Supplementary material (ESI) for Journal of Materials Chemistry

Electronic Supplementary Information

Smart block copolymer masks with molecule-transport channels for total wet nanopatterning

Ryoko Watanabe[1], Kaori Kamata[1, 2], and Tomokazu Iyoda[1, 2*]

[1]Division of Integrated Molecular Engineering, Chemical Resources Laboratory, Tokyo Institute of Technology, R1-25 4259 Nagatsuta, Midoriku, Yokohama, kanagawa 226-8503, Japan. [2]CREST, Japan Science and Technology Agency, 4-1-8 Hon-cho, Kawaguchi, Saitama 332-0012, Japan

**email: iyoda.t.aa@m.titech.ac.jp*

Contents:

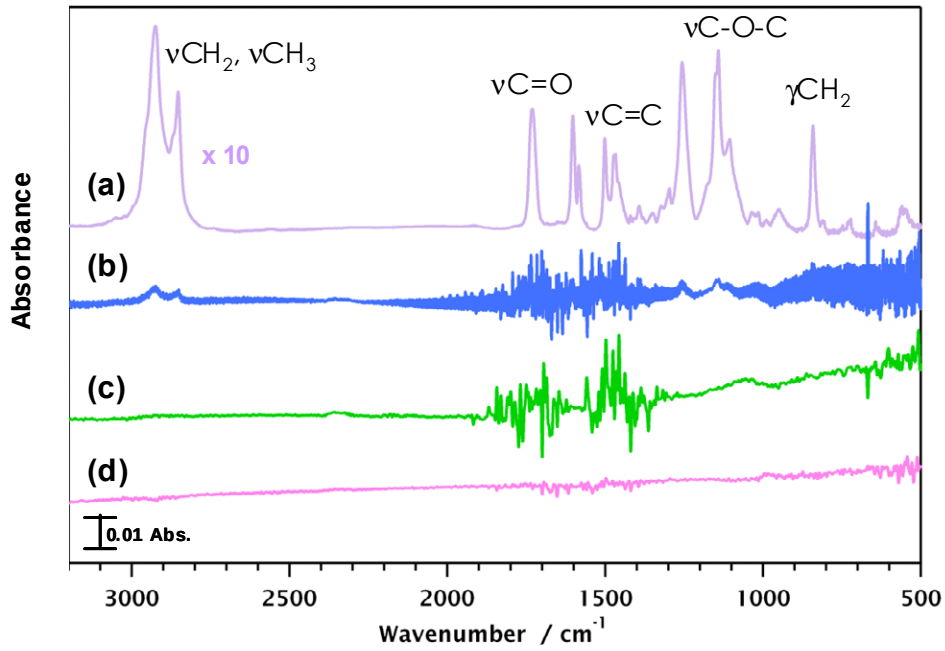

Fig. S1 Fourier transform infrared spectroscopy (FTIR) spectra of (**a**) cast film of PEO-*b*-PMA(Az), (**b**) spin-coated film of PEO-*b*-PMA(Az), (**c**) silicon wafer etched by NH_4F through EO-blended etching mask after THF/water rinse, and (**d**) bare silicon wafer. FTIR measurement was carried out by an FT/IR-660 plus (JASCO). The reference was a bare non-doped silicon wafer.

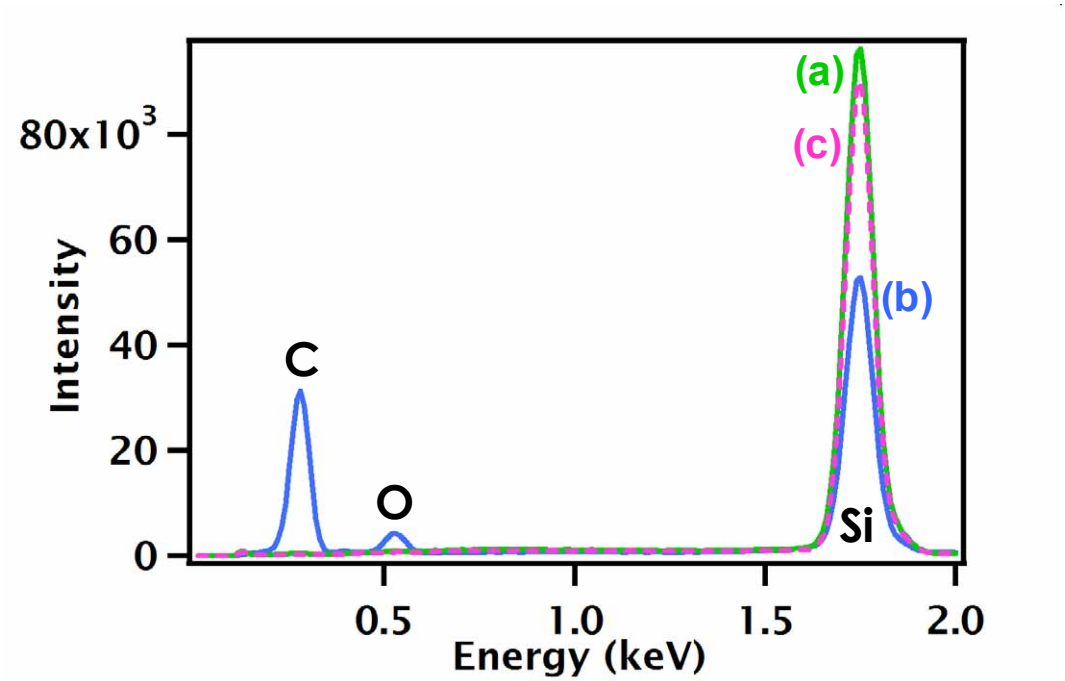

Fig. S2 Energy dispersive X-ray (EDX) profiles of (a) etched silicon wafer through the PEO-*b*-PMA(Az) mask, (b) spin-coated film of PEO-*b*-PMA(Az), and (c) bare silicon wafer. EDX analysis was performed using Genesis 2000 (EDAX INC.) equipped with a scanning electron microscope S-3000N (Hitachi High-Technologies Co.)

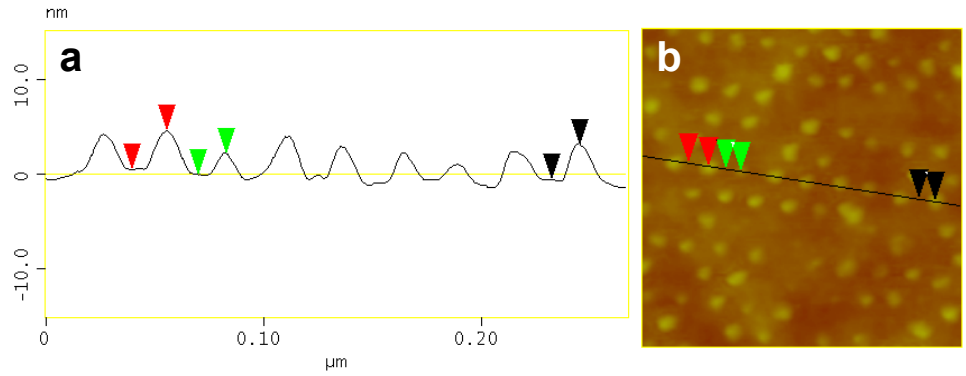

Fig. S3 (**a**) Topographic profile of the nano-cone array fabricated on silicon wafer by immersion into 33 wt% of NH_4F aqueous solution for 15 min. The mask used was EO-blended PEO_{114}-*b*-$PMA(Az)_{67}$ with blend ratio of 55 %. (**b**) The corresponding image of the profile.

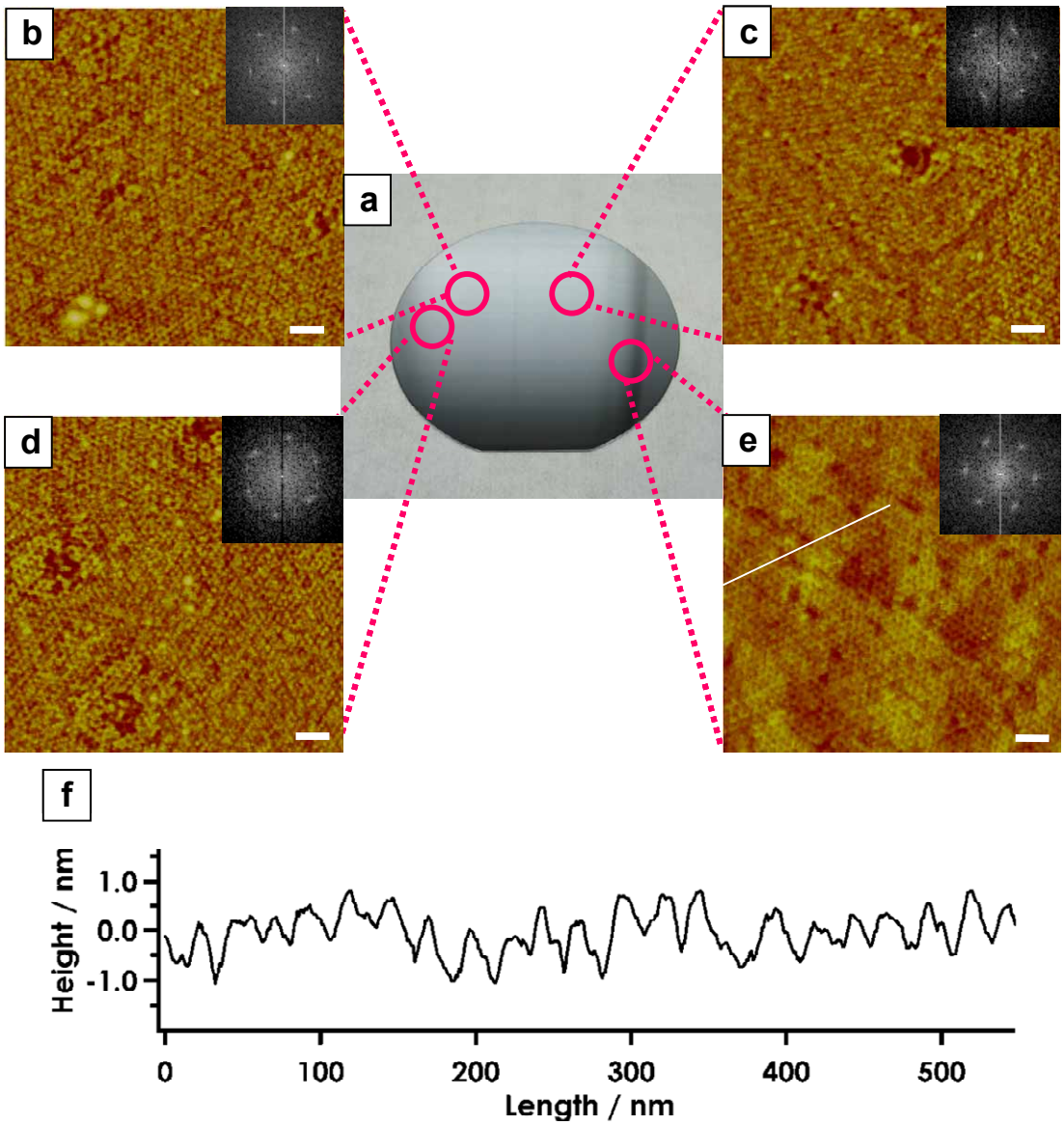

Fig. S4 Nanopattern transcription on a large area of silicon wafer surface by total wet nanopatterning with NH_4F for 5 min through EO-blended mask of PEO_{114}-*b*-$PMA(Az)_{54}$. (**a**) Photograph of 4-inch silicon wafer to be etched. (**b-e**) Tapping mode AFM height images of the surface indicated with circle on (**a**). The inset is FFT image of each height image. Scale bar is 100 nm. Z scale is 10 nm. (**f**) Cross-sectional profile along the white line in the image (**e**).

It takes only a few hours to demonstrate such a large-area nanopatterning by using a 4-inch silicon wafer as a large substrate. The whole procedure consisted of the mask preparation including spin-coating and annealing for 1 h, the etching for 3 min, removal of the mask, and AFM observation of the resulting nanohole array.

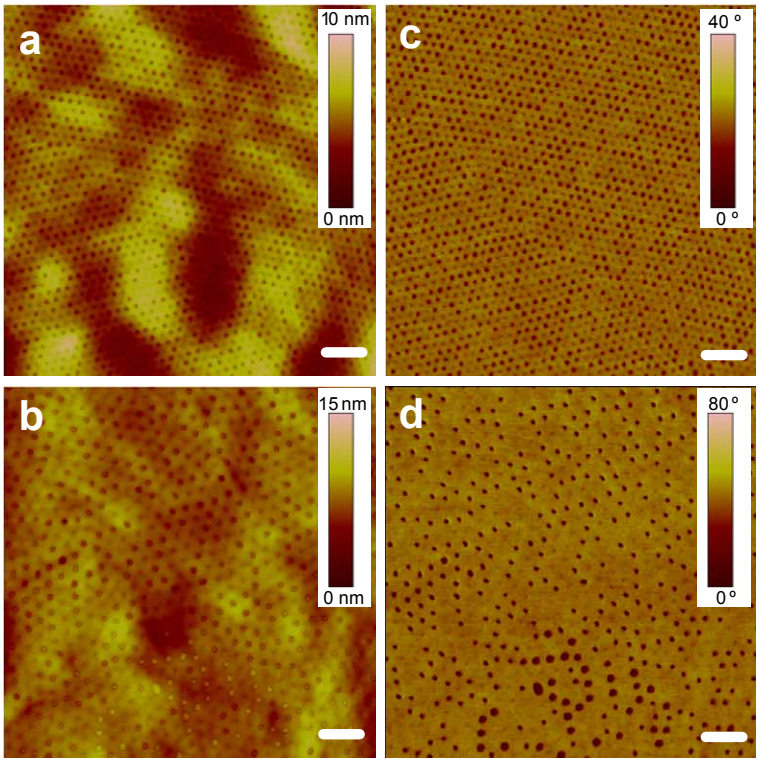

Fig. S5 Tapping mode AFM height (**a** and **b**) and phase (**c** and **d**) images of the EO-blended PEO_m-*b*-$PMA(Az)_n$ etching masks after annealing. (**a** and **c**) PEO_{114}-*b*-$PMA(Az)_{54}$, blend ratio= 55 %. (**b** and **d**) PEO_{272}-*b*-$PMA(Az)_{116}$, blend ratio= 54 %. Scale bars, 100 nm.

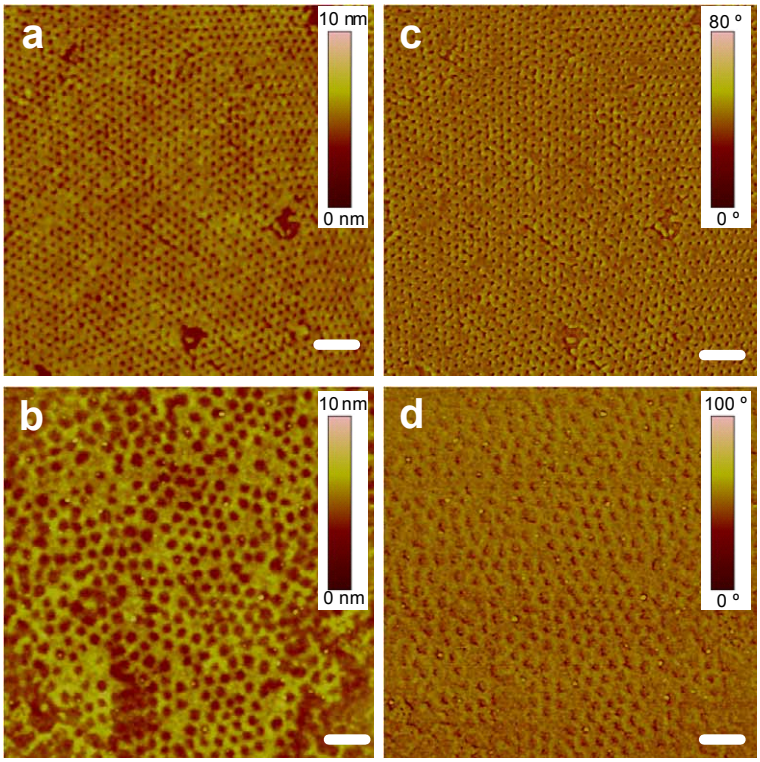

Fig. S6 Tapping mode AFM height (**a** and **b**) and phase (**c** and **d**) images of the resulting silicon wafer surfaces after wet chemical etching by 33 wt% of NH_4F aqueous solution. The mask used was PEO_{114}-*b*-$PMA(Az)_{54}$, blend ratio= 55 % (**a** and **c**), and PEO_{272}-*b*-$PMA(Az)_{116}$, blend ratio= 54 % (**b** and **d**). The etching time was 4.5 min (**a** and **c**) and 4 min (**b** and **d**). Scale bars, 100 nm.

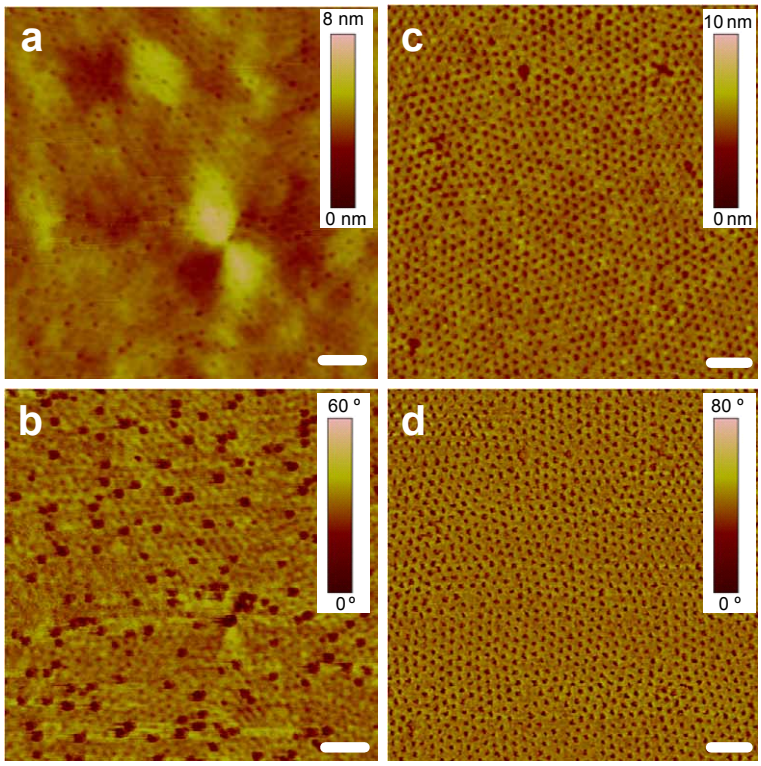

Fig. S7 Tapping mode AFM images of the 55 % EO-blended PEO_{114}-*b*-$PMA(Az)_{54}$ etching masks blended with $PMA(Az)_{97}$ homopolymer (**a** and **b**) and the resulting silicon wafer surfaces after wet chemical etching by 33 wt% of NH_4F aqueous solution (**c** and **d**). $PMA(Az)_{97}$ was blended so that PMA(Az) weight composition accounted for 88 % of the mask. Mask was annealed at 105 ºC for 1 h. The etching time was 3 min. **a** and **c** are height images. **b** and **d** are phase images. Scale bars, 100 nm.

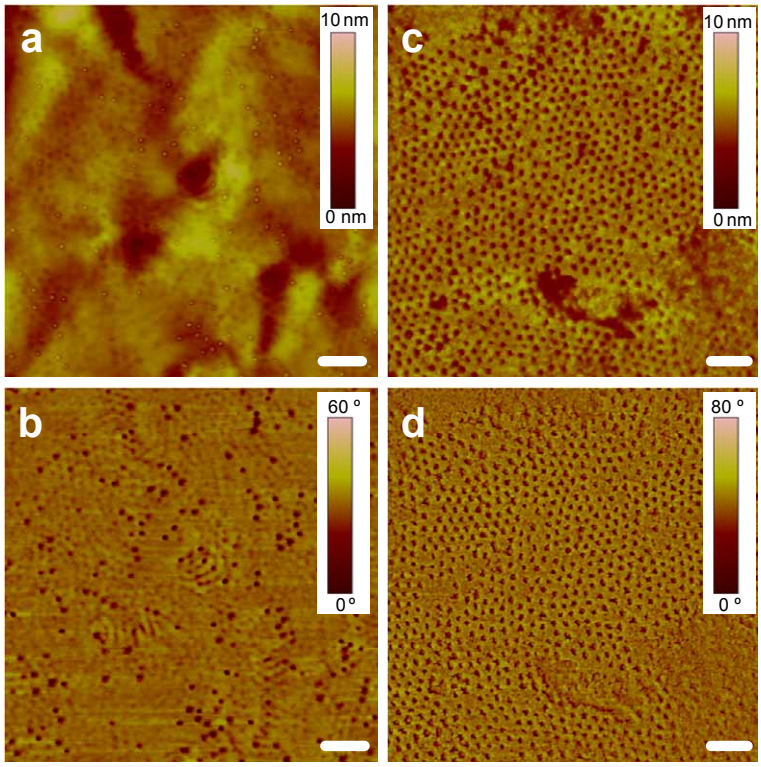

Fig. S8 Tapping mode AFM images of the 55 % EO-blended PEO_{114}-*b*-$PMA(Az)_{54}$ etching masks blended with $PMA(Az)_{97}$ homopolymer (**a** and **b**) and the resulting silicon wafer surfaces after wet chemical etching by 33 wt% of NH_4F aqueous solution (**c** and **d**). $PMA(Az)_{97}$ was blended so that PMA(Az) weight composition accounted for 91 % of the mask. Mask was annealed at 105 ºC for 1 h. The etching time was 3 min. **a** and **c** are height images. **b** and **d** are phase images. Scale bars, 100 nm.