Transfer of Sub-30-nm Patterns from Templates Based on Supramolecular Assemblies

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The controlled generation of nanopatterns on functional substrates is an essential process step in nanotechnology. Serial methods such as electron beam lithography yield precisely positioned structures a few tens of nanometers in size with low throughput. Conventional optical lithography allows generating feature sizes in the 100-nm range on a large scale. Their downscaling to the 50-nm range is associated with a large increase in technical complexity and costs. Block copolymer (BC) lithography has emerged as an inexpensive high-throughput alternative for creating patterns with periods in the sub-50-nm range.[1−8] To this end, thin BC films[1,9,10] are coated onto the substrates to be patterned. The BC templates thus obtained contain hexagonal arrays of either spheres or cylinders oriented normal to the film plane, which consist of the minor component. This pattern can be transferred into the underlying substrate by reactive ion etching (RIE).[1−4,11] The etch contrast between the blocks of BCs is usually too low for efficient pattern transfer. To overcome this problem, the stability of the resist domains under RIE conditions can be improved by staining them with heavy elements.[1] BC templates with sufficient etch contrast may also be prepared from BCs containing blocks of organometallic polymers, taking advantage of the higher stability of the organometallic domains with respect to organic domains.[2] However, the metal contaminations thus introduced deteriorate the electronic properties of the patterned substrates.[12] An alternative approach involves the production of continuous nanoporous films as etch resists by the selective removal of the minor component. In polystyrene-*block*-polybutadiene (PS-*b*-PB) and polystyrene-*block*-polyisoprene (PS-*b*-PI) templates, the PB and PI domains can be removed by ozonation.[1] Thin polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) films containing cylindrical PMMA domains oriented perpendicular to the film plane are accessible if the surface interactions of the blocks are balanced by coating the substrate with a random copolymer.[9,10] Application of UV light degrades the PMMA and cross-links the PS matrix.[3,4,13] Because of this easy access to nanoporous PS masks, PS-*b*-PMMA is a widely used BC template for processes involving pattern transfer into underlying substrates. Asymmetric PS-*b*-PMMA with an overall mass average molecular weight $M_w \approx 70\,000$ g/mol yields porous PS films with a period $L \approx 42$ nm, even though the BC is in the weak segregation regime.[14] Further reduction of L requires smaller degrees of polymerization.[15,16] This in turn further reduces the repulsion between the PS and PMMA blocks, thus preventing the evolution of a highly ordered domain structure with a period in the sub-30-nm range.

It is highly desirable to extend the range of available templates exhibiting patterns in the sub-30-nm range that can easily be developed into nanoporous masks for pattern transfer. Here we demonstrate the transfer of sub-30-nm patterns from templates based on supramolecular assemblies (SMAs) consisting of poly(styrene-*block*-4-vinylpyridine) (PS-*b*-PVP) and 2-(4′-hydroxybenzeneazo)benzoic acid (HABA)[17,18] into underlying Si wafers. The Flory−Huggins interaction parameter for PS-*b*-PMMA is given by $\chi = 0.028 + 3.9/T$,[19] whereas that of PS-*b*-PVP is given by $\chi = 91.6/T - 0.095$.[20] Thus, independent of the temperature T, PS and PVP have significantly higher χ values than PS and PMMA. Correspondingly, the repulsive interactions between the blocks in PS-*b*-PVP are significantly stronger than in PS-*b*-PMMA. The strong driving force for microphase separation enables the use of PS-*b*-PVP templates even with periods in the sub-30-nm range.

The morphology of SMAs in thin film configurations based on the PS-*b*-PVP/HABA system was previously investigated in detail.[17,18,21,22] The SMA template initially consists of a PS matrix that surrounds cylindrical PVP/HABA nanodomains oriented normal to the substrate. Vertically oriented cylinders can be obtained for a film thickness up to 100 nm, whereas in thicker films vertically and horizontally oriented cylinders were observed. The HABA molecules form hydrogen bonds with the PVP repeat units so that HABA is evenly dispersed within the PVP/HABA domains. The alignment of the cylindrical nanodomains is insensitive to the composition of the confining surface due to the self-adaptive behavior of the SMA. Therefore, no pretreatment of the substrate is necessary.[17] The extraction of the low molecular weight additive HABA with selective solvents yields films with nanopores 8 nm in diameter arranged in a hexagonal lattice, which has a period of 26 nm. No staining or cross-linking of the developed SMA template is required to transfer the patterns into underlying substrates by RIE. Therefore, it should be possible to pattern a broad range of materials by means of SMA templates.

We prepared PS-*b*-PVP/HABA films with a thickness of 30 nm according to procedures described elsewhere.[17,18] In brief, a mixture of PS-*b*-PVP (M_n(PS) = 35 500 g/mol, M_n(PVP) = 3600 g/mol, $M_w/M_n = 1.06$; Polymer Source Inc.) and HABA (Fluka) in 1,4-dioxane (0.82 wt % PS-*b*-PVP; 0.18 wt % HABA) was deposited on (100)-oriented Si wafers by dip-coating. The wafers were withdrawn from the solution at a rate of about 1 mm/s. Subsequently, the samples were kept in a saturated atmosphere of 1,4-dioxane for 10−20 min. Thermal annealing cannot be applied to improve the order of the PS-*b*-PVP/HABA template because HABA is prone to thermal degradation. Subsequently, HABA was extracted by immersing the samples into methanol for 5 min. Figure 1a shows an atomic force microscopy (AFM) topography image of a nanoporous PS-*b*-PVP film after the extraction of HABA recorded with a Dimension 3100 AFM (Digital Instruments, Inc.) equipped with silicon cantilevers (NSC15, MikroMasch, resonant frequency 325 kHz) in the tapping mode. The inset is a Fourier transform of Figure 1a, which evidences the hexagonal order of the nanopore array. We determined the period of the nanoporous PS-*b*-PVP film by means of real space image analysis. The mean nearest-neighbor distance determined from the pair distribution function obtained from Figure 1a (Figure 1b) is about 26 nm (standard deviation 2.5 nm).

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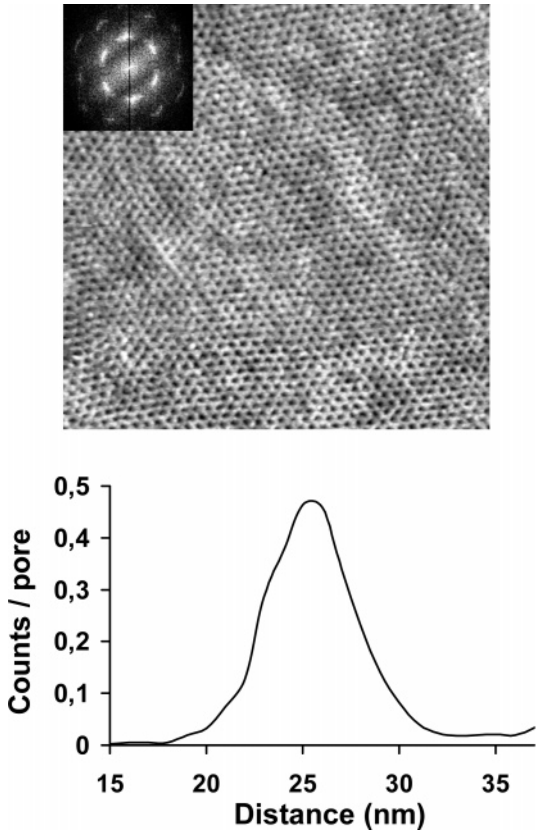

Figure 1. (a) AFM topography image of a nanoporous PS-*b*-PVP film on a Si waver after the extraction of HABA. The edge length is 1 μm. Inset: Fourier transform. (b) Nearest-neighbor peak of the pair distribution function of the image seen in (a). We plotted the number of counts normalized to the number of pores vs distance.

We transferred the pattern of the developed SMA template into the underlying Si wafer by RIE with a mixture of 10 vol % C_4F_8 and 90 vol % Ar (etching time: 30 s; overall gas flow: 100 sccm at 10 mTorr), using an inductively coupled plasma (ICP) reactor (Oxford PlasmaLab System 100) equipped with 2.1-MHz ICP380 and 13.56-MHz radio-frequency sources. After the RIE step, the samples were cleaned by sonification in tetrahydrofuran. Cross-sectional specimens of Si wafers thus patterned were prepared by slicing sections with a thickness of $\approx$400 μm from samples embedded in epoxy resin with a diamond wire. The sections were ground and polished to a thickness of $\approx$80 μm, dimple-ground, and further polished to a thickness of less than 15 μm. The samples were then thinned to electron transparency by etching with Ar ions from both sides (PIPS, Gatan). The specimens were investigated by transmission electron microscopy (TEM), using Phillips CM20T and JEOL 4010 microscopes operated at accelerating voltages of 200 and 400 kV, respectively. The wafers were homogeneously patterned over large areas, as obvious from Figure 2a. The period of about 26 nm is in line with that of the BC template. A detailed view (Figure 2b) reveals that the indentations have a depth of about 10 nm. No amorphous silica layer covering the Si is present.

The SMA resist used for the proof of concept reported here had pores with an aspect ratio (length/diameter) of about 3:1 to 4:1. This is close to the maximum aspect ratio of patterned resists used in industrial RIE processes, which have feature sizes one order of magnitude larger than that of the PS-*b*-PVP/HABA system. One the one hand, higher aspect ratios may impose limitations on the accessibility of the pore bottoms to the plasma. It is reasonable to assume that problems related to charging of the pore walls occur. On the other hand, too thin resist layers may exhibit insufficient etch contrast, hampering the pattern transfer.

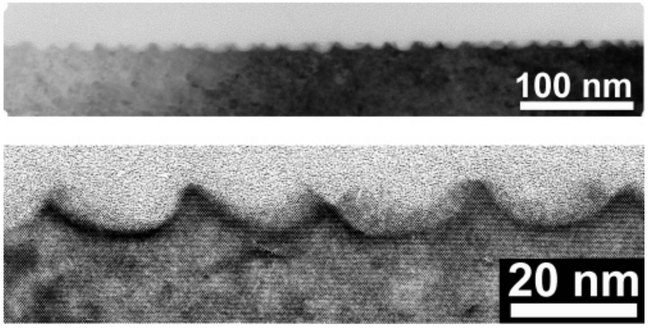

Figure 2. TEM micrographs of cross-sectional specimens of patterned Si wafers: (a) overview; (b) details.

Despite these difficulties, the pattern of the SMA template could directly be transferred into the underlying Si substrate by a standard one-step etching protocol. However, as obvious from Figure 2, the indentations thus generated are broader than the pores of the SMA template, whereas their aspect ratio is smaller than one. This leads to the conclusion that the polymeric resist was completely consumed during the RIE step. However, we anticipate that an additional inorganic resist layer on top of the Si wafer to be patterned will enable etching of features with aspect ratios up to 5:1, as previously shown in the case of nanoporous PS masks obtained from PS-*b*-PMMA templates.[8,23]

In conclusion, SMA templates based on PS-*b*-PVP and HABA with periods in the sub-30-nm range can easily be developed by extracting the additive HABA. No pretreatment of the substrates and no staining or cross-linking of the SMA templates are required for the pattern transfer by RIE. Therefore, SMA templates might be an interesting alternative to established BC templates.

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References and Notes

(1) Park, M.; Harrison, C.; Chaikin, P.; Register, R.; Adamson, D. *Science* **1997**, *276*, 1401−1404.
(2) Cheng, J. Y.; Ross, C. A.; Chan, V. Z. H.; Thomas, E. L.; Lammertink, R. G. H.; Vancso, G. J. *Adv. Mater.* **2001**, *13*, 1174−1178.
(3) Guarini, K. W.; Black, C. T.; Milkove, K. R.; Sandstrom, R. L. *J. Vac. Sci. Technol. B* **2001**, *19*, 2784−2788.
(4) Black, C. T.; Guarini, K. W.; Milkove, K. R.; Baker, S. M.; Russell, T. P.; Tuominen, M. T. *Appl. Phys. Lett.* **2001**, *79*, 409−411.
(5) Park, C.; Yoon, J.; Thomas, E. L. *Polymer* **2003**, *44*, 6725−6760.
(6) Hamley, I. W. *Nanotechnology* **2003**, *14*, R39−R54.
(7) Segalman, R. *Mater. Sci. Eng., R* **2005**, *48*, 191−226.
(8) Zschech, D.; Kim, D.; Milenin, A.; Hopfe, S.; Scholz, R.; Göring, P.; Hillebrand, R.; Senz, S.; Hawker, C.; Russell, T.; Steinhart, M.; Gösele, U. *Nanotechnology* **2006**, *17*, 2122−2126.
(9) Mansky, P.; Liu, Y.; Huang, E.; Russell, T.; Hawker, C. *Science* **1997**, *275*, 1458−1460.
(10) Ryu, D.; Shin, K.; Drockenmuller, E.; Hawker, C.; Russell, T. P. *Science* **2005**, *308*, 236−239.
(11) Blauw, M. A.; Craciun, G.; Sloof, W. G.; French, P. J.; van der Drift, E. *J. Vac. Sci. Technol. B* **2002**, *20*, 3106−3110.
(12) Feichtinger, H. In *Electronic Structure and Properties of Semiconductors*; Schröter, W., Vol. Ed.; Materials Science and Technology; VCH: Weinheim, 1991; Vol. 4, pp 143−195.
(13) Thurn-Albrecht, T.; Steiner, R.; DeRouchey, J.; Stafford, C. M.; Huang, E.; Bal, M.; Tuominen, M.; Hawker, C. J.; Russell, T. P. *Adv. Mater.* **2000**, *12*, 787−791.

(14) Guarini, K. W.; Black, C. T.; Yeung, S. H. I. *Adv. Mater.* **2002**, *14*, 1290−1294.
(15) Almdal, K.; Rosedale, J. H.; Bates, F. S. *Phys. Rev. Lett.* **1990**, *65*, 1112−1115.
(16) Madsen, M. W.; Bates, F. S. *Macromolecules* **1996**, *29*, 1991−1998.
(17) Sidorenko, A.; Tokarev, I.; Minko, S.; Stamm, M. *J. Am. Chem. Soc.* **2003**, *125*, 12211−12216.
(18) Tokarev, I.; Sidorenko, A.; Minko, S.; Stamm, M. *Polym. Mater. Sci. Eng.* **2004**, *90*, 292−293.
(19) Russell, T. P.; Hjelm, R. P.; Seeger, P. A. *Macromolecules* **1990**, *23*, 890−893.
(20) Schulz, M. F.; Khandpur, A. K.; Bates, F. S.; Almdal, K.; Mortensen, K.; Hajduk, D. A.; Gruner, S. M. *Macromolecules* **1996**, *29*, 2857−2867.
(21) Tokarev, I.; Krenek, R.; Burkov, Y.; Schmeisser, D.; Sidorenko, A.; Minko, S.; Stamm, M. *Macromolecules* **2005**, *38*, 507−516.
(22) Tokarev, I. Ph.D. Thesis, Technische Universität Dresden, 2004.
(23) Zschech, D.; Kim, D.-H.; Milenin, A. P.; Scholz, R.; Hillebrand, R.; Hawker, C. J.; Russell, T. P.; Steinhart, M.; Gösele, U. *Nano Lett.* **2007**, *7*, 1516−1520.

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