Fabrication of nano-patterns of photoresist by ultraviolet lithography and oxygen plasma

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Nanofluidic devices with two-dimensional nanochannels have many applications in biology and chemistry, however, it is still a challenge to develop a low-cost and simple method for fabricating nano-masks that can be used to produce two-dimensional nanochannels. In this paper, a novel low-cost and simple method, based on UV lithography and oxygen plasma, was proposed to fabricate nano-mask. The influence of exposure time on the photoresist mesas was investigated in the ultraviolet lithography process. The parameters of RF power and treatment time on the width reduction of photoresist mesas were analyzed by the oxygen plasma. In our work, in order to increase the efficiency controllability of photoresist removal, a RF power of 90 W, a pressure of oxygen plasma 60 Pa, and the time division method were adopted to remove photoresist by oxygen plasma. Finally, nano-patterns of photoresist mesas with bottom width of 330 nm were successfully fabricated. The proposed method provides a low-cost way to produce high-throughput two-dimensional nanochannels.

Key words: nano-patterns, fabrication, ultraviolet lithography, oxygen plasma

1 Introduction

Nanofluidic devices have drawn significant attention in applications of biochemical analysis [1, 2], environment detection [3], and health care [4, 5]. This is because special features existed in nanochannels, such as the overlap of electrical double layer [6, 7], and ultra-high ratio of surface-to-volume [8, 9]. Nanochannels are critical components of nanofluidic devices. These special features are even more pronounced in two-dimensional (2D) nanochannels. 2D nanochannels have width and depth in nanoscale. Moreover, the size of the 2D nanochannel is similar to that of biological macromolecules, such as DNA and protein, which has the irreplaceable advantages to detection, control and separation of biological macromolecules at single molecule level [10, 11]. The different methods so far developed for fabricating 2D nanochannels can be classified as follows:

- Some methods that do not require nano-masks have been reported. Nano-masks are defined here as patterns with nanoscale in width, which can be used as a mask for etching to transfer the patterns. These methods combine several processing techniques of Micro-electromechanical Systems (MEMS) to realize the fabrication of nanochannels. These methods mainly include self-sealing by deposition technology [12, 13], sacrificial layer technology [14], polydimethylsiloxane (PDMS) surface treatment/deformation molding technology [15, 16], and cracking technology [17, 18]. These methods mainly rely on the traditional ultraviolet technology (UV) and have the advantage of low cost, but they are difficult to precisely control the size and cross section shape of the nanochannels.

- Other methods that require the nano-masks for creating nanochannels have also been reported. In this class of methods, the fabrication of nano-masks is particularly important. The nano-masks were fabricated first, and then the 2D nano-mold can be produced easily by wet etching technique, finally the 2D nanochannels can be obtained by replicating technique [19]. By using proton beam [20, 21], electron beam [22, 23] or focused ion beam [24, 25], the nano-mask patterns can be fabricated directly with nano-resolution. However, these direct-writing techniques require expensive equipments, and they are time-consuming for nano-masks production. By using the sidewall technique [26-28], nano-masks patterns can be fabricated by traditional UV exposure technique, and they are low-cost. However, usually the fabrication process of nano-masks by sidewall technique is complicated, and they are not suitable for mass production. Therefore, it is still a challenge to develop a low-cost and simple method for fabricating nano-masks.

In this article, a novel low-cost and simple method, based on UV lithography and oxygen plasma, is developed to fabricate nano-mask. During the UV lithography, the influence of exposure time on the photoresist mesas was investigated. During the photoresist removal by oxygen...
Fig. 1. Process flows of the nano-patterns of photoresist fabrication: (a) – layer of oxide film was grown on the substrate, (b) – AZ703 photoresist was spin-coated on the oxide film, (c) – UV exposure of photoresist, and (d) – photoresist treatment with oxygen plasma.

Fig. 2. Cross sections of the photoresist mesas with different exposure time after development: (a) – 40 s, (b) – 45 s.

Fig. 3. Cross-section of photoresist mesas treated by oxygen plasma at different RF powers for 4 min, with a constant oxygen pressure of 60 Pa: (a) – 20 W, (b) – 50 W, (c) – 70 W, and (d) – 90 W.
Table 1. Bottom widths of photoresist mesas after treated by oxygen plasma

| RF (W) | Bottom Width (µm) | Reduction (µm) |
|--------|------------------|----------------|
| 20     | 1.30             | 0.20           |
| 50     | 1.09             | 0.41           |
| 70     | 0.57             | 0.93           |
| 90     | 0.90             | 0.60           |

plasma, the influence of the parameters of RF power and treating time on the width reduction of photoresist mesas were also studied. Finally, the nano-patterns of photoresist mesas with bottom width of 330 nm were obtained.

3 Results and discussion

3.1 Analysis of exposure time

In the experiment, the silicon substrate with oxide film was baked in the drying oven at 120°C for 15 min to remove moisture thoroughly. To improve the adhesion between the oxide film and photoresist, a layer of hexamethyldisilazane (HMDS) was evaporated on the substrate in the drying tower for 10 min. Then, the substrate was baked at 150°C for 3 min immediately. Then a layer of AZ703 photoresist was spin-coated on the substrate. After baking on the hot plate at 85°C for 30 min, photoresist was exposed to the UV light in a mask aligner (MA6, Karl Suss, Germany) at a dose of 6.0 mWcm⁻² with a photomask. The transparent spacing between the patterns of the photomask is 1.5 µm.

When the times of UV exposure were set to 40 s and 45 s - consequently, the development time was 51 s, the cross-section of the photoresist mesas were shown in Fig. 2(a) and Fig. 2(b). It can be seen from Fig. 2(a) that the sidewalls of the photoresist mesas were not perpendicular to the surface of the substrate. This was because the exposure time was insufficient. The bottom corners of the photoresist mesas were not fully developed during the UV lithography. In Fig. 2(b), the sidewalls of the photoresist mesas were perpendicular to the surface of the substrate, and the bottom corners of the photoresist mesas were fully developed in the developing solution. However, when the exposure time was set as 50 s or 55 s, the photoresist mesas were all disappeared with the same development time as above. According to the analysis above, we can conclude that the optimized parameters of exposure and development time were 45 s and 51 s, respectively.

3.2 Analysis of parameters of oxygen plasma treatment

For obtaining patterns of photoresist with nanoscale width, the AZ703 photoresist mesas were treated by oxygen plasma (Emitech K1050X). To optimize the treatment parameter of RF power, the impact of RF powers on the width of photoresist mesas treated by oxygen plasma was investigated. All the results were evaluated by the SEM (Scanning Electron Microscopy) images, as shown in Fig. 3.

Before treatment with oxygen plasma, the widths of top side and bottom side of photoresist mesas were both equal to 1.5 µm. When the treated parameters of RF powers of the oxygen plasma were 20 W, 50 W, 70 W, and 90 W with a constant treatment time of 4 min, the widths of top sides of the photoresist mesas were 1.30 µm, 0.93 µm, and 1.12 µm, respectively, Fig. 3(a) -3(d). The corresponding reduced widths of top side were 0.2 µm, 0.41 µm, 0.57 µm, and 0.38 µm, respectively. When the same treatment parameters of the oxygen plasma as above were employed, the widths of bottom sides of the photoresist mesas were 1.30 µm, 1.09 µm, 0.57 µm, and 0.90 µm, respectively. The corresponding reduced widths of bottom side were 0.20 µm, 0.41 µm, 0.93 µm, and 0.60 µm, respectively, as shown in Tab. 1. In Tab. 1, when the RF power was 70 W, the bottom width of 0.57 µm of photoresist mesas was the smallest and the corresponding bottom width reduction was also the largest. When the RF power was 20 W, the bottom width of 1.30 µm of photoresist mesas was the largest and the corresponding bottom width reduction was also the smallest. Table 1 shows that as the power increased from 20 W to 90 W, the bottom width reduction decreased first and then increased. This is because if the RF power is too large, the collision frequency of plasma will increase, and the actual plasma effectively participated in etching will decrease.

When the AZ703 photoresist mesas was treated by oxygen plasma for 9 min with the RF power of 20 W and oxygen pressure of 60 Pa, the photoresist mesas with top width of 1.22 µm was obtained, Fig. 4(a). With the same treated parameters for another 2 minutes, the photoresist mesas with top width of 1.12 µm were obtained, Fig. 4(b). As the sample was continued to be treated for 2 minutes, the top width of the photoresist mesas was reduced to 1.04 µm. In conclusion, when the photoresist mesas were treated by oxygen plasma for a longer time of 13 minutes, the width of photoresist mesas was still in microscale. Thus, the RF power of 20 W was not appropriate due to its corresponding removal rate was too slow.
When RF power was set to 70 W, the bottom width of the photoresist mesa was 0.57 µm after treating by oxygen plasma with 60 Pa for 4 min. With the same parameters of RF power and pressure of oxygen plasma, it was found that the photoresist mesas completely disappeared when the treatment time was increased to 4 min 20 s. When RF power was set to 90 W, the bottom width of the photoresist mesas was 0.90 µm with the treated parameters of 60 Pa, and 4 min (Fig. 5 a). When the treatment time was 4 min 30 s, and other parameters were same as above, the photoresist mesas were all disappeared, as shown in Fig. 5(b). This was because as the
3.3 Fabrication of nano-patterns of photoresist

In our work, in order to increase the efficiency of photoresist removal, parameters of 90 W, 60 Pa were selected to remove photoresist. Meanwhile, to increase the controllability, the time division method was adopted in the following work to remove photoresist by oxygen plasma. For obtaining photoresist mesas with bottom width in nanoscale, the photoresist mesas were treated with oxygen plasma by four steps, named time division method, under a fixed RF power of 90 W, and a constant pressure of oxygen plasma 60 Pa. Step 1: the photoresist mesas were treated by oxygen plasma with 4 min, and the microscope image of the photoresist mesas after treatment was shown in Fig. 6(a). The top width of the photoresist mesas was 1.0 μm. Step 2: after step 1, the sample was treated for another 1 min, and the top width of the photoresist mesas was 950 nm, as shown in Fig. 6(b). Step 3: after step 2, the sample was treated for another 1 min, and the top width of the photoresist mesas was 760 nm, as shown in Fig. 6(c). In the last Step 4: the sample after step 3 was treated for another 1 min, finally, the top width was 640 nm, the corresponding of the bottom width of the photoresist mesas was 330 nm, as shown in Fig. 7.

4 Conclusions

This paper presents a novel low-cost and simple method for fabricating nano-patterns of photoresist, based on UV lithography and oxygen plasma. During the ultraviolet lithography process, the effect of exposure time on the cross-section shape of photoresist mesas after development was studied. The experimental results show that photoresist mesas with the sidewall perpendicular to the bottom surface were obtained, and the width of the photoresist mesas was 1.5 μm after fully developed in the development process. To improving the efficiency and controllability of photoresist removal, RF power of 90 W and the time division method was adopted for removing photoresist mesas during the treatment of oxygen plasma. The four time periods for removing photoresist mesas were 4 min, 1 min, 1 min and 1 min respectively. Finally, the photoresist mesas with the bottom width of 330 nm were obtained by oxygen plasma treatment, with a RF power of 90 W, a pressure of 60 Pa, and a total time of 13 min. It can be clearly seen that the proposed method in this paper is a potential candidate for fabricating low cost 2D nanochannels, compared to most of the current fabrication methods.

Acknowledgements

This work was supported by Natural Science Foundation of Hebei Province of China (E2017202296), National Natural Science Foundation of China (No. 61802108, 51775088, and 11632004), and Young Teacher Innovation Fund of TUST (No. 2014CXLG25).

References

[1] Z. C. Fang, Y. Ding, Z. C. Zhang, F. Wang, Z. K. Wang, H. Wang, and T. R. Pan, “Digital microfluidic meter-on-chip”, Lab on a Chip vol. 20, no. 4, pp. 722-733, 2020.
[2] R. Oz, K. K. Siram, and F. Westerlund, “A nanofluidic device for real-time visualization of DNA-protein interactions on the single DNA molecule level”, Nanoscale vol. 11, no. 4, pp. 2071-2078, 2019.
[3] L. M. Fu, H. H. Hou, P. H. Chiu, and R. J. Yang, “Sample preconcentration from dilute solutions on micro/nanofluidic platforms: A review”, Electrophoresis vol. 39, no. 2, pp. 289-310, 2018.
[4] R. Li, W. Gai, D. Zhu, C. Lok, C. Song, J. Dong, N. Han, Y. Zhang, and X. Zhao, “Evaluation of a novel micro/nanofluidic chip platform for the detection of influenza A and B virus in patients with influenza-like illness”, Amb Express vol. 9, pp. 77, 2019.
[5] W. Q. Yue, Z. Tan, X. P. Li, F. F. Liu, and C. Wang, “Micro/nanofluidic technologies for efficient isolation and detection of circulating tumor cells”, Trac-Trends in Analytical Chemistry vol. 117, pp. 101-115, 2019.
[6] J. H. Yeh, Z. Y. Huang, Y. C. Liu, M. J. Deng, T. H. Chou, H. C. O. Yang, T. Ahamad, S. M. Alshehri, and K. C. W. Wu, “A nanofluidic osmotic power generator fabricated in polymer gel electrolytes with substantially enhanced performance”, Journal of Materials Chemistry A vol. 7, no. 47, pp. 26791-26796, 2019.
[7] S. Kim, G. H. Kim, H. Woo, T. An, and G. Lim, “Fabrication of a Novel Nanofluidic Device Featuring ZnO Nanochannels”, Acs Omega vol. 5, no. 7, pp. 3114-3115, 2020.
[8] S. Wang, Y. Liu, P. Ge, Q. Kan, N. Yu, J. Wang, J. Nan, S. Ye, J. Zhang, W. Xu, and B. Yang, “Colloidal lithography-based fabrication of highly-ordered nanofluidic channels with an ultra-high surface-to-volume ratio”, Lab on a Chip vol. 18, no. 6, pp. 979-988, 2018.
[9] J. Kim and H. Park, “Impact of nanofluidic electrolyte on the energy storage capacity in vanadium redox flow battery”, Energy vol. 160, pp. 192-199, 2018.
[10] B. R. Cipriany, R. Zhao, P. J. Murphy, S. L. Levy, C. P. Tan, H. G. Craighead, and P. D. Soloway, “Single Molecule Epigenetic Analysis in a Nanofluidic Channel”, Analytical Chemistry vol. 82, no. 6, pp. 2480-2487, 2010.
[11] X. Liang and S. Y. Chou, “Nanogap detector inside nanofluidic channel for fast real-time label-free DNA analysis”, Nano Letters vol. 8, no. 5, pp. 1472-1476, 2008.
[12] C. C. Wong, A. Agarwal, N. Balasubramaniam, and D. L. Kwong, “Fabrication of self-sealed circular nano/microfluidic channels in glass substrates”, Nanotechnology vol. 18, no. 13, pp. 135304, 2007.
[13] S. W. Nam, M. H. Lee, S. H. Lee, D. J. Lee, S. M. Rossnagel, and K. B. Kim, “Sub-10-nm Nanochannels by Self-Sealing and Self-Limiting Atomic Layer Deposition”, Nano Letters vol. 10, no. 9, pp. 3324-3329, 2010.
[14] N. R. Tas, J. W. Berenschot, P. Mela, H. V. Jansen, M. Elwenspoek, and A. van den Berg, “2D-confined nanochannels fabricated by conventional micromachining”, Nano Letters vol. 2, no. 9, pp. 1031-1032, 2002.
[15] K. D. Park, S. W. Lee, N. Takama, T. Fujii, and B. J. Kim, “Arbitrary-shaped nanochannels fabricated by polymeric
deformation to achieve single DNA stretching”, Microelectronic Engineering vol. 86, no. 4-6, pp. 1385-1388, 2009.

[16] D. Huh, K. L. Mills, X. Zhu, M. A. Burns, M. D. Thouless, and S. Takayama, “Tuneable elastomeric nanochannels for nanofluidic manipulation”, Nature Materials vol. 6, no. 6, pp. 424-428, 2007.

[17] M. Kim, D. Ha, and T. Kim, “Cracking-assisted photolithography for mixed-scale patterning and nanofluidic applications”, Nature Communications vol. 6, pp. 6247, 2015.

[18] J. Wang and Z. Yin, “SU-8 nano-nozzle fabrication for electrohydrodynamic jet printing using UV photolithography”, Materials Science in Semiconductor Processing vol. 84, pp. 144-150, 2018.

[19] E. Cheng, H. Zou, Z. Yin, P. Jurcicek, and X. Zhang, “Fabrication of 2D polymer nanochannels by sidewall lithography and hot embossing”, Journal of Micromechanics and Microengineering vol. 23, no. 7, pp. 075022, 2013.

[20] J. Gong, K. Ansari, H. Jin, and J. A. van Kan, “High-throughput fabrication of polymethylmethacrylate nano-hole arrays for structural coloration using proton beam writing made diamond stamp”, Microelectronic Engineering vol. 222, pp. 111213, 2020.

[21] J. A. van Kan, P. G. Shao, Y. H. Wang, and P. Malar, “Proton beam writing a platform technology for high quality three-dimesional metal mold fabrication for nanofluidic applications”, Microsystems Technologies-Micro- and Nano-systems-Information Storage and Processing Systems vol. 17, no. 9, pp. 1519-1527, 2011.

[22] Y. Chen, “Nanofabrication by electron beam lithography and its applications: A review”, Microelectronic Engineering vol. 135, pp. 57-72, 2015.

[23] T. Okino, Y. Kuba, M. Shibata, and H. Ohyi, “130 kV High-Resolution Electron Beam Lithography System for Sub-10-nm Nanofabrication”, Japanese Journal of Applied Physics vol. 52, no. 6, pp. 06GB01, 2013.

[24] R. P. Aloysius, S. Husale, A. Kumar, F. Ahmad, A. K. Gangwar, G. S. Papani, and A. Gupta, “Superconducting properties of tungsten nanowires fabricated using focussed ion beam technique”, Nanotechnology vol. 30, no. 40, pp. 405001, 2019.

[25] R. Ribeiro-Andrade, T. L. Vasconcelos, R. M. S. Kawabata, M. Pires, P. L. Souza, and W. N. Rodrigues, “Two-dimensional ordered growth of InAs nanowires assisted by randomly deposited silver nanoparticles on a topographically modified surface by a focused ion beam”, Applied Surface Science vol. 493, pp. 271-278, 2019.

[26] J. Sakamoto, H. Nonma, N. Fujikawa, H. Kawata, M. Yasuda, and Y. Hirai, “Strength enhancement of nano patterns from edge lithography for nanoimprint mold”, Microelectronic Engineering vol. 98, pp. 189-193, 2012.

[27] J. Hallstedt, P. E. Hellstrom, and H. H. Radamson, “Sidewall transfer lithography for reliable fabrication of nanowires and deca-nanometer MOSFETs”, Thin Solid Films vol. 517, no. 1, pp. 117-120, 2008.

[28] Z. Zhang, P. E. Hellstrom, J. Lu, M. Ostling, and S. L. Zhang, “A novel self-aligned process for platinum silicide nanowires”, Microelectronic Engineering vol. 83, no. 11-12, pp. 2107-2111, 2006.

Received 16 September 2020