Directed Self-Assembly of Perpendicularly Oriented Nano-Cylinders with Liquid Crystalline Block Copolymer

Hiroshi Yoshida, Yasuhiko Tada, Kouhei Aida
Hitachi Research Laboratory, Hitachi Ltd., Hitachi, Ibaraki 319-1292, Japan
hiroshi.yoshida.jz@hitachi.com

Motonori Komura, Tomokazu Iyoda
Chemical Resources Laboratory, Tokyo Institute of Technology, Midori-ku, Yokohama, Kanagawa 226-8503, Japan

Advances in chemical heteroepitaxy of block copolymer (BCP) are positioning directed self-assembly (DSA) as a promising next-generation lithographic candidate.[1,2] In conventional BCP, orientation of microdmains in thin films is governed by interfacial interactions between microdomains and free / substrate surfaces. This limits variation of block copolymers capable to form microdmains with perpendicular (out-plane) orientation in thin films, which is one of the important characteristics for precise pattern transfer. Homeotropic alignment of liquid crystalline moieties has been reported to induce microdomains to orient perpendicular against the free surface.[3] In this work, DSA of perpendicularly oriented cylindrical microdomains was successfully demonstrated using an amphiphilic block copolymer, PEO-*b*-PMA(Az), which contains liquid crystalline side-chain in one of the blocks (Fig. 1).[3]

The PEO-*b*-PMA(Az) applied in this study self-assembles into a hexagonal closed packed (hcp) array of perpendicularly oriented PEO cylinders in PMA(Az) matrix with lattice plane spacing d_0= 17 nm as demonstrated by a cross-sectional electron scanning micrograph (Fig. 2). DSA of the PEO-*b*-PMA(Az) was carried out by chemical heteroepitaxy. The PEO-*b*-PMA(Az) film was spin coated on a template with a sparse chemical contrast pattern prepared by e-beam lithography with hcp lattice plane spacing $d_{sub} = 35 \text{ nm} \approx 2d_0$ (Fig. 3a). A long-range ordered single lattice with lattice plane spacing of d = 17.5 nm was successfully obtained by assembling PEO cylinders on and in between the pre-patterned lattice points, thus multiplying the pattern density of the template by a factor of 4 (Figs. 3b ~ 3c).

Polystyrene (PS) and poly(methyl methacrylate) (PMMA) is one of a few combinations having almost neutral surface tension, which makes PS-*b*-PMMA as a unique and therefore widely applied material to form perpendicularly oriented structures. However, the minimum feature size of PS-*b*-PMMA is limited to ca. 25 nm because of its relatively small segregation power. PEO-*b*-PMA(Az) can assemble structures with sub 10 nm full pitch. Therefore, presented results suggest that introduction of liquid crystalline ordering, in addition to conventional microphase separation, provides not only robustness to the DSA process but also enhances resolution required for next generation nano-devices.

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[1] S. O. Kim et al. *Nature*, 424, 411 (2003)
[2] R. Ruiz et al. *Science*, 321, 936 (2008), Y. Tada et al., *Macromolecules*, 41, 9267 (2008)
[3] M. Komura et al., *Macromolecules* 40, 4106 (2007)

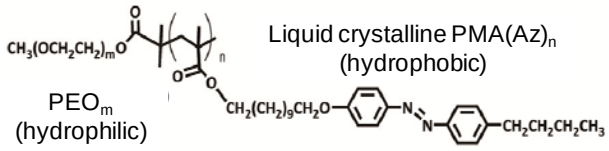

Figure 1. Structural formula of PEO-*b*-PMA(Az).

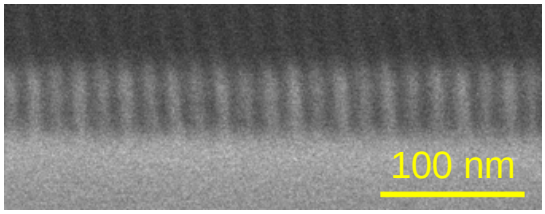

Figure 2. A cross-sectional SEM image of PEO_{114}-*b*-$PMA(Az)_{24}$ thin film self-assembled on Si substrate. Cylindrical microdomains of PEO were stained with RuO_2 and therefore appear whitish under SEM. Film thickness = 50nm

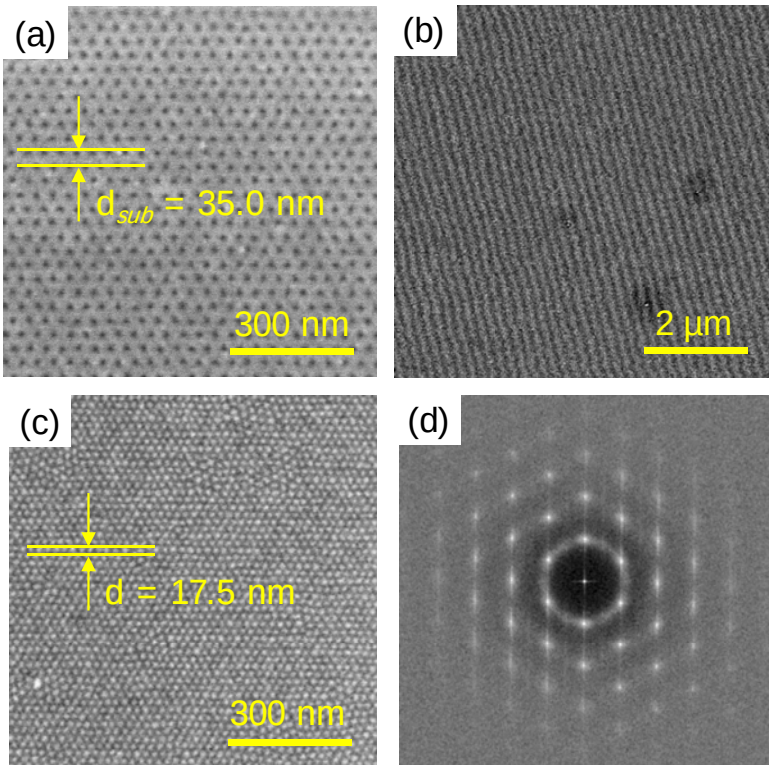

Figure 3. Chemical heteroepitaxy of cylinder forming PEO_{114}-*b*-$PMA(Az)_{24}$. (a) A top-down SEM image of resist mask prepared by e-beam lithography to pattern a chemical template. (b) A low magnification SEM image of self-assembled film showing moiré pattern demonstrating single grain structure. (c)(d) A top-down SEM image and the corresponding 2D-FFT image of self-assembled film.