Surface Patterning

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Cantilever-Free Scanning Probe Molecular Printing**

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cantilever-free methods · molecular printing · polymer pen lithography · scanning probe microscopy · surface chemistry

Over the past decade, molecular printing tools and techniques[1] that enable the direct transfer and constructive delivery of molecules to a surface with sub-micrometer resolution have undergone transformational developments. Such progress not only increases the accessibility and generality of molecular printing to a broad scientific audience, but it also allows researchers to study diverse and complex systems ranging from the natural to the applied sciences. The broad category of molecular printing can be divided into 1) soft lithography,[2] known also as microcontact printing, and 2) scanning probe-based approaches originating from dip-pen nanolithography (DPN).[3] The invention of each technique marks an important departure from conventional lithography approaches in the semiconductor industry, which rely on both the delivery of energy and destruction of material on a surface to achieve the desired patterning result.[4]

Scanning probe technology began with the inventions of scanning tunneling microscopy (STM)[5] in 1981 and atomic force microscopy (AFM)[6] in 1986. STM allowed one to spatially resolve individual atoms on metal and semiconductor samples under ultrahigh vacuum using the tunneling current between a biased tip and a substrate. The limitations of STM to specific conditions and conductive samples led to the idea that a similar metrology tool could be developed to visualize surfaces in ambient environments by relying on forces between the tip and the sample rather than electrical signals. In particular, the AFM tip is fabricated on the end of a cantilever that acts as the force sensor; it is sensitive and flexible in the z direction, but rigid in the x and y directions.

After the invention of STM and AFM, researchers recognized that these tools might be useful for constructing nanoscale architectures. Indeed, the idea and goal of high-resolution, high-throughput nanolithography under ambient environmental conditions posed a challenge. While the impressive but highly impractical use of an STM tip to pick up and place atoms one at a time on a surface demonstrated the ultimate capability these tools might provide in nanomanufacturing,[7] it was not until 1999 that a technique based on AFM was invented.

DPN is both fundamentally and practically different from the pick-and-place STM-based approach to nanofabrication and represents a departure from techniques that deliver electrical,[8] thermal,[4,9] mechanical,[10] and photochemical energy[11] to a surface (Figure 1). Specifically, DPN used an AFM tip as a lithography tool to directly deposit chemical adsorbates as monolayers on gold surfaces with resolution below 100 nm.[3] This discovery was an important milestone, as it demonstrated that an AFM tip coated with a transportable material and the meniscus[12] that naturally forms at the tip–substrate point of contact could be used to generate stable nanostructures on a surface through subsequent chemisorption events. Since then, DPN has proven to be a versatile and general technique for patterning many nanostructures, including DNA,[13] proteins,[14] polymers,[15] sol–gels,[16] and both inorganic and organic nanostructures on a variety of substrates.[17]

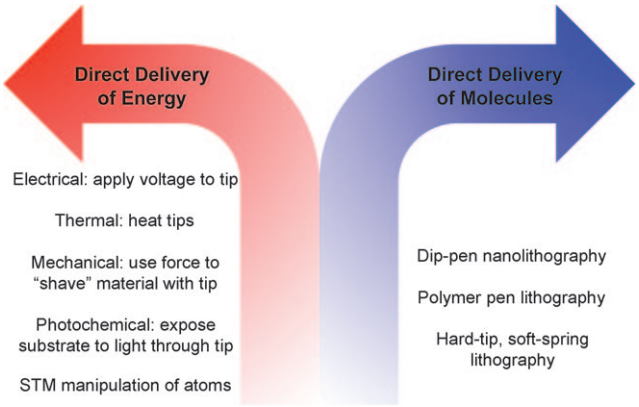

Figure 1. Different approaches to scanning probe-based nanofabrication, which can rely on the delivery of energy or molecules.

DPN has quickly evolved from a serial to a parallel technique, as one-dimensional[18] and two-dimensional Si cantilever pen arrays (Figure 2)[19] became available in 2000 and 2006, respectively. While this work demonstrates engineering feasibility of massively parallel arrays, practical

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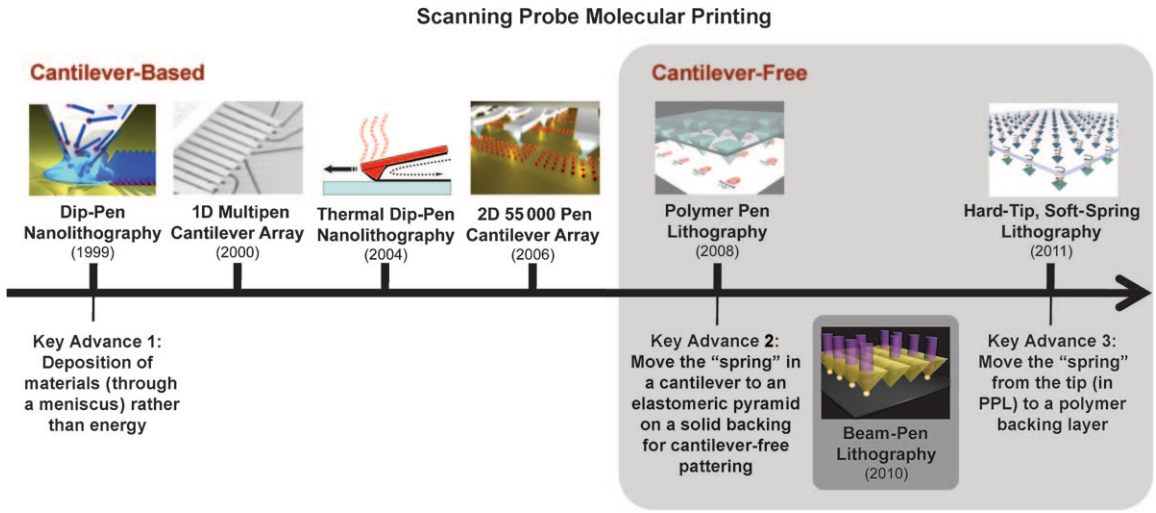

Figure 2. Timeline showing the evolution of scanning probe molecular printing from cantilever-based to cantilever-free techniques. Polymer pen lithography (PPL) merges the advantages of DPN and microcontact printing to enable highly parallel, simple, robust, and inexpensive delivery of molecules to a surface for generating nanoscale and microscale architectures. Hard-tip, soft-spring (HSL) lithography overcomes the feature size limits of elastomeric pens in PPL by moving the spring to a polymer backing layer and using an array of sharp Si tips. Though beam pen lithography (BPL) is not a molecular printing tool, it makes use of elastomeric pen arrays to control the distance between apertures and a surface for fabricating sub-diffraction-limit or larger features.

considerations and limitations exist with these cantilever-based designs in terms of fabrication complexity, pen density, associated costs, and array alignment strategies.

In 2008, a new concept within molecular printing was introduced that combined the strengths of microcontact printing and scanning probe approaches while eliminating the weaknesses—polymer pen lithography (PPL).[20] Twenty-two years after the invention of AFM and cantilever-based tools, PPL uniquely demonstrated cantilever-free patterning of nanoscale to microscale features by using an elastomeric array of inverted pyramids attached to a transparent glass backing layer, which could then be mounted in an atomic force microscope and finely controlled with piezoactuators. Like in DPN, when a polymer pen is in contact with a surface, ink diffusion causes feature size to increase with dwell time, but unlike DPN, the degree of elastomeric pen deformation can also dictate feature size (Figure 3 a). In PPL, tips are able to toggle between a sharp point and a flattened surface to generate features of different dimensions even while the tip–substrate contact time is held constant.[21] This important concept of integrating elastomeric pyramid arrays mounted on transparent solid backings with piezoactuators obviates the need for a cantilever, because the spring that a cantilever normally represents is built into the polymer pen itself. PPL is conceptually transformational because it marks the first time that cantilevers were not used in a scanning probe experiment to generate molecule-based nanostructures (Figure 2).

Moreover, the pen arrays used in PPL are quite forgiving, in part because of the poly(dimethylsiloxane) (PDMS) composition and properties, but also because of the elastomer base that adheres to the glass backing. This tolerance is observed when the pen array is subject to small *z*-piezo extensions, just when the tips make the slightest contact with a surface (Figure 3 a). Although the feature size might be expected to depend linearly on *z*-piezo extension, it does not change significantly for small extensions (less than 1 μm). These attributes allow the array to be aligned with a substrate of interest in a straightforward and simple manner by eye, though even more precise strategies of pen array force maximization can also be employed.[22]

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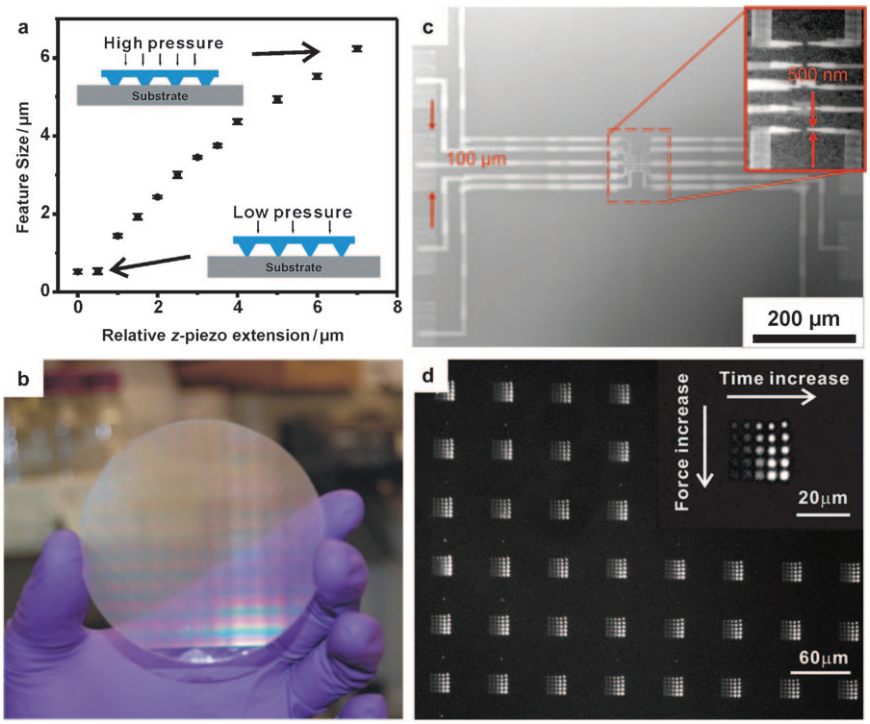

Figure 3. a) Force-dependent feature size increase in PPL. At low *z*-piezo extensions, the elastomer support layer is quite forgiving and allows the pen array to be aligned such that all tips are in contact with the substrate. b) Optical image of a four-inch (ca. 10 cm) wafer containing 11 million polymer pens. c) Optical micrograph of etched gold circuit patterns having nanometer- (inset) and micrometer-scale features fabricated by PPL.[20] d) Fluorescence optical micrograph of prostate specific antigen (PSA) arrays made by PPL and labeled with AlexaFluor 488-labeled anti-PSA antibodies. The magnified image (inset) shows the feature sizes as a function of increased time and force.[23]

The highly scalable and low-cost aspects of PPL make it an attractive technique for molecular printing. Molecular materials ranging from proteins[23] to polymers[24] that can be printed in DPN apply to PPL as well. Furthermore, conventional photolithography methods are used to fabricate the PPL mold; depending on the desired pen array specifications, the photolithography mask defines the array size, density, and pen height. As many as 11 million polymer pens have been fabricated on a four-inch (ca. 10 cm) wafer (Figure 3b).[20] Furthermore, PPL relies on commercial materials that are inexpensive and readily available. When used properly, each mold enables numerous pen arrays to be made; in the event that a mold or pen array is damaged or defective, it is not cost-prohibitive to make or use a new one. After fabricating and mounting the pen array into an AFM instrument, completely different designs ranging from circuit diagrams to complicated logos can be created without ever needing a new mask or mold, because the instrument controls the patterning (Figure 3c). Given the force-dependent properties of PPL, researchers can quickly generate combinatorial patterns over large areas by simply tilting the array; in a single experiment, one side of the pen array can produce nanoscale features while the other produces microscale ones.

The many advantages and abilities offered by PPL have recently opened the area of cantilever-free scanning probe approaches to complementary techniques (Figure 2). For example, the transparent nature of PDMS along with precise *z*-piezo control of pen distance can be exploited for massively parallel near-field scanning optical microscopy (NSOM) lithography; this extension of PPL, which is not a molecular printing tool, but important in its own right, is termed beam pen lithography (BPL).[25] In BPL, the same pen array used in PPL is coated with an opaque metal layer (e.g. Au) except at the tip, which acts as an aperture. The entire array can then be positioned in near-field or far-field distances of a photosensitive surface to produce sub-diffraction-limit (e.g. 100 nm features for an incident wavelength of ca. 400 nm) or larger features, respectively, when light illuminates the backside of the pens. Though all of the pens in the array make contact with the substrate, the ability to control which pens are illuminated in BPL provides another orthogonal parameter for patterning.

While both PPL and BPL are suitable for fabricating nano- and microscale features in a high-throughput manner, it is challenging to achieve feature dimensions smaller than 100 nm that are characteristic of DPN. In this regard, an approach reminiscent of PPL strategies has been reported, termed hard-tip, soft-spring lithography (HSL).[26] HSL relies on hard Si tips (diameter = 22 nm) attached to an elastomeric backing to easily produce patterns with features smaller than 50 nm. Unlike PPL, however, HSL exhibits no force dependence during patterning, because the elastomeric layer absorbs any z-direction deformation; thus as with DPN, ink diffusion from the tip governs feature size. The conceptual importance of HSL is that it demonstrates how the spring in a DPN or PPL experiment can be converted from a cantilever or pyramid, respectively, to a thin soft layer that supports incompressible tips.

The development of and progress within scanning probe cantilever-free lithography approaches such as PPL and HSL are transforming molecular printing and enabling advances in fundamental science and technology. These simple and robust techniques for high-throughput, high-resolution patterning can be easily utilized for numerous systems spanning biology, chemistry, physics, engineering, and nanotechnology. Indeed, the massively parallel pyramid-based arrays may become to scanning probe lithography and, in particular, molecular printing, what disposable razor blades are to shaving. In the coming years, it is likely that these cantilever-free scanning probe molecular printing tools will become the equivalent of rapid prototyping devices akin to a "desktop fab". Areas where they are likely to be exploited include the investigation of cell–protein interactions, fabrication and functionalization of biomolecule diagnostic tools, chemical sensors, catalyst

testbeds, and optoelectronic devices that range from the nano- to the microscale.

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