Nanofabrication and Characterization of Quasicrystal Metasurfaces Using Shadow-Sphere Lithography

Caroline Zellhofer

Mechanical Engineering, University of Maryland Baltimore County

NNIN REU Site: Center for Nanoscale Systems, Harvard University, Cambridge, MA

NNIN REU Principal Investigator: Professor George Whitesides, Dept. of Chemistry and Chemical Biology, Harvard University

NNIN REU Mentor: Dr. Alex Nemiroski, Nanotechnology Department, Illumina, Inc.
(Previously at Dept. of Chemistry and Chemical Biology, Harvard University)

Contact: caroz1@umbc.edu, gwhitesides@gmwgroup.harvard.edu, alex.nemiroski@gmail.com

Abstract:

Quasi-crystals may have useful optical characteristics with applications in biosensing, however they have previously been difficult to fabricate, characterize, and simulate, as well as involving processes that are costly and time-consuming. This project focused on optimization of the quasicrystal fabrication and characterization process using template self-assembly and shadow-sphere lithography (SSL), a process of depositing metal, particularly gold, at different angles, onto a pattern of silica microspheres. The angle of deposition creates "shadows" behind the spheres, places where gold has not been deposited. Once the spheres are removed, these complex shadow patterns are left behind, with features as small as 20 nm visible. The quasi-crystals are fabricated in an array of 78 different quasi-crystals to be created on a single 50 mm × 100 mm surface. Being able to produce many quasi-crystals rapidly allows for the crystals to be characterized faster than they can be simulated. The self-assembly and SSL process have drastically decreased the time required to fabricate quasicrystals, reducing the time from days to make one quasicrystal to hours to make hundreds. Characterization of these quasicrystals has revealed sharp peaks in reflectance, which is useful in biosensing.

Introduction:

Optical quasicrystal metasurfaces – patterned arrays of plasmonic nanoantennas that enable the precise manipulation of light – are emerging as critical components in many nanophotonic materials [1]. The development of these materials has been slowed by the difficulty of efficiently fabricating patterns with the required combinations of intricate nanoscale structure, high areal density, and/or heterogeneous composition. The only fabrication strategies that permit broad control over appropriate arrays use conventional photo-, electron-beam, and/or ion-beam lithography. These fabrication processes, however, are expensive, time-consuming, and often lack scalability. In addition, due to the small area of the quasicrystals fabricated, specialized equipment must be used to characterize the surfaces. Lastly, current technology is not robust enough to simulate the properties of the quasicrystals due to the complexity of the patterns.

To improve methods of processing quasicrystals, a previous method for processing, nanosphere lithography, was examined. Nanosphere lithography involved depositing gold directly onto spheres that were self-assembled in a hexagonal pattern. By depositing from directly above, the spheres create perfectly spherical shadows that block the gold and leave a pattern underneath. While simple, this method is limited in its complexity and customization, as it can only form honeycomb shadow patterns. The idea of using nanosphere lithography to leave shadow patterns was combined with a more robust self-assembly process and angular deposition in order to create more complex, smaller features that retain definition.

Experimental Procedure:

Templated Self-Assembly. Seen in Figure 1, the templated self-assembly reduces the time of fabrication from weeks to a few hours per sample, compared to more traditional methods [1]. The silicon template was created by first direct-writing a pattern into a mask using a micro pattern generator. The image on the mask was an array of 78 different quasicrystals, with various sizes and orientations. Being able to produce hundreds of quasicrystals in parallel allowed for these crystals to be fabricated and characterized within hours—much faster than they could be simulated.

The image on the mask was then projected five times smaller, using an i-line stepper, onto a 76.2 cm photoresist-covered silicon wafer. The pattern, each a single 3.5 × 7 mm rectangle, was repeated to cover the wafer. The wafer was then etched using a dry anisotropic etch, effectively etching the silicon where the photoresist was exposed. The spheres were assembled into the holes of the wafer, which measured slightly shallower than the diameter of the spheres, and then transferred to a glass slide using PDMS.

Proccess & Characterization

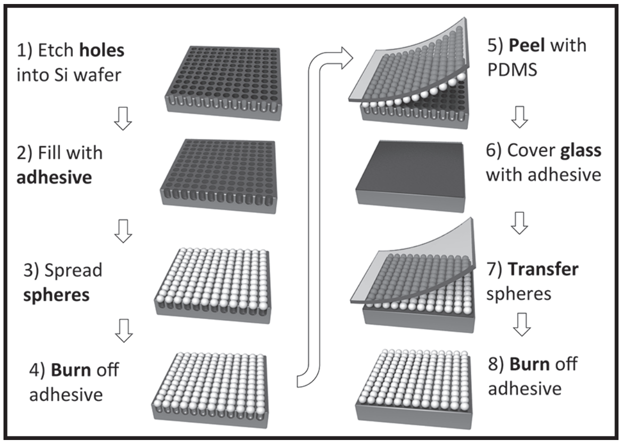

Figure 1: Diagram of the templated self-assembly process.

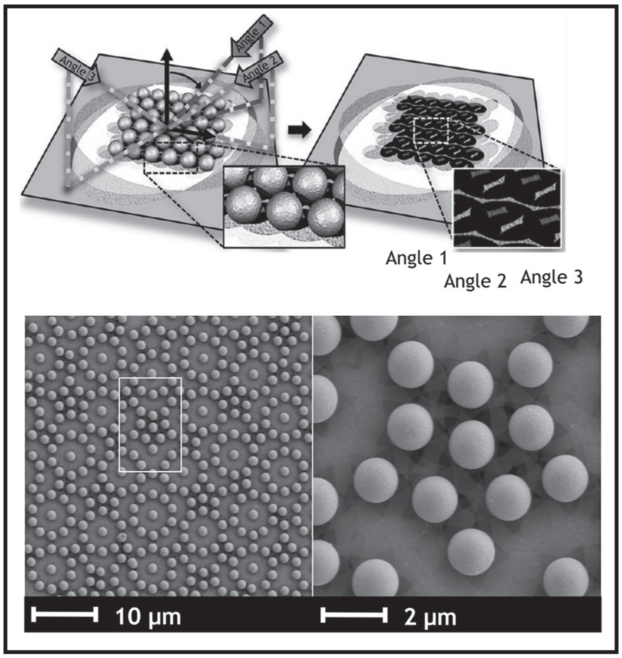

Figure 2: Top; Diagram of SSL process. Bottom; SEM of gold-coated microspheres, with shadow patterns visible underneath.

Shadow-Sphere Lithography (SSL). Shadow-sphere lithography was created by the Whitesides lab as a method to efficiently, cheaply, and quickly fabricate metasurfaces [1]. To fabricate, the glass substrate with the patterned microspheres on top was placed on a custom-made stage at anywhere between a 45°-70° angle to the horizontal inside an electron-beam evaporator. Using electron beam physical vapor deposition (EBPVD), a thin film of titanium was deposited onto the spheres. The titanium was deposited as an adhering layer between the gold and the glass. The sample was then rotated a set number of degrees and titanium was again deposited. The sample was rotated until all angles had been covered with titanium, and then gold was deposited at the same angles. The spheres were then removed using a simple piece of tape, leaving the shadow patterns — the places where the spheres blocked — behind, which can be seen in Figure 2.

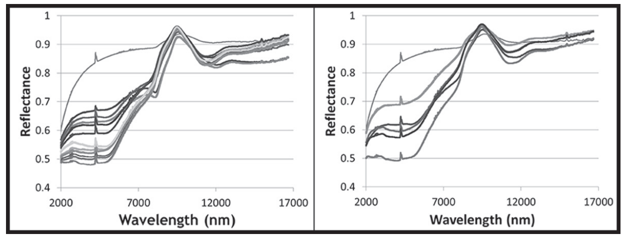

Figure 3: Left; Graph of reflectance from an FTIR scan from 2-17 µm of one column. The topmost line is the background reflectance of the substrate. As the other lines approach the background, the orientation of the quasicrystal is rotated. Right; Graph of reflectance from an FTIR scan from 2-17 µm of one row. The topmost line is the background reflectance of the substrate. The size of the spacing between the spheres is changed, creating more densely packed patterns and finer features. The lowest line belongs to the most densely packed pattern.

Results:

The combination of template self-assembly and SSL resulted in repeatable, defined features as small as 20 nm, covering a space as large as 50 mm by 100 mm. A Fourier transform infrared spectroscopy (FTIR) scan revealed nothing of significance for transmission. Changing the rotational orientation and the spacing of the spheres in the template both revealed differences in the reflectance spectrums. The difference in spacing led to a sharper peak for the patterns with more densely packed spheres, where the shadow patterns are finer. These trends can be seen in Figure 3. The difference in rotational orientation led to an even spacing between the resulting lines on the graph, but seemingly had little effect on the sharpness of the peak.

Conclusions:

In conclusion, templated self-assembly is possible and allows for a rapid, low-cost method of patterning spheres for the fabrication of quasicrystals. Shadow-sphere lithography creates fine features with replicable accuracy, and allows for quasicrystals to be created in parallel, which would be useful for high-throughput testing of sensors. Although more experiments are necessary to fully explore the properties of quasicyrstalline metasurfaces, trends can be seen in changing the spacing of the spheres and the rotational orientation in an array of quasicrystals.

Acknowledgements:

Special thanks to Dr. Baris Unal, and to the staff of Harvard University's Center for Nanoscale Systems. Funding was provided by the National Nanotechnology Infrastructure Network Research Experience for Undergraduates (NNIN REU) Program via the National Science Foundation, Grant No. ECCS-0335765.

References:

[1] Nemiroski A, Gonidec M, Fox JM, Jean-Remy P, Turnage E, Whitesides GM. 2014. Engineering shadows to fabricate optical metasurfaces. ACS Nano. 8(11), pp 11061-11070.