CHAPTER 13

Integrated Nanostructures and Nanodevices Fabricated by Dip-Pen Nanolithography

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Summary

The ability to tailor the chemical composition and structure of a surface at the nanometer length scale is essential for fabricating novel nanomaterials, understanding underlying nano-science and engineering, and developing integrated systems for demanding applications. Dip-pen nanolithography (DPN), based upon an atomic force microscope, has recently evolved as a unique tool that allows one to routinely pattern an extraordinary array of materials onto all manner of surfaces at the sub-100-nm to many-micrometer length scale. This chapter briefly reviews the rapid growth of the research field of DPN with particular emphasis on biological applications.

KEYWORDS: Surface, Patterning, Nanomaterials, Atomic force microscope, Dip-pen nanolithography.

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INTRODUCTION

Nanolithography is the art and science of etching, writing, or printing at the nanoscopic level, in which the dimensions of characters are on the order of nanometers (1). Recently, there has been considerable interest in developing lithographic methods for patterning nanostructures because of their scientific importance and potential technological applications in integrated molecular electronics, high density information storage devices, and ultrahigh sensitive biosensors (2). Conventional nanolithography techniques, including optical and electron beam lithography, have either fundamental limitations with respect to complex procedure or unsuitable to handle a large variety of organic and biological molecules that are indispensable building blocks in nanotechnology. To these regards, alternative nanolithography techniques, such as nano-imprint lithography and scanning probe microscope (SPM)-based lithography, have been developed over the past twenty years (3). In particular, SPM-based approaches offer both ultrahigh resolution and *in situ* imaging capabilities. However, most of these methods are indirect or surface "destructive" approaches in which a passivating layer as template for surface modification through etching, oxidation, and shaving, or grafting were required (4). In addition, these methods typically suffered from low throughput due to inherent limitations associated with the instrument (4).

Dip-pen nanolithography (DPN) is a departure from existing forms of scanning probe lithography (SPL), which allows the direct deposition of a diverse variety of materials via an AFM tip onto surfaces of interest with nanoscale resolution (5-7). Compared to other SPL methods, DPN is a direct-write lithographic technique that allows one to routinely pattern self-assembled monolayer (SAM) nanostructures with high registration and sub-50nm resolution. Since the introduction of DPN to the research community in 1999 (5), a significant progress has been made towards various applications of the method and fundamental understanding of molecular transport phenomena. A vast array of molecules, including small organic molecules (8,9), biological molecules (10-12), polymers (13,14), and metal ions (15,16), have been patterned via the DPN process. In addition, the patterning substrates have been expanded to include insulating, semiconducting, and metallic materials (5-7,9,17-19). Owing to the unique capabilities of DPN, the approaches, based upon a combination of the DPN and other techniques, have also been reported. More importantly, DPN can be used to pattern nanostructure arrays in a massively parallel fashion. Indeed, one and two dimensional arrays of probes with numbers up to

55,000 have been already developed and proved successful in the DPN process (20). The effort of parallelization will clearly make DPN a promising workhorse nanofabrication tool, and potentially open up many applications, including high throughput screening of cell-surface interactions (21, 22) and viral infectivity (23). The use of small sample amounts in DPN should be particularly attractive to biologists for significantly lowering limits of detection of target molecules. This chapter is designed to illustrate the fundamental applications of DPN for fabrications of nanostructures and nanodevices in the context of the current progress being made in this field.

SMALL ORGANIC MOLECULES AND POLYMERS

The first successful demonstration of DPN was reported by delivering alkanethiol molecules (octadecanethiol: ODT and 16-mercaptohexadecanoic acid: MHA) to Au substrates (5-7). The reason to choose molecules with thiol-terminal groups is because thiolated molecules strongly bind gold surface and form stable self-assembled monolayers (SAMs) as evidenced by highly ordered crystalline lattice structure. Additionally, high resolution and registration can also be readily achieved by DPN. With the advent of the DPN for these small thiolated molecules, it has been shown that the molecule transport in DPN process is complicated and likely influenced by many parameters, including the nature of chemical interactions between the ink and the substrate, patterning temperature, relative humidity, tip shape, and tip-substrate contact time, etc. In particular, the patterning temperature and relative humidity have been extensively studied in the hope that correlations between these parameters and the resulting nanostructures could be established. It is generally believed that under ambient conditions the volume of water meniscus formed at the tip-substrate interface increases with relative humidity for MHA patterning (24). In contrast, a water meniscus for ODT patterning is not required (25). This difference can be attributed to the varied hydrophilic properties of MHA and ODT. The ability to deposit molecules without a meniscus should be important in that water-sensitive molecules can be patterned under vacuum. Ratner *et al.* modeled the condensation of a liquid meniscus between an AFM tip and a surface using a grand canonical Monte Carlo simulation method (26). Recently, Hong *et al.* developed a model to describe the collective behavior of weak-surface-binding molecules in direct-deposition processes (27). All these theoretical contributions should provide

insights into a better understanding of the complex kinetics of molecular transport in DPN and allow one to design integrated systems with a great flexibility.

Although the methodology of DPN has been mostly applied to alkyl thiols and gold substrates, it is not limited to such a molecule-substrate combination. Indeed, small organic molecules with other terminal groups have been successfully patterned on a variety of substrates. For example, Ivanisevic *et al.* described a way of depositing organosilane molecules, such as hexamethyldisilazane (HDMS), on semi-conducting surfaces with sub-100nm spatial resolution (9). As shown in Figure 1, HDMS nanostructures were patterned on both GaAs and doped silicon substrates with sub-100 nm linewidth. In addition, Jung *et al.* have also successfully written 3'-mercaptopropyltrimethoxysilane (MPTMS) on a glass surface (28). Lines with width of 110 nm were achieved as shown in Figure 2 by using a surface-modified tip under optimum patterning conditions. Importantly, this study shows that patterning of organosilanes can be achieved under low relative humidity, at which condition silane polymerization is minimized. Moreover, the resulting nanostructures can be further used as templates to conjugate with biomolecules such as biotin-maleimide and Cy3-streptavidin that can be visualized by fluorescence microscopy (Figure 2).

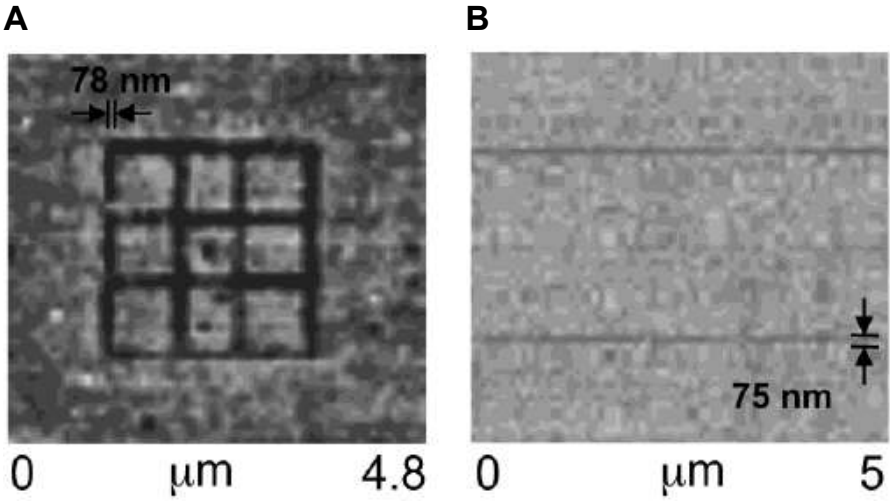

Figure 1. Lateral force microscopy (LFM) images of DPN-generated TMS monolayer patterns on semiconductor surfaces. (A) TMS grid on Si/SiOx substrate (2.4 μm edge width) and (B) a parallel line pattern on oxidized GaAs. (Reproduced with permission from Ref. 9)

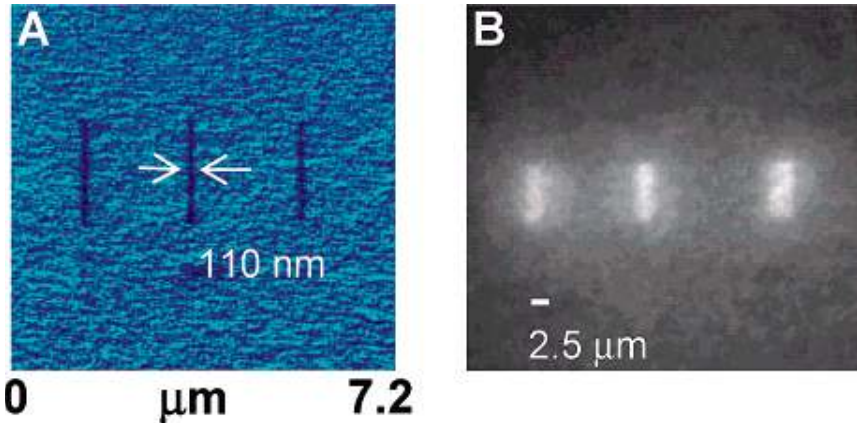

Figure 2. (A) Lateral force microscopy (LFM) image of 2-µm-long lines of MPTMS written by DPN on glass. (B) Fluorescent image of three 2.5 µm × 10 µm regions of MPTMS conjugated with biotin-maleimide and Cy3-streptavidin. (Reproduced with permission from Ref. 28)

In addition to small organic molecules, a broad range of macromolecules have been identified suitable for patterning nanostructures with sub-100 nm feature sizes by DPN. In particular, patterning of conducting polymers has received considerable interest due to their potential applications in areas as diverse as electronic devices to mechanical actuators (29-32). Maynor *et al.* reported that using the electrochemical dip-pen nanolithography (E-DPN) conducting poly(thiophene) nanowires can be fabricated on semi-conducting and insulating surfaces (33). Typically, the poly(thiophene) was formed at tip-substrate interface upon electrochemically polymerizing monomers while a negative bias voltage was applied between the tip and the substrate. The reaction scheme and as-synthesized line patterns were shown in Figure 3A and B, respectively. In another report, Mirkin *et al.* have explored using electrostatic interaction rather than the bias as a driving force to anchor conducting polymer to substrates (13). In general, charged polymers were transferred to oppositely charged surfaces via electrostatic interaction by DPN, resulting in patterns with 100 nm resolution. Interestingly, similar dependence of pattern size to tip-substrate contact time, which has been observed for small organic molecules, was also observed for the polymer. It should be noted that untreated silicon surfaces are not favorable to molecule patterning. The same strategy that uses electrostatic interaction as a driving force for depositing molecules has also been applied to pattern positively charged dendrimer onto negatively charge Si/SiOx substrates (34). In addition, Yang *et al.* reported a new technique, termed as thermal dip-pen nanolithography (tDPN), which can write molecularly ordered polymer nanostructures with control of both physical dimensions

and orientation (35). They demonstrated that polymer nanostructures can be directly written via layer-by-layer fashion. Other variants of DPN approaches, coupled with confocal microscopy, ring-opening metathesis polymerization, enzymatic catalysis, and photocatalysis, have also been reported, providing a general and versatile method for patterning polymers down to single molecules (14, 36-38).

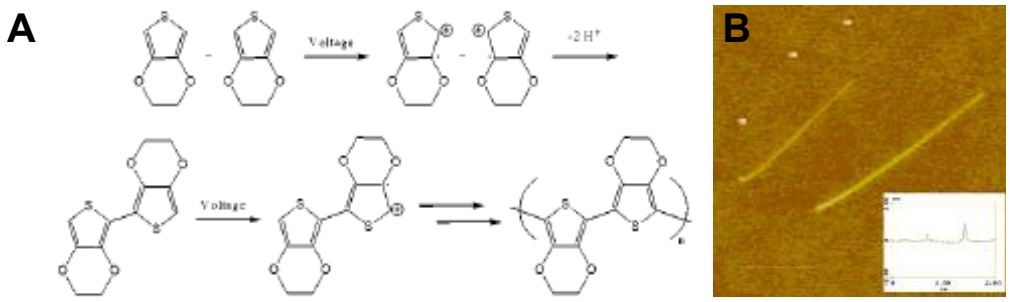

Figure 3. (A) Scheme for the oxidative polymerization mechanism of poly-EDOT. (B) Two poly-EDOT lines written with speed of 10 (left) and 1 nm/s (right). Line width: 50 nm. Inset: Cross-section of the two lines. (Reproduced with permission from Ref. 33)

INORGANIC FUNCTIONAL NANOMATERIALS

The delivery of functional nanomaterials such as metal nanoparticles into predefined architectures and patterns are of great interest in nanotechnology for their applications in miniaturized electronic circuits or in plasmon waveguides. The DPN-based nanofabrication has been routinely used for realization of such architectures composed of nanoparticles, nanowires, and nanotubes. The patterning processes can be generally divided into two methods. One is direct transfer method via an AFM tip coated with nanomaterials, while the other is based upon a template approach that typically consists of a two-step procedure. Nelson and co-workers described direct deposition of continuous metal nanostructures by thermal DPN (39). The tip is coated with indium metal and the deposition is controlled using a heater integrated into the cantilever. As for the template approach, functional organic molecules are first transferred from the tip to a substrate to generate nanostructured molecular templates. Subsequently, nanomaterials with appropriate surface functionalization are assembled onto the molecular templates via electrostatic interactions or chemical recognitions. Alternatively, the organic

templates can be used to initiate crystal growth of the nanomaterials. For example, Zheng *et al.* reported the patterning of Au nanoparticles on a silicon substrate via a combination of AFM-based local oxidation and chemical assembly of the nanoparticles (40). Moreover, Myung *et al.* demonstrated large scale precision assembly and alignment of V_2O_5 nanowire arrays (41). They firstly patterned a substrate with positively charged molecules. When the patterned substrate was immersed in an aqueous solution of negatively charged V_2O_5 for about 30 s, nanowires were assembled onto the patterned structures. Basnar *et al.* reported the synthesis of gold nanowires using DPN and biocatalytic "inks" (42). Recently, Lee *et al.* described a new approach to fabricate gold nanowires by electric-field-induced AFM-based lithography (43). In their approach, gold seeds are first deposited on a p-type silicon substrate and these seeds are then developed using a solution of $HAuCl_4$ and a reducing agent. Most recently, Wu *et al.* reported direct deposition and assembly of gold nanoparticles using a nanofountain probe (44). Their results indicate that the flow of nanoparticles is confined to the tip region of the probe (44). Wang *et al.* found that single-walled carbon nanotubes (SWNTs) can be assembled and manipulated via DPN-defined MHA templates (45). Unique and unusual structures, such as high strained dots, rings, and arcs, could be readily obtained by using appropriate molecular templates (45).

BIOLOGICAL MACROMOLECULES AND LIVING ORGANISMS

The analysis and manipulation of biological molecules such as DNA and proteins at the sub-zeptomolar level remains an elusive goal because most conventional techniques are simply not compatible to light sensitive molecules or require complex instrumentation. In contrast, DPN is a promising tool to fabricate biological nanopatterns with ultra-low-volume materials for biodetection down to single molecule level. This technique is particularly useful in case where sensitivity is a primary concern. Demers *et al.* demonstrated two alternative approaches that directly deposit DNA molecules on conducting and insulating substrates (10). Furthermore, the resulting DNA patterns were used to direct the assembly of individual oligonucleotide-modified nanoparticles via orthogonal assembly (46, 47). Indirect approaches, based upon self-assembly motifs, have also been used to generate DNA/nanoparticle hybrid nanostructures (48, 49).

In addition to DNA molecules, several papers described nanoscale patterning of proteins by DPN. Wilson and co-workers reported direct patterning of thiolated collagen on gold surfaces in

tapping mode (50). The deposited collagen was observed to possess helical structure conformation and retain its biological activity. They also reported that contact-mode AFM is not suitable for depositing biomolecules due to possible destruction to the fragile molecules by the AFM tip, which is consistent with another report by Agarwal *et al.* that involves patterning of peptides in both contact and tapping modes (51). In contrast to the direct writing of chemically modified collagen, protein nanoarrays fabricated via indirect approaches have been applied to study cellular adhesion at nanometer length scale. The indirect approach exploits DPN-generated MHA patterns as templates to adsorb proteins via selective binding of the proteins by carboxylic groups in MHA. In another report, Lee *et al.* have demonstrated writing of proteins using gold substrates and modified tips (11). Importantly, the resulting protein arrays retain their specific bio-recognition properties. Lim *et al.* reported direct depositions of proteins onto silicon oxide substrates that were either treated with base to yield a negatively charged surface or modified with aldehyde (12). The surface treatment leads to electrostatic interaction or covalent bonding for immobilization of the proteins once delivered by DPN. Recently, Li *et al.* reported the scission of single DNA molecules with non-specific endonuclease (DNase I) via a modified DPN approach, termed as combined-dynamic mode dip-pen nanolithography (CDDPN) (52). They found that digestion of DNA by the DNase I is effective even on an air-liquid-solid interface with ambient conditions. They contributed the efficient digestion to a high level local concentration of the DNase I deposited in a spatial confined area (52).

The DPN technique has recently extended to pattern peptides for cell adhesion studies. When compared to proteins, peptides can be much easily patterned because of their relatively small size. Agarwal *et al.* have used the tapping mode DPN to deposit a synthetic peptide on a nickel surface (Figure 4) (51). Ivanisevic *et al.* have systematically studied TAT peptides to generate their nanopatterns on different substrates, including SiOx, gold, and GaAs (53-55). Recently, Zhuang *et al.* reported controlled growth of peptides on SiOx surfaces that are modified with PAMAM dendrimers by ring-opening polymerization of Tryptophan-N-carboxyanhydrides (Trp-NCAs) (56). The unique advantage of this method is that the growth of peptide nanostructures can be well controlled by the feeding time and concentration of Trp-NCA solutions.

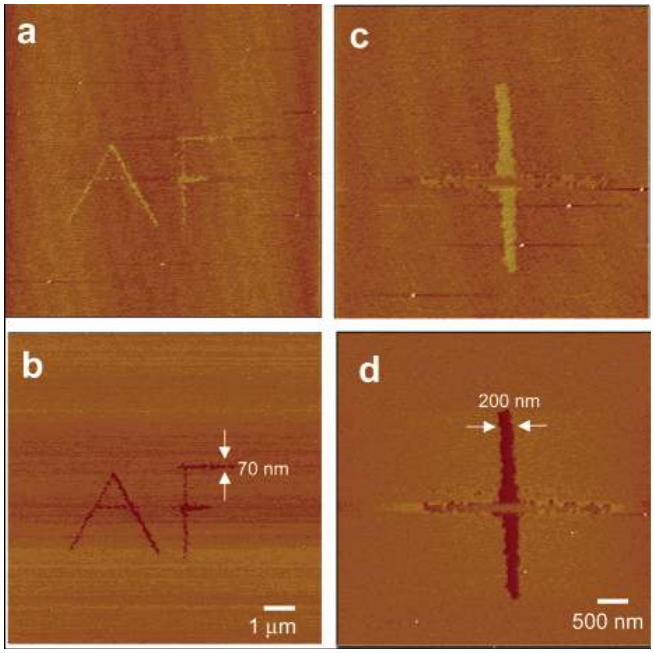

Figure 4. Nanoscale patterns written with the peptide MH2 on a gold surface using TappingMode DPN. (a) Height image of "AF" written using an aspect ratio of 1: 64 and various scan angles. The corresponding phase image (b) shows a darkened patterned region. (c) Height and (d) phase image of "+" written with aspect ratio of 1:32. Line widths of patterns are indicated. (Reproduced with permission from Ref. 51).

To demonstrate the capability of DPN-generated patterns used for studying the orthogonal assembly, proof-of-concept experiments related to metal ion-affinity templates will be discussed. Vega *et al.* have conducted a series of studies regarding the assembly of viruses and antibodies (23,57,58). Typically, metal ion-affinity template was first obtained by using MHA nanopatterns generated by DPN on a gold surface. The areas surrounding the nanopatterns were then passivated with thiol-PEG. Metal ions of Zn^{2+} was then selectively coordinated to MHA patterns through Zn^{2+}-carboxylic coordination chemistry. It was demonstrated that the metal ion templates showed binding activity towards virus particles of TMV as characterized by tapping mode AFM (57).

In another report, Vega *et al*. have used Zn^{2+} templates to immobilize antibodies onto substrates (58). The generality of the metal ion-mediated immobilization of antibodies was demonstrated by testing a series of different antibody subclasses, including polyclonal chicken IgY, polyclonal rabbit IgG, monoclonal mouse IgM, and monoclonal mouse IgG1. Notably, the antibodies retain their biological recognition as probed by incubating the antibody in solutions of their corresponding antigens and subsequently measuring the height increase of the antibody

patterns. Recently, this strategy was used to study single-cell infectivity by monitoring the cellular infection process in real time (23).

SOLID-STATE NANOSTRUCTURES

The ability to pattern solid-state nanostructures on various substrates is essential for fabrication of integrated nanodevices and nanosensors (49,59-62). A general scheme for patterning of solid-state nanostructures starts with deposition of MHA or ODT onto an Au/Ti/Si multilayered substrate, followed by selective etching of the exposed Au areas surrounding the MHA or ODT patterns by immersing the substrate in a ferri/ferrocyanide-based etchant. The residual very thin Ti and natively oxidized SiO_2 layers are then etched by using a solution of HF. Finally, the remaining Si is anisotropically etched with a KOH alcoholic solution, resulting in the formation of crystals with {111} crystallographic planes. Removal of the residual Au by aqua regia yields all-Si features. Using a combination of the DPN and a wet chemical etching technique, Zhang *et al.* generated sub-100 nm Au, Ag and Pd structures with controlled feature shapes as shown in Figure 5A (62). They also showed that miniaturized nanogap electrodes (down to 12 nm) can be generated on Si/SiOx surfaces via the same approach (Figure 5B) (61). Using multi-pen arrays, the mass production of these nanogap electrodes can be realized at a lower cost than conventional methods currently in use. Importantly, they demonstrated that the as-synthesized metallic nanostructures can be further used as templates to immobilize biomolecules such as DNA and proteins and form ultrahigh density nanoarrays for biological detections (49,63). By combining DPN, wet chemical etching and reactive ion etching techniques, Zhang *et al.* developed a method to fabricate nanosacle Si and SiOx structures, which could be used as nanoimprint lithography templates (60).

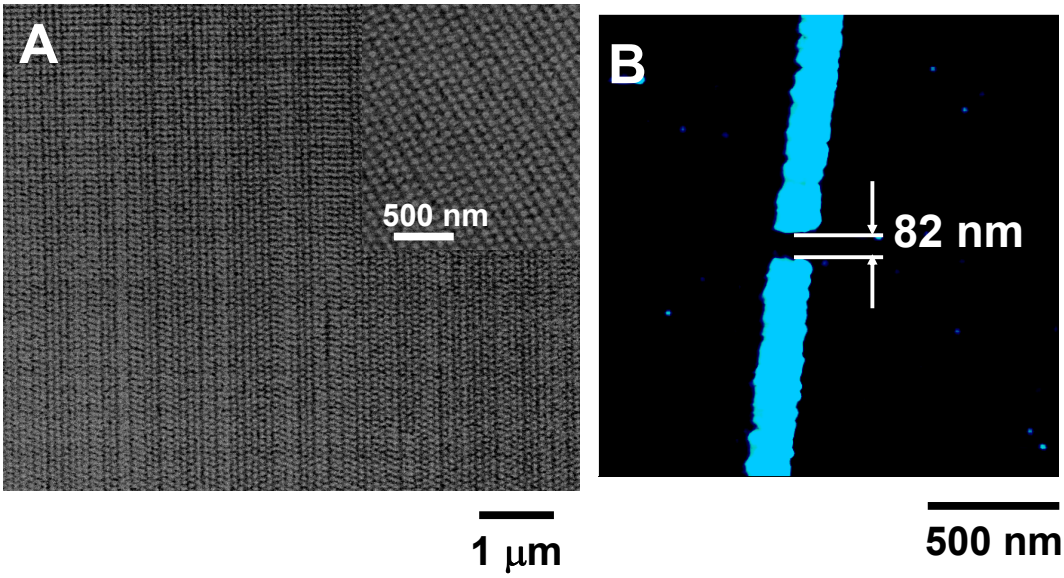

Figure 5. (A) SEM image of 45-nm gold nanodots and (B) TM-AFM image 12-nm gold nanogap. (Reproduced with permission from Ref. 61)

NANODEVICES

The ultrahigh registration of DPN has made it an ideal tool to fabricate or modify nanoscale electronic devices. An early example was demonstrated by Maynor *et al.* via E-DPN. They fabricated GaN nanowire heterostructures by a local electrochemical reaction between the nanowire and a tip-applied KOH "ink" (64). By controlling the ambient humidity, reaction voltage, and reaction time, they showed precise control over geometry of the heterostructures. They further demonstrated that site-specific surface modification of nanowires could lead to large changes in their electron transport properties. Chung *et al.* reported fabrication of nanoscale electrical circuits by DPN coupled with DNA-directed assembly of nanoparticles (65). They first modified lithographically defined electrodes and the gap between the electrodes with single stranded DNA molecules. Subsequently, the gap was selectively filled with complementary oligonucleotide-modified gold nanoparticles. Importantly, the approach allows one to assemble multiple, different nanostructures onto the same chip in a single chemical assembly step. These devices should provide opportunity to measure electrical transport through DNA/nanoparticle junctions and to develop label-free detection of biomolecules. It should be noted that there is considerable nonspecific binding of nanoparticles to the electrodes. In this regard, Zhang *et al.* developed a novel technique for transferring nanoparticles in a one-particle-at-a-time fashion

(66). This direct write technique, termed as single particle DPN, uses an AFM tip to physically catch individual nanoparticles on a substrate. The nanoparticles attached to the tip can be controllably released onto a different place. This approach should provide a convenient tool to fabricate single-nanoparticle-based devices for studying a variety of quantum phenomena such as coulomb blockade and quantum conductance.

POLYMER CRYSTALLIZATION

Crystallization is essential for the manufacture of products and the characterization of many materials. However, our understanding of the crystallization process remains limited because of the lack of spectroscopic or x-ray diffraction tools that allow *in situ* visualization crystal growth, particularly at the early stages. Several research groups have used AFM to study crystal nucleation and growth at microscopic length scales, but typically in the context of structures growing randomly on a surface from a bulk solution saturated with a feedstock of the molecules. Liu *et al.* reported a DPN-based method that allows one to control the initiation and kinetics of polymer crystal growth (67). By using DPN with an AFM tip coated with poly-DL-lysine hydrobromide (PLH), triangular prisms of the polymer epitaxially grow on freshly cleaved mica substrates, and their in-plane and out-of-plane growth rates can be controlled by raster scanning the coated tip across the substrate. This technique can also be used to study environment-imposed changes in crystal morphology. Indeed, low humidity favours the formation of smaller crystals, down to five orders of magnitude smaller than those observable by single-crystal x-ray diffraction. This tool should allow systematic determination of the optimum crystal growth conditions for molecules, especially proteins and organic macromolecules that are normally difficult to crystallize.

HIGH THROUGHPUT NANOPATTERNING

While DPN offers many advantages such as ease of implementation, biocompatibility, high resolution and registry, a significant challenge is the development of an integrated system that has high throughput and massive multiplexing capabilities. In fact, the Quate group first demonstrated that up to 50 conductive AFM tips bound to a single silicon nitride chip could be used to perform anodic oxidation of silicon surfaces (68). In addition, two-dimensional (2D) (32 × 32) probe arrays have been developed by IBM for the Millipede storage technology (69). DPN

was always limited in throughput by how many pens it could use to write molecules at the same time until recently the Mirkin group has developed both linear and 2D passive probe arrays that are now commercially available (70,71). Salaita *et al.* have used 55,000 passive-pen array, the highest density and largest working scanning probe array ever fabricated, to routinely pattern molecules over large areas with sub-100 nm feature size. The new array can draw 55,000 likenesses of Thomas Jefferson in a confined space and size of a nickel in less than 30 minutes. The images consist of 470 million dots of ~ 80 nm in diameter (20). The array was fabricated by modifying a microfabrication process developed for single AFM probes. The pens are roughly 7.6 μm high with tips about 60 nm across. Most importantly, the cantilevers are bended by coating with gold and annealing to yield curvatures that allow one to bring down all the pens in contact with their substrates using merely gravity, as opposed to a complex set of feedback systems. This system has overcome the challenges of adequately uniform inking of all the pens while obtaining registry between the substrate and all pens. The massively parallel DPN approach should open the technique up for many applications in areas from life sciences to integrated electronics. Another study by Lenhert *et al.* demonstrated the multilayer pattering of heterogeneously supported phospholipids via massively parallel DPN (72). They utilized the physical adsorption, rather than conventional chemical bonding interaction, between the phospholipids and substrates for patterning of lipid membranes.

To improve the throughput of DPN, it is also important to develop a parallel array of individually controllable cantilevers. In a proof-of-concept experiment, Bullen *et al.* reported the development of a probe array consisting of ten thermal bimorph actuated probes for DPN applications. The probe array was demonstrated by using it to write ten different ODT patterns on a gold substrate (73). The results suggest that, if ten features can be drawn separately, in principle, any set of controllable patterns can be generated via this approach. This also paves the way towards parallel SPLs, including DPN, which dispel the myths with regard to the throughput that weakens SPLs. Although an impressive demonstration of the active-pen array, the technique is far from perfect because the thermal fluctuation accompanying the technique affects the molecule transfer rate and limits the choice of links to be used. Thus, much work needs to be done to improve the application of the approach.

FUTURE CHALLENGES AND OPPORTUNITIES

This chapter presented a brief overview of recent development of DPN, a unique approach for positioning, manipulating and generating a variety of atoms, molecules, and materials with accuracy at the nanometer length scale. Although the passive- and active-pen arrays for patterning parallelization are far from perfection, the general approach that integrates knowledge and ideas across disciplinary boundaries has already evolved into a particularly useful tool to study the fundamental consequences of miniaturization. Furthermore, one has to meet the great challenge that involves the lack of efficient analytical tools for characterizing the patterned individual nanostructures on a surface or within the context of an integrated device. The integration of the advanced characterization tools and DPN should allow better understanding and prediction of the fundamental and cooperative properties of nanostructures. Further investigations are expected in this field.

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