Nanofabrication

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Massively Parallel Dip–Pen Nanolithography with 55 000-Pen Two-Dimensional Arrays**

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The last decade has witnessed the development of a dichotomy in scanning-probe lithographic (SPL) approaches and systems.[1–4] These techniques are either: 1) constructive, such as dip–pen nanolithography (DPN),[1,2] and involve the delivery of molecules or other materials that can chemically or physically anchor to the underlying substrate, or 2) destructive (e.g. anodic oxidation[5,6] and nanografting[7]) and involve the delivery of energy (in the form of heat, force, or current) to a surface that results in the physical change, chemical transformation, or displacement of the underlying material.[3,4] The design demands for parallelization of the two approaches are daunting but extremely different because of the fundamental difference between delivering energy and chemical materials. In fact, the only example of massively parallel SPL is the "millipede", which has been limited to destructive patterning involving polymer thermal indentation and annealing.[8–10] Since throughput is the biggest limitation of the constructive DPN technology, large area parallelization capabilities must be developed to realize its full potential.[3,4,11,12] However, parallelization must be accomplished with the constraints and capabilities of the DPN technique in mind. Herein, we describe a solution to DPN parallelization through the development, fabrication, and use of a novel 55 000-pen two-dimensional (2D) array to pattern gold

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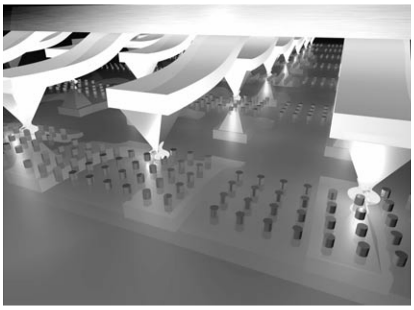
substrates with sub-100-nm resolution over square centimeter areas (Scheme 1).



Scheme 1. Massively parallel DPN with a passive, wire-free, 2D cantilever array.

Using photolithographic techniques,[13] we have fabricated a 55000-pen 2D array (yield > 98%; Figure 1A). With a pen spacing of 90 and 20 μm in the x and y directions, respectively, this array occupies 1 cm^2 and has the highest density and largest total number of cantilevers reported to date.[2] The 55000-pen array was developed so that it would be amenable to a lithographic approach that does not require independent feedback from each tip.

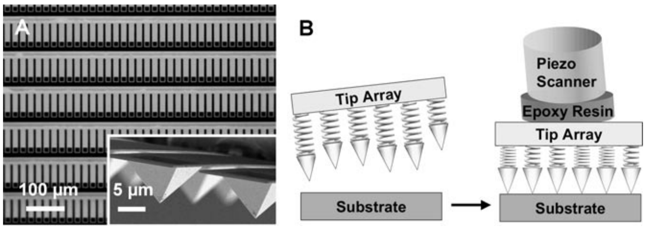


Figure 1. A) Optical micrograph of part of the 2D array of cantilevers used for patterning. Inset: SEM image of the cantilever arrays at a different viewing angle. B) Schematic of the gravity-driven alignment method used for massively parallel DPN with a 2D cantilever array. Each pen was brought into contact with the substrate under the weight of the whole pen array. Subsequently, the exact position of the pen array was locked to the AFM scanner head by an epoxy resin.

Large-area DPN is possible with this 2D array because of several features associated with the array architecture and a novel but easily adoptable gravity-driven alignment procedure (Figure 1B). First, the cantilevers were fabricated such that the apex of each pyramidal tip is (7.6 ± 0.2) μm taller than the cantilever base, and each tip has a square base with an edge length comparable to the cantilever width (Figure 1A). This pen structure gives the tip adequate spatial clearance for approaching the substrate. Second, the cantilevers are bent at an angle of approximately 20° (or a tip deflection of approximately 20 μm) from the supporting base by coating them with 25 nm of Au (and a 5-nm Ti adhesion layer) and then annealing at 300 °C for 2 h.[13] This curvature is a result of the different thermal expansion of gold and silicon nitride, and intrinsic stress arising from the annealing-induced restructuring of the Au/Ti/Si_xN_y multilayer.[14,15] The bent cantilever architecture provides greater tolerance to substrate morphology and inherent tip misalignment within the array (up to ± 10 μm). Third, gravity (ca. 20 nN/tip), instead of a complex set of feedback systems, is used to bring all of the tips in contact with a sacrificial substrate prior to use. Finally, the tip array is locked into position with respect to the piezo scanner head by taking advantage of the malleability of a rapidly curing epoxy resin (Figure 1B). This remarkably simple alignment procedure allows all of the tips within the array to be engaged and disengaged in a deliberate and controlled fashion without a feedback system or independent cantilever addressability. Once engaged, the pen array can be used to directly write virtually any pattern of molecules on the underlying substrate and simultaneously generate approximately 55000 duplicates at the resolution of single-pen DPN.

Structures made of several molecules (e.g. 1-mercaptohexadecanoic acid, 1-octadecanethiol (ODT), phospholipids[16]) in many different physical forms on vastly different substrates (gold and glass) have been fabricated using this array and alignment procedure.[13] As an illustration of the control afforded by the technique, we have uniformly coated the pen arrays with ODT and subsequently used them to pattern a polycrystalline gold-coated (25–50-nm thick with a 5-nm Ti adhesion layer) silicon substrate with one-molecule high features. The resulting ODT molecular patterns were converted, by wet chemical etching, to raised gold features with in-plane dimensions defined by DPN.[13,17–19] By converting molecular patterns into gold nanostructures, we could use an optical microscope to rapidly characterize the patterns over the entire 1-cm^2 area. Higher resolution scanning electron microscopy and AFM were used to analyze the fine structure of representative duplicates. Alternatively, the ODT patterns can be used as affinity templates to assemble proteins, such as fibronectin, to form arrays of such materials with feature size control on the sub-100-nm to many micrometer length scale (see Supporting Information).

In an initial experiment, the 55000-pen array was used to generate approximately 88 million dot features (Figure 2). Each pen generated 1600 dots in a 40 × 40 array, where the dot-to-dot distance was 400 nm. The dots had a diameter of (100 ± 20) nm, a height of 30 nm, and were spaced by 20 μm in the x direction and 90 μm in the y direction corresponding to the distances determined by the array architecture. Although smaller dots could be generated by reducing the hold time, the diameter of these features approaches the ultimate resolution

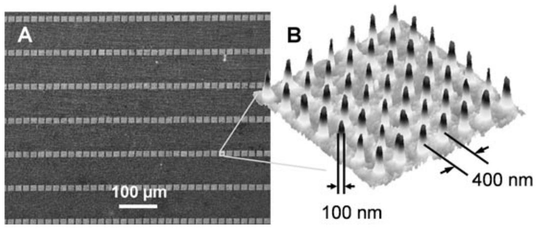


Figure 2. A) Large-area SEM image of part of an 88000000-gold-dot array (40 × 40 within each block) on an oxidized silicon substrate. B) Representative AFM topographical image of part of one of the blocks, where the dot-to-dot distance is 400 nm, and the dot diameter is (100 ± 20) nm.

under these conditions, which is limited by the radius of curvature of the tip apex (ca. 60 nm), as well as the grain size of evaporated Au (30–50 nm).

A remarkable attribute of this 2D DPN patterning approach is the rapid prototyping capability that can be used to, for example, generate a combinatorial array of molecular and solid-state features that systematically vary in size, spacing, and shape.[13] One can even generate very sophisticated structures using this approach along with integrated software that controls the relative movement of the tip array over the underlying substrate. Indeed, we were able to take the likeness of Thomas Jefferson from a 2005 US five-cent coin and duplicated it 55000 times by depositing 80 nm features of ODT according to a $14.5\times14.5\ \mu m^2$ bit map that contains 8773 dots (Figure 3 A). The pattern was created

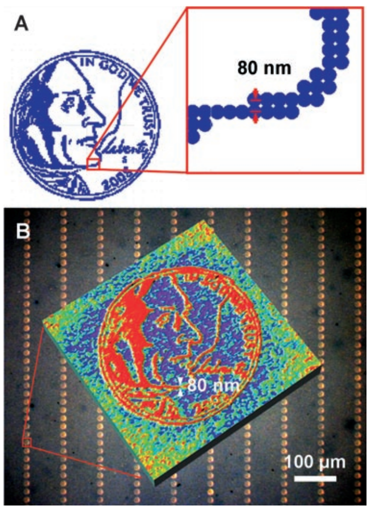


Figure 3. A) Dot matrix map representing the front face of the 2005 US five-cent coin. The coin bears a picture of Thomas Jefferson, who helped develop the polygraph, a letter duplicator that relies on an array of macroscopic pens. The lines of the chin are composed of dots of 80-nm diameter . B) Optical micrograph of a representative region of the substrate on which the approximately 55000 duplicates were generated. Each of the circular features is a miniaturized replica of the face of the five-cent coin. Inset: High-resolution topographical AFM image of a representative replica.

by holding the pen array at each spot for 0.08 s and traveling between spots at a speed of $60\ \mu m\,s^{-1}$. Figure 3 B shows a representative portion of the approximately 55000 copies of gold structures (yield >99%) across an area of $1\times1\ cm^2$. Importantly, approximately 4.7×10^8 features were used to generate the replicas, and the total time required to perform this fabrication was less than 30 min.

The bent-cantilever architecture and large pyramidal tip size provides for a very simple method of tolerating substrate roughness and thickness variations. To demonstrate this tolerance a gold-coated glass microscope slide (total thickness variation ca. $2.6\ \mu m\,cm^{-2}$) was patterned in place of a single-crystal silicon substrate (total thickness variation ca. $0.05\ \mu m\,cm^{-2}$). Figure 4 A is an optical image showing the iridescent reflection from arrays of gold disks of approximately 600-nm diameter patterned on a glass microscope

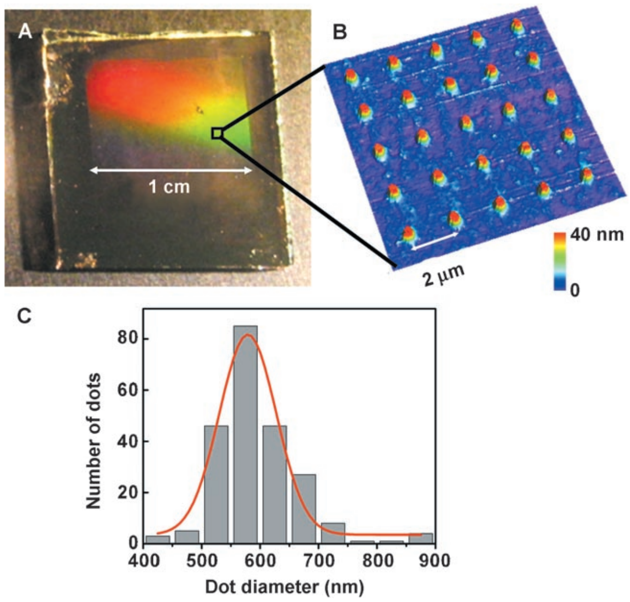


Figure 4. A) Iridescent reflection from arrays of gold disks patterned across a 1×1-cm² area of a glass slide. Each pen generated a 5×20 square-lattice array of disks of approximately 600-nm diameter at a pitch of 2 μm. B) Representative AFM image of part of a gold-disk array. C) Histogram analysis of the diameter of 240 disks randomly but uniformly selected from the sample shown in (A).

slide. To quantify the patterning fidelity, 240 features were randomly selected across the entire 1-cm² area and imaged by AFM, and histograms were constructed using the full-width at half maximum height (FWHM) of the height profile of the features (Figure 4). Significantly, >99% of the pens (excluding 1–2% of pens damaged during processing) are in operation. The standard deviation of the dot diameters for the features generated by the 55000 different pens was 16% across the 1-cm² area, which is a combined result of minor variations in substrate etching, tip morphology, and ink coating. In all patterning experiments AFM and SEM images confirm that registry and alignment are maintained within the field of view of each tip and between tips as well. This degree of registry and pattern fidelity are maintained even when the single-crystal silicon substrate is replaced with a glass microscope slide, thus confirming the flexibility and robustness of this molecular patterning technique.

Although still in its infancy, this parallel 2D DPN approach should be particularly useful for fabricating combinatorial libraries of structures, especially once independent tip-inking strategies have been developed. It is also useful for creating the types of structures that can be fabricated with a nanostamping approach but without the distortion effects that plague stamping and the need to fabricate a mask each time a new design is required.[3]

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