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

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). Hydrophobic methane PMO thin film was covered by masks and exposed to oxygen plasma to make 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 non-patterned 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 Aldrich. Reagents were used as received.

Synthesis of methane PMO thin films

The synthesis was performed accord 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 Si/CTACl/HCl/H_2O/EtOH = 1:0.15:2x10^{-4}:19.1:15. The solution 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

Stencil masks were cut out of 90um thick plastic films (PET) using a VersaLaser cutting system. Metallic letters were ordered from Gemini Sign Letters. Stencil masks or metallic letters were placed directly on top of the thin film as masks. Plasma exposure was performed under oxygen atmosphere for 20-40s on FEMTO plasma system from Diener Electronics.

Characterizations

Low angle X-ray diffraction was performed on Scintag XDS2000 diffractometer using Cu Kα radiation operated at 40 kV and 30 mA. Transmission electron microscopy was performed on JEOL 2100 TEM with an accelerating voltage of 200 kV. Ellipsometry data were collected on Woollam Spectroscopic Ellipsometer over the wavelength range of 500-900 nm. Photos and videos were taken on Cannon 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 whose organosiliceous pore walls 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 –CH_2– bridge, as an archetype to demonstrate our patterning technique because at a temperature higher than 400 °C, the transformation of bridging –CH_2– groups into terminal –CH_3 groups hydrophobizes the surface of the pore wall[10,16,17] and exposes the terminal methyl groups for subsequent plasma treatment. Another PMO that can be similarly hydrophobized is 3-ring PMO; in contrast, ethane and ethene PMO do not possess this ability.[10]

We choose 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 self-assembled monolayers (SAMs) on flat surface at length scales from sub-100 nm to centimeter.[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 patterning by masking only the top surfaces of the structures.[18-20] In this report, we use oxygen plasma to convert terminal methyl groups into silanol groups in thermally-treated methane PMO. This conversion switches the hydrophobic pore wall to a hydrophilic one, and enables us to create patterns of different wettability in one single material (Figure 1).

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 X-ray diffraction (XRD) and transmission electron microscopy (TEM) (Figures 2 and 3). The decrease in d-spacing (from 4.2 nm to 3.2 nm) and the increase in diffraction intensity after thermal treatment are due to anisotropic shrinkage in the out-of-plane direction[21] and increased electron density contrast.[22] Both worm-like[23] and 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 (Figure 4). As a specific example, the O-shaped pattern was revealed when 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±0.01 at 633 nm (repeated wetting by water could increase the refractive index up to 1.30±0.02 at 633 nm). Vapor condensation inside mesopores was studied previously in the context of the application of PMOs as low-dielectric constant materials in semiconductor microprocessors.[10] This vapor condensation increased the effective refractive index of the hydrophilic regions of the pores to the range of 1.4-1.5,[10] providing enough contrast of 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[23] and could lead to further design of novel vapor sensors.

The versatility of our technique is illustrated in the gallery of wetting patterns (Figure 5). The top two rows show that successive addition of water gradually diminished the un-wetted 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 movie 1-3). The vertical line and the horizontal line in these movies were exposed to plasma for 20s and 40s, 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 line (less hydrophilic) (Supplementary movie 1). Excess water was removed by the capillary action from the tip of a glass pipette (inside diameter ~1mm) (Supplementary 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 that at the end (Supplementary 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 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 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.

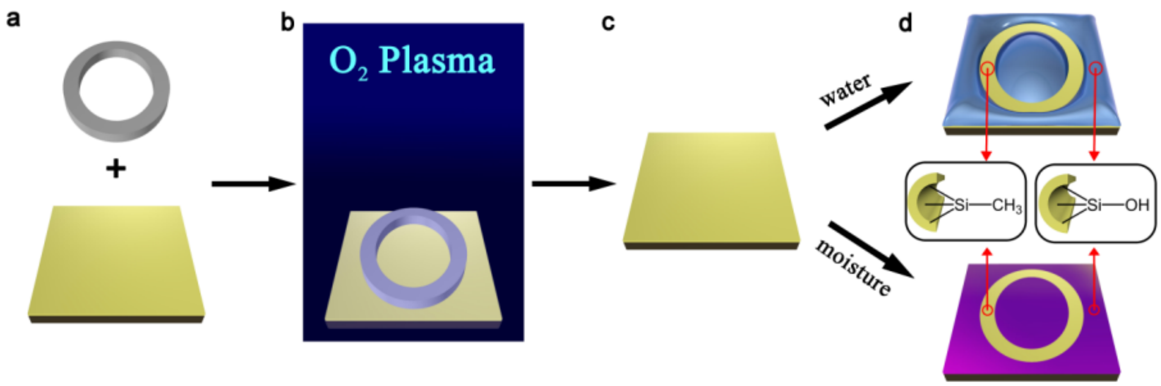

Figure 1 Scheme of the patterning experiments: (a) Methane periodic mesoporous organosilica thin film and an O-shaped mask, (b) plasma treatment; (c) resulting patterned thin film after plasma treatment is optically indistinguishable from the original film, (d) the pattern revealed by adding water droplets on the film or by exposing the film to water vapor.

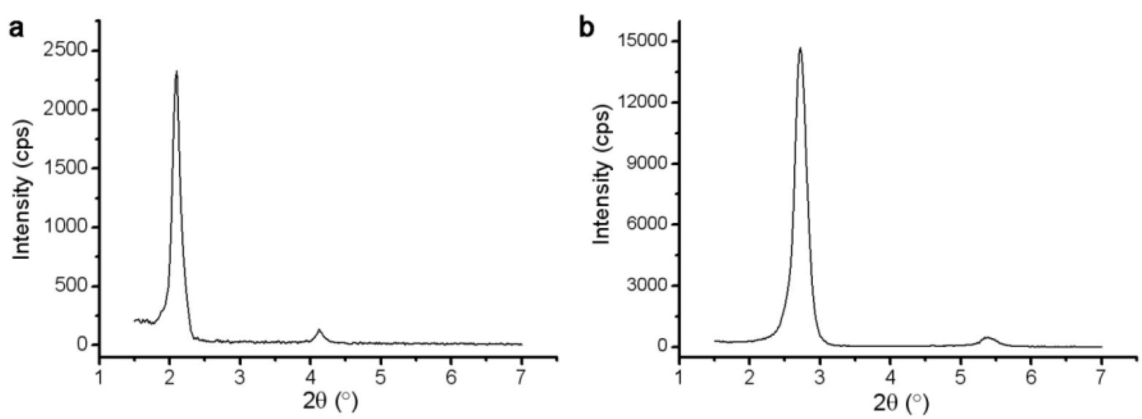

Figure 2 Low angle XRD diffractograms of methane periodic mesoporous organosilica thin films (a) before and (b) after thermal treatment at 500 °C. The d-spacings calculated from the main peaks are 4.2 nm and 3.2 nm for (a) and (b), respectively.

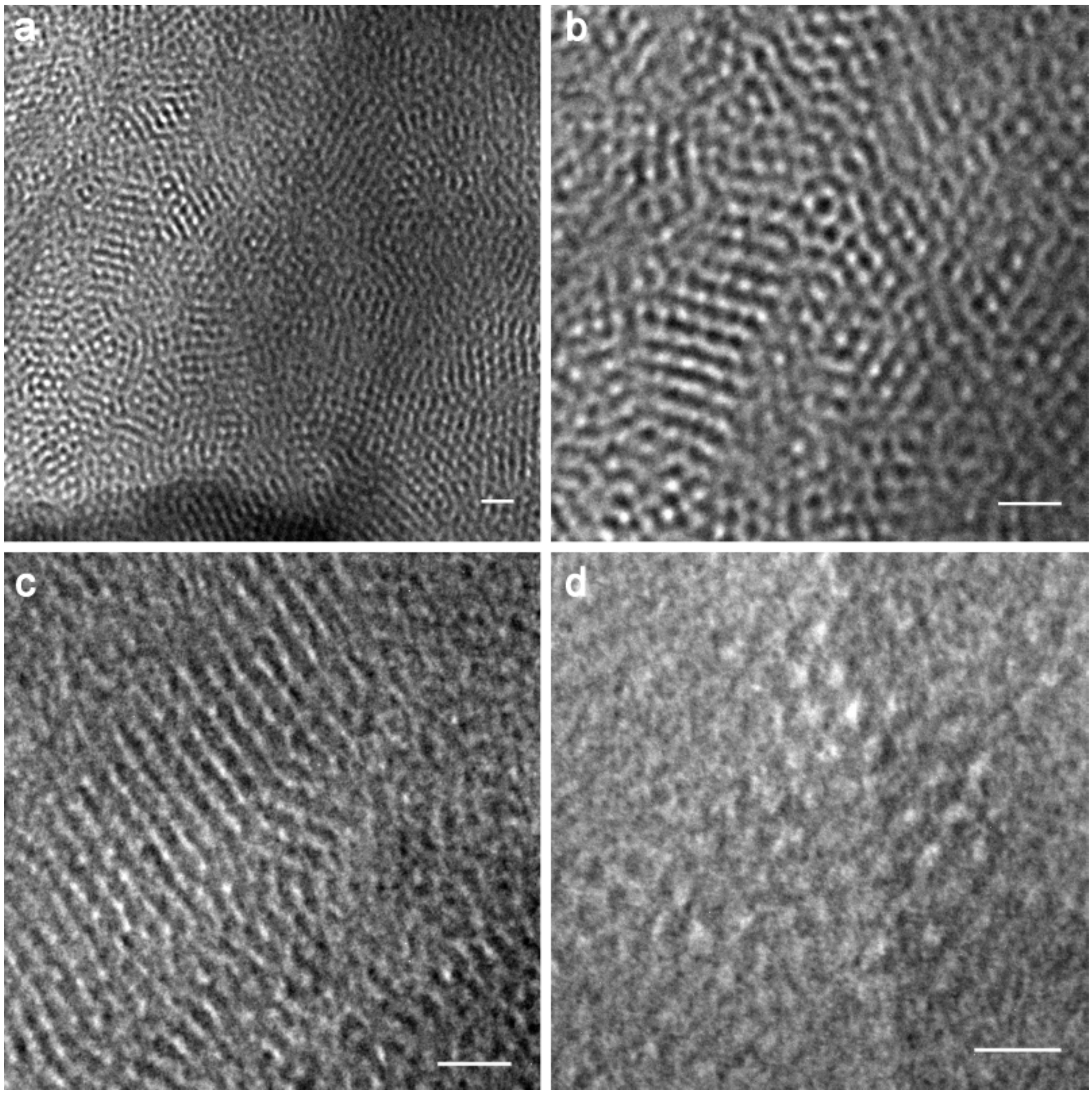

Figure 3 Representative TEM images of methane PMO after thermal treatment. Scale bar is 10nm.

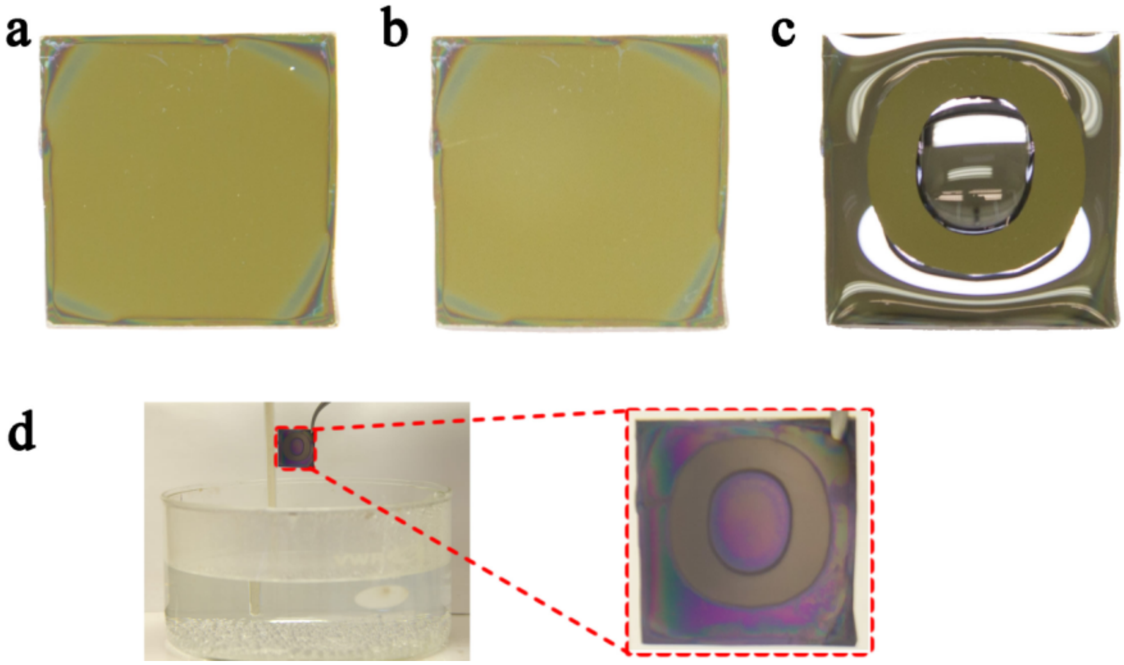

Figure 4 Photos of thin films (a) before and (b) after the plasma patterning treatment, and O-shaped pattern revealed (c) by wetting the thin film with water or (d) by exposing the thin film to the vapor above an 80 °C water bath.

Figure 5 Gallery of Wetting Patterns.

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