Achieving Ordered Nanoholes and Other Non-bulk Morphologies by Directed Self-Assembly of a Block Copolymer

A. Tavakkoli K. G.[1,2], S. M. Nicaise[1], A. F. Hannon[3], K. W. Gotrik[3], C. A. Ross[3], K. K. Berggren[1]

[1]*Department of Electrical Engineering and Computer Science, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA02139, USA*

[2]*NUS Graduate School for Integrative Sciences & Engineering (NGS), Singapore*

[3]*Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA02139, USA*

amirtkg@mit.edu

Physical and chemical templates can be used to guide block copolymer (BCP) self-assembly to fabricate nanoscale patterns. One of the limitations of these methods is that only a single morphology of the BCP is typically achieved by using one patterning step while in most of the applications we need to have multiple morphologies on a single substrate. In this study, we showed that by using an array of majority-block functionalized posts, we generated multiple morphologies on a single substrate; one such example is a morphology consisting of nanoholes in an in-plane lamella (sheet), instead of the cylindrical diBCP morphology expected in bulk. We used three-dimensional self-consistent field theory simulations to predict the formation of different morphologies and investigated the effect of post period vs. BCP morphology.

Figure 1-a shows a schematic of the major steps of the process. In the first step, an array of HSQ-resist posts was fabricated by electron beam lithography (EBL), and then the samples were chemically functionalized with a hydroxyl terminated polystyrene brush (1 kg mol^{-1}). Next, polystyrene-b-polydimethylsiloxane (PS-PDMS) diBCP (45 kg mol^{-1}, 32%vol PDMS) was spin coated on substrates and solvent annealed using a mixture of toluene and heptane (5:1). We used CF_4 reactive ion etch (RIE) to remove the top PDMS layer followed by oxygen RIE to remove the PS matrix and leave the resultant pattern of oxidized PDMS on the substrate.

Figure 1-b shows an example of an ordered array of nanoholes generated by this method. Two different morphologies, cylinders in the untemplated region and holes in the templated region appeared on a single substrate. The pitch of the holes is 0.58 times the post pitch and each post produced three holes. Figure 2 shows graphs of the hole size vs. the post diameter and pitch. As can be seen in these two graphs, we achieved ordered holes within a wide range of post diameter and pitch. The holes between the posts ("generated holes") had a constant size whereas the holes around the post ("post holes") increased in size with an increase in the pitch and size of the posts. In addition to forming nanoholes from a cylindrical diBCP, by changing the post periodicity and post arrangement, we fabricated and controlled different morphologies such as undulating cylinders, spheres, ellipsoids, periodic structures, bicontinuous cylinders, and perforated bicontinuous cylinders on the same substrate.

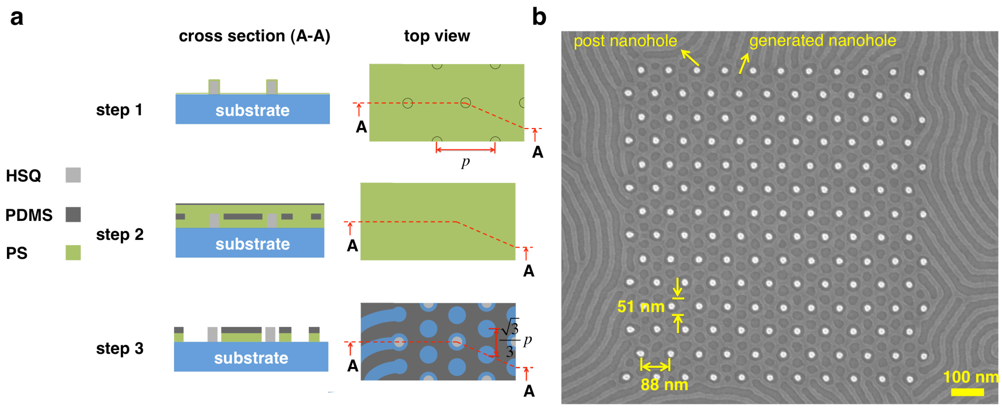

Figure 1: (a) The diagram of the major steps of the process, (step 1) fabrication of an array of posts by EBL of HSQ resist and functionalization using a PS brush, (step 2) spin coating and annealing of the PS-PDMS diBCP, (step 3) using CF_4 to remove the PDMS top layer and oxygen RIE to remove the PS matrix. Inside the template the morphology of the BCP is nanohole and outside the template is cylinder. In the diagram "p" refers to the pitch size. (b) SEM of ordered nanoholes. Light grey and white colors represent PDMS and HSQ, respectively.

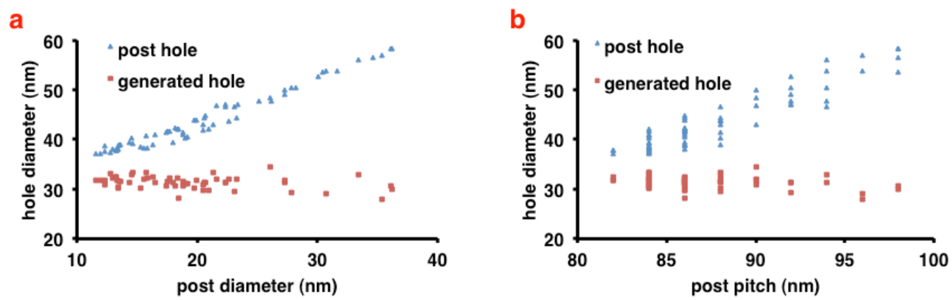

Figure 2: Graphs of changing the post-hole and generated-hole size by changing the post diameter and pitch. The generated hole diameter does not change, whereas the post hole diameter linearly increases with post diameter and post pitch.

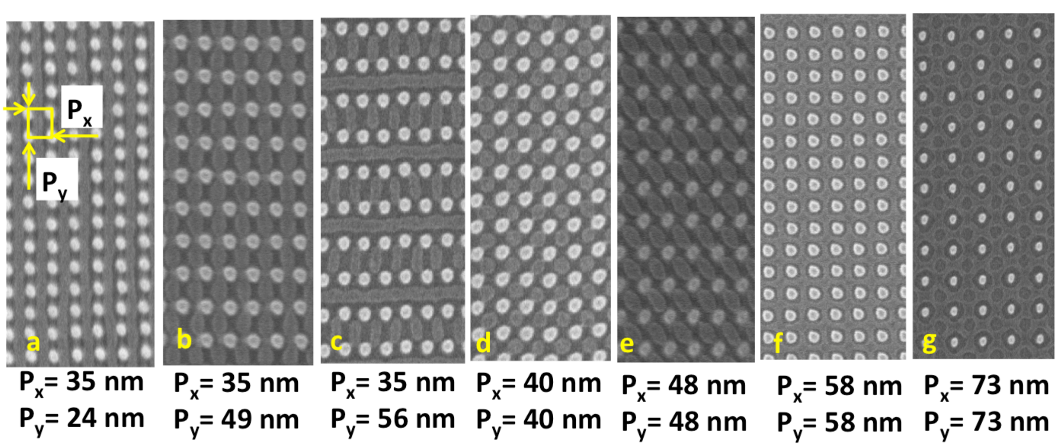

Figure 3: SEM of different morphologies of PDMS microdomains obtained by changing the periodicity of the posts. Light grey and white colors represent PDMS and HSQ, respectively.