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Fabrication of Nano Patterns on Various Substrates Using Nanosphere Lithography Technique

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This paper presents a procedure for fabricating large-area, size-tunable, metal arrays with a periodically different shape using Nanosphere Lithography (NSL). This technique has attracted considerable interest because of its important applications as diffraction devices, chemical and optical data recording. Their ordered arrays can be used for anti-reflection surfaces, bio-sensors and nanopatterning masks. Two different types of patterns, honeycomb and hexagonal patterns, could be fabricated on various substrates with different procedures. All steps for making different patterns employed a PS (polystyrene) monolayer by spin coating. Honeycomb patterns were fabricated by spin coating a PS monolayer on a glass substrate and depositing a metal followed by removal of the monolayer, whereas the hexagonal pattern was produced by the transfer of a gold deposited monolayer onto a GaN substrate using the same process. These processes allow simple and excellent control of the size and shape of the patterns. All experimental results on structure characterization and determination of the nanoparticle metrics were accomplished by atomic force microscopy and field emission-scanning electronic microscopy.

Keywords: Nanosphere Lithography (NSL), Nanopattern, Polystyrene (PS), Thermal Evaporator, Sputter, Reactive Inductively Etching (RIE).

1. INTRODUCTION

The fabrication of nanostructured materials is a promising avenue of research owing to their novel electric, magnetic, optical or biological characteristics, which cannot be obtained using conventional nanostructured materials. These materials have many applications in science and technology, such as low dimensional electronic¹ and magnetic systems,² photodetectors,³ photoemitters,⁴ enhanced Raman scattering,⁵ filtration,⁶ bioreactors,⁷ biosensors,⁸ and supports for enzyme immobilization.⁹ Electron beam lithography is the most popular method for this type of nanofabrication. Ion beam lithography, X-ray lithography, electron holographic lithography, laser interference lithography, etc. are also available.

Although these methods have many advantages, they require large, expensive systems. On the other hand, nanosphere lithography (NSL)¹⁰ is one of the simplest methods for fabricating 2D patterns. It is a low cost, high throughput, general nanofabrication technique that is capable of producing an unexpectedly wide range of nanoparticle structures and well-ordered 2D nanoparticle arrays.

This paper reports a spin-coating method to form two types of patterns (honeycomb and hexagonal) by regular polystyrene (PS). Three different types of uniform patterns can be easily obtained on a range of substrates, such as Si wafer, glass, GaN. Structure characterization and determination of the nanoparticle metrics were accomplished by atomic force microscopy (AFM) and field emission-scanning electronic microscopy (FE-SEM).

2. EXPERIMENTAL PROCEDURE

Polystyrene (PS) with diameter of 580 nm was used to fabricate all three different patterns, and three common steps were followed. The first step is to spin-coat a PS layer. The second step is the deposition of a metal. The final step is the removal of the metal deposited PS. The detail experimental procedures are reported.

2.1. Honeycomb Pattern

Figure 1 shows the general fabrication process for producing the honeycomb pattern. First, sodium dodecyl sulphate was diluted with methanol (1:400) followed by the addition of 580 nm PS beads (C37347, CureBio. Co., Ltd.) at a ratio of 1:1 to make a PS solution.¹¹

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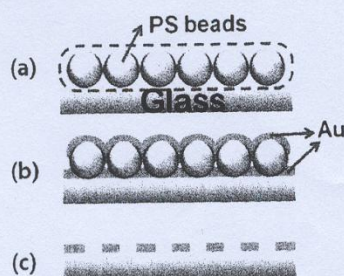


Fig. 1. Schematic diagram of honeycomb pattern fabrication by nanosphere lithography: (a) Polystyrene (580 nm) was spin-coated onto the glass substrate. (b) Au was then deposited on the glass substrate by thermal evaporation. (c) Au-PS was removed by sonication.

A glass substrate (Paul Marienfeld GmbH and Co. KG, Germany) was used to fabricate this pattern after RCA cleaning. The substrate was cleaned in an aqueous mixture containing 30% hydrogen peroxide, ammonium hydroxide and DI water with a volume ratio 1:1:5 at 80 °C, 30 min, followed by thorough rinsing with DI water and dipping into DI water until needed. After cleaning, the PS solution was spin-coated onto a glass substrate under the following conditions, which consisted of three stages:

- (i) 500 rpm for 30 s to spread the PS solution evenly;
- (ii) 1200 rpm for 1 min to spin away the excess PS solution;
- (iii) 3000 rpm for 10 s to spin off the excess materials from the edges.¹² A 50 nm Au layer was deposited by thermal evaporation in a vacuum (7.6×10^{-6} torr) at a deposition rate of 8~9 Å/sec. The Au coated PS beads were removed by sonication for 3 sec after deposition. After sonication, all Au deposited PS beads were removed. The honeycomb pattern, which is the exposed surface of the glass that had the spherical shape of the PS beads, could be obtained where the PS beads were removed.

2.2. Hexagonal Pattern

Figure 2 shows a schematic diagram of the entire fabrication process. First, an aqueous solution of 580 nm PS was diluted in methanol and spin-coated onto a glass substrate. The glass substrates were cleaned in $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ (1:1:5) at 80 °C for 30 min and stored in water until needed. The PS formed monolayers under the same conditions mentioned above. Subsequently, a ~50 nm thick Au film was deposited on the nanospheres by DC sputtering in a vacuum (1.0×10^{-6}) at a deposition rate of 1.5 Å/sec, plasma power of 30 W and Ar flow rate of 20 sccm (Fig. 2(b)), forming a continuous Au layer on the upper part of the hemispheres. The glass substrate coated with the nanospheres was immersed into DI water to separate the spherical layers from the substrate.

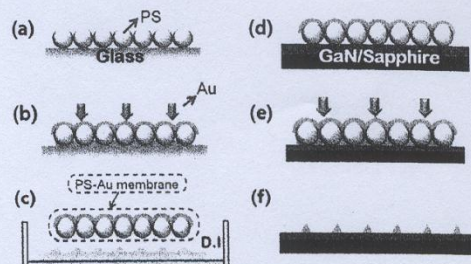


Fig. 2. Schematic diagram of the hexagonal pattern fabrication by nanosphere lithography: (a) polystyrene was spin-coated on glass substrate. (b) Au was sputtered onto the PS spheres (PS membrane). (c) The PS membrane was immersed in deionized water. (d) The PS membrane was transferred to the GaN substrate. (e) Au was again deposited with the PS membrane on GaN by thermal evaporation. (f) Au-PS was removed by sonicating the substrate-transferred Au-PS.

As a result, the free-standing membranes (Au-coated membranes of nanospheres) remained floating on the water surface Figure 2(c). The membranes were then transferred to the surface of GaN/sapphire by immersing the latter into the solution and lifting up the substrate together with the membrane. In conclusion, a hexagonal pattern was formed on a GaN substrate and the glass substrate used in the first step played an ancillary role in fabricating the pattern. As already mentioned, the direct deposition of PS nanospheres on GaN was difficult due to the hydrophobicity of GaN. The "mask transfer" technique¹³ was applied to address this problem. The nanospheres self-assembled on the hydrophilic substrate (glass in this case) were first connected by a thin metal coating, and then transferred to the GaN surface. For the hole pattern, the hydrophobic GaN substrate was changed to hydrophilic by plasma-enhanced chemical vapor deposition (PECVD) after an O_2 treatment for 2 min at 50 W. Finally, a 30 nm thick Au layer, which determined the shape of the pattern, was deposited on the GaN substrate with the PS membrane on the surface by thermal evaporation. Deposition was carried out in a vacuum (7.6×10^{-6} torr) at a deposition rate of 8~9 Å/sec. The shape of the pattern depended on the deposition rate. Finally, the pattern with a regular hexagonal array of triangular Au, was fabricated after sonication for 3~4 sec to remove the PS membrane.

3. RESULTS AND DISCUSSION

NSL is a widely used technique for producing a range of patterns on substrates with various nanomaterials, including ferroelectric,¹⁴ magnetic,¹⁵ and metal dots for the growth of carbon nanotubes¹⁶ and semiconductor nanowires etc. SEM showed that the spin-coated beads were packed mostly as monolayers of hexagonally closed packed domains with a domain size of $150 \mu\text{m} \sim 6 \text{ mm}$ on the substrates. Occasionally, holes with diameters of

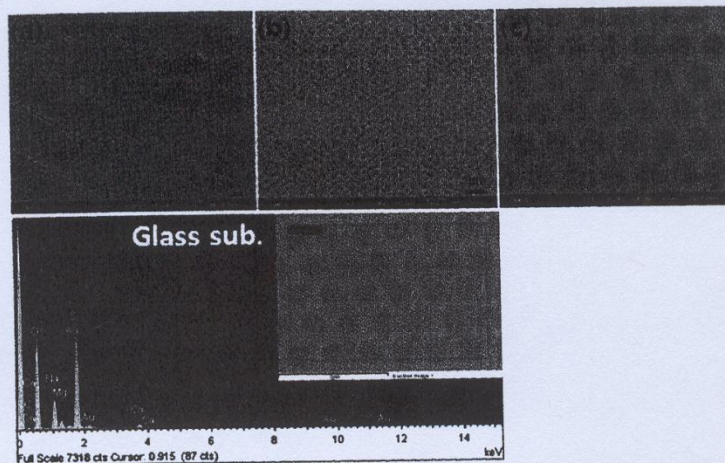


Fig. 3. Field Emission-Scanning Electronic Microscope of 60 nm Au evaporated on the glass substrate. (a) 580 nm polystyrene is spin-coated on glass substrate. (b) Au is evaporated onto PS spheres. (c) Honeycomb pattern. (d) EDS analysis of Au and glass substrate.

$\sim 1.5 \mu\text{m}$ were observed between the domains. Although dip-drying is a common technique for NSL, spin-coating was found to be a more controllable process. The patterns formed in this study will be introduced in this section.

3.1. Honeycomb Pattern

Fabricating the honeycomb pattern was quite simple. Spin-coating was a more controllable and convenient process, particularly for patterning a monolayer of beads on a range of substrates. Figure 3(a) shows closed-packed PS beads deposited by spin-coating. The same monolayers in Figure 3(b) showed different contrast due to the deposition of a ~ 50 nm thick Au layer onto the PS monolayer. Figure 3(c) shows the honeycomb pattern. PS-Au was removed by sonication for 5 sec. The hole size was approximately 480 nm. The glass composition and Au was confirmed in the EDS spectrum in Figure 3(d). The FE-SEM images confirmed the well ordered pattern. The AFM image in Figure 4 shows the uniformity of the honeycomb pattern and the uniformity of the hole diameter of approximately 480 nm and hole depth of approximately

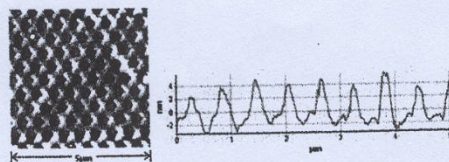


Fig. 4. AFM image of the honeycomb pattern.

50 nm throughout the entire pattern. The patterns can have a range of applications if the thickness or type of the deposited metals can be controlled.

3.2. Hexagonal Pattern

The major characteristic of the hexagonal pattern is to fabricate a pattern using "mask transfer" on an unmaneuverable substrate due to the hydrophobicity of its surface. The overall fabrication process is the same as the process for fabricating the above two patterns. Au metal was deposited after the formation of the PS monolayers to produce the shape of the pattern and the pattern was finally fabricated by removing the deposited PS. The membrane of the PS monolayers was fabricated by sputtering to move the closed-packed PS monolayers with its original shape to the GaN substrate. The GaN substrate was used after its hydrophobic surface was changed to hydrophilic by an O_2 treatment with PECVD, and the PS membrane was easily transferred to the GaN substrate. Figure 5 shows images of each step as well as the PS membrane on the GaN substrate (Fig. 5(c)). Considering the characteristics of FE-SEM, a relatively small size was selected for the entire area of the PS membrane, and this image was approximately $1174 \times 1642 \mu\text{m}$. Au deposition was performed by thermal evaporation. Au was deposited on a PS membrane and the surface between the PS beads. As shown in Figures 5(d, e), Au passing through the space in PS had a triangular hexagonal pattern, which depends on the deposition rate of the thermal evaporator. Figures 5(d and e) show the forms deposited at a $7 \sim 8 \text{ \AA/sec}$ and $2 \sim 3 \text{ \AA/sec}$ deposition rate, respectively. The thickness of each triangular Au was 30 nm and the pattern was relatively well

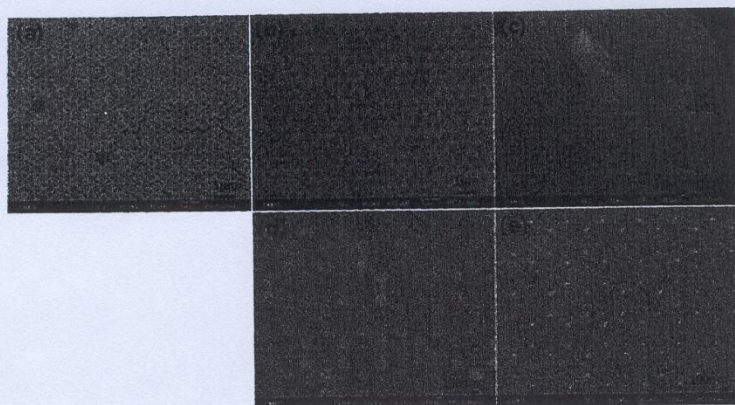


Fig. 5. FE-SEM image of the hole pattern on GaN substrate (a) Au deposited PS monolayers (b) the glass substrate after floating the PS membrane (c) PS membrane on the GaN substrate (d, e) hexagonal pattern images of different deposition rate.

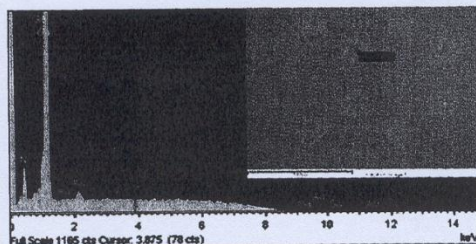


Fig. 6. EDS spectrum of Au pattern on GaN substrate.

ordered. The ED spectrum in Figure 6 shows that the GaN substrate was used for this pattern. AFM confirmed the well ordered Au pattern (Fig. 7).

The good separation and small size are another advantage of the mask transfer technique. In this method, the metallic coating of the PS spheres narrows the holes between the spheres, and subsequently the Au dot size. This is highly desirable for the subsequent growth of single nanowires on individual Au dots. This approach suggests the possibility of creating patterned one-dimensional nanostructures for applications as sensor arrays, optoelectronic devices and interconnects.

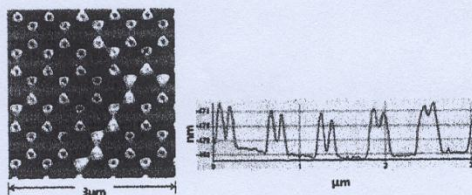


Fig. 7. AFM image of the hexagonal pattern.

4. CONCLUSION

Nanosphere lithography can be a suitable preparation method for large-scale, magnetic and periodic particle arrays, containing a very small quantity of structural defects. The main advantages of this technique are the short preparation time, high level of hexagonal, hole and honeycomb structures and the possibility of application of large, monolayered masks directly onto any type of surface. In the present study, the honeycomb and hexagonal patterns were produced using NSL. The period was determined by the initial diameter of the polystyrene beads. This method is expected to have a wide range of applications in science and technology. In the hexagonal pattern, the direct deposition of PS nanospheres on GaN was found to be difficult due to the hydrophobicity of GaN. The "mask transfer" technique was used to address this problem. The nanospheres were self-assembled on the hydrophilic substrate (glass in this case), connected with a thin metal coating, and transferred to the GaN surface. Mask transfer stabilized the self-assembled spheres, which reinforces the feasibility of large-scale Au nanodot arrays on GaN. This paper presented a possible approach to the direct production of biosensors, optical devices, and the indirect formation of magnetic recording media and bioreactors.

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