

# Large Area High Density Sub-20 nm SiO<sub>2</sub> Nanostructures Fabricated by Block Copolymer Template for Nanoimprint Lithography

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Thin films with nanometer scale patterns have many fascinating applications for novel material structures and devices. Among those, periodic pillar and hole structures of tens of nanometer pitch are potentially useful for applications in magnetic storage media, photovoltaic cells, organic semiconductors, plasmonic nanophotonics, and filtration membranes.<sup>1–5</sup> Electron-beam lithography and focused ion beam (FIB) lithography are widely used methods to fabricate these types of patterns for which conventional photolithography faces resolution limit. However, the time-consuming process and the high cost associated with such techniques seriously restrict the large-scale production of high density nanopatterns. As alternatives, nanotemplate approaches using track-etched membrane and anodized aluminum oxide (AAO) have been extensively used to produce tens of nanometer scale patterns. However, the poor adhesion of template to a substrate, the harsh processing conditions to remove the template, or the resolution of the patterns often limit these pattern transferring techniques.<sup>6,7</sup>

Recently, the self-assembly behavior of diblock copolymers has drawn significant attention for nanotemplate fabrication.<sup>8</sup> It is well-known that the self-organization of block copolymer can access extremely dense and complex nanostructures. The density and the dimension of such self-organized nanostructures are usually beyond the reach of typical conventional top-down nanofabrication techniques.<sup>9</sup> Furthermore, various techniques that have been developed to control the orientation of the nanoscale morphology in the thin film make it possible for these self-

**ABSTRACT** We developed simple fabrication methods to effectively transfer the block copolymer nanopatterns to a substrate material. High aspect ratio, sub-20 nm nanopillar and nanohole structures are successfully fabricated in a SiO<sub>2</sub> layer in large area format, and the versatile utilities of these nanostructures as nanoimprint molds are studied. Nanoimprint lithography using these molds makes it possible to easily replicate densely packed block copolymer nanotemplate patterns on arbitrary substrates in a short processing time by using a large variety of polymer materials, including functional materials such as conjugated polymers. In addition, the PDMS soft stamps with both nanohole and nanopillar pattern polarities, which are useful tools for soft lithography and transparent template applications, are also successfully fabricated using the pillar- and hole-type SiO<sub>2</sub> molds. These soft stamps provide an effective way to fabricate controllable as well as reproducible plasmonic metal nanostructures with tunable surface plasmon resonances.

**KEYWORDS:** nanoimprint lithography · self-assembly · block copolymer · conjugated polymer · soft lithography · plasmonic nanostructures

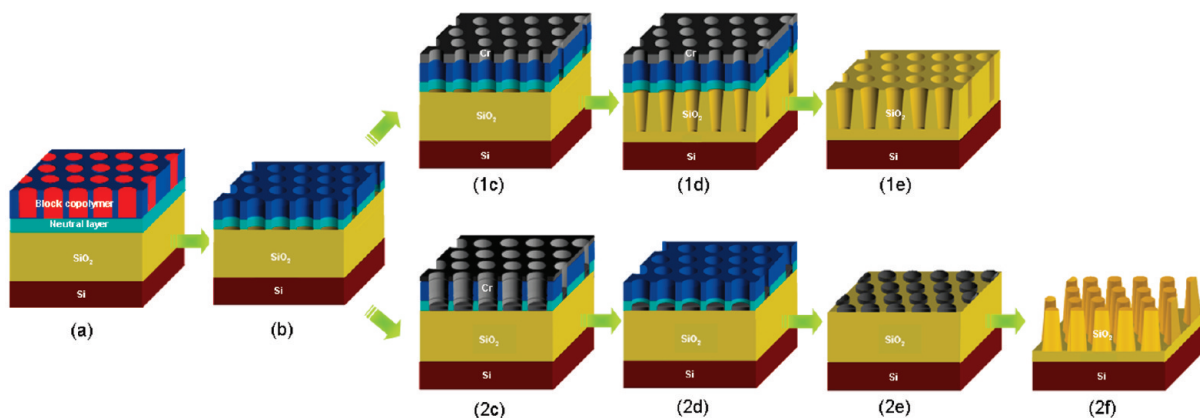
organized nanostructures to be used as templates for various applications.<sup>8,10,11</sup> Despite the numerous advantages offered by these nanotemplates fabricated by block copolymer self-assembly, the long processing time needed to develop the self-assembled structures has drastically reduced the potential impact of this versatile nanopatterning technique. To overcome this limitation, we report in this paper reliable and practical methods of fabricating SiO<sub>2</sub> molds for nanoimprint lithography (NIL) using the block copolymer template, which were then used in NIL for high-speed nanopatterning.<sup>12,13</sup> Such an approach represents a big step forward to mass production of nanostructures with dimension, density, and areal coverage only accessible by the block copolymer self-assembly process. We will also illustrate several examples of useful nanostructures fabricated by using this approach, including large area plasmonic nanoparticle arrays and nanopatterning of conjugated polymer material.

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**Figure 1.** Schematic of the process for fabricating both nanohole and nanopillar array patterns in SiO<sub>2</sub>: (a) cylindrical PS-*b*-PMMA morphology is developed on the substrate surface modified by the neutral PS-*r*-PMMA layer. (b) PMMA nanodomains are selectively removed by O<sub>2</sub> plasma etching. (1c–1e) Nanohole array fabrication process; (1c) Cr is selectively deposited on polymer template using shadow evaporation; (1d) SiO<sub>2</sub> layer is etched using Cr mask by RIE; (1e) Cr mask and polymer template are removed for SiO<sub>2</sub> and form nanohole arrays. (2c–2f) Nanopillar array fabrication process; (2c) Cr is deposited over the polymer template; (2d) top Cr layer is removed by Cr etching RIE; (2e) Cr nanodots remained after lift-off; (2f) SiO<sub>2</sub> layer is etched using Cr mask by RIE and Cr masks are subsequently removed.

NIL is a promising lithographic technique capable of replicating large area nanostructures with resolution down to a few nanometers. Though there have been previous reports to fabricate SiO<sub>2</sub> or Si nanostructures using a self-assembled block copolymer template, the processing methods were not straightforward for either pillar or hole polarity patterns and none has succeeded in applying those nanostructures to NIL.<sup>14–17</sup> In this work, polymer nanotemplate originated from poly(styrene)-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) diblock copolymer was successfully transferred to high density, high aspect ratio sub-20 nm SiO<sub>2</sub> nanopillar and nanohole structures over a large area using the novel processing techniques. Not only can NIL create resist patterns as in a lithographic process but it can also imprint functional device structures in various polymers, which can lead to a wide range of applications.<sup>18</sup> Our imprinting results show that densely packed sub-20 nm nanopillar and nanohole polymer patterns can be easily fabricated on arbitrary substrates. Also it is possible to develop sub-20 nm conjugated polymer patterns on ITO transparent electrodes, which are promising structures for photovoltaic cells. In addition, elastomeric stamps based on a combination of hard and soft poly(dimethylsiloxane) (PDMS), which can be used for soft lithography and transparent template applications, were also fabricated. Using the nanostructured flexible PDMS template and a metal transfer technique,<sup>19,20</sup> sub-20 nm dense plasmonic metal nanoparticles were fabricated and exhibited strong light extinction at the resonance wavelength. Such plasmonic particle arrays can be used in biosensors<sup>21</sup> and photovoltaic cells.<sup>22</sup>

## RESULTS AND DISCUSSION

**NIL Molds Fabrication.** The overall processes for fabricating the NIL molds are described in Figure 1. A SiO<sub>2</sub> layer, which was thermally grown on a Si wafer surface, was

first treated by poly(styrene-*ran*-methyl methacrylate) (PS-*r*-PMMA) random copolymer to produce the neutral surface to polystyrene (PS) and poly(methyl methacrylate) (PMMA).<sup>8,10,11</sup> Subsequently, PS-*b*-PMMA diblock copolymer with 0.7 volume fraction of PS was spin-coated and annealed above the glass transition temperature of the copolymer for the self-assembly process to proceed. This process results in the equilibrated morphology of hexagonally packed cylinders. The identical interfacial tension provided by the neutral PS-*r*-PMMA layer to each block of the PS-*b*-PMMA copolymer on the surface eventually led to vertically oriented cylindrical PMMA nanodomains surrounded by PS. This morphological structure could be used to fabricate a PS nanotemplate with hole arrays by removing the PMMA cylindrical nanodomain utilizing the etching selectivity between PS and PMMA, which is about 1:1.5–2 by typical O<sub>2</sub> plasma etching.<sup>23</sup> The resultant PS template with nanohole array patterns is shown in Figure 2a.

There have been previous attempts to directly use the PS template as an etching mask to transfer the block copolymer patterns to other materials;<sup>14,15</sup> however, the soft PS mask is not strong enough as an etch mask to produce structures with high aspect ratios. Here by using a few nanometer Cr deposited at an angle to the substrate (*i.e.*, shadow evaporation), we could successfully transfer the block copolymer patterns into the SiO<sub>2</sub> layer having an almost 1:10 aspect ratio. Cr was chosen because it is highly resistant to the reactive ion etching (RIE) gases used to etch oxide materials. Cr was selectively deposited on the top surface of the PS template by angled deposition, and this Cr layer acted as the actual mask to etch the SiO<sub>2</sub> layer rather than PS. The resultant SiO<sub>2</sub> hole arrays with 20 nm diameter and 150 nm depth are shown in Figure 2b.

The PS nanotemplate from the PS-*b*-PMMA block copolymer patterns was also used to fabricate SiO<sub>2</sub> nanopillars. Again, Cr was selected as an etch mask. Initially,

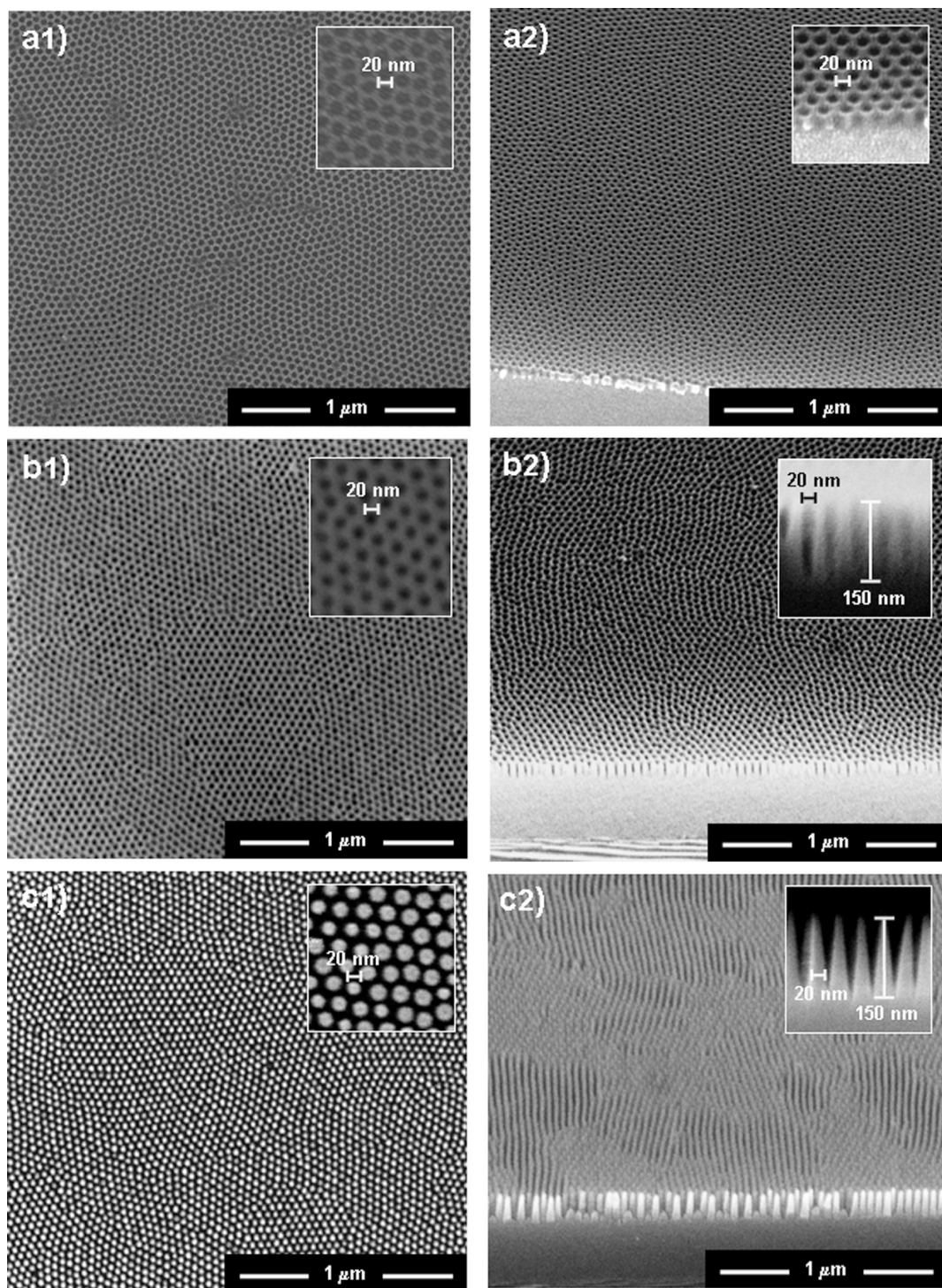


Figure 2. SEM micrographs of various nanostructures (left column, top view; right column, perspective view at 45° tilt angle). (a) PS template fabricated by etching away the PMMA nanodomains of the self-assembled PS-*b*-PMMA hexagonal patterns. (b) SiO<sub>2</sub> nanohole structure. (c) SiO<sub>2</sub> nanopillar structure. All of the inset images are high-magnification SEM images; and the inset images in b2 and c2 show the cross-section view of the nanostructure in the fabricated SiO<sub>2</sub> mold.

we tested the conventional lift-off process by depositing Cr on the PS template and subsequently dipping the sample into toluene in order to lift-off the Cr film on top of the PS template, while leaving the Cr pattern at the bottom of the nanoholes. However, even by harsh processing conditions, such as 3 h sonication at 60 °C, only small areas of PS template were dissolved

and most areas of PS template remained on the substrate. This is due to the Cr metal deposited on the side wall of the porous PS template because the profile of the nanoholes is not perfectly vertical to the substrate. These problems are usually solved by making undercut structure to prevent the metal from being deposited on the side wall; however, the weak etching property

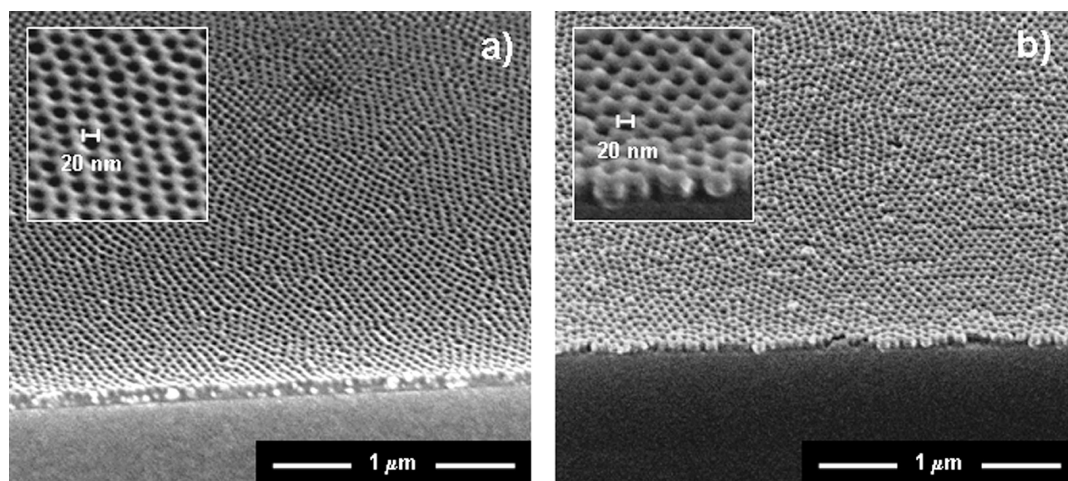


Figure 3. SEM micrographs of (a) PMMA nanotemplate imprinted by SiO<sub>2</sub> nanopillar mold. (b) PMMA nanotemplate of which the residual layer was removed by O<sub>2</sub> plasma using Cr mask deposited by angled evaporation. Both inset images are the high-magnification SEM images. All of the images are 45° tilted views.

of the PS template does not allow such process. Our solution to this problem is based on an observation that it is difficult for the ions in RIE plasma to reach the bottom of the nanoholes in the PS template under moderate conditions, which is due to the high aspect ratio of the nanoholes and the small hole openings. Therefore, by inserting a Cr RIE etching step before the lift-off in organic solvent, as shown in processing flows in Figure 1, we confirmed that the lift-off was thoroughly completed in only 1 min while leaving the Cr dots at the bottom of the nanoholes. Well-defined and uniform SiO<sub>2</sub> nanopillars, shown in Figure 2c, fabricated by further etching of the SiO<sub>2</sub> layer after the lift-off are clear evidence of this successful process, and we were able to fabricate densely packed SiO<sub>2</sub> nanopillar structures with 1:10 aspect ratio. Because of the freedom to insert a hard etch mask for the fabrication of both polarity patterns, the aspect ratio and the shape of the SiO<sub>2</sub> nanostructure are easily controllable, and the pattern transfers to the substrate materials other than SiO<sub>2</sub> are also possible, simply by choosing the appropriate metal masks that are resistant to the RIE chemistry for etching the target layer. Additionally, the dimensions of resultant SiO<sub>2</sub> nanostructures are also tunable using appropriate self-assembled block copolymer templates, of which the dimensions are controlled by the molecular weight and composition.<sup>9</sup>

**Nanoimprinting Polymer Resist on Arbitrary Substrates.** The nanoimprint molds of both pattern polarities made in SiO<sub>2</sub> described above can be used to fabricate various functional nanostructures. For example, using the nanopillar mold fabricated here, it is straightforward to reproduce the high density nanohole patterns similar to that produced by the block copolymer self-assembly process in essentially any polymers in a short time by using the NIL technique. As shown in Figure 3a, a PMMA template with densely packed nanoholes was generated by a simple thermal nanoimprinting step using a

nano-pillar mold at a temperature of 180 °C and a pressure of 600 psi within a few minutes. To use them as masks for further pattern transferring into a substrate or to produce a porous PMMA membrane, the residual layer of the imprinted PMMA pattern could be easily removed by a subsequent O<sub>2</sub> plasma after an angled deposition of a metal mask such as Cr on top of the imprinted PMMA to reinforce the etching resistance, as shown in Figure 3b.

**Conjugated Polymer Pattern Fabrication for OPV.** Vertically oriented sub-20 nm nanohole and nanopillar structures made in conjugated polymers are highly desirable structures for organic photovoltaic (OPV) cells. To achieve high efficiency OPV cells, it is most essential to produce interpenetrating networks of an electron-donor and an electron-acceptor material. It is desirable to limit the size of each domain to within the exciton diffusion length, which has been measured to be 4–20 nm.<sup>24–28</sup> By making such controlled nanoscale morphology between the donor and the acceptor, and having the donor–acceptor interface vertically oriented to the cathode and the anode,<sup>29</sup> the excitons can be fully dissociated to electrons and holes and can be efficiently transported to the electrodes before recombination. Here, as an initial effort to produce the ideal interdigitated interface structure, we attempted to imprint directly a regioregular poly(3-hexylthiophene) (rr-P3HT) polymer having high crystallinity. This material is one of the most widely used donor materials in making the OPV cells. Figure 4 shows that the fabrication of sub-20 nm hole- and pillar-type nanostructures in conjugated polymer is possible using the SiO<sub>2</sub> molds of both polarity patterns. Though there have been several works to fabricate rr-P3HT nanodomains using NIL,<sup>30,31</sup> the structures reported here are the smallest and approach the exciton diffusion length, which will permit us to effectively study the exciton diffusion length effect of the OPVs. The nanoimprint process, carried out at 185 °C

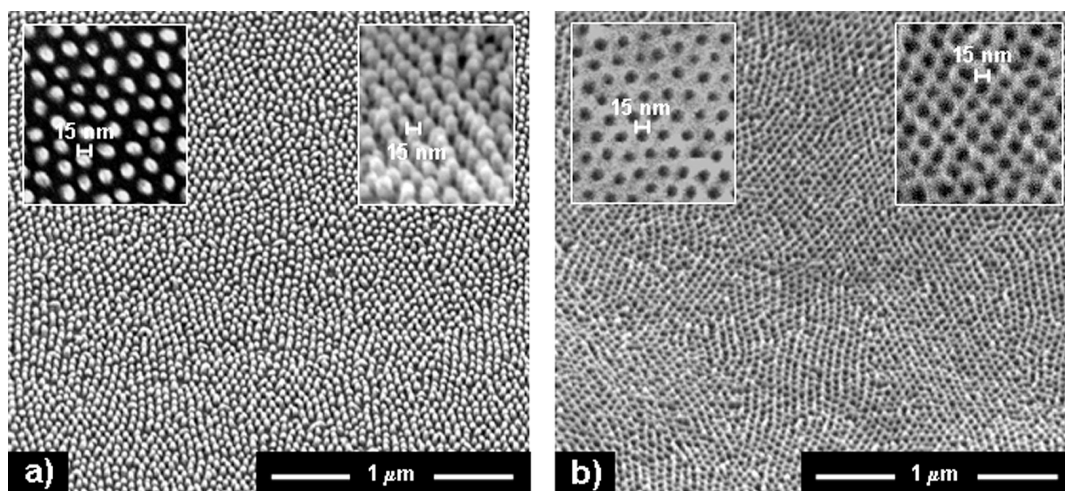


Figure 4. SEM micrographs of (a) imprinted P3HT nanopillars with 15 nm diameter (aspect ratio  $\sim 2.5$ ) taken at  $45^\circ$  tilted view. The inset images on the left and right provide high-magnification top view and  $75^\circ$  tilted view, respectively. (b) The  $45^\circ$  tilted view of imprinted P3HT nanoholes with 15 nm diameter. The left and right inset images are high-magnification top view and  $45^\circ$  tilted view of the structure, respectively.

and 750 psi, is successful despite the fact that the high crystallinity of the rr-P3HT may prevent the polymer chains from flowing easily. The aspect ratio of the imprinted P3HT nanostructures can be controlled by adjusting the imprint temperature, time, and pressure. The effectiveness of these ordered nanostructures to the performance of the OPV cell is currently under investigation.

**Application for Soft Lithography and Plasmonic Nanostructure Fabrication.** Flexible PDMS nanostructures, which are useful tools for soft lithography and transparent nanotemplate, were also successfully fabricated by using the  $\text{SiO}_2$  molds of both hole and pillar polarities. The soft lithography technique has been widely used for pattern transferring and capillary force lithography. However, the fabrication of soft mold with tens of nanometer scale has been very challenging. As shown in Figure 5, large area soft stamps having dense 20 nm features

of both pattern polarities were successfully fabricated. The nanoscale feature replication was possible due to the use of a hard PDMS layer possessing a higher modulus. Higher modulus is necessary to effectively prevent the collapsing of the replicated nanopatterns.<sup>32</sup> Our PDMS nanostructures can also act as transparent templates, and we discuss a simple technique to fabricate plasmonic metal nanostructures. Plasmonic nanostructures have been exploited in many photonic applications such as biosensors<sup>21</sup> and photovoltaics<sup>22</sup> due to their unique capabilities of localizing light at nanoscopic dimensions.<sup>33</sup> Though reproducible metallic nanoparticle arrays have been demonstrated by using the NIL technique,<sup>34</sup> creating denser and much smaller particle sizes for many practical applications has been very challenging by using this approach. We show that high density sub-20 nm size Ag and Au plasmonic nanostructures were successfully fabricated simply by

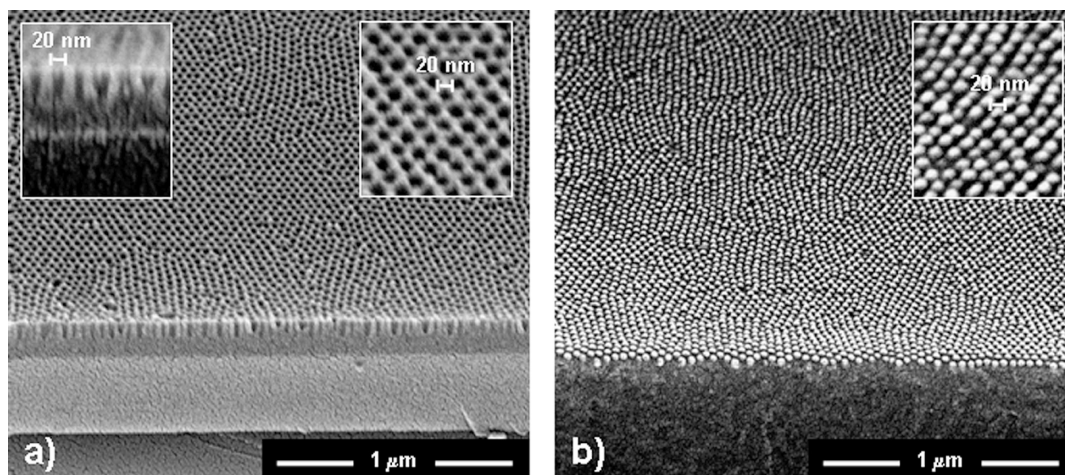


Figure 5. SEM micrographs showing (a)  $45^\circ$  tilted view of the nanohole-type PDMS soft stamp imprinted by  $\text{SiO}_2$  nanopillar mold. The left and right inset images are the high magnification  $85^\circ$  and  $45^\circ$  tilted views, respectively. (b) The  $45^\circ$  tilted view of the nanohole-type PDMS soft stamp imprinted by  $\text{SiO}_2$  nanohole mold. The inset image is the  $45^\circ$  tilted view with high magnification.

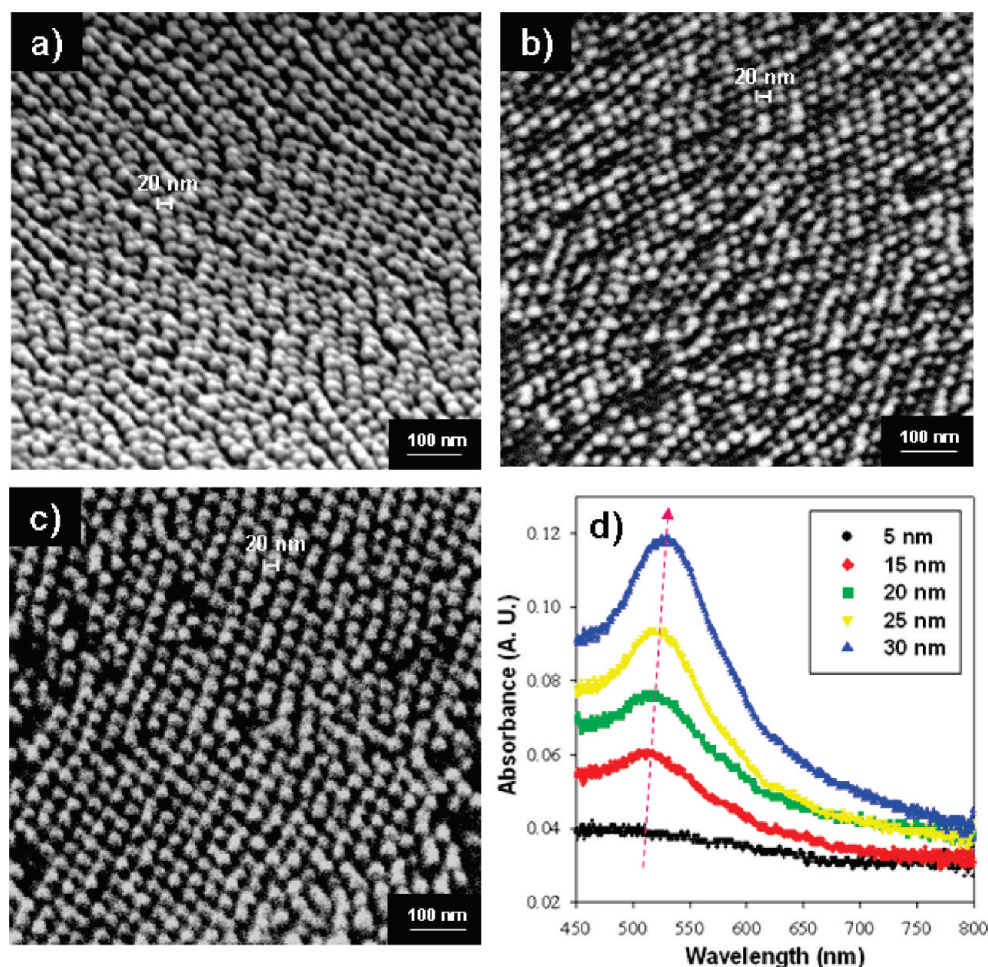


Figure 6. SEM micrographs of 45° tilted view of (a) Ag and (b) Au plasmonic nanoparticles deposited on nanopillar-type PDMS stamp by shadow evaporation. (c) Au nanoparticles transferred to a PMMA layer on a substrate. (d) Extinction spectra of the Au plasmonic nanoparticles for different Au thicknesses. With increasing Au thickness, the peak of the localized surface plasmon resonance is red-shifted along with an increase in the magnitude of light extinction.

an angled deposition of metal onto the nanopillar structures on the transparent PDMS (Figure 6a,b). Moreover, the position and the peak extinction of the localized surface plasmon resonance (LSPR) of our Au nanoparticles were tunable by changing the thickness of the metal, as shown in Figure 6d. Another strong merit of this approach is that it is possible to transfer those metallic nanostructures to arbitrary polymer layers by making use of the low surface tension property of the PDMS soft stamp. For example, a high density plasmonic Au nanoparticle was transferred onto a PMMA layer, as shown in Figure 6c. These unique advantages provide useful ways to fabricate large area controllable as well as reproducible plasmonic nanostructures on arbitrary polymer substrates in a short processing time. Currently, we are investigating the use of such plasmonic nanoparticles in OPV devices.

## CONCLUSIONS

In summary, densely packed, high aspect ratio nanopillar and nanohole SiO<sub>2</sub> structures were successfully fabricated using block copolymer template, and their versatile utilities for nanoimprint lithography were

demonstrated. Because it is well-known that the block copolymer pattern formation and the NIL are scalable, our process can be extended to large area applications. Block copolymer nanotemplate was used to produce a nanohole-type SiO<sub>2</sub> mold by using the angle-deposited Cr mask that reinforced self-assembled patterns formed in block copolymer and to produce a nanopillar-type SiO<sub>2</sub> mold using a novel lift-off method to utilize the Cr island masks left at the bottom of the template. Additionally, these successful applications of the Cr mask in these processes made it possible to freely control the aspect ratio of those etched structures by changing the RIE conditions. Nanoimprint lithography using those SiO<sub>2</sub> nanostructures provided an effective way to replicate block copolymer like high density and large area nanopatterns on arbitrary substrates using various polymers (e.g., conjugated polymers) in short processing time. In addition, the nanostructured PDMS stamps fabricated by using the SiO<sub>2</sub> molds are promising tools for soft lithography and can be applied to fabricate useful structures such as tunable plasmonic nanoparticles.

## METHODS

**Block Copolymer Nanotemplate.** Si wafers with 500 nm thick thermal oxide having the size of 1.2 cm × 1.2 cm were used as substrate for the block copolymer self-assembly and subsequently for NIL mold fabrication. Note that the process can be easily extended to larger substrates without degradation of pattern quality. These substrates were cleaned in a hot piranha solution (1:1 mixture of H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub>) for 1 h and were subsequently washed with deionized water for 30 min. After the cleaning process, the substrate surface was modified by using the PS-*r*-PMMA random copolymer. The PS-*r*-PMMA layer was spin-coated on the substrate and subsequently thermally annealed at 165 °C for 48 h in a vacuum. After the annealing, the substrate was washed by toluene to remove unreacted random copolymer. After the surface treatment, a thin film of PS-*b*-PMMA diblock copolymer (molecular weight 73 000 g/mol, polydispersity 1.07, PS volume fraction 70%, thickness ~30 nm) was spin-coated and annealed at 185 °C for 24 h to develop cylindrical nanodomains oriented normal to the surface. The PMMA domains in the nanostructure were selectively removed by O<sub>2</sub> plasma (20 sccm O<sub>2</sub>, 12 mTorr chamber pressure, and 30 W bias power). The resultant PS nanostructure was used as a starting template for the subsequent pattern transferring to the SiO<sub>2</sub> layer.

**Pattern Transfer into SiO<sub>2</sub> Layer for NIL.** To fabricate nanohole arrays in SiO<sub>2</sub>, a 5 nm thick Cr was deposited with an incident angle of 45° to the PS template at a rate of 2 Å/s using an electron-beam evaporator. After the Cr deposition, RIE (50 sccm C<sub>2</sub>F<sub>6</sub>/50 sccm He/60 sccm Ar/10 sccm O<sub>2</sub>, 60 mTorr chamber pressure, and 50 W bias power) was performed to etch the SiO<sub>2</sub> layer using the Cr pattern as an etch mask.

In order to fabricate a SiO<sub>2</sub> pillar structure, 5 nm Cr was deposited normal to the PS template at a rate of 2 Å/s using the electron-beam evaporator. Subsequently, RIE (25 sccm Cl<sub>2</sub>/5 sccm O<sub>2</sub>, 10 mTorr chamber pressure, and 30 W bias power) was used to etch the Cr layer that was deposited on the top and the side walls of PS template. Cr dots remained at the bottom of the PS nanoholes as discussed in the Results and Discussion section. Then a lift-off step was performed by immersing the sample in toluene for 1 min at room temperature. It was easily observed that all PS templates were quickly dissolved in toluene. Using the remaining Cr dots as an etch mask, the SiO<sub>2</sub> layer was etched by RIE to produce dense nanopillars by using the same etch condition as that used to fabricate the SiO<sub>2</sub> hole structures.

**NIL Using Molds of Both Pattern Polarities Made in SiO<sub>2</sub>.** In order to fabricate a nanoimprinted polymer nanotemplate, PMMA solution in toluene was spin-coated on a substrate to an appropriate thickness (as determined by the feature depth on the mold) and imprinted in a Nanonex NX2000 nanoimprinter (Princeton, NJ) at a pressure of 600 psi and a temperature of 180 °C for 5 min by using SiO<sub>2</sub> nanopillar mold. Every SiO<sub>2</sub> mold used in the NIL experiment was treated with surfactant, (tridecafluoro-1,1,2,2-tetrahydrooctyl)trichlorosilane (GELEST). After depositing a 5 nm thick Cr at a rate of 2 Å/s in an electron-beam evaporator with an incident angle of 45° to the substrate, the residual layer of the imprinted polymer template was removed by an anisotropic O<sub>2</sub> plasma etch (20 sccm O<sub>2</sub>, 12 mTorr chamber pressure, and 30 W bias power).

Both nanohole and nanopillar PDMS stamps were fabricated using the nanopillar and nanohole SiO<sub>2</sub> molds, respectively. After treating the substrate by methoxysilane having vinyl groups, a high modulus PDMS solution<sup>32</sup> was dropped on the substrate and subsequently covered by the SiO<sub>2</sub> mold. The PDMS was cured at 120 °C for 5 min under a pressure of 5 psi.

Poly(3-hexylthiophene) (P3HT) was purchased from Rieke metal (4002E grade) and spin-coated on a PEDOT:PSS layer (Clevis PH 500) that was also spin-coated on the ITO-coated PET. The P3HT layer was imprinted in a custom-built nanoimprinter (750 psi, 185 °C, 15 min). All of the area imprinted by SiO<sub>2</sub> molds showed the uniform nanostructure.

**Plasmonic Nanoparticle Fabrication.** Both Ag and Au nanoparticles were fabricated by depositing metals on PDMS nanopillar structures with an angle using an electron-beam evaporator at a rate of 1 Å/s. To transfer the metal nanoparticles to other sub-

strates, the nanostructured PDMS soft stamp, covered by the deposited metal nanoparticles, was pressed onto a polymer layer under 100 °C and 20 psi for 5 min in Nanonex NX2000 nanoimprinter.

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## REFERENCES AND NOTES

- Ross, C. A. Patterned Magnetic Recording Media. *Annu. Rev. Mater. Res.* **2001**, *31*, 203–235.
- Coakley, K. M.; McGehee, M. D. Conjugated Polymer Photovoltaic Cells. *Chem. Mater.* **2004**, *16*, 4533–4542.
- Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. Efficient Photodiodes from Interpenetrating Polymer Networks. *Nature* **1995**, *376*, 498–500.
- Henzie, J.; Lee, J.; Lee, M. H.; Hasan, W.; Odom, T. W. Nanofabrication of Plasmonic Structures. *Annu. Rev. Phys. Chem.* **2009**, *60*, 147–165.
- Striemer, C. C.; Gaborski, T. R.; McGrath, J. L.; Fauchet, P. M. Charge- and Size-Based Separation of Macromolecules Using Ultrathin Silicon Membranes. *Nature* **2007**, *445*, 749–753.
- Martin, C. R. Nanomaterials: A Membrane-Based Synthetic Approach. *Science* **1994**, *266*, 1961–1966.
- Shimizu, T.; Xie, T.; Nishikawa, J.; Shingubara, S.; Senz, S.; Gösele, U. Synthesis of Vertical High-Density Epitaxial Si(100) Nanowire Arrays on a Si(100) Substrate Using an Anodic Aluminum Oxide Template. *Adv. Mater.* **2007**, *19*, 917–920.
- Hawker, C. J.; Russell, T. P. Block Copolymer Lithography: Merging “Bottom-Up” with “Top-Down” Processes. *MRS Bull.* **2005**, *30*, 952–966.
- Bates, F. S.; Fredrickson, G. H. Block Copolymer Thermodynamics: Theory and Experiment. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525–557.
- Huang, E.; Rockford, L.; Russell, T. P.; Hawker, C. J. Nanodomain Control in Copolymer Thin Films. *Nature* **1998**, *395*, 757–758.
- Ryu, D. Y.; Shin, K.; Drockenmuller, E.; Hawker, C. J.; Russell, T. P. A Generalized Approach to the Modification of Solid Surfaces. *Science* **2005**, *308*, 236–239.
- Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. Imprint Lithography with 25-Nanometer Resolution. *Science* **1996**, *272*, 85–87.
- Guo, L. J. Nanoimprint Lithography: Methods and Material Requirements. *Adv. Mater.* **2007**, *19*, 495–513.
- Jeong, S.-J.; Xia, G.; Kim, B. H.; Shin, D. O.; Kwon, S.-H.; Kang, S.-W.; Kim, S. O. Universal Block Copolymer Lithography for Metals, Semiconductors, Ceramics, and Polymers. *Adv. Mater.* **2008**, *20*, 1898–1904.
- Black, C. T.; Guarini, K. W.; Breyta, G.; Colburn, M. C.; Ruiz, R.; Sandstrom, R. L.; Sikorski, E. M.; Zhang, Y. Highly Porous Silicon Membrane Fabrication Using Polymer Self-Assembly. *J. Vac. Sci. Technol., B* **2006**, *24*, 3188–3191.
- Gowrishankar, V.; Miller, N.; McGehee, M. D.; Misner, M. J.; Ryu, D. Y.; Russell, T. P.; Drockenmuller, E.; Hawker, C. J. Fabrication of Densely Packed, Well-Ordered, High-Aspect-Ratio Silicon Nanopillars over Large Areas Using Block Copolymer Lithography. *Thin Solid Films* **2006**, *513*, 289–294.
- Black, C. T.; Ruiz, R.; Breyta, G.; Cheng, J. Y.; Colburn, M. C.; Guarini, K. W.; Kim, H.-C.; Zhang, Y. Polymer Self Assembly in Semiconductor Microelectronics. *IBM J. Res. Dev.* **2007**, *51*, 605–633.
- Guo, L. J. Topical Review: Recent Progress in Nanoimprint Technology and Its Applications. *J. Phys. D: Appl. Phys.* **2004**, *37*, R123–R141.
- Kang, M.-G.; Guo, L. J. Metal Transfer Assisted Nanolithography on Rigid and Flexible Substrates. *J. Vac. Sci. Technol., B* **2008**, *26*, 2421–2425.

20. Kang, M.-G.; Kim, M.-S.; Kim, J.; Guo, L. J. Organic Solar Cells Using Nanoimprinted Transparent Metal Electrode. *Adv. Mater.* **2008**, *20*, 4408–4413.
21. Nath, N.; Chilkoti, A. A Colorimetric Gold Nanoparticle Sensor to Interrogate Biomolecular Interactions in Real Time on a Surface. *Anal. Chem.* **2002**, *74*, 504–509.
22. Morfa, A. J.; Rowlen, K. L.; Reilly, T. H., III; Romero, M. J.; van de Legemaat, J. Plasmon-Enhanced Solar Energy Conversion in Organic Bulk Heterojunction Photovoltaics. *Appl. Phys. Lett.* **2008**, *92*, 013504.
23. Ting, Y.-H.; Park, S.-M.; Liu, C.-C.; Liu, X.; Himpfel, F. J.; Nealey, P. F.; Wendt, A. E. Plasma Etch Removal of Poly(methyl methacrylate) in Block Copolymer Lithography. *J. Vac. Sci. Technol., B* **2008**, *26*, 1684–1689.
24. Halls, J. M.; Pichler, K.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. Exciton Diffusion and Dissociation in a Poly(*p*-phenylenevinylene)/C<sub>60</sub> Heterojunction Photovoltaic Cell. *Appl. Phys. Lett.* **1996**, *68*, 3120.
25. Pettersson, L. A. A.; Roman, L. S.; Inganäs, O. Modeling Photocurrent Action Spectra of Photovoltaic Devices Based on Organic Thin Films. *J. Appl. Phys.* **1999**, *86*, 487–496.
26. Theander, M.; Yartsev, A.; Zigmantas, D.; Sundström, V.; Mammo, W.; Anderson, M. R.; Inganäs, O. Photoluminescence Quenching at a Polythiophene/C<sub>60</sub> Heterojunction. *Phys. Rev. B* **2000**, *61*, 12957–12963.
27. Savenije, T. J.; Warman, J. M.; Goossens, A. Visible Light Sensitisation of Titanium Dioxide Using a Phenylene Vinylene Polymer. *Chem. Phys. Lett.* **1998**, *287*, 148–153.
28. Haugeneder, A.; Neges, M.; Kallinger, C.; Spirkl, W.; Lemmer, U.; Feldman, J.; Scherf, U.; Harth, E.; Gugel, A.; Mullen, K. Exciton Diffusion and Dissociation in Conjugated Polymer/Fullerene Blends and Heterostructures. *Phys. Rev. B* **1999**, *59*, 15346–15351.
29. Kim, M.-S.; Kim, J.-S.; Cho, J.; Stein, M.; Guo, L. J.; Kim, J. Flexible Conjugated Polymer Photovoltaic Cells with Controlled Heterojunctions Fabricated Using Nanoimprint Lithography. *Appl. Phys. Lett.* **2007**, *90*, 123113.
30. Cheyins, D.; Vasseur, K.; Rolin, C.; Genoe, J.; Poortmans, J.; Heremans, P. Nanoimprinted Semiconducting Polymer Films with 50 nm Features and Their Application to Organic Heterojunction Solar Cells. *Nanotechnology* **2008**, *19*, 424016.
31. Aryal, M.; Buyukserin, F.; Mielczarek, K.; Zhao, X.-M.; Gao, J.; Zakhidov, A.; Hu, W. Imprinted Large-Scale High Density Polymer Nanopillars for Organic Solar Cells. *J. Vac. Sci. Technol., B* **2008**, *26*, 2562–2566.
32. Pina-Hernandez, C.; Kim, J.-S.; Guo, L. J.; Fu, P.-F. High-Throughput and Etch-Selective Nanoimprinting and Stamping Based on Fast-Thermal-Curing Poly(dimethylsiloxane)s. *Adv. Mater.* **2007**, *19*, 1222–1227.
33. Maier, S. A. Plasmonics—Towards Subwavelength Optical Devices. *Curr. Nanosci.* **2005**, *1*, 17–22.
34. Lucas, B. D.; Kim, J.-S.; Chin, C.; Guo, L. J. Nanoimprint Lithography Based Approach for the Fabrication of Large-Area, Uniformly Oriented Plasmonic Arrays. *Adv. Mater.* **2008**, *20*, 1129–1134.