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Beam pen lithography

Fengwei Huo[1,2†‡], Gengfeng Zheng[1,2†‡], Xing Liao[2,3], Louise R. Giam[2,3], Jinan Chai[1,2], Xiaodong Chen[1,2†], Wooyoung Shim[2,3] and Chad A. Mirkin[1,2,3*]

Lithography techniques are currently being developed to fabricate nanoscale components for integrated circuits, medical diagnostics and optoelectronics[1–7]. In conventional far-field optical lithography, lateral feature resolution is diffraction-limited[8]. Approaches that overcome the diffraction limit have been developed[9–14], but these are difficult to implement or they preclude arbitrary pattern formation. Techniques based on near-field scanning optical microscopy can overcome the diffraction limit, but they suffer from inherently low throughput and restricted scan areas[15–17]. Highly parallel two-dimensional, silicon-based, near-field scanning optical microscopy aperture arrays have been fabricated[18], but aligning a non-deformable aperture array to a large-area substrate with near-field proximity remains challenging. However, recent advances in lithographies based on scanning probe microscopy have made use of transparent two-dimensional arrays of pyramid-shaped elastomeric tips (or 'pens') for large-area, high-throughput patterning of ink molecules[19–23]. Here, we report a massively parallel scanning probe microscopy-based approach that can generate arbitrary patterns by passing 400-nm light through nanoscopic apertures at each tip in the array. The technique, termed beam pen lithography, can toggle between near- and far-field distances, allowing both sub-diffraction limit (100 nm) and larger features to be generated.

Beam pen lithography (BPL) combines the concepts and advantages of near-field scanning optical microscopy (NSOM)-based lithography with polymer-based lithography. Although transparent polydimethylsiloxane (PDMS) stamps have been used to control light propagation in the context of surface patterning[24,25], this approach does not allow for the fabrication of sub-diffraction limit features in arbitrary geometries. Polymer pen lithography (PPL), however, is a direct-write method that uses transparent two-dimensional elastomeric tip arrays to deliver various ink molecules to a surface in a constructive manner with high throughput and nanometre registration over square-centimetre areas[19–21]. In principle, one could take advantage of the transparent polymer pens in a PPL array if they were coated with an opaque metal layer except at the point of each tip, to selectively pass light to a photoresist-coated surface. This approach would allow the creation of arbitrary patterns on a surface through the combined movement of the stage and selective illumination of desired tips. Moreover, because the pens are elastomeric and reversibly deformable, near-field distances could be guaranteed by bringing the BPL array into contact with the substrate without damage to the substrate or array. The creation of apertures for all gold-coated pens in the array could be easily achieved by placing the array in contact with an adhesive poly(methyl methacrylate) (PMMA) surface (Fig. 1a), but can also be fabricated by focused ion beam (FIB) lithography for diameters as small as 50 nm (Fig. 1b).

In a typical experiment, a PDMS array of pyramid-shaped tips was fabricated according to established literature methods[19]. Each pyramidal pen had a square base with edges several tens of micrometres in length, tapering to a tip with a diameter of ~100 nm. The entire array, including tips, was treated with oxygen plasma, and a layer of gold (~80-nm gold, with a 5-nm titanium adhesion layer) deposited by thermal evaporation. The tip array was then brought into contact with a glass slide coated with PMMA, which completely removed the gold layer from the apex of each tip to create an aperture exposing the transparent PDMS (shown in the dark-field optical microscopy image of Fig. 1c). Moreover, application of different external forces on the back side of the BPL tip array coupled with PDMS tip compression provided control over the contact area between the tips and PMMA surface, allowing the average aperture size to be selected. The aperture size did not change significantly from tip to tip (less than 10% variation), and could range between 500 nm and 5 μm in diameter, simply by controlling the contact force (0.002–0.2 N for a 1-cm^2 pen array).

In a proof-of-concept experiment, a BPL tip array (tip-to-tip spacing, 80 μm) was brought into contact with a silicon substrate that was pre-coated with a layer of positive photoresist (Shipley1805, MicroChem), followed by UV light exposure above the beam pen array. The opaque gold layer on the sidewalls of each tip allowed light to pass strictly through the apertures of the PDMS pyramidal tips, forming a single dot feature per tip for each light exposure (Fig. 2a). The diameter of each dot could be modulated by means of a number of lithographic parameters, including resist type and resist layer thickness. Another significant factor contributing to BPL resolution is the tip aperture size, which controls the area of resist exposed to light. With a ~400-nm halogen light source, 40-nm-thick photoresist layer, and FIB-fabricated BPL tips (aperture diameter, 50 ± 5 nm), we generated chromium dot features with diameters of 111 ± 11 nm, which are below the diffraction limit of the light source (Fig. 2b). Such small feature sizes can be attributed to near-field effects at the point of contact between the tip and surface, where each tip acts like a NSOM tip.

When using large-scale two-dimensional arrays of BPL tips (15,000 pens per cm^2) with an average aperture size of 700 nm, this approach can be used for high-throughput lithography, yielding thousands of duplicated patterns in a single experiment. To image these large-area results, a positive photoresist-coated substrate (~200 nm thick) was developed (30 s in MF319, Rohm & Haas Electronic Materials). Subsequent metal thermal evaporation (titanium, 5 nm; gold, 10 nm) and photoresist lift-off by acetone allowed us to visualize the dot features. The position of each dot reflects the tip position in the array, and there was no evidence of missing features. Note that large-area (~1 cm^2) dot feature arrays can be made by simply moving the substrate under the beam pen array with a piezo stage.

[1]Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA, [2]International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA, [3]Department of Materials Science and Engineering, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208-3113, USA; †Present address: School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798 (F.H. and X.C.); Laboratory of Advanced Materials & Department of Chemistry, Fudan University, 2205 Song-Hu Road, Shanghai, China, 200438 (G.Z.); ‡These authors contributed equally to this work. *e-mail: chadnano@northwestern.edu

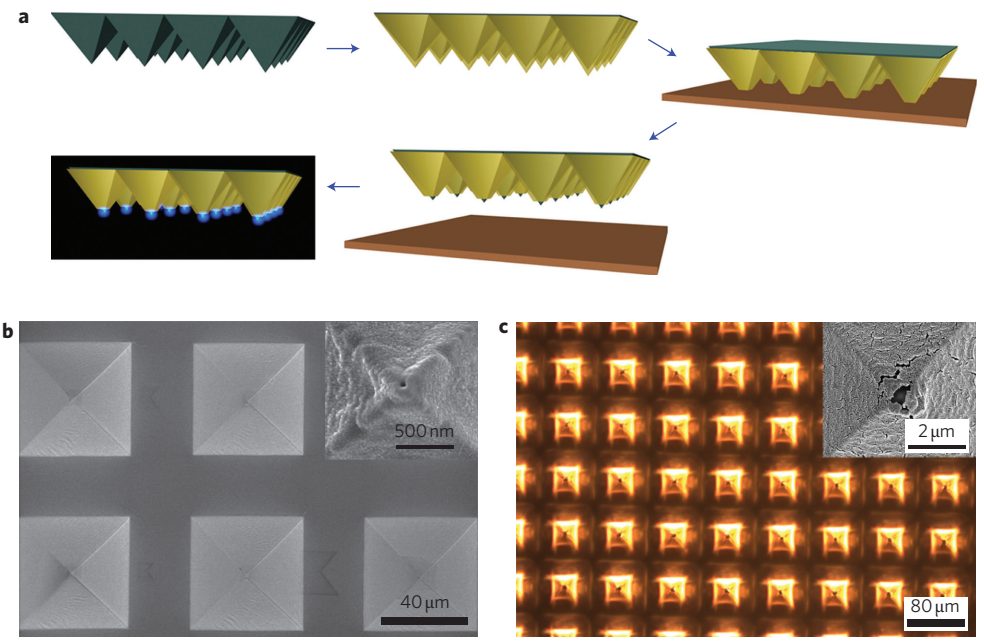

Figure 1 | Fabrication of a beam pen array. a, Schematic of the steps involved in fabricating a BPL tip array. **b**, SEM images of a BPL pen array in which the aperture (diameter, 50 ± 5 nm, inset) is fabricated by FIB. **c**, BPL pen array, where the aperture size is controlled by the amount of force made with an adhesive PMMA surface, as shown in **a**. Pen arrays as large as several square centimetres can be fabricated by this approach, where the size of the aperture can be controlled between 500 nm and 5 μm, simply by controlling the extent to which the beam pen array contacts the PMMA.

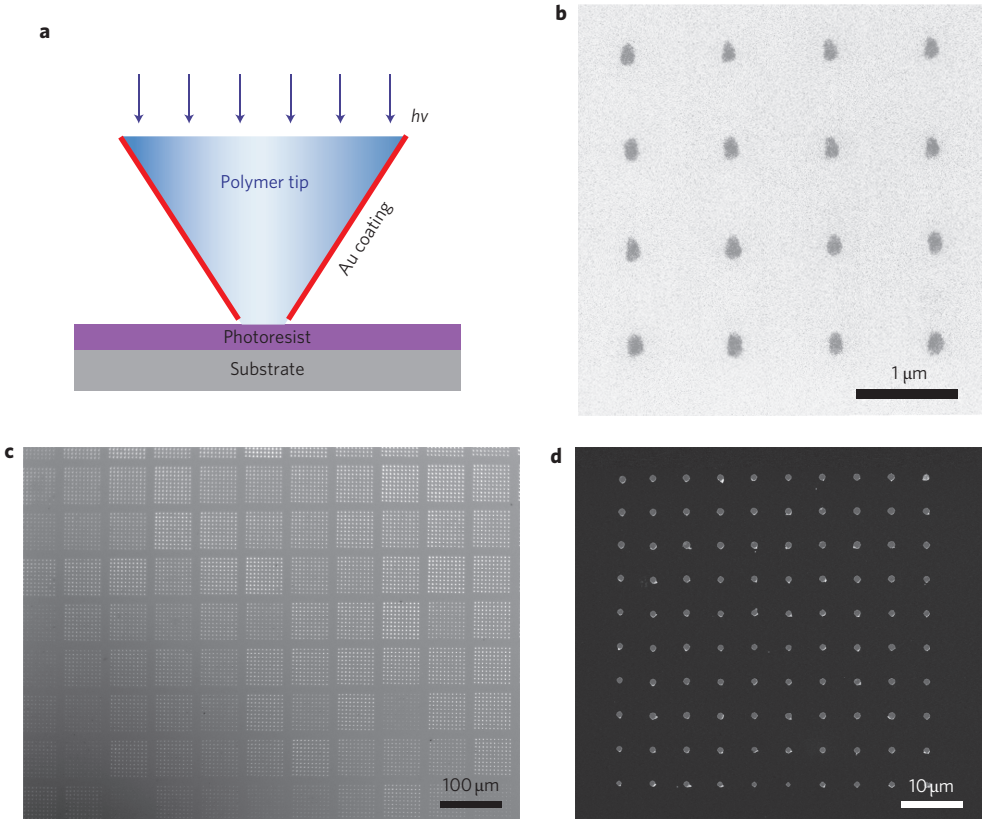

Figure 2 | Large-area patterning and sub-diffraction limit features. a, Schematic of BPL, where transparent polymer tips are coated with an opaque metal layer (gold) except at the end of the tips. In this way, light only exposes a light-sensitive photoresist-coated surface at the tip. **b**, SEM image of a chromium dot array created by BPL arrays (after metal evaporation and photoresist lift-off), in which the apertures were fabricated by FIB. Each feature diameter is 111 ± 11 nm. **c**, Optical microscopy image of gold dot arrays made by BPL (after metal evaporation and photoresist lift-off), in which the apertures were made by controlling the force between the beam pen array and an adhesive surface. **d**, Magnified SEM image of **c,** showing a 10 × 10 gold dot array made by one tip in the beam pen array after metal evaporation and photoresist lift-off.

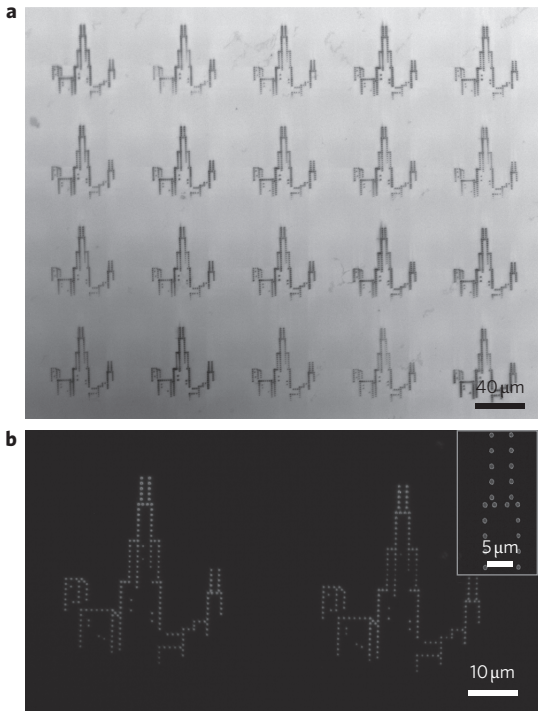

Figure 3 | Arbitrary pattern fabrication capability. a, Optical microscopy image of developed photoresist patterns showing a representative region of ~15,000 duplicates of a Chicago skyline pattern. **b**, Magnified optical microscopy image of the gold Chicago skyline pattern after metal evaporation and photoresist lift-off. The inset shows a magnified scanning electron microscopy (SEM) image of the gold features, which have diameters of 450 ± 70 nm.

Illumination of the backside of the beam pen array allows one to generate 15,000 patterns simultaneously in half an hour (to achieve a total of 1.5 million features). Specifically, we have generated 10 × 10 gold dot arrays using halogen lamp illumination (maximum power light intensity, 90%; exposure, 20 s; diameter, 750 ± 80 nm) with a feature spacing of 6 μm (Fig. 2c,d). It is important to note that, during the entire experiment, the light is turned on. To ensure that exposure of the photoresist areas that are not intended to be patterned is kept to a minimum, lateral and vertical movements of the beam pen array across the substrate were therefore rapid (60 μm s^{-1}).

Compared to conventional photolithography or contact printing, which only allow one to create and duplicate pre-formed patterns (that is, photomasks), BPL provides the flexibility to create arbitrary patterns through piezo-controlled movement of the beam pen array over a substrate. This advantage bypasses the need for, and costs associated with, photomask fabrication in conventional photolithography. Note that the maskless nature of BPL allows one to arbitrarily make many types of structures without the hurdle of designing a new master. For instance, BPL was used to create 15,000 replicas of the Chicago skyline, each pattern consisting of 182 dots. Each feature on the photoresist was created using a beam pen array with 500-nm diameter apertures and with light exposure of 20 s (Fig. 3a). As previously described, metal evaporation and photoresist lift-off yield gold dot features, which have diameters of 450 ± 70 nm and are spaced 600 nm apart (Fig. 3b).

Tip addressability has been one of the most significant challenges for scanning probe lithography (SPL) methods. With passive arrays, one simply achieves duplication—each tip does exactly what the other ones do. Many different methods of actuation, including thermal[26,27], mechanical[28] and electrical approaches[29], have been evaluated with limited success, especially where lithography is the primary goal. Although the beam pen tips are nanoscopic, the pyramidal bases are microscopic and can be addressed easily with light. For example, one can use a mask to illuminate certain bases (and therefore tips) during the BPL process. As a proof-of-concept, one can use a chrome photomask to cover select areas of the beam pen array. Under halogen lamp illumination, each tip in the array was used to fabricate the pattern 'NU', which was composed of 29 dots (maximum power, 90%; exposure for each dot, 20 s, Fig. 4a). When the light source was selectively illuminated on certain BPL tips (for example, a 'U' pattern) with a photomask, only the illuminated tips exposed the photoresist. Although all the tips made simultaneous contact with the substrate, no patterns were observed from masked pens (Fig. 4b). This approach provides two orthogonal levels of control: at the macroscale (with respect to the entire beam pen array), selective illumination allows for tip addressability; at the nanoscale (with respect to each pen), however, tip movement allows for arbitrary pattern generation. Importantly, when BPL is coupled with dynamic spatial light modulators, each tip may be individually addressed rapidly to fabricate various macroscale patterns[12,13].

In summary, BPL is a new lithography method, which uses polymer tip arrays coated with an opaque metal layer on the sidewalls of each tip. BPL can be readily integrated with conventional photolithography methods and allows for the fabrication of

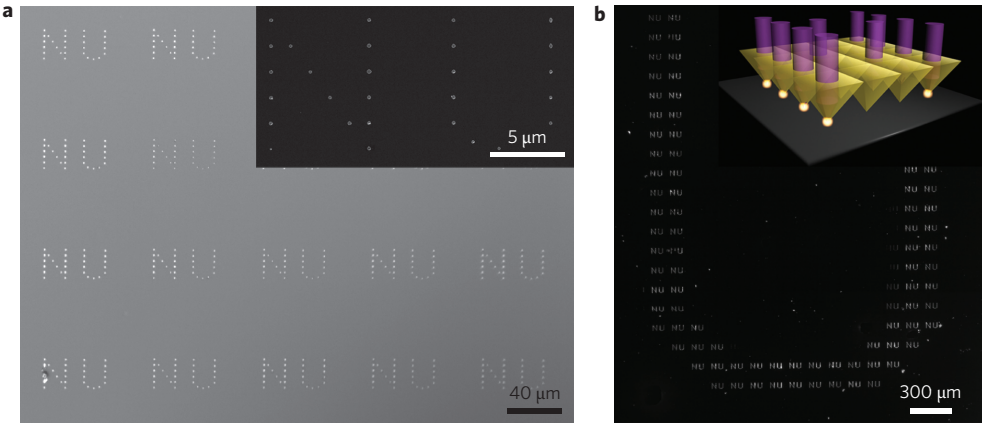

Figure 4 | Orthogonal levels of patterning control provided by macroscale addressability of pens. a, Optical microscopy image of 'NU' patterns generated by each tip. The inset shows a magnified SEM image of one pattern. Feature diameter, 430 ± 80 nm. **b**, SEM image showing the macroscale selective illumination of the beam pen array with a mask in the shape of a 'U' pattern as well as the nanoscale arbitrary pattern generation from each tip (small 'NU' patterns). The inset is a schematic of pen addressability.

feature sizes below the diffraction limit of light because of near-field alignment with the surface. Because the elastomeric pens allow one to control the distance between the apertures and an underlying surface, it is possible to switch between near-field and far-field modes for generating sub-diffraction and micrometre-sized features. Importantly, the combination of nanoscale tip movement for arbitrary pattern generation with macroscale selective illumination of desired pens provides a simple, flexible and low-cost tool, which is a step towards the realization of a 'desktop fab' that produces complex patterns relevant to rapid prototyping and studies of electronic, optical and metamaterial structures and devices.

Methods

Fabrication of polymer pen array masters. Shipley1805 (MicroChem) photoresist was spin-coated onto gold thin film substrates (10-nm chromium adhesion layer with a 100-nm layer of gold thermally evaporated on a pre-cleaned and oxidized silicon ⟨100⟩ wafer). Square well arrays were fabricated by photolithography using a chrome mask. The photoresist patterns were developed in MF319 (MicroChem), and then exposed to oxygen plasma for 30 s (200 mtorr) to remove residual organic material. The substrates were then placed in gold (10 min, Type TFA, Transene) and chromium (3 s, Type 1020, Transene) etching solutions, respectively. Copious rinsing with deionized water was required after each etching step to clean the surface. The photoresist was then washed away with acetone to expose gold patterns on a substrate. This substrate was placed in a KOH etching solution (30% KOH in H_2O:isopropanol (4:1 v/v)) at 75 °C for ~25 min with vigorous stirring. The uncovered areas of the silicon wafer were etched anisotropically, resulting in the formation of recessed pyramids. The remaining gold and chromium layers were removed by wet chemical etching. Finally, the pyramid master was modified with 1H,1H,2H,2H-perfluorodecyltrichlorosilane (Gelest) by gas-phase silanization.

Fabrication of polymer pen arrays. Hard PDMS (h-PDMS) was used for fabricating the polymer pen arrays. The h-PDMS was composed of 3.4 g of vinyl-compound-rich prepolymer (VDT-731, Gelest) and 1.0 g of hydrosilane-rich crosslinker (HMS-301). Preparation of polymers typically required the addition of 20 ppm w/w platinum catalyst to the vinyl fraction (platinumdivinyltetramethyldisiloxane complex in xylene, SIP 6831.1, Gelest) and 0.1% w/w modulator to the mixture (2,4,6,8-tetramethyltetravinylcyclotetrasiloxane, Fluka). The mixture was stirred, degassed and poured on top of the polymer pen array master. A pre-cleaned glass slide (VWR) was then placed on top of the elastomer array and the whole assembly was cured at 70 °C overnight. The polymer pen array was carefully separated from the pyramid master and then used for polymer pen lithography experiments.

Beam pen lithography. A Si/SiO_2 surface was first spin-coated with a layer of hexamethyldisilazane (HMDS) at 4,000 r.p.m. for 40 s, followed by spin-coating a layer of positive photoresist (Shipley1805, MicroChem) at 4,000 r.p.m. for 40 s. The Shipley 1805 was pre-diluted with propylene glycol monomethyl ether acetate (MicroChem): 30% for a 200-nm-thick photoresist layer and 10% for a 40-nm-thick photoresist layer. The photoresist-coated substrate was then baked on a hot plate at 110 °C for 5 min before being used. When combined with an atomic force microscopy (AFM) platform (Park XEP, Park Systems Co.), a halogen light source (Fiber-lite Illuminators MI150, Dolan-Jenner) was used to perform BPL. A typical illumination time for a ~400-nm halogen lamp at 90% of maximum power is 20 s, followed by photoresist development in MF319 (MicroChem). For macroscale selective beam pen illumination, quartz masks with different shapes (such as the 'U' pattern made by conventional photolithography) were placed between the light source and BPL tip arrays.

Alignment of BPL arrays. There are two methods by which the arrays can be aligned, applicable both to the formation of apertures and BPL light exposure to an underlying substrate. One method involves attaching the pen array to an AFM instrument and using motors to align the $x-y$ stage. Some of the pens on the perimeter of the array are not coated with gold. Because they are transparent, one can easily align the array by observing tip deformation of those pens with an optical microscope. We have also reported another more precise method, which achieves alignment by maximizing the force generated between the pen array and substrate; this approach does not rely on visual alignment[22].

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Author contributions

F.H. and G.Z. contributed equally to this work in designing and performing the experiments, analysing the results and drafting the manuscript. X.L., L.R.G., J.C., X.C. and W.S. also performed experiments and helped with revisions. C.A.M. helped design the experiments, analyse the results, and draft the manuscript.

Additional information

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