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Dip Pen Nanolithography®: A "Desktop Nanofab™" Approach Using High-Throughput Flexible Nanopatterning

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Summary: The ability to perform controllable nanopatterning with a broad range of "inks" at ambient conditions is a key aspect of the dip pen nanolithography® (DPN®) technique. The traditional ink system to demonstrate DPN is *n*-alkanethiols on a gold substrate, but the DPN method has found numerous other applications since. This article is meant to outline recent advances in the DPN toolkit, both in terms of research and patterning technology, and to discuss applications of DPN as a viable nanofabrication method. We will summarize new DPN developments, and introduce our concept of the "Desktop Nanofab." In addition, we outline our efforts to commercialize DPN as a viable nanofabrication technique by demonstrating massively parallel nanopatterning with the 55,000 tip 2D nano PrintArray™. This demonstrates our ability to overcome the serial nature of DPN patterning and enable high-throughput nanofabrication. SCANNING 30: 137–150, 2008. © 2008 Wiley Periodicals, Inc.

Key words: Dip pen nanolithography, alkanethiols, gold, water meniscus, nanofabrication, NSCRIPTOR, atomic force microscope, ink transport, MHA, ODT, scanning probe lithography, SPL, DPN, self-assembly, patterning, nanolithography, scanning probe microscopy, SPM, AFM, nanoscale lithography, nanoscale deposition, direct deposition, nanofabrication

Introduction

Since its inception eight years ago in the research laboratory of Mirkin and coworkers (Piner *et al*., 1999), DPN has gone from a single ink, single tip research technique to a multi-ink, multi-tip, versatile surface patterning system, in some cases capable of exceeding the throughput of e-beam lithography (10^1–10^4 μm^2/h) (Marrian and Tennant, 2003). Moreover, DPN's attributes and differentiating characteristics (explained below) position it as a technology able to fill needs and expand capabilities across a wide variety of disciplines. Clearly, a great deal of ground has been covered in these eight years; we will not attempt to entirely chronicle that body of work here, as several excellent reviews have already done so (Ginger *et al*., 2004; Rosner and Demers, 2005; Huck, 2007; Salaita *et al*., 2007; Lenhert, 2008). Rather, we seek to provide an overview of the trajectory of the technology based upon where it has been, recent new developments, and where we see it making the biggest impact in the near-term and mid-term.

We will begin by setting the stage—introducing the DPN technology via its key attributes—and generally noting the early work that established DPN's foothold as an important technique in alkanethiol DPN assisted template creation, biological patterning, and inorganic and hard-ink (metals) deposition. From there, we will detail DPN's evolution into a high-throughput patterning method—a crucial quantum leap for this technology. Along with this, we will discuss ancillary aspects of the DPN portfolio, namely microfluidic ink delivery systems, independently actuated cantilevers, and preformulated ink recipes targeted for potential applications (e.g., DNA arrays, or conductive metal traces using nanoparticle-based inks).

This naturally leads to our concept of DPN enabling the "Desktop Nanofab"—a system that allows a non-expert atomic force microscope (AFM) user to rapidly create high resolution, scalable nanostructures with a wide variety of materials, drawing upon well-characterized ink and substrate pairings. Moreover, this Desktop Nanofab approach can take direct advantage of the fact that DPN is fundamentally an AFM-based technique; in most cases, the user can get immediate information on critical components of the experiment through several different modes of AFM scans. Notably, this Desktop Nanofab approach does not incur the massive capital costs of techniques such as e-beam or photolithography.

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The versatility of DPN as a nanopatterning process consequently suggests unique families of applications. We recognize that DPN will always play a role as a fundamental research technique, examining natural phenomena in the life sciences or inorganic materials for their own sake, and making important contributions to a growing body of academic knowledge. On the other hand, we also recognize that there is a broad middle ground of applications where DPN can fill the needs of many, both in industry and in academia. As we continue to map this territory, we find that these are not just *capabilities* of DPN waiting to find a use, but actual *applications* of the technology where DPN is a means to an end. We will devote the final portion of this article to describing some of these applications, and the associated challenges for their development.

Attributes of Dip Pen Nanolithography

The road to crafting architecture at the nanoscale is often complex and replete with obstacles; valuable nanopatterning techniques are those that offer ways around these obstacles. Whether the architecture is physical or chemical, there are principally two approaches to building nanostructures: top-down or bottom-up. Dip pen nanolithography has emerged as a technique using the AFM tip to deposit molecules by direct-write on suitable substrates, enabling both approaches to nanofabrication. Further, precision nanoscale deposition is a fundamental requirement for much of current nanoscience research, and depositing a variety of materials as nanoscale features onto diverse surfaces is a challenging requirement for nanoscale processing systems. Dip pen nanolithography is an inherently additive SPM-based technique that operates under ambient conditions, making it suitable to deposit a wide range of biological, organic, and inorganic materials at specified locations. We should note that in 1995, Jaschke and Butt noticed 1-octadecanethiol (ODT) deposits on mica when trying to image with an ODT-coated AFM tip (Jaschke and Butt, 1995); however, their process was not well-controlled, particularly when trying to make lines, and was not successful with thiols on gold. By contrast, thiol-on-gold deposition was later perfected by Mirkin and coworkers and extended to the deposition of 16-mercaptohexadecanoic acid (MHA), among several other inks. This technique was found to be versatile enough for a variety of ink–substrate combinations and it was realized that it could be used to deposit controlled amounts of material at specific regions (e.g., for additive repair), and as a tool for template-directed assembly and biological material deposition, among other applications. As such, DPN is a flexible nanoscale patterning tool and we will detail this in the DPN capabilities section.

For a large subset of inks, the DPN transport process is understood to be water meniscus-mediated, wherein a water meniscus forms between the inked AFM tip and the substrate owing to capillary condensation. The ink molecules transfer from the tip to the substrate when the tip is either drawn across the substrate or kept in contact with it as shown schematically in Figure 1. Typically, the alkanethiol-on-gold ink/substrate system is used to demonstrate DPN, wherein the AFM tip is coated with the thiol ink by simply holding the probe with tweezers and dipping into an MHA-acetonitrile solution. However, the DPN method has been demonstrated to deposit a wide variety of inks (McKendry *et al*., 2002; Su *et al*., 2004; Zhang *et al*., 2004; Nafday *et al*., 2006), and reviews on the flexibility of this technique can be found in the literature (Ginger *et al*., 2004; Rosner and Demers, 2005; Huck, 2007; Salaita *et al*., 2007; Lenhert, 2008). These reviews have succinctly summarized the prior DPN work, including families of ink–substrate combinations, and categorized DPN patterning methods with respect to other deposition methods. Ginger and coworkers (Ginger *et al*., 2004) categorized DPN applications according to biomolecular micro and nanoarrays, controlling biorecognition processes from the molecular to cellular level, building nanostructured materials with DPN using templates for orthogonal assembly, and DPN-patterned etch resists. This review summarized the first five years of DPN applications, including DPN ink transport mechanisms and high-throughput parallelization efforts. Since then, the DPN technique has evolved both in terms of new hardware tools and new ink transport explanations. The Huck review (Huck, 2007) outlined alkanethiol-ink-on-gold-based microcontact printing and DPN methods to create nanoscale architectures, and further mentioned the rapid growth in DPN hardware since its invention. The review by Salaita and coworkers (Salaita *et al*., 2007) focused on developments leading to biological nanoarray fabrication with DPN and templated assembly of materials, and outlined the extended capabilities of DPN. Most recently, Lenhert's review (Lenhert, 2008) stresses DPN's ability to integrate different materials on scales (both in size and complexity) that appear impossible to reach using any other direct-write nanopatterning techniques. He highlights selective deposition and combinatorial chemistry as key attributes, and discusses the capabilities they bring to bear.

Inasmuch as the above reviewers have written about different *applications* in their articles, we herein understand the bulk of those discussions to be focused on *capabilities*. The Rosner review (Rosner and Demers, 2005) began making this distinction through its title "Dip pen nanolithography: Applications and Functional Extensions", and examined how various DPN tools (i.e., arrays of passive pens, devices for microfluidic ink delivery, actuated cantilevers) would enhance existing capabilities. Here, we will take this concept further and

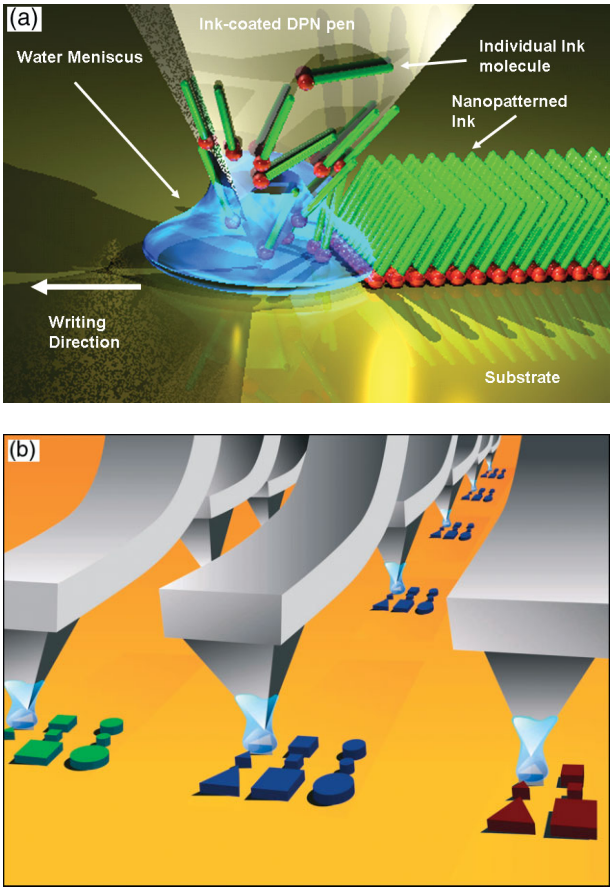

Fig 1. (a) Schematic representation of the DPN process. A molecule-coated single AFM tip deposits ink via a water meniscus onto a substrate. Reproduced with permission from Nature Publishing Group (Salaita *et al*., 2007). (b) Schematic representation of the DPN process scaled up for massively parallel nanopatterning. The graphic depicts the ultimate aim of rapidly creating a variety of structures on the fly, with different inks on each tip.

give our assessment of DPN *applications* in the final section of this review.

Table I provides an instructive look at DPN's place among nanopatterning techniques: it is highly scalable with the use of multipen arrays; it is a technique that enables both bottom-up nanofabrication (e.g., self-assembly, templating) (Demers *et al*., 2001) and top-down fabrication via etch resist-based "inks" (Zhang *et al*., 2003); and it is a high-resolution (14 nm line widths, 20 nm pitches) technique (Haaheim *et al*., 2005). Dip pen nanolithography 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 (Jang *et al*., 2001). In addition, because NanoInk's nanolithography platform—the NSCRIPTOR™—is based on scanning probe microscopy (SPM) technology, it is inherently capable of both pattern fabrication and immediate verification of the result by AFM imaging. This is frequently important, as current drawbacks of the DPN technique often relate to ink transport and overall process control. We view this as an area of necessary (and achievable) development for commercially viable applications. Further, we want to emphasize that we do not envision DPN *replacing* the techniques shown in Table I (i.e., photolithography, microcontact printing), but rather *complementing* them; the multiple overlap of attributes constitutes a powerful "sweet spot" for DPN as a nanopatterning method, and discussions below will clarify how applications take advantage of this.

To enhance the versatility and ease of use of DPN, NanoInk Inc. (Skokie, IL) has developed a suite of DPN tools including MEMS devices, software, and most notably a dedicated lithography instrument (NSCRIPTOR), with the object of developing new applications and commercializing this technique. The NSCRIPTOR platform (Haaheim *et al*., 2005) has been proved to be a suitable tool for top-down and bottom-up creation of architectures via DPN. In that work, we characterized the performance of the NSCRIPTOR DPN instrument and demonstrated 14 nm line widths, feature placement precision better than 10 nm, and size control better than 15% for sub-100 nm features as shown in Figure 2.

Ink Transport in DPN—Transferring Molecules from Tip to Substrate

One of the most fundamental aspects in DPN is to understand the ink transport of molecules from the inked AFM tip to the substrate, which has been a source of disagreement in recent literature. This disagreement was due in part to two reasons: first, it was not clear how a water meniscus could account for hydrophobic ink transport like 1-octadecanethiol (ODT), especially since the size of the meniscus is estimated from the Kelvin equation to be smaller than the height of thiol self-assembled monolayers (SAM). Second, thiol ink DPN was demonstrated at near 0% relative humidity (RH) where the conditions for water meniscus formation were not suitable, leading to the belief that the water menisci might not be important for ink transport (Sheehan and Whitman, 2002). To this end, studies have emerged that have contributed to determining how the water meniscus can affect ink transport (Jang *et al*., 2001; Schwartz, 2002; Nafday *et al*., 2006). Two possible modes of ink transport have emerged from these studies: (i) bulk meniscus, and (ii) air–water meniscus interface transport, which can lead to either filled or internally hollow structures respectively. The minimum width of the water meniscus has been estimated to be 5 molecular diameters (1.9 nm) by Lattice gas Monte Carlo simulations (Jang *et al*., 2004). Moreover, direct

TABLE I. A comparison of nanopatterning techniques; DPN's competitive advantages relative to other methods

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	>$10 M	high-masks
	E-Beam Lithography	serial	no	~15 nm	medium	high	days	>$1 M	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	highly scalable; (2D speed exceeds e-beam)	extremely high	hours - change on the fly	<$250k	LOW
Bottom up	Microcontact Printing (μCP)	parallel	yes	~100 nm	fast	low	days-week	~$200k	moderate - masks
	Scanning Tunneling Microscopy (STM)	serial	limited	atomic	very slow	extremely high	days	>$250k	low

imaging of the water meniscus performed using an environmental scanning electron microscope (ESEM) (shown in Figure 3), proved the meniscus (height of up to 2 μm at 99% RH) to exhibit variable size depending on the RH of the patterning environment. This clearly suggests that RH is an important factor in the DPN process (Schenk *et al*., 1998; Weeks *et al*., 2005). As such, the NSCRIPTOR tool allows precise control of the environmental conditions important for a typical DPN experiment (Peterson *et al*., 2004), using an environmental chamber capable of controlling temperature (from $-2\,^{\circ}$C below room temperature to $10\,^{\circ}$C above room temperature) and RH (0–75%) through a real-time feedback loop. Variations in the environmental conditions were $\pm 0.1\,^{\circ}$C, and $\pm 0.5\%$ RH when using the environmental chamber.

Dip Pen Nanolithography Capabilities Demonstrated in Prior Research

Dip pen nanolithography-generated nanostructures have been shown to be a viable template creation tool as resists for lithographic masters (Salaita *et al*., 2006). Using 1D Passive Pen Arrays as a fabrication tool, silicon (Si) nanostructures were generated using a combination of DPN, wet-chemical etching (WCE) and reactive ion etching (RIE) techniques (Zhang *et al*., 2007). Zhang and coworkers showed that thiol layers on gold/silicon substrates can serve as etch-resist layers (Zhang *et al*., 2003). In this way, patterns of metal, silicon, glass, or chrome nanostructures can be generated from a thiol-resist layer. This approach can then be coupled to patterning with large 1D or 2D pen arrays depending on the magnitude of multiplexing required. Salaita *et al*. (2006) used this approach with our multipen 1D arrays to create MHA patterns on a gold (Au) substrate, which were subsequently etched to produce gold/titanium/silicon features.

By contrast, Wang *et al*. (2006; Zou *et al*., 2007) created arrays of very precisely sized, positioned, and oriented single-walled carbon nanotubes (CNTs) by attaching them to pre-DPN-patterned MHA templates passivated by ODT. It is a powerful templating technique, especially considering the traditional difficulty in working with CNTs. Integrating the nanotube materials in all cases relies on one's ability to control the placement, orientation, and shape of the nanotube components; their work demonstrates all of these traits. Extending the technique using large area multipen patterning techniques, they created arrays of very precisely sized, positioned, and oriented single-walled CNTs. This CNT templating work has been further improved with greater chemical generality (Myung *et al*., 2005).

Su and coworkers (Su *et al*., 2004) demonstrated direct patterning of aluminum and tin oxides on silicon and silicon oxide substrates based on sol-gel chemistry. This approach took advantage of the water meniscus formation as a nanowater source to hydrolyze the metal precursors. Subsequent to patterning the sol-metal inks, the copolymer based sol was evaporated by heating to a high temperature ($\sim 400\,^{\circ}$C). This approach suggested potential DPN-based catalyst and waveguide applications, in addition to being a complementary technique to micromolding and stamping techniques.

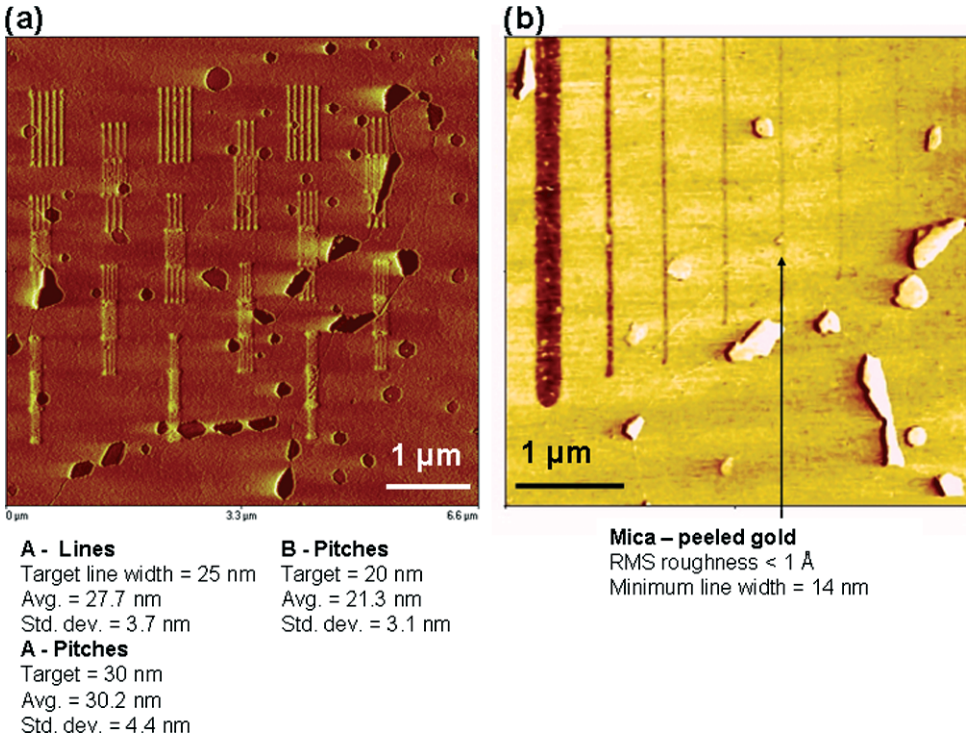

Fig 2. (a) Reverse channel lateral force microscopy (LFM) images of 16-mercaptohexadecanoic acid (MHA) lines written with a sharpened tip on mica-peeled gold, yielding a 14 nm minimum line width (4.0 μm scan). (b) Forward channel LFM image of interdigitated DPN line patterns of MHA written onto mica-peeled gold using a sharpened tip (6.6 μm scan). Total patterning time = 44 s. We observe pitches down to 20 nm, and placement precision better than 10 nm according to standard deviation measurements. Reproduced with permission from Elsevier (Haaheim *et al*., 2005). This figure is available in colour online at www.interscience.wiley.com/SCA.

When using oligomer or protein-based inks, the DPN method can produce nanoscale spotted features that are much smaller than conventional bioarrays (Lee *et al*., 2003). For example, Lee *et al*. 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 nonspecific binding of proteins to the passivated areas of the structure (Lee *et al*., 2002).

Other variants have since added to the capabilities of the DPN method. These include thermal cantilever DPN (tDPN), electrochemical DPN (eDPN) and nanofountain pen lithography (NPL) (shown in Figure 4). Thermal cantilever DPN (Figure 4(a)) can be used to deposit inks which are solid at room temperature (metals, polymers) by using a resistively heated cantilever to locally melt the inks and generate stable nanostructures on ink cooling (Nelson *et al*., 2006). Electrochemical DPN (Figure 4(b)) employs a voltage difference between the AFM tip and the substrate to drive ink molecule flow (Jegadesan *et al*., 2006). The NPL method (Lewis *et al*., 1999) is slightly different from DPN, tDPN, or eDPN, in that it uses a nanopipette tip design that relies on ink from microchannels linked to ink reservoirs for steady ink flow, as opposed to coating the tip itself (Figure 4(c)). We would like to note that

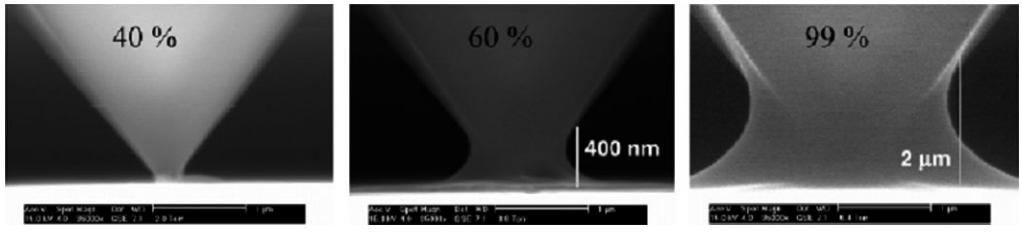

Fig 3. Environmental scanning electron microscope (ESEM) image of the water meniscus size at different relative humidity (RH) values. Reproduced with permission from (Weeks *et al*., 2005). Copyright (2005) American Chemical Society.

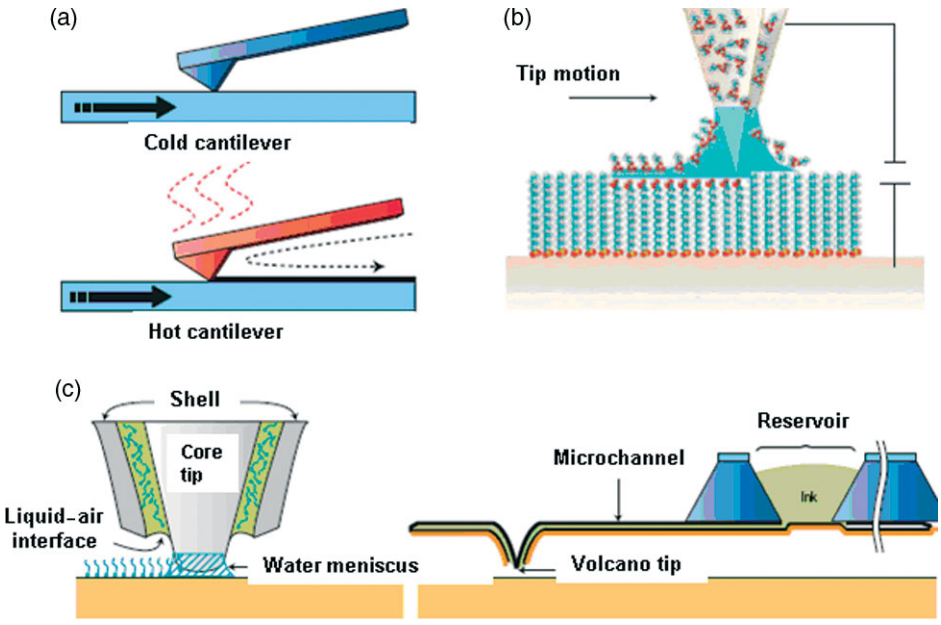

Fig 4. Variants of the DPN technique. (a) Thermal DPN, (b) electrochemical DPN, (c) nano-fountain pen lithography. Reproduced with permission from Nature Publishing Group (Salaita *et al*., 2007). This figure is available in colour online at www.interscience.wiley.com/SCA.

the concept of "the ink source" is a recurring and fundamental question for many unfamiliar with the body of DPN research; while many find it intuitively necessary to have tips with holes and a steady supply of liquid ink, this turns out to be unnecessary in the majority of patterning situations we encounter. Relative to the nanoscale amounts of material deposited onto the surface—using 1 or 55,000 tips—the amount of ink stored on the tip, or loaded in solvent on the underside of the cantilever, is more than adequate for many continuous hours of writing. We control this process of microfluidic ink delivery using Inkwell™ systems, described below. An updated DPN bibliography sorted according to application areas, with a chart listing various demonstrated ink and substrate combinations, is available at www.nanoink.net.

Ink Delivery Systems

The process of "inking" a DPN pen (i.e., an AFM probe with ink on it) can be as trivial as dipping it in a vial with a pair of tweezers. However, repeatability and process control are cornerstone elements of DPN applicability—where DPN serves as a means to an end—and there are two critical components of inking that must be addressed to achieve this overall process control: (i) selectively delivered ink, with no cross-contamination, and (ii) uniform cantilever loading. To ensure these, we have developed complementary tools—Universal Inkwell™ and DNA Inkwell™—systems to enable controllable inking by aligning microfluidic channels precisely with the cantilever arrays, keeping in mind the cantilever-to-cantilever spacing as shown in Figure 5. These devices represent the next generation of inkwell development. The design philosophy accommodates a variety of active and passive pens, and incorporates etch-isolated microwells that protrude from the surrounding chip, providing an "inking peninsula" of sorts to isolate the ink dipping event and prevent wicking or contamination. The "InkCliff" acts as a flow barrier, and the recessed InkCliff area extends to the back edge of the chip. This larger region provides ample clearance for the probe chip during inking. The microwells are fed by six reservoirs, which can contain six different inks. These devices are beneficial as we increasingly find it important to control cantilever ink-loading for inks that must be deposited with their native solvent (e.g., DNA, proteins, and/or metal nanoparticle-based inks). These Inkwells uniquely provide isolation, containment, and optimized fluid flow (to the microwell, and not *vice versa*).

Another approach to ink AFM cantilevers has been documented (Ryu *et al*., 2004), wherein a microfluidic chip inks multiple nanolithography tips in a high-density array in a parallel fashion. This chip consists of multiple precision patterned thin-film polydimethylsiloxane (PDMS) patches serving as porous inking pads. Inking chemicals are supplied from loading reservoirs to the inking pads through microfluidic channels. The gas-permeable thin PDMS membranes allow ink

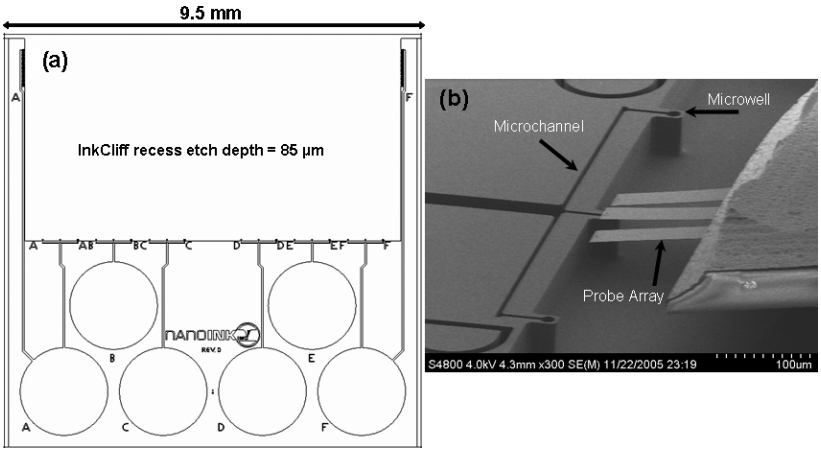

Fig 5. (a) Top view schematic of a Universal Inkwell. (b) An array of three cantilevers dipping into the microwell of a Universal Inkwell. The ink is selectively delivered only to the intended center tip, and cross-contamination is prevented by etch isolation.

molecules to diffuse through while preventing bulk liquid from overflowing or evaporating. The inking chip provides high-density inking, easy loading of inks, and reduced evaporation losses.

Actuated Cantilevers

Dip pen nanolithography patterns are often simply written and imaged with a single inked tip, contaminating the pattern even as it is imaged. This contamination can lead to reduced phase contrast with continued imaging, and eventual pattern overwriting. Furthermore, selective inking and individual cantilever actuation becomes even more important for the patterning of biological inks, where cross-contamination can lead to nonspecific binding, or interfere with later fluorescence characterization.

As such, initial prototypes of actuated AFM probes for DPN were thermally actuated probe arrays, which consisted of ten thermal bimorph cantilevers, each 300 μm long, with a lateral spacing of 100 μm. These cantilevers could be actuated by passing DC current through a heater embedded in the probe base. The array was demonstrated to sequentially write ten different ODT patterns on a gold surface (Bullen *et al*., 2004). We subsequently refined the cantilever actuation technology to provide a commercial device (Figure 6). We have developed current-driven Active Pen™ cantilever arrays that allow independent actuation and retraction of each cantilever, potentially enabling writing with multiple inks in a single pass. The writing/reading capabilities of each cantilever can be individually tailored depending on whether the cantilever has been turned on or off. The Active Pen tool is specifically engineered for flexible and multiplexed nanopatterning, with lateral tip spacing as low as 23 μm.

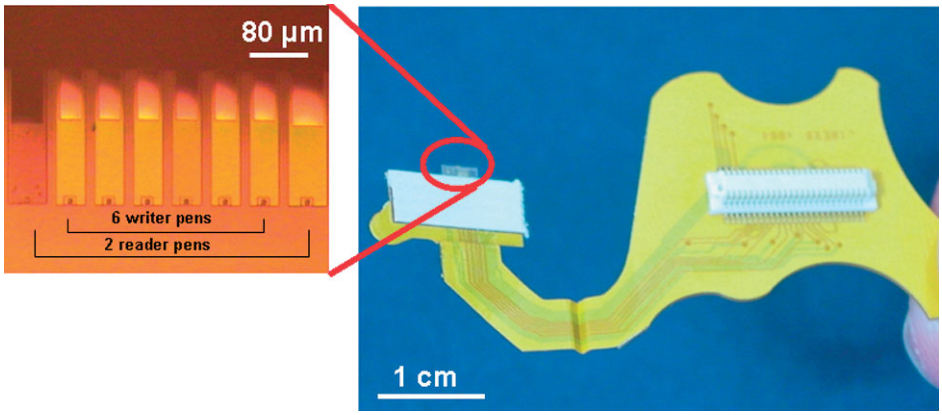

Fig 6. A commercially available active pen device, with electrical connector and flex circuit showing. Left inset: An expanded view of the eight cantilevers shows the far left reader pen actuated; its color changes because of the substantially different angle of the cantilever relative to its neighbors. This figure is available in colour online at www.interscience.wiley.com/SCA.

Using thermal bimorph technology, individual cantilevers can be actuated to enable multi-ink writing without any cross-contamination or unintended surface patterning. Additionally, "reader" tips can be left clean to image surface patterns, or address specific surface structures without unintentional inking. Active Pens are used in conjunction with our Universal Inkwells, which enable selective inking of individual pens without cross-contamination. As combined patterning of biological materials, small functional molecules, and inorganic nanoparticles becomes more necessary to produce functional nanostructures, such tools will be pivotal to nanotechnology research and development.

Commercially Available Massively Parallel Nanopatterning

Although the DPN process has been successfully demonstrated for a variety of applications in academic and government research labs, critics have 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. We generated internal prototypes throughout 2003 and 2004 that constituted an entire 4 in. wafer, and contained 1.3 million pens (Rosner and Demers, 2005). Although this device was beneficial as a MEMS exercise and a marketing tool, it could not realistically be implemented in that form.

Beginning in early 2005, researchers in the Mirkin group at Northwestern University (Evanston, IL) expressed interest about using the above-mentioned prototype, but dicing it into smaller pieces that could be reasonably affixed to an NSCRIPTOR scanner. The resulting collaboration 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 (Salaita *et al*., 2006). With throughput exceeding 1×10^7 μm^2/h, 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 as shown in Figure 7. In that work, an image 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, which was imaged optically as shown in Figure 8. They also used these DPN-generated thiol templates to create fibronectin arrays (NanoInk internal communication). Initial challenges included 2D planar surface alignment, which was overcome through a combination of taller tips and an epoxy-resin-based self-leveling technique. This massively parallel approach to DPN works because DPN is effectively force-independent, and thus 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). The highest cantilever density ever reported in 1 cm^2 is 55,000 tips. Fundamentally, this enables flexible direct writing with a variety of molecules, simultaneously generating 55,000 duplicates at the resolution of single-pen DPN.

This work was extended to direct writing of biomolecules by our collaborators at Forschungszentrum Karlsruhe (Lenhert *et al*., 2007). Working with the phospholipid 1,2-dioleoyl-sn-glycero-3-phosphocholine

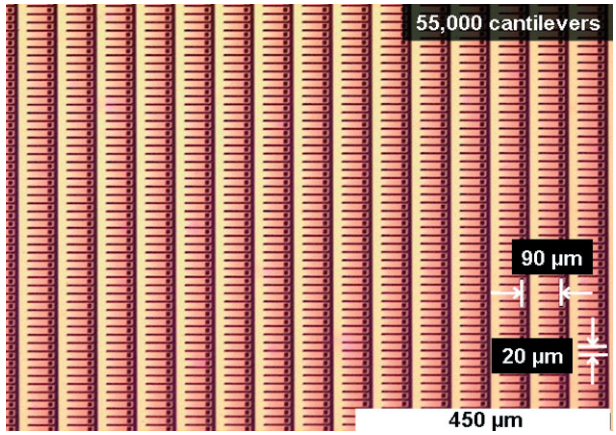

Fig 7. Optical microscope image of the 2D nano PrintArray (tips facing up) showing the pitch, spacing, and high yield. Here 832 cantilever tips are shown, roughly 1.5% of the entire array. (55,000 tips constituted of 110 rows by 500 columns).

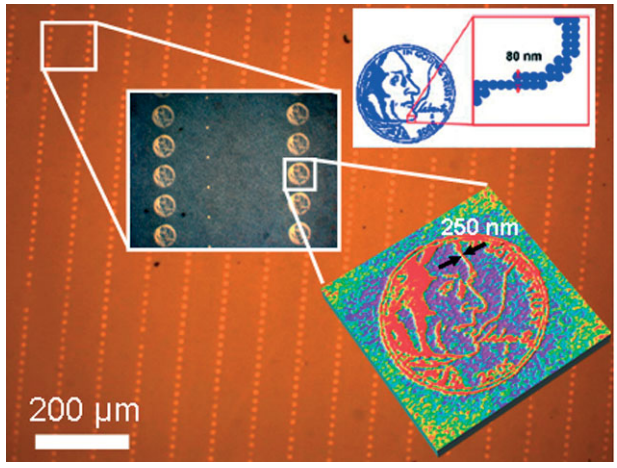

Fig 8. Jefferson Nickel Patterning data from the 2D nano PrintArray showing a region of 55,000 replicas of the Jefferson nickel. Inset: An high-resolution AFM image of a set of features produced by a single tip. Reproduced with permission from Nature Publishing Group (Salaita *et al*., 2007).

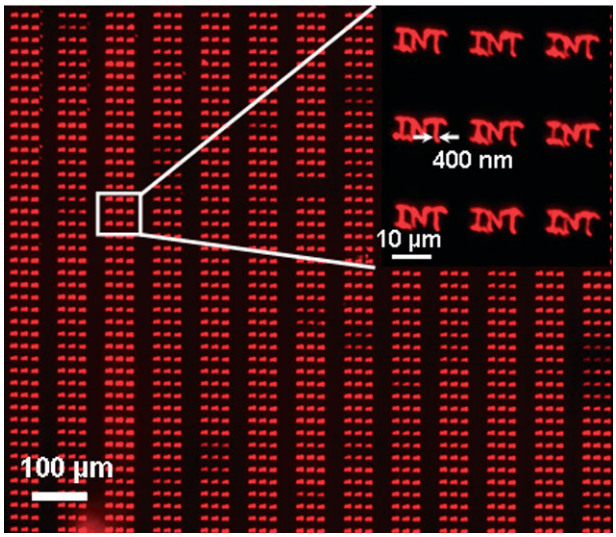

Fig 9. Fluorescence micrographs of phospholipid patterns generated by the 2D nano PrintArray. The substrate was a glass coverslip used as purchased, without further cleaning or treatment. Inset: A higher magnification of the area outlined by the white square. Reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA (Lenhert *et al*., 2007). This figure is available in colour online at www.interscience.wiley.com/SCA.

(DOPC), they were able to pattern complex features at an astounding throughput of 3×10^{10} μm^2/h, and showed that 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 (Figure 9). 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, and provides a way to make patterns for studying cooperative cell–substrate interactions. There is no other known method for generating heterogeneous, multivalent, planar supported lipid bilayers covering large areas with feature sizes smaller than a single cell.

In spite of the impressive results shown above, several prominent engineering hurdles stood between the devices these groups used and a robust commercial offering. Significant challenges still included leveling the array with respect to the substrate and 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. Either of these scenarios can result in nonuniform patterning or possible cantilever damage. Our collaborators' method for mounting the devices on the instrument involved setting the device on the sample surface (where it was naturally level), and then bringing the scanner in contact with the device with a small blob of epoxy in between. However, the epoxy takes more than one hour to set, and even still can introduce volume distortion that can affect the leveling. Additionally, if multiplexed ink delivery methods are used to address different inks to different tips, the surface contact time will introduce cross-contamination. Further, it is not commercially viable to spread epoxy onto an AFM scanner.

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 formation of a precision nanoscale pattern. We have engineered the device to be easy to use, wire-free, and fully integrated with the NSCRIPTOR scanner, stage, and sophisticated lithography routines. As a part of our commercial offering, we have introduced etched view ports (shown in Figure 10(a)) in a silicon handle wafer (instead of the pyrex used in the prototypes); coupled with a precisely machined magnetic wedge to attach the device to the NSCRIPTOR (Figure 10(b)), we have overcome the bulk of these hurdles. Leveling is accomplished by examining cantilever deflection through these view-ports at three different points, noting the z-height differences, and then using software routines to calculate and execute planarity with the three z-motors. Contrasted with earlier methods, the view-port leveling takes only a few minutes. (The NanoInk logo data shown in Figure 11 was generated in under 30 min, from mounting the probes to finishing the etch-resist process.) Mounting the device is very straightforward via the magnetic wedge, and prevents cross-contamination. Unlike the previous prototypes, with these new devices it is possible to view the substrate through the handle wafer, align to preexisting surface features (such as inkwells), and in principle even align a laser to a cantilever for imaging. Figure 12 shows a forest of these cantilevers, and the inset illustrates the degree of curvature achieved by the fabrication process. No metal coating or annealing was required for this, and the curvature provides a large freedom of travel (FOT) for the tips as they touch the substrate, making the leveling process even more forgiving. This is also important because not all chemistries are amenable to gold-coated tips, (i.e., gold-coated tips quench fluorescence, which can be a problem if trying to image fluorescently tagged molecules while on the array). The view-ports provide versatility for a variety of different samples, including samples of different thicknesses with the same array. They also provide the flexibility to move across larger samples that might not be perfectly flat, and quickly spot check to reachieve "level." Further, the fact that the silicon handle chip is not transparent (or even translucent) is beneficial because it prevents ambient light from bleaching biological inks. We should note a distinct difference between this approach of *direct deposition* over a large area, and *manipulating* the surface through independent actuation and heating of each cantilever as demonstrated in the case of the Millipede by IBM,

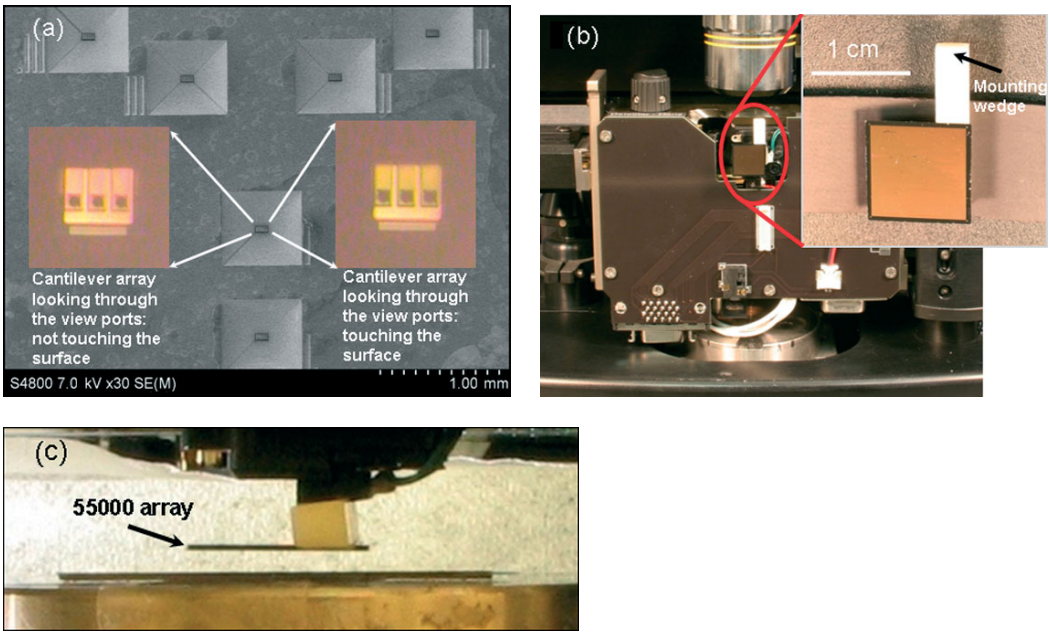

Fig 10. (a) SEM image of the view-ports etched into the 2D nano PrintArray handle wafer, enabling the user to monitor cantilever deflection to determine array leveling. (b) The device magnetically affixed to the Nscriptor scanner. Inset: Zoomed image of the device itself, showing the mounting wedge. (c) A side profile view of the device mounted to the Nscriptor via magnetic wedge, shown over 1,000 μm above the substrate.

which had an array of 32 by 32 cantilevers (Vettiger *et al*., 2000).

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: (i) rapidly and flexibly generating nanostructures (e.g., Au, Si) via etch-resist techniques; (ii) 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 (iii) directly writing biological materials. Using established templating techniques, these advances enable screening for biological interactions at the level of a few molecules, or of even single molecules. This in turn can enable engineering the cell–substrate interface at subcellular resolution. In addition to suggesting novel methods for studying the effectiveness of new drugs and delivery techniques, this technology allows users to routinely pattern libraries of small molecules over very large areas, and to realistically practice single-cell experimentation. Studies of cell adhesion, growth, motility, and differentiation can be easily conducted on custom, molecularly designed substrates. Using 2D nanopatterning, the process is scalable and can cover large areas for statistically significant investigations of these individual bioprocesses. The 2D DPN templating and biomolecule deposition opens up a completely new area of single-particle biology; it is possible to probe interactions between surfaces and single viruses, spores, or cells. For example, DPN-generated arrays have been demonstrated to monitor single-cell infectivity from virus-particle nanoarrays (Vega *et al*., 2007) as shown in Figure 13. In this work, Vega and coworkers immobilized antibodies on DPN-patterned MHA-Zn^{2+} regions. After initial MHA patterning, the unpatterned regions were passivated with polyethylene glycol (PEG), and the whole substrate was immersed in an ethanolic $Zn(NO_3)_2{\cdot}6H_2O$ solution. These MHA-Zn^{2+} regions were then exposed to rabbit antibodies creating nanoarrays, which were later incubated with fluorescent SV5 viral solution. The resulting virus nanoarrays were used for CV1 cell infection experiments. In this way, DPN-generated MHA patterns were used for subsequent cell infectivity measurements, thus demonstrating a bottom-up lithographic approach.

Further, because these inks can be used as etch-resist materials, we can perform maskless rapid prototyping across large areas, forming combinatorial arrays of metallic or solid-state features varying in size, spacing, and shape. Combined with universally applicable inks, these capabilities engender several of the applications we discuss below.

The Desktop Nanofab Approach

As noted above, a true Desktop Nanofab would be a system that allows a nonexpert user to rapidly create high-resolution, scalable nanostructures with a wide variety of materials, drawing upon well-characterized

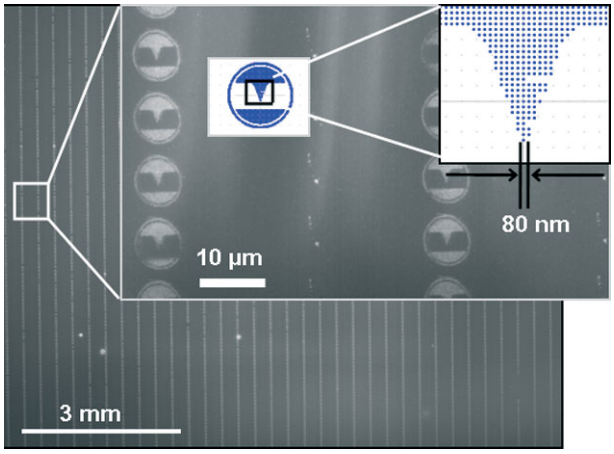

Fig 11. Optical images of the NanoInk logo following the successful process of mounting, leveling, and printing ODT with the 2D nano PrintArray. The design includes 2,250 dots of 80 nm diameters. Patterns were generated using ODT as the etch resist. Only a fraction of the 55,000 printed logos are shown. This figure is available in colour online at www.interscience.wiley.com/SCA.

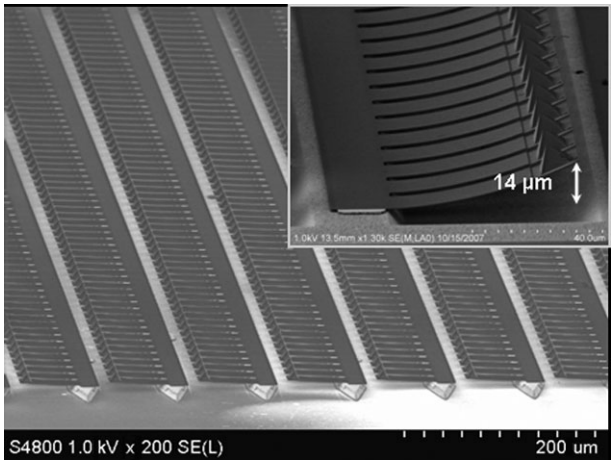

Fig 12. SEM image showing multiple rows of cantilevers attached to silicon ridges. The inset shows individual cantilevers, while also highlighting the 7.5 μm tall sharpened tips and inherent cantilever curvature ($\sim$ 14 μm bow).

ink and substrate pairings. To get uniform feature sizes and reliable tip inking in DPN, the development of a suitable ink carrier material is pertinent. Ideally, this carrier material will be deposited together with the ink of interest, resulting in uniform patterns after exclusion of the carrier material with subsequent processing steps. Potentially, there will be universal carriers for certain groups of inks—a suitable carrier for patterning biological molecules (DNA, proteins), and another for "hard inks" like metal nanoparticle DPN.

As a part of this work, our research teams have developed a novel ink for patterning certain types of

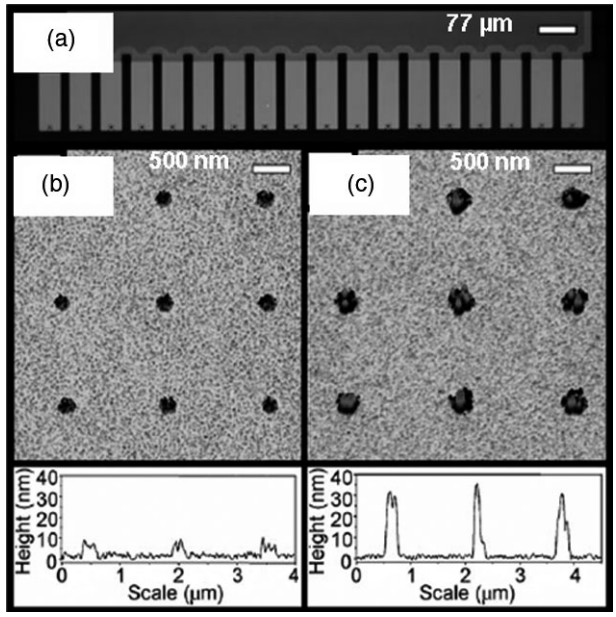

Fig 13. Monitoring single-cell infectivity from virus-particle nanoarrays created by parallel DPN. (a) Optical image of a NanoInk 18 cantilever 1D Passive Pen Array. (b) Tapping mode AFM topography image before, and (c) after encapsulation of SV5 virus particles. Reproduced with permission from Wiley-VCH Verlag GmbH & Co. KGaA (Vega *et al.,* 2007).

DNA onto substrates of interest such as SiO_2, gold, and glass (commercially available as "Just Add DNA™"). Spotting of short oligonucleotide chains of as many as 60 base pairs onto a chemically modified surface was optimized, and this carefully controlled DPN patterning process provides feature sizes as small as 200 nm in diameter. Using our DNA probes and Inkwells, these feature sizes allow simultaneous deposition of different DNA strands onto a single surface.

Beyond DNA, we are currently pursuing several tracks for the different classes of universal inks. Suitable carriers for biological ink DPN include Agarose (Rozkiewicz, 2007), PEG (NanoInk internal communication), phospholipids (Lenhert *et al*., 2007), and possibly gelatin nanoparticles (Truong-Le *et al*., 1999; Coester *et al*., 2000). All of these carriers would be ideally suited for biological patterning due to their characteristics of water retention, permeability to oxygen, and formation of weak bonds with the substrate facilitating easy removal subsequent to patterning. PEG has also been recently employed for preparing positive and negative nanostructures via (NanoInk internal communication).

The "Nanofab" to Enable a Family of Near-Term Applications: DPN as a Means to an End

Above we noted the broad middle ground of applications where DPN can fill the needs of many,

and that these are no longer simply capabilities of DPN waiting to find a use, but actual applications of the technology where DPN is a means to an end.

Deposition of biological materials onto detecting substrates

There is a general need to be able to detect biological materials at the single-molecule level, and these techniques provide an avenue via examining spectroscopic information. DPN's ability to place biologically active materials onto various engineered substrates with nanoscale precision will be a strong enabler as novel detection techniques such as surface enhanced Raman spectroscopy (SERS), surface enhanced resonance Raman spectroscopy (SERRS), and Total Internal Reflection Fluorescence (TIRF) continue the evolution toward single molecule detection. Achieving the highest levels of sensitivity will bring value in both diagnostic and research applications; research is already well underway to demonstrate high levels of sensitivity to important biomarker molecules. Dip pen nanolithography may be the only way to combine the small volumes of fragile samples necessary with the small spatial regimes required.

Direct deposition of conductive traces

We are currently investigating metal nanoparticle-based inks as a means to satisfy a definite market need. A wide variety of researchers and engineers inquire about conductive trace patterning, for everything from device interconnects to failure analysis probing. In these cases, their needs are satisfied by DPN's capabilities: producing nanoscale features flexibly, on the fly, in a cost-efficient manner, and registering them to existing surface features.

High-density protein nanoarrays

Current proteomics research is limited by the architecture of commercially available protein chips: several thousand spots, with 50–100 μm dot sizes. Dip pen nanolithography provides a way to pattern significantly smaller features in a smaller array, minimizing the volume of precious analyte required for the experiment (e.g., a patient's blood sample being screened for disease markers), all while maintaining the bioactivity of the proteins. Moreover, by harnessing DPN's nanoscale resolution it is possible to create arrays of single molecules. We are currently involved in research to demonstrate this application, although significant engineering challenges are involved in getting several hundred or thousand different proteins 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 protein inks of nearly identical properties to ensure even fluidic control, tip loading, and ink transport from the tip.

Peptide nanoarrays

Like proteins, peptide patterning fills an important need in the biological market. Current commercial systems pattern on custom cellulose substrates, but DPN can provide a way to pattern on much more commercially attractive glass slides, and at a resolution far below what is otherwise available.

Metal oxide sol-gel gas nanosensors

Above we noted the preliminary work (Su *et al*., 2004) showing sensor elements from sol gels. Companies are generally interested in cheaper, faster, and more sensitive sensors to detect harmful gases and/or biological warfare agents, and we have projects underway finalizing robust protocols for fabricating such sensor elements via DPN. These sensors become increasingly sensitive as the line width decreases, making DPN a very attractive method for generating these structures.

Rapid and flexible fabrication of functional nanostructures via etch resist

Taking advantage of etch-resist capabilities described above (Zhang *et al*., 2003; Salaita *et al*., 2006), 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 centimeter square area. Numerous researchers in the field of SERS would benefit from a method of quickly generating arrays of noble metal nanostructures. Many years of research into the origin of SERS have found that the most important requirement for a SERS substrate is its ability to increase the electromagnetic field at the surface. These researchers have found that 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 resonances and field enhancing properties of these metal 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. Currently, 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. In order for SERS to be used in future sensing devices, nanopatterned noble metal surfaces must combine reproducibility and maximized SERS enhancement; DPN methods offer a way to quickly fabricate such patterns. 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.

Summary and Outlook

This review presents the current state-of-the-art in DPN and illustrates our efforts to introduce DPN to new research areas and initiate applications development. Our assessment of bona fide DPN *applications* reflects our need to identify trends in academic research and elevate these to realizable commercial applications, both in the short term and midterm. Several longer term applications may include using DPN templates to study stem cell differentiation, direct-write DPN patterning onto medical devices, combinatorial discovery of functional nanomaterials, and patterning magnetic materials for data storage.

In less than eight years since its discovery, DPN has proved capable of patterning a variety of materials onto a variety of substrates. Dip pen nanolithography-deposited patterns have been used as a resist in an etching step, or as a template for bottom-up assembly. Because DPN works in ambient conditions, it offers a significant advantage for materials that are environmentally sensitive or incompatible with existing microfabrication techniques, such as biomolecules, conductive polymers, or ceramics (e.g., for sensors and molecular electronics). In effect, a whole DPN "toolkit" has been built, one that interfaces the inorganic with the organic, the world of microelectronics with the world of biochemistry and polymers. All of these attributes have become highly scalable with our development of a commercial 2D nanopatterning solution—one that is 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 proved and in practice, desirable future developments could include laser feedback on viewable cantilevers for immediate imaging, and automated step-and-repeat lithographic routines. Multiplexed ink delivery to a large number of tips remains a fundamental challenge—one that we are approaching 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.

References

Bullen D, Chung SW, Wang XF, Zou J, Mirkin CA, *et al*.: Parallel dip-pen nanolithography with arrays of individually addressable cantilevers. *Appl Phys Lett* **84**, 789–791 (2004).

Coester C, Kreuter J, von Briesen H, Langer K: Preparation of avidin-labelled gelatin nanoparticles as carriers for biotinylated peptide nucleic acid (PNA). *Int J Pharm* **196**, 147–149 (2000).

Demers LM, Park SJ, Taton TA, Li Z, Mirkin CA: Orthogonal assembly of nanoparticle building blocks on dip-pen nanolithographically generated templates of DNA. *Angew Chem Int Ed Engl* **40**, 3071–3073 (2001).

Ginger DS, Zhang H, Mirkin CA: The evolution of dip-pen nanolithography. *Angew Chem Int Ed Engl* **43**, 30–45 (2004).

Haaheim J, Eby R, Nelson M, Fragala J, Rosner B, *et al*.: Dip Pen Nanolithography (DPN): Process and instrument performance with NanoInk's NSCRIPTOR system. *Ultramicroscopy* **103**, 117–132 (2005).

Huck WTS: Self-assembly meets nanofabrication: Recent developments in microcontact printing and dip-pen nanolithography. *Angew Chem Int Ed Engl* **46**, 2754–2757 (2007).

Jang JY, Schatz GC, Ratner MA: How narrow can a meniscus be? *Phys Rev Lett* **92**, 2004,; Art. No. 085504-1—085504-4.

Jang JY, Hong SH, Schatz GC, Ratner MA: Self-assembly of ink molecules in dip-pen nanolithography: a diffusion model. *J. Chem. Phys* **115**, 2721–2729 (2001).

Jaschke M, Butt HJ: Deposition of organic material by the tip of a scanning force microscope. *Langmuir* **11**, 1061–1064 (1995).

Jegadesan S, Sindhu S, Advincula RC, Valiyaveettil S: Direct electrochemical nanopatterning of polycarbazole monomer and precursor polymer films: ambient formation of thermally stable conducting nanopatterns. *Langmuir* **22**, 780–786 (2006).

Lee KB, Lim JH, Mirkin CA: Protein nanostructures formed via direct-write dip-pen nanolithography. *J Am Chem Soc* **125**, 5588–5589 (2003).

Lee KB, Park SJ, Mirkin CA, Smith JC, Mrksich M: Protein nanoarrays generated by dip-pen nanolithography. *Science* **295**, 1702–1705 (2002).

Lenhert S: *Materials Integration by Dip-pen Nanolithography in Nanotechnology* Vol. 2, Nanoprobes, WILEY-VCH, Weinheim (2008).

Lenhert S, Sun P, Wang Y, Fuchs H, Mirkin CA: Massively parallel dip-pen nanolithography of heterogeneous supported phospholipid multilayer patterns. *Small* **3**, 71–75 (2007).

Lewis A, Kheifetz Y, Shambrodt E, Radko A, Khatchatryan E, *et al*.: Fountain pen nanochemistry: atomic force control of chrome etching. *Appl Phys Lett* **75**, 2689–2691 (1999).

Marrian CRK, Tennant DM: Nanofabrication. *J Vac Sci Technol A* **21**, S207–S215 (2003).

McKendry R, Huck WTS, Weeks B, Florini M, Abell C, *et al*.: Creating nanoscale patterns of dendrimers on silicon surfaces with dip-pen nanolithography. *Nano Lett* **2**, 713–716 (2002).

Myung S, Lee M, Kim GT, Ha JS, Hong S: Large-scale "surface-programmed assembly" of pristine vanadium oxide nanowire-based devices. *Adv Mater* **17**, 2361–2365 (2005).

Nafday OA, Vaughn MW, Weeks BL: Evidence of meniscus interface transport in dip-pen nanolithography: an annular diffusion model. *J Chem Phys* **125**, 4 (2006a).

Nafday OA, Pitchimani R, Weeks BL, Haaheim J: Patterning high explosives at the nanoscale. *Propell Explos Pyrotech* **31**, 376–381 (2006b).

Nelson BA, King WP, Laracuente AR, Sheehan PE, Whitman LJ: Direct deposition of continuous metal nanostructures by thermal dip-pen nanolithography. *Appl Phys Lett* **88**, 2006,; Art. No. 033104-1—033104-3.

Peterson EJ, Weeks BL, De Yoreo JJ, Schwartz PV: Effect of environmental conditions on dip pen nanolithography of mercaptohexadecanoic acid. *J Phys Chem B* **108**, 15206–15210 (2004).

Piner RD, Zhu J, Xu F, Hong SH, Mirkin CA: "Dip-pen" nanolithography. *Science* **283**, 661–663 (1999).

Rosner BT, Demers LM: *Dip Pen Nanolithography: Applications and Functional Extensions in Dekker Encyclopedia of Nanoscience and Nanotechnology*, Taylor and Francis Group, New York (2005).

Rozkiewicz DI: Covalent microcontact printing of biomolecules, PhD Thesis, University of Twente (2007).

Ryu KS, Wang XF, Shaikh K, Bullen D, Goluch E, *et al*.: Integrated microfluidic linking chip for scanning probe nanolithography. *Appl Phys Lett* **85**, 136–138 (2004).

Salaita K, Wang YH, Mirkin CA: Applications of dip-pen nanolithography. *Nat Nanotechnol* **2**, 145–155 (2007).

Salaita KS, Lee SW, Ginger DS, Mirkin CA: DPN-generated nanostructures as positive resists for preparing lithographic masters or hole arrays. *Nano Lett* **6**, 2493–2498 (2006a).

Salaita KS, Wang YH, Fragala J, Vega RA, Liu C, *et al*.: Massively parallel dip-pen nanolithography with 55000-pen two-dimensional arrays. *Angew Chem Int Ed Engl* **45**, 7220–7223 (2006b).

Schenk M, Futing M, Reichelt R: Direct visualization of the dynamic behavior of a water meniscus by scanning electron microscopy. *J Appl Phys* **84**, 4880–4884 (1998).

Schwartz PV: Molecular transport from an atomic force microscope tip: a comparative study of dip-pen nanolithography. *Langmuir* **18**, 4041–4046 (2002).

Sheehan PE, Whitman LJ: Thiol diffusion and the role of humidity in "dip pen nanolithography". *Phys Rev Lett* **88**, 2002,; Art. No.156104-1—156104-4.

Su M, Aslam M, Fu L, Wu NQ, Dravid VP: Dip-pen nanopatterning of photosensitive conducting polymer using a monomer ink. *Appl Phys Lett* **84**, 4200–4202 (2004).

Truong-Le VL, Walsh SM, Schweibert E, Mao HQ, Guggino WB, *et al*.: Gene transfer by DNA-gelatin nanospheres. *Arch Biochem Biophys* **361**, 47–56 (1999).

Vega RA, Shen CKF, Maspoch D, Robach JG, Lamb RA, *et al*.: Monitoring single-cell infectivity from virus-particle nanoarrays fabricated by parallel dip-pen nanolithography. *Small* **3**, 1482–1485 (2007).

Vettiger P, Despont M, Drechsler U, Durig U, Haberle W, *et al*.: The "Millipede" - More than one thousand tips for future AFM data storage. *IBM J Res Dev* **44**, 323–340 (2000).

Wang YH, Maspoch D, Zou SL, Schatz GC, Smalley RE, *et al*.: Controlling the shape, orientation, and linkage of carbon nanotube features with nano affinity templates. *Proc Natl Acad Sci U S A* **103**, 2026–2031 (2006).

Weeks BL, Vaughn MW, DeYoreo JJ: Direct imaging of meniscus formation in atomic force microscopy using environmental scanning electron microscopy. *Langmuir* **21**, 8096–8098 (2005).

Zhang H, Chung SW, Mirkin CA: Fabrication of sub-50-nm solid-state nanostructures on the basis of dip-pen nanolithography. *Nano Lett* **3**, 43–45 (2003).

Zhang H, Jin RC, Mirkin CA: Synthesis of open-ended, cylindrical Au-Ag alloy nanostructures on a Si/SiOx surface. *Nano Lett* **4**, 1493–1495 (2004).

Zhang H, Amro NA, Disawal S, Elghanian R, Shile R, *et al*.: High-throughput dip-pen-nanolithography-based fabrication of Si nanostructures. *Small* **3**, 81–85 (2007).

Zou S, Maspoch D, Wang Y, Mirkin CA, Schatz GC: Rings of single-walled carbon nanotubes: molecular-template directed assembly and Monte Carlo modeling. *Nano Lett* **7**, 276–280 (2007).