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Programmable Soft Lithography: Solvent-Assisted Nanoscale Embossing

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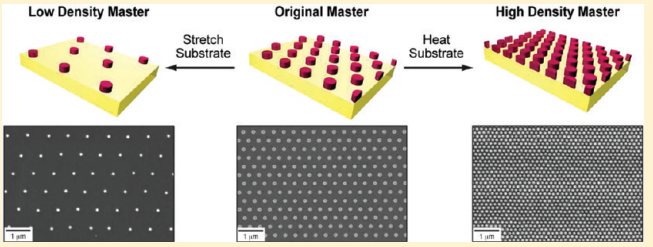
Supporting Information

ABSTRACT: This paper reports an all-moldable nanofabrication platform that can generate, from a single master, large-area nanoscale patterns with programmable densities, fill factors, and lattice symmetries. Solvent-assisted nanoscale embossing (SANE) could increase the spacing of patterns up to 100% as well as decrease them down to 50% in a single step by stretching or heating a polymer substrate. Also, SANE could reduce critical feature sizes as small as 45% compared to the master by controlled swelling of patterned molds with different solvents. These capabilities were applied to generate plasmonic nanoparticle arrays with continuously variable separations and hence different optical properties on the same substrate.



KEYWORDS: Nanopatterning, nanomolding, nanoparticle array, surface plasmon

Molding as a means to replicate functional and artisanal masters can be traced from the manufacturing of Mesopotamian tools to the casting of Renaissance statues. Recently, molding at the nanoscale has driven the production of high-density optical and magnetic storage media,[1,2] organic light-emitting diodes,[3,4] polymer photovoltaic cells,[5,6] and field-effect transistors.[7−9] Although rigid molds can imprint soft and semi-hard materials,[10,11] they are expensive to create and brittle at nanoscale dimensions. Elastomeric molds have also been used to pattern soft materials,[12−16] but their feature sizes are mostly limited to submicrometer dimensions.[17,18] However, what all current molding methods have in common is that their primary goal is to generate replicas of the master. Therefore, if different features are desired, new masters are necessary to create every new pattern.

Here we report an all-moldable nanofabrication platform that can generate, from a single master, nanoscale patterns with programmable densities, fill factors, and lattice symmetries. Solvent-assisted nanoscale embossing (SANE) was able to increase the spacing of patterns up to 100% as well as decrease them down to 50% in a single step. Furthermore, SANE could reduce critical feature sizes as small as 45% compared to the original master by controlled swelling of elastomeric SANE molds with different solvents. Both the pattern densities and fill factors can be tuned continuously at will. We applied these new capabilities to create plasmonic nanoparticle arrays[19] with variable separations and whose properties depend critically on particle spacing. SANE combines the strengths of serial fabrication techniques (prototyping patterns, high resolution) with those of parallel ones (high throughput, large patterned areas). Thus, SANE enables unprecedented opportunities to manipulate electronic, photonic, and magnetic properties of nanomaterials by providing a low-cost, scalable route to large-area, nanoscale patterns.

Figure 1 summarizes how SANE is an all-polymer, parallel nanofabrication technique that can create at least four classes of different patterns from a single master: (i) arrays with higher densities; (ii) arrays with lower densities; (iii) arrays with the same densities but with smaller critical feature sizes; and (iv) arrays with different lattice symmetries. SANE can thus generate a wide-range of new masters and patterns that are easily transferred into functional materials and devices by conventional fabrication methods. To demonstrate these inclusive capabilities of SANE, we selected a large-area (6 in. diameter) polyurethane (PU) master molded with hexagonal arrays of posts[16] (diameter d_0 = 180 nm, height h = 330 nm, pitch a_0 = 400 nm) (Figure 1A,B). The elastomer poly(dimethylsiloxane) (PDMS) was then cast against the master to create PDMS molds either for SANE, where the PDMS mold is first wet with solvent and then placed into contact with a photoresist-coated substrate, or for inSANE, the inverse strategy, where a PDMS mold is wet with photoresist and then placed into contact with a substrate (Figure 1C). Both SANE and inSANE can produce arrays of isolated photoresist nanopatterns.

inSANE is an approach for designing new substrates with array densities (while keeping the feature sizes constant) different from that of an original master. The critical step is that inSANE creates patterns on flexible substrates whose properties can be

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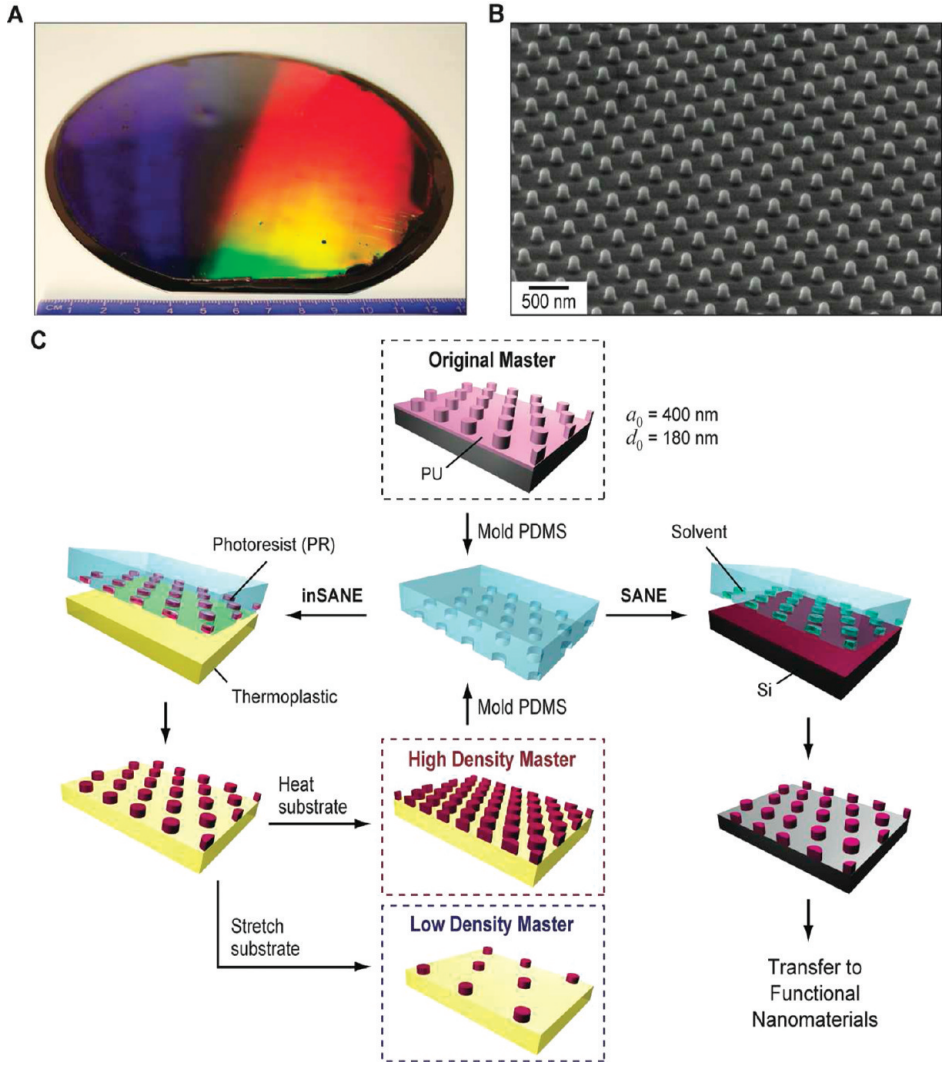

Figure 1. Programmable soft lithography: Solvent-assisted nanoscale embossing. (A) Optical micrograph of a 6 in. diameter PU master with pitch a_0 = 400 nm and feature size d_0 = 180 nm. (B) SEM image of a portion of the PU master in panel A. (C) Scheme of the nanofabrication procedure to create high-density and low-density masters using inverse SANE (inSANE) and to produce patterns with features smaller than (but with the same pitch as) a master using SANE.

manipulated by external means (Supporting Information Figure S1). Figure 1C depicts a scheme of inSANE on thermoplastic substrates (Shrink Film, prestressed polystyrene)[20] where the separation between adjacent photoresist patterns was decreased if the thermoplastic film was uniformly heated or increased if the thermoplastic was mechanically stretched. Depending on the array properties of interest, SANE molds could then be generated either from these new high- or low-density masters or from the original master. Typically, SANE was carried out on hard substrates such as silicon (Si) so that the photoresist nanopatterns could be transferred into functional materials for future applications.

Figure 2 highlights representative examples of how photoresist patterns (Shipley 1805) with lattice spacings different from the master (a_0 = 400 nm) can be created by inSANE. Note that the feature sizes remained the same as those on the original master (Figure 2A), but the total percentage change of separations possible was 400% (new spacings a = 200−800 nm). To wet the inSANE mold with photoresist without affecting the sizes of the patterned features, we reconstituted the Shipley 1805 resist with ethanol (Supporting Information); otherwise, the organic solvent[21] contained in the resist would swell the PDMS mold as well as dissolve the thermoplastic substrate. The inSANE mold was placed in contact with the substrate for 20 min at room temperature to solidify the photoresist patterns as the ethanol evaporated through the PDMS. Any residual photoresist film was removed with a short oxygen plasma (15 s).

To create patterns with higher array densities, we heated the patterned resist on Shrink Film in a convection oven at 115 °C; after 20 min, the thermoplastic substrate shrank by 30%, and the lattice spacing also decreased by 30% (Figure 2B, $a = 0.70 \times a_0$ = 280 nm). Hence a new master (covering >10 cm^2) was readily achieved with a density 100% higher ($\rho = 1.5 \times 10^9$ features/cm^2) than the original pattern ($\rho = 7.3 \times 10^8$ features/cm^2). After a longer heating time (40 min), the Shrink Film decreased in size by 50%, and the array spacing also decreased by 50% (Figure 2C, $a = 0.50 \times a_0$ = 200 nm). Thus another master with a density 300% higher ($\rho = 2.9 \times 10^9$ features/cm^2) than the original could be formed. Significantly, the percentage decrease on the nanoscale was easily determined by measuring the macroscale change.

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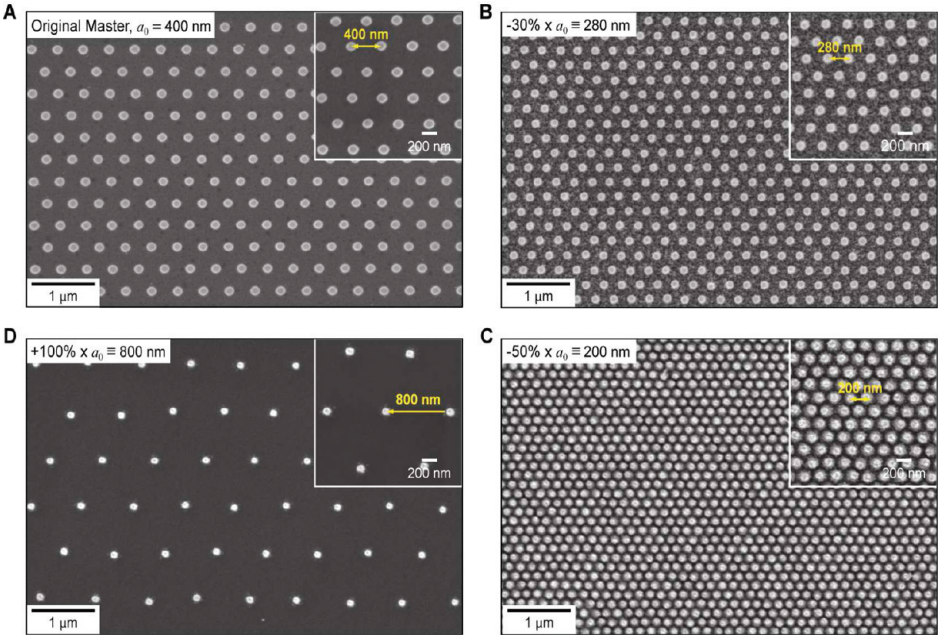

Figure 2. New masters with different pattern densities from the same original master using inSANE and tunable substrates. SEM images of (A) original master and new masters with pitches that are (B) smaller (−30%), (C) smaller again (−50%), and (D) larger (+100%) than that of the original master (a_0 = 400 nm).

The maximum shrinkage possible of the Shrink Film is around 60%.[20] This unique approach to reduce the distances between isolated features is not limited to the nanoscale; we also created microscale patterns and reduced their pitch to result in higher density microarrays (Supporting Information Figure S2).

To produce arrays with lower densities, we heated the inSANE-patterned photoresist on the Shrink Film at 115 °C and also mechanically stretched the substrate. Uniform stretching of the film in two perpendicular directions produced a low-density master with spacings up to 100% greater than the original pattern ($a = 2.0 \times a_0 = 800$ nm) (Figure 2D) and densities 75% lower ($\rho = 1.8 \times 10^8$ features/cm^2). The generation of low-density masters starting from a higher density pattern cannot readily be achieved by conventional soft lithography because (i) stretched PDMS molds will not only change the pitch but also the lateral and vertical sizes of the patterned features[22] and (ii) the decreased patterned heights prohibit further transfer to other materials. Low-density patterns with anisotropic lattice symmetries could also be fabricated by stretching in only one dimension (Supporting Information Figure S3).

In addition to increasing and decreasing pattern density (while preserving feature size) using inSANE, SANE can create patterns with the same density but with smaller feature sizes. Thus, SANE generates arrays with different fill factors. SANE works by transforming a perceived disadvantage of PDMS, that the polymer swells in the presence of different solvents, into an advantage. In a nanopatterned PDMS mold, as the polymer regions increase in volume because of the solvent, the voids decrease. SANE molds were first wet with solvent (Supporting Information) and then placed into conformal contact with a thin layer (t = 200 nm) of photoresist (Shipley 1805) on a Si(100) wafer. The solvent trapped in the recessed wells of the PDMS mold caused both a reduction in size of the mold patterns (from PDMS swelling) and a dissolution of the photoresist film to fill the solvent wells.[23] After the solvent evaporated for 15 min, the mold was removed, and any residual resist between posts was removed by a 15 s oxygen plasma. Large-area SANE molds (>2 in^2) produced SANE patterns in photoresist that were extremely uniform (Figure 3A).

Solvents with different swelling factors can be defined by the factor S, which is the ratio of the length D of PDMS in the solvent to the length D_0 of the PDMS in air ($=D/D_0$).[21] Using the same SANE mold (from Figure 2A; original master d_0 = 180 nm, a_0 = 400 nm) and different solvents, we controlled the sizes of the patterned photoresist on Si (Figures 3B−D). For example, SANE using dimethylformamide ($S \sim 1.02$) resulted in features that were reduced in size by 22% ($d = 0.78 \times d_0 = 140$ nm) with a corresponding fill factor reduction of 40% (Figure 3B). When a solvent with a higher S was used for SANE, such as isopropyl alcohol ($S \sim 1.09$), the sizes of the photoresist posts decreased by 33% ($d = 0.67 \times d_0 = 120$ nm), and the fill factor decreased by 55% (Figure 3C). The largest size reduction that we achieved (while maintaining the integrity of the patterned mold and array) was 44% ($d = 0.56 \times d_0 = 100$ nm) using dichloromethane ($S \sim 1.22$), and the fill factor decreased by 70% (Figure 3D). For all three solvents, the pitch remained nearly the same with only small changes in some areas (<3 nm) although there were substantial decreases in feature size.

SANE (and inSANE) offer a programmable strategy to access nanostructured surfaces with nearly any type of pattern size, density, or lattice symmetry so that the prototyping of nanopatterns no longer has to be separated from the scaling of them. However, the value of any nanofabrication technique is in its ability to transfer the patterns into functional materials. We demonstrate how SANE can create photoresist patterns that can then be converted into large-area arrays of metal nanostructures using PEEL.[19] Figure 4 illustrates how nanoparticle arrays with different lattice spacings on the same substrate can be achieved. First, nanoparticle arrays were fabricated by deposition of 50 nm of gold through a nanohole array film on a Shrink Film

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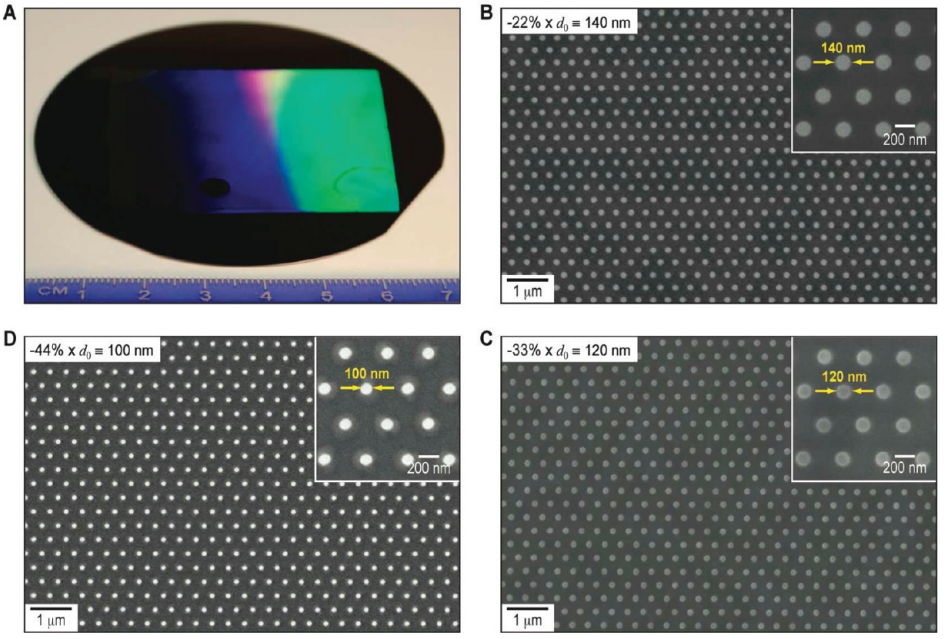

Figure 3. Reduction of feature sizes using SANE with different solvents. (A) Optical micrograph of a 3 in. Si wafer patterned with photoresist patterns by SANE. SEM images of patterns obtained after SANE using solvents with different swelling factors in PDMS (S): (B) dimethylformamide (S = 1.02, d = 140 nm), (C) isopropylalcohol (S = 1.09, d = 120 nm), and (D) dichloromethane (S = 1.22, d = 100 nm). The array spacing a_0 remained constant at 400 nm.

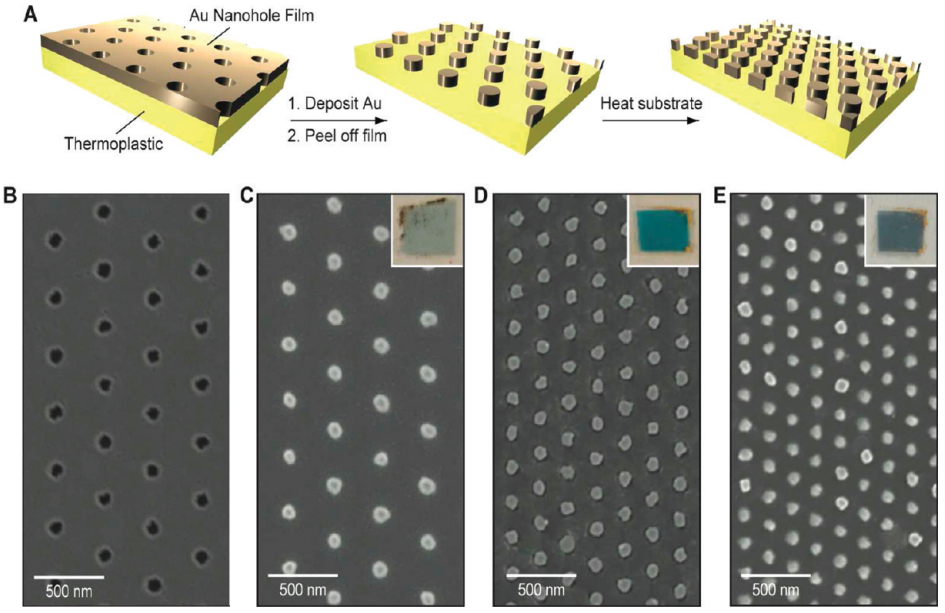

Figure 4. Nanoparticle arrays with different spacings on the same substrate. (A) Scheme to create high-density nanoparticle arrays starting from a gold nanohole array as a deposition mask followed by heating of the Shrink Film substrate. (B) SEM images of gold nanohole array mask (thickness = 100 nm) with 400 nm spacing. (C−E) SEM images of gold nanoparticle arrays with different pitches on the same Shrink Film substrate: (C) 400 nm (no heating), (D) 250 nm (film in (C) heated at 115 °C for 20 min), and (E) 200 nm (film in (D) heated for 20 min more). (Insets) Optical images of color change as the pitch between nanoparticles in the arrays was reduced.

(Figure 4B) followed by removal of the hole array.[19] The hole array was produced starting from SANE molds from the first master (a_0 = 400 nm, Figure 2A). Figure 4C indicates that the gold nanoparticles had diameters similar to those of the nanoholes (Figure 4B). Next, the Shrink Film substrate patterned with gold nanoparticles was heated to 115 °C for 25 min to reduce the separation between particles to a = 250 nm (Figure 4D). After a longer heating time (40 min), the Shrink Film further decreased the nanoparticle spacing to a = 200 nm (Figure 4E).

This reduction in array pitch (up to 50%) produced a large macroscopic difference in color (Figures 4C−E, insets). Optical transmission spectra of the nanoparticle arrays (superstrate water, n = 1.33) showed that the collective plasmon resonance blue shifted (Supporting Information Figure S4) because of

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dipolar coupling between particles in the array.[24] This nanoparticle array fabrication method opens a way to solve a challenge in plasmonics: to control the spacing between nanoparticles continuously on the same substrate. Typically, if different separations are desired, new samples must be prepared for each new separation; however, we have overcome this problem by patterning nanoparticles directly on the thermoplastic films.

In summary, we have developed a simple yet potentially transformative method to create new nanoscale masters with variable spacings and feature sizes starting from a single master pattern. This programmability offers significant advantages over nanoimprint lithography and other molding methods in terms of cost and over direct-write nanolithography methods in terms of scalability. The ability to control nanostructure array densities and fill factors allows for the rapid prototyping and testing of plasmonic structures with tunable resonances, photovoltaic cells with enhanced absorption, and storage media with high capacities. Moreover, SANE represents a new paradigm to introduce nanofabrication capabilities into any lab because all the materials used are inexpensive, and the procedures can be carried out on the benchtop.

■ ASSOCIATED CONTENT

Supporting Information. inSANE on the flexible substrates; control of microscale pattern densities; control of lattice symmetries: one-dimensional stretching; and optical transmission spectra of high density nanoparticle arrays. This material is available free of charge via the Internet at http://pubs.acs.org.

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