



# Three-dimensional nanomasks using block copolymers confined in the nanopores of anodic aluminum oxide templates



Chiang-Jui Chu, Chia-Hua Lin, Pei-Yun Chung, Ming-Hsiang Cheng, Kai-Sheng Jeng, Jiun-Tai Chen\*

Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30010, Taiwan

## ARTICLE INFO

### Article history:

Received 6 March 2015

Accepted 1 April 2015

Available online 28 April 2015

### Keywords:

Block copolymers

Nanolithography

Nanotubes

Solvent annealing

Three-dimensional

## ABSTRACT

Block copolymers have been widely studied over the last few decades because of their ability to self-assemble into well-ordered nanoscale structures. Here, we present a novel approach to fabricate nanostructures using block copolymer thin films as three-dimensional nanomasks. Polystyrene-block-polydimethylsiloxane (PS-*b*-PDMS) are coated in the nanopores of anodic aluminum oxide (AAO) templates via solvent-vapor induced wetting. The morphologies of the block copolymer thin films coated on the nanopores are controlled by the annealing solvents. The PDMS domains of the coated PS-*b*-PDMS thin films can then be etched selectively using HF solutions, and the patterns of the block copolymers can be transferred to the nanopore walls.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Block copolymers containing two or more polymer blocks have attracted great attention in the past decades because of their ability to self-assemble into well-ordered nanostructures [1,2]. These nanostructures show great promise for many applications, such as drug delivery, batteries, and solar cells [3–5]. A major research direction using block copolymers is to achieve perpendicular morphologies of block copolymers normal to the substrate surfaces [6,7]. One of the polymer blocks can then be etched or removed selectively because of their differences in UV resistance, plasma resistance, or solubility in different solvents [8]. As a result, block copolymer thin films can be used as nanomasks and the patterns of the block copolymers can be transferred to the underlying substrates [9].

Although the concept of using block copolymer thin films as nanomasks have been widely studied, it is mainly used for two-dimensional purposes. For future applications to construct lighter and smaller electronic devices, one strategy is to make the sizes of the nanopatterns smaller. But this research direction has become more difficult to achieve, especially when the pattern sizes are close to sub-10 nm [10]. Another feasible strategy is to go from two-dimensional to three-dimensional. Ideally, much more data can be stored using three-dimensional nanostructures instead of

two-dimensional nanostructures. Therefore, it is highly desirable to develop new methods for the generation of three-dimensional nanostructures. The three-dimensional nanostructures, in which more units can be stored at the same volume, can be used for data storage applications, such as hard disks [11,12].

Here, we present a novel approach to fabricate nanostructures using block copolymer thin films as three-dimensional nanomasks. Instead of coating block copolymer thin films on flat substrates, the block polymers are coated on the walls of cylindrical nanopores [13]. Polystyrene-*block*-poly(dimethylsiloxane) (PS-*b*-PDMS) with a high Flory–Huggins parameters ( $\chi = 0.27$ ) is used in the work [14]. There is also a high etching resistance difference between the PS and PDMS blocks, which enable PS-*b*-PDMS as an ideal material as masks for etching and forming nanostructures on underlying substrates [15].

PS-*b*-PDMS polymers are first introduced into the nanopores of anodic aluminum oxide (AAO) templates using a solvent-annealing-induced nanowetting in templates (SAINT) method [16,17]. In the past, different kinds of template wetting methods have been studied to introduce polymers into the nanopores of porous templates, including the melt method, the solution method, and the solvent-annealing method [18]. In the melt method, polymer films or powders are heated above the glass transition temperatures ( $T_g$ ) or the melting temperatures ( $T_m$ ) of the polymers [19,20]. Polymer nanotubes or nanorods can be produced, depending on the wetting conditions and the pore sizes of the AAO templates [21]. In the solution method, polymers are first dissolved in a suitable solvent and the polymer solution wets

\* Corresponding author. Tel.: +886 3 5731631.

E-mail address: [jtchen@mail.nctu.edu.tw](mailto:jtchen@mail.nctu.edu.tw) (J.-T. Chen).

the nanopores via capillary force [22]. Polymer nanotubes are usually obtained using the solution method [23,24]. It has also been studied that polymer nanorods, nanospheres, and undulated structures can also be obtained using the solution method by changing the experimental parameters such as the molecular weight or the type of the solvents [25,26]. A recently developed template wetting method is the solvent-annealing method, also called as the solvent-annealing-induced nanowetting in template (SAINT) method [16,27]. In the SAINT method, polymer films are brought into contact with porous templates and the samples are annealed in sealed chambers containing saturated solvent vapors. For homopolymers, it has been studied that polymer nanotubes or nanorods can be prepared by the SAINT method, depending on whether the samples are annealed at complete wetting or partial wetting regimes [16]. In the complete wetting regime, the spread coefficient of the swollen polymer chains is larger than zero ( $S > 0$ ) and polymer nanotubes can be obtained. In the partial wetting regime, the spread coefficient of the swollen polymer chains is smaller than zero ( $S < 0$ ) and polymer nanorods can be obtained [16,21].

Here, we apply the SAINT method to control the morphologies of the block copolymer thin films coated on the nanopores using different annealing solvents. The PDMS domains of the coated PS-*b*-PDMS thin films can then be etched selectively using HF solutions, and the patterns of the block copolymers can be transferred to the nanopore walls. The etched AAO templates can be refilled by other materials such as PMMA homopolymer, and nanostructures with surface patterns transferred from the block copolymers can be obtained. The concept developed in this work can be applied to other nanofabrication and nanolithography fields. The regular ordering of the nanopatterns can be extended to not only the XY directions along the substrates, but also the Z direction perpendicular to the substrates.

## 2. Experimental

### 2.1. Materials

PS-*b*-PDMS was used as received from Polymer Source Inc. with a polydispersity index (PDI) of 1.15 and a molecular weight of (31-*b*-14.5) kg/mol. PMMA homopolymers were purchased from Sigma-Aldrich with a PDI of 2.11 and a weight-average molecular weight of 75 kg/mol. Deionized water was obtained from Milli-Q system. Ethanol, acetone and isopropyl alcohol were bought from Echo Chemical. Toluene and hexane were purchased from TEDIA. Hydrogen fluoride (HF) was obtained from Union Chemicals. Ammonium hydroxide (NH<sub>4</sub>OH) was obtained from Merck. Four-inch Si (1 0 0) wafers were purchased from Guv Team International Co., Ltd. AAO templates (thickness ~60 μm, pore diameter ~150–400 nm) were obtained from Whatman. Polycarbonate filters (VCTP, pore size ~0.1 μm) were purchased from Millipore.

### 2.2. Fabrication of PS-*b*-PDMS nanostructures in nanopores

For coating PS-*b*-PDMS thin films on the nanopore walls, a 1 wt% PS-*b*-PDMS solution in toluene was first prepared. The polymer solution (50 μL) was then dropped onto a silicon wafer. After solvent evaporation, the polymer film on the silicon wafer was dried further using a vacuum pump. Subsequently, an AAO template was placed on top of the PS-*b*-PDMS film. The sample was later moved into a glass chamber, where an open bottle containing the annealing solvent was present. A parafilm was used to seal the chamber to prevent the leakage of the solvent vapors. The solvent annealing process was carried out in different solvent vapors for 24 h. During

the annealing process, the temperature was controlled at 30 °C to maintain the vapor pressures of the solvents.

After the solvent annealing process, the sample was taken out from the annealing chamber and dried using a vacuum pump. The AAO template was dissolved selectively by immersing the sample in a 5 wt% NH<sub>4</sub>OH solution for 6 h. The sample was then filtered using a polycarbonate membrane and washed with deionized water for several times.

### 2.3. Fabrication of etched AAO templates and PMMA nanostructures

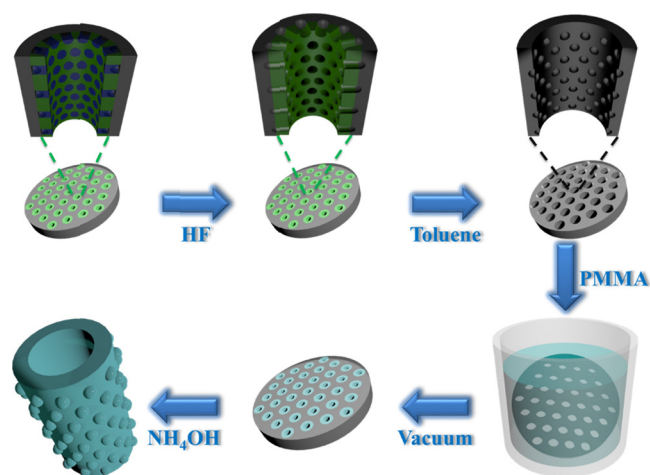
After the nanopore walls were covered by PS-*b*-PDMS thin films, the sample was dipped in a HF solution (diluted by water in the ratio of 3 to 1) with the dipping time of ~15–25 s. The sample was then washed with water and dried. For making PMMA nanostructures, an etched AAO template was dipped in a 5 wt% PMMA ( $M_w = 75$  kg/mol) solution in toluene. After the template was taken out from the PMMA solution and dried using a vacuum pump, a NH<sub>4</sub>OH solution was used to dissolve the template selectively. Finally, the sample was filtered using a polycarbonate membrane and washed with deionized water for several times.

### 2.4. Structure analysis and characterization

The polymer nanostructures were investigated by a scanning electron microscope (SEM, JEOL JSM-7401) at an acceleration voltage of 5 kV. Before the SEM examination, the samples were dried using a vacuum pump and coated with 4 nm of platinum. A transmission electron microscope (TEM, JEOL JEM-2100) with an acceleration voltage of 200 kV was also employed to investigate the polymer nanostructures. Before the TEM examination, the samples were deposited on copper grids coated with carbon or Formvar.

## 3. Results and discussion

Scheme 1 shows the graphical illustration of the experimental process to prepare the three-dimensional block copolymer nanomasks. At first, PS-*b*-PDMS thin film are coated inside the nanopores of AAO templates using the SAINT method [16]. Briefly,



**Scheme 1.** Schematic illustration of the fabrication process of etched AAO templates and PMMA nanotubes. PS-*b*-PDMS thin films are first coated inside the nanopores of AAO templates. The PDMS domains can be etched selectively using a HF solution, leaving nanopatterns on the walls of the nanopores. After the block copolymers are removed completely by toluene, the patterned nanopores of the AAO templates are refilled with a PMMA solution. Finally, the PMMA nanotubes with surface nanopatterns are obtained after the AAO templates are dissolved selectively using a NH<sub>4</sub>OH solution.

Download English Version:

<https://daneshyari.com/en/article/1586200>

Download Persian Version:

<https://daneshyari.com/article/1586200>

[Daneshyari.com](https://daneshyari.com)