Shadow Overlap Ion-beam Lithography for Nanoarchitectures

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ABSTRACT

Precisely constructed nanoscale devices and nanoarchitectures with high spatial resolution are critically needed for applications in high-speed electronics, high-density memory, efficient solar cells, optoelectronics, plasmonics, optical antennas, chemical sensors, biological sensors, and nanospectroscopic imaging. Current methods of classical optical lithography are limited by the diffraction effect of light for nanolithography, and the state of art of e-beam or focused ion beam lithography limit the throughput and further reduction less than few nanometers for large-area batch fabrication. However, these limits can be surpassed surprisingly by utilizing the overlap of two shadow images. Here we present shadow overlap of ion-beam lithography (SOIL), which can combine the advantages of parallel processing, tunable capability of geometries, cost-effective method, and high spatial resolution nanofabrication technique. The SOIL method relies on the overlap of shadows created by the directional metal deposition and etching angles on prepatterned structures. Consequently, highly tunable patterns can be obtained. As examples, unprecedented nanoarchitectures for optical antennas are demonstrated by SOIL. We expect that SOIL can have a significant impact not only on nanoscale devices, but also large-scale (i.e., micro and macro) three-dimensional innovative lithography.

Noble metal nanostructures have received increasing interest in nanoscale electronics,1,2 photonics,2−7,12 plasmonics,2−13 and biotechnology3−6 due to their unique physical, optical, chemical, and mechanical properties, which can be tuned by the structure, material, and size.7 Consequently, the development of cost-effective, high-throughput, and tunable fabrication techniques are essential.

The standard lithography techniques include optical photolithography,14,15 holographic lithography,16 electron beam lithography (EBL),17−19 and focused ion-beam lithography (FIB).20,21 However, since typical optical photolithography is limited in its resolution due to the diffraction of light, it is necessary to overcome this limit without complicated methods such as immersion techniques, double patterning, or other nonlinear techniques.14 Although EBL and FIB allow the fabrication of arbitrarily shaped nanostructures with high spatial resolution, the serial processing of these techniques inherently shows serious challenges in high-throughput and is responsible for their high cost. Nanosphere lithography (NSL),22−25 laser interference lithography (LIL),25,26 and shadow-based nanofabrication27,28 can be good alternative parallel and low-cost lithography methods, but in general these techniques are seriously limited to specific fabricated shapes such as prisms and disks.

Here, we present the shadow overlap of ion-beam lithography (SOIL), which is a tunable and parallel nanolithographic method. It is based on simple prepatterned micro/nanostructure arrays, shadows, and overlaps between shadows obtained by the angle of metal deposition using directional e-beam evaporation or ion-beam milling. This technique can provide several benefits to overcome the limitations of the previously described systems. First, this method has potentially a single digit of nanoscale spatial resolution since the nanostructures are fabricated by using the shadow area of prepatterned structures, which are generated by the directional metal layer deposition and etching. For example, a bow-tie structure with a gap of 10 nm or less is easily achieved with this lithographic technique (Figure 2a). Second, we can make many different shapes of nanostructure arrays, since the shadow shape or area can be changed with different prepatterned structures, the angle of metal deposition and etching, or the number of deposition cycles. Third, this technique allows batch nanofabrication; we can fabricate the same nanostructure in arrays over a large-area at one time. Fourth, SOIL is a relatively simple and cost-effective method.

The general concept of SOIL is illustrated schematically in Figure 1a. A metal layer is deposited with a specific angle on the substrate. As expected, metal is selectively covered on the surface of the substrate due to the shadows created by the angle of deposition and prepatterned structure. Because of the regular prepatterned array, a shadow of one structure can overlap the neighboring structure, and the metal deposited area becomes different from that of a single structure due to the shadow-structure overlap. Analogous to the angled deposition result, directional ion-beam etching process. 

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can remove metal layer except where a shadow is cast. The final nanostructure remains in the shadowed area and has a completely different shape compared to the conventionally fabricated nanostructure using angle deposition and etching because of the shadow-structure overlap. Moreover, a variety of nanostructure shapes can be fabricated by controlling the key factors, which are the zenith angle (i.e., the angle from the normal direction on the substrate to the deposition or etching direction in the cross-section view), the number of deposition or etching cycles, and the azimuth angle (i.e., the angle between the crystal line of the prepatterned array and the directions of the deposition and etching in the top view) (Figure 1b).

As a demonstration, polystyrene (PS) beads were selected as prepattern array for several reasons. (i) The selectivity and uniformity in size; from tens of nanometers to several micrometers, PS beads have a wide range in size and a highly uniform distribution in each size. (ii) Large-area uniform pattern; it is critical to get a uniform prepattern in a large-area to fabricate highly uniform nanostructures array by SOIL. As reported in many literatures, large-area, uniform, closed-packed patterning (over 1 cm²) has been accomplished.24,29,30 (iii) Size tunability by isotropic dry etching; the size is easily controlled by oxygen plasma etching (i.e., isotropic etching) while its shape remains a sphere. Consequently, the interparticle distance in the array can be controlled, which is one of the key factors of SOIL.

The transparency of the substrate is important for optical characterization of the fabricated SOIL pattern and future applications in optics. In order to satisfy this prerequisite, a microscope glass slide was selected as a substrate. Surfactant-free carboxyl-terminated PS nanospheres with a diameter of 477 nm were self-assembled on top of the glass substrate by using a drop-casting method (Supporting Information Figure S1I). Because the capability to fabricate various types of nanostructures by SOIL comes from the shadows and the overlap of the shadows induced by the directional metal deposition and etching, PS beads were isotropically etched with oxygen plasma to reduce their size by 85% (i.e., 405 nm in diameter) thus making space between them (Supporting Information Figure S1 II). Twenty nanometers of gold was directionally deposited with zenith angles of 10, 20, 30, and 40° based on the normal direction to the substrate (Supporting Information Figure S1 III). During depositions, gold was covered on a glass substrate except in the shadow area created by PS beads. Since this shadow is dependent on the deposition angle, the gold-patterned area is changed by the zenith angle also. A directional dry etching by ion-beam milling was applied to remove the gold film. While the etching was in progress, the shadows protected the gold structure (Supporting Information Figure S1 IV and V). The overlap of the deposition and etching shadows with hexagonally patterned PS bead array allowed us to generate many different nanostructure patterns.

We investigated fabricating nanostructures by SOIL as a function of the gold deposition angle and the number of deposition times. The zenith angle of ion-beam milling was fixed at 0°, which was the normal direction on the substrate. In the top view, the azimuth angle is one of the key fabrication parameters. Since the drop-casting method was used to obtain PS bead arrays in this work, PS bead arrays at each grain boundary showed different directions. However, as representative examples, we show two extreme cases named “matching” and “mis-matching”, which indicates the cases of the minimum and maximum (i.e., 0 and 30°, respectively) azimuth angle (Figure 2). At low zenith angle, a nanocrescent array was fabricated regardless azimuth angle. However, as representative examples, we show two extreme cases named “matching” and “mis-matching”, which indicates the cases of the minimum and maximum (i.e., 0 and 30°, respectively) azimuth angle (Figure 2). At low zenith angle, a nanocrescent array was fabricated regardless azimuth angle. In this regime, no advantage of SOIL can be obtained because there is no shadow overlap effect. However, as the zenith angle of the gold deposition increased, the metal deposition shadows from the neighboring PS beads started interfering with the etching shadow (i.e., the overlap of deposition and etching shadow). As a result, many different

Figure 1. The schematics and representative patterns by SOIL. (a) Schematic diagrams of the representative patterns based on spheres and cylinders. (b) Illustration of the representative nanostructures (left, nanobulls; right, nanodouble axes) by SOIL using PS nanosphere arrays, and corresponding SEM images. (c) The schematic and SEM images of the fabricated nanoarchitecture by SOIL using pillar array. The scale bar corresponds 500 nm.
shapes could be fabricated. In the matching case where the direction of deposition and crystal orientation is identical, the deposition shadow was overlapped at the middle area of the etching shadow of its neighboring PS bead over 20° of the zenith angle. Therefore, new nanostructures different from nanocrescents (i.e., nanoaxes) were fabricated by preventing the gold from being deposited in the middle area due to the shadow overlap. At higher azimuth angles, the nanoaxes were split into two identical parts. On the other hand, in the mismatching case, nanocrescents were obtained up to 20°, due to the longer distance from the deposition shadow of neighboring PS bead to the etching shadow. From 30°, unique structures (i.e., nanobulls) emerged and these structures were slightly broken into three pieces at 40°. In double deposition, we could increase the density 2-fold (Figure 2b).

Next, we evaluated the effect of the zenith angle of the etching with 0, 10, 20, and 30° (Figure 2c,d). The zenith angle of the gold deposition was fixed at 35°. As expected, nanobull array was fabricated with 0° in matching case. As the etching angle became higher, nanobulls were elongated in the direction of the etching angle. As an additional demonstration of SOIL, nanoneedle arrays were fabricated based on nanopillar array, which have 100 nm interparticle distance, 500 nm height, and 100 nm diameter. The small variance of prepatterned structure such as height and shape induced slightly nonuniform nanoarchitectures by SOIL. Systematic characterizations to reveal the relation between the divergence of the prepatterned array and the final fabricated nanostructures are currently underway (Supporting Information Figure S2).

To characterize the SOIL patterned arrays, near-field optical properties were first explored by using numerical simulation (Figure 3 and Supporting Information Figure S3). In the electric field (E-field) enhancement, which is the ratio of the amplitude of the output and input E-fields, the resonance peak position in each pattern was highly tunable

Figure 2. Tunable SOIL patterns as a function of the zenith angle of gold deposition and dry etching. Fabricated nanostructures depending on the gold deposition angle; (a) single and (b) double gold deposition. Deposition thickness was 20 nm. The direction of dry etching was fixed at 0°. The bar correspond 100 nm. SOIL pattern changes with varying the angle of dry etching; (c) mis-matching and (d) matching case. The angle of gold deposition was fixed at 35°. The bar correspond 200 nm. The zenith gold deposition angle is defined as the angle from the normal direction of the glass surface to the direction of the deposition or etching.
as a function of light-polarization, wavelength, and the zenith deposition angle. As expected, the polarization along the fabricated structure (i.e., longitude polarization) showed higher enhancement than latitude polarization and the maximum values were 160 and 155 for latitude and longitude polarization in the mis-matching case, respectively (Figure 3a). The amplitude of the E-field enhancement profile varied from 40 to 120 with latitude polarization and the peak position was changed without any consistent direction with respect to the zenith deposition angle. However, in the case of longitude polarization, the amplitude was relatively constant and the peak showed a blue shift up to 30°. Because of the splitting the fabricated nanostructures into 3 pieces at 40°, the profile was completely different. Until the fabricated structures were separated, the maximum enhancement happened at the tips, but after the SOIL structures were split, the position was moved to the divided area regardless of polarization.

Next, we examined the scattering spectra as a far-field optical characterization. The scattering images and spectra of the fabricated nanostructures by SOIL were acquired using a dark-field microscopy system with a true-color imaging charge-coupled device (CCD) camera and a spectrometer (Figure 4a, scattering image is not shown). The graphs of Figure 4 show the scattering profile of the SOIL patterns fabricated with different zenith deposition angles. Since the drop-casting method does not allow the precise control of the crystal orientation of the PS bead array, the fabricated nanostructure array on a glass substrate had all azimuth angles. As a result, the averaged data over azimuth angles are shown, and Gaussian fitted curves are presented with the raw scattering profile. We believe that the averaged data,
white light excitation (i.e., unpolarized light), and inherent difference of near-field and far-field optical characteristic could make slightly the different results between simulation and experiment. The scattering spectra had a major single peak which existed in the range from 580 to 680 nm. As the zenith deposition angle increased, the scattering peaks consistently increased (i.e., red-shifted) in the single deposition case. On the other hand, in the case of double deposition, the peak position shifts to longer wavelengths up to 30° of the deposition angle; however, after 30°, it became blue shifted.

In conclusion, we have demonstrated a cost-effective, high-throughput, and tunable lithography method with high spatial resolution by the shadow overlap from the directional metal deposition and etching in prepatterned polystyrene arrays. We found that various types of nanostructure arrays could be easily fabricated in large areas by changing the zenith and azimuth angle of the metal deposition and etching and the number of metal deposition times. Moreover, tunable and uniform nanostructure arrays with high spatial resolution such as bow-tie shape with 10 nm gap or modified crescent shape were achieved in parallel processing by SOIL. The fabricated structures showed high electromagnetic (EM) field enhancement and polarization dependent EM field distributions in the near-field, and the scattering peak position was tuned as a function of the deposition angle. Since it is obvious that different prepatterned arrays such as pillars or pyramids can generate completely different shapes by overlapping two shadows, this lithographic method can potentially be extended to fabricate a wide variety of nanostructure arrays with different prepatterned arrays. We believe that our SOIL method will have major impacts on the fields of photonics, nanoelectronics, and future quantitative chemical or biomolecular sensing.

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Supporting Information Available: Fabrication method, Ordered pillar array based SOIL pattern, Further simulation results. This material is available free of charge via the Internet at http://pubs.acs.org.

References

Figure 4. The far-field optical characterization for the fabricated SOIL pattern arrays. (a) The experimental configuration and the measured extinction coefficients as a function of gold deposition angle at (b) 10, (c) 20, (d) 30, and (e) 40° (left, single deposition; right, double deposition). (f) Rayleigh scattering resonance peak change.