Secrets revealed — Spatially selective wetting of plasma-patterned periodic mesoporous organosilica

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Abstract: We report a simple method to pattern wetting properties on thin films of periodic mesoporous organosilica (PMO). A hydrophobic methane PMO thin film was covered by masks and exposed to oxygen plasma to make the unmasked area hydrophilic. The wettability patterns could be revealed only when the films were immersed in water or exposed to moisture. We expect that our method would extend the utility of PMO to such areas as sensing and information security.

Key words: wetting, plasma, mesoporous materials, thin film.

Introduction

Spatially patterned porous materials combine the characteristics of a pattern, such as shape and dimensions, with the characteristics of a porous material, such as high surface area and large pore volume, to deliver functions that promise applications in sensors, catalysis, photonics, displays, microfluidics, and electronics.1–6 Patterns of ordered mesoporous materials have been produced using self-assembled monolayers (SAMs),2,7,8 photolithography,4 micromolding in capillary,1,6 direct writing,5 ink-jet printing,5 and scanning electrochemical microscopy.9 These patterns are produced either by selectively generating materials in the patterned area or by selectively removing materials from the nonpatterned area. In other words, they are distinguished by the physical presence or absence of materials. Here, we report a method to create patterns of different wettability on thin films of mesoporous organosilica. This method creates patterns of properties, in contrast to patterns of materials. These patterns only reveal themselves when the films are immersed in water or exposed to moisture. We expect our method could lead to applications in sensing and information security and also could provide a convenient platform for fundamental studies in wetting dynamics and nanofluidics.

Experimental

Materials
Bis(triethoxysilyl)methane was purchased from Gelest. Cetyltrimethylammonium chloride (CTACl) 25 wt % solution in water was purchased from Sigma-Aldrich. Reagents were used as received.

Synthesis of methane periodic mesoporous organosilica (PMO) thin films
The synthesis was performed according to a previous report.10 Briefly, bis(triethoxysilyl)methane was added into a solution of CTACl, HCl, water, and ethanol with moderate stirring. The molar ratio of the reactants was...
bridging –CH2– groups into terminal –CH3 groups at a temperature higher than 400 °C, the transformation of archetype to demonstrate our patterning technique because, 

range of 500–900 nm. Photos and videos were taken on a Woollam spectroscopic ellipsometer over a wavelength 

ating voltage of 200 kV. Ellipsometry data were collected on (TEM) was performed on JEOL 2100 TEM with an accelerated at 40 kV and 30 mA. Transmission electron microscopy 

Scintag XDS2000 diffractometer using Cu K

results was aged for 70–90 min. These as-deposited thin films 

were heated at 150 °C for 2 h (ramping 1 °C / min) and then at 500 °C for 2 h (ramping 1 °C / min) under continuous nitrogen flow.

Patterning by plasma treatment
Stencils masks were cut out of 90 μm thick plastic films (PET) using a VersaLaser cutting system. Metallic letters were ordered from Gemini Sign Letters. Stencils masks or metallic letters were placed directly on top of the thin film as masks. Plasma exposure was performed under oxygen atmosphere for 

20–40 s on a FEMTO plasma system from Diener Electronics. Plasma exposure was performed under oxygen atmosphere for 

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Characterizations
Low-angle X-ray diffraction (XRD) was performed on a Scintag XDS2000 diffractometer using Cu Kα radiation operated at 40 kV and 30 mA. Transmission electron microscopy (TEM) was performed on JEOL 2100 TEM with an accelerating voltage of 200 kV. Ellipsometry data were collected on a Woollam spectroscopic ellipsometer over a wavelength range of 500–900 nm. Photos and videos were taken on a Canon EOS Rebel T2i model.

Results and discussion
The material we choose is methane periodic mesoporous organosilica (PMO). PMO, invented in 1999, is a class of mesoporous materials with organosiliceous pore walls that have one organic bridging group covalently bonded to two or more silicon atoms.11–13 These bridging organic groups impart unique chemical, biological, optical, and dielectric properties to PMO and distinguish PMO from its pure siliceous counterpart.14,15 We use methane PMO, with a –CH₂– bridge, as an archetype to demonstrate our patterning technique because, at a temperature higher than 400 °C, the transformation of bridging –CH₂– groups into terminal –CH₃ groups hydrophobizes the surface of the pore wall10,16,17 and exposes the terminal methyl groups for subsequent plasma treatment. Another PMO that can be similarly hydrophobized is three-dimensional (3D) porous silicon inverse-opal structures by iterating silanization and shadow-masked oxygen plasma to produce spatial patterns of surface chemistry within the pores.19,20 The slow propagation of plasma oxidation fronts in porous structures enables pattern- 

We chose plasma treatment as the way to generate patterns. Plasma treatment with the aid of a preformed mask was shown to be a fast (on the order of minutes) and clean (liquid-free) method to create patterns of SAMs on a flat surface at length scales from sub-100 nm to centimetres.18 We have previously extended this technique to three-dimensional (3D) porous siliceous inverse-opal structures by iterating silanization and shadow-masked oxygen plasma to produce spatial patterns of surface chemistry within the pores.19,20 The slow propagation of plasma oxidation fronts in porous structures enables pattern- 

we produced thin films of methane PMO by spin-coating, followed by thermal treatment at 500 °C to remove surfactants and to initiate self-hydrophobization.10,17 The mesostructure of methane PMO was confirmed by low-angle XRD and TEM (Figs. 2 and 3). The decrease in d spacing (from 4.2 to 3.2 nm) and the increase in diffraction intensity after thermal treatment are due to anisotropic shrinkage in the out-of-plane direction21 and increased electron density contrast.22 Both wormlike23 and two-dimensional (2D) hexagonally ordered porous channels were observed in TEM.

We then patterned thin films in oxygen plasma treatment with preformed masks placed directly on their top surfaces. Masks were made out of metal, plastic, or glass. A flat smooth surface is required to provide a conformal contact with the underlying thin films. The plasma treatment did not alter the visible appearance of methane PMO thin films (Fig. 4). As a specific example, the O-shaped pattern was revealed when a water droplet was placed on the surface of the film or when the film was exposed to water vapor. The refractive index of the thermally treated thin film was 1.26. Vapor condensation inside mesopores was studied previously in the context of the application of PMOs as low-

dielectric constant materials in semiconductor microproces-
This vapor condensation increased the effective refractive index of the hydrophilic regions of the pores to the range of 1.4–1.5, providing enough contrast in refractive indices to make the pattern visible to the naked eye. The principle behind this vapor-phase response is different from most of the current sensing methods that exploit properties imparted by the physisorbed molecules on the porous surface and could lead to further design of novel vapor sensors.

The versatility of our technique is illustrated in the gallery of wetting patterns (Fig. 5). The top two rows show that...
successive addition of water gradually diminished the unwetted area and changed the shape of the pattern from a star to a circle as the result of a balance of surface tensions (glass substrates are used for optimum visual effect). The first image on the third row shows that the star-shaped pattern was visible when the whole thin film was covered with water (silicon wafer as the substrate). This visual contrast under water demonstrates that liquid water did not fill the mesopores in the hydrophobic regions. The star-shaped pattern and the letters “GAO” were made from positive masks (metallic letters), whereas the smiley face and the Canadian flag were made from negative masks (plastic sheets with patterned areas removed by laser cutting).

We also observed that an increase in the duration of plasma treatment increased the wettability of a pattern (Supplementary data, movies 1–3). The vertical line and the horizontal line in movies 1–3 (Supplementary data) were exposed to plasma for 20 and 40 s, respectively. Placing a droplet at the area where the two lines cross revealed that water wet the horizontal lines (more hydrophilic) faster than the vertical lines (less hydrophilic) (Supplementary data, movie 1). Excess water was removed by the capillary action from the tip of a glass pipette (inside diameter ~1 mm) (Supplementary data, movie 2). Water added at the end of the lines spontaneously transferred to the center because the curvature of a water droplet at the center was larger than the curvature of a water droplet at the end and, consequently, the Laplace pressure was smaller at the center than at the end (Supplementary data, movie 3). The transportation of water seems to occur inside the mesoporous thin films rather than along the surface of the thin film because no visible bulge exists along the line of water transportation. We further used these wetting phenomena in an interesting demonstration of hiding and revealing the pattern of a smiley face (Supplementary data, movie 4). Detailed analysis in quantifying the hydrophilicity after plasma treatment and further exploration on liquid transport phenomena are ongoing in our lab.

**Conclusion**

In conclusion, we have demonstrated that plasma treatment of thermally processed thin films of methane PMO is a fast and clean method to create patterns of wettability. These patterns can only be revealed when exposed to water or moisture. We also demonstrated a few interesting phenomena of wetting dynamics. Our technique may provide a way to study some fundamental aspects of wetting dynamics, such as fluid transport in the presence of a gradient of wettability and the complex geometry of wettability patterns, as well as some applications of this selective wetting phenomenon, such as hiding, revealing, and transforming shapes (and hence information), in sensing and information security.

**Supplementary data**

Supplementary data are available with the article through the journal Web site (http://nrcresearchpress.com/doi/suppl/10.1139/v2012-092).

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