Silicon nanodot arrays patterned using diblock copolymer templates

Gil Bum Kang · Seong-Il Kim · Young Hwan Kim · Yong Tae Kim · Jung Ho Park

Abstract Dense and periodic arrays of holes and Si nano dots were fabricated on silicon substrate. The holes were approximately 20–40 nm wide, 40 nm deep and 40–80 nm apart. To obtain nano-size patterns, self-assembling resists were used to produce layer of hexagonally ordered parallel cylinders of polymethylmethacrylate (PMMA) in polystyrene (PS) matrix. The PMMA cylinders were degraded and removed with acetic acid rinse to produce a PS. 10 nm-thick Au thin film was deposited by using electron beam evaporator. PS template was removed by lift-off process. Arrays of Au nano dot were transferred by using fluorine-based reactive ion etching. Au nano dots were removed by sulfuric acid. Si nano dots size and height were 24–70 nm and 20–30 nm respectively. Sequential oxidation-wet etching method reduced size of Si nano dots. Reduced sized silicon nano dots diameter and height were 18 nm and 12 nm, respectively. Nanopatterned holes sizes were observed by field emission scanning electron microscope (FESEM) and atomic force microscopy.

Keywords Diblock copolymer · Copolymer lithography · Reactive ion etching · Si nano dot · Nanotemplate

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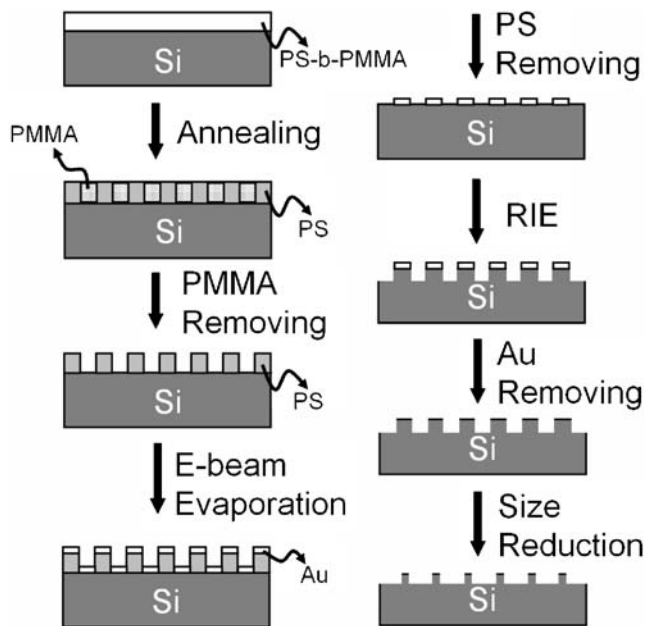Korea University,
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1 Introduction

Photolithography has played a predominant role in producing features of sizes greater than ~1000 nm for the past few decades. As industrial and academic fields have demanded smaller and denser features, electron beam lithography has been used to produce features as small as 30 nm in recent years. However, structures less than 30 nm in size are not easily obtained by standard optical lithography techniques. Because of the advantages of smaller and denser microelectronic circuitry, novel techniques for nanolithography with smaller feature sizes have been investigated [1–3].

Electronic circuits often require the fabrication of intricate and complicated structures. However, simple periodic patterning is sufficient for many devices. Various applications of nanometer periodic patterning include the fabrication of high-density magnetic recording devices [4], the fabrication of quantum dots or antidotes [5], and the creation of a periodic electric potential in a two-dimensional electron gas system [6]. For these applications, ordered microstructures observed in diblock copolymer films seem to be ideal because of lithography templates for their ~10 nm length scale and their ability to fabricate uniformly patterned and wafer-sized areas.

Diblock copolymers consist of two distinct polymer chains covalently bound at one end. They self-assemble to form well-ordered periodic microdomains at molecular length scales because of the tendency for unlike chains to separate and the constraint imposed by chain connectivity. The competition between interfacial energy and chain-stretching energy governs the bulk equilibrium-phase behavior, and the relative volume fractions of the block control the curvature, size, and periodicity of the microdomains. Diblock copolymers, which are composed of incompatible block segments, are attractive materials for

Fig. 1 Schematic procedures for fabricating Si nano dots

with a high aspect ratio through a pattern transfer process from the top layer of sphere-forming polystyrene-block-polyisoprene (PS-b-PI) diblock copolymer thin films to the polyimide bottom layer by multiple reactive ion etching. An array of gold dots with a real density of $\sim 10^{11}$ cm^{-2} was finally produced by electron-beam metal evaporation followed by a wet lift-off process [8].

In this paper, we introduce a fabrication method of Au and Si nano dots arrays using a diblock copolymer film for a template (Fig. 1). Specially, we fabricated Au nano dots for metal nano dots dry etching mask using the conventional lift-off process. PS-b-polymethylmethacrylate (PMMA) was used to fabricate nanopatterns on the Si surface. Au thin film was deposited on PS nano template using by electron beam evaporation. Uniformly distributed nano dots were fabricated on Si substrate using tetrahydrofuran (THF) sonication. By reactive ion etching (RIE), we tried to transfer the nanopattern to the substrate. After removing process of Au nano dots dry etching mask, Si nano dots were fabricated and size reducing process were performed. We confirmed that cylindrical nanostructures were generated on PS-b-PMMA, Au nano dots and Si nano dots were confirmed in Si substrates using a field-emission scanning electron microscopy and an atomic force microscopy (AFM).

2 Experimental procedure

Si substrates were cleaned by Pirhana cleaning to remove organic chemicals and hydrophilic surfaces. Si substrates with balanced interfacial interactions of PS and PMMA were prepared by anchoring 3-(p-methoxyphenyl) propyltrichlorosilane (MPTS, CH$_3$OPh (CH$_2$)$_3$SiCl$_3$, >95%) to the native silicon oxide layer [9, 10].

forming a wide variety of self-assembled microdomain morphologies composed of lamellar, cylindrical, or spherical structures [7]. To fabricate such nanostructures, one of the blocks in the diblock copolymer must be removed by chemical or physical etching, taking advantage of the difference in chemical properties between the two blocks.

Recently, many studies have demonstrated general strategies to pattern arrays of metal-dots (not necessarily magnetic) by block copolymer lithography, metal deposition, and lift-off. Park et al. demonstrated the large-area fabrication of a hexagonally ordered array of gold dots by combining block copolymer lithography and a trilayer resist technique (block copolymer thin film/silicon nitride/polyimide bottom layer). They generated a nanoporous template

Fig. 2 FESEM images of PS template on Si substrate; (**a**) Fabricated by using 77 k PS-b-PMMA diblock copolymer. (**b**) Fabricated by using 200 k PS-b-PMMA diblock copolymer
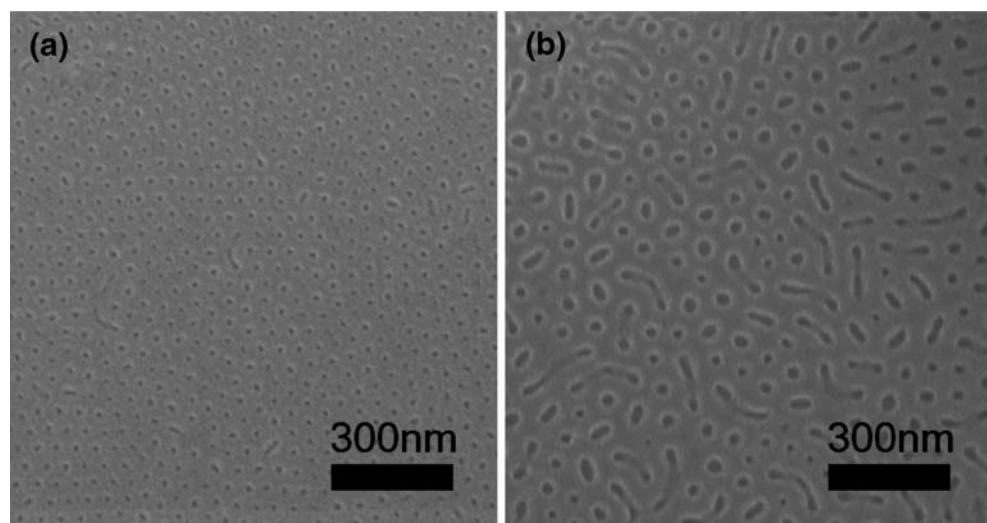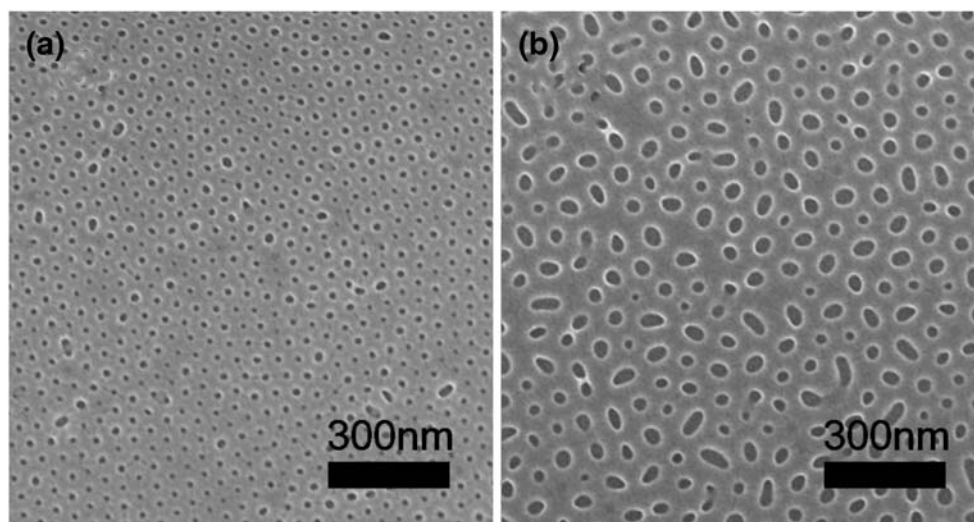
Fig. 3 FESEM images of Au coated PS template; (**a**) Fabricated by using 77 k PS-b-PMMA diblock copolymer. (**b**) Fabricated by using 200 k PS-b-PMMA diblock copolymer

A film of PS-b-PMMA (77 and 200 kDa, 70:30 by volume) was spin-coated on Si using 1% (w/w) toluene solution at 3000 rpm and annealed at 200°C for more than 48 h under vacuum to induce complete microphase separation. Then, the cylindrical PMMA blocks were selectively degraded by UV exposure (at 254 nm, 1 J cm^{-2}) and subsequently rinsed with acetic acid and deionized water to remove the degraded PMMA. After forming PS mask, 10 nm-thick Au thin film was deposited by using e-beam evaporator. PS template was removed by lift-off process. Arrays of Au nano dot were transferred by using fluorine-based RIE. Au nano dots were removed by sulfuric acid solution. Subsequently, Si nanodots annealed with rapid thermal annealing (RTA) in O$_2$ atmosphere and rinsed with buffered oxide etch solution.

The film thickness was measured by Alpha-step. The domain structures of the block copolymer thin films and Au

nano dots were imaged for each sample using a FEI-100 FESEM and XEI-100 AFM.

3 Results and discussion

The copolymer thin films have cylindrical PMMA micro-domains in the crosslinked matrix [11]. When the temperature is increased to above the glass-transition temperature of PMMA, the PMMA cylindrical domains release the stress exerted by the surrounding crosslinked PS matrix in the outer cylinder direction [11]. The crosslinking polymer, in general, causes volume contraction of the polymer due to the covalent coupling of adjacent chains.

From the FESEM image in Fig. 2, it is evident that nanoscopic holes are formed at the center of the cylindrical PMMA microdomains. The ordered nanometer-scale area

Fig. 4 FESEM images of Au nano dots on Si substrate; (**a**) Fabricated by using 77 k PS-b-PMMA diblock copolymer. (**b**) Fabricated by using 200 k PS-b-PMMA diblock copolymer
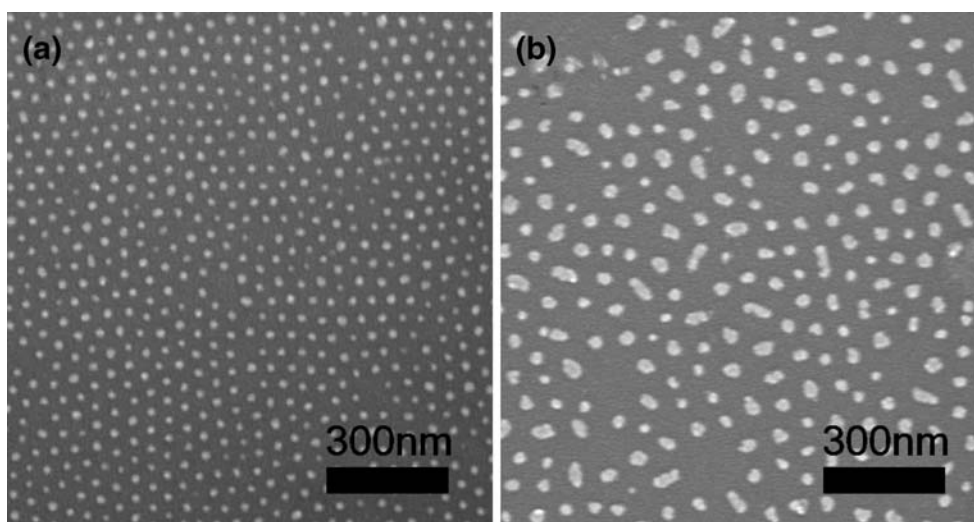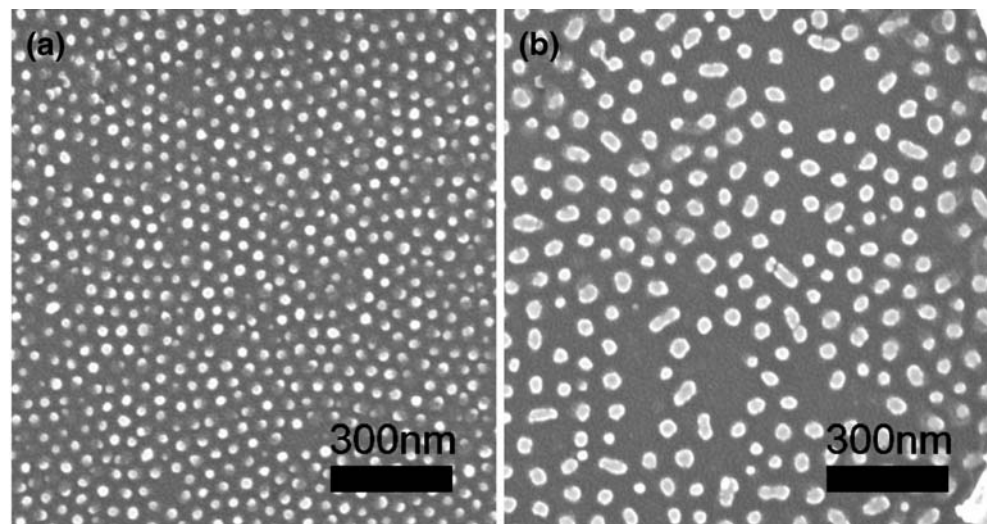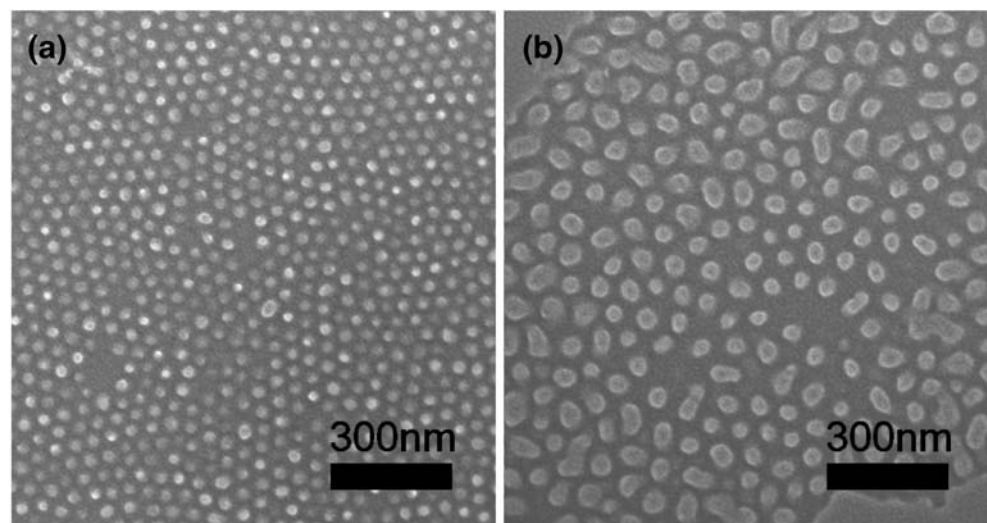
was made using simple processing tools. The sizes of the holes were about 20 nm fabricated by 77 k PS-b-PMMA block copolymer and 40 nm fabricated by 200 k PS-b-PMMA block copolymer [Fig. 2(a) and (b)]. The thickness of the films was 40 nm. It was possible to change the hole size by changing the molecular weight of the diblock copolymer [12]. The PMMA block was removed and PS-based patterns remained. In Fig. 2, the dark points are cylindrical empty spaces and brighter back ground is the template of the PS polymer.

PS template was coated with Au thin film using electron beam evaporator. Thickness of Au films was 10 nm. Figure 3 shows brighter image than Fig. 2 that affected by Au thin film. Order distribution of nano pattered hole was not changed in PS template fabricated by 77 k block copolymer [Fig. 3(a)]. However, in Fig. 3(b), better order distribution of nano patterned hole was observed than Fig. 2(b). Because, when Au thin film coated on PS

template, Au thin films separate a top side of arched structures on PS template fabricated by 200 k block copolymer thin film. Figure 4 is FESEM images of substrate after lift-off process. When the evaporation of Au thin film progressed, the PS nano-scale holes were coated by Au thin film. Therefore, Au thin films on Si substrate in nano scale hole remain in spite of lift-off process. Au nano dots were uniformly distributed on Si substrate [Fig. 4(a), (b)]. In Fig. 4(a), almost hexagonally distributed Au nano dots were observed but a part of dots were disappeared. Weak adhesion force of Si substrate and Au thin film caused removing of Au nano dots while lift-off process in THF sonication. This removing effect made empty space. Empty space was sporadically observed in Fig. 4(b).

Morphology of Au nano dots were transcribed on Si substrate using by RIE. Au nano dots were used as dry etching mask. We used SF_6-based plasma chemistry to etch

the Si substrate (flow rate 10 sccm SF_6, bias rf power 30 W, 35 mTorr and 30 s) [13]. Figure 5 is FESEM images of surfaces after RIE. If the etching space were broad area, etching process would be progressed in equal area. But, in this experience, exposed area of Si surface to the RIE process was to narrow to etch with the same rate of broad area. Therefore, etched area of Si was reduced [Fig. 5(a), (b)]. SF_6 RIE is isotropic etching process, but it was not enough time to etch to horizontal side. In dry etching process, equal effect of etching materials progressed on dry etching mask. In Fig. 5, the brightness of Au nano dots metal mask is faded.

Au nano dots dry etching mask were removed by solution of mixture of sulphuric acid and hydrogen peroxide. Figure 6 is FESEM image of Si nano dots images after Au nano dots removing. Au nano dots covered on Si nano dots in Fig. 5, but, Si nano dots were appeared on surfaces after Au nano dots were removed [Fig. 6]. In Fig. 6(a), the diameter of Si nano dots were 24 nm and height of Si nano dots were 20 nm fabricated by 77 k block copolymer. In Fig. 6(b), the diameter of Si nano dots were 30–70 nm and height of Si nano dots were 30 nm fabricated by 200 k block copolymer. Difference of Si nano dots height was caused by difference of empty space distance between Au nano dots and neighboring.

To obtain a smaller size of nano dots, additional annealing process was performed. In O_2 atmosphere, substrate was annealed (500°C, 60 s) and rinsed with BHF. Surface was oxidized in RTA process and thin oxide layer was removed with BHF rinse. After 10 times of oxidation-wet etching sequential process, diameter and height of Si nano dots were reduced (Fig. 7). FESEM images of Si nano dots were showed in Fig. 7(a) and (c). Hemispherical shape of Si nano dots (Fig. 7(a)) became dulled in Fig. 7(c). In Fig. 7(a) and (b), diameter and height were reduced after sequential wet etching process. Diameter and height of size reduced Si nano dots were 18 nm and 12 nm, respectively.

4 Conclusion

We fabricated nano scale silicon dots using a diblock copolymer. By using electron beam evaporation method, Au thin film was coated on PS nanotemplate. Au nano dots were fabricated on silicon substrate using lift-off in THF sonication. By RIE, we tried to transfer nano array of Au nano dots. During dry etching, the original order of Au nano dot was maintained: thus, nanoscopic Si nano dots were fabricated. Si nano dots size and height were 24–70 nm and 20–30 nm, respectively. Sequential oxidation-wet etching method reduced size of silicon nano dots. In this work, we fabricated reduced-sized silicon nano dots. Si nano dots diameter and height were 18 nm and 12 nm, respectively.

Fig. 7 Si nano dots were fabricated by using 77 k PS-b-PMMA diblock copolymer. (**a**) 40° tilted FESEM image and (**b**) 3D topography AFM image. (**c**) FESEM image, after size reducing process. (**d**) 3D topography AFM image, after size reducing process. Scale set value of 3D topography AFM was 5
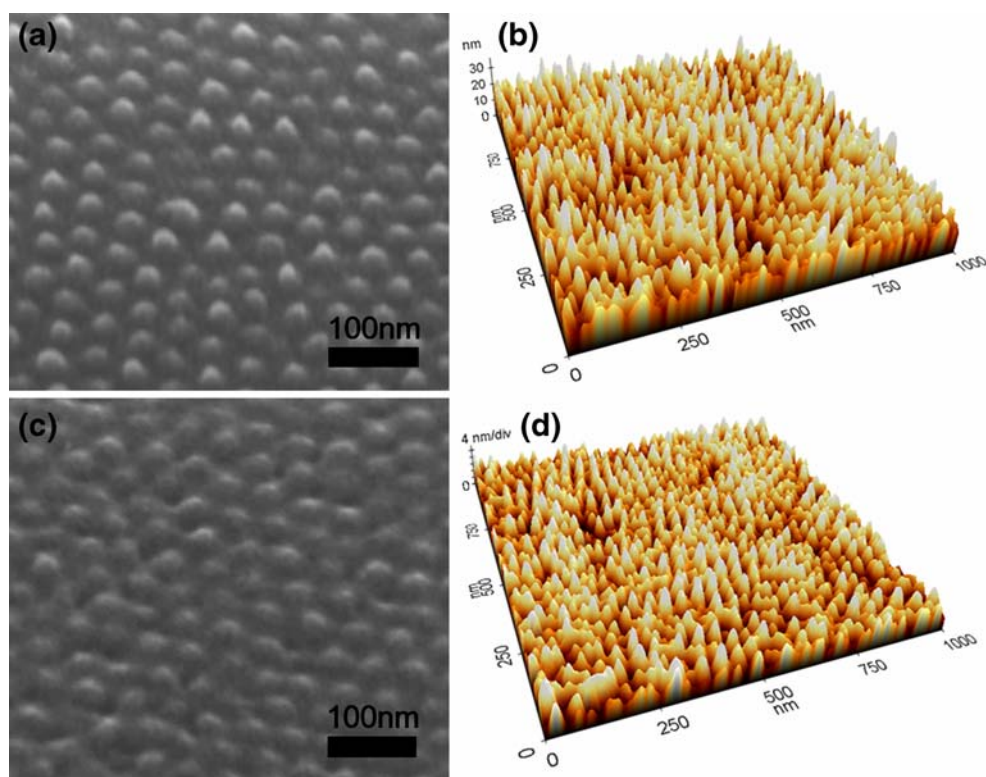
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