

Video Article

Fabrication of Periodic Gold Nanocup Arrays Using Colloidal Lithography

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Abstract

Within recent years, the field of plasmonics has exploded as researchers have demonstrated exciting applications related to chemical and optical sensing in combination with new nanofabrication techniques. A plasmon is a quantum of charge density oscillation that lends nanoscale metals such as gold and silver unique optical properties. In particular, gold and silver nanoparticles exhibit localized surface plasmon resonances—collective charge density oscillations on the surface of the nanoparticle—in the visible spectrum. Here, we focus on the fabrication of periodic arrays of anisotropic plasmonic nanostructures. These half-shell (or nanocup) structures can exhibit additional unique light-bending and polarization-dependent optical properties that simple isotropic nanostructures cannot. Researchers are interested in the fabrication of periodic arrays of nanocup for a wide variety of applications such as low-cost optical devices, surface-enhanced Raman scattering, and tamper indication. We present a scalable technique based on colloidal lithography in which it is possible to easily fabricate large periodic arrays of nanocup using spin-coating and self-assembled commercially available polymeric nanospheres. Electron microscopy and optical spectroscopy from the visible to near-infrared (near-IR) was performed to confirm successful nanocup fabrication. We conclude with a demonstration of the transfer of nanocup to a flexible, conformal adhesive film.

Video Link

The video component of this article can be found at <https://www.jove.com/video/56204/>

Introduction

The emergence of plasmonics in conjunction with improved nanofabrication and synthesis techniques have brought about a wide variety of exciting technologies such as sub-diffraction limited circuitry, enhanced chemical detection, and optical sensing^{1,2,3}. In this protocol, we demonstrate a scalable and relatively low-cost technique capable of fabricating nanopatterned plasmonic substrates using commercially available polymeric nanospheres and an etching step followed by metal deposition. Unlike other techniques for fabricating nanopatterned substrates, such as electron beam lithography⁴, this technique can quickly and efficiently be scaled to 300 mm wafers and beyond with minimal effort and uses a transfer step to produce flexible and conformal films⁵.

Since the Roman era, we have known that certain metals such as gold and silver can have brilliant optical properties when they are finely divided. Today, we understand that these metal particles exhibit an effect called the "localized surface plasmon resonance" (LSPR) when their dimensions approach the nanoscale. LSPR is analogous to a standing wave in which weakly bound electrons found in the metal oscillate coherently when light of certain frequencies illuminates the metal particles. Anisotropic nanostructures are of particular interest because unique optical resonances can emerge as a result of symmetry breaking^{6,7,8}.

The illumination of half-shell (nanocup) structures with light can excite electric dipole or magnetic dipole plasmon modes, depending on factors such as the deposition angle of the metal, the orientation of the substrate with respect to the incident light, and the polarization of the incident light⁹. Nanocup have often been considered analogous to three-dimensional split-ring resonators, in which the resonance frequency can be approximated as an LC-oscillator^{10,11}. The resonance frequency for the size of polymeric nanospheres used here (170 nm), the amount of deposited gold (20 nm), and the etch rates yield resonance frequencies spanning the visible and near-IR.

The optical properties of the gold nanocup can be measured either in transmission or reflection, depending on the substrate used for spin-coating. In the presented protocol, we chose to use 2 in. silicon wafers as the substrate and perform reflectance measurements after metal deposition. The measurements were performed using a microscope coupled to a dispersive spectrometer with a halogen light source. We have also had success with using glass substrates, allowing for both transmission and reflection measurements immediately following the metal deposition. Furthermore, this technique can easily be scaled and is not limited to 2 in. wafers. Due to the wide commercial availability of high-quality monodisperse polymeric nanospheres, it is straightforward to tune the optical properties of these structures by simply starting with differently sized nanospheres.

In this protocol, a technique to fabricate anisotropic half-shell (or nanocup) gold nanostructures using a method called colloidal lithography is demonstrated. Colloidal lithography uses self-assembly of highly monodisperse polymeric nanosphere to quickly pattern a substrate that can be further processed into a plasmonic substrate after sputter coating a thin layer of gold. Likewise, it is possible to tune the anisotropy of the

substrate by tilting the sample substrate during metal deposition. The resulting structures are polarization-sensitive because of the anisotropy of the formed nanostructure. Here, we demonstrate one particular case and perform optical characterization and lift-off to transfer the structures to a transparent, flexible film.

Protocol

1. Material Preparation

1. Place several 2 in. silicon wafers into a quartz carrier for cleaning and load the silicon wafers into the plasma etching system. Pump the vacuum chamber down until it reaches at least 75 mTorr. This may take a few minutes.
2. Begin the flow of O₂ (30 sccm) gas and allow the pressure to stabilize. Set the etch time to 15 min. Once the chamber pressure has stabilized initiate the radiofrequency (RF) 13.56 MHz 250 W plasma.
NOTE: This step cleans the silicon wafers of any organic contaminants and functionalizes the surface with hydroxylated (-OH) moieties thereby ensuring a hydrophilic surface.
3. While waiting for the plasma cleaning step to finish, remove the commercially purchased polystyrene nanospheres (170 nm diameter, 10% solids, 0.5% sodium dodecyl sulfate) from the refrigerator (4 °C). Allow the container to warm to room temperature.
4. Briefly vortex (1 min) and sonicate (35 kHz, 1 min) the polystyrene nanospheres to minimize nanosphere agglomeration.
5. Into a clean glass vial, measure 1.0 mL of the 170 nm polystyrene nanospheres and add 1.0 mL of H₂O to obtain a 5% solids colloidal suspension.
6. After 15 min, stop the flow of O₂, vent the vacuum chamber, and remove the freshly cleaned wafers.

2. Spin-coating of Polystyrene Nanospheres Template

1. Unload the cleaned silicon wafers from the plasma etcher. Then mount a 2 in. wafer onto the spin-coater. Ensure it is properly centered and that the O-ring is clear of any debris. Initiate the vacuum and ensure that the wafer is securely attached to the stage.
2. Set the spin parameters of the spin-coater. These parameters vary based on the nanosphere size. For a solution of 5% 170 nm nanospheres, set the spin-coater to a 1 step process with a spin time of 1 min, a speed of 3,000 rpm, and an acceleration of 2,000 rpm/s.
3. Using a disposable syringe, withdraw ~ 1 mL of colloidal suspension from the vial. Set aside the vial. Take a 5 µm syringe filter and place it at the end of the syringe. Depress the syringe until a droplet of suspension clears the tip. The filter removes undesirable aggregates and particulate that can significantly reduce film quality.
4. Deposit enough suspension directly on the center of the wafer such that approximately 2/3 of the surface is covered. Try to minimize bubbles because those can impact film quality. Close the spin-coater lid and press Start. During this process, it may be possible to see thin film interference effects on the surface of the wafer as the nanospheres self-assemble. This will vary based on the nanosphere diameter.
5. Remove the spin-coated wafer after deactivating the vacuum. Wipe the bowl and lid of the spin-coater to remove excess nanospheres.

3. Film Quality Assessment and Preparation for Etching

1. Visually assess the quality of the self-assembled film by looking for noticeable defects such as streaks or holes that may have been caused by particulate during the spin-coating process.
2. Assess the film quality by placing the wafer under an optical microscope. Grain boundaries and some defects are normal. If the wafer has large uncoated areas or obvious multilayers, it is necessary to adjust the spin parameters to obtain a more uniform film. Electron microscopy may also be used to assess film quality.
3. Turn on the light source to the microscope and focus onto the surface of the silicon wafer using a 20X objective. Assess the quality at several spots throughout the wafer to ensure uniformity.
4. The final film quality check is to use scanning electron microscopy (SEM) to visualize the nanosphere self-assembly at the nanoscale. It is possible to assess the degree of multilayers, holes, and grain boundaries/defects across small portions of the wafer relatively quickly using this technique.
5. Once a sufficient film has been obtained, place the wafer into an oven (107 °C) for 2 min to anneal the self-assembled nanospheres. This helps encourage adhesion to the substrate and yields a better nanopatterned surface after etching.

4. Etching, Metal Deposition, and Optical Characterization

1. Load the annealed wafer into the plasma etcher and initiate the pump down process.
2. Once the vacuum chamber reaches at least 75 mTorr, begin the flow of O₂ (20 sccm) gas and wait for the pressure to stabilize. Initiate the RF plasma (75 W) for 165 s.
3. Once the RF plasma cycle has completed, stop the flow of O₂ and vent the chamber.
4. The substrate is now etched and ready for metal deposition. Transport the sample to a sputter coater and deposit a thin (20 nm) layer of gold. Varying deposition angles may be used to alter the optical properties of the nanocups. In this case, metal deposition normally incident to the substrate was performed.
5. After the metal deposition, the substrate may be characterized using optical spectroscopy. Focus the microspectrophotometer onto the surface of the metallized substrate and measure the reflectance spectra. For 170 nm etched nanosphere arrays, the LSPR was at 615 nm.
6. Using pressure-sensitive adhesive tape, gently place the film in contact with the substrate. It may be necessary to remove any air bubbles that formed at the interface using a tweezers.
7. Once the tape is in contact with the substrate, the tape may be immediately peeled off to remove the nanocups from the substrate surface. Gently peel back the tape and the result is a flexible and conformal film of gold nanocups.

Representative Results

Gold nanocups were prepared using 170 nm diameter polystyrene nanospheres. After annealing for 2 min at 107 °C and etching with a 75 W, 20 sccm O₂ plasma for 165 s, the resulting film was characterized using SEM (**Figure 1**). To evaluate the quality of the spin-casted film, optical microscopy-in addition to visual inspection-may be used (**Figure 2**). High-quality films should be essentially free of defects. Grain boundaries are typically observed even in high-quality films, but with careful attention to detail, it is possible to nearly eliminate point defects. Deposition of 20 nm of gold using sputter coating resulted in a plasmonically-active film and was characterized using optical reflectance spectroscopy (**Figure 3**). The plasmonic film was transferred from the rigid silicon substrate to a flexible film using commonly available adhesive tape. The tape was placed in contact with the plasmonically-active film and allowed to adhere to the film for 1 min. The tape was then gently removed from the substrate, resulting in a transfer of the gold nanocups to the film (**Figure 4**).

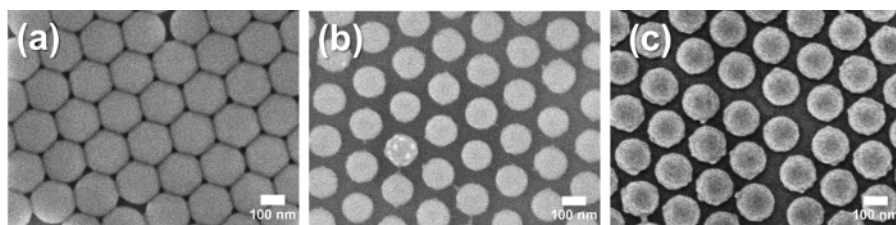


Figure 1: Representative scanning electron micrographs of self-assembled nanostructures fabricated using colloidal lithography. (a) Self-assembled monolayer of a typical array of polystyrene nanospheres before etching, (b) periodically spaced polystyrene nanospheres after annealing and etching (75 W, 20 sccm O₂ for 165 s), and (c) periodically spaced gold nanocups with 20 nm of gold (Au) deposited at a normal incidence with respect to the substrate. Scale bar: 100 nm. Magnification: 100 kX. [Please click here to view a larger version of this figure.](#)

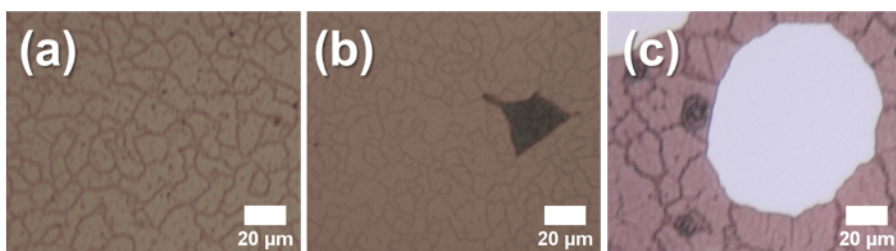


Figure 2: Optical microscopy of self-assembled films to evaluate quality. (a) Film with good monolayer coverage and minimal defects. Grain boundaries are observed with minimal defects and holes. (b) Film consisting of monolayer and multilayer regions. (c) Film with major defects and incomplete monolayer coverage. Scale bar: 20 μm. Magnification: 20X. [Please click here to view a larger version of this figure.](#)

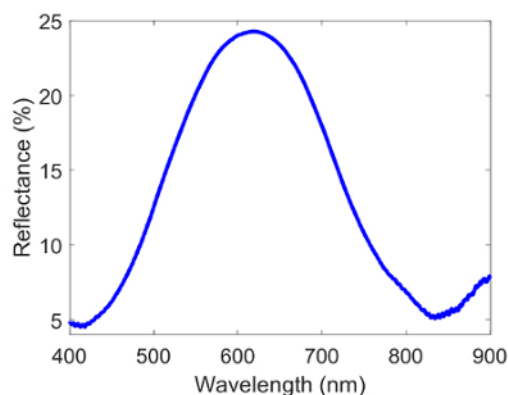


Figure 3: Optical reflectance characterization of the fabricated gold nanocup array. Optical reflectance spectra showing a strong plasmonic resonance at ~ 615 nm. [Please click here to view a larger version of this figure.](#)

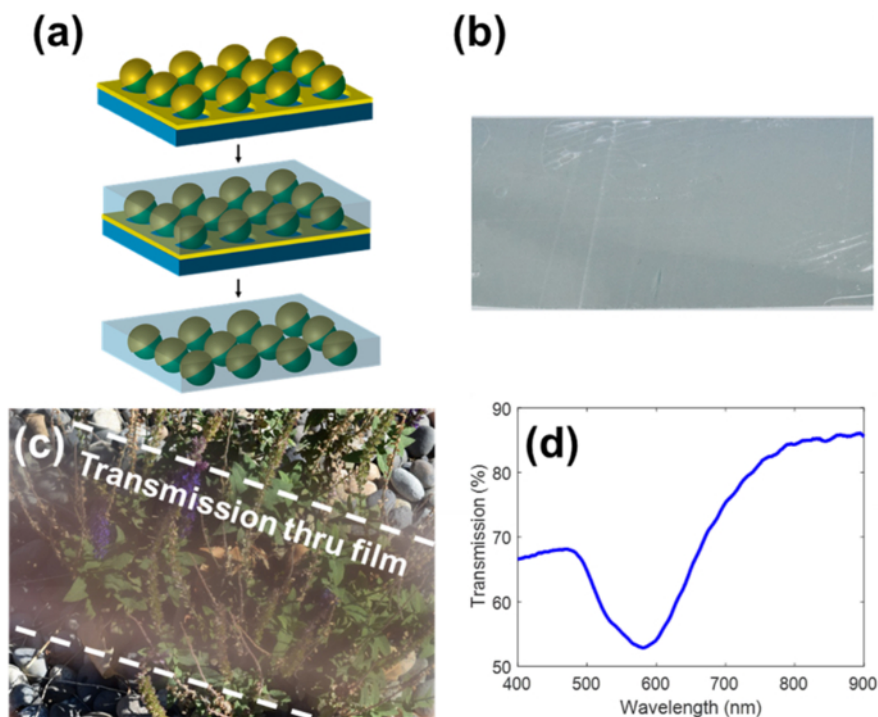


Figure 4: Resulting flexible, transparent film after peeling gold nanocups from sacrificial silicon (Si) wafer. (a) Schematic of lift-off procedure. (b) Optical image of peeled film. (c) Photograph focused past the film to demonstrate transparency. (d) Representative optical transmission spectra of a film after lift-off. [Please click here to view a larger version of this figure.](#)

Discussion

This protocol demonstrates a low-cost and efficient technique for fabricating periodic arrays of plasmonic gold nanocups. This technique is particularly advantageous because it avoids serial top-down processes such as electron beam lithography or focused ion beam milling. The presented technique shows that commercially available polymeric nanospheres can be self-assembled in a straightforward manner to serve as a nano-sized template for further processing.

Modifications and Troubleshooting:

If the film quality is poor, it may be necessary to pre-filter the nanosphere solution. Here, we used a 5 μm syringe filter but it may be advantageous to use syringe filters down to 0.22 μm , depending on the nanosphere diameter. The etching process can be adjusted to get the desired optical response. The quality of the etch should be evaluated using SEM to ensure non-touching and evenly spaced polymeric nanospheres. Once the etch parameters have been established for a particular system, it is possible to reproducibly manufacture several wafers in a batch with similar plasmon resonances. Metal deposition at varying angles will tune the nanocup's anisotropic optical properties.

Critical Steps:

The nanospheres must be properly stored and handled to achieve high quality films. Allow the nanospheres to warm to room temperature and briefly vortex followed by sonication to help ensure monodisperse nanospheres. The silicon substrate must be plasma cleaned and used immediately in order to ensure a highly hydrophilic surface. Finally, the self-assembled film should both be inspected by eye as well as through optical microscopy. Minimal defects should be observed, otherwise it will be necessary to adjust spin conditions.

Limitations:

This is a highly scalable technique but it does have several limitations that must be kept in mind. The self-assembly process is excellent at producing large arrays of nanospheres but it is challenging to fabricate nanostructures with three-dimensional anisotropy. Complex nanostructures are best fabricated by electron beam lithography or focused ion beam milling. These nanostructures, however, do not scale well and are exceedingly expensive to manufacture.

Overall, this protocol demonstrates how to fabricate nanoplasmonic films. Nanoplasmonic films have a variety of applications in areas such as nonlinear optical materials⁷, photovoltaics¹², and light emitting diodes¹³.

Disclosures

The authors have nothing to disclose.

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