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Fabrication of Periodic Square Arrays by Angle-Resolved Nanosphere Lithography

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Abstract

We investigate the fabrication of periodic square arrays of solid gold islands by angle-resolved nanosphere lithography (ARNSL) in conjunction with thermal evaporation and etching. By varying θ (the tilt angle between the direction of gold deposition beam and the substrate surface normal) and ϕ (the substrate rotation angle about the beam axis), adjacent islands on a deposited hexagonal gold array will have a constant and periodic difference in height. Upon etching, this height bias will result in the shorter structures being removed to produce an array with a different symmetry from the original hexagonal symmetry of the parent mask. By depositing at 3 directions of $\phi = 0^\circ, 120^\circ$ and -120° with a constant $\theta = 20^\circ$, experimental results show that deposited two-dimensional gold periodic arrays will have a measurable difference in height between adjacent islands. Etching of the resulting patterns produced periodic near-square arrays with triangular nanostructures. Thus the combination of ARNSL and etching can allow selective periodic nanostructures to be removed, increasing the diversity of array symmetries available through nanosphere lithography.

Keywords: Angle-resolved nanosphere lithography (ARNSL), square array, gold etching

1. INTRODUCTION

Arrays of nanoparticles, nanotubes or nanoparticles in the sub-100 nm size regime have been widely used in catalysis¹, optics², single molecule detection³ etc. Recently, metallic nanoparticle arrays have been used extensively in Localized Surface Plasmon Resonance (LSPR), which offers a convenient sensing capability for both chemical and biological applications^{4,5,6,7,8,9}. The shape, size, interparticle spacing and materials determine the LSPR wavelength. In addition, theoretical modeling has shown that sharp nanoparticle features give rise to hot-spots in the electromagnetic fields that increase the sensitivity to local refractive index¹⁰ and amplify surface-enhanced spectroscopies^{11,12,13}. Thus, the ability to fabricate nanoparticles by varying these parameters becomes a very important factor⁹. Although these fine and periodic nanoparticles can be produced by photolithography¹⁴, E-beam lithography (EBL)^{15,16} and dip pen nanolithography (DPN)^{17,18,19} combined with wet chemical etching^{20,21,22,23,24,25,26,27}, the low resolution of photolithography, and the serial nature of EBL and DPN make them unsuitable for production. An alternative cost-effective technique is nanosphere lithography (NSL), which makes use of a colloidal crystal mask to pattern the material required²⁸. One variant of this technique is angle-resolved NSL (ARNSL) which provides an additional degree of control by changing the angle between the surface normal of the sample assembly and the incident vector of the material deposition beam²⁹. This provides an increased flexibility to the nanoparticle shape obtained and a reduction in interparticle spacing^{30,31}. However, these techniques can only produce hexagonal lattices with triangular islands or square lattices with circular islands. Still lacking is a method to produce nanoparticles with different shapes, sizes, interparticle spacing and array symmetry.

To overcome these limitations, our study explores a fabrication method based on the combination of ARNSL, rotation of the sample substrate³² and etching^{33,34,35}. By rotating the substrate in two dimensions, the deposition occurs at multiple positions² to yield hexagonal arrays with a periodic difference in heights. With the resulting height variance, the shorter arrays can be etched away to achieve patterns other than the intrinsic hexagonal array. This is the first successful reported attempt to combine ARNSL and etching to expand the variety of particle array symmetries available from nanosphere lithography. This method can produce triangular nanostructures in a square array, unlike the circular nanostructures obtained in bilayer colloidal masks³⁶.

2. EXPERIMENTAL DETAILS

Silicon and glass substrates were pretreated in piranha solution (H_2SO_4 : H_2O_2 = 3:1) for 20 minutes. The substrates were then rinsed in deionised water and dried with nitrogen. Polystyrene (PS) monolayer colloidal mask was assembled via flow-controlled vertical deposition (FCVD) method³⁷. For fabricating a large area of closepacked self-assembled PS sphere monolayer, sodium dodecyl sulfate (SDS), which acts as a surfactant, was required because it changes the surface tension of the PS colloidal. However, the trace amount of SDS left on the Si substrate before Au deposition could come between the interface of the gold and the Si and weaken the Au-Si adhesion, resulting in the sonication removal of the gold nanoparticles along with the PS sphere mask. In order to solve this problem, the assembled sphere mask on glass with FCVD (with the presence of SDS) is first transferred on water, then to a Si substrate where the presence of SDS amount will be reduced³⁸.

Evaporation of gold take place in a thermal evaporator with a modified setup at a current of 26 A and pressure of 2×10^{-4} Pa for 2 minutes each at 3 different substrate positions spaced 120° apart. The basket, with the gold in it, was then placed face down towards the site of deposition or rotating sample assembly (Fig. 1), where θ is the angle between the direction of gold deposition beam and the surface normal of the sample assembly. The rotating sample assembly allows the sample to be rotated in 2 dimensions: it can be tilted by rotating its arm (z axis) with angle ϕ and by rotating along the axis perpendicular to paper (x axis) with angle θ . The silicon substrate was placed at a distance of 40 mm from the basket. Gold was evaporated at 3 different positions of the substrate respectively. Firstly, at the sample position of $\phi = 0^\circ$ and $\theta = 20^\circ$, secondly at $\phi = 120^\circ$ and $\theta = 20^\circ$ and lastly at $\phi = -120^\circ$ and $\theta = 20^\circ$. The substrate was then sonicated in ethanol to remove its nanosphere mask and dried with nitrogen stream.

Finally, the etching of gold array was done by using KI gold etchant. The etching rate of normal gold etchant is $0.5 - 1 \mu\text{m}/\text{min}$ at room temperature which is too fast for our purpose. Thus a diluted KI gold etchant ($\text{I}_2:\text{KI}:\text{H}_2\text{O} = 6:10:1600$ in volume ratio) was needed. The etching rate of this etchant is $\sim 5 \text{ nm}/\text{min}$, the time of this process depends on the thickness of the film, in our case the substrate was placed in the etchant for 2 minutes. It was then rinsed thoroughly with deionised water and dried with nitrogen stream. The final substrates were examined under field emission scanning electron microscope (FESEM) and atomic force microscope (AFM).

3. MODELING OF METHODOLOGY

The original nanostructures deposited in a monolayer mask are a hexagonal array of triangles (Fig. 2). To obtain a subset of this array pattern, either the blue or white members have to be removed. By making use of the mask spheres to aid or block the propagation vector of the gold beam r , one could choose certain directions of deposition ϕ to bias certain areas (in this case the blue areas) with a higher amount of deposition.

The illustration on Fig. 3 shows how a square array can be produced. D1, D2 and D3 are three designated directions spaced $\phi = 120^\circ$ apart. These directions are chosen because they allow channeling of Au flux in between the spheres. The rest of the gold propagation beam would be blocked by the PS spheres and those arrays would receive less deposition. As a result specific arrays would have a bias in deposition height relative to the rest

Originally the substrate was laid flat, normal to the direction of deposition. D1, D2 and D3 would be carried out. To obtain D1, the substrate was tilted at $\theta = 20^\circ$ about the x axis and gold deposition was done. In D2, the substrate was rotated $\phi = -120^\circ$ anticlockwise about z axis and tilted again $\theta = 20^\circ$ about x axis before deposition was carried out. Lastly, D3 involved a rotation of $\phi = 120^\circ$ clockwise about z axis from the original flat position and tilted again $\theta = 20^\circ$ about x axis before depositing gold. In summary, gold depositions at $\theta = 20^\circ$ were carried out in 3 directions of rotations $\phi = 0^\circ, 120^\circ$ and -120° on PS monolayer mask on silicon wafers.

4. RESULTS AND DISCUSSION

Fig. 4 shows the self-assembled PS sphere monolayer on a Si wafer. As shown, the PS sphere is highly ordered within an area of $25\ \mu\text{m} \times 25\ \mu\text{m}$, which is enough for our purpose.

A deposition bias within the hexagonal gold pattern can be seen in Fig. 5(a) which shows a height difference of 11.3 nm between 2 nanostructures after gold was deposited via ARNSL. There was a similar repeating height difference between surrounding arrays. After etching was performed, periodic square lattices were obtained (Fig. 5(b)). Although it is not a perfect square array with angle of 90° at the corner, it is a near-square array (parallelogram). The square array is defined here as the smallest repeatable unit of the lattice. As shown in Fig. 5(d), some square lattices were imperfect because the silicon substrate was sloping down, resulting in one end of the substrate being further away from the gold source than the other end. Thus the area further away from the gold source received less deposition, causing a range in height for the taller and shorter arrays respectively. As a result, shorter arrays that veer towards the tall end of range might not be etched totally while taller arrays at the short end of range could be etched away. Finally, the square lattice we obtained in this case is $150\ \mu\text{m}^2$. However, we believed that larger area of square lattice can be obtained by shifting the substrate in x, y direction during evaporation, so that the same thickness of gold is deposited.

Nanostructures in Fig. 5(b) were triangular in shape, unlike the circular shaped square arrays obtained through gold deposition via bilayer mask. Fig. 5(b) shows the distance apart between 2 nanostructures is 421.9 nm which is smaller than PS colloids with sphere size of 424 nm because the nanoparticle is located at slightly above or below the diameter of the sphere. The fabricated nanoparticle has a height and width of 27.9 nm and 175.8 nm respectively. The white circle marked in Fig. 5(b) shows the size of nanoparticle is bigger than the surrounding nanoparticles because of the grain boundary defect within the colloidal crystal mask. The grain boundary defect region has more

space than the closed pack region and results in larger or combined nanoparticles as shown in Fig. 5(d). In addition, the corners at the triangular nanoparticle are not as sharp as the previously reported nanoparticle fabricated using nanosphere lithography (NSL). We believe the rounded corner in our case comes from the little space left over due to the remaining SDS between the colloids. This problem can be solved if large area of closed pack PS sphere monolayer is self-assembled without using SDS. One of the possible ways is to use a template to guide the PS sphere for self-assembly.

5. CONCLUSIONS

In conclusion, a novel method to obtain a near-square array from a hexagonal nanoparticle array was demonstrated. Using a combination of ARNSL, rotation and etching, the resulting arrays tend to be triangular in shape and of a smaller size due to etching. Some remaining imperfections in the square lattice are due to sloping nature of the substrate or the defects generated during colloidal self-assembly process. This method allows an extension of the conventional NSL to produce 4-fold symmetry arrays of nano-deposits of any material that can be evaporated.

Figure Captions

Fig. 1. Schematic of setup of angle-resolved thermal evaporator. ϕ is the rotation angle about z-axis and θ is the tilt angle about the x-axis. Tungsten basket with melted gold facing downwards towards substrate and was deposited at an angle θ .

Fig. 2. Schematic illustration of (A) original nanostructure and (B) square array after etching.

Fig. 3. Schematic illustration of (A) spheres and chosen deposition directions and (B) blockage of deposition by spheres valleys.

Fig. 4. Large area of self-assembled monolayer to act as a colloidal mask.

Fig. 5. (a) AFM image of hexagonal array of gold nanoparticles deposited from 424 nm-PS spheres monolayer (before etching). The height difference of the nanostructure as shown is 11.3 nm. (b) AFM image of the square arrays after etching of (a). (c) & (d) high and low magnification FESEM of the square arrays (after etching) respectively.

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