Nanowell arrays

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Cicada Wings: A Stamp from Nature for Nanoimprint Lithography**

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Nanoimprint lithography (NIL) has been proposed as an alternative approach for the fabrication of nanostructures with critical dimensions on the wafer scale (sub 100 nm).[1] The smallest structures that have been successfully fabricated by NIL so far are 6-nm half-pitch lines.[2] Also, imprinting processes have already been demonstrated on 8-inch wafers with lines, dots and rings.[3] Compared with other lithography techniques, such as scanning-probe lithography (SPL), electron-beam lithography (EBL), and photolithography (PL), NIL has advantages of high throughput, high resolution, and low cost, and thus has proved to be a promising candidate for next-generation lithography.[4] However, a lot of challenges in terms of overprinting, imprinting with micro- and nanocombined structures, and imprinting on irregular surfaces remain.[5] Many efforts have been made to develop the alignment system[6,7] to resolve the problem of micro- and nanostructure imprinting,[8] and to perform the nanoimprint lithography on nonflat surfaces.[9]

Preparation of stamps with high resolution over a large area is a key procedure in NIL. Besides the traditional methods mentioned above, there are many other developed methods of preparing the stamps. For example, a stamp with a silicon-tip array has been fabricated by Ar^+ ions bombarding Ti dots on a silicon wafer.[10] Large-area pillar arrays have been prepared using polymer-colloid masks,[11] and biomolecules can also act as a stamp in imprinting.[12] However, these are usually time-consuming and complicated and in some cases, expensive to carry out.

Many nanostructures exist in nature.[13–16] A very good example is the micro- and nanostructures that exist on the *Morpho sulkowskyi* butterfly scale, which, through light-scattering and diffraction, result in the butterfly's charming blue color.[17,18] Combined micro- and nanostructures found on the surface of the leaves of some plants exhibit superhydrophobicity, which is described as the "lotus effect".[19,20] In addition, arrays of tapered pillars have also been found on cicada wings and moth eyes, which can greatly minimize the reflectivity on their surfaces over broad angles or frequency ranges.[21–23] In fact, many efforts have been made to replicate or directly utilize these bionanostructures for special applications.[24,25] In this work, the direct use of these nanostructures as stamps for NIL is reported. With these natural stamps, nanowell arrays (negative structures of cicada wings) have been fabricated on a polymer support. Furthermore, the nanowell arrays can be transferred to the silicon substrate by reactive ion etching (RIE), and thus exhibit an antireflective property. With patterned poly(methyl methacrylate) (PMMA) as a mold, hexagonal gold-pillar arrays similar to the surface of cicada wings can also be obtained by thermodeposition.

The cicadas (*Cryptympana atrata Fabricius*) are either captured locally or bought from specimen factories. As shown in Figure 1, the microscopic structures of the cicada

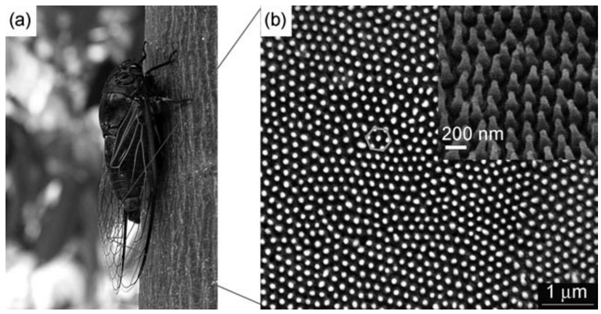

Figure 1. a) Photograph of *Cryptympana atrata Fabricius*. b) Scanning electron microscopy (SEM) image of the surface of cicada wings. The space between each pillar is about 190 nm. The pillars are arranged in a hexagonal array. Inset: SEM image showing a tilt of about 30°.

wings consist of ordered hexagonal close-packed arrays of pillars with a spacing of about 190 nm. The height of the pillars is about 400 nm and the diameters at the pillar top and bottom are about 80 and 150 nm, respectively. On the original surface of the cicada wings, there are many stains, which may stick these pillars together. We found that these stains affect the quality of imprinting patterns, thus it is important to remove them first.

Before imprinting, the cicada wings are cleaned to get rid of the stains. The cleaning procedure consists of two steps, whereby the wings are sonicated in acetone for 15 min to remove the organic compounds, followed by soni-

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cation for 20 min in ultrapure water. According to the scanning electron microscopy (SEM) images, there is no notable change of profile of the cleaned wings compared with the untreated wings. However, with the stains cleaned off, the sticking pillars are restored. We also noticed that there is a smaller electric-charging effect during SEM imaging of the cleaned wings than the untreated wings (see Figure S1 in the Supporting Information). This means the surface has changed to become more conductive. Normally, the surface of the wings is covered with wax and improper treatment might destroy the special layer,[26] which will affect the profile of the structures. The reason for the reduced electric charging may be due to the fact that the insulative wax layer on the surface is partially removed by the cleaning process. Fortunately, as will be shown here, the surface tension remains low even after the treatment, which is very important for NIL.

Figure 2 is a schematic diagram showing nanoimprint lithography with cicada-wing stamps, fabrication of gold pillar arrays, and transfer of the pattern to a silicon substrate. The veins in the wings have been removed before imprinting because their diameter is about 70 μm (the wing membrane is only 20-μm thick; see Figure S2 of Supporting Information) and will affect the uniformity of the patterned PMMA. PMMA was chosen because it is widely used in NIL due to its high resolution and low shrinkage under large variations of temperature or pressure. The thickness of the resist spun on the substrate (silicon) was about 450 nm, higher than the height of the pillars on the wings. The glass-transition temperature (T_g) of PMMA (weight-average molecular weight $M_w = 95000$) is 120 °C. An assistant template was necessary to provide uniform pressure on the cicada wings during imprinting. The imprinting pressure applied was around 40 bar. The temperature was around 190 °C, 70 °C higher than the T_g, at which PMMA has low enough viscosity. Meanwhile, sufficiently softened PMMA would not destroy the structures on the wings. The pressure was applied for about 180 s. Figure 3a and b are typical SEM images of the patterned PMMA and Figure 3c is an atomic force microscopy (AFM) image of the structures. From these images, it can be seen that the negative structures of the stamp have been successfully fabricated by NIL and a nanowell array has formed. The largest homogeneous area on PMMA is up to hundreds of square micrometers after imprinting. The pitch between the wells is about 190 nm, the well diameter is about 150 nm, and the depth is found to be about 400 nm; these parameters are consistent with the stamp. We also performed direct imprinting with untreated wings: there are many defects on the patterned PMMA layer (see Figure S3 of Supporting Information). Additionally, cicada-wing stamps can be used several times although the quality of the imprinting results may decline due to the material of the cicada wings and hot embossing conditions.

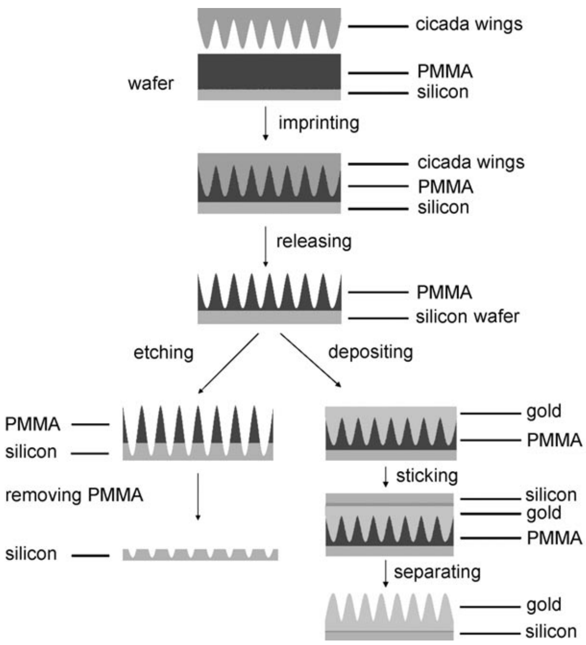

Figure 2. Schematic diagram of NIL, showing cicada-wing stamps, fabrication of gold pillar arrays, and transfer of the pattern onto a silicon substrate.

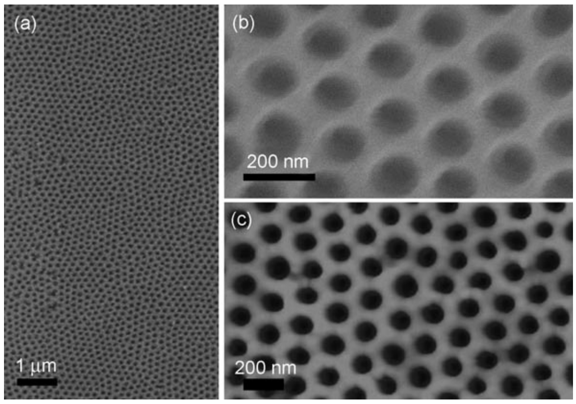

Figure 3. Results after imprinting using cicada wings as the stamp. (a) and (b) are SEM images of patterned PMMA with different scales. (c) is an AFM image of the patterned PMMA surface.

This experiment shows that cicada wings have sufficient stillness, chemical stability, and low surface tension[27] to carry out NIL. These properties originate from the special composition of cicada wings. Similar to the cuticle of other insects, the main components of cicada wings consist of an arrangement of highly crystalline chitin nanofibers embedded in a matrix of protein, polyphenols, and water, with a small amount of lipid. Crystalline chitin interacts with the protein matrix via hydrogen bonding, which imparts stillness and chemical stability to the structure. The Young's modulus of these cicada wings can be as high as 7–9 GPa.[27] Although this number is still far lower than traditional stamps used in NIL, such as silicon (up to 131 GPa), it is sufficient for imprinting PMMA while still maintaining the original profile.

In addition, these cicada-wing stamps have very low surface tension. If the surface tension is too high, after imprinting, the patterned polymer will be destroyed during stamp release due to conglutination.[28] In traditional NIL, a layer of low-surface-tension material, called the antiadhesive layer, has to be deposited on patterned silicon or silica stamps.[29] The efficiency of this anti-adhesive layer determines the lifetime of the stamp. This step affects the throughput of nanoimprint lithography. There is no such problem when we use the cicada wings as imprinting stamps. The notable low surface tension of the wings originates from a layer of wax on the surface of the wings,[26] which contains esters, acids, alcohols, and hydrocarbons. The cicada wings, therefore, do not need to be treated before imprinting and can be directly removed by small tweezers after imprinting.

The imprinting structures can be transferred to the silicon substrate by RIE. Figure 4a is an SEM image of the structures on the silicon substrate transferred by 3-min RIE. Different etching times were investigated; the longer etching time will over-etch the structures but shorter times do not etch the silicon substrate sufficiently (see Figure S4 of

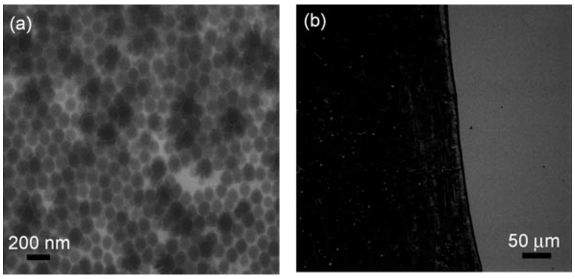

Figure 4. a) The result of pattern transferal to the silicon substrate. b) Optical microscopy image of nonstructured (right) and structured (left) silicon substrate, the latter showing some antireflective ability.

Supporting Information). From the image, it can be seen that the structures are not very uniform and some of the wells are connected to one another. This is possibly due to the fact that the etching is isotropic. PMMA is not an ideal mask for such an RIE process. Other resists will be investigated further. Figure 4b is an optical microscopy image of the structure compared with a normal Si substrate, showing the antireflective property of the structural surface. This is consistent with a previous report.[30]

The gold pillar arrays similar to the structures in the cicada wings can be fabricated by using the patterned PMMA as a mold. Figure 5a is the SEM image of fabricated gold pillar arrays. About 400 nm of gold was deposited onto the patterned PMMA and then this gold layer was adhered to another silicon or glass wafer. The gold layer was transferred to the wafer after separation from the mold. From the SEM images, the height of the pillars is found to be about 400 nm, the bottom diameter is about 150 nm, and the pitch is about 190 nm, which is consistent with the features of the original stamps. Other metals can also be deposited onto patterned PMMA and various metallic pillar arrays can be easily fabricated by this method. Such metallic pillar arrays can be useful in optical imaging or in surface-enhanced Ramon scattering (SERS).[31,32]

In summary, we have demonstrated that the cicada wings can be used as a new type of imprinting stamp. Nano-

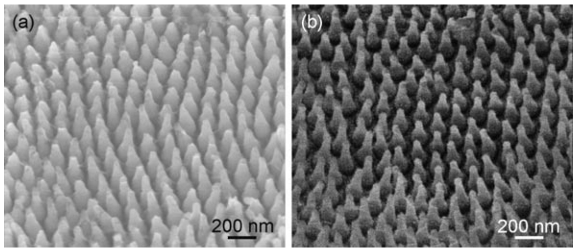

Figure 5. Result of replicating cicada-wing structure by imprinting with Au. a) SEM image, taken after replication, showing tapered Au pillar array with 30° tilt. b) SEM image of cicada wings, showing 30° tilt.

well arrays have been successfully fabricated by NIL and the structures can be transferred to the silicon substrate by RIE, subsequently showing antireflective properties. Patterned PMMA can also be used as a mold to fabricate the hexagonal gold tapered pillar arrays mimicking the structures on cicada wings. This method can also be extended to other metals, even other materials, which will be useful in optical imaging or SERS. This may prove much cheaper for NIL because the cicada wings are abundant in nature and easy to obtain. Our work serves as an example of using natural nanostructures for NIL as well as related technologies such as step and flash imprint lithography.

Experimental Section

Cicada wings were cleaned before use as stamps. First, the wings were sonicated in Milli-Q water for about 15 minutes to remove contaminants absorbed physically on the surface; the wings were then sonicated in acetone for 20 min to remove the stains that stick the pillars together, and lastly the wings were sonicated in Milli-Q water again for 15 min to remove residual acetone, followed by nitrogen blow-drying. Subsequent SEM characterization showed that the details on the surface of the wings were not changed.

PMMA ($M_w = 95\,000$, $T_g = 120\,^{\circ}C$) was purchased from Acros Organics and dissolved in toluene (Acros Organics) to form a 5 wt% solution. The solution was spun with onto a $2 \times 2\ cm^2$ silicon wafer. After hard-baking, the thickness of the layer was found to be about 450 nm. Imprinting was carried out with a 2.5-in. Nanoimprinter (Obducat AB, Malmö, Sweden). The loaded pressure was about 40 bar and the imprinting temperature was 190 °C. The pressure was released after 180 s, and the wing stamp was carefully removed with tweezers.

To transfer the pattern to the substrates, RIE was carried out using a Plasmalab Oxford 80plus system (Oxford Instrument Co., UK). The processing gases used were SF_6 (30 sccm) and O_2 (6 sccm), the RF power was 50 W, and the chamber pressure was 30 mTorr. The etching time was about 3 min.

The patterned PMMA layer served as a mold to fabricate gold pillar arrays similar to the structure on the surface of the cicada wings. A 400-nm-thick layer of gold was thermally deposited onto the PMMA surface with the thin-film coating system (Auto 306, BOC Edward, Inc.). The gold layer was then glued onto a silicon or glass piece (cleaned in SC-1 solution: $NH_3/H_2O_2/H_2O =$

1:1:5, by volume) by EPO-TEK 377 (Epoxy Technology Co., Ltd., USA). The sample was baked at 150 °C for one hour to harden the glue. The Au film was transferred to the top silicon or glass piece after separation from the PMMA mold. The residual PMMA on the sample was removed by boiling in acetone for 15 min. It was found that cleaning with O_2 plasma was more effective.

All AFM images were acquired using a Nanoscope IV multimode atomic force microscope (Digital Instruments, Santa Barbara, USA) in tapping mode under ambient conditions. SEM images were obtained with LEO 1530 VP (LEO Elektronenmikroskopie GmbH, Oberkochen, Germany) and Strata DB 235 (FEI, USA).

Keywords:
biophysics · cicada wings · imprint lithography · nanostructures · reactive ion etching

[1] a) S. Y. Chou, P. R. Krauss, P. J. Renstrom, *Appl. Phys. Lett.* **1995**, *67*, 3114 – 3116; b) B. Heidari, I. Maximov, E. L. Sarwe, L. Montelius, *J. Vac. Sci. Technol. B* **1999**, *17*, 2961 – 2964.
[2] M. D. Austin, W. Zhang, H. Ge, D. Wasserman, S. A. Lyon, S. Y. Chou, *Nanotechnology* **2005**, *16*, 1058 – 1061.
[3] C. Perret, C. Gourgon, F. Lazzarino, J. Tallal, S. Landis, R. Pelzer, *Microelectron. Eng.* **2004**, *73–74*, 172 – 177.
[4] L. J. Guo, *J. Phys. D* **2004**, *37*, R123 – R141.
[5] a) S. Zankovych, T. Hoffmann, J. Seekamp, J. U. Bruch, C. M. S. Torres, *Nanotechnology* **2001**, *12*, 91 – 95; b) M. Beck, F. Persson, P. Carlberg, M. Graczyk, I. Maximov, T. G. I. Ling, L. Montelius, *Microelectron. Eng.* **2004**, *73–74*, 837 – 842.
[6] D. L. White, O. R. Wood, *J. Vac. Sci. Technol. B* **2000**, *18*, 3552 – 3556.
[7] X. Cheng, D. W. Li, L. J. Guo, *Nanotechnology* **2006**, *17*, 927 – 932.
[8] L. Jiao, H. Gao, G. Zhang, G. Xie, X. Zhou, Y. Zhang, B. Gao, G. Luo, Z. Wu, T. Zhu, J. Zhang, Z. Liu, S. Mu, H. Yang, C. Gu, *Nanotechnology* **2005**, *16*, 2779 – 2784.
[9] X. Y. Sun, L. Zhuang, W. Zhang, S. Y. Chou, *J. Vac. Sci. Technol. B* **1998**, *16*, 3922 – 3925.
[10] T. Borzenko, M. Tormen, V. Hock, J. Liu, G. Schmidt, L. W. Molenkamp, *Microelectron. Eng.* **2001**, *57*, 389 – 396.
[11] C. W. Kuo, J. Y. Shiu, Y. H. Cho, P. Chen, *Adv. Mater.* **2003**, *15*, 1065 – 1068.
[12] J. P. Hulme, J. Gwak, Y. Miyahara, *J. Am. Chem. Soc.* **2006**, *128*, 390 – 391.
[13] A. R. Parker, V. L. Welch, D. Driver, N. Martini, *Nature* **2003**, *426*, 786 – 787.
[14] S. Yang, J. Ford, C. Ruengruglikit, Q. R. Huang, J. Aizenberg, *J. Mater. Chem.* **2005**, *15*, 4200 – 4202.
[15] S. Yang, G. Chen, M. Megens, C. K. Ullal, Y. J. Han, R. Rapaport, E. L. Thomas, J. Aizenberg, *Adv. Mater.* **2005**, *17*, 435 – 438.
[16] J. Aizenberg, A. Tkachenko, S. Weiner, L. Addadi, G. Hendler, *Nature* **2001**, *412*, 819 – 822.
[17] K. Kumazawa, H. Tabata, *Zool. Sci.* **2001**, *18*, 1073 – 1079.
[18] S. Kinoshita, S. Yoshioka, *ChemPhysChem* **2005**, *6*, 1442 – 1459.
[19] W. Barthlott, C. Neinhuis, *Planta* **1997**, *202*, 1 – 8.
[20] R. Blossey, *Nat. Mater.* **2003**, *5*, 301 – 306.
[21] G. S. Watson, J. A. Watson, *Appl. Surf. Sci.* **2004**, *235*, 139 – 144.
[22] E. B. Grann, M. G. Moharam, D. A. Pommet, *J. Opt. Soc. Am. A* **1995**, *12*, 333 – 339.
[23] A. Kaless, U. Schulz, P. Munzert, N. Kaiser, *Surf. Coat. Technol.* **2005**, *200*, 58 – 61.
[24] M. H. Sun, C. X. Luo, L. P. Xu, H. Ji, O. Y. Qi, D. P. Yu, Y. Chen, *Langmuir* **2005**, *21*, 8978 – 8981.
[25] P. Vukusic, I. Hooper, *Science* **2005**, *310*, 1151 – 1151.
[26] P. Kreuz, W. Arnold, A. B. Kesel, *Ann. Biomed. Eng.* **2001**, *29*, 1054 – 1058.
[27] J. F. V. Vincenta, U. G. K. Wegst, *Arthropod Struct. Dev.* **2004**, *33*, 187 – 199.
[28] a) J. Taniguchi, T. Kawasaki, Y. Tokano, Y. Kogo, I. Miyamoto, M. Komuro, H. Hiroshima, N. Sakai, K. Tada, *Jpn. J. Appl. Phys. Part 1* **2002**, *41*, 4194 – 4197; b) M. Beck, M. Graczyk, I. Maximov, E. L. Sarwe, T. G. I. Ling, M. Keil, L. Montelius, *Microelectron. Eng.* **2002**, *61–62*, 441 – 448.
[29] S. Park, C. Padeste, H. Schift, J. Gobrecht, *Microelectron. Eng.* **2003**, *67*, 252 – 258.
[30] Y. Kanamori, K. Hane, H. Sai, H. Yugami, *Appl. Phys. Lett.* **2001**, *78*, 142 – 143.
[31] A. Ono, J. Kato, S. Kawata, *Phys. Rev. Lett.* **2005**, *95*, 267407.
[32] Y. P. Zhao, S. B. Chaney, S. Shanmukh, R. A. Dluhy, *J. Phys. Chem. B* **2006**, *110*, 3153 – 3157.

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