Top-Down Approaches to the Formation of Silica Nanoparticle Patterns

Deying Xia, Dong Li, Zahyun Ku, Ying Luo, and S. R. J. Brueck*

Center for High Technology Materials, University of New Mexico, 1313 Goddard, SE, Albuquerque, New Mexico 87106

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This article reports a simple, versatile approach to the fabrication of lithographically defined mesoscopic colloidal silica nanoparticle patterns over large areas using spin-coating, interferometric lithography, and reactive-ion etching. One-dimensional nanoparticle films (bands) and 2D discs, diamonds, and holes with sub-micrometer periodicity, high quality, and excellent uniformity were successfully fabricated over large areas. The well-defined shape and period of the patterned nanoparticle film were controlled in the interferometric lithography step, while the thickness of nanoparticle film was easily tuned in the spin-coating step. This approach can extend to other deposition methods such as convective self-assembly, electrostatic self-assembly, and other materials such as metallic and ferromagnetic nanoparticles. We have also been able to generate sparse, random, isolated particle patterns, using a combination of interferometric lithography and layer-by-layer deposition as an extension of this approach to another deposition method, and to generate disc nanoparticle patterns using colloidal lithography as an extension of this approach to another lithography technique. These patterned films will find important applications in the fields of material growth, biosensors, and catalysis, as well as serving as building blocks for further fabrication.

Introduction

The fabrication of colloidal particle arrays in 2D and 3D arrangements has been extensively explored due to important applications in electronics,1,2 optical devices,3 chemical and biosensors,4,5 catalysis,6,7 and high-density magnetic and optical data recording materials.8,9 Nanoparticle arrays also serve as templates for designed nanostructures.10-12 In particular, patterned arrays and films consisting of colloidal particles are of practical significance in the fabrication of structures for photonic crystals13,14 and patterned material growth.15 Most reports have focused on template-directed colloidal self-assembly, as recently reviewed.14-17 It remains challenging to fabricate large-area mesoscopic patterns of nanoparticle films on flat surfaces with high quality and uniformity. Such control impacts macroscopic film properties, especially those important to sensor, catalytic, and optical applications. Lithographically defined self-assembled nanoparticle films on micro- and nanoscales have been reported only infrequently, and have not been studied in detail.18 In addition, patterns of randomly distributed, isolated particles will find applications in materials growth and biosensors.

Directed self-assembly combines “top-down” lithographic techniques such as laser interferometric lithography19 and electron-beam lithography,20 with “bottom-up” self-assembly techniques relying on chemical or physical driving forces. Most reports of directed self-assembly have focused on “bottom-up” oriented fabrication approaches in which optical lithography or nanosphere lithography21,22 is used to define a hard (e.g., SiO2)12,23 or a soft template (e.g., photolithography),24 and the colloidal particles are deposited in preferential locations on these patterned surfaces.14 Although well-defined patterns using large colloidal particles (>1 μm diameter) have been reported for research laboratory-scale production, the tedious fabrication processes, and nonuniform or noncontrollable thickness over a large area are restrictions for mass-fabrication and practical application of these approaches. Hard-template, directed self-assembly has issues with local defects and significant process overhead for etching into patterned surfaces and is inappropriate for formation of large regions of nanoparticle films (with at least one dimension >> nanoparticle diameter). The soft-template directed self-assembly we have reported previously has drawbacks including an “edge-high” effect (lifting of the nanoparticle pattern from the substrate at pattern edges), the difficulty of filling 2D patterns, and poor uniformity for films with small nanoparticles over large areas.24 A technique that enables fabrication of large area patterns

* To whom correspondence should be addressed. E-mail: brueck@chtm.unm.edu.

of nanoparticle films on flat surfaces with high-quality, controllable thickness, and high uniformity has yet to be demonstrated. A variety of approaches such as gravity sedimentation,20 electrostatic self-assembly,25,26 convective deposition,27 and physical confinement12,28 have been developed to deposit colloidal particles into periodic 2D patterns and 3D crystals. The spin-coating-driven assembly of colloidal particles is fast, inexpensive, consumes very small volumes of colloidal suspension, and is suitable for the wafer-scale batch microfabrication.29–31 Using spin-coating, it is easy to fabricate particle films and porous structures with high uniformity and controllable thicknesses over large, wafer-scale areas.32,33 Electrostatic self-assembly [layer-by-layer (LbL) deposition] is an alternative process for forming nanoparticle films with controlled thicknesses. The LbL method provides accurate control of the deposition density and thickness at the expense of a relatively long deposition time and the consumption of larger volumes of material.

Interferometric lithography (IL), the interference of a small number of coherent optical beams, is a powerful technique for fabrication of a wide range of samples of interest for nanoscience and nanotechnology.34–36 IL provides an inexpensive, large-area capability as a result of its parallelism.

Reactive-ion (plasma) etching (RIE) is widely used in semiconductor processing. Even though RIE also has been used to transfer patterns in nanoparticle lithography,37,38 it remains a challenge to use RIE to transfer mesoscopic patterns into continuous nanoparticle films with lithographically defined patterns as masks.

Here, we report a simple, inexpensive approach to combining bottom-up self-assembly and top-down lithography to fabricate nanoparticle film patterns with sub-micrometer periodicity. A uniform nanoparticle film is first self-assembled, and then lithographically defined photoresist patterns are formed atop the nanoparticle film and transferred by etching. In this work, we primarily make use of spin-coating-driven self-assembly, IL, and RIE to define mesoscopic patterns of silica nanoparticles on a flat surface. 1D and 2D patterns of nanoparticle films have been successfully demonstrated. We also employed LbL deposition as an example of the extension of this approach to deposit sparse, localized, random particle distributions and thin nanoparticle films. Finally, we employed colloidal nanoparticle lithography (CL) as an example of the extension of this approach to fabricate disc-shaped nanoparticle film patterns.39 CL uses self-assembled arrays of colloidal particles as masks to fabricate various nanostructures with deposition and/or etching through the interstitial pores between the particles. CL is inexpensive, is inherently parallel, and is capable of high throughout, but long-range order is less certain than for a top-down lithographic approach.

A major aspect of the work reported here is the demonstration of a manufacturable technology for the production of nanoparticle patterns with high uniformity across large, wafer-scale areas. This is a significant step toward the capabilities required for realistic applications.

**Experimental Section**

The experimental procedure for producing lithographically defined, mesoscopic colloidal nanoparticle patterns on flat surfaces includes three main steps: spin-coating, IL, and RIE (see illustration in Figure S1 in Supporting Information). The resulting film morphology was observed by scanning electron microscopy (JEOL 6400F).

**Formation of Silica Nanoparticle Films via Spin-Coating.** Si wafers were used for these experiments. A Si wafer was cleaned with piranha solution with a volume concentration ratio of H₂SO₄/H₂O₂ of 3:1 (caution: corrosive, dangerous) to remove any residual organic contamination. A thin layer of a metal such as Cr was deposited on the clean samples by e-beam evaporation to a thickness of ~10 to 50 nm. The metal layer served as an etch stop in the final etch step to prevent the reactive-ion etching of the Si substrate, since the RIE gas mixture of O₂ and CHF₃ etches both Si and SiO₂. If a different substrate material such as sapphire is used, the metal layer is not necessary.

The next step was to spin-coat the wafer with aqueous suspensions of colloidal nanoparticles. Silica nanoparticle films were used in these experiments because they are commercially available, inert to most organic solvents, and compatible with both silicon microfabrication and biological processes.40,41 Both 50- and 15-nm diameter silica nanoparticles (Nissan Chemical America Corp.) were used. In most cases, a ~5 wt % 50-nm silica suspension was spun at 4000 rpm for 30 s. The thickness of the resulting colloidal nanoparticle film was determined by the particle size, colloidal concentration, spin speed, and number of cycles of the spin-coating process. After spin-coating, the sample was baked for 5 min at 95 °C to drive off any absorbed water.

**Preparation of Polymer Photoresist Patterns on Silica Nanoparticle Films Using IL.** IL was used to produce photoresist (PR) patterns atop the nanoparticle films. After the nanoparticle film was deposited on the substrate, an antireflection coating (ARC) layer and a PR layer were spun onto the samples. The ARC layer is used to minimize reflection of the IL beams from the substrate, eliminating vertical standing wave patterns. Two different ARCs (XHRiC-16, Brewer Science, Inc.; wet-i 10-7, Brewer Science, Inc.) were used. In most experiments, the wet-i ARC was used due to its simpler process requirements (wet-i ARC is removed selectively in the photore sist develop step, eliminating the need for a separate ARC etch step). An isotropic O₂ plasma-etch process was used to etch the XHRiC-16, resulting in the decrease of the photoresist feature size in both the horizontal and vertical directions. Either positive PR (SPR 505A, Shipley, Inc.) or negative PR (NR7-500P, Futurrex, Inc.) was applied to the ARC layered samples. Subsequently, IL was used to produce the PR patterns. The patterning process involved exposure, postexposure bake, and develop. The pattern period was adjusted by changing the angle between the two coherent laser IL beams. For square 2D patterns, a double exposure with a 90° rotation of the sample was performed; all the other steps were the same as those for the 1D patterns. Hole patterns were fabricated using negative PR 500P, while post (disc) patterns were formed using positive PR 505A. Hexagonal patterns (holes or discs) were produced when the second exposure was applied to the sample.
with a 60° rotation; rectangular patterns of holes or discs could be produced when the second exposure was applied to the sample with a different period from that of the first exposure at a 90° rotation; the relative doses of the two exposures controlled the ellipticity of the holes (posts).

RIE. RIE was used to remove the exposed silica particle regions, while the IL-defined photoresist protected mesoscopic regions of the silica particle film from the RIE. A mixture of O₂ and CHF₃ (50:130) was used to etch the silica particles at a power of 100 W. The etching time is a function of the particle film thickness and particle size. After the RIE step, piranha solution was used to remove the PR/ARC patterns. In some cases, particularly for larger features, ARC was not used, and then acetone was used to remove the PR after the RIE step. A high-temperature calcination (700–900 °C) was also suitable for removal of the PR/ARC patterns.

Formation of Random Particle Distribution and Nanoparticle Film Using a LbL Approach. The polyelectrolytes for LbL were products of Alfa-Aesar. The polycation was poly(allylamine hydrochloride) (PAH) with 6 k molecular weight (MW), and the polyanion was poly(styrene sulfonate acid) sodium (PSS) with MW 70 k. The polycation (PAH) and polyanion (PSS) aqueous solutions were ~3 mg/mL. In LbL, the sample was immersed into polyelectrolytes aqueous solution to alternately adsorb oppositely charged components. At the beginning of the process, three layers of linear polyelectrolytes are adsorbed onto substrate to make the surface uniformly charged. Next, negatively charged silica particles were assembled in alternation with an oppositely charged polycation solution. The typical sequence of the alternate immersion was: PAH (10 min) + PSS (20 min) + PAH (10 min) + silica particle suspension (10 min). For these experiments, the silica particle diameter was 80 nm. After each immersion in polycation, polyanion, silica aqueous solution, the sample was rinsed with DI water for 1 min to drive away any unadsorbed polyelectrolytes and silica particles. We also performed multiple-cycle depositions with the LbL method. The experimental procedure for forming thick nanoparticle film with multiple-cycle deposition is: after the first sequence of PAH/silica, repeat of PAH/silica alternative deposition was carried out to form the nanoparticle film with multiple-cycle depositions with the LbL method. The experimental procedure for forming thick nanoparticle film with multiple-cycle deposition is: after the first sequence of PAH/silica, repeat of PAH/silica alternative deposition was carried out to form the nanoparticle film with multiple-cycle depositions with the LbL method.

Results and Discussion

1D Silica Nanoparticle Films. IL is a very promising low-cost, reliable, and scalable technology for the fabrication of nanoscale periodic patterns over large areas. IL Defined Nanoparticle Patterns. Silica nanoparticles (50 nm diameter) were spin-coated at 4000 rpm for 30 s onto a Si substrate with a thin Cr layer using a 5 % silica suspension. PS particles (460 nm diameter, Bangs Laboratories, Inc.) were then spun on top of the silica nanoparticle film using ~5 wt % PS suspension with 4000 rpm for 30 s. The subsequent RIE was the same as above to etch the silica nanoparticle films.

A thin metal layer such as Cr was deposited on a Si substrate prior to spin-coating the nanoparticle film to avoid etching the Si substrate during the RIE process as a result of the poor selectivity for RIE between Si and SiO₂. The RIE duration, t, for complete etching of unprotected film regions depends on the film thickness; the partially etched particles were formed in the upper particle layer in the unprotected regions while a spherical-particle array was preserved in the PR-protected regions. In preliminary experiments, the etching results with time for 90-nm thick silica nanoparticle films were carried out on a Si substrate in the absence of a metal protection layer (see Figure S2 of the Supporting Information). At shorter etching times, the etching is obviously incomplete; cleared 1D patterns were formed at an appropriate etching time. If further etching was performed, nearly vertical edge profiles were achieved and partial etching into the Si substrate was observed. The poor selectivity between Si and SiO₂ was confirmed after HF removal of silica particle films in the PR-protected region.

If a metal layer was used as a stop barrier to eliminate etching of the substrate, the width of silica particle bands after RIE etching was the same as the original width of PR walls over a relatively large range of RIE times due to the thick PR/ARC layers and the directional properties of the RIE process. 1D mesoscopic nanoparticle films were easily fabricated with this approach using Cr metal as an etch-stop barrier. Figure 1 shows several examples of 1D patterns of nanoparticle films. Figure 1A,B shows images of a thin film (90–100 nm, roughly corresponding to a two-layer-thick nanoparticle film) pattern after one cycle of spin-coating with ~5 wt % 50-nm silica particle suspensions. The etching time was 6 min, which was estimated from the experimental etching parameters in Figure S2. The thickness of silica particle films was more easily controlled by the number of cycles of spin-coating rather than by the spin speed. Even thinner films can be obtained through higher spin speed or more dilute particle suspension, even though it is difficult to form a perfect monolayer-thick film because of the large-diameter variations of the available silica nanoparticles.

Smaller silica nanoparticles and a smaller period pattern were also tested for this approach, as shown in Figure 1C–F. The smaller silica nanoparticles were 15 nm in diameter, and the period of the 1D patterns was about 350 nm. With such small silica nanoparticles, the uniformity of films was much improved.
and the final patterned film bands displayed excellent uniformity over a large area. The thickness of films was also more easily controlled with these smaller nanoparticles. Narrower film bands could be obtained with the use of undevelopable ARC (XHRiC-16) and RIE etching through the ARC layer, as well as through the nanoparticle film, as shown in Figure 1C,D. An isotropic O₂ plasma etch process was used to etch the XHRiC-16, resulting in a decrease of the photoresist feature size in both the horizontal and vertical directions. After the RIE step for an ARC layer, the width of the unprotected bands was increased and thus the width of final particle bands became narrower. The ratio of the width of particle occupied bands to the width of unoccupied bands was decreased to 1:3, as shown in Figure 1C. The sharply defined thick nanoparticle bands are clear as shown in Figure 1D. Much thinner film bands are easier to fabricate using these smaller nanoparticles and dilute nanoparticle suspension, as shown in Figure 1E,F. The concentration of 15-nm silica nanoparticle suspension used here was ~1 wt %, and the thickness of films was ~30 nm (~2 particle thick) after 4k rpm for 30 s. For such thin films, the RIE time for complete removal of silica particle films in unprotected regions was dramatically decreased to ~1 min. Finally, thin, wide bands of silica nanoparticle films (high aspect ratio in x-direction) were fabricated. The period and width of nanoparticle bands with such smaller silica nanoparticles can be extended to the nanoscale (less than 50 nm) with recent developments in immersion IL, as well as with a shorter-wavelength laser source. 

Patterned silica nanoparticle films can be formed on other types of substrates. If a sapphire substrate was used for the formation of silica nanoparticle film patterns, the metal layer was not necessary, as shown in Figure 2. Patterned films with high uniformity could be formed over a typical sample size as large as 2 × 2 cm², as seen in Figure 2A (set by practical considerations in our laboratory-scale system and not a limiting value for the technique). For a silica particle pattern on a sapphire substrate without a metal layer, almost perfectly clean regions of final particle bands became narrower. The ratio of the width of particle bands to the width of unoccupied bands was decreased to 1:3, as shown in Figure 1C. The sharply defined thick nanoparticle bands are clear as shown in Figure 1D. Much thinner film bands are easier to fabricate using these smaller nanoparticles and dilute nanoparticle suspension, as shown in Figure 1E,F. The concentration of 15-nm silica nanoparticle suspension used here was ~1 wt %, and the thickness of films was ~30 nm (~2 particle thick) after 4k rpm for 30 s. For such thin films, the RIE time for complete removal of silica particle films in unprotected regions was dramatically decreased to ~1 min. Finally, thin, wide bands of silica nanoparticle films (high aspect ratio in x-direction) were fabricated. The period and width of nanoparticle bands with such smaller silica nanoparticles can be extended to the nanoscale (less than 50 nm) with recent developments in immersion IL, as well as with a shorter-wavelength laser source.

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Spin-Coating. The three steps (spin-coating, IL, and RIE) in this approach determine the morphology of the final patterned films. The only special feature for IL in this approach compared with our previous work is that the polymer patterns were produced on silica nanoparticle films instead of on flat Si or SiO₂ surfaces. The roughness of silica nanoparticle films (~50 nm) was not a significant factor for the current pattern feature (~500 nm) and silica nanoparticle sizes (~50 nm). Even for the pattern feature size between 300 and 500 nm, the influence of surface of silica nanoparticle film on IL-defined patterns was minimal. Here, we focus on the step of spin-coating of silica nanoparticle suspension.

Spin-coating is used to produce very thin and uniform films of photoresist as an important step in semiconductor fabrication. This process is also finding applications in the production of optical, magnetic recording media, and other material processing. The spin-coating technique described here has a number of advantages over other self-assembly techniques for the formation of (ordered) particle films. First, it is rapid and highly manufacturable; second, spin-coating is applicable to both large and small diameter spheres. For large silica spheres, the spin-coating technique overcomes the rapid gravitational sedimentation issues encountered with other deposition methods. For small silica spheres, the particle film using spin-coating technique has high uniformity and tunable thickness over wafer-scale areas.

Bornside et al. divided spin-coating (for a homogeneous material such as photoresist) into four stages: deposition, spin-up, spin-off, and evaporation. An excess of liquid is dispensed on the surface during the deposition stage. In the spin-up stage, the liquid flows radially outward. In the spin-off stage, excess liquid flows to the perimeter and leaves as droplets. As the film thins, the rate of removal of excess liquid by spinning slows down because the viscosity increases with the increased concentration of the nonvolatile components. Finally, evaporation takes over as the primary mechanism of thinning. During spin-up, inertia overpowers the force of gravity. During spin-off, the tendency to form uniform thickness of liquid arises due to the balance between the two main forces: inertia, which drives flow radially outward, and viscous force (friction), which acts radially inward. The change in concentration of the nonvolatile components during the evaporation stage affects the hydrodynamics through the dependence of viscosity on concentration of the nonvolatile components. In general, the viscosity of many of these solutions has been reported to be a power-law function of the concentration.

The spinning procedure creates a steady forced convection in the vapor above the substrate. The evaporation rate in spin-coating tends to be quite uniform. A spun film arrives at its final thickness by evaporation after the film becomes so thin and viscous that its radial flow is halted. According to this model of spin-coating, the final thickness for Newtonian fluids (linear relationship between shear stress and shear rate) is

\[ h_{\text{final}} = c_0 \left( \frac{3\eta e}{\rho_0 \omega^2 (1 - c_0)} \right)^{1/3} \]

where \( c_0 \) is the initial concentration of the nonvolatile components, \( \eta \) is the viscosity, \( e \) is the evaporation rate that depends on the mass transfer coefficient, \( \rho_0 \) is initial value of the mass of volatile solvent per unit volume, and \( \omega \) is spin speed. Even though this model was designed to address continuum fluids, we find that it provides useful insight into the spin-coating deposition of nanoparticles (of diameter comparable to the film thickness) from a colloidal suspension.

The evaporation rate, \( e \), in eq 1 depends strongly on how fast the vapor phase above the liquid is removed and, therefore, is


dependent on the spin speed. The simplest model suggests that the rate of evaporation is related to the rate of airflow over the surface as \( \dot{e} \propto \omega^{1/2} \). Substituting into eq 1, the final thickness, \( h_{\text{final}} \), is proportional to the \(-1/2\) power of the spin speed. This is true especially for high spin speed, and there is no dependence on initial height of the liquid.\(^{47}\) In addition, the final thickness is linearly proportional to initial concentration, \( c_0 \), if \( c_0 \) is sufficiently small.

We have investigated the final thickness of silica nanoparticle films as a function of spin speed, concentration, and particle size on a flat surface. The spin speeds tested were 3k, 4k, 5k, and 6k rpm. Two concentrations (5 and 10 wt %) and two particle sizes (50 and 15 nm diameter) were examined. The thickness of films was measured with both ellipsometry and SEM images. In the ellipsometer technique, a nine-point measurement was performed across a relatively large area of the sample. In SEM examination, the thickness of films was measured from cross section views at 6–10 different positions across a relatively small area of each sample. The trend of thickness for silica nanoparticle film as a function of spin speed was the same for both measurement methods (see Table S1 and S2 of the Supporting Information). We believe that the data for film thickness was accurate for high speed, small particle size, and high concentration because at these experimental conditions, the thickness of nanoparticle film over large area was more uniform and easier to measure.

The film thickness is inversely proportional to the square root of spin speed, as shown in Figure 3 for SEM measurements. This agrees well with the model prediction. Both the packing density and the particle size distribution impact the observed film thicknesses. As the water evaporates past each layer of nanoparticles, capillary forces drive the particles into contact and form the final pattern; both particle size distributions and defects in the pattern leave spaces between particles, so that the final thickness deviates from ideal, hexagonal close-packed, digital expectations. Overall, these depositions resulted in three- and four-layer thick films of silica nanoparticles for 50-nm particles, and 6- to 12-layer thick films for 15-nm particles. In addition to the control of nanoparticle film thickness with concentration and spin speed, multiple cycles of spin-coating processing is a simple way to control the film thickness. There is a linear relationship of film thickness to the number of cycles of spin-coating. Therefore, the nanoparticle film thickness can be controlled easily by changing the spin speed, concentration, and number of cycles of spin-coating.

2D Films of Silica Nanoparticles. An important advantage of IL is that it is easy to produce 2D patterns using double exposures. After the first exposure, the sample was rotated by 90° and exposed for a second time to produce the 2D square array patterns with holes or posts depending on photoresist types and doses. If the angles between two beams of laser were same for these two exposures, the holes or posts are circular; if the angles between two beams of laser were different for these two exposures, the holes or posts are elliptical. In addition, a hexagonal 2D pattern could be prepared with the rotation angle 60° for the second exposure.

Figure 4 shows an example of 2D square patterns of holes obtained using negative PR. Connected PR periodic patterns (period: ~500 nm) with empty holes (~350 nm diameter) were formed on 180-nm thick films composed of 50-nm silica nanoparticles, as shown in Figure 4A. The PR patterns were formed over a large area with high uniformity, as shown in Figure 4B. The thick PR patterns served as protective layers for the silica nanoparticle films during the RIE process. After RIE and removal of PR/wet-i, connected periodic patterns with empty holes were produced. With sufficient RIE time, the holes were clean without particles and the feature sizes were maintained after etching, as shown in Figure 4C.D. Square patterns of these 2D structures over a larger area are shown (Figure 4E). From the side view, we can see that about four layers of silica nanoparticles were kept after etching as in Figure 4F.

Isolated 50-nm silica nanoparticle film discs and diamonds with a 1000-nm period were fabricated using this approach with positive PR, as shown in Figure 5. The images in Figure 5A–C show diamond-shaped films using a shorter develop time with wet-i ARC in IL, while the image in Figure 5D show disc-shaped films using a relatively long developing time with wet-i ARC in IL. After double exposures with positive PR, isolated PR posts were formed in a well-connected wet-i network at first with a relatively short developing time (Figure 5E, classified as a type-I pattern); as the developing time increases, the wet-i patterns became isolated diamond patterns while the PR was developed to round posts (Figure 5F, type-II pattern); for longer develop times, the wet-i diamond decreased to a size smaller than the top layer PR post patterns (type III patterns). During the RIE processing, the PR post patterns are thinned in both height and diameter. However, the O2 etching did not etch the wet-i patterns. Therefore, for type I and II patterns, the wet-i layer controls the final silica film pattern; while for type III patterns, the PR layer determines the final film pattern. With accurate
control of the develop time and the wet-i prebake step which controls the develop characteristics, different silica film patterns were formed using this approach. The wet-i ARC layer forms a relatively larger square shape which determines the final film patterns in the RIE processing, as shown in Figure 5A–C (type II pattern). The diamond has a $5 \times 5$ or $6 \times 6$ array of 50-nm diameter silica nanoparticles. In Figure 5D (type III patterns), each disc has $\sim 16 - 20$ silica nanoparticles. The number of particles within each disc is determined by the ratio $D/r$ of the disc $D$ and particle $r$ diameters. Type III patterns are the most tolerant to variations in the lithography process and could be formed with better uniformity over larger areas than the other patterns.

The evolution of patterned films with develop time was confirmed, as well for the samples with 15-nm silica nanoparticles, as shown in Figure 6. Figure 6A shows an image of well-connected patterned films (type-I) even though the positive PR was used. The transition state between type I pattern and type II pattern is indicated in Figure 6B. The type II pattern is shown in Figure 6C, while the type III pattern is clearly seen in Figure 6D. As we mentioned above, the smaller the silica nanoparticles and the larger the pitch of pattern, the more uniform the film patterns are as seen in Figure 6E. The thickness of 15-nm silica nanoparticle film was about 30 nm (Figure 6F, $\sim 2$ particles high).

In the IL step, other patterns can easily be fabricated. Figure 7 shows two examples of these nanostructures. 2D hexagonal patterns of connected networks with empty holes are shown in Figure 7A–C. To form the hexagonal patterns, the second exposure was rotated by 60° instead of the 90° used for square patterns. After double exposure and development, a hexagonal pattern of empty holes with exposed underlying silica nanoparticle films was produced. After RIE and removal of PR/wet-i, hexagonal patterns on silica nanoparticle films were formed on flat surfaces. From the top view image shown in Figure 7A, we can see that perfect hexagonal patterns of connected silica nanoparticle network with empty holes were obtained over a large area. The patterned silica films were easily observed from the images of tiled and side views, as shown in Figure 7B,C. Two-layered silica nanoparticle films were maintained after formation of hexagonal patterns with the processing of RIE and piranha treatment as shown in Figure 7C. The pitch based on the angle between two laser beams in IL step is the height of the equilateral triangle rather than the length of a side of the triangle. So, if the pitch in IL was $P$, then the lattice constant, $a$, in the hexagonal pattern was $(2\sqrt{3}/3)P$. An example of a different nanostructure is the elliptical hole pattern shown in Figure 7D–F. In the preparation of this kind of structure, the second exposure was rotated by 90° but exposed at a different pitch than the first exposure. Thus, the resulting pattern consists of elliptical holes with different periods in the $x$ and $y$ directions. After spin-coating and lithography, elliptical hole patterns were formed using negative PR. From top view image as in Figure 7D, the elliptical hole patterns are obvious with a long axis of 1000 nm (black arrow direction) and short axis of 500 nm (white arrow direction). Rectangular patterns of elliptical holes in a two-layer packed nanoparticle film were easily fabricated. By controlling the exposure parameters, rectangular patterns of circular holes can be prepared as well.

**Extensions of This Approach.** In the current experiments, we have adopted spin-coat driven self-assembly to deposit nanoparticle films on the flat surface of the Si wafer. Other deposition methods besides spin-coating, such as electrostatic and convective self-assembly are also applicable for the film formation. The patterned silica particle structures can be used for fabrication of hybrid microstructures from aligned carbon nanotubes and silica particles as in a recent demonstration by Ramanath et al. Convective deposition is an effective approach for the formation of colloidal crystals with monodisperse particle distributions. Convective and electrostatic deposition methods...
are much slower than spin-coating and consume a bulk volume of the particle suspension.

A random layer of nanoparticles has applications in the life sciences; patterning would improve the detection capacity and sensitivity for biomolecular species. We explored electrostatic deposition (LbL) instead of spin-coating driven deposition as one example of the extensibility of this approach. The IL and RIE steps are same as the above experiments. The results are shown in Figure 8. Patterned, isolated particle islands were formed using spin-coating with dilute particle suspension. The LbL is an effective method for pattern formation of random isolated particles. Images in Figure 8A–C show 1D patterned random 80-nm silica nanoparticle using the combination of LbL, IL, and RIE. Before the IL step, randomly placed, isolated silica particles were deposited on a Si substrate atop a thin metal layer, as shown in Figure 8A. The density of particles depends on the deposition time, particle surface charge, particle concentration, particle size, and polyelectrolyte. We used a large period (1.4 μm) for 1D patterns to define the PR in IL step in order to have obvious patterns superimposed on the random particle distribution. After the IL step, the 1D bands of random particles were clearly observed in Figure 8B. After a 5-min RIE and removal of PR/wet-i patterns, the desired 1D bands of random, 

Figure 6. SEM images of evolution process with developing time for 2D hole, diamond, and disc patterns of 15-nm silica nanoparticle films with 1000 nm period using positive PR 505A and wet-i after RIE 6 min: (A–E) top views; developing time increases from (A) to (D); (A) holes; (B) pseudo-diamond; (C) diamond; (D) discs; (E) magnified images of diamond patterns; (F) tilted 45° view of a single diamond.

Figure 7. SEM images of 2D hole patterns with 90-nm thick 50-nm silica nanoparticles after 6 min RIE. (A–C) 2D hexagonal hole patterns with 1000-nm period: (A) top view; (B) tilted 45° view; (C) side view; (D–F) 2D rectangular patterns of elliptical holes with 1000- (black arrow direction) and 500-nm (white arrow direction) periods; (D–E) top view with a long period along horizontal direction; (F) tilted 45° view with the long period in the vertical direction.

Figure 8. SEM images of 1D patterns on Si substrates above a thin Cr layer using LbL deposition. (A–C): 80-nm silica random and isolated nanoparticles with a 1.4 mm period; (A) random distribution formed by LbL before using IL and RIE, tilted 45° view; (B) PR/wet-i patterns on random silica particles after IL step, side view; (C) 1D bands of random silica nanoparticles after 5-min RIE and removal of PR/ARC layer; (D—F) 15-nm silica nanoparticles with 1000-nm period, (PAH/silica) 5 LbL deposition and 1.5-min RIE; (D) tilted view of PR patterns on silica nanoparticles; (E) top view of 1D bands; (F) side view of 1D bands.

isolated silica particles were obtained, as shown in Figure 8C (also see Figure S3A of the Supporting Information). Here, we not only confirmed that this approach can extend to other particle deposition methods such as LbL, but also we can produce the 1D bands of random, isolated particles. We believe that complex patterns (1D and 2D periodic patterns) with micrometer-scale and nanoscale resolution of the periodic non-close-packed colloidal crystals can be made by combination of spin-coating, IL, and RIE for potential device applications.\(^{33}\)

We further used the LbL approach to deposit monolayer film of small silica nanoparticle (~15 nm) to form patterned nanoparticle films. The experimental results are shown in Figure 8D–F. When a 50 mg/mL silica nanoparticle suspension was used with the LbL approach, 1D bands of non-close-packed monolayer-thick silica nanoparticles were successfully fabricated at a 500-nm period (see Figure S3B of the Supporting Information). Compared with spin-coating driven deposition, the LbL approach is likely to form loose- or non-close-packed monolayers because the electrostatic force in LbL approach acts primarily in the vertical direction while the capillary forces in spin-coating act in the horizontal direction. The 1D patterns with isolated, random nanoparticles were also formed with diluted silica suspension (10 mg/mL) (see Figure S3C of the Supporting Information). The silica nanoparticle films could be formed with LbL approach through repeating the immersion the sample in PAH and silica solution. Figure 8D–F shows the example of (PAH/silica)\(_{n}\) deposition. Dense, thick silica nanoparticle films were deposited on a flat substrate with multiple depositions. Thus, we can control the thickness of nanoparticle film through the number of bilayer of PAH and silica, as well as the adsorption time.\(^{49}\) After IL, RIE, and removal of PR, 1D bands of nanoparticle films with ~30-nm thickness were formed with period of 1000 nm.

We also explored CL as an alternative to IL as a second example of the extension of this approach.\(^{39}\) The spin-coating driven deposition and RIE steps are same as the above experiments. The results are shown in Figure 9.

After deposition of 50-nm silica nanoparticle film, we used spin-coating to deposit 460-nm diameter PS spheres atop the silica nanoparticle films. A monolayer of hexagonally close-packed 460-nm PS spheres was formed atop a two-layer 50-nm silica nanoparticle film, as shown in Figure 9A. Defect-free domains of several to a few hundred square micrometers (see Figure S4 of the Supporting Information) were formed.\(^{50}\) There are many well-developed and mature deposition methods to form large-area, uniform monolayer or multiple-layer colloidal spheres crystals in this range of particle diameter.\(^{27,51–53}\) After a 5-min RIE with O\(_2\) and CHF\(_3\), non-close-packed hexagonal silica nanoparticle discs with etched PS spheres were formed on a substrate, as shown in Figure 9B. While the RIE with O\(_2\) and CHF\(_3\) was carried out through the interstices between PS spheres, the PS spheres would be etched down small size due to the composition of RIE. The degree of shrinkage of the PS spheres and their morphology depend on the RIE conditions (time, composition, power, etc.) and PS crystal orientation.\(^{38}\) After removal of etched PS particles with piranha solution or high-temperature calcination (400 °C, 2 h), non-close-packed hexagonal silica nanoparticle film discs were obtained with ~2-layer thick nanoparticle patterned films, as shown in Figure 9C,D. Additional silica nanoparticle film patterns will be achieved with the number of PS layers, crystal orientation, and RIE conditions in CL defined nanoparticle film. With combination with conventional lithography (tens or hundreds of micrometers), we can realize hierarchical patterning with nanoscopic and microscopic length scales so that multi-scale nanopattern-based devices can be fabricated for applications.\(^{54}\)

Conventional optical lithography is also suitable for pattern formation. Because the feature size in conventional lithography can be adjusted from the ~50 nm scale (currently) to micrometers and even millimeters, the pattern and particles sizes for formation colloidal patterns and crystals can be extended across this entire range of sizes. A combination of spin-coating of approximately hundreds of nanometer diameter silica—monomer solution, proximity photolithography and RIE has been developed to produce well-defined features of macroporous polymer film and planar colloidal crystals for potential device applications.\(^{32,33}\) The combination of convective deposition of approximately hundreds of silica particles, photolithography, and RIE also could pattern the colloidal crystal into a microscale device for specific device applications.\(^{55}\) We believe that the microphotonict crystal devices and chips can be developed using some deposition methods, photolithography, and RIE.\(^{56}\) Furthermore, it is easy to fabricate hierarchical structures combining IL for nanoscale features with conventional optical lithography for larger features.

In the etching step, patterned nanoparticle films with other kinds of materials may be formed through wet etching process using appropriate solvents or through other gas compositions in RIE. For example, Au and Ag particle films can be wet-etched with aqueous Fe\(^{3+}/\text{thiourea}.\(^{40}\) Another example is FePt particle pattern formation with wet removal with an appropriate solvent such as hexane.\(^{57}\) In these cases, probably, the metal protection layer is not necessary due to the selectivity of the etching processes.

This method overcomes the "edge-high" effect (lifting of the film at feature edges) and difficulty in filling nanoscale holes in

template-directed self-assembly using IL. Colloidal nanoparticle films are formed on flat surface instead of patterned surface. Using this approach, patterned films were formed over large areas with high uniformity.

Conclusions

We report a simple, versatile approach for fabricating lithographically defined mesoscopic colloidal silica nanoparticle patterns over large areas using spin-coating, IL, and RIE. 1D nanoparticle film bands and 2D discs, diamonds, and holes with sub-micrometer periodicity and excellent uniformity were successfully fabricated over square centimeter and larger areas. The thin nanoparticle film patterns with a short period, and some unique nanostructures such as hexagonal 2D patterns, and 2D rectangular patterns of elliptical holes can be generated through controlling processes in the IL step. This approach is very suitable for formation of patterned nanoparticle films with a low defect density and high uniformity. The thickness of the nanoparticle film can be controlled easily in the spin-coating step. This approach can extend to other deposition methods such as convective and electrostatic deposition, other lithography methods such as colloidal lithography, and other kinds of nanoparticles such as metals. We believe the approach can be extended to pattern formation with larger particles in range of ~200 nm and above using appropriate colloidal particle deposition methods, optical lithography, and RIE. We have demonstrated the formation of the patterned isolated particles, and patterned nanoparticle films with the combination of LbL deposition, IL, and RIE. Using LbL deposition in this approach, a thin nanoparticle film, as thin as a monolayer, could be generated with the various patterns and the patterned sparely isolated particle distribution was fabricated as well. We also have demonstrated the formation of non-close-packed hexagonal nanoparticle discs with combination of spin-coating, CL, and RIE with monolayer PS spheres. We believe various types of patterning of nanoparticle films will be achieved with CL of multiple-layer and different orientation of PS crystals. These patterned films will find technological application in material growth, biosensors, catalysts, nanodevice, and as building blocks for further nanofabrication.

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Supporting Information Available: SEM images of etching results of patterned films on Si substrate without a metal layer, LbL, CL approach and tables of thickness of silica nanoparticle film vs spin speed. This material is available free of charge via the Internet at http://pubs.acs.org.