Templated Self-Assembly of 5 nm Gold Nanoparticles

L. E. Ocola, X.-M. Lin

Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL

ABSTRACT

Combining top-down electron beam lithography and bottom-up colloidal chemical assembly can potentially lead to large scale patterning of nanocrystals on arbitrary substrates. We report on the templated self-assembly of 5 nm gold nanoparticles in both trenches and in geometries that lend themselves to large area self-assembly. Preliminary results show that templates that retain the self-assembly symmetry can be used to induce self-assembly at distances significantly larger than trench geometry constraints.

Further progress in templated self-assembly will lead to novel nanophotonic and chemical sensing devices, along with the means to extend top-down nanofabrication below the 10 nm barrier.

1. INTRODUCTION

Large-area self-assembly from colloidal solutions has been a topic of ever increasing research. Initial attempts used biomaterials such as DNA to act as locators for the dispersed nanostructures [1-3]. Langmuir Blodgett and other kinetically driven self-assembly of nanostructures [4-7] have also been used as bottom-up approaches for large area self-assembly. Most of these methods though have been unsuccessful to cover large areas without defects or grain boundary formation.

Solvent dewetting, combined with top-down lithography, has also been used to align particles in topographically defined surfaces [8, 9] with single particle resolution. However, this has only been achieved in very narrow area templating using particles larger than those used here. Combining top-down electron beam lithography and bottom-up colloidal chemical assembly can potentially lead to large-scale patterning of nanocrystals on arbitrary substrates if the constraint of large amount of patterning requirement can be avoided. In this paper we provide initial results on attempting to induce large-area self-assembly by fabricating template constraints that mimic the natural self-assembly symmetry of the nanostructures. In this particular case the nanostructures are 5-nm gold nanoparticles, the symmetry is hexagonal closed-pack, and the template constraints used are triangles.

2. EXPERIMENTAL

Line trench and equilateral triangle pillar templates were fabricated on silicon wafer substrates of about 20 mm x 10 mm per side. The substrates were pre-treated with a mild Piranha etch with a ratio of sulfuric acid to peroxide of 1:1, for about 5 minutes. This made the surface hydrophilic. The samples were spin coated with about 80 nm to 100 nm of hydrogen silsesquioxane (HSQ) negative resist, without a subsequent bake. The resist was then exposed using a 100 KV JEOL 9300 FS electron beam lithography system with doses between 1100 $\mu C/cm^2$ and 1800 $\mu C/cm^2$. The patterns used were a variety of linear gratings and arrays of equilateral triangles of different sizes, ranging from 10 nm to 200 nm per side in the design layout. After exposure the sample was developed in a TMAH solution 0.26 N (MF-CD 26, Microposit) for 45 seconds and rinsed in an IPA:DI water solution 1:5, both at 55 ^oC. Finally the sample was dried with a nitrogen gun. A second set of sample substrates were treated to be hydrophobic by triple surface priming with hexamethyldisilazane (HMDS) after exposure and development.

A colloid dispersion of monodisperse (<5%) dodecanethiol-ligated gold nanocrystals in toluene [6], with a typical size of 5 nm to 6 nm, was applied to the template surface via pipette. Toluene wetted the hydrophilic substrate surface very well, two to three drops were sufficient to cover the entire surface. Meanwhile on a hydrophobic surface the contact angle was about 70 degrees and only the center of the sample was covered.

Two methods of colloid deposition were used. The first one, called “drop-and-flow”, consists of applying drops of solution, waiting for about 30 s, and then tilting the sample so the excess liquid would flow off the substrate. The second method, called “intermittent-spin”, used a spin coater. The sample was placed in the spin coater before the solution drops were applied. After waiting about 60 s, the sample was spun at 300 rpm for 15 sec, then stopped for another 15s, for at least 3 cycles, and then a final fast spin at 1000 rpm to remove excess liquid was applied. This method was efficient in providing uniform thin films on the entire substrate for both hydrophobic and hydrophilic samples. The drop-and-flow method had problems with the hydrophobic surface because the solution did not wet the surface well. Results of both methods are discussed in the next section.

3. RESULTS AND DISCUSSION

Using the drop-and-flow technique, assembly of 5 nm nanoparticles in sub-50 nm trenches was achieved (Fig 1). The gratings were patterned with variable spaces ranging from 30 nm to 110 nm. The purpose of the design was to

NSTI-Nanotech 2008, www.nsti.org, ISBN 978-1-4200-8503-7 Vol. 1

determine what was the maximum trench opening at which the gold nanoparticles could self assemble without grain defects appearing over large distances. In figure 1, it is clear that the 30-nm trench at the right is narrow enough that the nanoparticles pack in with no defects. The tilt technique did not yield good results for the large-area templates. We observed evidence that fluid flow was dominant and interactions with the triangles were not significant, as illustrated in Figure 2.

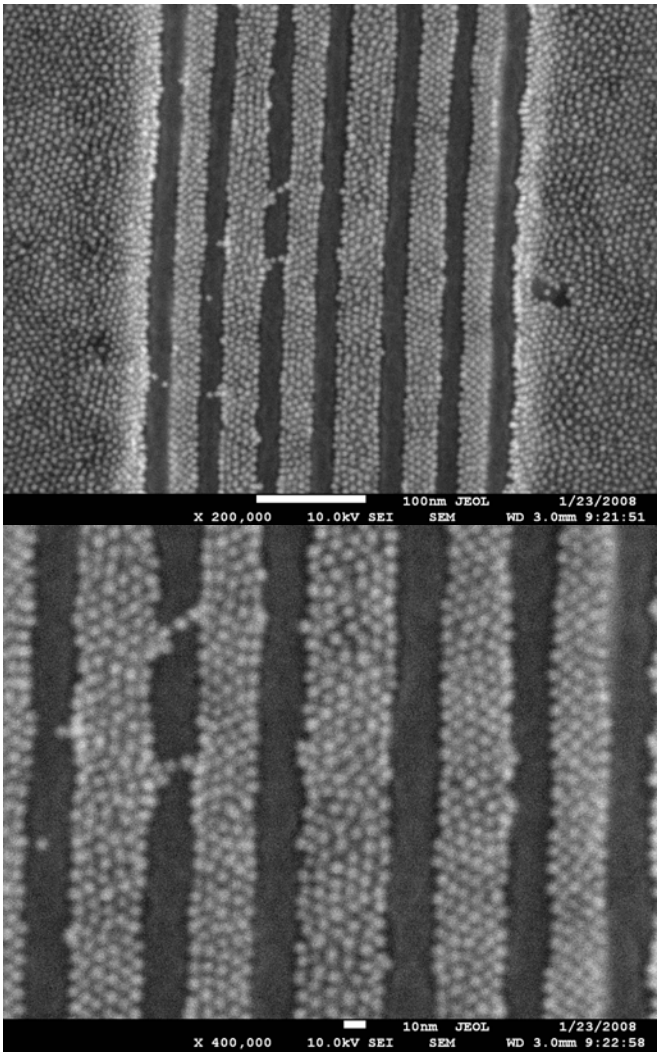

Figure 1. Gold nanoparticles arranged inside trenches defined by a grating of seven lines of HSQ using drop-and-flow deposition. The gold nanoparticles outside the grating show traditional grain boundary structures. (top) SEM micrograph at 200 KX magnification. (bottom) SEM micrograph at 400 KX magnification.

When the dispersion was allowed to sit longer on the sample surface, as in the intermittent spin method, better results for large area templating were obtained for both hydrophilic and hydrophobic surfaces. The results are shown in Figure 3 for a hydrophobic surface sample and Figure 4 for a hydrophilic surface sample.

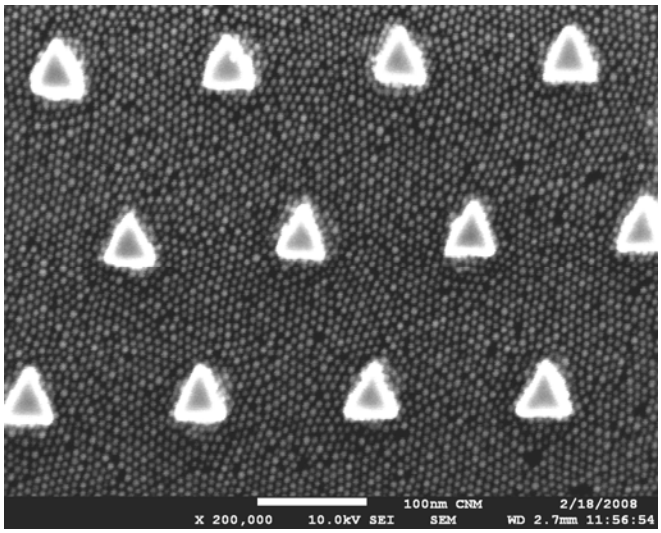

Figure 2. Gold nanoparticles after drop and flow application on a pattern on a hydrophilic surface with 50 nm equilateral triangles.

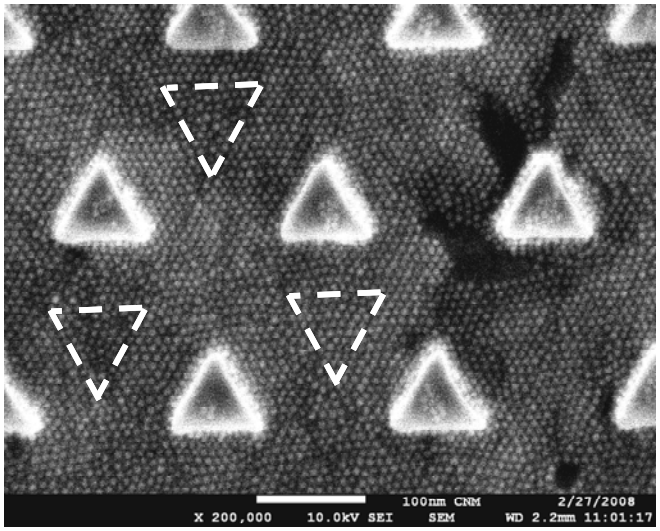

Figure 3. Gold nanoparticles arranged on around 100 nm (top) triangular pillars of HSQ using intermittent-spin deposition on a hydrophobic surface. Dashed triangles are placed for visual assistance to highlight template influence of pillars.

Although similar self-assembly results were obtained on both the hydrophobic and hydrophilic surfaces, the film quality was superior on the hydrophilic surface. The hydrophobic surface exhibited significant amount of coverage defects as seen in the gaps in Figure 3.

Both Figures 3 and 4 show that nanoparticle ordering influenced by templates that reflect the hexagonal closed pack symmetry that is inherent to nanoparticle spheres can be achieved at distances larger than the size of the templates themselves. Improvement on line edge definition and

deposition technique should be able to permit then registered templated self-assembly covering wafer size areas, instead of the small gaps found in the trench experiments, due to the high precision pattern placement capabilities of current lithography tools over large areas. In addition, the symmetry based template approach can be extrapolated to nanoparticles with different symmetries, such as cubes or nanorods. In those cases, squares or rectangular templates may be used.

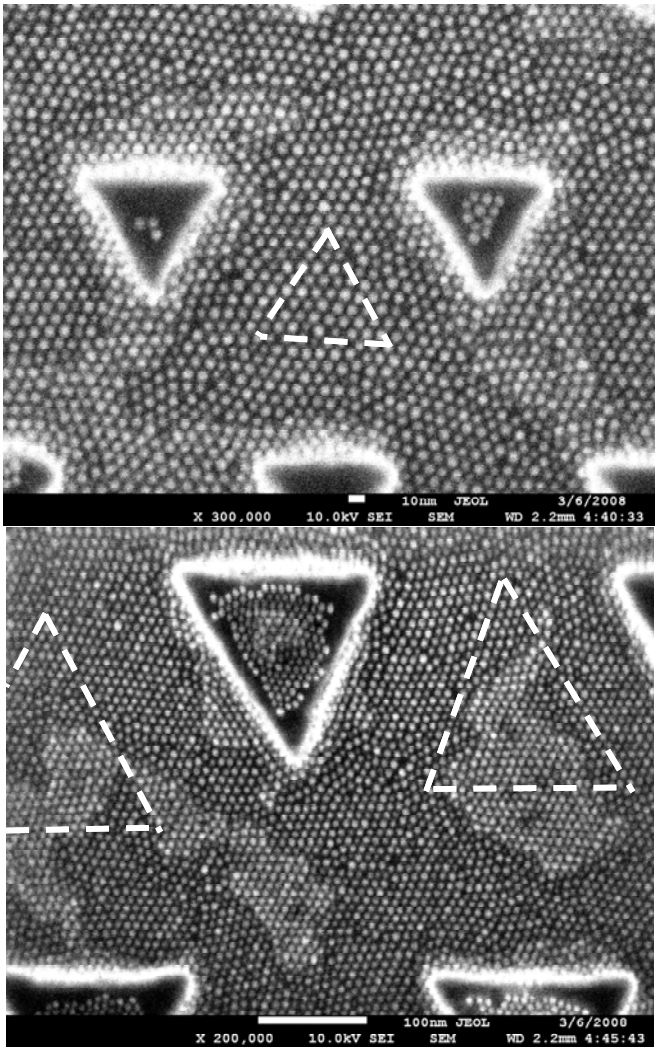

Figure 3. Gold nanoparticles arranged on around 80 nm (top) and 120 nm (bottom) triangular pillars of HSQ using intermittent spin deposition on a hydrophilic surface. Dashed triangles are placed for visual assistance to highlight template influence of pillars. Bottom image is skewed due to sample charging.

4. SUMMARRY AND CONCLUSIONS

We have reported on the templated self-assembly of 5 nm gold nanoparticles in both trenches and in geometries that lend themselves to large-area self-assembly. Preliminary results show that templates that retain the self-assembly symmetry can be used to induce ordered self-assembly at distances significantly larger than trench geometry constraints and larger than the size of the template size. This method may be applied to nanoparticles of other shapes, such as cubes and nanorods.

5. ACKNOWLEDGEMENTS

This work was supported by UChicago Argonne, LLC and the Department of Energy under Contract No. DE-AC02-06CH11357.

Use of the Center for Nanoscale Materials was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

REFERENCES

1. N. Kossovsky, D. Millett, A. Gelman, E. Sponsler, H. J. Hnatyszyn, Nature Biotechnology 11, 1534, 1993
2. C. A. Mirkin, R. L. Letsinger, R. C. Mucic, J. J. Storhoff, Nature 382, 607, 1996
3. E. Braun, Y.Eichen, U. Sivan, G. Ben-Yoseph, Nature 391, 775, 1998
4. F. Caruso, R. A. Caruso, and H. Möhwald, Science, 282, 1111, 1998
5. A. Stein, Microporous and Mesoporous Materials, 44-45, 227, 2001
6. T. P. Bigioni, X.-M. Lin, T. T. Nguyen, E. I. Corwin, T. A. Witten and H. M. Jaeger, Nature Materials, 5, 265, 2006
7. X.-M. Lin, A. C.S. Samia, Journal of Magnetism and Magnetic Materials 305, 100, 2006
8. J. A. Liddle, Y. Cui, and P. Alivisatos, J. Vac. Sci. Technol. B, 22, 3409, 2004
9. T. Kraus, L. Malaquin, H. Schmid, W. Riess, N. D. Spencer, H. Wolf, Nature Nanotechnology 2, 570, 2007