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Direct Patterning of Self Assembled Nano-Structures of Block Copolymers via Electron Beam Lithography

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Abstract: This study describes a method where the match of two different length scales, i.e., the patterns from self-assembled block copolymer (<50 nm) and electron beam writing (>50 nm), allow the nanometer scale pattern mask. The method is based on using block copolymers containing a poly(methyl methacrylate) (PMMA) block, which is subject to be decomposed under an electron beam, as a pattern resist for electron beam lithography. Electron beam on self assembled block copolymer thin film selectively etches PMMA microdomains, giving rise to a polymeric nano-pattern mask on which subsequent evaporation of chromium produces the arrays of Cr nanoparticles followed by lifting off the mask. Furthermore, electron beam lithography was performed on the micropatterned block copolymer film fabricated by micro-imprinting, leading to a hierarchical self assembled pattern where a broad range of length scales was effectively assembled, ranging from several tens of nanometers, through submicrons, to a few microns.

Keywords: block copolymer, electron beam lithography, nanopattern mask, self assembly.

Introduction

Development of engineering processes for patterning densely packed nanometer scale structures is crucial for many potential applications of nanotechnology including high density memory devices, high sensitive biochemical sensors.[1] Lithography is usually the most critical procedure for defining structures successfully with such dimensions.[2] Dip-pen nanolithography, micro-contract printing, and block copolymer lithography are examples of non-conventional methods to structure materials into nanoscale features.[3,4] Colloidal lithography makes use of the gaps between laterally touching colloids on the interfaces by evaporating metals through the gaps onto the underlying substrate. Subsequent removal of the colloidal structure results in hexagonally patterned nanostructure.[5]

Techniques based on self assembly of polymeric materials provide some means to control molecular features with even higher resolution down to a few nanometers and are convenient methods to use because the various nanostructures are pre-determined thermodynamically in synthesizing macromolecules. For instance block copolymers can self-assemble into ordered periodic structures at the molecular scale (~5 to 100 nm), and many types of nanostructures can be achieved, depending on the ratio of the volume between two blocks.[1]

The periodic nanostructures of block copolymers in thin films are useful as templates for nanolithography when one of the blocks is removed chemically. The resulting patterns may be transferred to a substrate either through reactive ion etching or by thermal evaporation or electroplating of a metal into the previously removed regions. Dense, periodic arrays of holes and troughs have been fabricated in silicon, silicon nitride, and germanium.[1] A block copolymer-hard mask-magnetic layer scheme was recently used for creating nanoscale magnetic dots for single bit magnetic media storage.[1]

Up to now UV, ozone and oxygen plasma have been utilized to etch one of the blocks selectively.[6,7] For fabricating a block copolymer thin film in which the etched area is micropatterned, the etching methods mentioned above require either a pattern mask through which block etching agent can selectively pass or a pre-patterned substrate on which block copolymer structure is selectively formed.

E-beam lithography is a common method for direct writing sub-micrometer structures. Although a beam of electrons may be focused to less than 1 nm in diameter, the resolution is limited by the interaction of the beam with the resist material and by the radius of gyration of the macromolecules. In general it is still difficult to accurately

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manipulate structures which are less than approximately 20 nanometers wide. New development in using self assembled monolayers overcomes these restrictions inherent with standard e-beam resist materials.[8] Recently Spatz *et al.* have introduced a direct process by applying monolayered block copolymer micelle films as a negative e-beam resist. Micelles irradiated by electrons are chemically modified and can hardly be dissolved from the substrate while non-exposed micelles can be readily lift-off by suitable solvents.[9]

Here we present a simple, convenient way to fabricate a micropatterned block copolymer nanopattern mask. The method is based on using direct writing of electron beam lithography on self assembled block copolymer thin films. We use a block copolymer, which contains a block component much more vulnerable for e-beam, as an e-beam resist material. Exposure of e-beam on a self assembled block copolymer thin film gives rise to the selective etching of the microdomains composed of the more decomposable blocks. Direct writing capability of e-beam lithography allows the block copolymer microdomains not only to be etched selectively but also to have an arbitrary pattern formation with sub-microns in size. We also demonstrate that micropatterned arrays of metal nanoparticles are fabricated using metal evaporation through a micropatterned block copolymer mask followed by lift-off process. Furthermore, e-beam lithography performed on the micro-imprinted block copolymer thin film leads to a hierarchical self assembled pattern where broad range of length scales was effectively assembled from several tens of nanometers to sub-microns, a few microns.

Experimental

Materials and Film Preparation. Two poly(styrene-*block*-methylmethacrylate) block copolymers: PS/PMMA (25/26) and PS/PMMA(30/290) were purchased from Polymer Source Inc. Doval, Canada. The PS/PMMA (25/26) has a total molecular weight of 51,000 g/mol, a polydispersity of 1.06, with PS and PMMA blocks of 25,000 and 26,000 g/mol, respectively. The block copolymer presents a bulk lamellar microstructure (evidenced by small-angle X-ray scattering (SAXS): $d_{100\ lam}$~39 nm), consistent with the 49% volume fraction of the PS block. The PS/PMMA(30/290) has a total molecular weight of 320,000 g/mol with PS and PMMA blocks of 30,000 and 290,000 g/mol, respectively. Since the volume fraction of the PS block is 12%, the bulk sample displays a closely packed spherical microstructure of the minority PS component.

We produced thin block copolymer films by spin-coating polymer solutions with two different concentrations (1 and 3 wt% in toluene) onto silicon wafer. The silicon wafers (100) were rinsed with acetone, methanol, and deionized water, then dried with N_2 for cleaning. Thin block copolymer films with approximately 30 and 200 nm in thickness were prepared with the 1 wt% solution (spin speed: 5,000 rpm) and the 3 wt% solution (spin speed: 2,000 rpm), respectively. In particular we confirmed that spin coating of 1 wt% solution of PS/PMMA(30/290) with the spin rate of 5,000 rpm produced a monolayer of PS sphere microdomains in PMMA matrix. A uniform monolayer of spherical PS microdomains was confirmed by Atomic Force Microscope (AFM). An AFM image in phase contrast displayed self assembled spherical PS microdomains while an image with height contrast did not show any microstructure, indicating that the polymer film surface is extremely flat with the roughness of approximately 3 nm. The spin coater (SPIN 1200 Midas-system, Korea) was used and the film thickness was measured from the cross section profile in AFM and confirmed with ellipsometer (Gaertner Scientific Co. USA). The block copolymer films were annealed for 2 days under vacuum at 170 °C, which is above the glass transition temperatures of both blocks.

Electron Beam Lithography. Electron beam lithography was performed on thin PS/PMMA block copolymer films with an acceleration voltage of 20 kV and an aperture of 30 μm in Raith plus (Raith GmbH, German). The PMMA microdomains were selectively decomposed by electron beam due to much faster chain scission rate than that of PS ones. The films were developed with a 3:1 mixture of methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA) at room temperature and washed with IPA for several times. 1 D periodic lines were produced by electron beam writing with the width and periodicity of 300 and 600 nm, respectively. The etching was mainly adjusted by the exposure time and dose factor of electron beam. Thin Cr layer of approximately 10 nm in thickness was thermally evaporated on the block copolymer thin film which had been treated with e-beam. The evaporation was performed with the rate of 1 nm/sec under high vacuum (~10^{-6} mmHg). The e-beam treated film was spun at 10 rpm and chilled down through water cooling system during the evaporation. Finally the block copolymer thin film was lift-off by being dissolved in toluene. A procedure of the pattering method is schematically depicted in Figure 1.

Micro-Imprinting Lithography. Electron beam lithography was also performed on a micro-imprinted block copolymer thin film. The spin coated PS/PMMA (30/290) thin film (3 wt% solution in toluene) was topographically patterned with the micro-imprinting apparatus developed in our laboratory. When the conformal contact is formed with a poly(dimethylsiloxane) (PDMS) master pattern, the temperature is raised well above the glass transition temperatures of both blocks (200 °C). The pressure applied depends on both the load and the contact area of the micropattern on the block copolymer film. The pressure used is approximately 156,800 Pa. The micro-imprinting was performed for 20 min, resulting in the micropatterns with topographic thickness variation in large areas (~1 × 1 cm^2). The elasto-

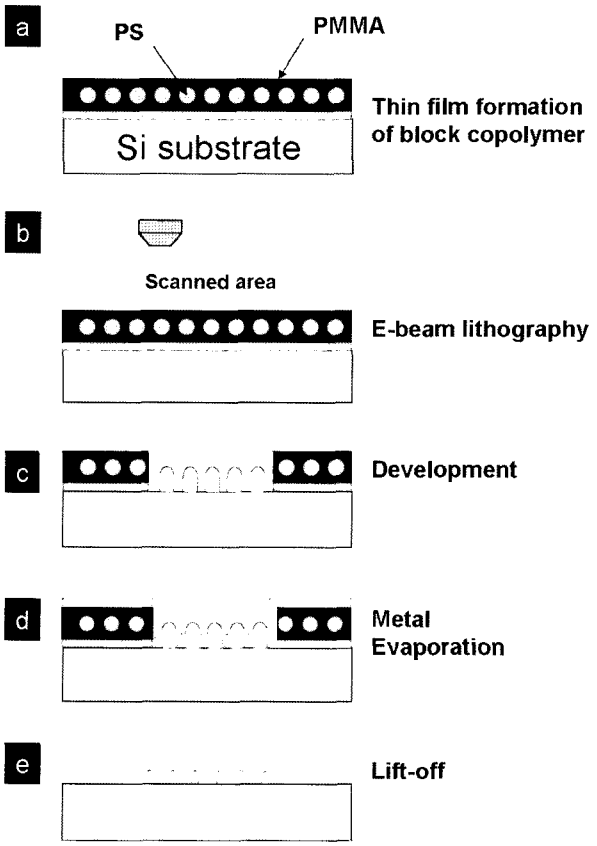

Figure 1. Schematics of nanometer scale pattern mask fabrication of block copolymer thin film using electron beam lithography. (a) Thin film formation of a PMMA containing block copolymer. (b) Electron beam writing and (c) selective removal of PMMA microdomains. (d) Deposition of metal layer, and (e) lift-off process.

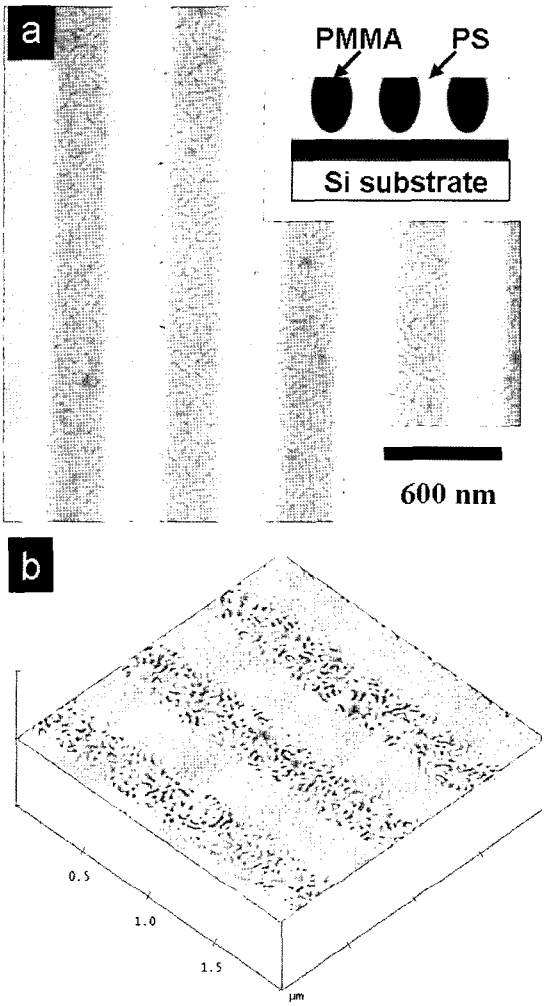

Figure 2. Tapping mode AFM images in height contrast of thin PS/PMMA(25/26) block copolymer film exposed to electron beam. Periodic lines with the width and periodicity of 300 and 600 nm, respectively were formed. (a) Plan-view image of the film. It is obvious that the block copolymer was formed with the edge-on lamellar structure. PMMA microdomains are selectively removed by electron beam. An inset depicts schematic of cross-sectional view of lamellar structure. (b) A surface view image shows almost zero height difference between the exposed regions and the unexposed ones, indicating that PS microdomains are intact during electron beam exposure.

meric PDMS mold was fabricated by curing a PDMS precursor (Sylgard 184, Dow Corning Corp) on a prepatterned silicon master. We used a mixture of PDMS precursor and curing agent (10:1 by weight). The prepatterned photoresist master was prepared by standard photolithography, and the surface was fluorinated before casting the PDMS precursor on the master. After the PDMS precursor was cured at 40 °C for 12 h using vacuum oven, the mold was separated from the master. The 2 dimensional PDMS mold was prepared which has cylindrical posts with the diameter of 2 μm arrayed into a square structure. The center-to-center distance is 4 μm.

The micropatterns fabricated were examined by AFM (Nanoscope III from Digital Instrument) in tapping mode.

Results and Discussion

The microstructures of the block copolymer films after e-beam lithography were investigated by AFM in tapping mode with phase contrast (Figure 2). Alternating PS and PMMA lamellar microdomains oriented perpendicular to the substrate (edge-on lamellae) were observed (Figure 2(a)). Lamellae orientation with respect to a substrate has been known to strongly depend on film thickness and interfacial energy among the constituent blocks, air and the substrate.[10] PS/PMMA(25/26) has asymmetric boundary condition on a Si substrate; PMMA block favors the Si surface while PS block prefers air surface, perpendicular orientation of the lamellae is obtained when the film thickness is less than $3d/2$ and larger than $d/2$ where d is periodicity of lamellae. The film thickness of approximately

30 nm measured by ellipsometry ensures edge-on lamellae orientation. The explicit self consistent field calculation[10] demonstrates that the edge-on lamellar structure obtained, however, has thin bilayer of PS and PMMA where PS lies on PMMA layer in contact with Si surface as shown in the inset of Figure 2(a).

Selective etching of PMMA microdomains can be controlled by various parameters in e-beam lithography such as accelerating voltage, aperture size, writing line width, and the dose factor of electron beam. Proper conditions for effective e-beam writing should be determined by combining all these parameters for each specific material system. We found that dose factor mainly influenced the etching properties of block copolymer domains. Various dose factors ranging from 0.5 to 1.5 were tested to optimize the selective etching of PMMA domains.

Figures 2(a) and (b) show PS/PMMA(25/26) thin film on which the lines of 300 nm in width with the periodicity of 600 nm were written with electron beam scanning. Electron-beam writing with the dose factor of 0.8 provided optimum removal of PMMA microdomains without significantly damaging PS ones. Independent electron beam exposure experiments on homopolymers of PS and PMMA indicate that, under equivalent etching conditions, a 20 nm thick PMMA film is completely removed, while approximately 75% of a 20 nm thick PS film remains, yielding an approximate etch ratio of PMMA to PS of 4. Thus microphase separated edge-on lamellae structure is clearly visible on the electron beam exposed regions. The surface profile obtained from Figure 2(a) shows that the height difference between the e-beam exposed regions and the unexposed ones is approximately 5 nm, which indicates that PS microdomains were also a little removed under electron beam. Although the current patterning conditions were sufficient to etch PMMA microdomains, it should be noted that in order to fabricate a pattern mask with completely etched nanostructure the patterning conditions must be more severe to remove the thin PS layer formed below the edge-on lamellae as explained previously. As will be shown later, the complete microdomain etching to the bottom of the substrate occurs only on some areas of even e-beam treated regions where the thin PS layer is removed by e-beam.

We also employed another block copolymer PS/PMMA (30/290) of a PS sphere forming block copolymer. The 300 nm line pattern with the periodicity of 600 nm on the block copolymer thin film produced by electron beam writing is

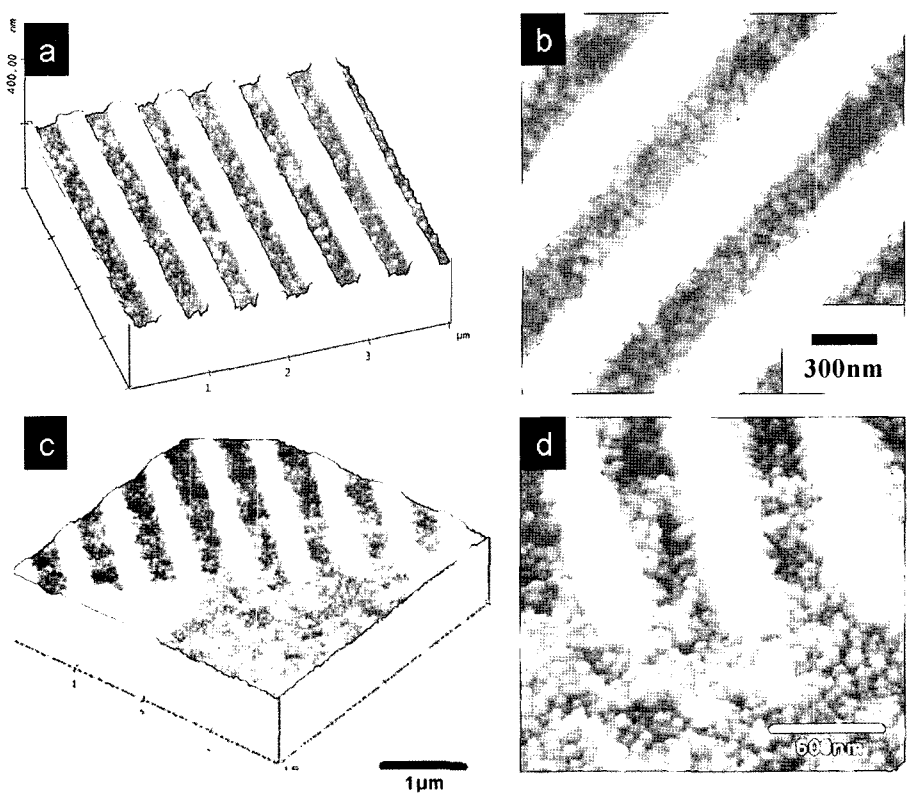

Figure 3. Tapping mode AFM images in height contrast of thin PS/PMMA(30/290) block copolymer film exposed to electron beam. Periodic lines with the width and periodicity of 300 and 600 nm, respectively were formed. It is obvious that spherical PS microdomains exist after the removal of PMMA block by electron beam. (a) Surface view and (b) plan view images of the film. Patterned structures of the block copolymer film overexposed to electron beam with dose factor of 1 are shown in (c) and (d). Overexposure gives rise to non uniform etching with rough surface profile.

shown in Figure 3. The several dose factors were employed to this sample for measuring adequate dose since the over-dosed sample in electron beam degraded the polymer thin film even the PS domains as well as PMMA phase and the electron beam having deficient dose was not capable of removing PMMA phase. Figure 3(a), (b) clearly show the spherical PS microdomains with approximately 40 nm in diameter in the regions where electron beam was exposed with dose factor of 1. The distinct contrast between line patterns (e-beam treated and untreated lines) in Figure 3(a), we believe, results from the selective etching of PMMA matrix. As shown in Figure 1(c), the removal of the PMMA matrix above the spherical PS microdomains provides the distinct height difference from the un-etched regions. Since the edge-on lamellae shown in Figure 2, however, do not have the removable PMMA top layer, the contrast between e-beam etched regions and un-etched ones is relatively weak, compared with the spherical block copolymer. Fewer defects were observed compared with overdosed sample in electron beam shown in Figure 3(c), (d). As shown in Figure 3(c) and (d), the PS spheres in the valley were partially etched due to strong electron beam with dose above 1.

E-beam lithography on self assembled block copolymer thin film was combined with micro-imprinting for better control of microstructure. Micro-imprinting is a simple, convenient non-lithographic way to produce polymeric micropatterns with topographic thickness variation. We employed micro-imprinting to block copolymer followed by e-beam writing for selective etching of block copolymer microdomains. We first used a PDMS mold in which cylindrical posts with 2 μm in diameter were arrayed with a *4mm* symmetry. The micropattern generated by imprinting thin PS/PMMA (30/290) film spin coated on a Si substrate is shown in Figure 4(a). The imprinting allowed us to fabricate a large area pattern (~1 × 1 cm^2) with ease. The imprinted square array pattern displays clearly the thickness variation in height mode AFM image (Figure 4(a)). The thickness profile obtained in AFM software indicates that the maximum height difference is approximately 200 nm. Cross-section view by scanning electron microscope revealed that the thinner region (circular region) is approximately 50 nm in thickness while the thicker one is 250 nm (data not shown). It would be useful to fabricate a topographical micropattern of the PS/PMMA block copolymer where thinner areas have monolayered PS microdomains and the elevated ones have double or triple layered PS ones. E-beam lithography on the topographic micropattern could allow us to fabricate a micropatterned block copolymer mask when the e-beam etches the PMMA domains completely to the bottom substrate only in the thinner regions.

The lines with the width of 300 nm were produced by e-beam onto the micro-imprinted square pattern (Figure 4(b)). Lines are apparent in both the thinner and the thicker regions. A magnified image shown in Figure 4(c) displays

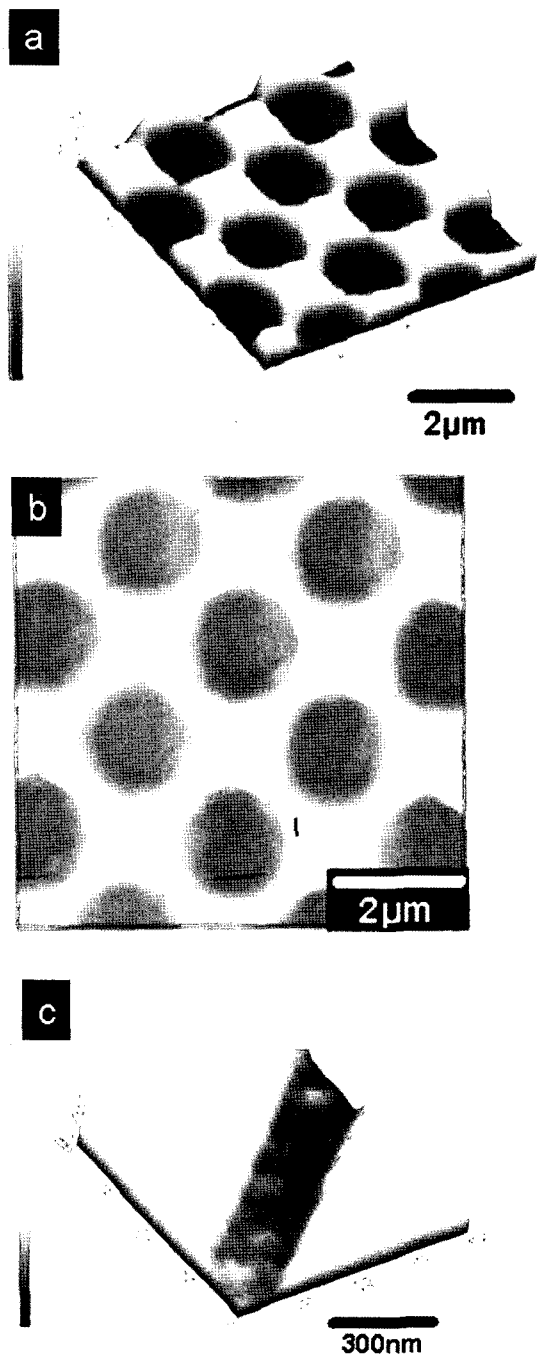

Figure 4. (a) A tapping mode AFM image of micro-imprinted PS/PMMA(30/290) thin film. Circular holes with 2 μm in diameter are arranged with 4 mm symmetry. (b) Periodic lines with 300 nm in width were written by electron beam on the imprinted pattern. (c) Magnified image of line pattern produced by electron beam on the micro-imprinted block copolymer thin film. The line formed on the elevated region of the imprinted pattern was chosen.

single line formed outside circular regions, i.e. the thicker regions by the selective etching of PMMA microdomains. In contrary to the pattern formed on homogeneous block

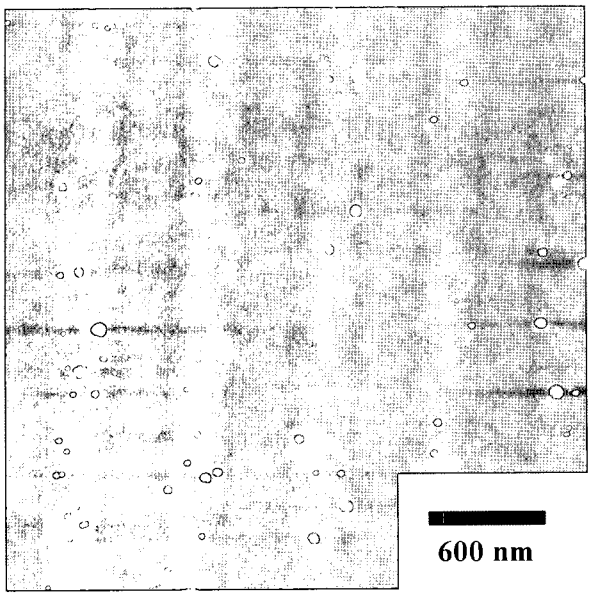

Figure 5. A tapping mode AFM image in height contrast of Cr nanoparticles formed by deposition of Cr layer on thin PS/PMMA(25/26) film exposed to electron beam and subsequent lift-off of the block copolymer mask. Nanometer scale particles are shown only in the patterned areas by electron beam.

copolymer thin film (Figure 3), the spherical PS microdomains did not appear clearly inside the line, which arose from the fact that in thicker regions at least 4 layers of the spherical PS microdomains were stacked with low positional ordering. E-beam on a monolayer of the block copolymer film etches PMMA phase much more uniformly along thickness.

In order to utilize the block copolymer thin film exposed to e-beam as a nanopattern mask, thin layer of a metal was thermally evaporated on the film which was subsequently removed by being dissolved in toluene. A pattern mask prepared with the lamellar forming PS/PMMA(25/26) was used as previously shown in Figure 2. We thermally evaporated chromium (Cr), which is known as an adhesive layer on a Si substrate, with a thickness of approximately 10 nm on the block copolymer film. Although a disordered edge-on lamellae structure of Cr was expected similar to the block copolymer pattern mask shown in Figure 2(a), the evaporation and lift-off process produced randomly deposited Cr dots on the regions where e-beam was exposed (Figure 5). We assume that the formation of Cr nanoparticles arose from incomplete etching of the thin PS layer formed underneath the edge-on lamellar PMMA microdomains (the inset of Figure 2(a)). Since e-beam is also capable of etching the PS microdomains in spite of very low etching rate, the edge-on lamellae were completely etched in some areas where the thickness of the bottom PS layer is relatively thinner than other regions and the subsequent evaporation of Cr on the block copolymer mask produced irregular deposition of Cr nanoparticles as shown in Figure 5. The size of Cr dots varied from 20 to 40 nm. The line pattern with 300 nm in width is clearly visible. The thickness of Cr-dots is approximately 10 nm.

Conclusions

We fabricated nanometer scale pattern masks by combining self assembled PS/PMMA block copolymer structures with electron beam lithography which selectively etched the PMMA microdomains. Self assembled periodic lamellar and spherical masks were easily fabricated with the typical pattern dimension of less than 30 nm which was still difficult to obtain routinely using e-beam lithography itself. Writing capability of e-beam lithography allowed us to design an arbitrary pattern on which block copolymer nanometer scale mask was selectively formed. In addition, our method does not require additional etching step such as plasma and reactive ion because e-beam itself etches the PMMA domains selectively. We demonstrated that thermal evaporation of Cr on a block copolymer mask and the subsequent lift-off produced Cr nanoparticles selectively deposited on the patterned regions where e-beam had been exposed. Furthermore, we demonstrated that electron beam lithography could be combined with other lithographic techniques such as micro-imprinting for more versatile utilization of self assembled block copolymer nanopatterns.

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