Lithographic Patterning with Block Copolymers

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1. Introduction

Polymers with block architectures have been investigated for use as microlithographic photoresist since the late 1980s. The majority of early research focused on polymers having a silicon-containing block^[1] because of their improved etch resistance and the superior solubility properties provided by controlled microstructures. This early work also permitted exploration of unusual developers such as supercritical CO₂. With structural dimensions for nanotechnology pushed to ever-smaller limits, block copolymers have been of great interest as templates in lithographic processes for potential fabrication of quantum devices^[2], magnetic storage media^[3,4], nanowires^[5], nanoelectrode assemblies^[6], selective membranes^[7] and photonic crystals^[8]. In general, two approaches have been used in the nanofabrication process: First, the periodic microstructures in block copolymer thin films can be transferred to a substrate through reactive ion etching because of the different etching sensitivity of the two building blocks. Several kinds of organic block copolymers^[9,10] or organic-organometallic block copolymer^[3,11] templates and processes were developed to improve the etching contrast of the two blocks and thus the aspect ratios of the fabricated features. Second, nanoporous^[12,13] or nanorelief^[5,14] structures were fabricated by selectively removing one block and subsequently introducing an active component into the removed region through thermal evaporation or solution diffusion.

Control over the orientation of the block copolymer microdomains, however, is very important for the optimal use of nanoscopic patterns. In particular, for cylindrical

microdomains, an orientation normal to a substrate surface is highly desirable. Various strategies have been used for inducing macroscopic orientation of block copolymer microdomains. For example, one can influence the orientation by: (1) the use of externally applied fields^[15–18] (mechanical, electric, thermal, eutectic solidification etc.) (2) chemical modification of the surface^[19] to change the substrate-polymer interactions, (3) controlling the film thickness^[20] or substrate physical constraints^[21] (topography) to induce long range ordering.

The template nanolithography process can provide periodic patterning with feature sizes on the order of tens of nanometers. However, in many applications, simple periodic patterning is insufficient and spatial control of the microdomains is necessary to form integrated multilevel structures^[4]. Here we describe an approach we utilized that combines advanced photolithography with template nanolithography processes using a novel photopatternable block copolymer system. This combination is attractive because it provides spatial control of the block copolymer microdomains with favorable orientation for nanolithography. We are able to generate uniform nanometer sized pores in submicron-sized photopatterns with simple processing steps.

2. Experimental

2.1 Materials

Materials were obtained from Aldrich and used without further purification, unless otherwise noted.

Tetrahydrofuran (THF) was distilled from sodium/benzophenone under nitrogen and titrated

with *sec*-butyl lithium before polymerization. Monomers of α -methylstyrene and 4-*tert*-butoxystyrene were successively distilled from calcium hydride and dibutylmagnesium under high vacuum prior to use.

2.2 Polymer synthesis and characterization

The reactions used for the preparation of poly(α -methylstyrene-*b*-4-hydroxystyrene) (PMS-*b*-PHS) are shown in Scheme 1.

Scheme 1. Synthesis of PMS-*b*-PHS block copolymer.

Block copolymers of poly(α -methylstyrene-*b*-4-*tert*-butoxystyrene) (PMS-*b*-PtBuS) were synthesized by sequential anionic polymerization in THF at -78°C with *sec*-butyl lithium as the initiator. The PMS block was polymerized first for 12 hrs and an aliquot of poly(α -methylstyryllithium) was isolated for analysis after termination with degassed methanol. The 4-*tert*-butoxystyrene monomer was then introduced into the reactor and the reaction was terminated with degassed methanol after 12 hrs.

The PMS-*b*-PtBuS was converted to poly(α -methylstyrene-*b*-4-hydroxystyrene) (PMS-*b*-PHS) by a hydrolysis reaction. The block copolymer was first dissolved in dioxane, and 10 molar fold amount of hydrochloric acid was added. The mixture was reacted at 80°C under an atmosphere of nitrogen overnight and precipitated into water. After neutralization with a 5 % NaOH solution, the resulting polymer underwent a dissolve-precipitate cycle from a THF solution to methanol/water (1:1 v/v) mixture twice and freeze-dried from dioxane. The Molecular weight of the block copolymer was determined by a GPC equipped with a Waters 486 UV detector and 410 differential refractive index detector. The molecular weight of PMS block was determined to be 13,000 g/mol and polydispersity index is 1.09. The molecular weight of PtBuS was calculated based on relative intensity of aromatic groups and aliphatic groups in $^1\text{H-NMR}$ and determined to be 47,500 g/mol.

2.3 Lithographic processing of patternable block copolymer PMS-*b*-PHS

Block copolymer films were made by spin coating a PMS-*b*-PHS solution (solvent: propylene glycol methyl ether acetate, PGMEA) onto a silicon wafer in the presence of the additives (tetramethoxymethyl glycouril (TMMGU) as crosslinker (CL) and photoacid generator (PAG)). Photoimaging experiments were performed using a JBA 1000 DU Resist Cure Ramp (450 mJ/cm^2 @ 250 nm) and Nikon 248nm stepper ($\text{NA} = 0.42$ and $\sigma = 0.5$) equipped with a KrF excimer laser (Cymer CX-2LS) for the first irradiation. Heating (115°C for 60 sec) was applied afterwards to make the PHS matrix rigid and a mixed solvent (cyclohexanone / isopropanol = 1/2 in volume) was then used as a developer to form a negative-tone photoresist patterns. A second strong irradiation step was subsequently carried out under high vacuum (70 J/cm^2 @ 365 nm) to depolymerize the PMS minor phase in the patterned region.

AFM measurements were performed on the polymer film using a Digital Instrument Dimension 3100 before and after removal of the PMS materials.

3. Results and Discussion

PMS-*b*-PHS is a unique block copolymer combining the photopatternable properties of the PHS block with the controlled depolymerization of the PMS building block. PHS is a negative-tone photoresist when a crosslinker (CL) and a photoacid generator (PAG) are used in combination. First UV irradiation produces a strong acid as a result of the photochemistry of the PAG, which catalyzes crosslinking between PHS and the CLs, rendering the exposed region insoluble. Since the T_g of PHS itself is $\sim 180^\circ\text{C}$, crosslinked-PHS can be used as a robust, continuous matrix. Subsequent strong UV irradiation on the developed pattern activates the depolymerization process of the PMS building block, thus nano-sized holes in spatially controlled micron-sized patterns can be generated.

AFM measurements of block copolymer films were taken after spin coating from PGMEA onto a silicon wafer (Figure 1). Film thickness was measured to be 152nm. Cylinders having a diameter of 25nm were found standing up throughout the wafer, which is favorable for the template nanolithographic process.

0 1.0

Figure 1. AFM height image obtained from thin films of PMS-b-PHS on a silicon wafer before removal of the PMS block. Bright dots represent vertical cylinders of PMS.

Weak irradiation of the thus formed block copolymer films on a 248 stepper and subsequent development gave high resolution images with features as small as 300nm (Figure 2a). Final strong irradiation using a 365nm UV source under high vacuum generates uniform vertical holes on the patterns as shown in Figure 2b.

Figure 2. AFM height images obtained after removal of the PMS block. (a). A photopatterned thin film on silicon wafer (thickness: 140nm); (b) A magnification of the 1.5μm line. Black dots represent holes. The diameter of the holes was measured to be 18 nm.

4. Conclusion

A combination of advanced photolithographic and nanolithographic processes on a PMS-b-PHS block copolymer system can produce spatially defined microdomain templates with favorable orientation. Nano-sized holes were created in the micron-sized photopatterns without any pattern collapse when a complete optimization of materials, formulation, exposure condition, and developer selectivity is carried out.

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