Fabrication of Nanopatterns by Using Diblock Copolymer

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Abstract

Thin films of diblock copolymers may be suitable for semiconductor device applications since they enable patterning of ordered domains with dimensions below photolithographic resolution over wafer-scale area. We obtained nanometer-scale cylindrical structure of dibock copolymer of polystyrene-block-poly(methylmethacrylate), PS-b-PMMA, also demonstrate pattern transfer of the nanoporous polymer using both reactive ion etching. The size of fabricated naonoholes were about 10 nm. Fabricated nanopattern surface was observed by field emission scanning electron microscope (FESEM).

1. Introduction

Feature size less than 30 nm are not easily obtained by standard semiconductor lithography techniques. Because of the technical trend is smaller, faster, and denser microelectronic systems, different novel techniques for nanolithography have been investigated by many researchers[1,2]. Diblock copolymer lithography is a useful technique in the nanopattern fabrication for the microelectronic devices and biotechnology applications such as microelectrode arrays, well defined polymer patterns, memory devices, and biosensors[3].

Diblock copolymers consist of two distinct polymer chains covalently bound at one end. They self assemble to form well-ordered periodic microdomains on molecular length scales because of the tendency for unlike chains to phase separate and the constraint imposed by chain connectivity. The competition between the interfacial and chain-stretching energies 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 composed of incompatible block segments are attractive as materials to form a wide variety of self-assembled microdomain morphologies composed of lamellar, cylindrical, or spherical structures[4]. To fabricate such nanostructures, one of the blocks in the diblock copolymer must be removed by chemical and/or physical etching, taking advantage of the

difference in chemical properties between two blocks.

In this article, we report simple and effective technique for fabricating nanopatterns on semiconductor surface using a diblock copolymer. By using a polystyrene-block-poly(methylmethacrylate), PS-b-PMMA for fabricate nanopatterns on the SiO_2/Si surface. And by using a reactive ion etching (RIE), we tried nanopattern transfer into a substrate. We confirmed cylindrical nanostructures are generated on PS-b-PMMA by field-emission scanning electron microscope (FESEM).

2. Experiments

SiO_2 substrate is prepared by chemical vapor deposition (CVD) on Si substrate. SiO_2/Si substrates is cleaned by Pirana cleaning that for removing organic chemicals. Poly(styrene-b-methylmethacrylate), PS-b-PMMA is prepared by living anionic polymerization in THF at -78 ℃. Polystyrene macro-anions were end capped with a unit of diphenyl ethylene(DPE) before adding methylmethacrylate(MMA) monomer. The scheme of the reaction is illustrated in Fig 1. The number of molecular weight of PS and PMMA were 46,100 g/mol and 21,000 g/mol. Diblock copolymer was spin-coated on to SiO_2/Si by using a 1 %(w/w) toluene solution at 3000 rpm and annealed at 200 ℃ for more than 48 hr under vacuum to induce complete microphase separation. Then, the cylindrical PMMA blocks were selectively degraded with a deep UV exposure (at 248 nm, 1 J cm^{-2}), and subsequently rinsed with acetic acid and deionized water to remove the degraded PMMA. After forming the PS mask, we using flourine-based reactive ion etching(RIE) techniques to transfer the microdomain pattern in the monolayer to the underlying SiO_2/Si, with the copolymer it self as the etching mask.

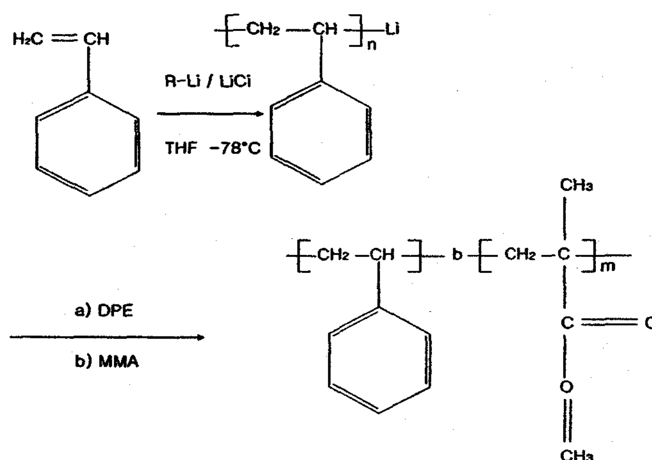

Fig. 1. Scheme of the synthesis procdure of PS-b-PMMA.

Film thickness is measured by Alpha-step and it was about 30 nm. The domain structures of block copolymer thin films were imaged in each sample using a Hitachi S-4300 field emission scanning electron microscope (FESEM).

3. Result and discussion

The copolymer thin films have cylindrical PMMA microdomains within the crosslinked matrix. When the temperature is elevated above glass-transition temperature of PMMA, the PMMA cylindrical domains can locally realease the stress exerted by the surrounding crossrlinked PS matrix by the outer cylinder direction[5]. Cross rinking polymer, in general, causes a volume contraction of the polymer due to the covalent coupling of adjacent chains.

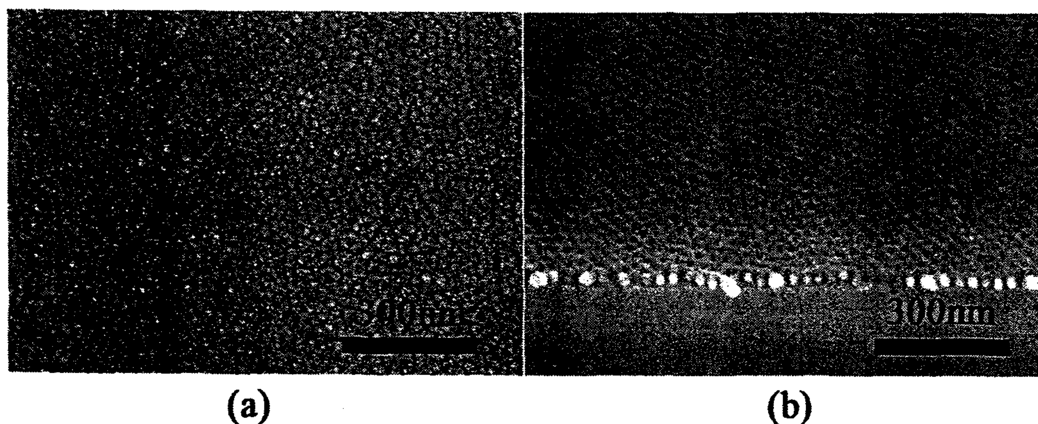

Fig. 2. SEM images of thin PS-b-PMMA films on substrate. (a) Planar SEM image of thin PS-b-PMMA films on SiO_2 substrate. (b) Cross-sectional SEM image of thin PS-b-PMMA films on SiO_2 substrate.

From the FESEM image in Figure 2-(a), it is evident that nanoscopic holes were formed at the center of the cylindrical PMMA microdomains. This ordered nanometer-scale areas using simple processing tools, with out the need for high-resolution lithography tools which are tools which are very expensive. The size of holes are about 10 nm. Changing of the size is possible by change the molecular weight of diblock copolymer[6]. PMMA block was removed and only PS based patterns are remained. Dark point is cylindrical empty space and brighter back ground is template of PS polymer. Clear image of cylindrical structure can be observed in Fig. 2-(b).

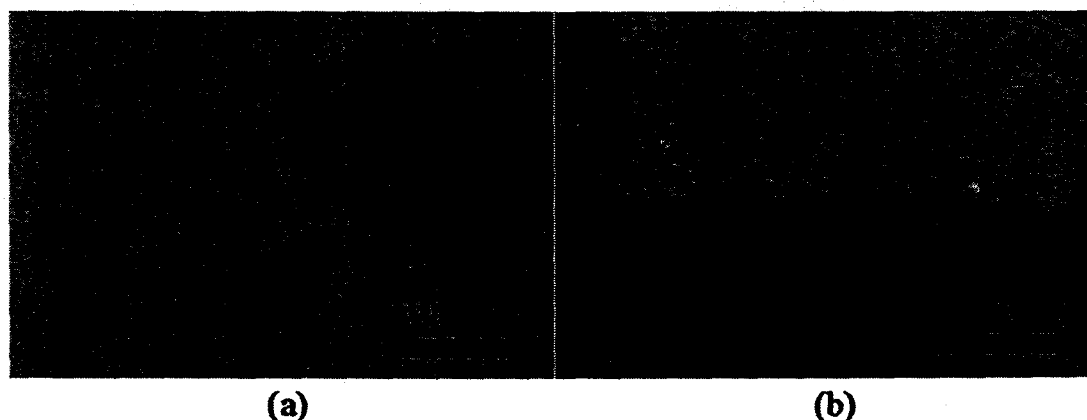

Fig. 3. SEM images of reactive ion etched (RIE) thin PS-b-PMMA films on substrate. (a) Planar SEM image of thin PS-b-PMMA films on SAMs of MPTS interface on SiO_2. (b) Cross-sectional SEM image of thin PS-b-PMMA films on SiO_2 substrate.

The porous PS template serves as a mask for RIE transefer of the hexagonal pattern into the silicon. We used SF_6 based plasma chemistry to etch the silicon[Fig. 3-(a)] (flow rate 10 sccm SF_6, bias rf power 10 W, 10 mTorr and 2 min). In planar view of RIE etched sample, it appaers that the size of holes are about 20.5 nm. Figure 3-(b) shows a cross-sectional SEM image of etched PS nanopatterned template. It appears that half the thickness of the PS has been removed. However, Si substrates seems to be sub-nanometer etched or not. Recently, Russell and coworkers[7] showed that 30 nm PS template as a mask for RIE ething. Size of cylinder radious get 66 % reduced(30 nm to 10 nm) than Russell group, etched trancefered nanopatern depth get reduced, too. Therefore, it seems to be hard to etch using via small sized PS nanopatterned templates.

4. Conclusions

In this work, we fabricated regularly formed nanopatterens by the using diblock copolymer. The size limit of the pore in block copolymer thin films can be extended well beyond block copolymer it self. Producing nanopores in block copolymer films by crosslikng the matrix is shown very simple, highly reproducible, and predictable. Via this route, the original ordering of the copolymer is maintained, providing a template in which nanoscopic holes can be produced. The polymer template pattern can be used as an etching mask, which opens opportunities to intergrate diblock copolymers for semiconductor processing at dimensions below photolithigraphic resolution limit.

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