SAND2011-9451C

Fabrication of Large Arrays of Plasmonic Nanostructures via Double Casting

Joanne C Lo[1,2], David A. Horsley[2], Jack L. Skinner[1]
[1]Sandia National Laboratories, Livermore, CA; [2]University of California, Davis, CA

ABSTRACT

Large arrays of periodic plasmonic nanostructures are widely used in various applications, including ultra-sensitive particle sensing, optical nanoantennas, and optical computing. However, creating large-scale arrays *via* current fabrication processes (*e.g.*, e-beam lithography and nanoimprint lithography) remains time consuming and expensive. To overcome this issue, here we present a double casting fabrication methodology. We demonstrate this technique by creating large 150 nm-nanohole and 150 nm-nanopillar arrays (0.5 cm x 1 cm) from one silicon master template with nanopillars. Previously, researchers have demonstrated double casting methods for microscale features; however, employing these techniques at the nanoscale has remained a challenge due to cracking and incomplete transfer of the nanofeatures. Here, we preclude cracking and incomplete transfer problems by using a hard-PDMS/soft-PDMS (h-PDMS/s-PDMS) composite stamp to replicate the features from: (*i*) the silicon template, and (*ii*) the resulting PDMS template. Our double casting technique can be employed repeatedly to create positive and negative copies of the original silicon template as desired. By drastically reducing the cost, time and labor associated with creating separate silicon templates for large arrays of different nanostructures, this methodology will enable rapid prototyping for diverse nanotechnology applications.

Keywords: Nanofabrication, Plasmonics, Nanophotonics, Double casting, h-PDMS, Composite stamp

1. INTRODUCTION

Sub-wavelength nanofeatures have shown interesting and valuable properties that would enable advancement in many research fields [1-3]. The developments of optocomputing[4], single-particle sensing[5, 6], or optical cloaking [7, 8] rely on the capability to manipulate light in the nanoscale. The fundamental building blocks of many nanophotonic devices are nanopillars and nanoholes [1-3, 5, 8, 9]. By controlling the material, height, aspect ratio, and pitch of nanopillars and nanoholes, a wide range of nanodevices can be realized [10, 11]. E-beam lithography and interference are two major ways to create nanofeatures of silicon wafers. These methods allow researchers to fabricate nanofeatures of specific size and pitch that are tailor to their applications. However, fabricating silicon templates with e-beam lithography and interference lithography are usually expensive and time-consuming. Moreover, many small research laboratories cannot afford to purchase the expensive equipment required for these processes, and are forced to purchase silicon templates commercially. Depending on the sizes of the array and nanofeatures, silicon templates are generally quite expensive. A times-efficient and cost-effective way to replicate two molds, a positive and a negative, from the expensive silicon template would be hugely beneficial. In this paper, we will present a double casting method that would allow researchers to use soft lithographic method to create two molds from one single silicon template, obviating the need for lengthy chemical etching processes.

Polydimethylsiloxine (PDMS) is widely used in various nanophotonics applications such as plasmonic sensors[12] and optofluidics[13]. The inexpensive material cost and ease of fabrication makes PDMS a good candidate for rapid prototyping. However, the success of PDMS device fabrication depends heavily on the quality of the master template, which is usually made of silicon, glass, or SU-8. The quality of the master template is determined by 1) the material compatibility between the template and mold materials, and 2) the reusability of the template [14-16]. The material properties of the template, such as coefficient of thermal expansion and surface chemistry, dictate the success of mold releasing. Since silicon and glass have lower coefficient of thermal expansion (~3.2 ppm/°C) than PDMS (310 ppm/°C), the baking temperature of PDMS has to be increased slowly to prevent the breakage of the template [17-19]. The mismatch between the coefficients of thermal expansion also affects the amount of polymer mold shrinkage. This often cause the dimensions (i.e. width and pitch) to differ significantly (>10%) from the template[19]. For nanophotonic applications, where 1-2 nm of difference in the feature size could create a dramatic change in the photonic response, the features size and pitch changes have to be considered in the fabrication process [20]. Additionally, care must be taken to ensure the surface of the template would not adhere to the mold material[16]. When fabricating nanofeature, a passivation material is usually deposit onto the template to lower the surface energy. This process allows the complete release of the mold, and the template to be reused multiple times. The rigidity and durability of the template material also affect the reusability of the template. Silicon and glass templates are durable, but they require higher cost and longer labor hours to create. Although polymer templates (i.e. SU-8 and PDMS) are not as durable as silicon and glass template, they generally require much less time to fabricate [14, 16, 19]. The cost-effectiveness of polymer templates allow them to be created from the silicon template, used to create other molds, and disposed after a certain number of cycles. It is desirable for polymer template to have comparable resolution as silicon and glass templates (i.e. able to retain the integrity of the nanofeatures). This is a challenge for polymer template since most polymers have lower Young's Modulus, which cause nanofeatures to sag or collapse [17, 20].

Because of these considerations, the fabrication of the template is a nontrivial step in developing a cost-effective bench-top rapid prototyping process for nanopatterned PDMS devices. In order to minimize the number of costly equipment, chemicals, and materials, our proposed double casting process only utilizes one material – PDMS. Although two variants of PDMS (hard-PDMS and soft-PDMS) were used to optimize the transfer of nanofeatures, no invasive chemical etchants, high temperature (>70°C), nor high pressure were used. In this paper, we demonstrate the fabrication of a PDMS mold with 150-nm nanoholes from a silicon master template, and the subsequent repeated use of this template to create PDMS stamps with 150-nm nanopillars. To the authors' knowledge, no prior studies have demonstrated double casting with PDMS producing features smaller than 500nm.

In order to replicate large arrays of nanofeatures, composite PDMS stamps were utilized. A composite stamp consists of a thin hard-PDMS (h-PDMS) and a thick Sylgard 184 soft-PDMS (s-PDMS) layer. It has been previously demonstrated that composite stamps are better suited for replicating nanofeatures compared to Sylgard 184 PDMS stamps [17, 21]. The h-PDMS has shorter polymer chains, and therefore is less viscous than the commonly used Sylgard 184 PDMS [21]. This property allows h-PDMS to conform to the nanofeatures of the silicon and PDMS mold, which makes it a good candidate for replicating dense nanopillars and nanoholes. Additionally, the high Young's modulus (~9MPa) of h-PDMS enables the stamp to retain the nanofeatures after demolding. Despite h-PDMS excellent ability to replicate nanofeatures, it is prone to cracking if no proper support is provided [17]. Since s-PDMS has a low Young's Modulus (~2MPa), it can serve as a flexible backing for the h-PDMS. For the PDMS nanohole template, an extra piece of silicon is placed on top of the s-PDMS for extra support. The silicon backing supports the mold and enables the template to be used multiple times.

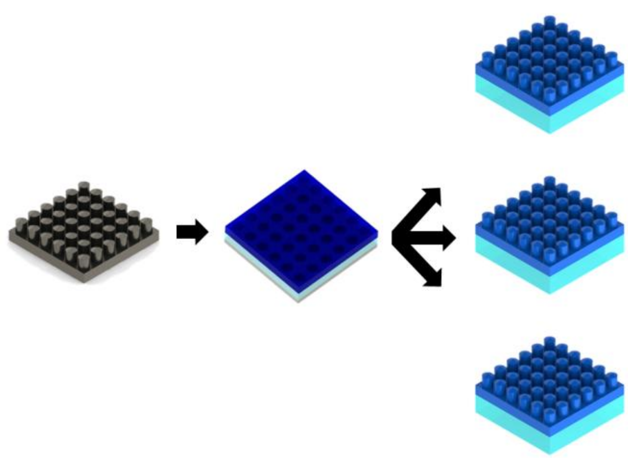

Figure 1. Double casting with PDMS. One PDMS template with a large array of 150-nm nanoholes is created from a silicon nanopillar array. Subsequently, the PDMS nanohole is used to create three nanopillar arrays.

2. EXPERIMENTAL DETAILS

2.1 Passivation of the master silicon template

The double casting fabrication procedure begins with a conventional silicon master template. The silicon master used in this study contains a large array (0.5 cm x 1 cm) of 150nm-nanopillars create by interference lithography, which was described in a previous paper [22]. The template was first passivated by molecular vapor coating (MVC) with Nanonex Ultra-100. Passivation was a necessary step in replicating small features (<1µm) in order to reduce adhesion between the template and the stamp. This is particularly important in this double casting procedure since PDMS is used in both the template and mold material; the surface chemistry would cause the mold and the template to strongly adhere to one another if caution was not taken in treating the surface of the template. MVC was chosen over a silanization passivation process for its short processing time (20 minutes instead of 10 hours) [16]. After the silicon template was passivated, it was rinsed with deionized water to remove any loosely bound molecules.

2.2 Fabrication of the PDMS nanohole template

To create the PDMS composite stamps, h-PDMS and s-PDMS was mixed and outgassed separately. The h-PDMS mixture was prepared by mixing 3.4 g of a vinyl PDMS prepolymer (VDT-731, Gelest Corp.), 18 µl of Pt catalyst (platinum divinyltetramethyldisiloxane, SIP 6831.2, Gelest Corp.), and one drop of a modulator (2,4,6,8-tetramethyltetravinylcyclotetrasiloxane, 396281, Sigma-Aldrich). The mixture was outgassed, and combine with 1 g of hydrosilane prepolymer(HMS-301, Gelest Corp). The resulting h-PDMS was again outgassed and spun onto the passivated silicon template at 2000 rpm for 30 seconds. Care was taken to ensure the smoothness of the h-PDMS layer, which had found to be essential in creating an uniform array of nanofeatures. The thin (20 µm) was h-PDMS examined with an ellipsometer for consistency of thickness. The thin h-PDMS was then partially cured at 65 ºC for 30 minutes until it was slightly tacky. To fabricate the flexible support layer, the two-part (10:1) mixture of s-PDMS (Sylgard-184, Dow Corning) was poured onto the h-PDMS to form a 1 mm layer. A small piece of silicon wafer was put on top of the s-PDMS as an additional support for the template. The whole composite stamp assembly was fully cured at 65 ºC for 2 hours, and was carefully demolded from the silicon template with a razor blade. The s-PDMS/h-PDMS composite stamp, which was patterned with a large nanohole array, was characterized with SEM.

2.3 Fabrication of the PDMS nanopillar mold

In the second casting procedure, the aforementioned composite stamp patterned with a nanohole array was used as the template. The PDMS template was passivated with a vapor-phase anti-stiction coating with Nanonex Ultra-100. In the passivation procedure, the PDMS template was coated with 90ºC vapor for 10 minutes, which was determined to be harmless for the nanofeatures of the PDMS template. A thin layer of h-PDMS (prepared with previously mentioned procedure) was then spun onto the passivated PDMS template. The thin h-PDMS layer was partially cured at 65ºC for 30 minutes, and a 2mm s-PDMS layer was poured onto the h-PDMS layer. The whole assembly was fully cured at 65ºC for 2.5 hours, and the second PDMS composite stamp was carefully demolded from the PDMS template. The resulting PDMS composite stamp, which was patterned with a large nanopillar array, was characterized with SEM.

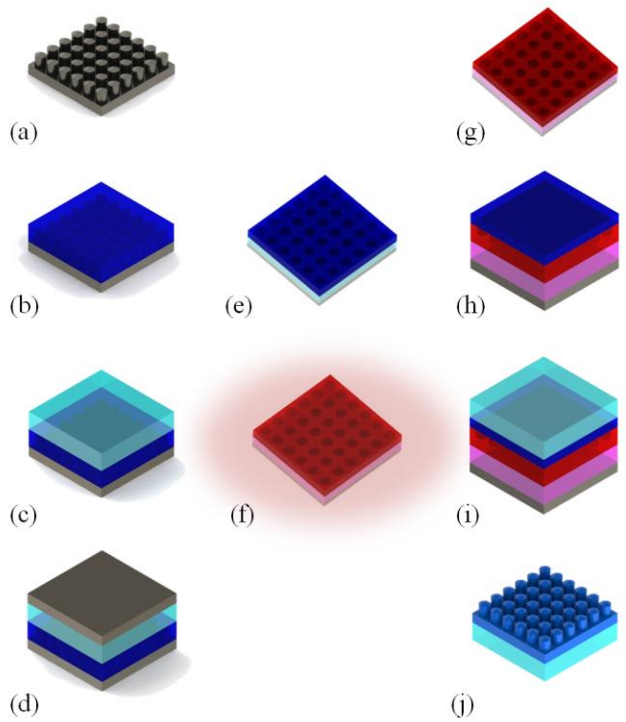

Figure 2. Fabrication procedure. (a) A silicon template was cleaned and passivated. (b) A thin layer (20μm) of h-PDMS was spun onto the passivated silicon template, and partially cured at 65°C for 30 minutes. (c) A thick layer (2mm) of s-PDMS was poured on top of the partially cured h-PDMS. (d) A small piece of silicon wafer was put on top of the s-PDMS for additional template support. The composite PDMS stamp was cured at 65°C for 2 hours. (e) The nanohole array template was carefully demolded from the silicon template with a razor blade. (f) The nanohole array template was passivated with molecular vapor coating (MVC). (g) The passivated nanohole template was rinsed with DI water to remove excess molecules. (h) A thin layer (20μm) of h-PDMS was spun onto the passivated PDMS template, and partially cured at 65°C for 30 minutes. (i) A thick layer (2mm) of s-PDMS was poured on top of the partially cured h-PDMS. The composite PDMS stamp was cured at 65°C for 2 hours. (j) The nanopillar array was demolded from the PDMS nanohole template with a razor blade.

3. RESULTS AND DISCUSSION

To demonstrate that the PDMS template can be used repeatedly to create nanophotonics features, the template was replicated three times to create three individual nanopillar arrays. In order to verify the integrity of the PDMS stamps and the success of pattern transfer, small pieces of the nanohole template and the resulting nanopillar stamps were cut out with a sharp razor blade and examined with SEM. The nanohole PDMS stamp meets the criteria for a template for replicating nanofeatures. As shown in the figures, the nanohole template shows defined, sharp nanofeatures with no sagging around the nanoholes. The nanoholes are 150nm in diameter, and 500nm in pitch. After three replications, the nanohole template still retains strural integrity. A side picture of the nanohole template was taken to show the depth of the nanoholes, demonstrating the success of nanopillar stamp demolding. The resulting nanopillar stamps also have clear and defined nanofeatures. The nanopillars are 150nm in diameter, and 500nm in pitch. Since the coefficient of thermal expansions and the template and the mold are exactly the same, the resulting mold has nanofeatures with the same dimensions and pitch as the template.

4. CONCLUSION AND OUTLOOK

In this paper, we presented a PDMS double casting method that can create sub-500 nm nanofeatures. In this fabrication procedure, high quality stamps were created without the assistance of high heat or high pressure. The stamps contain 150-nm nanopillars with 500-nm pitch, which is an accurate negative copy of the PDMS nanohole template. Three nanopillar stamps were created from one nanohole template, and the template retained structural integrity. This paper is not an exhaustive study of this double casting method; more nanopillar stamps could have been created from the one hanohole stamp. However, this experiment serves as a good first step for future investigation. This double casting procedure does not involve expensive equipments and numerous chemicals, which drastically reduces the cost for materials and labor. This fabrication method enables researchers and scientists to fabricate a positive and a negative copy from one single silicon template, creating more opportunities for investigations in various nanotechnology fields.

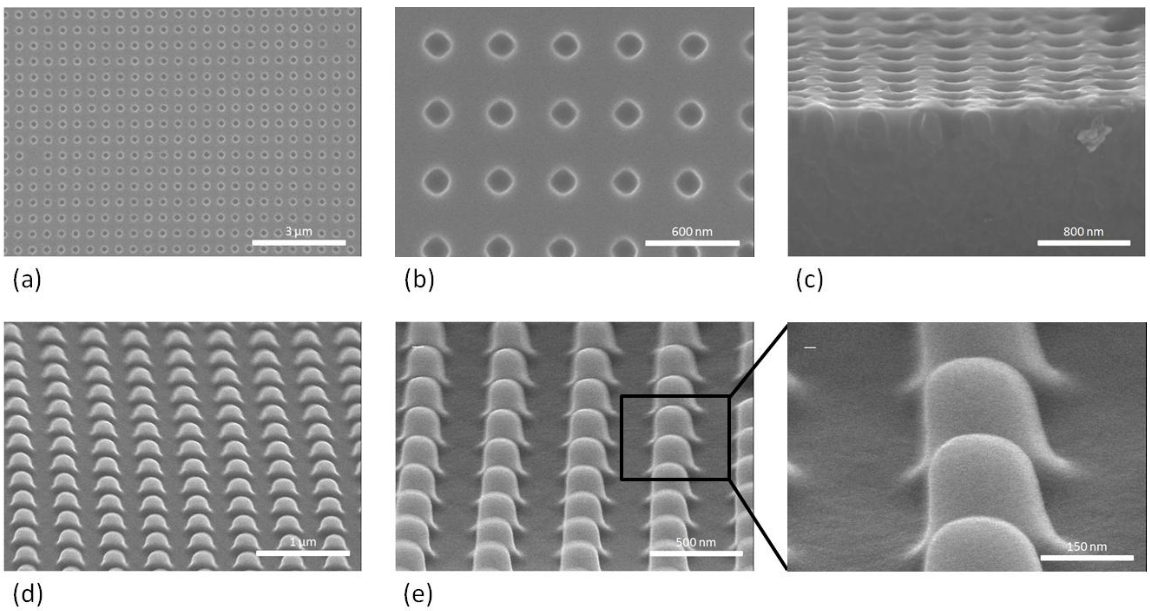

Figure 3. SEM images of the PDMS templates. (a) The PDMS nanohole template created from the silicon template. (b) A close-up image of the nanoholes. The nanoholes are 150nm in diameter, and 500nm in pitch. (c) A side-view of the nanohole template, showing the depth of the nanoholes after demolding. (d) The PDMS nanopillar template created from the PDMS nanohole template. (e) Close-up image of the nanopillars. The nanopillars are 150nm in diameter, and 500nm in pitch.

REFERENCES

1. Alaverdyan, Y., et al., *Optical antennas based on coupled nanoholes in thin metal films.* Nat Phys, 2007. **3**(12): p. 884-889.
2. Wang, K., et al., *Trapping and rotating nanoparticles using a plasmonic nano-tweezer with an integrated heat sink.* Nat Commun, 2011. **2**: p. 469.
3. Caldwell, J.D., et al., *Plasmonic Nanopillar Arrays for Large-Area, High-Enhancement Surface-Enhanced Raman Scattering Sensors.* ACS Nano, 2011. **5**(5): p. 4046-4055.
4. Engheta, N., *Circuits with Light at Nanoscales: Optical Nanocircuits Inspired by Metamaterials.* Science, 2007. **317**(5845): p. 1698-1702.
5. Anker, J.N., et al., *Biosensing with plasmonic nanosensors.* Nat Mater, 2008. **7**(6): p. 442-453.
6. Liu, N., et al., *Nanoantenna-enhanced gas sensing in a single tailored nanofocus.* Nat Mater, 2011. **10**(8): p. 631-636.
7. KocamanS, et al., *Zero phase delay in negative-refractive-index photonic crystal superlattices.* Nat Photon, 2011. **5**(8): p. 499-505.
8. Gabrielli, L.H., et al., *Silicon nanostructure cloak operating at optical frequencies.* Nat Photon, 2009. **3**(8): p. 461-463.
9. Walker, B.N., et al., *Tailored Silicon Nanopost Arrays for Resonant Nanophotonic Ion Production.* The Journal of Physical Chemistry C, 2010. **114**(11): p. 4835-4840.

10. Riedrich-Moller, J., et al., *One- and two-dimensional photonic crystal microcavities in single crystal diamond.* Nat Nano, 2011. **advance online publication**.
11. Sameshima, H., et al. *GaN pitch-variable grating fabricated on Si substrate*. in *Optical MEMS and Nanophotonics (OPT MEMS), 2010 International Conference on*. 2010.
12. Cattoni, A., et al., *λ3/1000 Plasmonic Nanocavities for Biosensing Fabricated by Soft UV Nanoimprint Lithography.* Nano Letters, 2011. **11**(9): p. 3557-3563.
13. Luciano De Sio, J.G.C., Andreas E. Vasdekis, and Demetri Psaltis, *All-optical switching in an optofluidic polydimethylsiloxane: Liquid crystal grating defined by cast-molding* Appl. Phys. Lett., 2010. **96**: p. 131112.
14. Gitlin, L., P. Schulze, and D. Belder, *Rapid replication of master structures by double casting with PDMS.* Lab on a Chip, 2009. **9**(20): p. 3000-3002.
15. Pan HA, H.Y., Sui YP, Huang GS, *Topographic control of the growth and function of cardiomyoblast H9c2 cells using nanodot arrays.* Biomaterials, 2011.
16. Kutter, G.Z.a.J.P., *Anti-stiction coating of PDMS moulds for rapid microchannel fabrication by double replica moulding.* J. Micromech. Microeng., 2011. **21**: p. 105020.
17. Odom, T.W., et al., *Improved Pattern Transfer in Soft Lithography Using Composite Stamps.* Langmuir, 2002. **18**(13): p. 5314-5320.
18. Wes WTooley, S.F., Sangyoon J Han, JunlanWang and and N.J. Sniadecki, *Thermal fracture of oxidized polydimethylsiloxane during soft lithography of nanopost arrays.* J. Micromech. Microeng, 2011. **21**: p. 054013.
19. Suleski, A.T.C.a.T.J., *Characterization of hybrid molding and lithography for SU-8 micro-optical components.* J. Micro/Nanolith. MEMS MOEMS, 2010. **9**: p. 013025.
20. Hui, C.Y., et al., *Constraints on Microcontact Printing Imposed by Stamp Deformation.* Langmuir, 2002. **18**(4): p. 1394-1407.
21. Schmid, H. and B. Michel, *Siloxane Polymers for High-Resolution, High-Accuracy Soft Lithography.* Macromolecules, 2000. **33**(8): p. 3042-3049.
22. Jack L. Skinner, L.L.H., A. Alec Talin, J. Provine, David A. Horsley, *Large-Area Subwavelength Aperture Arrays Fabricated Using Nanoimprint Lithography.* IEEE Trans. Nanotechnol., 2008. **7**(5): p. 1536.

ACKNOWLEDGMENT: Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.