Fabrication of enclosed nanochannels using silica nanoparticles

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We report a simple and inexpensive approach to the fabrication of enclosed nanoscale channels composed of silica nanoparticles on planar Si surfaces using interferometric lithography to define the long-range pattern in a photoresist film followed by spin-coating self-assembly of colloidal silica nanoparticles and high-temperature calcination to remove the photoresist leaving open nanochannels. Channel structures with channel width and height ranging from ~100 nm to over 1 μm were formed over large areas with different particle sizes and channel profiles. The dimensional scale of these ordered arrays of enclosed channels can be easily controlled through the parameters in the photoresist patterning and the spin-coating steps. Complex, multilayer structures have been generated using this approach as well. This process opens a route to fabricating ordered enclosed nanochannels with potential uses in photonics, molecular/biological sensors, biological separations and catalysis. © 2005 American Vacuum Society. [DOI: 10.1116/1.2130358]

I. INTRODUCTION

Microparticle and nano-particle assembly with two- and three-dimensional periodicity may find applications in photonic crystals, chemical sensors, catalysts, and biotechnology. Patterned surfaces can be used as hard templates to assist the self-assembly of not only relatively simple clusters but also complex and unique crystallization structures. Soft, polymer templates have been used for directed self-assembly of particle arrays on flat substrates. Using two different sizes of colloidal particles, binary colloidal crystals were fabricated. Microparticle and nanoparticles also have been used as templates for the preparation of porous metallic nanostructures and monodisperse colloidal crystals. Nanoscale porous metallic wires and tubes can be grown and prepared from alumina membranes through directed assemblies of nanoparticles. Three-dimensional structures with lattice constants and sizes ranging from several micrometers to millimeters, assembled with microparticle and nano-particles, also have been reported. Even though nanochannel structures for nanofluidic applications had been fabricated using thermal oxidation or nanoimprint, there are only a few reports of the fabrication of enclosed channels formed from nanoparticles. Here, we describe a simple and inexpensive approach to the fabrication of enclosed channels using silica nanoparticles on planar Si surfaces using standard semiconductor processing including spin-coating and interferometric lithography.

Interferometric lithography (IL) is an established, top-down, scalable technology for the fabrication of large areas of nanoscale periodic patterns. At the same time, bottom-up self-assembly techniques have been very successful at and below the nanoscale. The combination of these two approaches, directed self-assembly, is an interesting alternative for fabrication of complex micro- and nanostructures.

II. EXPERIMENTS

Figure 1 illustrates the scheme for directed self-assembly of silica nanoparticles into periodically enclosed channels on flat surfaces using interferometric lithography and spin coating. A developable bottom antireflection coating (BARC, wet-i) layer was spun onto a precleaned sample to minimize reflection of the IL beams from the substrate, eliminating vertical standing wave effects. The sample was baked at 200 °C for 90 s after spin coating the BARC layer. Both positive (Shipley SPR510A) and negative-tone (NR7-500P, Futurrex, Inc.) photoresists (PR) were used with appropriate spin and pre-bake conditions. IL with a 355 nm tripled...
yttrium–aluminum–garnet (YAG) laser source was used to produce the periodic patterns on this PR/wet-i film stack. Parallel PR/wet-i lines [one-dimensional (1D)] were formed on the Si wafer surface after the expose, bake, and develop cycle. After the PR patterning, silica nanoparticle colloidal dispersions were spin coated onto these samples at 4000 rpm for 30 s. Suspensions of three size distributions of silica nanoparticles were utilized for directed self-assembly of 1D periodic buried channel structures on flat surfaces. The suspensions were Snowtex colloidal silica (ZL~78 nm diameter; OL~50 nm diameter, and C~15 nm diameter) from Nissan Chemical Industries. Ltd diluted to a concentration of ~5 wt%. Each suspension was agitated for 5 min in an ultrasonic bath before spin coating. Several cycles of spin coating were employed to fill the spaces between walls of PR, and to form and control the thickness of the top sealing layer. The final fabrication step was to remove the PR/wet-i patterns, leaving 1D patterns of silica nanoparticles on the flat surface of the Si wafer. Calcination at high temperature was successful in completely removing the PR/wet-i while retaining the enclosed channel structures without collapse. Calcinations were carried out at 800 °C for 1.5–2 h. The multilayer channel samples (discussed below) were prepared by repeating multiple cycles of the PR patterning, spin coating and calcination. The resulting structures were characterized by field-emission scanning electron microscopy (FE-SEM) at 30 kV.

**III. RESULTS AND DISCUSSION**

The method presented here for the formation of channels with silica particle walls and tops was modified from the approach to directed self-assembly of patterns of nanoparticles reported previously. Additional cycles of spin coating with silica nanoparticle suspensions were employed to fill the voids between the photoresist (PR)/wet-i walls, and to cap the channels. High temperature calcination at 800 °C was used to remove the sacrificial polymers (PR/wet-i). Another advantage of the high temperature calcination was that it enhanced the mechanical stability of the structures as a result of some degree of sintering between the silica nanoparticles. Although, neck growth between silica particles between 700 and 950 °C was quite slow so that the overall shrinkage of lattice, which could lead to cracking, was small.

Figure 2 shows SEM images of the (a) photoresist and (b) and (c) of an enclosed silica nanoparticle channel array at different magnifications. While standing wave patterns on the PR sidewalls were minimized by the use of the wet-i layer, as seen from Fig. 2(a), minor standing wave patterns were observed. Additionally, the wet-i layer was somewhat over-developed (undercut). Aligned sidewalls of PR and wet-i could be achieved through careful control of the pre-exposure bake and the development parameters. Thin PR/wet-i walls (linewidth<space width) were formed using positive PR while thick PR/wet-i walls (linewidth>space width) were formed using negative PR. After the PR/wet-i grating was formed over a large sample area (~1 cm²), silica nanoparticle suspensions were applied to the photoresist-patterned sample using spin coating. Several cycles of spin coating with diluted silica suspensions were employed instead of one cycle of spin coating with a more concentrated silica suspension since this made it easier to ensure complete filling of the spaces between PR walls as well as to establish the thickness of the top layer.

The interaction of the colloidal suspension with the surface provided important feedback on the status of the deposition. For these 1D PR patterned samples for the first three cycles of spin coating, the colloidal fluid formed an elongated drop along the direction of the PR lines after the drop of suspension was applied on the patterned sample before...
spinning due to the hydrophobic surface properties of the Si and PR. This anisotropic wetting phenomenon was also observed on 1D macropatterned surfaces and explained by Morita et al. At about the third or fourth spin-deposition cycle, partial wetting was observed. Once the channel tops formed, the surface became hydrophilic because only silica surfaces were exposed. This provides a simple diagnostic for the stage of the colloidal nanostructure formation.

Figures 2(a) and 2(b) show enclosed channels with 50-nm-diam (OL) silica nanoparticles after six cycles of spin coating, and a 2 h calcination at 800 °C. Dense-packed silica particles are arranged around the original PR/wet-i wall to form enclosed nanochannels as shown in Fig. 2(b). The shape and size of PR/wet-i patterns were preserved even with the high temperature processing. The channel was ~300 nm high, 120 nm wide and ~1 cm long for this sample. The neck growth between silica particles at 800 °C was minimal as seen in Fig. 2(b). Figure 2(c) shows a continuous seal over a large area with six cycles of spin coating. The thickness of sealing layer was 100–150 nm (~2–3 particles) in this case. Our preliminary experiments on a planar Si wafer indicated that roughly one layer of OL silica particles was assembled at 4k rpm for 30 s for the concentration of particles we were using. The number of cycles of spin coatings provides a simple way to control the thickness of the top seal. The uniformity of silica nanoparticle channels was very good over a large area [Fig. 2(c)]. The extra particles evident in Fig. 2(c) were formed in the preparation of the sample for SEM investigation (cleaving) and are not inherent to the deposition process. Using this approach, large-area samples (several cm²) with uniform silica nanoparticle channels were obtained.

There are many degrees of freedom in this process sequence. First, in the preparation of the PR patterns, the period, shape, and size of channels can be controlled by varying the lithographic parameters such as photoresist type and thickness, IL period, exposure and development times, development parameters (postbake time and temperature, developer concentration, temperature, and time). The second controlled step is the spin coating where we have control over the spin program and the number of deposition cycles. Third, the colloidal concentration and particle size affect the channel profile. The relative sizes of the silica particles and the gap widths to be filled are important. A large silica particle compared to the gap width was not a good choice because of the limited conformality to the edge of the PR, resulting in a larger density of pattern defects.

Figure 3 shows examples of the flexibility of this approach. A ~500-nm-thick, negative PR was used. Thicker PR walls and narrower void spaces were formed in this case.
as compared with the positive photoresist. High aspect-ratio particle walls and thin top seals were observed after six cycles of spin coating followed by a high-temperature calcination. The supporting silica particle walls have aspect ratios as high as four. However, the silica particle patterns without sealing had many defects and nonuniformity for this high aspect-ratio sample. The sealing connects the walls together to minimize the defects and strengthen the overall pattern. Even though six spin-coating cycles were applied, only a thin top seal was formed. For the deep trenches between PR walls in this sample, the spin-coating cycles were used primarily to fill the deep voids. The ratio between the width of the channel and the particle wall is about 2:1. Some local defect regions without complete sealing were observed on this sample. These local defect regions could have been eliminated with additional spin-coat cycles.

The period of the enclosed channel structures can be easily controlled in the PR preparation step. The enclosed channel structures in Fig. 3(b) have a large period (~1 μm) and a large channel width/height. The choice of particle size also affects the channeled profiles. Figure 3(c) shows enclosed channels fabricated with larger silica particles (~80 nm diameter). In this case, the channel profiles had a relatively low fidelity to the square PR patterns even though the period was 1 μm. Fewer layers of large silica particles were needed for filling the voids between PR walls and sealing the top compared with medium and small silica nanoparticles. Smaller silica nanoparticles (~15-nm diameter) also were used for fabrication of enclosed channels with positive PR and 500 nm period as shown in Fig. 3(d). Even though the channels formed with these smaller silica nanoparticles had higher fidelity to the photoresist patterns, serious cracking occurred in the sealing layer. In most of the cases, the cracking was directed parallel to the channels and opened exactly on top of a channel. The mechanism for the occurrence of these cracks is still under investigation; we clearly observed that the cracking developed before the high-temperature calcination step. The accelerated evaporation of water during the spin-coating process and the smaller size of silica particles may lead to the cracks in the sealing layer. It may be possible to minimize or avoid the cracking for smaller silica nanoparticles through increasing the suspension concentration,18 adding some bonding agents,13 or increasing the ambient humidity during the spin coating to slow the drying process.

This approach can also yield more complex structures. To demonstrate some of the possibilities, we show several two-layer channel samples fabricated with 50 nm silica nanoparticles through repeat processing on a single substrate. Figure 4 shows three examples of such two-layered complex structures. After the first layer of buried channels was fabricated...
as described above, the full process, including application of the ARC and PR films, IL pattern definition and development, spin coating, and calcination, leads to the second (top) layer of enclosed channels. Figure 4(a) shows two layers of ~100-nm-wide, parallel channels. A sharp interface between the two layers is clearly evident. Figure 4(b) shows a two-layer stack with crossed channels. Examining the sidewall of the upper layer channel, it is clear that the silica particles were arranged into a dense, close-packed structure with pseudo-hexagonal patterns due to the large variation of particle size. The channels in the two layers can be at any relative angle by adjusting the sample rotation in the second exposure. We also fabricated the two-layered channels with different periods in these two layers as shown in Figs. 4(c) and 4(d). The large channels with a long period (~1 μm) in the underlying layer were perpendicular to the small channels with a short period (~500 nm) in the upper layer. More complex multiple layered stacked can be easily fabricated through this approach with multiple cycles. We can also vary the particle sizes to, for example, control porosity between different layers.

In this approach, conventional lithography techniques are used while avoiding costly and complicated processing steps such as etching and metallization. Thus, this approach is flexible, rapid and inexpensive. The channels can be extended to a nanoscale (less than 50 nm) with recent developments in immersion IL as well as with additional processing such as thinning of photoresist lines with plasma-ashing processes. We are investigating ways to eliminate the cracking observed using the 15 nm silica nanoparticles.

The as-prepared structures with silica particles may be applicable to high temperature processing (as high as 1000 °C). The enclosed channels have potential applications in microfluidics and nano-fluidics, as well as in biosensors due their broad transparency range, possibilities for functionality, and biocompatibility. More detailed studies of the fluid behavior in these channels are under way and will be reported elsewhere. Such controlled hierarchical structures as enclosed channels with gold nanoparticles or coating in inner surfaces with specific materials may be particularly suitable for catalytic applications, as they have a combination of efficient transport and high surface area. Multilayer channeled structures can be used as infiltration templates for further fabrication of complex structures.

An advantage of this approach over other methods for forming channels is that the particles can be functionalized to modify their chemical reactivity. After formation of channeled structures, we can modify the surface of particles to provide additional functionality. Thus, they can bind biologically active molecules for optical or for electrical analysis. More complex, core-shell nanoparticles can provide additional functionality. The resultant structures are similar in structure to organisms such as diatoms without the use of a biological template. The resultant channeled structure can be used to mimic biological channels with porous membranes to investigate their fluid transport behavior. The hierarchical structures may also be used to separate different sizes of biological species. We believe there are many potential applications for these channeled structures with porous walls.

IV. CONCLUSIONS

We have presented a simple, inexpensive, rapid, and reliable approach to the fabrication of enclosed channels composed of silica nanoparticles over large areas. This approach is also applicable to other materials such as gold nanoparticles. The morphology of entire ordered enclosed channels can be easily controlled through the parameters in the photoresist patterning, spin-coating, and calcination steps. The scale of channels can be extended further into the nanoscale by controlling the parameters in the interferometric lithography step and by using smaller nanoparticles. Complex multilayer structures were demonstrated. This process opens a new route to fabricating ordered, enclosed channels of nanoparticles, potentially useful in sensor, separation, catalytic, and photonic crystal applications.

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