# Simple Fabrication of Micropatterned Mesoporous Silica Films Using Photoacid Generators in Block Copolymers[†]

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Mesoporous metal oxide films have been the subject of extensive research because of their potential utility in sensors,[1a] microfluidics,[1b] microelectronics, optoelectronics, microelectromechanical systems,[1c] and catalysis.[1d] Many of these applications require the patterning of the mesoporous device layers to integrate other components necessary for intended applications. Patterning of mesoporous materials has been accomplished to date using a broad range of strategies including soft lithography,[2a–c] micropen lithography,[2d] ink-jet printing,[2d] micropatterned self-assembled monolayer templating,[2e] photochemical variation in acid concentration,[2f] and surfactant degradation.[2g,h] In all these approaches, mesoscopic structures are prepared through cooperative assembly of the hydrolyzed silica precursor species and organic surfactants or block copolymers in the presence of acid and excess amount of alcohol. The alcohol is required to slow the condensation of tetraethyl orthosilicate (TEOS) to permit adequate time for assembly to occur, which can result in long processing times and incomplete network condensation.[3] Because the structure evolution and precursor condensation occur simultaneously in this approach, the final film morphology cannot be completely prescribed before silica network formation. Moreover, because assembly occurs in solution or in solvated films, rapid diffusion of reactants and catalysts can result in poor resolution of patterning techniques that rely on spatial discrimination. One potential solution is to decouple structure generation from precursor condensation. Such an approach provides the potential for complete definition of desired hierarchical structure in a suitable template followed by precursor condensation to translate the defined architecture into the inorganic network.

Recently, Watkins and co-workers developed a new approach to mesoporous materials that involved 3D replication of preorganized block copolymer templates in supercritical carbon dioxide ($scCO_2$).[4a] The templates are prepared via spin-coating amphiphilic block copolymers from solutions that contain a trace amount of organic acid. Upon drying and annealing, the acid catalyst segregates into the hydrophilic domain of the block copolymer template. The template is then exposed to a solution of metal alkoxides in $scCO_2$, whereupon the precursor is infused into the template and undergoes hydrolysis and condensation polymerization selectively within the acid-doped hydrophilic domains to yield a silica network. Transport and diffusion of precursor into the template is enhanced by modest dilation of the template with $scCO_2$.[4b] The template is then removed by calcination at 400 °C or by reactive plasma etching to produce mesoporous metal oxide films having the morphology of template block copolymer film. One advantage of this approach is that separation of template preparation from inorganic network formation enables manipulation of the template prior to domain selective metal oxide formation. For example, the use of block copolymer templates with cylindrical domains orientated normal to the substrate yields arrays of open perpendicular nanochannels in silica[4c] or titania[4d] films that are likely inaccessible or difficult to achieve by a conventional cooperative self-assembly approach.

Here, we report a simple and rapid method to fabricate patterned mesoporous silica films by defining the desired hierarchical structure in the block copolymer template and then performing the domain selective precursor condensation. In our approach, the domain selectivity in precursor condensation was achieved by segregation of acid catalyst into the hydrophilic domain. To prepare patterned mesoporous metal oxide films, we used a photoacid generator in place of organic acids, like *p*-toluene sulfonic acid, previously used in our approach. A schematic of preparation of patterned mesoporous silica films is shown in Figure 1.

To validate this scheme, we initially used the well-studied, commercially available block copolymer, Pluronic F108, as a template and the commonly used and commercially available salt, triphenyl sulfonium triflate (TPST), as photoacid generator. Pluronic F108 is a triblock copolymer of

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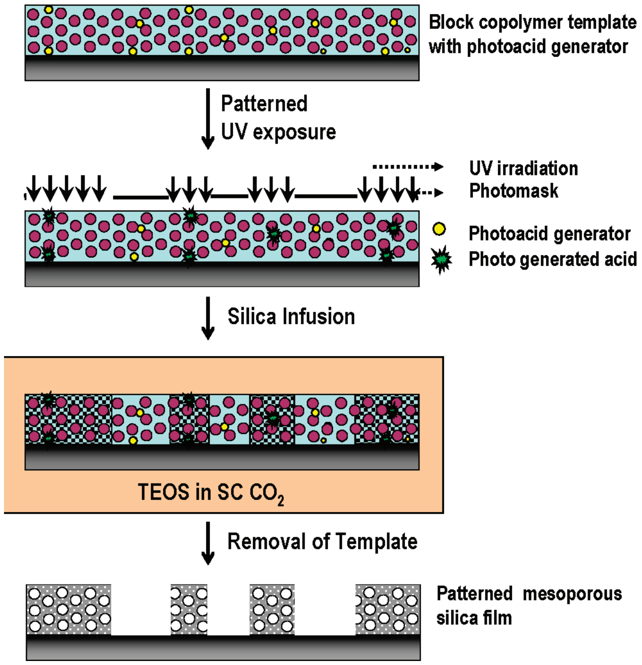

**Figure 1.** Schematic showing the steps involved in the preparation of micropatterned mesoporous silica with domain (nanoscopic) and device level (microscopic) definitions.

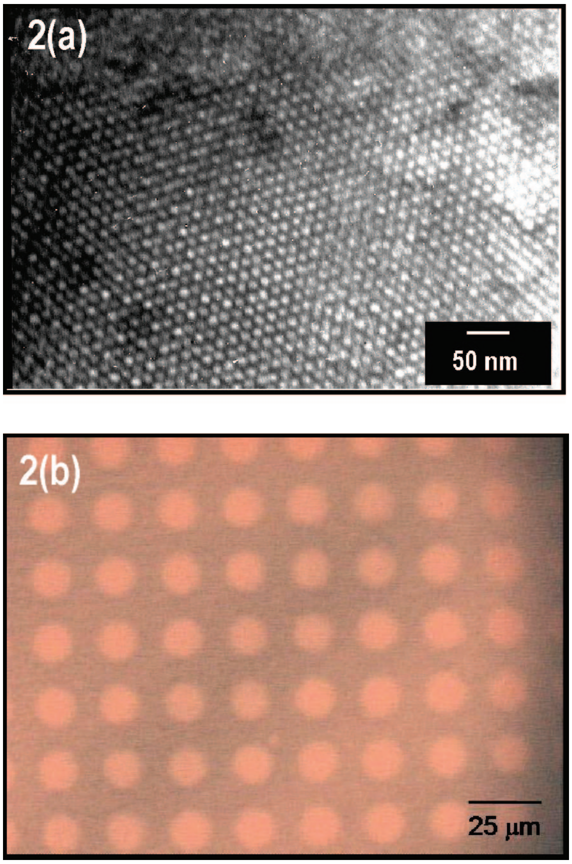

**Figure 2.** (a, b) Transmission electron and optical micrographs showing the domain and device level structures present in the mesoporous silica film templated from Pluronic F108 film, respectively.

poly (ethylene oxide) (PEO) and poly (propylene oxide) (PPO) in which the PEO volume fraction is approximately 80%. TPST generates triflic acid upon exposure to deep UV radiation ($\lambda = 254$ nm) as shown in the Supporting Information, Scheme 1. A 6 wt% solution of F108 was prepared in anhydrous methanol, containing 6 wt % (with respect to polymer) TPST. Films $\sim$200 nm thick were spun from this solution onto Si substrate. UV patterning was performed using a contact aligner and a photomask patterned with cubically packed metal dots, whose diameter is $\sim$13 $\mu$m. After exposure, the template was exposed to a CO$_2$ solution of TEOS at 125 bar and 60 °C. Following infusion, the composite film was removed from the reactor and calcined at 400 °C to remove the template. Images a and b in Figure 2 show the TEM and optical micrograph of the mesoporous silica film, respectively. Domain level replication can be seen in (Figure 2(a)), wherein well-ordered nanoporous structures templated from self-assembled F108 films are evident.

This observation indicates that the triflic acid generated from TPST segregates to hydrophilic PEO domain, where it serves as an effective silica condensation catalyst. Device level replication can be seen in (Figure 2(b)), wherein the micrometer-scale pattern transferred from the photomask is noticeable. Although domain level replication was excellent in F108 template films, device level replication was less effective. The features present in the optical micrograph (Figure 2b) lack sharp boundaries, which suggests that the generated acid readily diffused from the exposed portion to the unexposed portion of the film. This result is not entirely unexpected. Both the PEO and PPO domains in the template are well above their glass-transition temperatures during exposure and scCO$_2$-assisted infusion. Better resolution at the device level requires better control of acid diffusion. To limit the diffusion of acid, a high $T_g$, chemically amplifiable block copolymer system is used as a template.

To improve device scale resolution, we employed poly(t-butoxycarbonyloxystyrene) (PtbocSt) copolymers as a template. The choice of the PtbocSt block is based, in part, in its well-known utility as a chemically amplified resist.[5] The chemical amplification process involved in the PtbocSt system is shown in the Supporting Information, Scheme 2.

Upon generation of the photoacid, via exposure and a postexposure bake, the PtbocSt (hydrophobic) block is deprotected to yield poly(4-hydroxystyrene) (PHOST) domains, which are hydrophilic. In a typical photoresist application, this polarity switch would provide the basis for development by dissolution in a selective solvent. In our approach, we do not develop the template, but rather infuse the exposed template directly with TEOS in CO$_2$ solution.

The chosen template for our study is an anionically synthesized diblock copolymer comprised of PtbocSt and polystyrene (PS), wherein the weight fraction of the former is $\sim$55%. A 3% solution of PS-b-PtbocSt was prepared in propylene glycol monomethyl ether acetate (PGMEA), containing 5% (with respect to polymer) TPST. Approximately 250 nm thick films were spun onto Si wafer and

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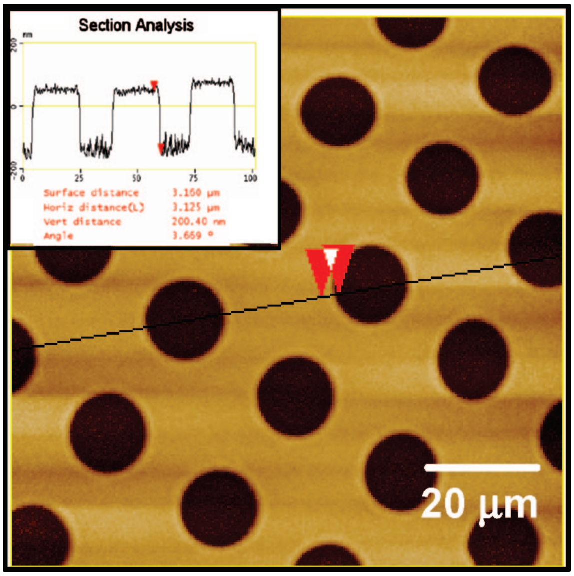

**Figure 3.** Atomic force micrograph showing the device level structures in the mesoporous silica film templated from P(S-b-tbocSt); its section profile is shown in the inset.

irradiated through a photomask. After UV exposure, postexposure bake and the domain selective silica deposition were done simultaneously in the presence of TEOS dissolved in $scCO_2$ at 125 bar and 60 °C. After depressurization, the film was etched in oxygen plasma to remove the organic components of the film and further calcined thermally at 400 °C in a nitrogen atmosphere for 6 h to complete condensation of the silicate framework. Figure 3 shows the AFM image of the calcined silica film, showing the micrometer-scale holes templated from the photomask. A section profile of the AFM image showed in the inset of Figure 3 reveal sharp sidewalls within the ~200 nm deep features.

Figure 3 suggests that during TEOS infusion at 60 °C, hydrolysis and condensation of TEOS proceeded simultaneously with deprotection reactions in the exposed regions, whereas little if any condensation was noted in the unexposed regions. It is worth mentioning that diffusion of generated acid catalyst from unexposed to exposed regions in chemically amplifiable polymers is highly limited compared to that in low-$T_g$ polymers, like Pluronic F108. In the case of former polymers, the acid diffusion is coupled with deprotection reaction front at the junction of exposed and unexposed regions, whereas in the case of latter polymers, diffusion proceeds freely at the junction. In addition, the glass-transition temperature of the PS-b-PtbocSt block copolymer domains are each well above room temperature, which mitigates acid diffusion after exposure and prior to supercritical $CO_2$ infusion. Figure 3 clearly indicates the high-fidelity replication of device level structures using a chemically amplifiable block copolymer as a template. Domain level replication was verified from the TEM image in Figure 4, which shows the mesoporous structures templated from block copolymer microphase segregation. However, the pores are not ordered. This can be attributed to weak phase segregation inherent to the underlying block copolymer template that has been faithfully reproduced in the silica film.

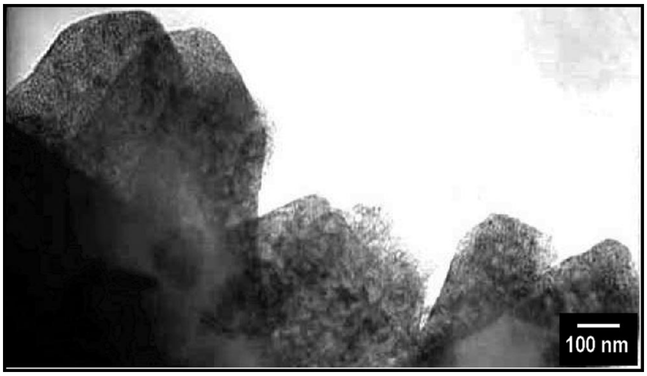

**Figure 4.** Transmission electron micrograph showing the domain level structures in the mesoporous silica film templated from P(S-b-tbocSt).

In conclusion, we have demonstrated a simple method to fabricate micropatterned mesoporous silicate films by a discrete two step approach. Microscopic (device level) and nanoscopic (domain level) structures can be defined in the template by the right choice of photomask and block copolymer. Low-$T_g$ block copolymer templates (Pluronic F108) resulted in excellent domain level replication and marginal device level replication, which is due to the diffusion of generated acid. Diffusion of acid catalyst was controlled by using chemically amplifiable block copolymer templates (PS-b-PtbocSt), which resulted in high-fidelity replication of device and domain level features. This simple method to pattern mesoporous silica films can be easily integrated into existing fabrication processes and reduce the number of process steps by eliminating the need for subsequent etching. Such an approach may reduce the cost, resources, and waste generation, for example, in fabrication of thick lines for BEOL (back end of the line) processes and potentially lower metallization layers as well. It should be noted that the resolution of features reported here is largely driven by our choice of mask and the limits of contact exposure. We are currently pursuing better resolution at the device scale by optimizing the resist chemistry and patterning with an optical stepper rather than a contact mask.

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**Supporting Information Available:** Detailed experimental procedure and two schemes. This information is available free of charge via the Internet at http://pubs.acs.org.

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