyama, E. J. Kramer, *Adv. Mater.* **13**, 1152 (2001).
17. P. Mansky *et al*., *Macromolecules* **31**, 4399 (1998).
18. Z. Lin *et al*., *Adv. Mater.* **14**, 1373 (2002).
19. N. Sundararajan *et al*., *Chem. Mater.* **12**, 41 (2000).
20. See supporting data on *Science* Online.
21. K. J. Hanley, T. P. Lodge, C.-I. Huang, *Macromolecules* **33**, 5918 (2000).
22. R. R. Gupta, V. S. RamachandraRao, J. J. Watkins, *Macromolecules* **36**, 1295 (2003).
23. B. D. Vogt *et al*., *Macromolecules* **36**, 4029 (2003).
24. P. D. Condo, S. R. Sumpter, M. L. Lee, K. P. Johnston, *Ind. Eng. Chem. Res.* **35**, 1115 (1996).
25. K. Maex *et al*., *J. Appl. Phys.* **93**, 8793 (2003).
26. J. M. DeSimone, *Science* **297**, 799 (2002).
27. D. L. Goldfarb *et al*., *J. Vac. Sci. Technol. B* **18**, 3313 (2000).
28. H. Namatsu, *J. Photopolymer Sci. Technol.* **15**, 381 (2002).
29. G. L. Weibel, C. K. Ober, *Microelectron. Eng.* **65**, 145 (2003).
30. J. M. Blackburn, D. P. Long, A. Cabanas, J. J. Watkins, *Science* **294**, 141 (2001).
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Materials and Methods
Figs. S1 to S3

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