Commercially Available High-Throughput Dip Pen Nanolithography®

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ABSTRACT

Dip Pen Nanolithography® (DPN®) is an inherently additive SPM-based technique which operates under ambient conditions, making it suitable to deposit a wide range of biological and inorganic materials. Massively parallel two-dimensional nanopatterning with DPN is now commercially available via NanoInk's 2D nano PrintArray™, making DPN a high-throughput, flexible and versatile method for precision nanoscale pattern formation. By fabricating 55,000 tip-cantilevers across a 1 cm^2 chip, we leverage the inherent versatility of DPN and demonstrate large area surface coverage, routinely achieving throughputs of $3x10^7$ μm^2 per hour. Further, we have engineered the device to be easy to use, wire-free, and fully integrated with the NSCRIPTOR's scanner, stage, and sophisticated lithography routines. We herein discuss the methods of operating this commercially available device, subsequent results showing sub-100 nm feature sizes and excellent uniformity (standard deviation < 16%), and our continuing development work. Simultaneous multiplexed deposition of a variety of molecules is a fundamental goal of massively parallel 2D nanopatterning, and we will discuss our progress on this front, including ink delivery methods, tip coating, and patterning techniques to generate combinatorial libraries of nanoscale patterns. Another fundamental challenge includes planar leveling of the 2D nano PrintArray, and herein we describe our successful implementation of device viewports and integrated software leveling routines that monitor cantilever deflection to achieve planarity and uniform surface contact. Finally, we will discuss the results of 2D nanopatterning applications such as: 1) rapidly and flexibly generating nanostructures; 2) chemically directed assembly and 3) directly writing biological materials. We will demonstrate flexibly generated nanostructures that are useful in that they complement and exceed the capabilities of existing techniques (e.g., nano imprint lithography and e-beam lithography); we will also demonstrate nanostructures that are valuable for plasmonics surface studies, particularly SERS enhancement.

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] (Fig. 1a). Fig. 1b demonstrates this concept scaled to portray two-dimensional (2D) arrays of tips. 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 [2] 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 [3].

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,

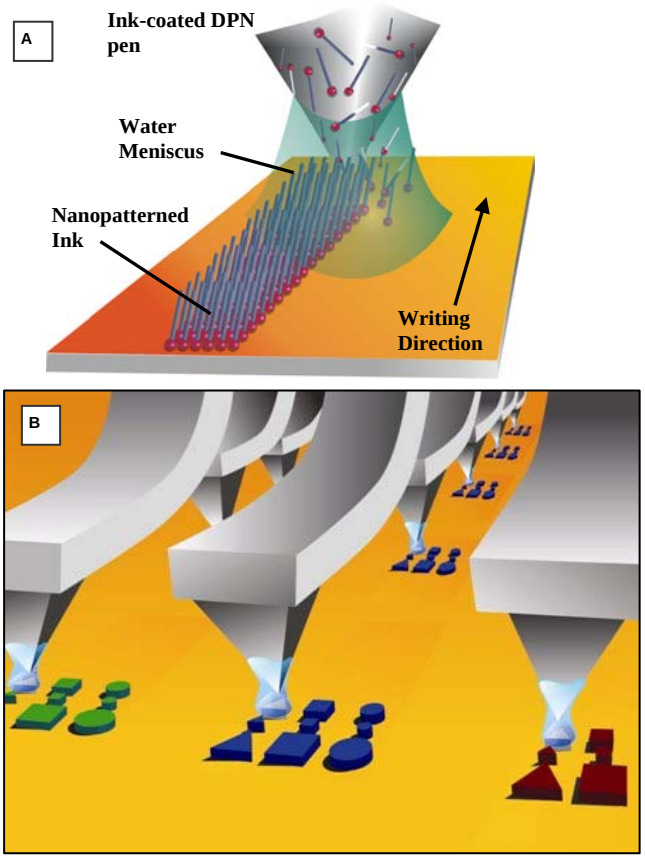

Fig. 1: (a) Schematic of the Dip Pen Nanolithography (DPN) process. A molecule-coated AFM tip deposits ink via a water meniscus onto a substrate. (b) Schematic representation of the DPN process scaled up for massively parallel nanopatterning. The graphic depicts the ultimate aim of rapidly creating a variety of structures on the fly, with different inks on each tip.

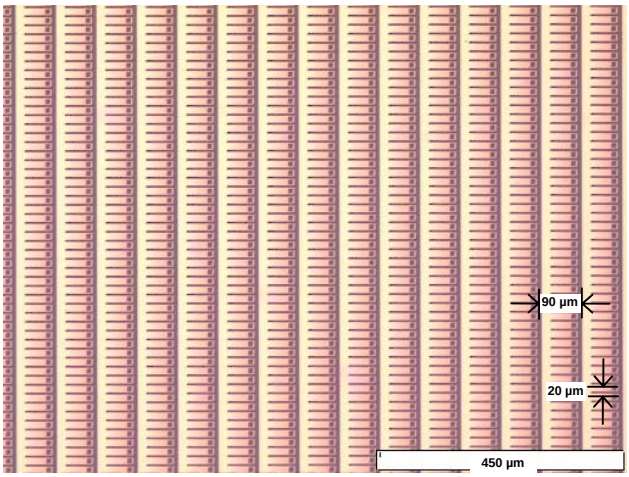

Fig. 2: Optical microscope image of the 2D nano PrintArray (tips facing up) showing the pitch, spacing, and high yield. 832 individual tips are shown, roughly 1.5% of the entire array.

templating) [4] and top down fabrication via etch resist-based "inks" [5]; and it is high resolution (14 nm line widths, 20 nm pitches) [6]. 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, 7, 8]. 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.

Since DPN's inception in 1999 [1], a great deal of research territory has been explored; we will not attempt to chronicle that body of work here, as several excellent reviews have already done so [9-14]. Rather, we will focus on the development of enabling technology – namely, NanoInk's 2D nano PrintArray. From that point we will elaborate several applications enabled by this fundamental capability of massively parallel nanopatterning.

2 MASSIVELY PARALLEL NANOPATTERNING INNOVATIONS

While the DPN process has been successfully demonstrated with a variety of capabilities in academic and government research labs, critics had naturally pointed out its initially serial nature, and as such have argued against its commercial viability. Recently, with a view to overcome the serial nature of the DPN process, we initiated efforts to perform massively parallel nanopatterning with cantilever arrays. The resulting collaboration with the Mirkin group at Northwestern University produced a vital proof-of-principle: massively parallel DPN patterning over cm^2 areas retains essentially all of the critical attributes of single pen DPN [15]. With throughput exceeding 1×10^7 μm^2/hr, and a dot size standard deviation of only 16%, they demonstrated sub-100 nm massively parallel nanoscale deposition with a 2D array of 55,000 pens on a centimeter square probe chip (Figs. 2-3). In that work [15] an image

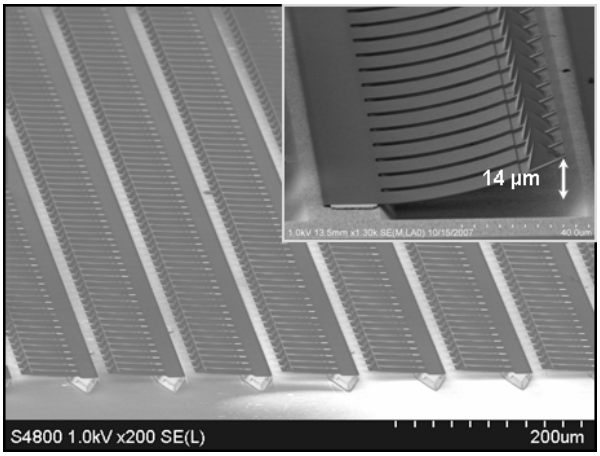

Fig. 3: SEM image showing multiple rows of cantilevers attached to silicon ridges. The inset shows individual cantilevers, while also highlighting the 7.5 um tall sharpened tips and inherent cantilever curvature (~ 14 µm bow).

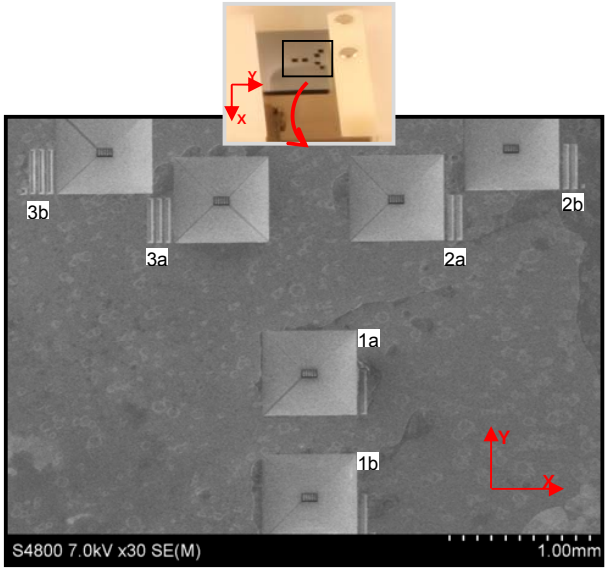

Fig. 4: SEM image of the top side of a 2D nano PrintArray, showing all six viewports as oriented when looking through the NSCRIPTOR optics. An optical image of the device with the wedge is shown for reference and orientation.

of the Jefferson nickel was imported into InkCAD™ software (the NSCRIPTOR system interface), transformed to a map of dots, and then 55,000 identical patterns were generated with ODT ink. The patterned ODT later served as an etch resist on the gold layer. This massively parallel approach to DPN works because DPN is effectively force-independent, and thus generally forgiving with respect to probe array leveling with low-spring-constant silicon nitride cantilevers. To date, there is no other way to flexibly pattern a variety of materials at this unprecedented resolution (80 nm). Additionally, 55,000 tips in 1 cm^2 is the highest cantilever density ever reported. Fundamentally, this enables flexible direct-writing with a variety of molecules and simultaneously generating 55,000 duplicates at the resolution of single-pen DPN.

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In spite of the impressive results detailed above, several prominent engineering hurdles stood between the devices these groups used and a robust commercial offering. Significant challenges included facile device mounting, routinely and accurately leveling the array with respect to the substrate, ensuring uniform contact of all of the tips when the array is meant to write, and making sure no tips are touching when the array is retracted. To overcome these challenges, we introduced etched viewports (Fig. 4), a precisely machined magnetic attachment wedge (Fig. 4 inset), and semi-automated leveling routines. We have engineered the device to be easy to use, wire-free, and fully integrated with the NSCRIPTOR scanner, stage, and sophisticated lithography routines. Unlike previous prototypes, it is now possible to view the substrate through the handle wafer, align to pre-existing surface features (such as inkwells), and in principle even align a laser to a cantilever for imaging. Massively parallel two-dimensional nanopatterning with DPN is now commercially available via NanoInk's 2D nano PrintArray™ (Figs. 2-3), making DPN a high-throughput, flexible and versatile method for precision nanoscale pattern formation.

Fig. 5 shows the results of this type of nanofabrication with the 2D nano PrintArray. Leveling is one of the most important aspects for successfully using the 2D nano PrintArray. The 2D nano PrintArray exists as a flat 1 cm^2 square chip whose goal is to be brought into uniform contact with a substrate. The sophisticated software control (Fig. 6a) easily enables the degree of planarity required to level the device, and to fine-tune the *z*-positioning prior to lithography. Leveling is accomplished by examining cantilever deflection through these viewports (Fig. 6b) at three different points, noting the *z*-height differences, and then entering these numbers into the software to calculate the planarity corrections of the three *z*-motors. Contrasted with earlier methods, the viewport leveling takes only a few minutes; the NanoInk logo data shown in Fig. 5 was generated in under 30 minutes, from mounting the probes to finishing the etch-resist process.

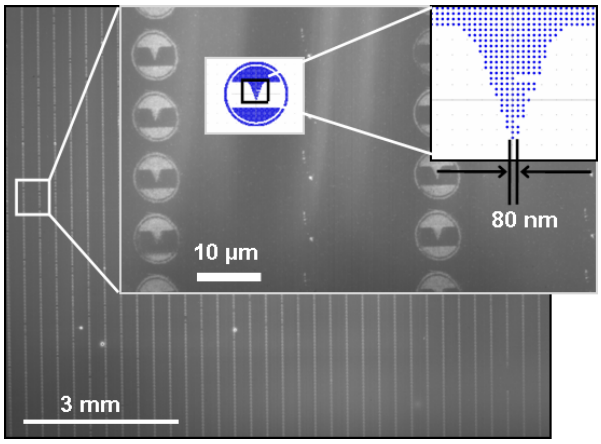

Fig. 5: Optical images of the NanoInk logo following the successful process of mounting, leveling, and printing ODT with the 2D nano PrintArray. The design includes 2250 dots of 80 nm diameters. Patterns were generated using ODT as the etch-resist. Only a fraction of the 55,000 printed logos are shown.

3 APPLYING 2D DPN

The 2D nano PrintArray's capabilities are constantly evolving, and the above represent only a sampling of what is possible. 2D nanopatterning currently falls into three broad categories: 1) rapidly and flexibly generating nanostructures (e.g., Au, Si) via etch resist techniques; 2) chemically directed assembly and patterning templates for either biological molecules (e.g., proteins, viruses, cell adhesion complexes), or inorganics (e.g., carbon nanotubes, quantum dots); and 3) directly writing biological materials.

Using established templating techniques, these advances enable screening for biological interactions at the level of a

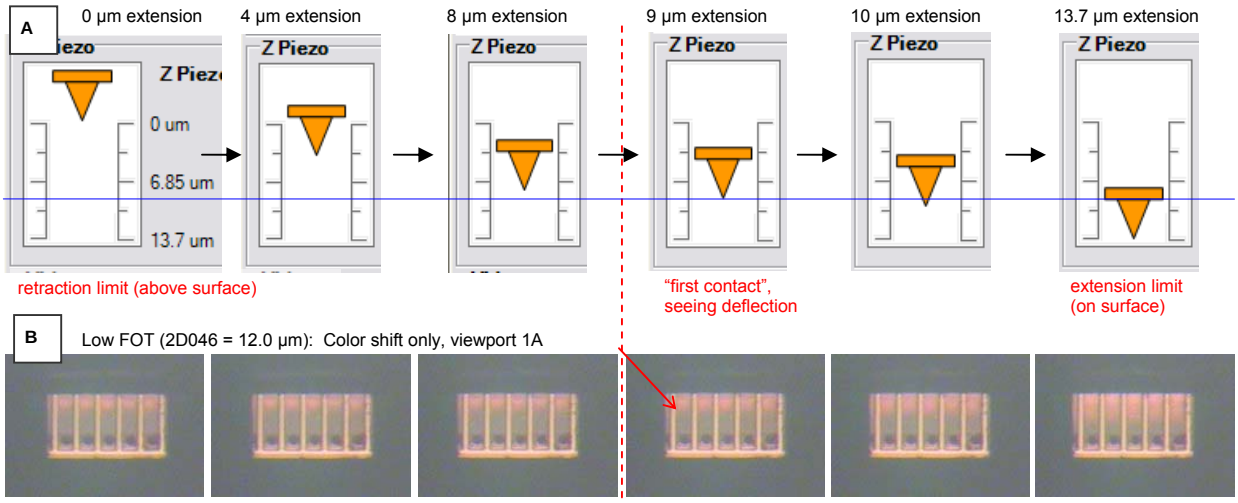

Fig. 6: Mapping the visual progression of cantilever deflection for a viewport; (a) The sequence of positions of the Z-piezo tool used to bring the cantilevers of a given viewport into contact with the surface. (b) These cantilevers are less curled (FOT = 12.0 µm), but display a dramatic color shift across the whole cantilever. At the point of first contact, note the subtle color and shade change at the base of the cantilever (shown inset). These subtle shifts become obvious when the Z-piezo is repeatedly extended to 9.0 µm and retracted. The shift becomes dramatic at an extension of 13.7 µm.

few molecules, or even single molecules. This in turn can enable engineering the cell-substrate interface at sub-cellular resolution. This technology allows users to routinely pattern libraries of small molecules over very large areas, and realistically practice single cell experimentation. Using 2D nanopatterning, the process is scalable and can cover large areas for statistically significant investigations of these individual bioprocesses. For example, DPN-generated arrays have been demonstrated to monitor single-cell infectivity from virus-particle nanoarrays [16]. In this work, Vega and coworkers immobilized antibodies on DPN-patterned MHA-Zn_2^+ regions. These nanoarrays were later incubated with fluorescent SV5 viral solution. The resulting virus nanoarrays were used for CV1 cell infectivity studies.

Further, because these inks can be used as etch-resist materials [17],[18], we can perform maskless rapid prototyping across large areas, forming combinatorial arrays of metallic or solid-state features varying in size, spacing, and shape. There are a variety of useful things one can do once one has the capability to rapidly generate arbitrary gold nanostructures on silicon oxide across a cm^2 area. Numerous researchers in the field of SERS would benefit from a method of quickly generating arrays of noble metal nanostructures. The most important requirement for a SERS substrate is its ability to increase the electromagnetic field at the surface; nanoscale noble metal structures (e.g., Ag, Au) have this ability through their interaction with light that has been tuned to the resonance frequency of the conductive electrons surrounding the metal. The field enhancing properties of these structures are particularly sensitive to the structures' size, shape, environment, inter-structure distance, and inter-particle distance. As such, it is extremely desirable to have the ability to fabricate such arbitrary metallic patterns – a clear strength of massively parallel DPN. Such patterns are typically fabricated by slow and often costly serial e-beam lithography. More crude methods, such as nanosphere lithography (i.e., "polystyrene drop-coating"), have reduced costs considerably, but only by sacrificing reproducibility. Further, this 2D etch-resist technique can generate very small metallic structures next to very large ones – something Nano Imprint Lithography (NIL) has a difficult time accomplishing. Finally, this 2D patterning method is not limited to any particular shape: notably, we can generate closely spaced arcs and circles, which is a weakness of e-beam lithography. All of these approaches are maskless with a quick-turn time, flexible, inexpensive, and require little to no chemistry expertise.

4 SUMMARY AND OUTLOOK

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, and automated step-and-repeat lithographic routines. But simultaneous multiplexed deposition of a variety of molecules remains a fundamental goal of massively parallel 2D nanopatterning. We are currently involved in research to demonstrate this application, although significant engineering challenges are involved in getting several hundred or thousand different molecules onto different tips. Massively parallel multiplexed DPN, enabled by multiplexed selective ink delivery, is a fundamental requirement of a variety of biological applications, and a direction of important development. In this regard, we anticipate the need for universal inks of nearly identical properties to ensure even fluidic control, tip loading, and ink transport from the tip. We are approaching this ink delivery challenge through a variety of methods, including InkTrough™ channels and different vapor coating techniques. Such a capability would enable multiplexed combinatorial libraries of nanoscale patterns across large areas.

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