Microelectronic Engineering 110 (2013) 350–353

Contents lists available at SciVerse ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Assembling polystyrenes spheres arrays in specified regions for required nanophotonic structures

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ARTICLE INFO

Article history:
Available online 26 February 2013

Keywords:
Nanophotonics
Nanstructures fabrication
Localized PSs assembly
Hydrophilic treatment

ABSTRACT

We present an effective method to assemble the PSs in specified regions by hydrophiling the substrate in designed regions for the nanophotonics with nanostructures in well-definite regions. A hydrophilic positioning template which carries designed metal structures is prepared by lithography according to the specified requirement. Following that, the structured metal surface is treated to be hydrophobic by a 184 polydimethylsiloxane (PDMS) membrane. After self-assembly and metal lift-off process, the PSs can be assembled only in the well-defined pattern regions. The corresponding experiments were performed and PSs were assembled in the different shapes regions.

1. Introduction

Combining with reactive ion etching (RIE) and lithography, polystyrenes spheres (PSs) self-assembly can fabricate kinds of nanostructures such as triangle, rhombus, hole and cone etc. [1–5]. Those nanostructures can realize some functional devices such as biosensors chip [6], color filter [7,8] and photonic crystal [9]. It has the advantages of high efficiency, simplicity, economy and ease for large area fabrication etc. However, the PSs are usually assembled into a uniform array in a large area [10–13]. It is difficult to assemble the PSs in the designed regions. This restricts the application of self-assembly method in functional devices with structures in well-defined regions, such as photosieve [14] and the multichannel biosensor chip [15] etc.

In 2001, Yadong Yin presented a template-assisted self-assembly method which can assemble the PSs into holes by capillary force coupled with the confining effect of the template [16]. Fung Ling Yap replaced the template by a pattered hydrophobic parylene layer and assembled the PSs into holes in the same mechanism [17]. In this method, the distance between the glass and the template is very crucial to the capillary forces. But it is very short and difficult to be controlled. Additionally, the concentration of the PSs injected and the movement rate are very crucial to the formation of the close packed PSs in monolayer. But they are also difficult to be controlled precisely. This limits the popularization of the template-assisted self-assembly method. In 2009, Shaoli Zhu reported a multichannel biosensor which was fabricated based on the PSs self-assembly. However, it has not illuminated how to assemble the PSs only in the designed regions [18]. In other words, it has not told us how to ensure there are no PSs outside the designed regions.

Usually, PSs self-assembly is realized using the affinity of the water-soluble PSs and the hydrophilic surface of the sample. The PSs can be arranged in ordered array on the hydrophilic surface. At the same conditions, it is difficult to be well arranged on the hydrophobic surface. Therefore, the hydrophilic treatment of the substrate is essential in the PSs self-assembly process. Generally, the hydrophilic treatment is realized by immersing the sample into special liquid [19,20] and the whole surface of the sample is treated to be hydrophilic. This results in the PSs being assembled on the whole surface but not only in the expected regions.

From the analysis on the PSs self-assembly technique, hydrophilic treatment the substrate surface only in the well-defined regions is the key problem to realize localized PSs assembly. So far, several approaches were reported to treat a sample surface in well-defined regions to be different from the complementary regions. Jeonggi Seo made pattered hydrophilic by modifying photoresist patters using plasma surface modification [21]. However, the contrast in sample surface wettability is low for the photoresist and the bare substrate both being modified. Chang-Soo Lee realizes pattered hydrophilic by photoresist sacrificial protecting the patterns regions when the hydrophobic film forms and followed by a lift-off process [22]. Although the surface wettability of protected regions is high, it is decreased during the followed photoresist dissolving process by acetone. In reference [23,24], to selective deposition of metal, self-assembled monolayers of $C_{18}H_{37}SiCl_3$ were patterned on a substrate. It is realized in the approach that a patterned/flat 184 polydimethylsiloxane (PDMS) film which carried monolayers of $C_{18}H_{37}SiCl_3$ was brought into contact with a flat/patterned substrate. The patterned monolayers can be realized in large area for the stickiness and flexibility properties of PDMS.

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http://dx.doi.org/10.1016/j.mee.2013.02.056

But it cannot be used to self-assemble PSs in patterns, because it is difficult to be well arranged PSs on the hydrophobic PDMS surface.

In this paper, a novelty method is presented to hydrophilic treatment the substrate surface only in the well-defined regions. A structured metal layer is used to protect the designed regions being free from hydrophobic treatment. A hydrophilic treating process makes the metal surface and bare substrate surface both hydrophilic. For the larger height of the metal structure than the bare substrate, the metal film surface can be treated to be hydrophobic independently using a PDMS membrane. A template with hydrophilic only in the designed regions can be obtained and can realize most of PSs being assembled in the specified regions. Additionally, a metal lift-off process can ensure wipe out the PSs on the metal surface thoroughly. The substrate treating process and assembling PSs in the well-defined regions method are illuminated in detail. The PSs are assembled into all kinds of shaped regions.

2. Method and experiments

Fig. 1 shows the schematic illustration of PSs self-assembly in well-defined regions. It consists of four steps such as preparing the positioning template, treating the template to be hydrophilic only in the designed regions, the PSs assembling and metal lift-off. Using this method, we assembled PSs in all kinds of shaped regions in experiments. We will describe every fabrication step in the following respectively.

2.1. The preparation of the positioning template

Positioning template is the sample that the regions of PSs want to be assembled in is well-defined and marked by metallic patterns. Regions with arbitrary shapes and dimensions can be designed according to the specific requirement. The positioning template preparation process is illustrated as Fig. 1(a)–(e).

A cleaned glass substrate was prepared and a 100 nm chromium film was deposited on it. Following that, an i-line photoresist (AZ3100 PR) was spun onto the chromium film with thickness of 1.5 μm and baked with temperature of 95 °C for 20 min to mark the designed regions. A mask with the designed regions in patterns was pressed onto the PR film and illuminated by light with emission peaks at 365 illuminated from the top. The designed regions in PR patterns were obtained after a 30 s development process. For bearing the strong acid in the following hydrophilic treatment, the sample was put into a chromium etching liquid for a few seconds and followed by the photoresist dissolving process in acetone. The patterns were transferred into the chromium film. The positioning template was obtained. The patterned regions can be dealt with independently in the following substrate treatment process and the outside pattern regions were isolated by the chromium.

2.2. Treating the template to be hydrophilic only in the designed regions

Treating only the designed regions to be hydrophilic is the most critical step in the whole PSs assembly process. Firstly, the positioning template was cleaned in the mixed liquor of H_2O_2 and H_2SO_4 with volume ratio 1:3 at 90 °C for 30 min. After that, it was hydrophilized by ultrasonic vibration in the mixed liquor of H_2O, NH_4OH, and 30% H_2O_2 with volume ratio 5:1:1. The positioning template surface was treated to be hydrophilic. For hydrophilic property only existing in the patterned regions, the chromium film surface need to be further treated to be hydrophobic independently.

A membrane of 184 PDMS was prepared by mixing the prepolymer and the curing agent with ratio of 10:1 and followed by a baking process with the temperature of 70 °C for 1 h. The PDMS membrane has the properties of good hydrophobicity, stickiness and flexibility. It was pressed onto the surface of the positioning template firmly and then peeled off. The chromium film surface was treated to be hydrophobic for the transfer of the hydrophobic molecules. On the other hand, the concave patterned regions were not contacted by the membrane for the spatial height difference and kept the hydrophilic property. Then the positioning template with hydrophilic property only in the well-defined regions was obtained. It can be used to capture the PSs only in the designed regions.

2.3. PSs self-assembly in the designed regions

A chemical solution of polystyrene spheres (400 nm diameter, 10%) was spin-coated onto the positioning template surface at

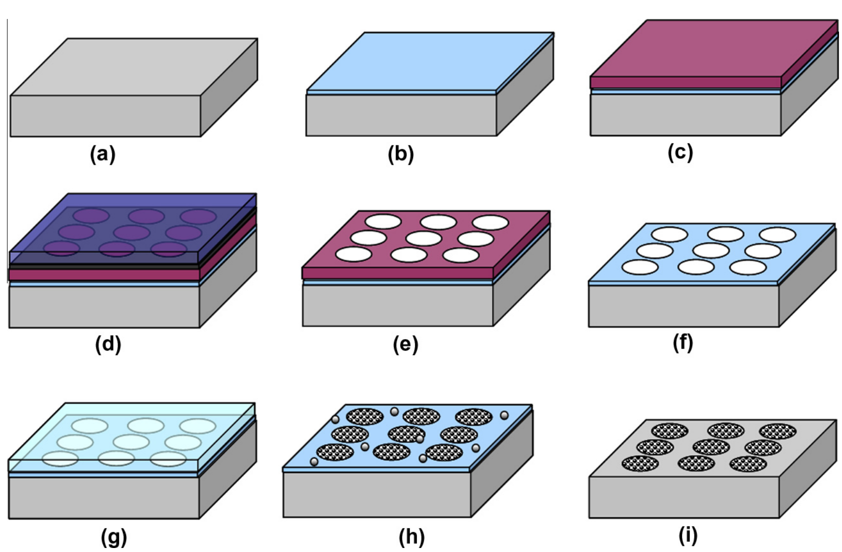

Fig. 1. The process of PSs self-assembly in the well definite regions. (a) Cleaning substrate. (b) Chromiumdeposition. (c) PR is spun on the chromium film. (d) The designed regions is marked using photoresist patterns by photolithography. (e) The patterns are transfered into the chromium film. (f) Photoresist is washed off and the sample is treated to be hydrophilic. (g) The sample is treated to be hydrophobic at outside the patterned regions by 184 PDMS membrane. (h) Most of the PSs are assembled in the patterned regions. (i) Metal and dispersed PSs on the metal are wiped out by a lift-off process.