Nanopillar and nanohole fabrication via mixed lithography

Seung Hee Baek$^{1,2}$, Sunwooong Lee$^{1,2}$, Ju-Hyun Bae$^{1,2}$, Chang-Won Hong$^3$, Mae-Ja Park$^4$, Hong Sik Park$^{3,5}$* and Sung-Wook Nam$^{1,2}$

$^1$Department of Molecular Medicine, School of Medicine, Kyungpook National University, Daegu 41405, Republic of Korea
$^2$Exosome Convergence Research Center (ECRC), Kyungpook National University, Daegu 41944, Republic of Korea
$^3$Department of Physiology, School of Medicine, Kyungpook National University, Daegu 41944, Republic of Korea
$^4$Department of Anatomy, School of Medicine, Kyungpook National University, Daegu 41944, Republic of Korea
$^5$School of Electronics Engineering, Kyungpook National University, Daegu 41566, Republic of Korea

E-mail: nams@knu.ac.kr

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Abstract

We report a fabrication method for the production of nanopillar (NP) or nanohole (NH) arrays together with a micrometer-sized structure within a single layer. On a 200 mm silicon wafer, we produced 200–400 nm NP or NH arrays using electron beam lithography (EBL). The EBL patterns on a positive-tone EB resist—either a poly(methyl acrylate) or chemically semi-amplified resist—were transferred to a hard mask oxide (HMO) layer using reactive-ion etching (RIE), as the first etching step. We used the HMO as an intermediate layer to connect the EB patterns to photolithography patterns. On the EB-patterned HMO layer, large-scale photolithography patterns were produced on a photoresist (PR), and transferred to the HMO layer using the second RIE step. After removing the PR, the mixed EB and photolithography patterns in the HMO layer were transferred to the target layer in the third RIE step. Our method offers an efficient way to combine nanometer-sized EBL patterns with high-throughput photolithography patterns in a single layer.

Introduction

Mixed lithography allows for the fabrication of extremely small features alongside large-scale features within the same layer [1–4]. In nanofluidic devices, it is essential to connect nanometer-scale functional channels with micrometer-scale fluid-guiding structures [5–12], and mixed lithography offers an effective way to accomplish this. Recently, the use of nanostructure-mediated fluidic devices has been demonstrated in a wide range of biomedical applications, including particle sorting, nucleotide sequencing, and single-cell culturing [13–15]. In these applications, mixed lithography can be employed in the fabrication of a variety of biochips, including nanopillar (NP) devices used to separate or sort biomarker molecules, which require the arrangement of nanometer-scale sorting channels together with micrometer-scale fluid-guiding channels [4, 16–19].

Electron beam lithography (EBL) is a proven method for the highly accurate fabrication of sub-100 nm structures [1–4, 20–26]. However, due to its high costs and low throughput, the use of EBL has been limited for producing nano-scale patterns in the extremely localized area. To overcome this issue, in the present study, we combine EBL with conventional semiconductor processes, including photolithography, reactive ion etching (RIE), and thin-film deposition. This approach enables the fabrication of multi-scale features (nanometer to millimeter) within the same layer. The primary goal of this study is to propose an efficient strategy for the production of both NP and nanohole (NH) array channel structures, which play a pivotal role in the separating and/or sorting of many biomolecular species, including cells, proteins, vesicles, and nucleotides.

In the present study, we developed a mixed lithography process based on a positive-tone electron beam (EB) resist. A chemically semi-amplified resist (CSR) and a ZEP resist, which are conventional positive-tone EB resists, have a sensitivity of $\sim 300 \, \mu C \, cm^{-2}$ for high-contrast development at an accelerating voltage of 100 keV, which is much lower than that of negative-tone resists such as hydrogen silsesquioxane (HSQ, $\sim 1000 \, \mu C \, cm^{-2}$) or calixarene [20–25]. Positive-tone EB resists are also more stable in terms of chemical aging and process...
optimization because breaking polymerized bonds has a simpler mechanism than cross-linking monomers via EB or UV exposure \[24\]. For these reasons, a systematic approach to positive-tone based mixed lithography would be useful.

Recently, negative-tone EB resists such as HSQ have been used for mixed lithography \[25\]. To connect HSQ nanopatterns with photolithography patterns, researchers have used an anti-reflective coating (ARC) as an intermediate layer to project both the EBL and photolithography patterns into the target layer. Similarly, when using a positive-tone EB resist for mixed lithography, the resist film can be exposed to electrons first then to photons. However, the simultaneous optimization of both electron and photon exposure is very difficult. Therefore, we employ a simpler technique in which the pattern is transferred to a hard mask oxide (HMO) layer in two etching steps. First, we etch the small EB pattern, then the EB resist is removed. Next, the larger pattern is printed using photolithography and etched into the same HMO layer. The combined patterns in the HMO layer are finally transferred to the Si layer in the third etching step.

**Experimental and results**

We present methods for the fabrication of both NP and NH array structures in figures 1(a) and (b), respectively. The use of a positive-tone EB resist means that the EB-exposed region is removed during the development process. Therefore, the layout design in figure 1(a) produces NP structures, while that in figure 1(b) produces NH structures. It should be noted that the NP and NH arrays in figures 1(a) and (b) are slightly tilted when compared to the horizontal line, which corresponds to the direction of flow for the fluid. The tilted NP and NH arrays are used as a deterministic lateral displacement (DLD) structure, which has the potential to be used to separate or sort particles \[4, 16–19\].

To connect the EBL patterns to the large-scale photolithography features, we coordinate multiple RIE steps for the NP and NH arrays, as depicted in the left and the right panels, respectively, of figure 2. To fabricate the NP and NH array channels, we used an HMO layer, as shown in the first step in figures 2(a) and (b). Thermally grown 100 nm thick silicon oxide was used as the HMO layer, and two positive-tone EB resists, the CSAR and poly(methyl methacrylate) (PMMA) resist, were used in the mixed lithography process.

Figure 1. Layout designs for (a) nanopillar (NP) and (b) nanohole (NH) arrays for a positive-tone electron beam (EB) resist. The colored regions (green or blue) represent the EB-exposed area.
To create the NP array structure, the green-colored region depicted in the upper left box in figure 2 is exposed by an EBL system (JEOL, JBX-9300FS, 100 keV, National NanoFab Center in Daejeon, Korea) with a positive-tone EB resist, in this case, a CSAR. The EB-exposed regions are removed with the development process, as shown in figure 2(c), and the NP array pattern (colored purple) in the EB resist is then transferred to the HMO using a reactive ion etching (RIE) process (Lam Research, EXELAN-HPT), as shown in figure 2(d). To connect the EBL features with the large-scale photolithographic features, we printed a photoresist (PR) pattern in the HMO layer so that the NP array channel is located in the center of the large-scale micrometer structure.

In the mixed lithography process, the overlapped region is inevitably exposed to RIE plasma twice. To circumvent this issue, we used RIE conditions that were highly selective for silicon oxide ($C_4F_8/Ar/O_2$ gas) rather than the Si layer. This allows for the efficient transfer of the patterns and minimizes the loss of the bottom Si layer. After the EBL and photolithography patterns are combined in the HMO layer, the third RIE step is highly selective for Si ($SF_6/H_2/Ar$ gas) rather than silicon oxide to transfer the combined patterns into the Si layer.

Figure 2. Schematics for the proposed positive-tone mixed lithography process. (a), (b) On a bare silicon (Si) wafer, thermal oxide (100 nm) is deposited. The oxide layer serves as a hard mask oxide (HMO) layer. Nanopillar (NP) array fabrication is described in (c)–(h). (c) A positive-tone electron beam (EB) resist (CSAR) is spin-coated, and the green-colored area in the upper left box is exposed to the EB. (d) The EB resist pattern is transferred to the HMO layer using reactive ion etching (RIE). (e) In the photolithography process, a photoresist (PR) pattern is printed that is aligned with the EBL pattern on the HMO. Note that both ends of the EBL pattern should overlap with the PR pattern to connect the EBL and photolithography patterns. (f) The PR pattern is transferred to the HMO using RIE. (g) The PR is removed using oxygen plasma. (h) The combined EBL and photolithography patterns on the HMO are transferred to the Si layer underneath using RIE. Nanohole (NH) array fabrication is described in (i) to (n). (i) After spin-coating the positive-tone polymethyl methacrylate (PMMA) resist onto the wafer, the blue-colored area in the upper right box is exposed to the EB. (j)–(n) The following process sequence is the same as for (d)–(h) except for the EBL and photolithography layer alignment, in which the EBL pattern on the HMO is protected by the PR pattern, as shown in (k).
To produce the NH array, we introduce a similar process to that for the NP array but with differences in terms of the tone of the layout design for the EBL pattern and the connecting mechanism between the EBL and photolithography patterns, as shown in figures 2(i) to (n). In figure 2(i), the NH array pattern is generated according to the design in the upper right box, which has the opposite tone to that of the NP array pattern, with a positive-tone PMMA resist exposed to an EBL system (Raith EBPG, 100 keV, Yale Institute for Nanoscience and Quantum Engineering in New Haven, Connecticut, USA). The NH array pattern in the EBL resist is transferred to the HMO using RIE (figure 2(j)), after which a photolithography pattern is generated in the PR (figure 2(k)). Note that the EBL-produced NH array in the HMO is protected by the PR, with the NH array pattern outside of the PR erased during the second RIE step (figure 2(l)). This PR protection strategy differentiates the NH array fabrication process from that of the NP array. After the PR is removed using oxygen plasma (figure 2(m)), a combined pattern is formed in the HMO layer. This combined pattern in the HMO is then transferred to the bottom Si wafer (figure 2(n)).

It is worth noting that the etching process for both the NP and NH arrays is the same except for the layout connecting mechanism between the EB and photolithography patterns. Therefore, our proposed method would be useful when a particular feature and a corresponding inverted feature, such as NP and NH array structures, are required on the same wafer via mixed lithography. In addition, the NP and NH arrays can be used as nanofluidic structures. When sealed with a capping layer, such as borosilicate glass, the NP array can serve as a fluidic channel [19], while the NH array can serve as a soft lithography mold upon which a polydimethylsiloxane chamber can be fabricated [27, 28].

Figure 3 presents detailed results of the proposed mixed lithography process for the NP array. Figure 3(a) shows a 200 mm wafer on which NP arrays have been fabricated using positive-tone mixed lithography. Twelve biochips (40 mm by 40 mm), each of which has an NP array pattern in the middle of the chip, have been arranged on the wafer. Figure 3(b) presents the layout design, with the EBL pattern in green and the photolithography pattern in orange. The magnified image in figure 3(c) shows that the ends of the EBL pattern (green) overlap with the photolithography pattern (orange) by ~5 micrometers, which is approximately equivalent to the manual alignment margin.

Figures 3(d) and (e) present optical microscopy (OM) images after the NP array in the CSAR EB resist has been transferred to the HMO layer. Following this, figures 3(f) and (g) present the aligned PR pattern printed using photolithography. Most of the EBL pattern in the HMO layer is covered with the unexposed PR, but the ends of the EBL pattern overlap with the open area of the PR pattern, as indicated by the red arrow in figure 3(g). This overlap between the EBL pattern in the HMO and the PR pattern is essential for the mixed lithography of NP array channels. During the second RIE step, the PR pattern is transferred to the HMO layer. In the transfer of the pattern, the overlapping region is re-exposed to RIE plasma, which can lead to a problem that the overlapping region is etched twice. However, the highly selective RIE conditions for the silicon oxide layer minimizes the removal of the Si layer underneath. This finely tuned etch-stop design is critical to the success of positive-tone mixed lithography. When the PR pattern is transferred to the HMO, the EBL and photolithography patterns are combined. This combined pattern is finally transferred to the Si layer in the third RIE step, as shown in figures 3(h) and (i). The OM image in figure 3(i) verifies the combination of the EBL and photolithography patterns, with traces of the overlapping region removed.

The scanning electron microscopy (SEM) image in figure 3(j) shows the combined zone and confirms the presence of trench-type structures. The atomic force microscopy (AFM) image in figure 3(k) shows that the depth of the trench is 1.2 μm, which is presented in profile in figure 3(l). Figure 3(m) presents an SEM image of the red rectangular area in figure 3(h). Figure 3(n) presents a 30°-tilted-SEM image of the red rectangular area in figure 3(m), showing the interfacial region between the large and small pillar arrays. Given the SEM tilting angle, the pillar height is estimated to be 1.1 μm.

Figure 4(a) presents a piece of a 150 mm wafer on which mixed lithography has been used to fabricate an NH array. On one wafer, there are 12 NH array chips, each of which has dimensions of 40 mm by 20 mm. Figure 4(b) presents a camera image of the orange rectangle in figure 4(a). In figure 4(b), the chip is designed to have one inlet and five outlet structures, meaning it is capable of sorting an analyte into five groups. It is worth noting that the NH array chip in figure 4(b) has a mesa-type structure that extends out from the wafer surface.

Figure 4(c) presents the layout design for the combined EBL and photolithography region. The blue-colored dots represent the NH array structure to be produced using EBL, while the yellow-colored block represents the lane structure to be produced using photolithography. In this layout design, the dot array extends outside of the lane structure within the approximate alignment margin (~5 micrometers). This part of the array outside of the lane structure is eliminated during the second RIE step.

Figures 4(d)–(f) present OM images of the orange rectangle shown in figure 4(b). Figure 4(d) shows the slit-shaped pattern in which the NH array is generated in the HMO layer after the first RIE step. The PR pattern is printed on top of the NH array using photolithography (figure 4(e)). After the second RIE step, the PR pattern is transferred to the HMO layer, and the remaining PR is stripped away by oxygen plasma. The third RIE step
Figure 3. Mixed lithography process for the fabrication of nanopillar (NP) array channels. (a) Digital image of a 200 mm wafer, on which electron beam lithography (EBL) patterns have been combined with photolithography patterns for NP array fabrication. (b) Layout design for the combined EBL and photolithography pattern region. The green-colored region is exposed to electron beam (EB), while the orange-colored pattern is printed using photolithography. (c) Magnified version of the layout design displayed in (b) showing that the end of the EBL pattern overlaps with the photolithography pattern. (d) Optical microscopy (OM) image of the EBL pattern in the hard mask oxide (HMO) layer after the first RIE step. (e) Magnified OM image of the red rectangular region in (d). (f) OM image of the EBL pattern in the HMO layer aligned with the PR pattern. (g) A magnified OM image showing the connecting region between the EBL and PR patterns. The red arrow indicates the overlapping region. (h) OM image of the area where the EBL and photolithography patterns are combined after the third RIE step. (i) A magnified OM image of the combined patterns. (j) Scanning electron microscopy (SEM) image of the mixed zone between the EBL and photolithography patterns. (k) Atomic force microscopy (AFM) image of the red rectangular area in (j). (l) The surface profile of the photolithography pattern reveals a depth of 1.2 μm. (m) SEM image of the NP array shown in the red rectangle in (h). (n) Tilted SEM image showing that the NP array consists of pillars with diameters of 450 nm and 220 nm.
performed to transfer the combined EBL and photolithography pattern in the HMO layer to the Si layer. Figure 4(f) shows that the EBL and photolithography patterns are combined in the Si layer, with the NH array located inside the micrometer geometry.

The SEM images in figures 4(g) and (h) show the NH array pattern before and after being combined with the photolithography pattern, respectively. Figure 4(g) shows the NH pattern in the HMO layer defined by EBL. Most of the NH array is protected by the PR, while the NH pattern outside of the upper and lower boundaries of the remaining PR is erased during the second and the third RIE steps (figure 4(h)). The orange rectangular region in figure 4(h) is magnified as a tilted SEM image in figure 4(i). The NH pillars have diameters of 450 nm and 220 nm; these are also visualized in the AFM image in figure 4(j). Figure 4(k) shows the surface profiles along the green and red lines in figure 4(j). The NH array has a depth of 220 nm.
Conclusions

We presented a mixed lithography method to produce both NP and NH array structures that are suitable for nanofluidic applications. We generated an NP array using EBL in which both ends of the NP channels were connected to a large-scale photolithography pattern by overlapping the two within the manual alignment margin. Even though the overlapping region was exposed to RIE plasma at least twice, the finely tuned etching selectivity of the RIE process and the introduction of an HMO layer minimized the loss of Si underneath. We also used EBL to fabricate an NH array, which was subsequently protected by a PR during the multiple RIE steps. We believe that our proposed method offers a systematic approach to the fabrication of EBL-based patterns combined with photolithography patterns within a single layer.

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ORCID iDs

Hong-Soon Nam © https://orcid.org/0000-0003-2582-2230
Sung-Wook Nam © https://orcid.org/0000-0002-2306-6032

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