Dip Pen Nanolithography®: A Maturing Technology for High-Throughput Flexible Nanopatterning

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ABSTRACT

Precision nanoscale deposition is a fundamental requirement for much of current nanoscience research. Further, depositing a wide range of materials as nanoscale features onto diverse surfaces is a challenging requirement for nanoscale processing systems. As a high resolution scanning probe-based direct-write technology, Dip Pen Nanolithography® (DPN®) satisfies and exceeds these fundamental requirements. Herein we specifically describe the massive scalability of DPN with two dimensional probe arrays (the 2D nano PrintArray™). In collaboration with researchers at Northwestern University, we have demonstrated massively parallel nanoscale deposition with this 2D array of 55,000 pens on a centimeter square probe chip. (To date, this is the highest cantilever density ever reported.) This enables direct-writing flexible patterns with a variety of molecules, simultaneously generating 55,000 duplicates at the resolution of single-pen DPN. To date, there is no other way to accomplish this kind of patterning at this unprecedented resolution. These advances in high-throughput, flexible nanopatterning point to several compelling applications. The 2D nano PrintArray can cover a square centimeter with nanoscale features and pattern 10^7 μm^2 per hour. These features can be solid state nanostructures, metals, or using established templating techniques, these advances enable screening for biological interactions at the level of a few molecules, or even single molecules; this in turn can enable engineering the cell-substrate interface at sub-cellular resolution.

Keywords: Dip Pen Nanolithography, DPN, Scanning Probe Lithography, SPL, Scanning Probe Microscopy, SPM, AFM, nanoscale lithography, nanoscale deposition, direct deposition, nanofabrication

1 INTRODUCTION

Dip Pen Nanolithography is NanoInk's patented process for deposition of nanoscale materials onto a substrate. The DPN process uses a coated scanning probe tip (the "pen") to directly deposit a material ("ink") with nanometer-scale precision onto a substrate [1, 2]. The vehicle for deposition can include pyramidal scanning probe microscope tips, hollow tips, and even tips on thermally actuated cantilevers. It is an amazingly robust and versatile technique, and can deposit a variety of organic and inorganic molecules onto a variety of substrates [3] under ambient conditions (Fig. 1). Further, thermal DPN (tDPN) grants access to an even wider range of ink materials by enabling solid ink deposition via a heated tip [4].

Table 1: Comparing Nanopatterning Techniques – DPN's Competitive Advantages

Approach	Nanopatterning Technique	Serial / Parallel	Material Flexibility	Litho Resolution	Litho Speed	Registration Accuracy	Cycle Time	Cost	
								Purchase	Operation
Top down	Photolithography	parallel	no	~ 35 nm	very fast	high	weeks	>$10M	high - masks
	E-Beam Lithography	serial	no	~ 15 nm	medium	high	days	>$1M	high
	Nanoimprint Lithography (NIL)	parallel	no	~ 10 nm	fast	high	days-week	>$500k	moderate - molds
enables both	**Dip Pen Nanolithography (DPN)**	serial or parallel pens	yes	14 nm	slower, but highly scalable	extremely high	hours – change on the fly	>$250k	LOW
enables both	Microcontact Printing (μCP)	parallel	yes	~100 nm	fast	low	days-week	~$200k	moderate - masks
Bottom up	Scanning Tunneling Microscopy (STM)	serial	limited	atomic	very slow	extremely high	days	>$250k	low

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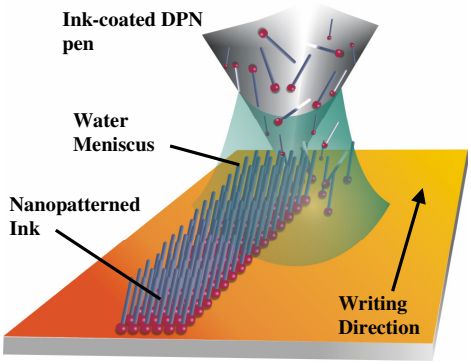


Fig. 1: Schematic of the Dip Pen Nanolithography (DPN) process. A molecule-coated AFM tip deposits ink via a water meniscus onto a substrate.

Table 1 provides an instructive look at DPN's place among nanopatterning techniques: it is highly scalable with the use of multi-pen arrays; it is a technique that enables both bottom up nanofabrication (self-assembly, templating) [5] and top down fabrication via etch resist-based "inks" [6]; and it is high resolution (14 nm line widths, 20 nm pitches) [7]. DPN is a direct-write technique, so materials of interest can be placed exactly (and only) where desired. Among sub-50 nm techniques – such as e-beam lithography – DPN is the only one that can directly deposit molecules under ambient conditions [1, 2, 8, 9]. Further, NanoInk's platform system, the NSCRIPTOR™ (Fig. 2), is an instrument and software package enabling nanoscale registry and alignment, sophisticated CAD design, and high quality AFM imaging.

Applications of this technology are diverse. DPN applications can be broadly categorized according to NanoBio (biomolecular nanoarrays, and controlling biorecognition processes from the molecular to cellular level); Nanoelectronics (materials, CNT manipulation, conductive inks); and fundamental nanofabrication techniques, such as templated assembly and etch resist methods, which support development in the first two areas. In this respect, the DPN process displays extraordinary chemical versatility; it is very general with respect to the molecules that may be transferred from the probe to the surface: small organic surfactants, charged macromolecules such as conjugated polymers and proteins, sol-gel precursors, metal oxides, direct metal deposition,

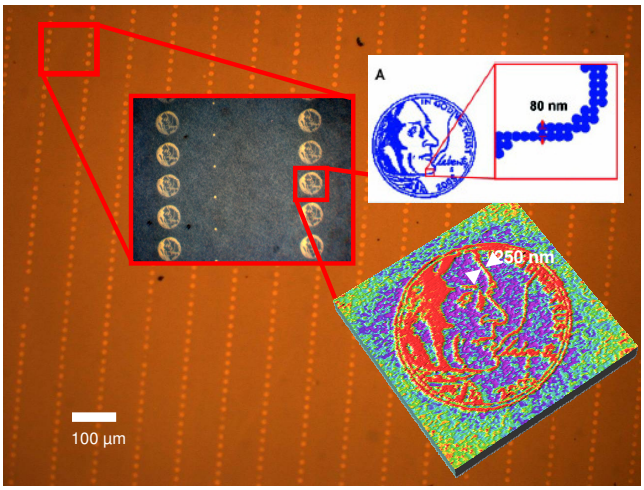


Figure 3: Patterning data from the 2D nano PrintArray showing a portion of 55,000 replicas of the Jefferson Nickel. (Courtesy of Salaita, K., et al. Angew. Chem. Int. Ed., 2006.)

and even nanoparticles [1,2, 5-9]. Substrates include metals (gold), insulators (aluminum oxide, silicon oxide) and semiconductors (GaAs). When using oligomer or protein-based inks, the DPN method can produce nanoscale spotted features which are much smaller than conventional bio-arrays [10]. For example, Lee et al. [11] generated Lysozyme and Immunoglobulin G (IgG) nanoarrays. The arrays featured structures as small as 100 nm in diameter and were shown to exhibit an almost complete absence of non-specific binding of proteins to the passivated areas of the structure. Wang et al. [12] created arrays of very precisely sized, positioned, and oriented single walled CNTs by attaching them to pre-DPN-patterned MHA templates, passivated by ODT. And Vega et al. [13] generated nanoscale site-specific arrays of Tobacco Mosaic Virus (TMV) on MHA templates, maintaining almost 100% bioactivity. This technique has also been demonstrated with Influenza A, and HIV [14].

2 TWO-DIMENSIONAL NANOPATTERNING

With the advent of DPN and its early research, speed and scalability were identified as key roadblocks; these

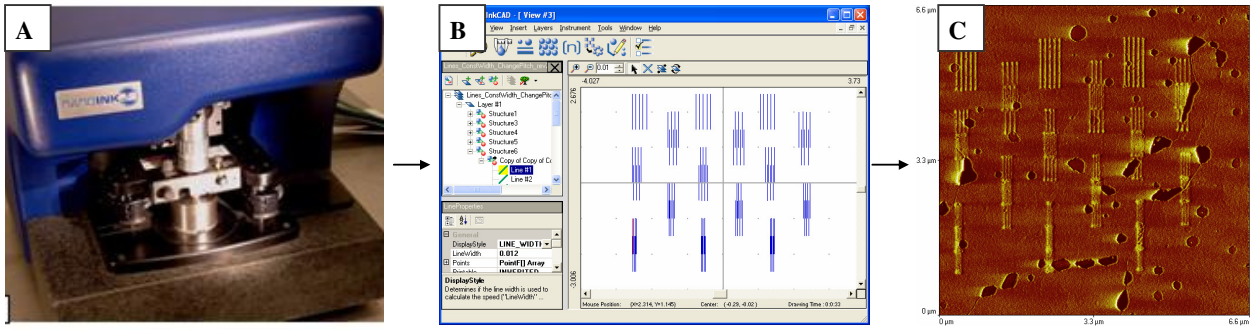


Fig. 2: (a) The NSCRIPTOR DPN instrument. (b) Screen capture of InkCAD™ software showing nanoscale interdigitated line patterns. (c) Forward LFM image of interdigitated DPN line patterns of MHA written onto mica-peeled gold. We observe line widths and pitches down to 20 nm, and placement precision better than 10 nm according to standard deviation measurements.

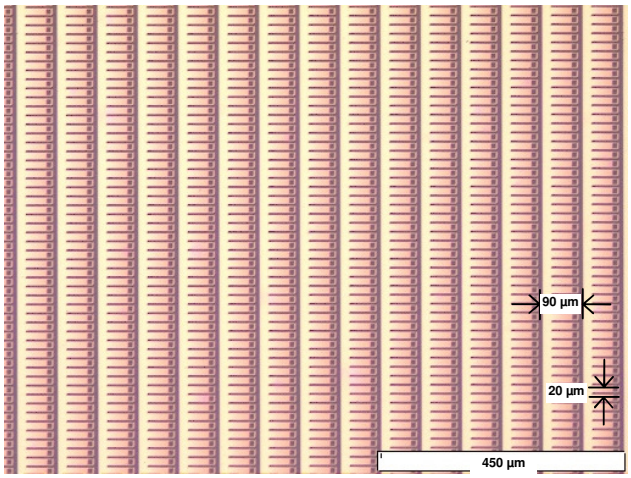
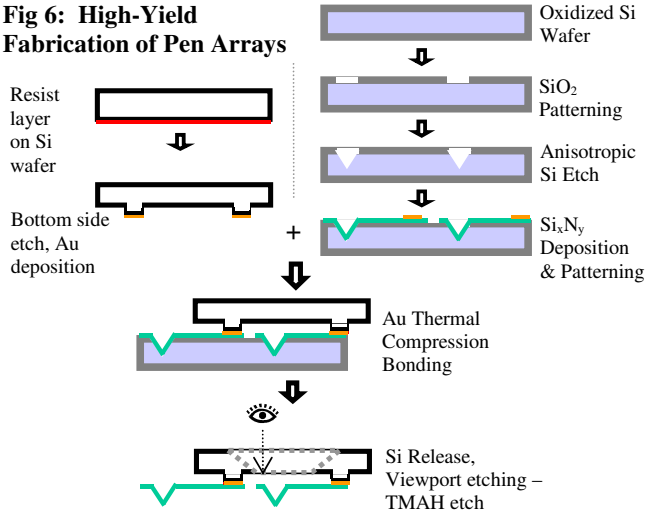


Fig. 4: Optical microscope image of the 2D nano PrintArray (tips facing up) showing the pitch, spacing, and high yield. 832 individual tips are shown, roughly 1.5% of the entire array.

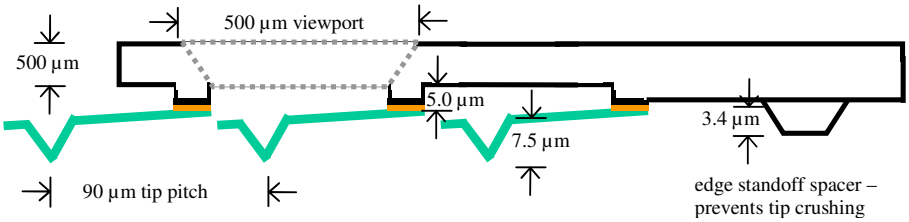
Fig 6: High-Yield Fabrication of Pen Arrays



have now been largely overcome. 2D nanopatterning currently falls into three broad categories: rapidly and flexibly generating nanostructures (i.e., Au, Si), patterning templates for biological molecules (proteins, viruses, cell adhesion complexes), and directly writing biological materials. DPN templating and biomolecule deposition, coupled with advances in 2D nanopatterning, opens up a completely new area of single particle biology. It is now possible to probe interactions between surfaces and single virus, spores or cells. In turn, it is possible to engineer the cell-substrate interface at sub-cellular resolution. Studies of cell adhesion, growth, motility and differentiation can be easily conducted on custom, molecularly designed substrates. And single particle site isolation is critical for studying the behavior of individual viruses, while also leading to new methods studying the effectiveness of new drugs and new delivery techniques. Using 2D nanopatterning, the process is scalable and can cover large areas for statistical investigations of these individual bioprocesses.

In collaboration with researchers at Northwestern University, we have demonstrated sub-100 nm massively parallel nanoscale deposition with a 2D array of 55,000 pens on a centimeter square probe chip [15] (Figs. 3-5). This enables direct-writing flexible patterns with a variety of molecules, simultaneously generating 55,000 duplicates at the resolution of single-pen DPN. In this work, patterns were generated with ODT and MHA, later using these thiol templates to create fibronectin arrays.

Fig 7: Critical Dimensions of 2D nano PrintArrays (not to scale)



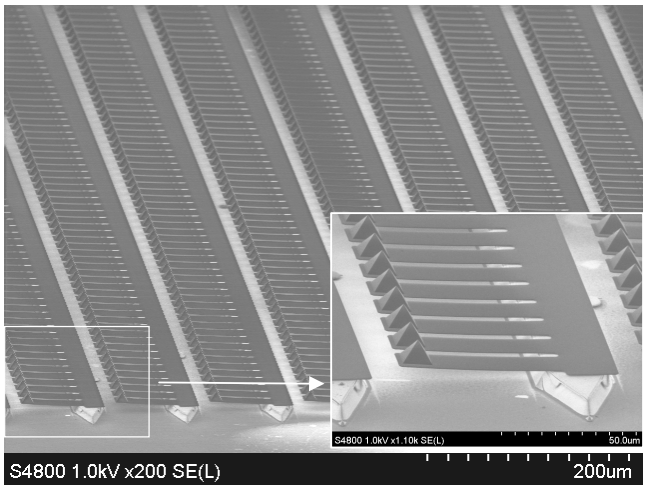


Fig. 5: SEM image showing multiple rows of cantilevers attached to the silicon ridges depicted in Fig. 7. The inset shows individual cantilevers, while also highlighting the 7.5 um tall tips and inherent cantilever curvature (~ 6°).

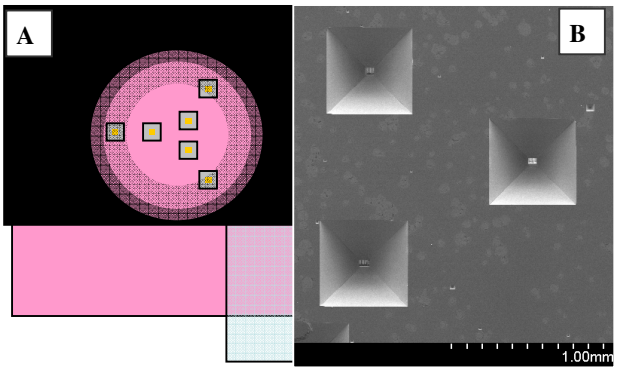


Fig. 8: (a) Top view schematic of the 2D nano PrintArray viewport configuration, as viewed through the Nscriptor scanner. (b) SEM top view image of the 3 central 2D nano PrintArray viewports.

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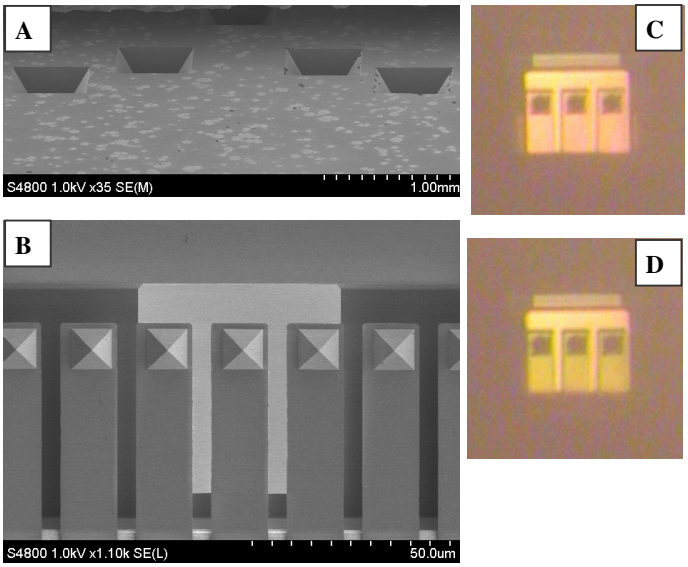

Fig. 9: (a) SEM top angled view of the etched viewports depicted in Fig. 5. (b) Bottom view of three cantilevers in front of the viewport aperture. (c) With the device mounted on the NSCRIPTOR scanner, we can see the cantilevers through the viewport both before the tips touch the gold surface, and (d) after.

To achieve this patterning, the 2D nano PrintArray is attached directly to the NSCRIPTOR scanner, covering a square centimeter with these nanoscale features (dot size standard deviation = 16%), and writing with a throughput of 1×10^7 μm^2 per hour.

This work was extended to direct biomolecule patterning by Lenhert et al. [16]. Working with the phospholipid 1,2-dioleoyl-*sn*-glycero-3-phophocholine (DOPC), they were able to pattern complex features at an astounding throughput of 3×10^{10} μm^2 per hour. Generally, phospholipids are an essential component of biological membranes, and arrays of them can be used as cell-surface models. Now, high resolution DPN patterning creates model systems capable of mimicking the structural complexity of biological membranes. (DOPC) can be used as a universal ink for noncovalent patterning on silicon, glass, titanium, and hydrophobic polystyrene, with lateral resolution down to 100 nm.

3 CONTINUING DEVELOPMENT

Preliminary work in 2D patterning encountered several obstacles, notably the inability to clearly see the substrate or cantilevers through the handle wafer. We subsequently changed the original design to incorporate the viewports depicted in Figs. 6-8, while maintaining the critical design features from the first generation (Fig. 7), notably the combined heights of the silicon ridges and edge standoff spacers which make it impossible to crush the tips against the underside of the silicon handle wafer.

Fig. 8 shows the 2D nano PrintArray from a top perspective, as viewed when attached to the instrument. The cluster of viewports is specifically arranged to fit within the optical viewing area of the NSCRIPTOR; all that is necessary is to examine the cantilever deflection through several windows to establish surface planarity. This is accomplished shown in Fig. 9, where 9c and 9d clearly differentiate the cantilevers' appearance when above the surface and when in contact. The method is fundamentally enabled by the inherent force independence of DPN, and the low *k* flexible silicon nitride cantilevers. However, we have taken this technology to the next step as a commercial product, making it wire-free, easy to use, and fully compatible with the NSCRIPTOR. The array is subsequently manipulated in the same fashion as NanoInk's 1D multi-pen arrays, with sophisticated lithography enabled by our InkCAD software.

4 SUMMARY AND OUTLOOK

We have developed a commercial 2D nanopatterning solution, easy to use, and readily implemented on any NSCRIPTOR. With the 2D nano PrintArray, we are advancing DPN as a technique for high-throughput nanopatterning. With such technology now proven and in practice, desirable future developments could include laser feedback on viewable cantilevers for immediate imaging, automated step-and-repeat lithographic routines, and sophisticated inking methods for addressing groups of tips (or individual tips) with different inks. It would then be possible to fabricate combinatorial libraries of arbitrary nanostructures over large areas.

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