Supporting Online Material for

Density Multiplication and Improved Lithography by Directed Block Copolymer Assembly

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This PDF file includes:

Materials and Methods
Figs. S1 and S2
References
**Materials and Methods:**

We use thin films of poly(styrene-block-methyl methacrylate) (PS-b-PMMA) to demonstrate both density multiplication and pattern quality rectification on substrates pre-patterned by e-beam lithography. Two copolymers are used to generate hexagonal arrays of perpendicularly oriented PMMA cylinders in a PS matrix at two different densities: 1) $M_n=64$Kg/mol, $f=0.7$ and $L_o=39$nm, and 2) $M_n=39$Kg/mol, $f=0.7$ and $L_o=27$nm, where $f$ is the weight fraction PS and $L_o$ is the block copolymer natural lattice constant. The assembly process is illustrated in Figure 1. A brush of hydroxyl-terminated polystyrene(S1, S2) ($M_n=6$ Kg/mol) is deposited on a SiO$_x$ substrate. We then apply and anneal a PMMA (950Kg/mol) e-beam resist layer. We use electron beam to write the closest possible match to a hexagonal pattern(S3) with a lattice constant $L_s$ such that $L_s=nL_o$ with $n=1, 2$ [Fig. 1(A)] over a total area of 100$\mu$m x 100$\mu$m (for $L_s=39$ and 78nm, we made additional patterns covering 3000$\mu$m x 50$\mu$m). Patterns with both $n=1$ and $n=2$ were written on the same sample. After developing the e-beam resist, representative samples are saved for imaging and metrology of the patterns created by traditional e-beam lithography. Samples for block copolymer assembly are then subjected to a brief dose of oxygen plasma (5sec, 95mTorr, 40W) followed by a rinse with toluene at 60 $^\circ$C and sonicated for 10 min to remove the bulk of the resist [Fig. 1(B)]. We then spin-coat a block copolymer film at a thickness of 1.1-1.3$L_o$ [Fig. 1(C)] and bake it in vacuum (220 $^\circ$C for $L_o=39$nm and 190 $^\circ$C for $L_o=27$nm) for 1hr [Fig. 1(D)]. The areas of the surface (arrays of spots) exposed to the oxygen plasma are preferentially wet by the PMMA block, and background areas are slightly preferential towards the PS block. (Perpendicular cylinders with defects including short sections of parallel cylinders are observed on areas of the sample adjacent to the patterned regions). The PMMA domains are then selectively removed from the film by exposing the sample to UV radiation and rinsing in acetic acid(S4). We use scanning electron micrographs (SEM) with a resolution of ca. 1.2nm/pixel to quantify the feature size uniformity of both block copolymer and e-beam features.

**Image Analysis.**

Image analysis was done on high resolution SEM micrographs. At least three images were taken on random areas in the patterns. Each image comprising at least 5000 dots for a total of at least 15000 dots analyzed per pattern. The resolution was chosen such that each dot would have ~250 pixels. We filtered the images using a band-pass filter to cut low and high frequency noise. We then used the histogram of the filtered image to identify the black and white levels of the data and set a binary threshold at the midpoint. We use the binary images to extract dot size distributions taking care not to include dots cut by the image edges.

We also extracted the center of mass of each dot to perform placement analysis. For each image we first find the set of lines that best fits all the rows of dots with all best-fit lines having a constant slope. The x-direction is then defined along the row lines. We first quantify placement error or jitter along the x-direction (downtrack direction). For each row, $i$, the distance of the $n$th dot to an arbitrary origin is $d_n=nL_p+x_i$ where $n$ is the dot...
number \( (n=0, 1, 2\ldots) \), \( L_p \) is the block copolymer pitch and \( x_i \) is the position of the first lattice point along the row. The placement error along the x-direction is therefore given by \( \delta_{x,n} = (d_i - x_i) - nL_p \). We define \( \sigma_x \) as the standard deviation of \( \delta_x \) and is reported in Table 1 for the various assembly patterns. Similarly, the placement error along the y-direction \( \delta_{y,n} \) is the perpendicular distance from the \( n \)th dot in row \( i \) to the best fit line to row \( i \). \( \sigma_y \) is the standard deviation of \( \delta_y \) (Table 1).

Fig. S1. Large area SEM micrographs of density multiplied patterns with (A) \( L_s=78\text{nm}, L_p=39\text{nm} \), and (B) \( L_s=54\text{nm}, L_p=27\text{nm} \).
Fig. S2. Moiré interference patterns formed by the superposition of the block copolymer grid with the SEM scanning grid. (A) \( L_s=78\,\text{nm} \), \( L_p=39\,\text{nm} \). The uniformity of the Moiré pattern in the pre-patterned area (zone 1) is indicative of the long range ordering of the block copolymer pattern. Outside of the pre-patterned area (zone 2) there is no long range ordering and the interference patterns have multiple orientations. (B) Interference pattern for \( L_s=54\,\text{nm} \), \( L_p=27\,\text{nm} \). Arrows indicate domains where the block copolymer pattern is defective or randomly oriented limiting defect density to \( \sim 10^{-3} \).

References:

S3. The chemical patterns are written on a rectangular lattice and not on a hexagonal lattice. This is due to the fact that the e-beam moves in an x-y grid with discrete steps along the x and y axis. The e-beam pre-pattern consists of a rectangular lattice with two dots in the unit cell that are the closest match to the natural hexagonal lattice of the block copolymer.