Scanning Probe Microscopy-Based Nanofabrication for Emerging Applications

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The ability to tailor the chemical composition and structure of a surface at the nanometer scale is essential for fabricating novel nanomaterials, understanding underlying nano-science and engineering, and developing integrated systems for demanding applications. The unique imaging and nanomodification capabilities of scanning probe microscopes have prompted the emergency of scanning probe microscopy (SPM)-based nanofabrication. This article reviews the rapid growth of the research field of SPM-based nanofabrication and highlights most recent developments with particular emphasis at the interface between biological and physical science. The fundamental principles of various approaches as well as their capabilities are introduced.

Keywords Scanning Probe Microscopy; Nanofabrication; Nanolithography; Nano-shaving and grafting; Dip-pen Nanolithography; Local Oxidation Nanolithography

1. Introduction

Scanning probe microscopy (SPM), including scanning tunnelling microscopy and atomic force microscopy, is a branch of microscopy originally used for visualizing surface structures from the atomic to the micron level using a probe that scans the sample [1,2]. In general, all SPMs contain the components shown in Fig. 1. Recently, SPM has evolved into an essential tool for surface modification and structure manipulation at the nanometer scale [3-7]. This development is driven largely by the need to fabricate, position, and interconnect nanostructures within complex systems. Unlike conventional nanolithography techniques such as photolithography and electron beam lithography, the SPM-based lithography is cost-effective, and particularly suitable to handle a large variety of organic or inorganic molecules and to initiate site-specific local chemistry. These capabilities have led to emerging applications ranging from high-throughput nanostructure patterning, single molecular synthesis and manipulation, quantum structure fabrication, nanocatalysis, biopolymer crystallization, single nanoparticle-based biosensors to miniaturized device fabrication (Fig. 2). The purpose of this concise review is to discuss general strategies of SPM-based nanofabrication in the context of the current progress being made in this field. Comprehensive reviews describing detailed instrumentation designs and experimental procedures have been reported elsewhere [3-7]. Herein, we intend to highlight some of most recent developments, with particular emphasis on applications of SPM-based nanofabrications at the interface between biological and physical sciences.

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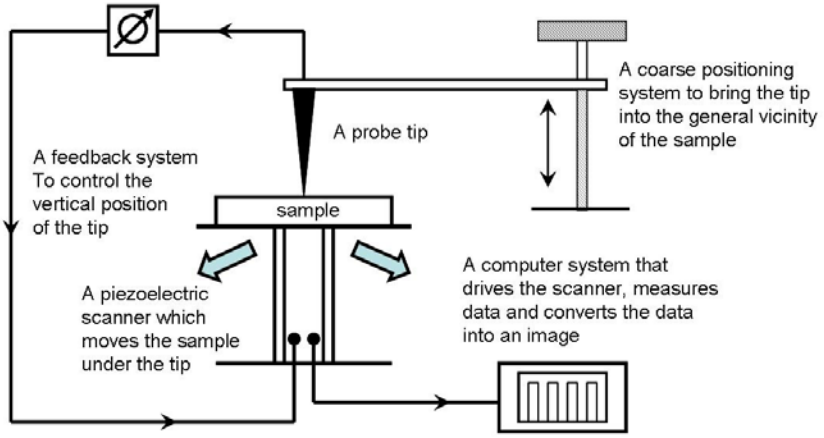

Fig. 1. Schematic of a generalized SPM.

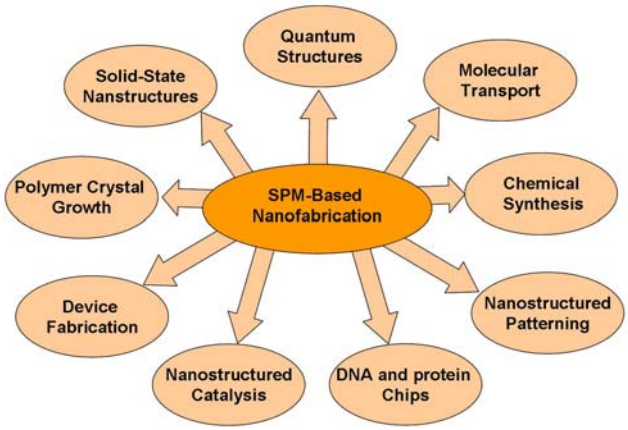

Fig. 2. Applications of SPM-based nanofabrication.

2. Scanning Tunnelling Microscopy

The scanning tunnelling microscopy (STM), invented in 1981 by Gerd Binnig and Heinrich Rohrer at IBM Zurich, is the ancestor of all scanning probe microscopes [2]. The STM uses a sharpened, conducting tip with a bias voltage applied between the tip and a conductive or semiconductive sample. When the tip is brought within about 10Å of the sample, electrons from the sample begin to "tunnel" through the 10Å gap into the tip or vice versa, depending on the sign of the bias voltage. The magnitude of the resulting tunnelling current can be tuned by adjusting the tip-to-sample spacing. In recent years, STM has been developed from an imaging instrument to a tool capable of controlled manipulation of single atoms and molecules on surface. It has been used to modify surfaces by locally pinning molecules to a surface and by transfer of an atom form the tip to the surface. Moreover, this technique allows pulling an atom to travel across the surface via an STM tip while the atom remains bound to the surface. An early example of STM-based nanomanipulation was demonstrated by Eigler and Schweizer for moving single xenon atoms on nickel (110) in an ultra-high-vacuum system and at 4K [8].

2.1. Patterning of Quantum Structures

Manipulations of single atoms by STM have led to various methods for confining electrons to artificial structures at the nanometer lengthscale. Crommie *et al.* first demonstrated that surface state

electrons on a Cu(111) surface can be confined quantum corrals defined by barriers built from iron adatoms [9]. A circular corral of radius 71.3 mathrm was constructed out of 48 iron adatoms. Braun and Rieder reported the patterning of Ag atoms in a triangular shape [10]. They then measured the lifetime of the surface electrons within the atomic structure. By constructing quantum corrals, the standing-electron waves and quantum transport phenomenon can also be studied. Manoharan *et al.* observed 'quantum mirage' of a magnetic Co atom surrounded by an elliptical quantum corral [11]. They detected a strong Kondo signature not only at the atom, but also at the empty focus. In addition, the ability of STM to manipulate single atoms is used to build quantum wire structures. Ho *et al.* reported a method for fabricating well-defined gold chains on NiAl(110) [12]. These structures provide insight into a better understanding of the interrelation between geometric structure, elemental composition, and electronic properties in metallic structures.

2.2. Molecular Transport and Manipulation

In addition to the inorganic atom manipulation, controlled molecular transport and manipulation have been demonstrated for a large collection of gaseous and organic molecules. Heinrich *et al.* investigated the hopping mechanism of CO molecules in molecule cascades through studies of the hopping rate as a function of temperature, isotope, and local environment [13]. Their studies revealed that at temperature below 6k the hopping motion of CO molecules can be attributed to quantum tunnelling of the molecule between neighboring binding sites on the surface. Hla *et al.* reported a molecular shooting technique that allows transportation of a sexiphenyl molecule across a Ag(111) surface [14]. It should be noted that this technique works only when the molecule is manipulated along its long-molecular axis in the closed-packed surface direction. Recently, Ho *et al.* demonstrated the atomic-scale coupling of photons to a single molecule in a double-barrier junction of STM through a two-step process of photo-induced resonant tunnelling [15]. This technique provides a novel route to explore molecular dynamics with the combined capabilities of lasers and STM that enable simultaneous spatial, temporal, and energy resolutions.

2.3. Initiation of Chemical Transformations

The STM-based nanomanipulation has been used to catalyze surface reactions and to synthesize single molecules or molecular complexes. Somorjai *et al.* showed that an STM tip catalyzes with high spatial resolution the rehydrogeneration of carbonaceous species on the Pt(111) surface [16]. They also showed that catalytic performance of the tip is closely related to the tip-surface distance. As the tip is closer to the surface, the tip catalysis is enhanced, indicating a proximity effect required for the transfer of H atoms to the surface. Lee and Ho demonstrated that it is possible to manipulate the bonding of a carbon monoxide (CO) molecule with individual iron (Fe) atoms by STM [17]. In their experiment, a CO molecule was transferred from a surface to an STM tip and bonded with an Fe atom to form Fe(CO). Importantly, a second CO molecule can be sequentially transferred and bonded with Fe(CO) to form $Fe(CO)_2$. The ability to control step-by-step bond formation of adsorbed chemical species at the single-molecule level and to *in situ* analyze the vibrational property of the products provides real-space understanding of the nature of the chemical bond [17]. Subsequent to Ho's report, Hla *et al.* demonstrated that by employing the STM-based nanomanipulation technique, a typical Ullmann reaction can be induced on single molecules, resulting in the formation of new individual molecules [18].

2.4. STM-Based Nanolithography

Kleineberg *et al.* carried out extensive studies on various self-assembled monolayers (SAMs) used as ultrathin resists for STM nanolithography [19]. The SAMs are manipulated by STM-writing in ultrahigh vacuum and the structure is subsequently transferred into the underlying substrate by selective wet etch procedures. Iwasaki *et al.* described a method of patterning SiO_2 overlayer on Si using STM through

irradiating the oxide overlayer by field-emitted e-beam from the STM tip at a moderate temperature [20]. In contrast to conventional high-energy electron beam techniques, this STM e-beam nanolithography technique has several advantages. First, one can *in situ* examine the patterned nanostructures by using the same STM tip as used for the patterning. Second, much less defect formation is expected for this technique due to the use of much lower electron energies. Song *et al.* reported SPM-based nanofabrication using a synchronization technique [21]. The technique allows transfer of a given pattern into an encoded voltage pulse series that are synchronized with SPM scanning. Their system can be operated in lift or normal imaging mode and used for patterning nanostructures on insulating and conductive substrates. Zhang *et al.* reported unusual "crater-like-pit" and "mound-in-pit" structures fabricated by STM [22]. They suggested the coexistence of field emission and tip-substrate direct contact during the nanolithography process.

3. Atomic Force Microscopy

Although STM-based nanofabrication has been used to control chemistry at the level of individual atoms and molecules, there are inherent limitations associated with these techniques including the need of a complex instrumentation, stringent operation conditions (e.g. ultra-high vacuum and ultra-low temperature, *etc.*), and time-consuming processing steps. In contrast, atomic force microscopes (AFM) that scans the surface of a sample with a sharp tip can be operated in air, and liquids. The AFM tip is located at the free end of a cantilever typically 100 to 200 μm in length. Forces between the tip and the sample surface cause the cantilever to bend or deflect. A detector measures the cantilever deflection as the tip scans over the sample. Unlike STM, AFM-based nanomanipulation can be operated on insulators and semiconductors as well as electrical conductors. In addition, the AFM-based lithographic techniques are suitable for patterning a variety of organic and biological molecules on surfaces at ambient conditions. More importantly, parallel patterning of multicomponent nanostructures can be obtained with probe arrays. These attributions open the possibility for a wide range of applications highlighted in the following.

3.1. Patterning of Self-Assembled Monolayers

The AFM-based nanolithography has been extensively studied for patterning SAMs. These studies have led to several unique approaches that include nano-shaving and grafting technique (NSGT), dip-pen nanolithography (DPN), and local oxidation nanolithography (LON) [21-23]. Specifically, NSGT developed by Liu and co-workers requires flat surface morphology and uses soft SAMs as sacrificial layers [23]. Usually removal of the sacrificial layers is accompanied by the displacement of selected molecules with a higher concentration than the displaced molecules. The DPN approach was developed by Mirkin and co-workers [24]. In DPN molecule "inks" are first coated on an AFM tip, and then transferred to nanoscopic regions of a target substrate. DPN could be used to pattern alkanethiol SAMs onto gold surfaces with high-resolution and registration. It was recently shown that it is possible to pattern multiple nanostructures with remarkable throughput via 1D or 2D arrays. Sugimura and coworkers pioneered the protocol for LON to pattern mixed SAMs. It typically involves a two-step process [25]. The first-layer monolayer is self-assembled on a surface. Then a local oxidation is performed on a selected area of the monolayer to remove the SAMs using conductive AFM. The modified region is then selectively passivated with different molecules. The abovementioned techniques and their variations are complementary to each other and can be applied to fabricate a variety of SAMs with various feature shapes, sizes, and compositions ranging from small organic molecules to biological macromolecules such as oligonucleotides.

3.2. Patterning of Biological Molecules

Various AFM-based techniques, including nanografting and DPN, have been used to precisely pattern biological molecules. An example of protein nanopattering via AFM was reported by Wadu-Mesthrige *et al.* on a gold substrate by nanografting [26]. Case *et al.* also utilized the nanografting technique to manipulate structural orientation of metalloproteins to the surface [27]. They showed that the three-helix bundle metalloproteins incorporating C-terminal thiol groups can be designed to orient vertically on an Au(111) surface. As a direct-write and biocompatible technique, DPN is particularly well suitable for pattering biological molecules on surfaces. Because of its ultrahigh-density capacity, DPN has a great potential to revolutionize the technology of surface-based biomolecular assays, including array-based DNA and protein detections. The first example of patterning of biological molecules by means of DPN was shown by Wilson *et al.* on gold substrates [28]. They patterned collagen and a collagen-like peptide down to 30-50-nm line widths and found these molecules preserved their structure and functionality, suggesting a new strategy to study the hierarchical assembly processes of biological systems. Lee *et al.* used DPN to construct nanoarrays of mercaptohexadecanoic acid (MHA) SAMs which were used as templates to adsorb Retronectin proteins [29]. They further demonstrated that these protein nanoarrays can be used to study surface-mediated biological recognition processes such as cellular adhesion at the submicrometer scale [29]. Demers *et al.* reported direct patterning of modified oligonucleotides on metals and insulators by DPN [30]. The oligonucleotide nanopatterns were used to direct the assembly of complementary oligonucleotide-modified Au nanoparticles onto the substrates. The method may opens up new routes for generating ultrahigh density DNA arrays and for developing novel scanning probe-based schemes for DNA detection. In addition to oligonucleotides and proteins, DPN has also been reported to deposit enzymes and peptide compounds on surfaces [31,32].

3.3. Patterning of Functional Nanomaterials

The AFM-based nanofabrication has been routinely used for patterning nanomaterials such as nanoparticles, nanowires, and nanotubes. The patterning processes can be generally divided into two methods. One is direct deposition of nanomaterials via an AFM tip, while the other is based upon a templating approach that consists of a two-step procedure. Nelson and co-workers described direct deposition of continuous metal nanostructures by thermal DPN [33]. The AFM tip is coated with indium metal and the deposition is controlled using a heater integrated into the cantilever. As for the templating approach, functional organic molecules were first transferred from an AFM 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 [34]. Moreover, Myung *et al.* demonstrated large scale precision assembly and alignment of V_2O_5 nanowire arrays [35]. They first patterned a substrate with positively charged molecules. When the patterned substrates were 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 synthesis of gold nanowires using DPN and biocatalytic “inks” [36]. Recently, Lee *et al.* described a new approach to fabricate gold nanowires by electric-field-induced AFM-based lithography [37]. 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.

3.4. Patterning of Solid-State Nanostructures

The ability to pattern solid-state nanostructures on various substrates is essential for fabrication of integrated nanodevices and nanosensors. Using a combination of DPN and a wet chemical etching technique, Zhang *et al.* generated sub-100 nm Au, Ag and Pd structures with controlled feature shapes

[38]. They also showed that miniaturized nanogap electrodes (down to 12 nm) can be routinely generated on Si/SiOx surfaces via the same approach [39]. 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 to form ultrahigh density nanoarrays for biological detections [40]. 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 [41].

3.5. Manipulation of Single Nanoparticles

One of the biggest challenges in the physical and engineering sciences is to develop a general method that allows one to pattern single nanoparticles in a one-at-a-time fashion and integrate them into nanoscale junctions in a controlled manner. From the experimental point of view controlled studies of the interaction between single nanoparticles are very challenging due to the complex nature of the experiment and the lack of reliable miniaturized tools. There are procedures of patterning nanoparticles that involve in assembling nanoparticles on pre-designed lithography-generated patterns. However, patterning of single nanoparticle arrays with control over particle size, composition, and inter-particle spacing remains a forbidding challenge because of the lack of reliable, reproducible fabrication methods. Manipulation of nanoparticles with SPM has been reported by Resch *et al.* to build a three-dimensional pyramidal structure [42]. It has also been reported that capturing nanoparticles could be realized with a conductive tip and a substrate by applying a voltage between the tip and substrate [43]. However, this kind of manipulation is limited to conductive nanomaterials, and in many cases the applied voltage alters surface properties of the nano-objects. To these regards, Zhang *et al.* developed a novel technique for transferring nanoparticles in a one-particle-at-a-time fashion [44]. This 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 substrate. This approach should provide a useful tool to fabricate single-nanoparticle-based devices for studying a variety of quantum phenomena such as coulomb blockade and quantum conductance.

3.6. Single Macromolecule Manipulation

Hu *et al.* showed that AFM can be used to manipulate DNA and perform DNA sequencing [45]. They utilized a combination of “molecular combing” and “molecular cutting” to isolate the DNA strands with single-base resolution. In a typical experiment, DNA molecules were first pulled to form a stretched line shape. They then cut, push, and fold the molecules in a highly precise fashion. Importantly, they successfully demonstrated transportation of the isolated molecules from the substrate to the tip. Upon PCR amplification, the sequence of the isolated strands can be identified. Most recently, they reported scission of single DNA molecules with non-specific endonuclease via a modified DPN approach [46]. 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 the high local concentration of the DNase I when confined in an extremely small area.

3.7. Manipulation of Polymer Crystal Growth

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 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 [47]. Liu *et al.* reported a DPN-based method that

allows one to control the initiation and kinetics of polymer crystal growth. This technique can also be used to study environment-imposed changes in crystal morphology [48]. Indeed, low humidity favors 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.

3.8. Device Fabrication

LON has been used to fabricate functional nanoelectronic and micromechanical devices including silicon microlenses, metal-oxide tunnelling transistors and quantum rings. Fuhrer *et al*. reported magnetotransport experiments on quantum ring structure fabricated by LON [49]. They argued that even in many-electron Coulomb blockaded systems a detailed understanding of the energy spectrum can be obtained. They also believed that such quantum rings could be used to investigate spin effects in a circular one-dimensional system. Chung *et al.* reported fabrication of nanoscale electrical circuits by DPN couple with DNA-directed assembly of nanoparticles [50]. 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.

4. Near-Field Scanning Optical Microscopy

Near-field scanning optical microscopy (NSOM) is a novel type of microscopy that uses a sub-wavelength light source as a scanning probe [51]. The probe scans over a sample surface at a fixed tip-sample distance using shear force feedback. This technique is a bridge between AFM and optical microscopy that allows optical excitation of materials at spatial resolutions well below the diffraction limit. NSOM can be used as a tool for photolithography on the submicron length scale. In this application the fiber optic probe is used as light source to expose a photoresist, and patterns are fabricated by scanning the probe over the resist surface. Because this technique is not diffraction-limited, it has the potential to generate features substantially smaller than the wavelength of the light used by conventional far-field optical lithography. Indeed, Leggett *et al.* showed that coupling a UV laser to NSOM enables patterning of lines featuring line width down to ~ 25 nm [52]. The technique, termed as scanning near-field photolithography, may provide a convenient and rapid method that is complementary to other AFM-based nanolithography. Taha *et al.* demonstrated that using a NSOM confocal system proteins can be delivered to a substrate through a nanopipette and subsequently imaged with NSOM [53]. One advantage of this approach is that parallel writing capability can be easily achieved by attaching the nanopipette to standard high performance liquid chromatography instrumentation [53].

5. Concluding Remarks

SPM-based nanofabrication is a unique approach for positioning, manipulating and generating a variety of atoms, molecules, and materials with accuracy at the nanometer scale. The approach that integrates knowledge and ideas across disciplinary boundaries has evolved into a particularly useful tool to study the fundamental consequences of miniaturization. On the basis of the development of high-throughput systems and massive multiplexing capabilities, the new instrumentation is to be developed as evidenced by the emergency of parallel DPN [54]. Such instrumentation, if accessible, will open up a wide range of applications in areas as diverse as drug discovery to the fabrication of ultrahigh density electronic devices. Furthermore, one has to meet the great challenge that involves the lack of efficient analytical

tools for characterizing patterned individual nanostructures on a surface or within the context of an integrated device. The integration of advanced characterization tools and SPM-based nanofabrication should allow better understanding and prediction of the fundamental properties and the potential applications of nanostructures.

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