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Photochemical Pattern Transfer and Enhancement of Thin Film Silica Mesophases

Andrew M. Dattelbaum,[†] Meri L. Amweg,[†,‡] Laurel E. Ecke,[†] Chanel K. Yee,[‡] Andrew P. Shreve,[†] and Atul N. Parikh[‡,*]

Bioscience Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, and Department of Applied Science, University of California, Davis, California 95616

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ABSTRACT

Here we present a spatially directed calcination approach based on masked UV exposure to pattern mesoporous regions within a mesostructured matrix in a rapid, single-step, and inexpensive manner. Subsequent chemical treatment of the film can selectively remove the mesostructured regions, leading to patterned mesoporous structures. Such tunability in the processing under near room-temperature conditions allows for spatial control and patterning of function related to optical properties, topology, porosity, hydrophobicity, and structural morphology of the mesoscopic thin film material on a wide range of substrates.

The ability to pattern thin films of mesostructured and mesoporous materials is important for many emerging technologies, including sensor microarrays, photonic applications, catalyst screening, and nanochemistry.[1−6] Mesostructured materials, both bulk[7,8] and thin film,[8,9,10] are formed by cooperative self-assembly of surfactant microphases and inorganic phases from solution precursor molecules[11] and are converted to mesoporous materials through thermal calcination of the organic phase. Although several soft-lithography and directed self-assembly-based patterning methods have been explored,[12−18] methods for creating patterned mesostructured/mesoporous composite films are still unavailable. Furthermore, restrictions imposed by an ultimate reliance on thermal calcination remain. We present a spatially directed calcination approach based on masked UV exposure to pattern mesoporous regions within a mesostructured matrix in a rapid, single-step, and inexpensive manner. We also show that subsequent chemical treatment of the patterned mesostructured/mesoporous film can exploit the differential reactivity of each region, up to and including complete selective removal of the mesostructured phase. Thus, spatially directed UV exposure can be used to create composite patterns of mesoporous/mesostructured films or isolated mesoporous islands, each with associated functions, with no need for thermal calcination.

In the past, patterning of mesostructured films has been accomplished through directed self-assembly methods, such as the use of polymer stamps,[12−14] micropen lithography, and ink-jet printing.[17] The use of patterned self-assembled monolayers[16] provides another approach, as does patterned condensation of the silica phase through photoinitiated superacid generation followed by chemical removal of uncondensed regions of the mesostructured film.[15] In all such cases, subsequent generation of patterned mesoporous structures can be achieved by removal of the templating surfactant phase using thermal calcination. Several limitations persist for all these approaches. Thermal calcination processes are not suitable for temperature-sensitive substrates, such as gold. In addition, none of the approaches described are useful for the generation of patterned mesostructured/mesoporous films. Also, chemically based methods, such as localized pH-induced condensation,[15] must be optimized for each specific inorganic precursor and depend on the ability to incorporate exogenous photochemically active species into the reaction mixture without perturbing the overall assembly process.

Recently, a nominally room-temperature photochemical method that does not require addition of exogenous species has been shown to provide a useful alternative to thermal calcination, leading to well-ordered, mesoporous silica thin films.[19] This method uses deep ultraviolet (187−254 nm) illumination of thin-film sample in air from a simple Hg source. It was suggested that UV light, in conjunction with the ensuing production of activated oxygen and ozone, both removes the surfactant phase and strengthens the silicate phase by fostering the condensation of unreacted silanols.[20] This process has an advantage over the recent use of vacuum ultraviolet light for surfactant removal[18,21] in that no specialized light source or expensive vacuum equipment is needed.[22]

* Corresponding aurthor. E-mail: anparikh@ucdavis.edu
† Los Alamos National Laboratory.
‡ University of California Davis.

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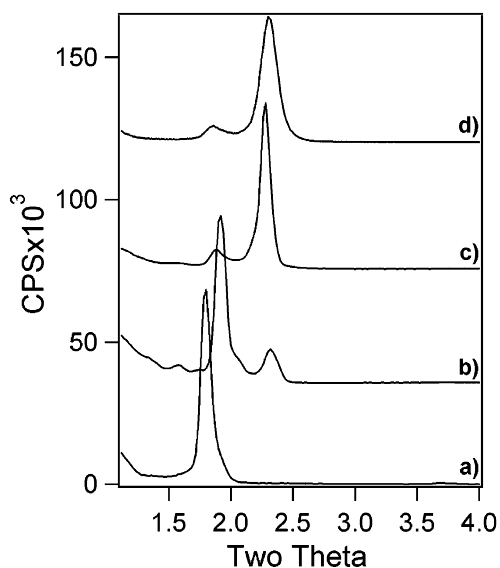

Figure 1. Typical XRD patterns for (a) an as-prepared mesostructured film and (d) a UV-exposed mesoporous film. Patterns (b) and (c) were collected on either side of the boundary between the unexposed and UV-exposed regions of the film, respectively.

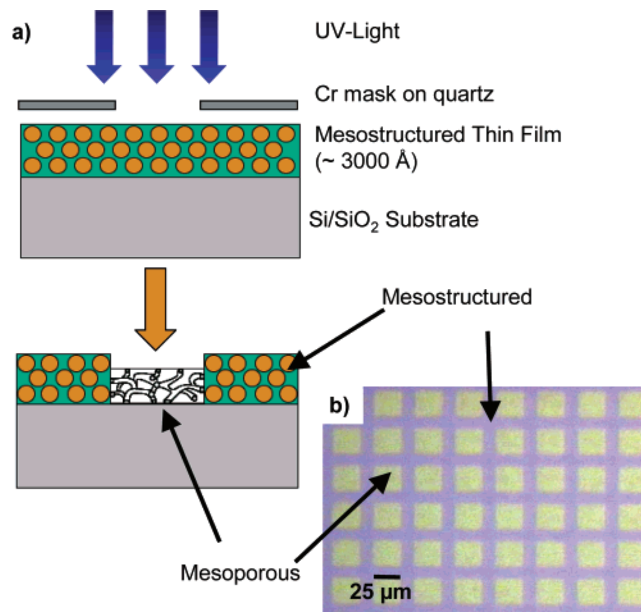

Figure 2. (a) Schematic of the preparation for patterned mesostructured/mesoporous silica thin films. (b) Optical microscope image showing contrast difference between mesostructured (purple) and mesoporous (yellow) regions.

Here, we show that the use of this UV-induced photochemical process together with a physical mask can lead to patterned mesoporous regions in a mesostructured film. Further, subsequent chemical treatment of the film can selectively remove the mesostructured regions, leading to patterned mesoporous structures. Such tunability in the processing under near room-temperature conditions allows for spatial control and patterning of function related to optical properties, topology, porosity, hydrophobicity, and structural morphology of the mesoscopic thin film material on a wide range of substrates.

Following Lu, et al.,[8] we prepared thin films of mesostructured silica on planar silicon substrates using an evaporation-induced self-assembly process.[23] An ethylene oxide based surfactant, $C_{16}H_{33}$ $(OCH_2CH_2)_{10}OH$ (Brij56), was used as a templating agent and tetraethyl orthosilicate (TEOS) as the silica precursor. Previous studies have shown that use of Brij56 produces an ordered hexagonal phase for the mesostructured material.[24,8] The initial structure of the film was confirmed using X-ray diffraction (Figure 1a), FTIR, and ellipsometry measurements. Exposing the film to ultraviolet light (187−254 nm) for ∼120 min, completely removes the surfactant phase as monitored by FTIR.[19] During this process a hexagonal to cubic transformation occurs as indicated by the X-ray diffraction pattern shown in Figure 1d, also confirming previous reports.[19] If ultraviolet light is blocked from specific regions of the surface using metal foil as a simple physical mask, then the surfactant is selectively removed from only the parts of the film exposed to UV light. X-ray diffraction patterns obtained on either side of the boundary region of a patterned mesostructured/mesoporous film are shown in Figures 1b and c, in which peaks associated with both hexagonal and cubic phases are observed.

More complex structures can be generated using chromium patterns deposited onto a quartz window as the physical mask (Figure 2a).[25] After the UV exposure, mesostructured/mesoporous patterns were easily visualized using standard optical microscopy (Figure 2b). Optical contrast results from both the thickness decrease and index of refraction change that accompany the UV exposure (see below), similar to those observed for thermally calcined samples.[8] Patterns as small as 3 μm could be observed in our simple optical microscopy measurements. As this resolution was limited by the mask used, it is not known if this represents the limiting feature size achievable by this approach. Future studies could address the question of whether significantly smaller sizes of pattern features can be obtained.

Following UV exposure, subsequent chemical processing of the films can be used to enhance the observed patterns through preferential etching of the mesoporous regions as indicated by the results presented in Figures 3 and 4. A mesostructured thin film was exposed to the UV treatment through a mask containing 1 mm square apertures (Figure 3a). The patterned mesoporous/mesostructured film was then exposed to an aqueous 0.1 M NaOH solution for a series of fixed exposure periods (t = 0, 10, 75, and 3525 s); cumulative exposures were 0, 10, 85, and 3600 s. Between consecutive exposure periods, the sample was removed from the solution, imaged optically (Figure 3b−d), and probed with spatially resolved FT-IR spectromicroscopy and imaging ellipsometry (Figure 4).

These experiments provide clear evidence confirming the two key results reported here. First, prior to exposure to the NaOH solution, the presence of surfactant in the mesostructured material and its absence in the UV-exposed mesoporous material are readily observed from the relative infrared absorption intensity of the surfactant-specific peaks in the methylene and methyl CH stretching frequency range[26] (2800

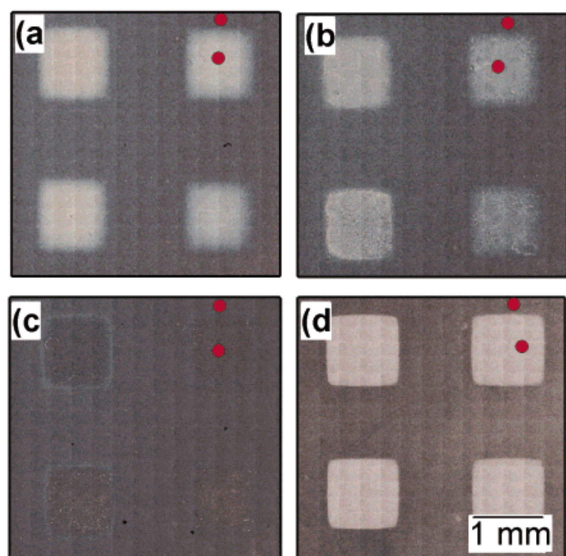

Figure 3. Optical images of a patterned mesostructured/mesoporous film prepared by masked deep-UV exposure (a), and the same film immersed in a 0.1 M NaOH solution for 10, 85, and 3600 s (Figure 3b−d, respectively). The red dots on each image indicate regions of the film interrogated by spatially resolved FT-IR spectroscopy and imaging ellipsometry (see Figure 4).

to 3000 cm^{-1}) as shown in Figures 4a,b. Second, upon exposure to the NaOH solution, the mesostructured material is more efficiently removed relative to the mesoporous material as is evident by the rapid decrease in mesostructured infrared intensity (Figure 4c) and ellipsometrically determined thickness (Figure 4d). This preferential removal reaches an end point in which the entire mesostructured region has been completely removed, as shown by the changes observed in ellipsometric thickness and FTIR intensities (Figure 4), while the UV-exposed mesoporous regions remain.

Ellipsometric thicknesses and FTIR (Si−O−Si stretches) intensity trends in Figures 4c,d further reveal a subtle but notable effect of the chemical enhancement step. At long exposure periods, the mesoporous material also begins to etch away, albeit at a significantly lower rate. We suggest that despite this etching, structural morphology and overall porosity of mesoporous silica films are preserved based on a closely related study by Doshi and co-workers.[15] There it was shown using transmission electron microscopy that mesoporous silica films retained their structural and porosity character, even upon etching in a more basic solution

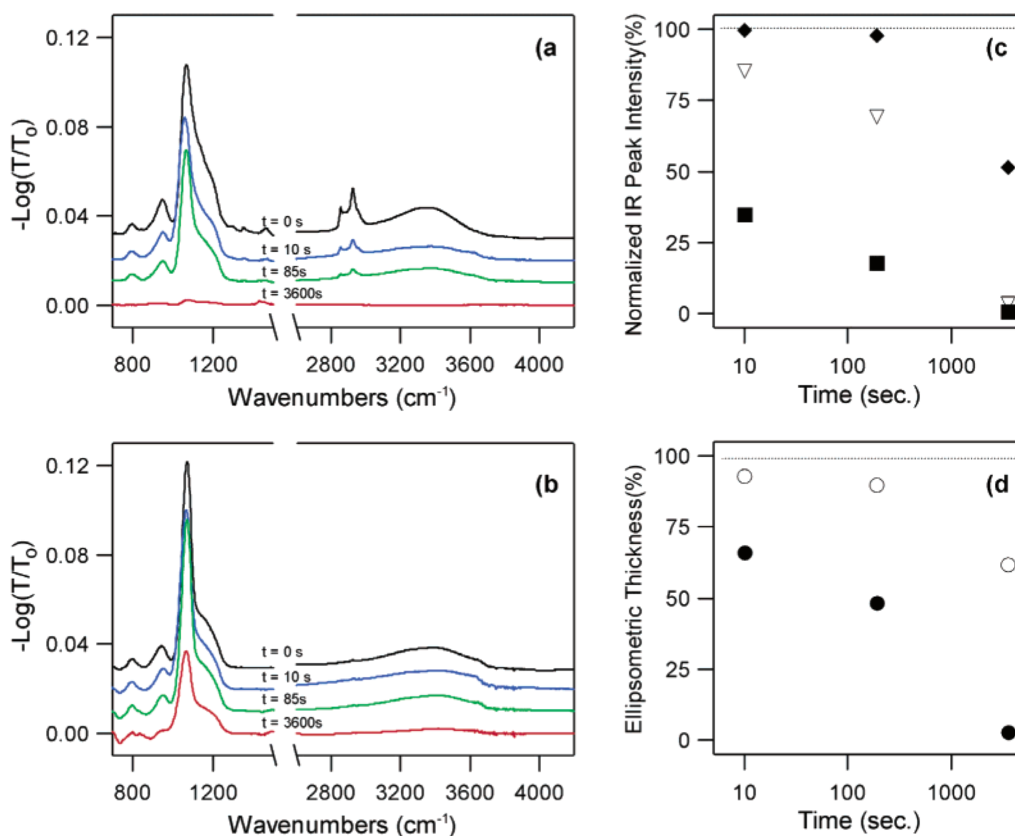

Figure 4. (a,b) Spatially resolved FT-IR spectra taken as a function of immersion time in 0.1 M NaOH (aq). The FT-IR data for the mesostructured regions (a) were obtained at the lower red point indicated in panels a−d. Correspondingly, the FT-IR data for the mesoporous regions (b) were obtained at the upper red point indicated in panels a−d. The integrated infrared absorption intensities of the methylene and methyl CH stretching modes (2800−3000 cm^{-1}) and the Si−O−Si stretching modes (1000−1250 cm^{-1}) for the mesostructured material are presented as closed squares and open triangles, respectively, in (c). In the same panel, the integrated intensities of the Si−O−Si absorption region for the mesoporous material are presented as closed diamonds. For each spectral region, the integrated intensities are plotted on a relative scale with 100% corresponding to the intensity of that region in the zero time spectra. Spatially resolved elliposometric data collected during the NaOH immersion of the patterned film shown in Figure 3 are presented in (d) on a normalized scale where the thickness in each region determined prior to immersion in NaOH solution is 100%; closed circles correspond to mesostructured regions, while open circles correspond to mesoporous regions.

(0.2 M NaOH) than the one (0.1 M NaOH) used in this study. Immersion of films in even solutions that are less basic than the one used here can minimize etching of the mesoporous material but require significantly longer periods of time to completely remove the mesostructured portion of the patterned film.

In summary, we have shown that a spatially directed impingement of ultraviolet light (187−254 nm) is effective in selectively removing surfactant molecules from mesostructured thin films to generate patterns as small as three microns. Further, the contrast of the patterned films generated can be tuned. In particular, enhancement by immersion in a NaOH solution preferentially and completely etched the mesostructured material from the surface, leaving patterned islands of mesoporous material. This process has been fully characterized using optical microscopy, spatially resolved FT-IR, and spatially resolved ellipsometry. The patterning techniques described in this paper, when coupled with the range of functionalities associated with mesoporous materials and applied in repeated cycles, will be useful in the design of patterned functional and multifunctional arrays incorporating electronic, optical, catalytic, sensing, and fluidic functions. Moreover, the approach is directly amenable to patterning mesoporous structures (and associated functions) in nonplanar geometries (e.g., fibers and beads). Such applications are currently being explored.

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(23) Surfactant/silicate thin films were prepared following a previously reported two-step process that was designed to minimize silicate condensation and promote facile silica/surfactant self-assembly during film deposition. Initially a silica sol was prepared by refluxing a mixture of tetraethyl orthosilicate (TEOS, from Aldrich, 61 mL), anhydrous ethanol (Fisher, 61 mL), >18 MΩ deionized water (0.44 mL), and 0.07 N hydrochloric acid (HCl, 0.2 mL) at 60°C. Upon cooling to room temperature, a portion of the above solution was diluted with ethanol, water, and hydrochloric acid (0.07 N). A nonionic surfactant, $C_{16}H_{33}(OCH_2CH_2)_nOH$.; $n \sim 10$ (technical name: Brij56, Aldrich), was then added to the silica sol solution at ~4.0 wt. %, significantly below the critical micellar concentration (cmc). During the addition of the surfactant, the water, ethanol, and hydrochloric acid concentrations were adjusted to yield the final reactant mixture in the mole ratios of 1 TEOS: 22 C_2H_5OH: 4 H_2O: 0.004 HCl: 0.085 Brij56. Mesostructured thin films were then deposited onto freshly oxidized single-crystal silicon (100) with native oxide overlayer (SiO_2/Si) by withdrawing the substrate from the 4 wt % Brij56/TEOS solution at 5−20 cm/min.
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