Ion Beam Patternning of Block Copolymer Thin Films

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Hierarchical nanostructures are generated on substrates by combining a top-down ion beam lithography with a bottom-up self-assembly of block copolymers. The ion beam lithography images micron sized patterns of block copolymer thin films which contain nanometer sized microdomains. This approach provides a simple route to fabricate structures containing two different length scales, i.e. micrometers and nanometers, which may find a variety of potential applications in nanoscience and technology.

Keywords: block copolymers, self-assembly, ion beam lithography, hierarchical structures

1. Introduction

The fact that block copolymers self-assemble into well defined periodic nanostructures of 5 ~ 50 nm due to microphase separation between blocks makes them very attractive, in particular, as an alternative patterning method to conventional lithography [1-4]. With the simplest molecular architecture of block copolymers, i.e. diblock copolymers, one can create line/space patterns or arrays of dots on a substrate. Cylindrical microdomains oriented parallel to the surface and lamellar microdomains oriented perpendicular to the surface generate line/space patterns; spherical microdomains and cylindrical microdomains oriented perpendicular to the surface provides arrays of dots. Extensive studies have been performed by many research groups to control the orientation and lateral placement of microdomains on surfaces [5-8].

It is of great interest to relate the nanoscopic microdomains of block copolymers with micron sized features which make it easy to access the nanoscopic features. This can be achieved by using conventional lithography to image the block copolymer thin films that serve as a photoresist. Previously, Ober and coworkers reported achieving spatial control through a high-resolution deep UV lithography process using a novel block copolymer system, poly(α-methylstyrene-b-4-hydroxy styrene) [9]. In the present work, we apply ion beam lithography using He or Ne ions to explore the patterning of block copolymer thin films using three different material systems: poly(styrene-b-methyl methacrylate) (PS-b-PMMA), poly(styrene-b-ethylene oxide) (PS-b-PEO), and PS-b-PEO/organosilicate (OS) hybrid.

Ion irradiation of polymers using high energy ions has been shown to significantly alter surface-sensitive properties [10, 11]. Upon ion beam exposure of polymers, both crosslinking reactions and molecular chain scission into smaller fragments may take place, depending on the ion mass and energy, and the polymer structure. Ion beam exposure has been used in lithography by exposing only certain areas and removing either the exposed or unexposed portions. Figure 1 schematically represents the ion beam patterning process used in this study. The thin films of block copolymers are prepared on silicon substrates. The orientation of microdomains is controlled by modifying surface energy of the substrate or using solvent vapor during spin coating. The films are then covered with a stencil mask for selective-area irradiation by the ion beam. Wet development of ion beam patterns using organic solvents or commercially available photoresist developer (e.g. CD-26) selectively removes the area
exposed to the ion beam (or the area not exposed, depending on the polymer, the solvent, and the ion beam parameters). Subsequently the microdomains of the block copolymer can be selectively removed either by solvent rinsing or by thermal treatment. The final samples contain hierarchical patterns of micrometer scale and nanometer scale on the substrate.

BCP thin films

He$^+$ or Ne$^+$ ions

contact mask patterning

Two step pattern development
(ion beam patterns
and block copolymer microdomains)

Fig. 1. Schematic representation of the patterning process in this study.

Ion beam is applied to the copolymer thin film in selected areas defined by a contact mask. Ion beam defined patterns can be obtained after the first development process. Subsequent development (second development process) selectively removes block copolymer microdomains, and creates a nanoporous structure within the ion beam defined features.

2. Method

Three block copolymer systems were used to create the nanoscopic patterns. The first system involved a diblock copolymer of polystyrene and poly (methyl methacrylate) (PS-b-PMMA, from Polymer Source, Inc) with 58,000 g/mol for PS and 25,000 g/mol for PMMA molecular weight. 1 wt% toluene solution of PS-b-PMMA was spun cast onto a silicon wafer substrate where the surface energy was controlled to be neutral to both PS and PMMA. The film contained cylindrical PMMA domains oriented perpendicular to the surface. The second system was a PS-b-PEO with 19,000 g/mol PS and 6,400 g/mol PEO. The PS-b-PEO was dissolved in toluene to 1 wt% and the solutions were spun-cast at 3,000 rpm on a SiOx surface under a H$_2$O vapor. The film contains PEO cylinders oriented perpendicular to the surface. The third system was PS-b-PEO (19,000 g/mol PS, 12,300 g/mol PEO) and an organosilicate (OS) hybrid. More details on the preparation of this hybrid have been described elsewhere [12-15]. The organosilicate in the mixtures of PS-b-PEO/OS is selectively miscible with PEO and the hybrid shows a two phase structure. In each case, the solution (PS-b-PEO in toluene, OS in propylene glycol propyl ether, PGPE) was spun cast at 1,000 rpm on SiOx under a chloroform vapor to trap the copolymers in a non-equilibrium state. The resulting morphology was PS spheres.

The ion beam was generated by a Penning ion source (National Electrostatics Corporation). Helium (He) ions, accelerated to 10 keV, were used to irradiate the first two systems. Neon ions sent at 20 keV were used for the third hybrid system. The exposure fluences ranged from $10^{13}$ ions/cm$^2$ to $3 \times 10^{15}$ ions/cm$^2$. Each of several separate areas of the polymer on each sample was exposed to a different fluence of ions, in order to identify the influence of ion dose on the polymer. Patterns were created using a contact mask consisting of 400 nm thick silicon, with a geometrical pattern of circular holes etched through it. The thin Si areas containing the pattern extended for about 1 mm $\times$ 1 mm. Pattern development varied for the three systems. The PS-b-PMMA samples were rinsed with acetic acid followed by a toluene rinsing for 30 seconds and 20 seconds respectively. The PS-b-PEO samples were rinsed with toluene for 20 seconds. The PS-b-PEO/OS samples were developed using a dilute solution of CD-26 (1 part CD-26, 2 parts H$_2$O) for 3 minutes. The samples were then baked to 450°C, increasing
the temperature at 5°C/minute, and remaining at this temperature for two hours. All three systems were characterized using an AFM in tapping mode using standard silicon cantilevers (Dimension 3100, Digital Instruments). SEM micrographs were obtained using a FESEM (Hitachi S-4700).

3. Results and Discussion
3.1. PS-b-PMMA

Figure 2 shows a height contrast AFM image of PS-b-PMMA thin films patterned with 10 keV He ions with dose of $10^{15}$ ions/cm$^2$. The ion beam patterns were developed with toluene for 20 sec. (It is noted that CD-26 is not an effective developer for the PS-b-PMMA.) As shown in Figure 2, the ion beam exposed area has cylinders of approximately 1 µm in diameter (corresponding to the mask holes) and 27 nm in height. Figure 2 (b) shows a cross-sectional profile of the patterns.

As the He ion beam crosslinks the PS while at this moderately low dose it decomposes PMMA, the cylindrical PMMA microdomains can subsequently be removed using a PMMA-selective solvent. Figure 3 shows an AFM height contrast image of ion beam patterned PS-b-PMMA after acetic acid treatment. Acetic acid is a selective solvent for PMMA and, as shown in Figure 3, it removes PMMA cylindrical domains distributed within micro meter sized ion beam patterned dots. This suggests that the approach in this study can be used as an effective method for creating hierarchical structures containing different structural length scales.

3.2. PS-b-PEO

Figure 4 shows AFM images of PS-b-PEO thin films patterned using 10 keV He ions with dose of $10^{15}$ ions/cm$^2$. Figure 4 (a) shows the height contrast AFM image, and Figure 4 (b) shows height (left) and phase (right) contrast images of higher magnification. Patterns were developed by rinsing with toluene for 20 sec. CD-26 can not be used for PS-b-PEO since it removes the entire block copolymer thin film. It should be noted that the quality of ion beam
patterns of PS-b-PEO is poorer than that for PS-b-PMMA. This is partly attributable to the significant volume shrinkage of PEO upon ion beam irradiation. We observed that the thickness of the PEO homopolymer changes from 125 nm to 25 nm by exposure to 10 keV He ions with dose of $10^{15}$ ions/cm$^2$. It is believed that the ion beam irradiation causes scission of PEO and the scission products that have mostly been volatile have gone away, which results in deformation of patterns. As shown in Figure 4, a thick residual layer in the non-exposed area is also observed after toluene development of ion beam patterns. Attempts to selectively remove entire PEO microdomains were not successful due to the difficulty in finding a good selective solvent for PEO microdomains.

Fig. 4. Ion beam patterned PS-b-PEO thin films. (a) height contrast AFM image. (b) high magnification height contrast (left) and phase contrast (right) AFM images. Partly removed PEO microdomains are shown in the phase contrast image.

3.3. PS-b-PEO/OS Hybrid

Previously we reported ordering behavior of the PS-b-PEO/OS hybrid system [12-15]. In this study, we used spherical microdomains of PS for ion beam patterning. The mixing composition of 20/80 (wt/wt) PS-b-PEO/OS gives PS spherical domains dispersed in an OS matrix. Upon exposing the hybrid films, there was no significant difference between the effects of the different fluences of ions or between the effects of He and Ne ions. Figure 5 shows a height contrast AFM image of the PS-b-PEO/OS hybrid, patterned using a 20 keV Ne ion beam with $10^{15}$ ions/cm$^2$ dose. While both PS-b-PMMA and PS-b-PEO patterns can be developed using toluene, the patterns of PS-b-PEO/OS were not able to be developed with organic solvents such as toluene or PGPE. Instead, we found that a commercial photoresist developer, CD-26, is a very effective developer for the PS-b-PEO/OS hybrid system. The bright dots within approximately 1 μm diameter ion beam pattern features are PS microdomains which are very likely crosslinked by the Ne ion beam irradiation. The dimension of PS microdomains was measured as approximately 20 nm in diameter.

Fig. 5. Height contrast AFM image of ion beam patterned PS-b-PEO/OS thin film.

It was not possible to selectively remove the crosslinked PS microdomains in ion beam patterns using common organic solvents, which indicates that the PS domains were crosslinked. To selectively remove the PS microdomains, we
used thermal treatment on the samples. Samples were heated to 450°C for two hours under a nitrogen environment, which induces simultaneously thermal crosslinking reaction of OS and decomposition of PS. Figure 6 shows SEM micrographs of the ion beam patterned PS-b-PEO/OS hybrid films after thermal treatment. As shown in Figure 6 (a), patterns are retained without significant damage after baking at 450°C. A high magnification micrograph in Figure 6 (b) shows a well developed nanoporous structure within the ion beam patterned micrometer sized features. The formation of this nanoporous structure clearly indicates that the PS microdomains were removed by the thermal treatment.

4. Conclusion

We have demonstrated that it is possible to combine two well studied concepts, ion beam irradiation and block copolymer self-assembly, to effectively create micrometer sized patterns without damaging the nanoscopic microdomains of block copolymers. All three material systems investigated in this study can effectively be created into a pattern within a pattern, although the PS-b-PEO system could not create the ideal result of removal of the PEO cylinders. Instead, it has been shown that an ion beam will have a major effect on PEO, greatly decreasing its thickness. The combination of top-down ion beam lithography and bottom-up block copolymer self-assembly is a promising route to hierarchical structures comprising both μm and nm length scales.

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