Ordered Hybrid Nanomaterials from Self-Assembled Polymeric Building Blocks

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Introduction

Self-assembly has attracted increasing attention as a platform toward well-defined, ordered complex structures on the nanometer scale. In particular, block copolymers (BCPs) offer a significant potential as nanomaterials since they self-organize to form well-ordered, periodic nanoscale morphologies depending on the relative volume fraction of the constituent blocks. There have been numerous efforts to use self-assembled BCPs as templates or scaffolds for the fabrication of functional nanostructures and an increasing number of novel nanomaterials are being reported from this unique class of polymers.[1,2]

In particular, thin films of diblock copolymers with cylindrical microdomains oriented normal to the surface are attractive due to the tunability of large aspect ratios of the cylindrical microdomains. In this article, selective etching and subsequent annealing of thin films of mixtures of asymmetric PS-*b*-PMMA with cylindrical PMMA microdomains and PMMA homopolymer in which PMMA microdomains oriented normal to the film surface, was employed to produce nanoporous thin films with arrays of discrete pores. The films served as planar waveguide layers in the experimental setup known as Kretschmann prism coupling configuration. Here, we report an unprecedented route to quasi-reversible nanostructures with capped nanopores obtained from sequential selective swelling and re-annealing process. Specifically, the change in porous morphology occurring simultaneously inside and on top of the film was detected independently by monitoring guided optical modes under *p*- and *s*-polarization conditions.

Experimental

Optical Waveguide Spectroscopy (OWS). We performed OWS experiments based on the Kretschmann prism coupling technique.[3,4] A home-built surface plasmon resonance (SPR) based optical detection setup was used. A HeNe laser (5mW, Uniphase) beam passed through a chopper that is connected to a lock-in amplifier (EG&G). A polarizer (Glan-Thompson) for either *p*- or *s*-polarization was used. The substrate containing the waveguide layer was attached to the prism base with an index-matching oil. Consequently the glass prism and the substrate form an optically continuous medium. The incident laser is reflected off the base plane of the coupling prism and the reflected intensity focused by a lens (L2, f = 50 mm, Ovis) is collected by a photodiode. The sample is mounted onto a 2-phase goniometer (Huber) that can be moved in 0.001° steps operated by the connected personal computer.

Fabrication of the Waveguide Layer. A silver (Ag) substrate was prepared on glass substrates in order to excite surface plasmon between the metal and the underlying waveguide layer. Chromium (Cr, ~2 nm) and silver (Ag, ~50 nm) layers were deposited by thermal evaporation. 3-MPS was then introduced as an adhesion-promoting layer between the Ag and the following silicon dioxide (SiO_2) layer. Silicon dioxide (SiO_2) substrates were prepared by a sol-gel process. A typical precursor solution for SiO_2 is composed of 163 μL H_2O, 55 μL methanol, 81 μL 0.1M HCl, and 20 μL TMOS. An energetically neutral surface for PS-*b*-PMMA films was then anchored to the SiO_2 layer using P(S-*r*-MMA) via the covalent coupling between the hydroxyl groups and the SiO_2 surface. Thin films composed of PS-*b*-PMMA and PMMA homopolymer mixtures, containing 25 wt% PMMA homopolymers with respect to the amount of the PMMA block, were prepared by spin coating 5 wt% toluene solutions at 500 rpm onto the P(S-*r*-MMA) surface. The films were annealed at 155 °C for 2 days under vacuum, and then quenched to room temperature.

Results and discussion

The entire process discussed in this work is schematically illustrated in Figure 1 and analysed by OWS as summarized in Figure 2. It is observed that the removal of homo PMMA due to selective etching and swelling results in shifts in the coupling angles to lower values in both *s*- and *p*-polarization, respectively, which is characteristic of a decrease in the ε_{eff} (blue curves). The porosity of the film, obtained by comparing the experimental data and the theoretical calculation derived from the effective medium theory, was measured to be ~ 5.4%. The reversible change at the air/film surface due to the rearrangement of PMMA block chains was selectively reflected in *s*-polarization during the sequential selective solvent swelling/re-annealing process.

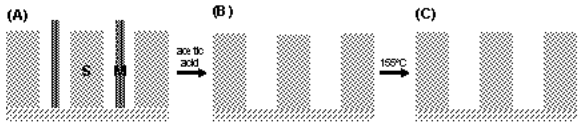

Figure 1. Schematic cross-sectional representation of the nanopore formation in PS-*b*-PMMA/PMMA film by selective solvent swelling

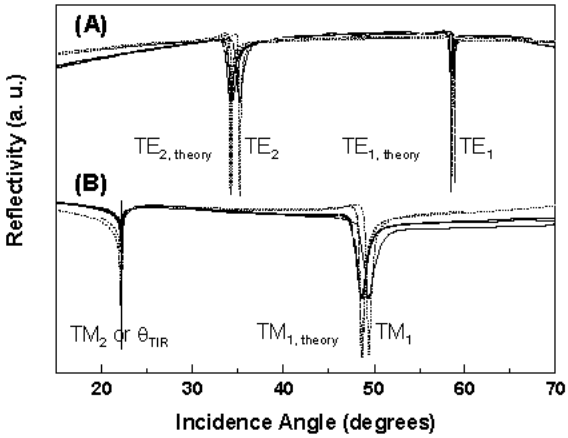

Figure 2. Waveguide mode patterns of the PS-*b*-PMMA/PMMA mixture film for each step of the process described in Figure 1 under *s*-polarization (a) and in *p*-polarization (b), respectively. The black, blue, and red curves indicate the waveguide patterns of the initial, swelled, and re-annealed films, respectively. The dotted curves are the best fits to the respective experimental data. The green curve represents the hypothetical pattern obtained from the Fresnel calculation assuming a complete removal of PMMA homopolymers.

Conclusions

In summary, we presented a simple route to unprecedented nanoporous structures, i.e., arrays of capped pores with controllable volume fraction, by a combined selective swelling and annealing, and verified the morphologies for each step of the fabrication process by AFM, TEM, FESEM and OWS studies. Based on the methodology discussed in this work, complex events that can occur in nanoporous materials such as growth of one-dimentional nanomaterials inside or functionalization/adsorption on top of the BCP templates can be investigated by static or in-situ kinetic mode OWS. Similar experimental strategies applied for porous aluminum oxide templates demonstrated the sub-angstrom sensitivity of OWS for such processes. This work demonstrates the potential applications of BCP films in integrated optical devices and suggests that OWS provides a significant advance over conventional analytical tools, e.g., microscopic or scattering methods, in terms of cost-effective, simple home-built experimental setup and high sensitivity.

References

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