Three-Dimensional Nanolithography Guided by DNA Modular Epitaxy

Three-dimensional nanolithography guided by DNA modular epitaxy

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Abstract Lithographic scaling of periodic three-dimensional patterns is critical for advancing scalable nanomanufacturing. Current state-of-the-art quadruple patterning or extreme-UV lithography produce line pitch down to around 30 nm, which can be further improved to sub-20 nm through complex post-fabrication processes. Herein, we report the use of three-dimensional (3D) DNA nanostructures to scale the line pitch down to 16.2 nm, around 50 % smaller than current state-of-the-art results. We use a DNA modular epitaxy approach to fabricate scaled 3D DNA masks with prescribed structural parameters (pitch, shape, and critical dimensions) along a designer assembly pathway. Single-run reactive ion etching then transfers the DNA patterns to a Si substrate at a lateral resolution of 7 nm and a vertical resolution of 2 nm. The DNA modular epitaxy-directed lithography achieves smaller pitch than the projected values for advanced technology node in field-effect transistors, and provides a potential complement to the existing lithographic tools towards advanced 3D nanomanufacturing.

By shaping materials into in silico designed patterns with high fidelity, lithography techniques build the manufacturing foundations for electronics[1], photonics[2,3], nanofluidics[4] and nanoelectro-mechanical systems[5]. In semiconductors processing[6], photolithography has been used over the decades to scale the pitch of gates and contacts (i.e. proportionally shrink their center-to-center spacing), to meet the projected milestones of integration densities. Recent advances in pitch scaling beyond the diffraction limit of photolithography are mostly ascribed to the multi-patterning techniques. For instance, a typical 10-nm node (with a 34 nm fin pitch[7]) uses self-aligned quadruple patterning consisting of 6 successive steps of depositing and etching. Such complicated processes could increase the risks of patterning failures.[8] Multi-patterning techniques also require aligning multiple photolithography layers for scaling pitch and constructing multilayered three-dimensional (3D) patterns, and the alignment accuracy (i.e. overlay control) is limited to 5 nm.[9] Alternative patterning approaches, either top-down or bottom-up, have been explored to advance lithography scaling, including extreme-UV (EUV) lithography[10], e-beam lithography[11], directed self-assembly of block copolymers[12] and nanoimprinting[13]. Despite its costly instruments and materials, EUV lithography will be used to replace quadruple patterning at 30-nm-scale pitches.[14] However, at sub-20-nm-scale pitches, current EUV approaches need to be replaced by either the high-numerical-aperture EUV or multi-patterning EUV techniques, which are still yet to be well-estabulished.[14]

Through encoding the spatial positioning information into the designable single-stranded DNA (ssDNA) components, structural DNA nanotechnology[15], in particular DNA origami[16-20] and DNA bricks[21-24], enables self-assembling of complex designer DNA nanostructures with single-nanometer feature modularity. This advantage allows self-assembled DNA templates to align[25,26] or *in situ* synthesize[27,28] inorganic nanostructures in solution, at a spatial resolution beyond the pitch limit of photolithography.[7] However, the durability of DNA-directed inorganic nanostructures/patterns relies on both the integrity of DNA templates and the presence of buffer. Current DNA templates have limited success in dry lithography, which uses reactive ion etching (RIE) to fabricate free-standing inorganic nanostructures.[29,30] Three technical barriers present challenges to DNA-based lithography: (1) Limited DNA pattern dimensions. Most of DNA origami structures are smaller than 0.01 μm^2 with a monolayer thickness of double-stranded DNA (dsDNA).[31] Hierarchical self-assembly method could laterally conjugate DNA origami structures to reach a total area of 0.6 μm^2,[32] but it is hard to precisely stack up multiple DNA origami into a thicker pattern. (2) Susceptible 3D DNA nanofeatures. Ordinary RIE masks should be thick enough to resist etchants, but high aspect ratio (height-to-width) DNA nanofeatures often collapse after being dried.[23,24,33] (3) Uncontrolled self-assembly pathways. Self-assembly of DNAs into micron-scaled 3D DNA patterns may involve competing seeding-growth pathways that lower the yield and introduce defects.[23,24] Thus, previous explorations of DNA-based lithography have relied on only 2D DNA patterns as masks, and been applied in either wet etching by hydrofluoric acid vapor[33,34] or indirect RIE after coating with metal[29] or silica[35]. Notably, these inorganic coatings sacrifice the spatial resolution of DNA masks.

Herein, we demonstrate scalable 3D nanolithography, which directly use 3D DNA masks in RIE without any auxiliary inorganic coating (such as metal or silica). We invent a DNA modular epitaxy paradigm to promote the pattern complexities and lower the structural defects of 3D DNA patterns. The DNA modular epitaxy begins with a flat DNA brick crystal as a substrate, followed by seed-mediated growth of 3D DNA modules on top of the substrate. The assembled 3D DNA masks are stabilized by Ni^{2+} ions, which prevent DNA feature collapse after air-drying on Si substrate. Finally, using the Ni^{2+}-stabilized 3D DNA masks, we apply a single-run RIE to directly produce the ultra-scaled Si patterns. The pitch and the critical dimension (CD) of Si patterns have been scaled as small as 16.2 ± 0.6 nm and 7.2 ± 1.0 nm, respectively, about 50 % smaller than current values using quadruple patterning or extreme-UV lithography. Individual 3D DNA mask also enables one-step lithography for multilayered 3D Si pattern at a vertical resolution of 2 nm. Towards future ultra-scaled 3D manufacturing, DNA modular epitaxy-directed lithography could potentially perform in synergy with other conventional lithographic tools for rational shaping of diverse substrates.

Strategy overview

Fig. 1 illustrates the workflow of DNA modular epitaxy-directed lithography for a multilayered grid pattern. To fabricate such pattern in silicon, we first designed a 3D DNA mask using the 32-nucleotide (nt) DNA bricks.[22,23] We then performed a three-stage DNA modular epitaxy synthesis in Tris/EDTA/$MgCl_2$ buffer, starting from a DNA substrate (yellow) to 3D modules of higher line (blue) and lower line (green). Next, the as-synthesized 3D DNA mask was deposited on a Si substrate, incubated with $NiCl_2$ solution, and then fully dried. After a single-run fluorine-based RIE and the removal of the mask residuals, the etched Si pattern exhibited the prescribed multilayered grid geometry.

Mask design details

Fig. 2a illustrates the design of the example grid DNA mask (named as 12H-grid). The mask exhibited two layers of cross-lines along the *x*- and *z*-directions, and both layers of lines were designed at an equal pitch (ca. 32 nm). The lines and spaces had equal designed width (ca. 16 nm). We converted the repeating unit of the grid pattern into unit cell of an *x*-*z* extending DNA brick crystal[23], as in the LEGO® and cylinder model of Fig. 2a (also in Supplementary Fig. 1). The hybridized 8-base pair (B) domain from two neighboring DNA bricks is designated as a voxel, with a volume of 2.7 nm × 2.4 nm × 2.6 nm (dimension data obtained from liquid-mode AFM, Supplementary Fig. 13). The unit cell consisted of three DNA modules, including the substrate (12 helices (H) × 4H × 94B in yellow), the higher line (6H × 8H × 94B in blue) and the lower line (6H × 5H × 47B in green), as shown in Fig. 2a. The three DNA modules had complementary ssDNAs dangling on their attachment interfaces to propagate the unit cell in the *x*-*z* plane.

DNA modular epitaxy

One-pot DNA self-assembly faces the difficulty of controlling the seeding-growth pathway.[36,37] Micron-scale 3D DNA patterns may exhibit more uncontrollable seeding-growth pathways than 1D and 2D DNA nanostructures,[38,39] which compete for ssDNA components and lower the assembly yield.[23,24] Inspired by molecular-beam epitaxy of inorganic crystalline films[40] and seed-mediated epitaxy growth of inorganic nanocrystals[41], we invented DNA modular epitaxy to activate designer seeding-growth pathway during 3D DNA self-assembly. Without controlling the assembly dynamics for individual ssDNAs, we adjusted the assembly orders of 3D modules, which simplified the pathway design and improved the yield and the quality for micron-scale 3D DNA masks. Fig. 2b illustrates the three-stage DNA modular epitaxy for 12H-grid mask. We first assembled DNA substrates as seeds using concentrated ssDNAs in Stage-1, and then stepwise introduced additional ssDNAs to grow 3D DNA modules in Stage-2 and Stage-3. To inhibit the competing seeding pathways during epitaxial growth stages, we gradually decreased the ssDNA concentrations and the reaction temperatures.

Epitaxial Stage-1 initiated the seeding and composed the DNA substrate (12H × 4H× 94 module) with an initial concentration of ca. 310 nM for each ssDNA component. The growth of DNA brick crystal was thermodynamically favorable along the base-pair stacking direction (*z*-direction), therefore leaf-like DNA substrates were produced with average pattern area of ~ 0.2 ± 0.1 μm × 1.5 ± 0.5 μm (Fig. 2c). Epitaxial Stage-2 constructed the higher line module (6H × 8H × 94B) that propagated along the *z*-axis on the DNA substrate. Besides the ssDNA components of the higher line modules (ca. 220 nM each ssDNA), Stage-2 introduced a second batch of the substrate ssDNA components to enlarge the dimensions of the DNA substrates. The Stage-2 product displayed parallel DNA lines with an average pattern area of 0.3 ± 0.1 μm × 2.5 ± 0.5 μm (Fig. 2c). Epitaxial Stage-3 introduced ssDNA components (ca. 180 nM for each) of the lower line module (6H × 5H × 47B) for assembling. The final product displayed a cross-line grid pattern in SEM and AFM images (Fig. 2c, 2d). We calculated a gross yield of 86 %, based on the remaining ssDNAs concentration (see Supplementary Method S2.6). Cryo-EM image of the DNA mask 12H-grid (Fig. 2e) validated a single-crystal-like dsDNA lattice with highly ordered 6H-wide lines and 6H-wide

spaces. We did not observe blank DNA substrates or discrete DNA lines in 12H-grid products, indicating the effective pathway controllability of DNA modular epitaxy.

DNA mask deposition and characterization

Rigid inorganic coating could prevent drying-induced collapse of 3D DNA patterns,[23,24,28] but such coating could lower the initial pattern resolution and disturb subsequent RIE procedures. We develop Ni^{2+}-assisted DNA mask deposition to stabilize dried 3D DNA mask patterns on a Si substrate without forming an inorganic coating layer. 3D DNA masks solution was first added onto a Si substrate and incubated with $NiCl_2$ solution (50 mM) for 1 hour. Besides promoting DNA masks adsorption onto the Si substrate, Ni^{2+} cations chelated with adjacent DNA helices to enhance the structural stiffness of 3D DNA modules.[42] After DNA mask deposition, the Si substrate was rinsed in ethanol to remove water and salt residuals while ethanol prevented dsDNA de-hybridization. Then the DNA mask-deposited Si substrate was air-dried to evaporate all ethanol. Energy dispersive X-ray (EDX) spectroscopy on SEM validated that low-dose Ni^{2+} were homogenously distributed within the dried DNA mask (Supplementary Method S2.5, Supplementary Fig. 20).

The Ni^{2+}-chelated 3D DNA mask maintains its intrinsic geometries after being dried. Taking the mask 12H-grid for example (Extended Data Fig. 5), SEM line-scan profiles indicated an *x*-axis pitch at 32.3 ± 0.9 nm for the higher lines and a *z*-axis pitch at 32.1 ± 0.9 nm for the lower lines. Their line widths were 13.2 ± 0.6 nm and 12.9 ± 1.0 nm, respectively. AFM profiles indicated three different thicknesses of 4.5 ± 0.3 nm, 14.5 ± 0.9 nm and 19.2 ± 0.7 nm for the DNA substrate, the lower and the higher lines, respectively (Fig. 2d). The increment of line widths in AFM profiles came from the artifact of AFM probe radius.

SEM measurements further indicated that Ni^{2+}-chelated 12H-grid exhibited different drying shrinkages in the mask lines and substrate modules. The DNA substrate was tightly immobilized with Ni^{2+} onto the Si surface and exempted from the lateral shrinkage during the drying process. Therefore, DNA substrate maintained an *x*-axis periodicity of 32.3 ± 0.9 nm regardless of the drying process, which equaled to the *x*-axis pitch of the higher lines (Extended Data Fig. 5d). The corresponding effective *x*-axis diameter of the dried substrate dsDNA was 2.7 nm. In contrast, *x*-axis width of the freestanding 6H-wide higher line reduced to 13.2 nm after drying, corresponding to an effective dsDNA diameter of 2.2 nm in the *x*-axis (Extended Data Fig. 5c). Because drying shrinkage tensions were proportional to volumes of 3D DNA modules, the cumulative tension from the higher lines stretched the lower lines, producing effective dsDNA diameter of 3.2 nm in the lower lines in the *x*-axis. Additionally, our control tests showed that Ni^{2+}-free deposition of mask 12H-b *grid* resulted in collapsed DNA lines and variable pitch shrinkages (Supplementary Fig. 23).

Mask pattern diversity

Based on DNA modular epitaxy, we designed and prepared DNA brick crystals with three commonly used periodic lithographic patterns. The detailed characterization results, including gross yields, dimensions and defect rates are summarized in Supplementary Table 1 and 2.

For line/space pattern at a 32 nm pitch, DNA mask 12H-a (Fig. 3a) was composed of a 12H-periodic substrate module (12H × 4H × 94B) and a 6H-wide line module (6H × 8H × 94B). Its two-stage epitaxial assembly resulted in a gross yield of 82 %. The DNA lines in the dried mask 12H-a did not collapse on Si substrate (Supplementary Fig. 4), showing 12.2 ± 0.5 nm in line width and 1.5 nm in line width roughness (LWR, defined as three times the width standard deviation, see Supplementary Method S2.8). The line pitch of DNA mask 12H-a was 32.2 ± 0.6 nm. At an equivalent line pitch, the LWR of DNA mask 12H-a was smaller than the benchmarking LWR of EUV lithography patterned resist.[43]

DNA mask 12H-pillar (Fig. 3b) exhibited a rectangular array of DNA pillar module (6H × 8H × 47B) on a 12H-periodic substrate (12H × 4H × 94B). The dried mask 12H-pillar had an *x*-axis pitch at 32.5 ± 1.6 nm and a *z*-axis pitch at 32.1 ± 1.9 nm (Supplementary Fig. 12d, g). The DNA pillars measured 16.5 ±

1.1 nm × 19.1 ± 1.1 nm in the *x*- and *z*- dimensions (Supplementary Fig. 12c, f). The missing or collapsed pillars, defined as feature defects, were around 4.6 defects per μm^2. At similar pitches and aspect ratios (height/width) of DNA mask 3D modules, 12H-pillar had more defects than 12H-grid and 12H-a (0.8 and 0 defect/μm^2). We consider that the large surface-to-volume ratio of DNA pillars made them more susceptible to the capillary-force-induced collapse during the drying process.

Contact hole mask 8H-hole-a was prepared by a subtractive DNA modular epitaxy approach, which etched contact holes in a pre-formed DNA substrate (Fig. 3c). With subtractive DNA modular epitaxy, each hole had well-formed sidewalls and free-of grain boundary defects (Supplementary Fig. 3). The DNA substrate for 8H-hole-a was prepared by a two-stage additive DNA modular epitaxy, using an *x*-*z* recurring DNA module of 8H × 8H × 94B. In Stage-3, we added antisense ssDNAs to etch away a contact hole module of 4H × 8H × 47B in the DNA substrate module, which was driven by hybridization between DNA bricks in the substrate module and their sequence-complementary antisense ssDNAs. The dried DNA mask 8H-hole-a displayed an array of contact holes at an *x*-axis pitch of 21.6 ± 1.0 nm and a *z*-axis pitch of 32.2 ± 0.9 nm (Supplementary Fig. 8d, e). The cross-section dimensions of the holes were measured as 12.4 ± 1.3 nm ×17.9 ± 1.5 nm in the *x*-*z* plane (Supplementary Fig. 8b, c). Some contact holes didn't allow an AFM probe to reach the Si substrate beneath (AFM profile in Fig. 3c), probably because of the steric hindrance between the AFM probe and the hole sidewalls.

DNA masks scaling

Fig. 4 illustrates the scaling for both the *x*-axis pitches in the line/space DNA masks and the CDs in the contact hole DNA masks. The epitaxial assembly workflows are summarized in Supplementary Fig. 2. The measurements of each DNA masks are summarized in Supplementary Table 1 and 2.

For line/space patterns, DNA mask 12H-b, designed with 6H × 12H × 94B line module and 12H-periodic DNA substrate module, exhibited a pitch of 32.3 ± 0.6 nm and a line width of 14.9 ± 0.4 nm (Extended Data Fig. 1). Compared with 12H-a, 12H-b was 4H higher in its line module, resulting in an increased mask thickness of 24.4 ± 0.7 nm. DNA masks 10H-a (Supplementary Fig. 5) and 10H-b (Extended Data Fig. 2) used 10H-periodic DNA substrate module (10H × 4H × 94B) to produce 27.0 ± 0.8 nm pitch line/space patterns. Their thicknesses difference (19.5 ± 0.8 nm and 24.2 ± 0.5 nm) originated from the 4H difference between the line modules 6H × 8H × 94B and 6H × 12H × 94B. DNA masks 8H-a (Supplementary Fig. 6) and 8H-b (Extended Data Fig. 3) used an 8H-periodic DNA substrate module (8H × 4H × 94B) to grow 10.4 ± 0.5 nm-wide lines at a pitch of 21.5 ± 0.9 nm. We used the line modules of 4H × 6H × 94B and 4H × 8H × 94B to adjust their mask thicknesses to 15.8 ± 0.7 nm and 18.2 ± 0.7 nm, respectively. DNA mask 6H-a (Supplementary Fig. 7) and 6H-b (Extended Data Fig. 4) produced 11.0 ± 0.8 nm-wide line (4H × 4H × 94B) at a pitch of 16.2 ± 0.8. We adjusted the substrate module thickness (6H × 4H × 94B and 6H × 2H × 94B) to control their mask thicknesses to 11.3 ± 0.5 nm and 9.3 ± 0.4 nm nm, respectively.

The three contact hole masks, 8H-hole-b, 8H-hole-c and 8H-hole-d, were the derivatives of the mask 8H-hole-a (Supplementary Fig. 2e). The contact hole cross-sections of 8H-hole-b, 8H-hole-c and 8H-hole-d were designed as 3H × 32B, 3H × 24B and 2H × 24B in the *x*-*z* plane, respectively. The designed hole depths along the *y*-axis were 8H. Their corresponding hole CDs in the cross sections were 9.3 nm × 13.9 nm, 8.5 nm × 11.7 nm and 7.9 nm × 9.2 nm after drying, respectively (Supplementary Fig. 9-11). Their pitch sizes and mask thicknesses were consistent with the measurements of 8H-hole-a.

Pattern transfer to silicon

Fluorine-based RIE directly transfers the lithographic pattern from a 3D DNA masks to a Si substrate. The DNA 3D features were gradually eroded along the *y*-axis and protected the underlying silicon from radical/ion etching. The thickness contrast in DNA mask (defined as the maximal vertical helices of DNA mask divided by the vertical helices of substrate module) led to distinct etching depths in silicon, such that the resulting Si pattern inherited the geometry from the 3D DNA mask. As the scheme shown in Fig.

5a, when RIE etchants depleted the DNA substrate at the line space of mask 12H-b and further etched the underlying silicon, the DNA line features still remained to protect the silicon beneath. The etched Si pattern, named as Si-12H-b, showed parallel Si lines at a pitch of 32.4 nm (Fig. 5b, Extended Data Fig. 6), which were consistent with the mask geometry. The tilted SEM image indicated the Si lines had no cracks on top and sidewalls (Fig. 5c). The EDX mapping test hasn't detected Ni^{2+} contaminations from the etched Si patterns (Supplementary Fig. 21). For stricter anti-contamination control, we could sandwich an amorphous carbon or SiO_2 layer between DNA mask and Si substrate to prevent metal ions diffusion during RIE.

The RIE process was implemented using 5 sccm (standard cubic centimeter/minute) of CHF_3, 13 mbar of chamber pressure, 200 W of coil power, and 10 W of plate power. This RIE protocol produced a vertical etch rate of 12 nm/min in silicon, with a Si-to-DNA etch selectivity (ratio of etch rates) above 1. The optimizations of RIE parameters considered the following guidelines: (1) Feed gas species. Compared with SF_6 and CF_4, we found CHF_3 had the best etching controllability on DNA masks due to its low output of fluorine radicals. Additionally, polymeric fuorocarbon byproducts from the ionized CHF_3 could be beneficial to DNA masks stablization.[44] (2) Gas flow and pressure. Both parameters were proportional to the radical concentrations and inversely proportional to ion free paths. Optimizing these two parameters could adjust the radical/ion ratio for balancing the radical-directed chemical-selective etching and ion-directed anisotropic physical etching. (3) Coil and plate power. The operating power of inductively coupled plasma coils and plate electrodes determined the etchants yields and the ion bombarding energies, respectively. These two parameters were responsible for the fine adjustment to chemical/physical etching activities to maximize Si-to-DNA etch selectivity and etch smoothness.

Silicon patterns scaling

The etched Si pattern products from single-run RIE demonstrated the rational scaling of pitches and CDs (see detailed measurements in Supplementary Table 3). Fig. 5d illustrated SEM and AFM images of Si line/space patterns (Si-12H-b, Si-10H-b, Si-8H-b and Si-6H-b, named after the corresponding DNA masks) at the prescribed pitches of 32.3 ± 0.4 nm, 27.0 ± 0.4 nm, 21.6 ± 0.6 nm and 16.2 ± 0.6 nm, respectively (see also Extended Data Fig. 6-9). Radical-directed sidewall etching made the etched Si lines slightly narrower than the DNA mask lines. For example, the CD line widths of DNA mask 12H-b and the corresponding RIE product Si-12H-b were 14.9 ± 0.4 nm and 12.2 ± 0.4 nm, respectively. Based on the Si line height in Si-12H-b (35.5 ± 0.7 nm) and the DNA line height in 24.4 ± 0.7 nm, the aspect ratio (height/width) for the etched Si line was 3, and the Si-to-DNA etch selectivity was 1.4.

The Si contact hole patterns, including Si-hole-a, Si-hole-b, Si-hole-c and Si-hole-d, displayed an *x*-axis pitch at 21.6 ± 0.7 nm and a *z*-axis pitch at 32.2 ± 0.9 nm, both values consistent with the DNA mask geometries. The CD cross-sections of Si contact holes were sequentially scaled to 12.8 nm × 19.2 nm, 10.7 nm × 15.4 nm, 8.3 nm × 12.1 nm and 7.2 nm× 8.6 nm along the *x*- and *z*-axes (Fig. 5e-g, see also Supplementary Fig. 16-19).

We also adjusted CDs of Si lines by controlling radical-dominant sidewall etching for DNA masks 8H-b. We mixed H_2 into CHF_3 feed gas to decrease radical yield, while ion-directed vertical etching was merely affected (Fig. 5h). The decrease of radical concentration then led to sidewall deposition of fuorocarbon polymers and increased the effective CD of DNA lines (Fig. 5i). Therefore, the CDs (widths) of Si lines were proportionally increased from 11.4 ± 0.6 to 13.6 ± 0.6 nm by raising H_2 flow rate from 0 to 1 sccm (Fig. 5j, k, see also Supplementary Fig. 14, 15).

High-resolution 3D lithography

The conventional single-mask 3D lithography methods, such as grayscale e-beam or grayscale UV lithography, are limited to submicron-level vertical (*y*-axis) resolutions in 3D patterning of polymer resists.[45] Therefore, for manufacturing multilayered 3D Si nanostructures, people have to overlay several layers of planar patterns via repeating lithography-etching processes. Here we demonstrated a direct 3D

nanolithography with single-run RIE, which transfers the precise thickness contrast of an individual DNA mask into multilayered 3D Si nanostructures (Extended Data Fig.10). The model DNA mask, 12H-grid, had three layers of thicknesses, and the thickness difference between higher DNA line and lower DNA line was 4.7 nm. Using the model DNA masks, Fig. 6a, b illustrates the time-series RIE process for 3D Si patterns. The final Si pattern displayed three-layered cross-line grid geometry, with feature heights of 6.1 ± 0.9 nm, 17.5 ± 0.8 nm and 19.6 ± 0.6 nm for the space, lower lines and higher lines, respectively (Fig. 6c, d). The 2-nm height difference between the higher and lower Si lines demonstrated the vertical (*y*-axis) resolution of our 3D nanolithography for silicon processing. Tilted SEM imaging showed the lower Si lines had stochastic cracks with a rate of 8.1 per μm^2 (Fig. 6f), which were probably induced by DNA mask failures under internal stress and RIE heating effects. Increasing DNA mask elasticity with poly-T spacer ssDNAs and using cryogenic RIE instead could improve the quality of etched Si patterns.

Outlook

Complex component interactions within 3D DNA self-assembly produce diverse possible assembly pathways. Our DNA modular epitaxy approach simplifies the complicated 3D DNA pattern into several basic 3D modules, and then adjusts temperature and ssDNA concentrations to regulate the seeding-growth pathways for sequentially connecting individual DNA modules. Therefore, DNA modular epitaxy could be experimentally implemented via a designer seeding-growth pathway, and enables further complexity scaling up for more complicated ssDNA components and 3D geometries.

Using DNA modular epitaxy-assembled DNA patterns as lithography masks, our DNA nanolithography enables: (1) High-precision pitch scaling. DNA modular epitaxy produces 3D DNA masks with pitches as small as 16.2 nm, exceeding the values from conventional lithography. Through one-step RIE, the ultra-scaled DNA mask features can be directly transferred to Si patterns, without using complicated multiple patterning or expensive EUV optical system. (2) High-resolution 3D lithography. Besides the scaling of pitches and CDs, DNA modular epitaxy could precisely control the thicknesses of multilayered 3D DNA mask, resulting in multilayered Si nanostructures at a vertical resolution of 2 nm, from a single-run RIE.

We find that increasing the thickness contrast of line/space DNA masks results in higher aspect ratios and smaller LWR of etched Si lines. For instance, the etched Si line products of mask 12H-a (thickness contrast 8H : 4H = 2) and mask 12H-b (thickness contrast of 3) exhibit height/width aspect ratios of 1.9 and 2.9, respectively. And the etched Si line products of mask 6H-a (thickness contrast of 1) and mask 6H-b (thickness contrast of 2) showed LWR of 3.3 nm and 2.1 nm, respectively (see Supplementary Table 3). Although increasing vertical (*y*-axis) thickness of 3D DNA modules may promote the thickness contrast of 3D DNA masks, such designs may decrease the stiffness of 3D DNA modules and fail to resist the capillary-force-induced collapse. Potentially, capillary force during drying 3D DNA masks could be eliminated when introducing supercritical CO_2 to rinse out ethanol.[46] This rinsing method could stabilize high contrast 3D DNA masks on Si substrate to enable high quality RIE products.

The next step for DNA modular epitaxy-directed lithography would be wafer-scale registration with DNA mask arrays. Wafer-scale registration may be achieved through aligning pre-assembled DNA masks onto a pre-patterned substrate[47] or in situ growing DNA masks with precisely designed orientations[48]. In particular, surface-aligned mono-dispersed sub-100 nm DNA structures may potentially be used as seeds in DNA modular epitaxy on surface. Therefore, wafer-scale lithographic masks with complex non-periodic features, prescribed positions and uniform sizes will be constructed.

The DNA modular epitaxy-directed lithography bridges biomolecule self-assembly and RIE manufacturing. Not limited to silicon, this lithography method could be applied into to other RIE substrates. Additionally, 3D DNA masks could be used in chemical vapor deposition[35], physical vapor deposition[49] and atomic layer deposition[50]. Therefore, towards future ultra-scaled 3D devices, DNA modular epitaxy-directed lithography may provide a complement to existing nanomanufacturing approaches.[2,4]

Data availability

The data represented in Figs. 2–6 and supplementary information are provided with the paper as source data. All other data that support results in this article are available from the corresponding author on reasonable request.

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Author contributions

J.S. conceived, designed, conducted the lithography study and wrote the manuscript. W.S. conceived, designed, conducted the DNA modular epitaxy study and wrote the manuscript. D.L. performed cryo-EM analysis. D.L. and T.S. analyzed the data and co-wrote the manuscript. P.Y. conceived and supervised the study and wrote the paper. All authors reviewed, edited, and approved the manuscript.

Competing interests

A patent based on this work was issued to J.S., W.S. and P.Y.

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Methods

3D DNA mask preparation. The DNA mask 12H-grid was synthesized by the following procedure. At epitaxial Stage-1, ssDNAs component of the substrate (ca. 310 nM each) were mixed into 16 μL TE/Mg^{2+} buffer (5 mM Tris, 1 mM EDTA, and 40 mM $MgCl_2$, pH 7.9). The mixture was sequentially incubated at 44 °C for 12 h and 39 °C for 24 h. At epitaxial Stage-2, ssDNA components of the substrate (ca. 190 nM each) and the higher line component (ca. 280 nM each) were mixed into the 54 μL TE/Mg^{2+} buffer and added into the product solution of Stage-1. Then their corresponding effective ssDNAs concentrations were ca. 150 nM and 220 nM, respectively. The mixture was sequentially incubated at 38 °C for 48 h and 33 °C for 8 h. At epitaxial Stage-3, ssDNA components of the lower line was mixed in 13 μL TE/Mg^{2+} buffer, and added into the product solution of Stage-2 (ca. 180 nM each). The mixture was incubated sequentially under 33 °C for 48 h and 31 °C for 8 h. The epitaxy products were stored in the reaction buffer and kept at 4 °C without further purification.

Pattern transfer to silicon. A100-fold diluted 3D DNA masks (2 μL, 10 mM $MgCl_2$) was added onto a 5 mm Si substrate, and incubated with $NiCl_2$ solution (2 μL, 100 mM) for 1h. Then the DNA mask-

deposited Si substrate was rinsed sequentially in 70 %, 90 % and 99.5 % ethanol followed by drying in air. Without further treatments, the DNA mask-deposited Si substrate was sent to an inductively coupled plasma etching system (STS ICP-RIE) for pattern transfer. The etched Si substrate was sonicated in acetone and then washed in a hot piranha solution (a mixture of 98 % sulfuric acid and 25 % hydrogen peroxide in a 3 : 1 volume ratio) to remove the residual masks and fluorocarbon polymers. The cleaned Si substrate was rinsed by DI water and dried in air for AFM and SEM characterizations.

Defect rate analysis. The defects of dried 3D DNA masks and Si pattern products were counted by SEM. For each sample, we randomly selected 20 pieces of discrete DNA or Si patterns within a 100 μm scale region, and calculated the ratio of defect amounts versus the sum of pattern area. The overlapped and upside-down laid DNA masks, and their corresponding RIE products were not involved in defects counting (examples shown in supplementary Fig. 22).

Figure legends.

Fig. 1: Strategy overview. a, In silico design of target pattern into 3D DNA mask from 32-nt DNA bricks (illustrated by cylinder/strand and LEGO® models). **b**, Multi-staged DNA modular epitaxy assembly for 3D DNA mask. The gray arrows indicated the extending directions of DNA mask. **c**, Pattern transfer to silicon via a single-run RIE.

Fig. 2: DNA modular epitaxy. a, Design for the DNA mask 12H-grid, illustrated by LEGO® model and cylinder model. **b**, Assembly flowchart for 12H-grid, together with the measured time course of ssDNA concentrations. **c**, SEM images of the DNA modular epitaxy products in each reaction stage. **d**, AFM characterization of the fully dried DNA mask 12H-grid. **e**, Cryo-EM image of 12H-grid at a resolution of single dsDNA helix. The fast Fourier transformation (FFT) patterns of cryo-EM images indicated the effective diameter of the hydrous dsDNA helix. All scale bars are 100 nm.

Fig. 3: **Pattern diversity**. Schemes of the epitaxial assembly and cryo-EM/SEM/AFM characterizations for line/space mask 12H-a (**a**), pillar array mask 12H-pillar (**b**), and contact hole mask 8H-hole-a (**c**). SEM line-scan profiles were extracted from the red dash lines. AFM profiles were extracted from the blue dash lines. All scale bars are 100 nm.

Fig. 4: **Scaling pitch and CD of DNA masks**. Schemes of epitaxial assembly and SEM/AFM characterization results for DNA masks with prescribed pitches and CDs, listed in an order of downscaled *x*-directional pitches. All scale bars are 100 nm.

Fig. 5: Pattern transfer to silicon. a, Schematic mechanism of single-run RIE with DNA mask 12H-b. **b**, SEM images of the etched Si patterns, Si-12H-b. **c**, Tilted SEM images of Si-12H-b pattern. **d**, SEM and AFM images of line/space Si pattern Si-12H-b, Si-10H-b, Si-8H-b and Si-6H-b, respectively. **e**, Schematic of DNA contact hole mask and the etched Si pattern, D_x and D_z are the hole diameters along the *x*- and *z*-axes. **f** & **g**, Statistical CD analysis and SEM images of Si contact hole pattern Si-8H-hole-a, Si-8H-hole-b, Si-8H-hole-c and Si-8H-hole-d, respectively. **h** & **i**, Schematic mechanism of hydrogen mediated RIE with 3D DNA mask. **j**, SEM images of serial Si line/space patterns etched from DNA mask 8H-b. **k**, SEM measurements of line widths and pitches. Scale bars are 1 μm, 200 nm and 200 nm in **b**. All other scale bars are 100 nm.

Fig. 6: **3D lithography with single DNA mask**. Schematic (**a**) and SEM characterization (**b**) of the time-series RIE products from the DNA mask 12H-grid. AFM image (**c**), AFM line scan profiles (**d**), 3D AFM profile (**e**), and tilted SEM images (**f**) of the etched Si-12H-grid pattern. All scale bars are 100 nm.