Periodic Nanowell Array using Template-Assisted Nanosphere Lithography

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ABSTRACT

Nanosphere lithography (NSL) has been studied as the effective method of fabricating nano-scale array. This paper presents template-assisted NSL to obtain high-quality crystal in regularity and coverage. A periodic array of 100 nm deep nano trenches with two different widths, 400 and 450 nm was fabricated by nano imprint lithography (NIL), and used as the template. When polystyrene nanospheres with the diameter of 100 nm were spin-coated on the substrate with the template morphology, they formed a crystal array with improved periodicity in both lateral and longitudinal directions. We also demonstrated nanowell array through subsequent deposition and etching steps.

Keywords: nanosphere lithography, template-assisted NSL, nano imprint lithography, nano fabrication

1 INTRODUCTION

Nano-scale fabrication has been developed for scaling down in microelectronics, sensors, and many other applications. The conventional lithographic methods have been used for nano patterns. Photolithography, most widely used in modern microelectronic fabrication, is parallel, simple, quick, and inexpensive process. Photolithographic resolution is, however, limited by the diffraction of the UV light. Many approaches such as electron beam lithography, X-ray lithography, extreme UV lithography, and scanning probe lithography have been studied in order to overcome this problem [1-4]. However, high cost, complexity, and long process time still prevent the wide use of above approaches to reduce the features.

Among non-optical lithographic methods studied as alternatives in recent days, nanosphere lithography (NSL) has been proved useful when a regular pattern on a large area was needed [5-8]. Advantages include low cost, quick process, and the freedom in choosing various materials on diverse substrates [5, 6]. In NSL, many approaches have been developed such as drop-coating, spin-coating, Langmuir-Blodgett method, and electrical method [9-12].

Many studies have been reported for nanosphere array above 300 nm in diameter using the above methods. No previous method, however, claims successful results with well-defined 100 nm features on a reasonably large area. The large variation of bead sizes and strong Van der Waals force between beads prevent the formation of a single domain, leading to multiple, fragmented domains.

This paper introduces template-assisted NSL that is the new method combined the morphology-driven arrangement with spin coating. We show 100 nm patterning over a large area through the optimization of spin coating and the use of nano trench on a substrate fabricated by nano imprint lithography (NIL). Also demonstrated are the fabrication of nanowell array by the shrinkage of nanosphere, metal deposition, and lift-off process.

2 EXPERIMENT

2.1 Preparation of Substrate

The nano-trench on a substrate was prepared using NIL (NANOSYS 420, NND co., Korea) [13, 14]. The mold was fabricated by electron beam lithography and inductive-coupled plasma (ICP) etching of silicon. Completed mold was coated with self assembled monolayer (SAM, heptadecafluoro-1,1,2,2-tetrahydrodecyl trichlorosilane) for an easy removal of the mold from the substrate after imprint. A silicon wafer with 100 nm-thick SiO_2 was used as the substrate. Thermoplastic polymer (mr-I 8010, Micro Resist Technology, Germany) was coated on the substrate. The NIL was performed at 190 ºC and 40 bars. The NIL was followed by the removal of residual polymer. The SiO_2 layer was etched with reactive ion etching (RIE) until the silicon surface was exposed. Finally polymer was stripped with piranha treatment (4:1, H_2SO_4:H_2O_2).

After diced into 1 mm ×1 mm pieces, the substrate with the nano-trench was pretreated with piranha for 3 h @ 120 ºC to clean the substrate and grow the native oxide on the silicon surface. These treatments changed the silicon surface into a hydrophilic one. The surface was further treated with RCA treatment (5:1:1 H_2O: NH_4OH: H_2O_2) with sonication for 30 min to increase the hydrophilicity of the substrate. To maintain cleanliness and wettability, the completely treated substrate was stored in deionized water until next continues.

2.2 Assembly of Nanospheres

Polystyrene nanospheres (Duke Scientific Co., USA) with the diameter of 100 nm were spin-coated on the substrate. In our approach, spin coating was completed in three steps as shown in Figure 1. First, 60 µg nanosphere solution was spin-coated on a substrate at 500 rpm for 10 s to spread the solution. Second, the substrate was rotated at a critical spin rate for 2 min to form and arrange the crystal of nanospheres. Various spin rates from 100 rpm to 1500 rpm were used to find the optimal condition for crystal formation. Finally, to remove the nanosphere solution from the substrate except for the nanospheres assembled in the trench, the spin rate was ramped up to 2000 rpm at the acceleration of 100 rpm/s.

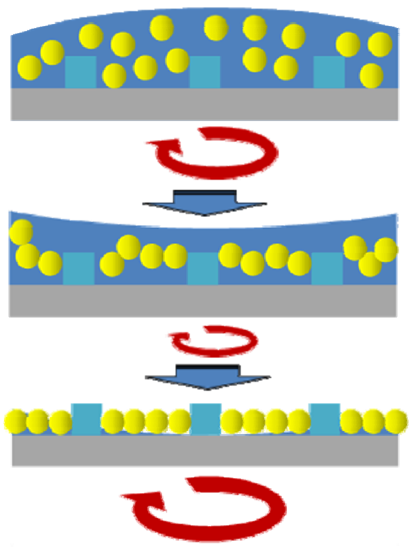

Figure 1. Schematic of template-assisted NSL that consists of spin coating with three steps: 1) spreading, 2) arrangement, 3) removal

2.3 Fabrication of Nanowell Array

The nanosphere array produced through template assisted NSL was shrunk by O_2 plasma to reduce the diameter of the nanospheres. The ashing with the plasma continued for 20 s at flow rate of 50 sccm, RF power 50 W, and pressure 50 mTorr. After the shrinkage, 10 nm-thick chromium was deposited on the spaced nanosphere array by e-gun evaporator (ZZS550-2/D, Maestech Co., Korea). The deposition rate was kept very low to obtain a uniform metal layer. Then the nanospheres were lifted off using toluene with sonication for 30 min.

3 RESULTS & DISCUSSION

The quality of the template-assisted NSL method heavily depends on spin coating. To obtain optimal spin rate for the best formation of nanosphere array with 100 nm in diameter, nanospheres were coated on the substrate without the nano template at various spin rates; 100, 200, 500, 800, 1000, 1200, and 1500 rpm.

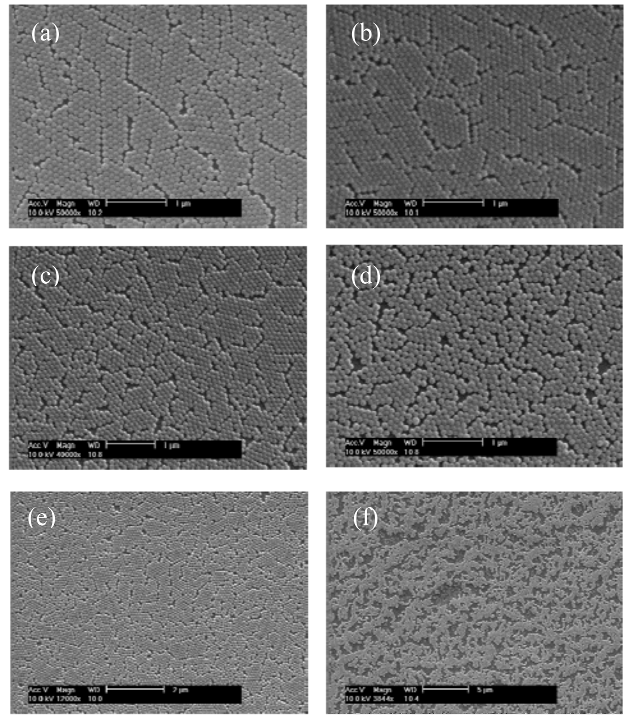

Figure 2. The SEM images of nanosphere array without nano template using spin rate of (a) 200, (b) 500, (c) 800, (d) 1000, (e) 1200, and (f) 1500 rpm. As the spin rate increased, the coverage was poorer and more domains were generated.

The relationship between the spin rate and the formation of nanosphere crystal is shown in Figure 2. The increase of the spin rate raised the number of the cracks, while reducing the domain size and the coverage on a substrate. Lower spin rate enabled better coverage and larger single domain. However, spin rate lower than 200 rpm deteriorated the formation of nanosphere crystal. This trend means that there exists the critical spin rate for the best crystal formation of nanospheres. For current process 200 rpm was determined as an optimum spin rate.

The perfect nanosphere crystal, however, could not be achieved using spin coating only. Even the best result at the spin rate of 200 rpm among the above ones had many cracks. It is likely that there was no force to rearrange the imperfect nanospheres without cracks. The breaking of the domains and reformation into the single domain were needed to produce the large scale patterning. We introduced a nano-template to enforce the periodic, crack-free arrangement of the nanospheres. Dimensions of the trench fabricated by NIL were 100 nm in depth with two different widths, 400 and 450 nm as shown in Figure 3.

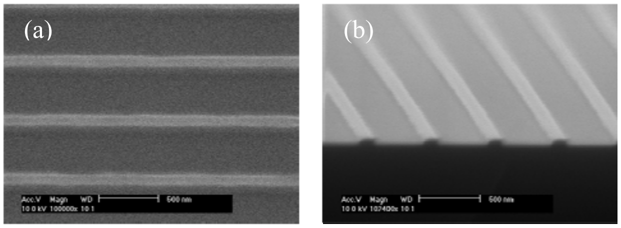

Figure 3. The SEM images of the nano template used in this experiment: (a) top view and (b) side view of nano template. The nano-template was 100 nm in depth with two different widths, 400 and 450 nm.

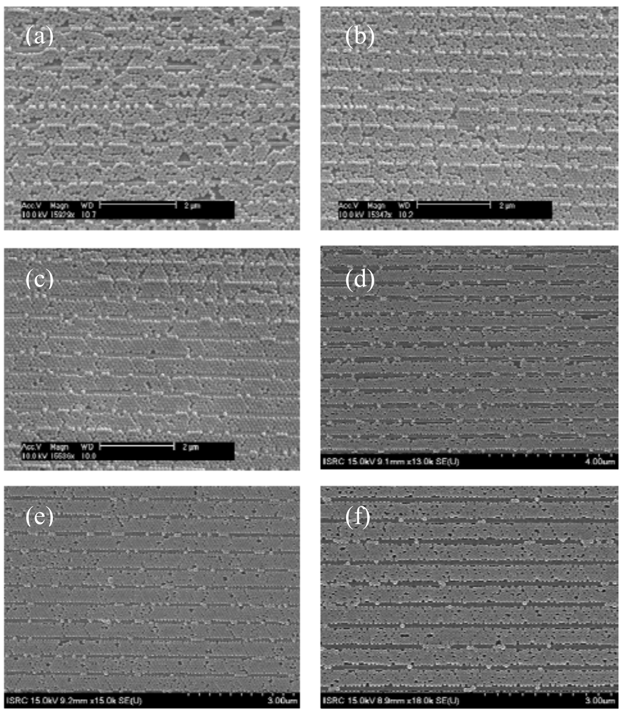

Figure 4. SEM images of template-assisted NSL at a spin rate of (a) 1500, (b) 1200, (c) 800, (d) 500, (e) 200, and (f) 100 rpm.

Figure 4 shows the results of template-assisted NSL at various spin rates. Like previous results of spin coating, crystal at 200 rpm produced the best coverage. There are additional advantages due to the use of nano-template. The nano-template helped the rearrangement of crystals as a passive guidance. The crystals of nanospheres were formed from several spots throughout the substrate at the early stage of arrangement process. Without any guidance, the crystals combined by Van der Waals interaction were never broken and rearranged, resulting in multiple domains. However, when guided by the template, the crystals could be relocated in the trench. The nano-template broke and rearranged the crystals by fitting them in the trench. Also, the cracks in the crystal array were reduced by the nano template. The cracks were almost always formed during the crystal formation of nanospheres on the substrate. Generally the crack is produced by (1) the distribution of nanoshpere diameters, (2) the collision between domains, and (3) the spots missing nanospheres in the array. In the template assisted NSL, however, the cracks were not continued on in the array and the effect of the crack, if any, was kept small. The template allows the freedom in one dimension, and the crack stops when bumping against the wall.

The gap size of the nano-templates was also a key factor for the crystal formation as the gap size is determined by

$$l_g = [(n-1)\sin 60^\circ + 1]d \quad (1)$$

,where n is the number of nanosphere rows per gap and d the average diameter of nanospheres. We used nano trench with two types of widths. One was 450 nm which was calculated with 100 nm in diameter and 5 nanosphere rows per gap. The other was 400 nm which was not suited with the current dimension of the nanosphere.

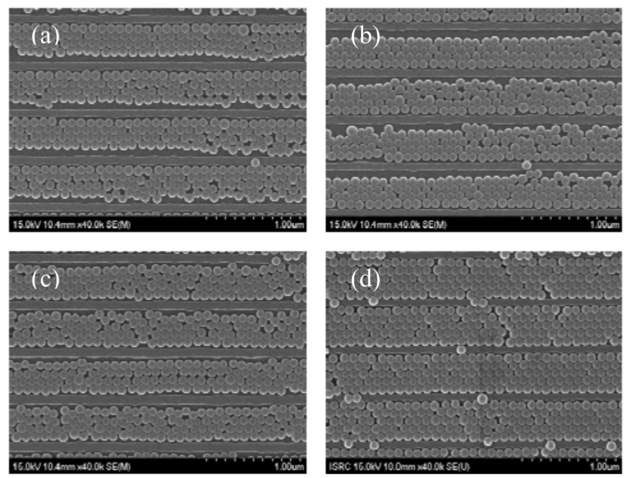

Figure 5. The crystals in 400 nm in width were placed (a) at the top or (b) at the bottom or (c) randomly. (d) 450 nm trench was packed perfectly. These results show the importance of the correct dimension of width.

Figure 5 (d) clearly shows that the nano template with precisely calculated width (450 nm) resulted in the formation of highly periodic nanosphere crystal. In contrast, the crystals were placed on the either side (Figure 5 (a), (b)) or randomly (Figure 5 (c)) when the width was 400 nm. In case of (a) and (b), biased side was determined by the direction of the centrifugal force.

Figure 6 shows the results of the fabrication process of nanowells. Shrunk nanospheres with O_2 plasma were shown in Figure 6 (a) and (b). The diameter of nanospheres after the plasma was reduced by 30 % in size. The periodic nanowell array was produced by the metallization and lift-off process as clearly shown in Figure 6 (c). We obtained the nanowell array extended in lateral direction through template assisted NSL.

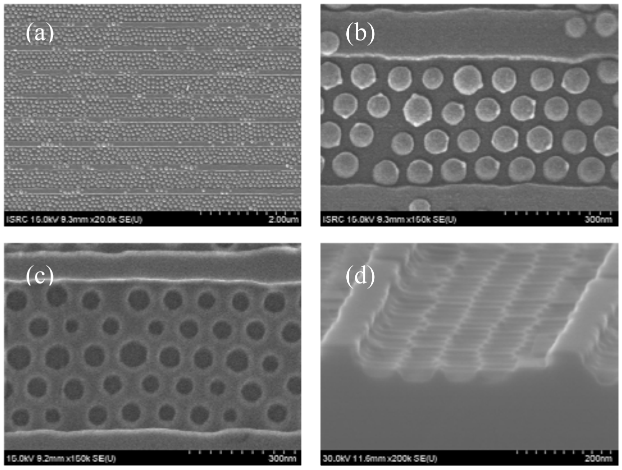

Figure 6. (a) and (b) shrunk nanospheres with O_2 plasma. (c) and (d) the nanowell array after metallization and lift-off process.

4 CONCLUSION

In this paper, we developed the template-assisted NSL which combines the active coating method (spin coating) and the passive guidance (nano-template). The nano-template fabricated by NIL helped the periodicity of nanosphere array. The nanowell array was fabricated through the subsequent steps of shrinkage, metallization, and lift-off process. We believe our methods will enable many applications that need a precise periodic nano pattern with simple process.

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