Nanoscale materials patterning and engineering by atomic force microscopy nanolithography


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Abstract

This review article aims to provide an updated and comprehensive description on the development of atomic force microscopy (AFM) nanolithography for structuring and fabrication at the nanometer scale. The many AFM nanolithographic techniques are classified into two general groups of force-assisted and bias-assisted nanolithography on the basis of their mechanistic and operational principles. Force-assisted AFM nanolithography includes mechanical indentation and plowing, thermomechanical writing, manipulation and dip-pen nanolithography. Bias-assisted AFM nanolithography encompasses probe anodic oxidation, field evaporation, electrochemical deposition and modification, electrical cutting and nicking, electrostatic deformation and electrohydrodynamic nanofluidic motion, nanoexplosion and shock wave generation, and charge deposition and manipulation. The experimental procedures, pattern formation mechanisms, characteristics, and functionality of nanostructures and nanodevices fabricated by AFM nanolithography are reviewed. The capabilities of AFM nanolithography in patterning a large family of materials ranging from single atoms and molecules to large biological networks are presented. Emphasis is given to AFM nanolithographic techniques such as dip-pen nanolithography, probe anodic oxidation, etc. due to the rapid progress and wide applications of these techniques.

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1. Introduction

Nanotechnology encompasses many processes that are important in the fabrication of integrated circuits, memory devices, display units, biochips and biosensors. One of the key processes in nanofabrication is the creation and construction of functional units in the size regime of less than 100 nm. Two approaches namely top-down and bottom-up, have been used to categorize the generation of nanostructures. The top-down approach applies various

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**Abbreviations:** AFM, atomic force microscopy; cAFM, conductive atomic force microscopy; CNT, carbon nanotube; 2DEG, two-dimensional electron gas; DPN, dip-pen nanolithography; EDPN, electrochemical dip-pen nanolithography; F–N, Fowler–Nordheim; HMDS, hexamethyldisilazane; I–V, current–voltage; MHA, 16-mercaptohexadecanoic acid; NC-AFM, non-contact atomic force microscopy; NTS, 18-nonadecenyltrichlorosilane; ODT, 1-octadecanethiol; OTS, octadecyltrichlorosilane; PEO, polyethyleneoxide; PMMA, polymethyl methacrylate; PS, polystyrene; PVK, polyvinyl carbazole; SAM, self-assembled monolayer; SEM, scanning electron microscope; STM, scanning tunneling microscopy; Tg, glass transition temperature; TMS, trimethylsilyl

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lithographical techniques to create nanoscale patterns from a featureless bulk starting material, while the bottom-up route often uses the interactions of molecules and colloidal particles to assemble two- and three-dimensional structures. The conventional techniques for nanofabrication are based on various lithographical methods in the top-down approach. Typical examples include photolithography [1,2], electron beam lithography [3,4] and focused ion beam lithography [5,6], and are widely implemented in semiconductor manufacturing. However, the applicability of these techniques is often limited by their high capital and operating cost, multiple-step processes, and poor accessibility. Several newly developed methods appear to be flexible alternatives for nanoscale patterning and fabrication, such as nano-imprint lithography [7–9], soft lithography [10], and atomic force microscopy (AFM) nanolithography [11,12]. These novel methods have the potential to be future low-cost techniques for nanoscale pattern formation and replication.

Among these newer techniques, AFM nanolithography has shown itself to be a unique tool for materials structuring and patterning with nanometer precision. AFM was invented in 1986 for use as a microscope to directly image the surface morphology with atomic and molecular resolution [13]. The morphological image of a surface is obtained by recording and regulating the forces felt by a probe as it scans the surface. AFM can be used to study both insulating and conducting materials, and can be operated in liquid, air or vacuum. The working principle of AFM nanolithography is based on the interaction between the probe and substrate. The typical radius of curvature of the probe is 20–60 nm, and the probe–substrate separation in close contact condition is <1 nm. When suitable forces are exerted, and/or external fields applied, the probe can induce various physical and chemical processes on the substrate surface. Consequently, localized nanostructures are generated through physical modifications and/or chemical reactions of the surface materials. AFM nanolithography possesses the versatility to pattern a wide range of materials including metals, semiconductors, polymers and biological molecules in different media. Due to its nanoscale positioning and imaging capability, AFM nanolithography is uniquely able to create site-specific and localized functional structures. Moreover, the morphological and physical properties of patterns formed can be immediately characterized with AFM by integrating additional measurement modules. This combined fabrication and characterization function in AFM nanolithography allows convenient in situ and in-line pattern creation and characterization.

Numerous AFM-based lithographic techniques have been developed in the last two decades. Generally, these techniques can be classified into two groups in terms of their operational principles: (i) force-assisted AFM nanolithography; (ii) bias-assisted AFM nanolithography (see Fig. 1). In force-assisted AFM nanolithography, a large force is applied to the tip for pattern fabrication, and the tip–surface interaction is mainly mechanical. Typical methods in this category include mechanical indentation and plowing [14], thermomechanical writing [15], nanomanipulation [16], and dip-pen nanolithography (DPN) [17]. During force-assisted nanolithography, forces larger than those used for AFM imaging are loaded onto the tip. The initially featureless surface is then patterned by mechanically scratching, pulling, or pushing the surface atoms and molecules with the probe. In DPN, instead of manipulating the existing molecules on the surfaces, the tip is used as a nanoscale pen to directly deposit collections of ink materials onto the substrate to define a functional structure. As for bias-assisted AFM nanolithography, the AFM tip is biased to create a localized electric field in the regime of $10^8$ V/m to $10^{10}$ V/m, and the tip acts as a nanoscale electrode for current injection or collection. Under such a high localized field, electrostatic, electrochemical, field emission, dielectric breakdown and explosive gas discharge processes can be initiated to facilitate pattern formation. Depending on the magnitude of tip bias and substrate materials, the application of tip voltage can lead to anodic oxidation [12],

![Fig. 1. (a) Force-assisted and (b) bias-assisted AFM nanolithography.](image-url)
electrochemical deposition [18], electrostatic attraction [19], and nanoscale explosion and shock wave propagation [20,21]. In anodic oxidation, the tip is negatively biased, and the local field induces the ionic dissociation of a water meniscus formed between the tip and sample surface. The oxidative OH\(^-\) anions migrate along the field and react with the substrates to form oxide structures. Electrochemical deposition is capable of generating positive structures with distinct physico-chemical properties from the precursor materials through bias-induced local chemical reactions.

Research into AFM nanolithography is fast growing, and it continues to attract increasing interest in nanotechnology. There have been quite a number of reviews [22–29] in the scientific literature, but these articles have either focused on a specific method such as DPN [22] and local oxidation [23,24], or generally described AFM nanolithography in the broader context of other techniques including scanning tunneling microscope (STM) lithography and soft lithography [25–28]. The objective of this review article is to provide a comprehensive and updated description on the progress and development in AFM nanolithography. We will review the methods, mechanisms and applications of typical techniques in force- and bias-assisted AFM nanolithography. In particular, we will summarize the theories and models related to the complicated lithographic processes, e.g., the nature of the forces during nanomanipulation, and the role of the water meniscus in ink transport and electric conduction. We will also describe the wide range of materials that can be patterned by AFM nanolithography, and the specific physico-chemical properties, functionalities and performances of structures and devices fabricated. In addition, nanofabrication strategies based on single-step direct AFM nanolithography and multiple-step pattern transfer will also be discussed. Finally, some concluding remarks are provided to briefly summarize the achievements and challenges in AFM nanolithography. Due to the broadness and diversity of AFM-based nanofabrication, it is not possible to cover all the valuable nanolithographic work in this review. Readers are referred to previous articles for literature emphasizing different aspects of AFM nanolithography such as molecular deposition [22], local chemical reaction [23,24], and biological structure manipulations [29].

2. Force-assisted AFM nanolithography

2.1. Mechanical indentation and plowing

Indentation, static plowing and dynamic plowing are three typical methods used in AFM to fabricate structures through the mechanical interactions of the tip and substrates. Indentation is the simplest way for single structure formation in which the tip is immobilized at a specific surface site, and a large force is then applied to the tip to indent the surface. In static plowing, the tip is operated in contact mode, and is scanned with a large load across the surface to define features in the shape of lines, rectangles, and squares. Dynamic plowing involves scratching the surface with a vibrating tip in tapping mode, and the force of the tip is modulated by adjusting the amplitude of the cantilever oscillations. Since a low force is used to image and modify soft polymers in tapping mode, the pattern irregularities caused by cantilever torsion under high contact forces are minimized in dynamic plowing. During a dynamic plowing operation, the cantilever driven by the piezo vibrates near its resonance frequency, and its oscillation amplitude depends on the distance between the tip and sample. Modification of substrate materials is achieved by increasing the modulation amplitude. As the tip approaches the sample surface, structures are created by elastic and plastic deformations of the substrate. In the following paragraphs, we review the application of the mechanical indentation and plowing techniques in patterning various materials such as polymers, metals, inorganic compounds, and semiconductors.

2.1.1. Polymers

Since polymers are soft materials and widely used as masks or resists in many device fabrication processes, there has been strong interest in the patterning of polymers by AFM mechanical nanolithography [14,30–34]. Cappella and Sturm addressed the patterning mechanism and the physico-chemical characteristics of polymer structures formed by AFM mechanical lithography [14]. They compared nanoindentation and dynamic plowing by performing these two techniques on polymethyl methacrylate (PMMA) and polystyrene (PS) polymeric films. The authors found that dynamic plowing is faster and more practical than nanoindentation in patterning polymers. Dynamic plowing is able to modify the stiffness and hardness of polymers, and create large border walls surrounding the patterned structures. The border walls can be subsequently eliminated by dissolving them in solvents that do not alter the other parts of the sample. Cappella et al. reported that the volume of the border walls is bigger than that of the structures carved out by
dynamic plowing (see Fig. 2) [30]. They ascribed such an increase in volume to changes in polymer density caused by a loosening of the polymer entity due to fast indentation of the AFM tip. Force–displacement curve measurements were performed to compare the adhesion forces between the modified and unmodified regions on PMMA and PS films. It was observed that the AFM tip could induce polymer chain breaking during dynamic plowing, and the newly exposed hydrophobic PS end groups were oxidized and became hydrophilic. This change in chemical binding configuration leads to a decrease of adhesion force measured for the modified PS. The energy dissipated by the tip during polymer plowing was found to be sufficient to break covalent bonds (e.g., >1–2 eV). The patterned polymer was also analyzed by size exclusion chromatography, and the results confirmed the scission of polymer structure and formation of shorter chains [30]. In the case of static indentation, Jung et al. estimated that the energy deposited into the polymers is much higher than the typical energy of covalent bonds [31]. Therefore, indentation may be caused by rupturing covalent bonds, or by plastic flow which is a well-known mechanism for polymers.

Nie et al. observed that a scanning of polyethyleneoxide (PEO) films with a large force led to regular stripes perpendicular to the scanning direction [32]. The stripes showed increased elastic stiffness and chain density which was attributed to the rearrangement of the PEO folding structures. During the large-force scanning, the tip pushes folding molecular chains down to some extent depending on the applied forces. The scanning process induces restoring forces (strains) in folding molecular chains, which force them back toward their initial positions. The balance of applied, lateral, and restoring forces determines the arrangement of folding molecular chains. From a model of molecular deformation, the authors estimated that there is some difference between the pristine and large-force scanned PEO. In addition to depressed structures, raised patterns were created by Jin et al. who observed modified areas 1–1.5 nm above the starting surface after raster scanning the tip over the sample surface [33]. They suggested that viscoelastic effects may play a role since the raised patterns were formed only under loads smaller than the yield strength of the polymer. Alternatively, the mechanism may be related to a morphology change induced by localized heating due to the rupture of adhesive force between the tip and sample. The measured force between the Si$_3$N$_4$ tip and polymer is in the range of 40–120 nN. The authors estimated that if all the energy was dissipated within one tip radius of the surface, the surface temperature would increase by up to several hundred degrees Kelvin. Heyde et al. developed a scan-linearized AFM instrument capable of 250 μm × 250 μm scan size for large scale dynamic plowing lithography [34]. The system permits one to operate the microscope in several modes, and allows the addition of desired functions such as force modulation, Kelvin force microscopy, and adhesion mode. Using this set-up, they were able to write straight lines up to 50 μm long by performing dynamic plowing on PMMA film. Fig. 3 shows three straight grooves embossed by the tip, and the accumulation of carved PMMA by the sides of the grooves. The authors discussed the dependence of lithography efficiency on scanning parameters such as the set-point amplitude, scanning directions, and feedback status.

2.1.2. Metals and insulating compounds

Nanolithography by AFM indentation and plowing has been reported for various metals and inorganic compounds such as Al, Au, mica, and KBr [35–41]. Fang and Chang created multiple furrows on an Al thin film using different
They studied the effects of AFM plowing on the roughness, fractal dimension, and bulge edge of the patterned Al surface. It was observed that the average surface roughness of the Al surface was improved after the AFM nanomachining process, and a smoother surface could be obtained under optimized load forces. The bulge edge becomes pronounced after plowing the surface under a fixed load for increased cycles. Filho et al. showed that the depth of a patterned Al film by a diamond tip increases with the applied normal force, while it decreases with increasing tip scanning velocity [36]. In addition, the plastically deformed indentation depth increases with prolonged duration of force application. Kato et al. scratched an oxide-covered Al surface with an AFM probe in various solutions including water, CuSO₄, and NaOH [37]. Grooves with increasing depth were fabricated by performing mechanical lithography in solutions under repeated plowing cycles (Fig. 4(a)). The authors found that the groove depth strongly depends on the load force, scratch cycles, solution pH values and chemical compositions. Fig. 4(b) shows the proposed mechanism for groove formation by AFM plowing in an aqueous solution. Scratching in dilute NaOH solution gives the highest groove development rate due to the high dissolution rate of Al. Wear of the Si probe was also examined by conducting the scratching experiments many times in water and NaOH solution. Irmer et al. defined superconducting constrictions by plowing a deposited Al film with a hard diamond-like AFM probe [38]. Highly transparent Josephson
junctions with a minimum contact length of 50 nm were fabricated, and their behavior was examined by a dc (direct current) superconducting quantum interference device. The authors demonstrated that the junctions can be easily integrated in mesoscopic devices as local radiation sources, and could be used as tunable on-chip millimeter-wave sources. The fabrication of nanochannels (~50 nm wide and 5 nm deep), nanosquares (50 nm wide and 5 nm deep) and complex nanostructures on a single Au nanowire was reported by Li et al. Such structures were created by directly scratching/sliding the Au wire surface with an AFM probe. Nanoscale surface polishing was also achieved by the implementation of the probe wear technique. Performing the wear procedure on the Au nanowire reduces the root mean square (RMS) surface roughness from 2 to 0.7. It is believed that creating nanostructures directly on nanowires may have applications in the fields of fluidics and biotechnology, as the patterns could be utilized to perform nanoscale fluidic pumping, fluid separation and chemical sensing.

As for insulating compounds, Gnecco et al. utilized a Si tip to scratch a KBr (1 0 0) surface in ultrahigh vacuum condition, and observed the abrasion of KBr down to the atomic scale. The damaged surface is smoothly modified by the tip pressure, and the debris is rearranged in an epitaxylike process, which leads to the creation of mounds with the same structure as the underlying surface. The depth of grooves and pits increases at high load, whereas the velocity does not significantly affect the scratching process. The authors suggested that the KBr ions are detached pair by pair, and moved by the tip to form ordered structures. Müller et al. reported the controlled and reproducible structuring of a mica surface by a silicon nitride tip operated in contact mode under ambient conditions. By repeated scanning of the tip along a predefined pattern at forces between 100 nN and 4 μN, mechanically induced etching was observed on the atomic scale. In contrast to the observation under ultrahigh vacuum condition, no tip wear and debris was found on the surface, indicating the atomic scale nature of the wear process. Line width down to 3 nm was achieved, and patterns on a wide range of length scales between 5 μm and 100 μm were generated. Their results were explained in terms of the local frictional force induced by chemical reactions, and the abrasive wear on the atomic and molecular scale. The observed threshold value of the force needed for surface modification provides important information concerning the structuring mechanism and may indicate a corresponding activation threshold for relevant processes of mechanically induced atomic scale etching. Fig. 5(a) and (b) displays the AFM images of a simple groove rectangle and complex groove structures generated by plowing the tip on atomically flat mica surfaces. The width of the groove rectangle is about 3 nm, and the depth is ~1 nm which corresponds to the height of one monolayer mica lattice.

2.1.3. Semiconductors

The application of AFM mechanical nanolithography on semiconductors ranges from creating simple patterns to fabricating electronic devices. Hyon et al. used commercial AFM tips to generate patterns as narrow as 10 nm on a GaAs surface. The formation of nanostructures with fully controlled width and depth was achieved by adjusting the feedback gain and the scan speed of the plowing operation. Schumacher et al. used an AFM tip to locally deplete the two-dimensional electron gas (2DEG) of a GaAs/AlGaAs heterostructure. As shown in the inset of Fig. 6(a), the line writing process was carried out by scanning the AFM tip against the surface under a load force of

![AFM morphology images of (a) a groove rectangle (image size: 1600 nm × 1600 nm), and (b) larger scale complex groove structures (image size: 27 μm × 27 μm) written into the mica surfaces by AFM mechanical plowing. Reproduced with permission from Ref. [41], © 2004 John Wiley & Sons, Ltd.]
The tip was repeatedly scanned over the Hall bar with a scan velocity of \( \sim 100 \mu m/s \), leading to a stepwise depletion of the 2DEG underneath the tip, and an increase of the electrical resistance. The plot in Fig. 6(a) shows the relationship between the resistance of the 2DEG and the number of scans during the fabrication of a typical line. The authors ascribed the evolution of resistance to the step-by-step depletion of the 2DEG resulting from the continuous removal of the GaAs/AlGaAs layers. The weak depletion observed at the initial stages is due to the removal of the undoped GaAs layer. The continuous thinning of the doping layer leads to a stronger depopulation of the 2DEG in the vicinity of the line. Eventually, the 2DEG is completely depopulated and the resistance increases to the background resistance of the wafer. Based on this technique, the authors fabricated an in-plane-gate transistor with mechanically written gates. Current–voltage (\( I-V \)) curves between the source and drain of the transistor were collected at low temperature, and nonlinear and linear \( I-V \) behaviors were observed for different side-gate voltages. A single-electron transistor was further fabricated by writing two tunneling barriers across the conducting channel.

Rosa et al. employed AFM to directly pattern the 2DEG of InAs/AlSb surface quantum wells [44]. They chose soft InAs semiconductor as the top layer to facilitate the direct modification of the InAs surface by the AFM tip with a relatively weaker force compared to that used for patterning Si and GaAs surfaces. Sharpened and sturdy electron beam deposited tips were used for reliable mechanical lithography and high resolution imaging. Fig. 6(b) depicts an array of directly patterned holes with a period of 55 nm and hole depth of 3 nm fabricated into a 8 nm-thin quantum well. Such AFM-fabricated holes are a few nanometers in diameter, and are much smaller than those (40–50 nm in diameter) fabricated by the authors through wet etching [44]. Magnetoresistance measurements indicated that the action of the direct patterning on the electron system is essentially restricted to the holes visible in the topographical image. Regul et al. fabricated quantum point contact devices by engraving a constriction into a GaAs/AlGaAs heterostructure with Si and diamond tips [45]. The electronic properties of the devices fabricated by different tips were then characterized by measuring the differential conductance of the devices. Flat quantized plateaus indicative of the formation of ballistic quantum point contacts were observed on diamond tip-patterned devices. In contrast, only a few poorly resolved conductance plateaus were detected on the Si tip-patterned sample. Further examination of the subband spacing of the diamond tip-patterned device indicated that the shape of the confinement inside the constriction remains nearly unaffected by the gate voltage. Furthermore, the depletion length observed for the diamond tip-patterned device is roughly two times smaller than that for the silicon tip-fabricated device. The authors concluded that diamond tips are almost perfect for not only fast and simple processing, but also in forming proper potential profiles for the investigation of electron transport behaviors.

2.1.4. Pattern transfer

In addition to direct AFM indentation and plowing, numerous groups have reported indirect nanofabrication schemes based on the transfer of AFM-generated patterns through wet-etching or lift-off techniques [46–52]. Klehn and Kunze coated polymer resist on various materials including SiO\(_2\), Si, GaAs and Au, and fabricated furrows in the resist using a vector-scan controlled dynamic plowing technique [46,47]. They showed that the penetration depth of
the tip into the resist depends on the duration and force of the tapping action. The depth is large when high driving amplitude and slow scanning speeds are used. An optimized amplitude is needed for the tip to completely penetrate the resist without scratching the underlying substrate, thus also degrading the tip quality. The resist patterns were then transferred to other materials by wet-chemical etching, followed by the removal of the resist layer in organic solvents.

Fig. 7(a) displays the scanning electron microscope (SEM) image of a pattern transferred to a 1.5 nm-thick SiO2 by the above procedures. The line width of the pattern is 30–40 nm, and the dark contrast represents the exposed Si surface due to the etching of oxides. The important factors limiting the resolution are the unavoidable underetching, attack of the resist by the etchant, imperfect resist notching due to lateral tip vibration, and the shape of the tip. Further transfer of SiO2 trenches into the Si substrate was achieved by anisotropic etching in 25 wt% tetramethylammonium hydroxide (TMAH), which is a preferential etchant of Si over SiO2. Resist patterns were also transferred to GaAs, Ti and Au surfaces using different etchants followed by stripping the resist in organic acetone. Fig. 7(b) displays the line patterns fabricated on GaAs (0 0 1) using bromine methanol solution as etchant. Magno and Bennett demonstrated the patterning of III–V compound semiconductors, such as GaSb/InAs and InSb/GaSb, by cutting lines in thin layers using AFM probes [48]. Cuts up to 10 nm deep which pass through 2–5 nm thick epilayers of both GaSb and InSb were formed. Selective etchants and GaSb etch masks were used to transfer patterns onto the InAs epilayer. Wendel et al. described a technique for integrated AFM lithography on various mask materials covering a mesa-etched GaAs/AlGaAs heterostructure [49]. The generated patterns were transferred to the 2DEG by wet chemical etching or by ion beam irradiation. They fabricated hole arrays with a periodicity of down to 35 nm and a hole diameter of only a few nanometers. Their magnetoresistances studies of the antidot device confirmed the successful pattern transfer to the electron system. Pyo et al. employed the polymer plowing technique to fabricate bottom-contact pentacene organic thin-film transistors (OTFTs) with a submicrometer channel length [50]. Source and drain electrodes were defined by mechanically scratching the Au layer on SiO2/Si with an AFM probe. The sample was then treated with hexamethyldisilazane (HMDS), and pentacene was evaporated onto the system to complete the OTFTs fabrication. In the above procedures, the scratching of Au layer by AFM probe determines the channel length, and the uniformity of the channel can be controlled by adjusting the probe load forces. The output characteristics of their OTFTs showed a typical p-type behavior with a lack of current saturation due to the short channel length. The field-effect mobility and inverse subthreshold swing of the device were also examined.

Beside device fabrication, the AFM-generated structures have also been used as templates to direct the growth of nanostructures. Chen et al. presented the formation of polypyrrole nanowires by combined AFM mechanical lithography and electropolymerization [51]. PMMA nanochannels were created on an ITO (indium tin oxide) substrate by means of static plowing technique. The width and depth of the nanochannels were controlled such that the polypyrrole monomer can penetrate through the PMMA layer and be in contact with the conducting ITO substrate. The nanochannels were subsequently used as a template for the electrochemical synthesis of polypyrrole nanowires. Fig. 8(a) and (b) displays the AFM images of the PMMA nanochannels and polypyrrole nanowires grown after electropolymerization, respectively. It can be seen that the growth of polypyrrole nanowires is strictly confined within the PMMA patterns defined by AFM plowing lithography. Conductive AFM (cAFM) measurements showed higher electric current from the patterned polypyrrole nanowires compared to the unpatterned region. Similarly, template-
directed metal nanowire growth can also be achieved by AFM nanoscratching coupled with evaporation and lift-off procedures. Chen et al. demonstrated the fabrication of various metallic nanowire patterns by depositing metals onto the AFM-generated PMMA grooves followed by dissolving the PMMA resist in acetone [52]. A range of nanowires, including Au, Cu, Ni, Al and Ti with widths down to 50 nm, were grown on SiO$_2$/Si substrates.

2.2. Thermomechanical writing

2.2.1. Heat transfer and mechanical behaviors

In thermomechanical writing, a resistively heated AFM probe writes a data bit by scanning over a polymer surface. The combined heat and mechanical force of the tip causes the polymer to soften and flow, thus facilitating the writing of data bits in a storage medium. This technique was pioneered by the IBM Zurich research group, and systematic descriptions on its working principles and applications can be found in their numerous publications [15,53–65]. Here, we briefly summarize their work and highlight a few key issues including the heat transfer and the physical behaviors of the polymer medium during thermomechanical indentation. Fig. 9(a) and (b) shows the schematic and SEM image of the resistively heated cantilever used for thermomechanical writing. The Si cantilever legs are made highly conductive by high-dose ion implantation, whereas the heater region (including the Si tip) remains low-doped for high resistivity. An electrical current is passed through the cantilever, and a large force is loaded on the hot tip to indent the polymer medium. Vettiger et al. reported that initially the heat transfer from the tip to polymer through the small
contact area was very poor, and it improved as the contact area increased [53]. In their experiments, the tip was heated to a relatively high temperature (~400 °C) to initiate the polymer softening. The tip was then pressed into the polymer to increase the volume of softened polymer and hence the bit size. According to the estimation of King et al., at the initial stage of the writing process, only ~0.2% of the heat power is utilized in the nanoscale contact zone (10–40 nm²) to soften the polymer [54]. About 80% is wasted through the cantilever legs to the chip body, and ~20% is radiated from the heater platform through the air gap to the medium/substrate. After the polymer has been softened and contact area increased, the percentage of the heating power transferred from the tip to the polymer increases to 2%. The IBM groups explored the use of very thin polymer layers deposited on Si substrate to improve heat transfer, and to achieve small tip penetration and small bit size [55]. The hard Si substrate prevents the tip from penetrating farther than the film thickness, and it enables more rapid transport of heat away from the heated region due to the higher thermal conductivity of Si. By coating a 40 nm-thick PMMA layer on Si, they obtained bit sizes ranging from 10 nm to 50 nm. A 70 nm-thick SU-8 stop layer was also introduced between the Si substrate and PMMA to prevent the tip wear possibly caused by the direct contact of the tip and substrate. Data bits 40 nm in diameter on such layered storage medium were written using a 1 μm-thick, 70 μm-long, two-legged Si cantilever. For bit writing, an electrical pulse 2 μs in duration was applied to the cantilever for a period of 50 μs. A 40 nm bits can be written with a 120 nm pitch, implying a potential bit areal density of 400 Gb/in.².

The IBM Zurich group further demonstrated that the heater cantilever originally used for writing can also function as a thermal readback sensor to read the data bits through its temperature-dependent resistance [53]. The resistance R increases nonlinearly with heating power/temperature from room temperature to a peak value of 500–700 °C. The peak temperature is determined by the doping concentration of the heater platform, which ranges from 1 × 10¹⁷ cm⁻³ to 2 × 10¹⁸ cm⁻³. Above the peak temperature, the resistance drops as the number of intrinsic carriers increases because of thermal excitation. For sensing, the resistor is operated at ~350 °C, a temperature that is not high enough to soften the polymer as is the case for writing. Vettiger et al. explained that the principle of thermal sensing is based on the fact that thermal conductance between the heater platform and the storage substrate changes according to the distance between them. The medium between a cantilever and the storage substrate transports heat from one side to the other. When the distance between the heater and sample is reduced as the tip moves into a bit indentation, the heat transport through air will be more efficient, and the heater’s temperature and resistance will decrease. Thus, changes in temperature of the continuously heated resistor are monitored while the cantilever is scanned over data bits, providing a means for detecting the bits.

According to Vettiger et al., the physical behavior of the polymer during indentation obeys the time–temperature principle [53]. In this principle, the time and temperature scales are considered to be interdependent variables that determine the polymer properties such as shear modulus. The authors plotted the threshold-temperature against heating-time for the bit writing process, and observed that the curve indeed shows the characteristics of time–temperature superposition. In addition, at constant heater temperature, the time for writing a bit was found to be inversely proportional to the load force. Their results indicate that the internal friction due to the high-frequency viscosity is the rate-limiting step in thermomechanical indentation. It was suggested that the time needed to heat the polymer above its glass transition temperature (Tg) is another rate-limiting step, as the spreading resistance of the heat flow and the thermal contact resistance are most critical factors in thermal conduction. Although simulations showed that thermal equilibrium in the polymer can be reached within 1 μs, the thermal coupling efficiency across the tip/polymer interface remains unknown. It was indicated that the heat transfer between the tip and polymer plays a crucial role. When the polymer is in contact with the heated tip, its temperature approaches the glass transition temperature asymptotically, leading to a substantial temperature gradient between the heater and medium.

Vettiger et al. also studied the detailed shape of the pile-up of materials surrounding the indentation [53]. They suggested the pile-up originates not only from the materials pushed aside during indentation as a result of volume conservation, but also an increase of the specific volume of the polymer induced by the flash heating and rapid cooling of the polymer. The outer perimeter of the pile-up corresponds to the Tg isotherm, and the temperature in the enclosed area has certainly reached values above Tg during the indentation process. The interaction of two successive pile-ups was further demonstrated by Vettiger et al. as shown in Fig. 10. When two indentations are located at certain separations, the pile-up regions can overlap each other without disturbing the indentation. If the two indentations are closer, the pile-up region of the latter indentation would extend over the pitch of the former indentation, leading to a significant decrease of the indentation depth (or erasing of the bit). However, when the spacing of the two bits is decreased even further, the erasing process ceases, and instead, a broader indentation would be formed.
Thermomechanical writing is a reversible nanofabrication technique in which data bits can be written, erased, and re-written. Data erasing is simply achieved by thermal reflow of the storage field as a whole. Binnig et al. reported that small bits (≤100 nm) can be erased very easily by heating the polymeric media to ~150 °C for a few seconds [55]. No alteration of the polymer film was observed after repeated writing and erasing. With this approach, storage fields of a few hundred microns can be erased en bloc.

2.2.2. Millipede technique

In the early 1990s, researchers at IBM first demonstrated the writing of storage bits by thermomechanical indentation based on a single AFM probe [56–59]. They achieved a storage density of up to 30 Gb/in.², which represents a significant advancement in that period. A single AFM can typically operate on the microsecond time scale, while the conventional magnetic storage operates on the nanosecond time scale. It is clear the AFM data rates have to be improved by three orders of magnitudes to be competitive with current and future magnetic recording. To solve this problem, the IBM researchers fabricated 5 × 5 probe arrays, and later invented the millipede technique which is based on 32 × 32 probe arrays for highly parallel data writing [53,60–65]. In this technique, the ultimate locality is given by the tip, and high data rates are achievable through the massive parallel operations of such tips. Fig. 11(a) shows the configuration of a 2D AFM cantilever arrays fabricated by the IBM groups [63,64]. Either the entire cantilever array or the polymer medium can be scanned in the x and y directions. The contact between the probe arrays and the polymer sample is realized by adjusting the z-piezo voltage, and only one feedback is used to control all the probes. Additional approaching sensors are integrated into the corners of the array chip to control the approach of the chip to the storage medium. These sensors can provide feedback signals to adjust the z-actuator until uniform contact with the medium is established. During data writing, the chip is raster-scanned over an area called the storage field, and each cantilever of the array writes and reads data only in its own storage field. A 32 × 32 array chip can generate 1024 storage fields on an area of less than 3 mm × 3 mm. The corresponding data capacity of the 1024 storage fields is 0.9 Gb assuming an areal density of 500 Gb/in.². Fig. 11(b) shows the photograph of the fabricated
chip, on which the 32 × 32 cantilever array is located at the center with bond pads distributed on either side. In general, the storage capacity of the system scales with the areal density, the cantilever pitch, and the number of cantilevers in the array.

The IBM group fabricated cantilevers entirely of Si for good thermal and mechanical stability [53]. Soft and high-resonance-frequency cantilevers were chosen for low loading force and low tip/medium wear, and high-speed scanning. Sufficiently wide cantilever legs were designed for a small thermal time constant, which is partly determined by cooling via the cantilever legs. Cantilevers were released from the crystalline Si substrate by surface micromachining through plasma or wet-chemical etching. The cantilevers within the array were electrically isolated from one another using integrated Schottky diodes. It was shown that the current response to an addressed cantilever in an array is nearly independent of the size of the array. The power applied to address a cantilever is not shunted by other cantilevers, and the reading sensitivity is not degraded. Their wear investigations suggested that a tip-apex height uniformity across the tip of less than 500 nm is required, with the exact number depending on the spring constant of the cantilever. For parallel operation on a large scale, Vettiger et al. developed a microscanner which is able to control the parallelism between the probe array and the sample [53]. The key element of the microscanner is a mobile platform which is supported by springs and contains integrated planar coils. Their PC-controlled write/read scheme addresses the 32 cantilevers of one row in parallel. Writing is performed by connecting the addressed row for 20 μs to a high, negative voltage and simultaneously applying data inputs to the 32 column lines. The row-enabling and column-addressing scheme supplies a heater current to all cantilevers. Selected cantilevers heated to high temperatures generate an indentation, while those with low temperatures make no indentation. When the scan stage has moved to the next bit position, the process is repeated, and this is continued until the line scan is finished.

Although the first high-density storage operation by the largest 2D array chip has been demonstrated, there are a number of issues to be addressed before the Millipede technique can be considered for commercial applications. According to Vettiger et al. [53], some of the unsolved key issues include: (i) overall system reliability, such as bit density, tip and medium wear, erasing and rewriting; (ii) limits of data rate, areal density, array and cantilever size; (iii) CMOS integration; (iv) optimization of write/read multiplexing scheme; (v) array-chip tracking; (vi) data rate versus power consumption tradeoffs. The IBM Zurich group is currently developing a functional prototype to investigate these important aspects. They have identified the fundamental physical mechanism of polymer deformation pertaining to the correlations between polymer properties and millipede operational parameters. The fact that bit writing is a robust process in terms of polymer selection may open up wide opportunities for medium optimization and for complementary technical requirements.

2.3. Manipulation

In AFM nanoscopic manipulation, the tip is used to mechanically cut, push, and transport materials to form desired patterns on a substrate. The materials manipulated by AFM range from single atoms, nanoparticles, nanocrystals and nanotubes to biological molecules such as DNA [16,66–75]. The manipulations can be operated in contact, tapping, and non-contact modes with the feedback loop on or off. Theoretical modeling was performed to understand the motion behaviors during manipulation. Experiments have also been carried out for nanoscale tribology and friction investigations, and for the fabrication of patterns and devices.

2.3.1. Modeling and protocols

In their modeling of pushing manipulation, Sitti and Hashimoto analyzed the interaction forces among the AFM tip, nanoparticle and substrate before and during pushing manipulation (Fig. 12) [66]. Two main phases during the manipulation, static and kinetic friction, were computed, and the conditions required for enabling the particle pushing were identified. At the beginning, due to static friction, the particle and tip follow the stage motion to the point where the applied cantilever load exceeds the static friction between the particle and substrate. After the initiation of lateral movement, the particle motion involves pure sliding, rolling and rotation. Their results indicate that the frictional properties of the particle/substrate interface, the adhesional force, and the nanoparticle fixation chemicals are crucial and specific factors in nanoscale pushing manipulations.

Ramachandran et al. presented techniques for the direct and controlled manipulation of nanoscale three-dimensional features using non-contact AFM (NC-AFM) [67]. They proposed two protocols for nanomanipulation by switching on and off the AFM feedback during the patterning processes. In the first protocol, the NC-AFM feedback is
switched off as the tip approaches the nanostructures. This leads to the close contact between the tip and structure, and the movement of the structure with the tip when the tip scans across the surface. In the second protocol, the feedback loop is switched on during the manipulation, and contrast reversal (from positive to negative images) is produced due to the feedback instability. The second protocol is advantageous because it allows easier identification of the operation regime and the manipulation of small features a few nanometers in size. It was indicated that pushing of the nanostructure by the tip via repulsive forces is the mechanism for manipulation in both protocols. The authors further demonstrated the viability of these two protocols by directly manipulating Au nanoparticles (5–15 nm in diameter) into pre-designed patterns on a mica surface. The limitation of both techniques is the tip and/or nanostructure damage due to the repulsive forces during manipulation. Indeed, the authors observed surface damage and changes to the tip shape as manifested by changes in the apparent shape and size of the imaged particles [67].

2.3.2. Single atoms and nanocrystals

The smallest structure manipulated by AFM is a single atom as reported by Sugimoto et al. [16]. In their work, the authors demonstrated the ability of AFM nanolithography to manipulate single atoms laterally for artificial structure creation and two-dimensional nanoengineering at room temperature. Atom inlays were created which are artificial atomic patterns formed from a few embedded atoms in the plane of a surface. Fig. 13 shows an atom inlay fabricated by laterally rearranging substitutional Sn adatoms on Ge (1 1 1)-c(2 × 8) to compose the letters associated with the Sn element. The creation of this nanostructure required more than 120 single-atom manipulation events during a continuous 9 h microscope operation. Such artificial atomic structures could remain stable on the surface at room

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Fig. 12. (a) Schematic showing the interaction forces among the tip, particle and substrate before pushing manipulation. (b) Schematic showing the contact pushing mechanism during manipulation. Reproduced with permission from Ref. [66], © 2000 IEEE.

Fig. 13. AFM height image (7.7 nm × 7.7 nm) of an atom inlay in the form of Sn patterned by single-atom manipulation. Reproduced with permission from Ref. [16], © 2005 Macmillan Publishers Ltd.
temperature for relatively long periods of time, and a minimum mean lifetime of 25 h was estimated for the atom inlay shown in Fig. 13.

The manipulation of larger structures such as nanospheres was reported by Ritter et al. [68]. With a vibrating tip, the authors translated and rotated in-plane submicron-sized latex particles to form two-dimensional patterns from randomly arranged arrays of particles on a given substrate (Fig. 14). The pattern formation involves the pushing and sliding of structurally unchanged nanoparticles on the surface by the tip operated in dynamic mode. The starting point, direction and end point of the nanoparticle movement were readily defined using the manipulation vectors. The controlled sliding and dislocation of nanoparticles also gives access to the study of their frictional and adhesional properties. In this case, the motion of the nanoparticles is dominated by sliding rather than rolling. The threshold amplitude needed to overcome the static friction of a single latex sphere was shown to be dependent on the size of the manipulated spheres. Using a similar technique, Resch et al. fabricated a pyramid-like Au structure by pushing one nanoparticle up between two adjacent particles [69]. The three-dimensional structure could be disassembled by pushing the top Au particle away from the base particles with the same AFM probe. The manipulation procedures can also lead to the formation of dimers by connecting separate Au particles together.

Flower-shaped antimony clusters on a graphite surface were manipulated by Heyde et al. [70]. The nanoclusters were displaced under high amplitudes of tip oscillation with a precision of ~20% of their sizes. Branchlike structures were found to split up during the dislocation operation. Using AFM manipulation, groups of antimony islands were separated, and surface areas were cleaned. Hsieh et al. studied the AFM manipulation of micelle-capped Au nanorods deposited on silicon oxide (SiO₂) surfaces [71]. They observed that translational manipulation of a nanorod without rotation took place whenever the tip hit the nanorod at its center. It was easier to translate the rods when the pushing direction was along the longitudinal axis than when pushing was performed transverse to the axis. This is because it is easier to locate the highest point across the width of the rod than to precisely determine the center of the rod along the axis of the rod. Therefore, longitudinal manipulation often led to perfect rod translation, while transverse operation was always accompanied by both translational and rotational movements.

Sheehan and Leiber employed AFM manipulation for nanotribology studies and nanofabrication applications [72]. They used an AFM tip to slide molybdenum oxide (MoO₃) nanocrystals on single-crystal molybdenum disulfide (MoS₂) surfaces. They observed highly anisotropic friction when MoO₃ nanocrystals moved in specific directions on the MoS₂ surface lattice. The extreme friction anisotropy was exploited by the authors to fabricate multicomponent MoO₃ nanostructures. By combining lattice-directed sliding with nanomachining, the authors defined interconnects and lock crystals together. In their AFM experiments, they manipulated two MoO₃ nanocrystals that have different preferred sliding directions on the MoS₂ substrate. As illustrated in Fig. 15, a 52 nm notch in crystal 2 was first opened by AFM nanomachining. Second, a rectangular latch was defined in crystal 1, and crystal 2 was translated by AFM so that its notch was almost aligned with the latch. The authors then enlarged the notch by 11 nm to make it wider than the

Fig. 14. AFM images (2 μm x 2 μm) showing the initial randomly arranged particles (a) and the “HU” patterns (b) formed by laterally manipulating the particles using an AFM tip. Reproduced with permission from Ref. [68]. © 2002 American Chemical Society.
latch. By sliding the latch into the notch of crystal 2, the two crystals were effectively locked, because crystal 2 could no longer move along its preferred direction on the MoS2 surface. Hence, a nanometer scale mechanical lock was fabricated by AFM manipulation. Such locking is reversible, e.g., the lock and unlock of crystals 1 and 2 could be repeated several times. The authors also tested the strength of the latch by determining the force required to slide crystal 2 perpendicular to the latch axis. A lateral force of 41 nN was estimated to break the latch, and this force is relatively large considering the small contact area of the latch.

A single-electron transistor was fabricated by Roschier et al. through the manipulation of carbon nanotubes (CNT) [73]. In the manipulation process, they first imaged the surface in non-contact mode with the feedback loop on. Then the tip was positioned to scan a single line over the CNT end, and the feedback loop was subsequently switched off, and the tip–surface distance was decreased in small steps of 1–10 nm. As the distance was decreased, the vibration amplitude decreased and the tube location could be observed in situ. At the moment when the tube was hardly visible in the amplitude signal, the CNT was usually moved. At the beginning, the tip was pushed very hard against the surface to loosen the tube. The tube was then moved by rotations around a pivot point on the surface. The moving procedures involved iterative dragging and pushing of the CNT over a distance of 1 μm. Fig. 16 shows the fabrication of a transistor by moving the CNT and putting it over the electrodes using the AFM manipulation technique. The I–V characteristics of the device exhibited single-electron charging effect, and a band gap of 15 meV was derived for the semiconducting CNT on the basis of their measurements. The authors also observed the Coulomb staircase structure in the I–V curve obtained from their asymmetric tunnel junction.

2.3.3. Biological molecules

The application of AFM nanomanipulation in fabricating biological structures was demonstrated by Hu et al. who described the cutting, shaping and folding of DNA strands by an AFM tip to form artificial DNA patterns [74]. In their work, they first used threshold forces of 20–100 nN to break the DNA strands at selected sites, and then they swept...
away the residues using a force smaller than the threshold loads. Fig. 17(a) shows an initial regular DNA network formed on a mica surface by the molecular combing technique. In Fig. 17(b), the DNA strands were cut at specific sites, and the DNA network was partially disconnected. Fig. 17(c) displays the successive cutting of the DNA strands at more sites, such that an isolated DNA square was defined in the center of the network. The authors also found that DNA strands are highly elastic and could bear a large change to their shape. As shown in Fig. 17(d), a wavy DNA structure was formed by delicately manipulating an initially straight DNA strand. It was observed that the DNA pattern did not shrink back to its original length, but rather remained on the surface after the deformation process. The length of the curved part was estimated to be 1.6 times that of the straight part. Such a large increase in DNA length originates from the overstretching of the strands, which leads to an irreversible change of the helix structure. The AFM probe can also induce DNA folding to convert DNA strands into spherical nanoparticles and nanorods. As seen in Fig. 17(e), the DNA strand was first broken by AFM cutting, it was then pushed forward in the vertical scan direction and folded up by starting the scan at the broken site in the horizontal direction. According to Hu et al. the pushing operation can be performed step by step at a precision of 10 nm, depending on the tip size [74]. By controlling the length of folded DNA strand through the scanning distance in the vertical direction, small and long DNA fractions can be converted into nanoparticles and thick nanorods, respectively. Fig. 17(f) shows an example of a 150 nm-long nanorod converted from a 600 nm-long DNA strand. The rods are at least partially ordered, as a periodic structure resembling a helix structure was observed in the longitudinal direction [74]. Although the detailed mechanism for the DNA patterning is not clear, it appears that the DNA adhesion, tip shape, and the scanning direction are key factors controlling the DNA manipulation. On the basis of DNA cutting, Lü et al. further demonstrated the isolation of DNA fragments for
biochemical analysis using an AFM kneading technique [75]. Single-molecule amplification experiments verified that the DNA fragment was kept active during the manipulation process.

2.4. Dip-pen nanolithography (DPN)

In 1999, Mirkin’s group invented the DPN technique to deliver collections of molecules in a positive printing mode [17]. DPN is an AFM-based direct-write lithographic technique in which the AFM probe is used as a pen to directly deliver materials (inks) to a nanoscopic region on a target substrate (Fig. 18). In most cases, the transport of ink molecules from the tip to the substrate is mediated by a water meniscus which is formed through capillary condensation. Depending on the selection of ink molecules, DPN is capable of creating structures made of various
materials such as metal, inorganic compounds, organic molecules, and biological species [17,76–101]. The fabrication of a wide range of functional structures by DPN has been demonstrated, and some of the typical structures include high resolution organic features, metallic and magnetic patterns, polymer brush arrays, and biological devices. A comprehensive and dedicated description on the evolution of DPN can be found in a recent review article by Mirkin and co-workers [22]. Here, we discuss the work related to the mechanism of ink transport and the applications of DPN in nanofabrication.

2.4.1. Meniscus formation and ink transport

While significant progress has been achieved in DPN-based nanofabrication of patterns and devices, there is an ongoing debate on the detailed mechanism for ink transport and diffusion. Theoretical and experimental results showed that the transport and deposition of inks depends on several factors such as the formation of water meniscus, the properties of the tip and the substrate, and the ink deposition time and temperature. In their Monte Carlo simulations, Jang et al. addressed the mechanism for liquid meniscus condensation in the confined tip–substrate geometry [76]. They showed how the equilibrium density profile changes from a gaslike state to a liquid meniscus as the saturation increases at constant temperature and tip–substrate distance. When the saturation is increased, an initial diffusive liquid meniscus is formed near the tip apex as a result of the accumulation of dense vapor. The meniscus then broadens continuously until it fills up the region outside its initial radius. For a tip–substrate spacing of 1.3 nm, the simulated width of the meniscus can be continuously extended from 4.5 nm to 32 nm if the humidity is increased. Small menisci are very unstable, with size fluctuations being much larger than their average width. The instability decreases with the broadening of the meniscus, and it finally converges at certain values of width. The size of the tip also has an impact on the formation of liquid meniscus: the width of the meniscus can be dramatically reduced for a better DPN resolution if a sharper tip is used. Moreover, changing the wettability of the tip has an even more dramatic effect than the tip size effect. The calculated width of the meniscus will be reduced by 10 times if the wettability is reduced from complete wetting to partial drying. A shorter tip–substrate spacing would favor the formation of meniscus, as the authors observed a linear decrease in meniscus width with increasing tip–substrate distance. The temperature effect on the meniscus width is not as significant as that arising from saturation, tip curvature, tip wettability, and tip–substrate distance. In general, the meniscus becomes smaller when the temperature is raised. A nascent meniscus formed by a tip at its closest contact with the substrate is independent of the tip geometry and wettability. When converted to a physical dimension relevant to DPN, the minimum meniscus width for the shortest tip–substrate spacing was estimated to be 2.3 nm [76].

In another work, Jang et al. investigated the ink diffusion dynamics in DPN using random walk simulation and analytical theory [77]. Fig. 19 displays the model used in their simulation which involves ink molecule transport and lateral diffusion. For a tip generating a constant flux of ink molecules, patterns such as circles, lines and letters were

Fig. 19. Proposed transport mechanism of ink molecules from the tip to the substrate. The incoming molecular flux from the tip creates a concentration gradient around the tip, and ink molecules subsequently diffuse over the region already occupied by other ink molecules (drawn as filled circles) to be finally trapped by the bare surface. Reproduced with permission from Ref. [77]. © 2001 American Institute of Physics.
studied by varying the deposition rate of ink molecules and the tip scan speed. In the case of circular structure formation, their results showed that the circle size grows linearly with the ink deposition time. Deviation from linearity was observed at the end of slow deposition processes, while it was detected at a relatively earlier time in fast deposition processes. The post-deposition ink diffusion was found to be negligible for slow deposition, but quite significant in fast deposition. In their simulation, when the tip was moved to generate patterns of lines and letters, broader and fuzzy lines were obtained at a slower scan rate, while disconnected lines consisting of isolated dots were obtained when the scan speed was increased. The diffusion of ink molecules on the bare substrate surface was also simulated by introducing finite diffusivity [77]. It was found that any pattern deposited would eventually diffuse over the entire surface, and no distinct pattern could be formed at prolonged times. The experimental results of Manandhar et al. showed an anomalous surface diffusion in the ink deposition process [78]. In their work, the authors used 1-dodecanethiol (DDA) as ink molecule which has weak binding to the mica substrate. Such a weak binding system allowed the authors to study the details of ink lateral diffusion by avoiding the surface binding events. Small and isotropic patterns of DDA were formed for short-time deposition, while large and anisotropic DDA structures were observed after long-time deposition. The fractal patterns cannot be explained by the random walk model proposed by Jang et al. [77]. Manandhar et al. attributed the anomalous diffusion to the rapid crystalline growth of DDA molecules on the mica surface: at the initial stage, the DDA structure remains circular because the pattern formation is dominated by the isotropic velocity distribution of the molecules coming from the tip [78]. When the pattern gets larger than the domain size, the lateral diffusion of DDA takes effect. The randomly diffusing molecules can sprout new crystalline domains at the edges of old domains, leading to the formation of fractal structures.

A double-molecular-layer (DML) model was proposed by Cho et al. to explain the molecular transport through the nanoscale tip–substrate junction [79]. By analyzing the temperature dependence of the pattern growth rate, they identified a phase transition which involves the melting of molecular ink layers during DPN deposition. In the DML model, the molecular ink on the AFM tip consists of a bulk solid part and a thin mobile layer. Above the melting temperature of the ink, the solid part of the molecular coating melts and the DML of the molecular ink becomes just a single molecular layer. Based on this model, previous contradicting experimental results were interpreted in terms of the dependence of pattern growth on solvents, absorbed water, and temperature [79]. Weeks et al. investigated the effects of humidity, tip speed, and dwell time (the duration of tip–sample interaction in static writing) on feature size during DPN writing [80]. Their experimental observations indicated that a transition between two distinct deposition regimes occurs at a dwell time independent of humidity. At low humidity, the meniscus does not form, thus the ink transport from the tip to the substrate is inhibited. The feature size increase with humidity, but the relative increase is independent of dwell time. The authors proposed a model based on self-assembled monolayer (SAM) to account for their observations. In this model, ink molecules dissolve from the tip into the meniscus, diffuse through the meniscus, and attach to the surface forming a continuous SAM. When the tip is removed from the water film, ink molecules are both attached to the surface and dissolved in the meniscus. Through diffusion, the dissolved ink molecules will eventually reach the edge of the SAM, forming the final size of the features. According to this model, for short dwell times, the most important parameter controlling the feature size is the activation energy for ink molecular detachment.

Rozhok et al. studied the effects of temperature and humidity on DPN patterning of 1-octadecanethiol (ODT) and 16-mercaptophexadecanonic acid (MHA) [81]. They observed that the ink deposition rate increases when the temperature is raised, and this dependence is strongly affected by other factors such as humidity, the chemical binding between the ink molecule and substrate, and the tip scanning speed. Ink solubility is a key parameter in determining temperature and humidity dependence of the pattern growth rate. Under typical DPN conditions, water is always present in the tip–substrate gap, and its impact on pattern formation is closely related to the solubility of ink materials in water.

New insights were presented by Hampton et al. who used long dwell times ranging from 15 s to 2 h to pattern ODT and MHA thiols on Au [82]. The transport rate for smaller patterns was found to be different from that of larger structures. Their results indicated that measurements with short dwell times are insufficient to determine transport rates for large structures. The transport of thiol inks can be significantly affected by the state of the substrate. The presence of inks already deposited on the surface can slow the transport rate of additional inks. Any surface adsorbates, either purposely patterned or unintentionally introduced, can affect the ink transport and even cause the failure of patterning. Hampton et al. further elucidated the significance of surface conditions by performing double-ink depositions [83]. When ODT was written on top of a pre-existing MHA structure, the ODT was observed at the periphery of the MHA pattern, and the transport rate increased (Fig. 20(a)). In the reverse case, when MHA was deposited on top of a written ODT structure, it also appeared outside of the ODT pattern, but the transport rate was
reduced. In addition, the shapes of the pre-existing patterns of one ink were not changed by the deposition of the other ink. The authors proposed that when ODT is patterned on top of MHA, the water meniscus spreads out, and the insoluble ink molecules are transported more easily (Fig. 20(b)). When MHA is patterned on top of ODT, the water meniscus is compact, and transport of the more soluble ink molecules is inhibited (Fig. 20(c)). In an earlier work by Salaita et al., when the two inks were deposited simultaneously from a double-inked tip, the binary ink mixtures exhibited near complete phase-separation (Fig. 20(d)) [84]. The more hydrophilic ink molecule always forms the interior phase, while hydrophobic ink molecule tends to form the outer phase. The results of Salaita et al. highlighted the important role of hydrophobicity of both the inks and substrates in determining transport properties and pattern fabrication.

While the above literature [76–84] addressed the role of water meniscus in facilitating ink transport, the work of Sheehan and Whitman showed that ink diffusion is independent of humidity, and water meniscus is not required for pattern formation in DPN [85]. To understand how hydrocarbons, which are essentially insoluble in water, would be transferred through the water meniscus, they investigated the diffusion coefficient for alkanethiol deposition on Au under various humidity conditions. In their experiments, the radii of thiol spots deposited on Au were measured as a function of tip–surface contact time and relative humidity. The humidity was adjusted by placing the DPN system in a dry bag and filling the dry bag with mixtures of filtered dry nitrogen and water-wetted nitrogen at different ratios. Monotonic plots of spot radii versus contact time were obtained, and the plots were not affected by the variation of humidity in the range of 0–62%. The diffusion coefficient was extracted from the radii versus contact plots by modeling the tip as an infinite reservoir of ink molecules. Such a reservoir was assumed to maintain a constant concentration along the perimeter of the tip–surface contact. Deposited molecules then diffuse radially outwards across the surface. It was observed that the surface diffusion coefficient of ODT on Au is independent of humidity. On the basis of their results, the authors concluded that thiol deposition does not occur through the water meniscus.

### 2.4.2. Pattern fabrication by inorganic inks

DPN has been applied to fabricate nanostructures made of inorganic materials such as metals, oxides, and magnetic compounds. To form a pattern, the inorganic inks are either taken as end materials for single-step deposition, or used as precursors for simultaneous reactions or post-treatments. Ali et al. demonstrated the direct transfer of Au nanoparticles from the tip to a silica substrate [86]. Thomas et al. directly deposited Au and Pd nanocrystals onto a mica substrate using hydrosols inks [87]. The deposition of Au nanoparticles on SAM-covered Au surface through S-Au linkage was presented by Garno et al. [88]. It was reported that Au ionic species could also be used as ink species for DPN writing [89]. In this case, an initial Au(III) ion was deposited onto the substrate to form elemental Au(0) nanostructures without applying electrochemical conditions through tip biasing. The conversion of soluble Au(III) ion to insoluble Au(0) metal was ascribed to surface-induced reduction of noble metal ions when they adsorb on the substrate. Fig. 21(a) and (b) displays the schematic for Au ionic ink transport, and patterns “DU” generated using the reductive deposition technique, respectively.
In addition to single metallic inks, magnetic inorganic compounds can also be transported from the tip to the substrate. Gundiah et al. utilized γ-Fe₂O₃ nanocrystal inks to fabricate magnetic nanostructures [90]. Magnetic lines with typical widths of 140–200 nm and lengths exceeding 10 μm were obtained, and no lateral diffusion of ink nanocrystals was observed on mica and silicon substrates. Fu et al. described the fabrication of hard magnetic barium hexaferrite (BaFe) nanostructures through precursor transport and post-heat treatment [91]. In their experiments, the BaFe precursor was coated on the tip, and transported to the substrate to form a precursor pattern. Subsequent thermal annealing of the precursor at elevated temperatures yielded solid-state magnetic features consisting of BaFe in its hexagonal magnetoplumbite structure. Su et al. presented an approach to fabricating oxide nanostructures by means of the simultaneous reaction of precursor inks during the DPN process [92]. The formation of oxide patterns is based on the hydrolysis of metal salt precursors in water meniscus through the reaction 2MClₙ + nH₂O → M₂O + 2nHCl. The main ingredient of the ink is inorganic chlorides MClₙ (M = Al, Si, and Sn) which are dissolved in surfactants in the form of sol–gel-like dispersion. Using a similar approach, Ding et al. patterned the cadmium sulfide (CdS) compound, a II–VI semiconductor with potential applications in the fields of solar cells, and light-emitting diodes [93]. The deposition of CdS structures involved the chemical reaction between Cd²⁺ and S²⁻ precursors during ink transfer. The authors used thioacetamide (CH₃CSNH₂, TAA) as the sulfide source to react with Cd²⁺ on mica and negatively charged silicon surfaces, respectively. Fig. 22(a) and (b) displays the reaction scheme of the precursors in forming solid-state CdS features and CdS patterns generated by this scheme, respectively. Several parameters such as surface charge, sulfide source and temperature were found crucial for the fabrication of semiconductor nanostructures. It was observed that freshly cleaved mica or silicon surfaces newly treated with piranha solution are more suitable for the deposition of CdS patterns. The authors proposed that the static interaction between the negatively charged surface and the positively charged CdS nanospecies facilitates the deposition of CdS onto the substrate. If Na₂S or (NH₄)₂S were used as the sulfide source, the speed of CdS formation would be too fast for the inking of the AFM tip. Instead, the use of TTA made the violent reaction controllable and compatible with the DPN process. As for temperature, it not only affects the solubility and diffusion of the precursors, but also changes the formation speed of CdS products.

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Fig. 21. (a) Schematic showing the conversion of Au(III) ink to Au(0) pattern. (b) AFM image of patterns “DU” fabricated by DPN. Reproduced with permission from Ref. [89], © 2001 American Chemical Society.

Fig. 22. (a) Schematic showing the generation of CdS features through the simultaneous reaction of ink precursors. (b) AFM morphology image of CdS patterns created. Reproduced with permission from Ref. [93], © 2005 American Chemical Society.
2.4.3. Pattern fabrication by organic inks

The DPN process is compatible with the delivery of many organic materials ranging from thiols and silazanes to alkynes and silanes. These organic inks can either supply materials for direct nanostructure deposition, or provide templates in multiple-step processes. In the first case, alkylthiol inks such as ODT and MHA have been used to create high resolution patterns on Au and mica surfaces. Silizane inks were found to be very suitable for patterning semiconductor surfaces with native or thermal/wet oxides. In the multiple-step processes, redox-active ferrocenyl-based inks were employed to fabricate templates for the orthogonal assembly of nanoparticles. In addition, monomer inks were also utilized in DPN as precursors for the formation of polymeric nanobrushes through subsequent activation and polymerization. Piner et al. demonstrated the DPN deposition of ODT on Au/mica substrates [17]. Lattice-resolved ODT SAM was obtained by raster scanning an ODT-coated tip across the surface. They prepared molecular dot features by holding the engaged tip at a fixed position for certain periods. Larger ODT dots were generated in prolonged contact time through the isotropic diffusion of ODT ink. ODT arrays and grids were fabricated by either holding the tip stationary at one point or sweeping the tip for line scans. The authors also discussed the possible factors affecting the pattern resolution such as the substrate roughness, diffusion of the ODT ink, and environmental humidity. Later, Hong et al. generated chemically pristine patterns of multiple ink organic molecules with near perfect alignment and 5 nm spatial separation [94]. As shown in Fig. 23, they demonstrated the registration capability of DPN by generating two sets of MHA dots on an atomically flat Au (1 1 1) surface. The first set of MHA dots (15 nm in diameter) was arranged in the shape of the letter “N” (Fig. 23(a)). The second set of dots was fabricated by depositing additional MHA dots in-between the neighboring dots of the first set according to pre-calculated coordinates (Fig. 23(b)). The nanoscale registry of the two sets of dots indicates a nanostructure alignment with a thermal drift of less than 1 nm/min under ambient conditions. In addition, they also showed that patterns written by an organic ink could be overwritten by a different ink. As seen in Fig. 23(c), three geometric structures of MHA, a triangle, square, and pentagon, were fabricated using the MHA-coated tip. The tip was then changed, and the area containing the MHA patterns was overwritten with an ODT-coated tip by raster scanning four times across the substrate.

Ivanisevic and Mirkin used HMDS as ink to pattern organic materials on Si/SiO$_x$ and oxidized GaAs semiconducting substrates [95]. They selected HMDS instead of trichlorosilane to avoid polymerization during ink deposition. Using HMDS ink, robust nanostructures can be fabricated due to the irreversible chemisorption of trimethylsilyl (TMS) which arises from the reaction of the silazane end group and surface oxides. It was observed that the writing times required for HMDS on oxidized surfaces are much longer than those for thiol-based inks on Au substrate under nearly identical conditions. However, increasing the temperature of the HMDS ink and substrates can dramatically reduce the writing time needed to generate features. In another work, Ivanisevic et al. showed how one can use redox-active ferrocenylalkylthiol inks to trigger and guide the assembly of modified nanoparticles in an

![Image](Fig_23.png)

Fig. 23. (a) LFM image of the first set of MHA dots on Au. (b) LFM image showing the insertion of the second set of MHA dots in the first one. (c) MHA polygon patterns and the overwritten ODT pattern. Reproduced with permission from Ref. [94], © 1999 AAAS.
orthogonal manner [96]. The ferrocenyl-based inks were designed to exhibit nonoverlapping redox processes by virtue of the alkylthiol and acylthiol functional groups directly attached to the cyclopentadienyl rings. Such inks allowed them to selectively address the ink structures by sweeping the potential of an electrode modified with them in linear fashion. Liu et al. reported the direct delivery of monomers from the tip to the substrate for the formation of polymer brushes on the nanometer scale [97]. In this work, the tip was coated with norbornenylthiol monomers and brought into contact with the Au substrate to define monomer structures. The DPN patterned surface was then used as a template for subsequent molecular passivation, catalyst activation, and ring-opening metathesis polymerization. Line and dot arrays of the polymer brushes comprised of exo-5-norbornen-2-ol were constructed through the combined DPN and polymerization approach. The feature size, shape, and composition of the polymer brushes could be varied by controlling the choice of the monomer ink, the DPN template, and the polymerization time.

2.4.4. Pattern fabrication by biological inks

The nanoscale patterning of biological materials is of great significance in fabricating biodevices such as biosensors, gene chips and proteomic arrays. There are several key factors in creating bionanostructures using DPN. First, the effective deposition of biomolecules requires a suitable modification of the AFM probe for the adsorption and desorption of the biomolecular inks. Second, the choice of suitable biomolecules and substrates is crucial, as the formation of immobilized biological structures relies on the strong interaction between the ink and substrate. In addition, the key is whether the patterned proteins and DNAs can maintain their original bioactivities. The DPN process should be designed and optimized to ensure the biological integrity and functionality of the resulting patterns.

Wilson et al. reported positive printing of collagen and collagen-like peptide down to 30–50 nm line widths with thiolated collagen and peptide inks [98]. The inks were coated on the tip by dipping it into an aqueous ink solution, and then deposited on a Au substrate using DPN. The thiolation modification of the collagen was found to be very necessary to ensure coupling to the Au surface. Firm attachment of the deposited collagen ink to the gold substrate was established by the sulfhydryl addition. Fig. 24(a) shows the AFM phase image of collagen patterns in the form of “TU” on a Au substrate. Biological structures fabricated in this way could preserve the triple-helical structure and biological activity of collagen, and even exhibit the formation of characteristic higher level of structural organization. The confined structure formation was attributed to tip-induced local liquid-crystalline organization in a process similar to fiber drawing. Using protein inks, Lim et al. directly wrote antirabbit IgG (immunoglobulin) patterns on different classes of silicon oxide substrates [99]. In their experiments, the AFM tip was modified with a biocompatible and hydrophilic layer which inhibits protein adsorption and reduces the activation energy required for protein transport from the tip to substrates. The substrates used are either negatively charged or aldehyde-modified oxide surfaces, so that protein inks can attach to the surface through electrostatic interaction or covalent bonding. Protein features with line widths ranging from 55 nm to 550 nm have been fabricated by the authors. Fig. 24(b)–(d) exhibits the fluorescence images of various DPN-generated IgG patterns labeled with a fluorophore. The biorecognition activity of the IgG patterns was also examined, and it was found that antirabbit IgG could selectively bond to rabbit IgG patterns.

Fig. 24. (a) AFM phase image of thiolated collagen patterns on Au substrate. (b and c) Fluorescence images of various antirabbit IgG patterns. (a) Reproduced with permission from Ref. [98], © 2001 National Academy of Sciences, USA; (b–d) reproduced with permission from Ref. [99], © 2003 Wiley–VCH Verlag GmbH & Co. KGaA, Weinheim.
Nam et al. reported a straightforward method for the preparation of biologically active protein nanoarrays on nickel oxide surfaces [100]. Ubiquitin and thioredoxin proteins were chosen as inks for DPN because they are biologically important species in proteolytic destruction and the reduction of disulfide bonds in proteins. The tip was coated with a Ni layer to promote the wetting of the tip by His-tagged protein inks through the interaction between the nickel oxide surface and the polyhistidine tag. High humidity conditions were used to effect uniform and rapid protein diffusion, and to prevent the denaturation of the resulting protein structures on the substrate. N-terminal His-tagged ubiquitin nanoarrays were constructed in a direct-write fashion in the form of dots and lines. It was found that protein transport is facilitated on Ni substrate because of the high hydrophilicity of the oxidized surface and its ability to support a water meniscus. The bioactivity of the patterned proteins was confirmed by the observation of the specific binding of labeled anti-ubiquitin molecules to the immobilized ubiquitin nanostructures. Demers et al. described the direct generation of covalently anchored patterns of oligonucleotides on both metallic and insulating substrates using DNA inks [101]. DNA molecules modified with hexanethiol groups were patterned on Au substrates, while those containing acrylamide were deposited on silica. Oligonucleotide structures with feature sizes ranging from micrometers to sub-100 nanometers were fabricated under different conditions. DNA patterns were found to exhibit sequence-specific binding behavior, and can be used as a template for the direct assembly of individual particles modified with oligonucleotides. Several key factors affecting DNA patterning were identified, and they include the surface modification of the tip, and the selection of suitable ink molecules which may have desired affinity to the specific substrates used.

3. Bias-assisted AFM nanolithography

In biased-assisted AFM nanolithography, a bias is applied to the AFM probe to create a localized electric field in the nanometer-sized tip–sample gap. Since the gap is usually less than a few nanometers, a moderate tip bias of several volts would generate a field of 10^8 V/m to 10^10 V/m. Such an extremely high field can initiate various physical and chemical processes which facilitate pattern formation through field emission, charge injection, Joule heating, electrostatic attraction, explosive discharge, and electrochemical reactions. In this section, we review the various bias-assisted techniques such as anodic oxidation, electrochemical deposition, electrochemical modification and functionalization of molecules, nanoexplosion and shock wave generations, and charge deposition and manipulation.

3.1. Probe anodic oxidation

Probe anodic oxidation is one of the earliest and most extensively studied techniques in bias-assisted AFM nanolithography. In this method, the water meniscus formed in the tip–sample gap is dissociated by the negative tip bias, and the O\(^-\) and OH\(^-\) oxidative ions react with the substrate to form localized oxide nanostructures. Because the molecular volume of the oxides is usually larger than that of the substrate materials, raised nanopatterns are formed after the oxidation reaction. AFM-based anodic oxidation has been applied to produce oxide structures on semiconductors, metals and other materials. The extensive research in this area is aimed at fabricating nanoscale devices such as metal-oxide-semiconductor (MOS) transistors through the precise control of the local oxide growth by the AFM probe. In addition, the anodic oxide features can act as reactive sites for the further assembly of molecules and nanoparticles through chemical linkages and affinities. Alternatively, the anodic oxides can also be etched to produce negative structures on the substrates for pattern transfer.

3.1.1. Oxidation of semiconductors

The first attempt at the oxidation of Si surface using a biased AFM probe was reported in 1993, although the principles of the oxidation process were not discussed [102]. Day and Allee later demonstrated the selective oxidation of a Si surface with sub-100 nm resolution [103]. Campbell et al. used a Ti-coated tip to oxidize regions of H-passivated Si (1 0 0) to fabricate nanoscale side-gated Si field effect transistor (FET) [104]. The uniform probe-grown oxide may serve as an effective mask for pattern transfer into the substrate by selective wet etching. Snow et al. subsequently produced oxide patterns 2–4 nm deep with line widths down to ~10 nm [105]. Fig. 25 shows AFM images of a set of etch lines with different widths after the AFM oxides were dry etched with an electron cyclotron resonance source [105]. The authors also demonstrated high speed patterning of platinum (Pt) silicide using AFM oxide as barrier to Pt diffusion during the formation of the silicide layer [106,107].
In 1995, Dagata briefly described the potential and progress of AFM probe oxidation nanolithography of different materials and in the fabrication of nanoscale devices [108]. He and co-workers then introduced an alternate probe anodic oxidation technique involving voltage modulation which can lead to an increased growth rate and higher aspect ratio of oxide features [109–112]. They also studied the formation of Si nanostructures after anisotropic TMAH etching of anodic oxides on Si (1 1 0) [110,112]. Etched structures with a pitch of 100 nm, positive- and negative-contrast structures, and feature with heights greater than 100 nm have been produced on bare silicon, Si$_3$N$_4$-coated and silicon-on-insulator wafers.

García et al. investigated the formation, reproducibility, voltage dependence, and kinetics of oxide structures using a dynamic AFM [113]. In their method, the tip and sample are separated by a gap of a few nanometers, thus the wear of the tip is reduced, and its lifetime increased due to the minimization of lateral forces. The authors observed that a threshold voltage must be exceeded to initiate the oxidation process, in agreement with previous observations with non-contact AFM lithographic method. Calleja and García studied the voltage and pulse duration conditions under fixed tip–sample separation [114]. They found that the application of short pulses at high voltages can produce high feature aspect ratios. A comparison between the oxidation in contact and non-contact modes was made later [115]. A slower oxidation rate was observed in contact mode lithography, and this was attributed to an effective energy barrier that includes the mechanical work done by the growing oxides against the cantilever. Fig. 26 displays two sets of oxide dots produced by AFM oxidation in contact and non-contact modes, respectively.

Minne et al. modified their AFM lithography system especially for high speed and large area writing purposes [116–119]. They demonstrated the fabrication of 0.1 μm metal oxide semiconductor field effect transistors on amorphous silicon (α:Si) films [116]. The probe-induced oxide pattern was transferred onto α:Si by plasma dry etching. The gate contact pad was masked by the photoresist and the gate was masked by AFM oxide, leaving the α:Si in these regions intact. They later reported parallel lithography by coupling the direct oxidation process with arrays of cantilevers (maximum 50 cantilevers) [117–119]. These authors showed that the area scanned by cantilever arrays

![AFM image of Si wires of varying line width after dry etching the AFM oxides. Reproduced with permission from Ref. [105], © 1995 American Institute of Physics.](image1)

![AFM image of a sequence of oxidation experiments performed for different pulse durations and constant voltage (20 V) at RH = 36%. (a) Contact AFM oxidation; (b) non-contact AFM oxidation. Reproduced with permission from Ref. [115], © 2001 American Institute of Physics.](image2)
can be simultaneously patterned, and centimeter scale lithography and imaging is achievable using the parallel lithography technique. Wilder and Quate introduced a cantilever with integrated MOSFET as a current source for on-chip control of the exposure current [120]. This integrated current source eliminates the need for external feedback control circuitry and simplifies the lithography process. In addition, probe anodic oxidation of Si wafers with different surface orientations and passivation under various AFM working modes have been reported by numerous groups [121–125].

In addition to Si, AFM probe oxidation has been extended to other semiconducting materials such as silicon nitride (Si$_3$N$_4$), silicon carbide (SiC), SiGe, and GaAs. Chien et al. conducted systematic studies of the oxidation of Si$_3$N$_4$ [126,127]. They discussed the oxide growth behavior and kinetics, and analyzed the chemical composition of the anodic oxides formed on Si$_3$N$_4$. Their micro-Auger analysis of the selectively oxidized region revealed the formation of SiO$_x$. Bo et al. patterned Si/SiGe heterostructures, and observed the direct oxidation of SiGe alloys which led to oxide features with only 20 nm line widths [128]. Ishii and Matsumoto performed the oxidation of GaAs, and found that the oxidized GaAs could be selectively etched in water [129]. A series of works on the oxidation of GaAs and Ga[Al]As compounds have been reported by several authors [130–132]. Dorn et al. demonstrated the fabrication of high quality antidot lattices which are particularly appealing for studying quantum signatures in chaotic systems [131].

Fig. 27(a) shows a 20 × 20 antidot array with a lattice period of 300 nm fabricated by these authors. Low-temperature magnetoresistance measurements showed well-developed commensurability oscillations as well as a quenching of the Hall effect around zero magnetic field. Sasa et al. presented a nanoscale fabrication strategy on InAs/(Al)GaSb heterostructures [133]. Their nanofabrication is based on oxidizing the GaSb surface layer and selectively etching the oxidized GaSb in water. Maynor et al. demonstrated an oxidation approach which combines local oxidation and DPN [134]. They created GaN nanowire heterostructures via the local electrochemical reaction between a n-type GaN nanowire and a tip coated with KOH ink. Their oxidation scheme involves the reaction $2\text{GaN} + 6\text{OH}^- + 6\text{h}^+ \rightarrow \text{Ga}_2\text{O}_3 + 3\text{H}_2\text{O} + \text{N}_2$. In this case, the oxidative reactant OH$^-$ is not from water ionic dissociation, but supplied by the

![Fig. 27](image-url)

Fig. 27. (a) Overview of the entire AFM patterned area. The bright areas mark the oxidized regions below which the electron gas is depleted. (b) Close-up of a 3 × 4 period segment. (c) Line scan along the direction indicated in (b). (d) Four-terminal magnetoresistance (left-hand scale) and Hall resistance (right-hand scale) at $T = 51.7$ K through the finite antidot geometry. The inset shows a close-up of the Hall effect around $B = 0$. Reproduced with permission from Ref. [131], © 2002 American Institute of Physics.
KOH ink which is delivered to the GaN nanowire by the AFM probe. There are also reports on AFM probe oxidation of diamond [135,136] and diamond-like carbon (DLC) films [137,138]. Tachiki et al. demonstrated the precise control of electrical conduction on hydrogenated diamond where the p+ (strong p-type semiconducting) region and insulating region are H- and O-terminated, respectively [136]. Their oxidation of diamond is controlled to the topmost monolayer, and the layers below are not oxidized. Based on the separation of C–H and C–O bonded surface, a single-electron transistor was constructed.

Xie et al. reported bias-assisted patterning of SiC semiconductor substrates [139,140]. They observed that the biased AFM tip can induce both the native oxide decomposition and direct oxidation of SiC. In the first case, when the probe was scanned across surface areas of 1 μm × 1 μm, the native oxide on SiC was decomposed and the debris was assembled into line patterns. By analyzing the electric current and line height as a function of tip voltage, they revealed that the electrons emitted from the negatively biased tip supplies the energy for the decomposition and assembly of native oxide on SiC (see Fig. 28(a)). The line height increases exponentially with increasing tip voltage due to the enhanced decomposition under larger tip biases. The preferential oxide decomposition at negative tip bias was attributed to the stronger field enhancement when the tip is negatively biased. Only the electrons injected from the AFM tip have high enough energy above the threshold for oxide decomposition. Besides tip bias, the scan rate also influences the assembly of decomposed native oxide. As shown in Fig. 28(b), a slower scan rate allows a higher flux of electron injection at one surface position, thus enhancing the decomposition process and facilitating high and uniform line assembly at the edge.

In the second case, when the AFM probe was immobilized at one surface site and a longer bias duration was applied, localized oxide growth was induced on SiC substrate (see Fig. 28(c) and (d)). It was observed that the aspect ratio of oxides grown on SiC is at least four times that formed on Si. The role of water meniscus in oxidation was simulated by finite element calculations, and was experimentally investigated by carrying out anodic oxidation under different humidity conditions. The results suggest that the water meniscus does not significantly affect the field distribution. Rather, oxide growth is more related to chemistry, i.e., water supplies the necessary oxidative species such as OH− and O2− ions for the oxidation. A bigger water meniscus can provide more OH− and O2− reactants for the anodic reaction, and the enriched oxidative species available at higher humidity facilitates the increase in both vertical and lateral oxide growth. The oxidation of SiC was found to be dependent on the surface orientation of the substrate which influences the anisotropic diffusion of OH− in the polar and nonpolar directions. The dielectrical properties of the

Fig. 28. (a) Schematic showing the native oxide decomposition on SiC by electron injection. (b) AFM image of lines L1–L3 of decomposed native oxide assembled with different scan rate. (c) Schematic showing the localized oxide growth on SiC by probe anodic oxidation. (d) AFM image of oxide dot arrays fabricated on SiC. Adapted from Refs. [139,140].
anodic oxides grown on SiC were further investigated by analyzing their $I-V$ characteristics. The occurrence of current shooting and breakdown events is closely related to the density of defects in the anodic oxide. Thicker oxides grown under high tip bias and long oxidation times exhibit better dielectric strength against degradation and breakdown under electrical stress [141–143].

3.1.2. Oxidation of metals

AFM local oxidation has been applied to different types of metals including Ti [144–146], Al [147], Cr [148], Nb [149,150], Ni [151,152], Ta [153], Mo [154], Zr [155,156], and Co [157]. For example, Snow and Campbell described the use of *in situ* electrical measurements to control the fabrication of metal-oxide devices on thin Ti films (~7 nm) [144]. In their experiments, a biased tip was scanned across the designated area to form a wire which could restrict current flow. The tip was then repositioned at the unoxidized side of the wire and scanned towards the oxidized region. The electrical resistance of the structure will therefore increase as the current is slowly constricted by the oxidation process. The width of the wires and resistance of the junctions were controlled by real-time, *in situ* measurements of the device resistance during fabrication. Structures with critical dimensions of less than 10 nm were fabricated with precisely tailored electrical properties.

In the work of Hsu et al., oxide structures were grown on nickel substrates, and the unoxidized part was etched away in diluted nitric acid solution [151]. Lin et al. then used the probe-grown nickel oxide as a catalytic template for selective growth of CNTs (see Fig. 29) [152]. Vertically aligned bunched or single CNTs with diameters of 30–80 nm were selectively grown on the oxide structures by chemical vapor deposition. It was also shown that the tube diameter could be effectively controlled by the size of the oxides. Rolandi et al. introduced the oxidation of molybdenum (Mo) film to form MoO$_3$ patterns and performed subsequent etching by simply using water [154]. The patterned Mo thin films were then used as resist to pattern the underlying substrate through wet chemical etching, or to fabricate metal nanostructures through a Mo/polymer bilayer resist and lift-off approach.

3.1.3. Oxidation of molecularly functionalized/passivated surfaces

In recent years, various approaches to use SAM [158–168] or Langmuir–Blodgett (LB) films [169–171] as a resist for AFM local oxidation have been proposed. The work pertaining to the oxidation of molecularly functionalized/passivated surfaces has also been previously reviewed [24,172]. Here we selectively discuss the effect of SAM and LB films on probe anodic oxidation, and their applications in post-oxidation nanostructuring and nanofabrication. Early work by Sugimura et al. [158] involved the anodic oxidation of Si covered by organosilane TMS monolayer. This resist was locally degraded during oxidation due to electrochemical reactions induced in the tip–sample junction. The oxide patterns generated were then transferred to the Si substrate by chemical etching. Tully et al. explored the use of poly(benzylether) dendrimers terminated with both benzyl and *tert*-butyldiphenylsilyl ether groups as resists for AFM oxidation lithography [161]. Sugimura et al. reported a pattern transfer process by applying AFM local oxidation on an octadecylsilyl (ODS) monolayer-passivated surface [162]. Following the removal of oxide, the sample was treated in

![Fig. 29. SEM images of (a) an oxide square before growth. (b) The vertically aligned multiwalled CNTs selectively grown on the square. Reproduced with permission from Ref. [152]. © 2004 Elsevier.](image-url)
Au electroplating bath to form Au nanostructures. They also fabricated coplanar nanostructures composed of two types of organosilane molecules by combining probe oxidation and self-assembly [164].

Ara et al. reported the anodic oxidation of a Si (1 1 1) surface which is covalently bonded to an alkyl monolayer [165]. Lee et al. examined the oxidation of surfaces passivated by mixed SAM layer comprising 1,12-diaminododecane-dihydrochloride (DAD-2HCl) and n-tridecylaminehydrochloride (TDA-HCl) [166]. Kim and Lee used various metal phosphate monolayers as resist [167], while Rolandi et al. presented the oxidation of dendrimer monolayer as negative tone resists on Ti films [168]. Lee and Ahn et al. systematically studied the local oxidation of surfaces passivated by various LB films [169–171]. They initially studied the conditions for the fabrication of nanostructures on poly(3(2(5choloro-benzotriazolo)ethyl)thiophene) (PCBET) polymer LB film [169]. The comparison of the conditions for oxide growth and degradation was made on mixed LB film of hexadecylamine (HAD) and palmitic acid (PA) [170,171].

Xie et al. performed anodic oxidation on an alkylsilated native-SiO2/Si surface [173]. Fig. 30(a) and (b) shows the oxide patterns fabricated on OTS (octadecyltrichlorosilane) passivated Si surfaces. The oxide growth rate on the OTS SAM-passivated surface is slower compared to that on the bare SiO2/Si surface. This is attributable to the higher hydrophobicity of the OTS SAM surface which is terminated by –CH3 end groups. The formation of water meniscus is less favorable on the hydrophobic OTS surface than on the hydrophilic SiO2/Si surface. Therefore, the presence of OTS SAM on the surface tends to inhibit the anodic oxidation of Si substrate. Sudden current increases were observed in the forward direction of the I–V curves recorded during oxidation (see Fig. 30(c)). It was suggested that the current increase is correlated to the local depletion of OTS molecules, and the depletion is completed in the forward voltage ramp. The dielectric properties of AFM anodic oxides, thermal oxides, and OTS molecules were investigated by comparing the I–V curves recorded for these samples (see Fig. 30(d)). The interface barrier height of the oxides and OTS SAM were determined using the Fowler–Nordheim (F–N) model.

Fig. 30. (a) and (b) AFM images of oxide patterns fabricated on the OTS/SiO2/Si surface. (c) Forward and reverse currents recorded during anodic oxidation. (d) I–V curves collected for AFM anodic oxides, thermal oxides, and OTS SAM, respectively. Adapted from Ref. [173].
3.1.4. Mechanistic and kinetic aspects of oxide growth

The mechanism of probe anodic oxidation has been addressed by several authors. Generally, it is suggested that the oxidation mechanism and kinetics are closely related to electrical field, surface stress, water meniscus formation, and OH\(^{-}\) diffusion [174–185]. Specifically, various models including the Cabrera–Mott model, power-law model, direct-log kinetic model, and space charge model have been proposed to account for the oxidation behavior. There is an ongoing debate on the limiting-factors of oxide growth due to the complexity of such nanoscale oxidation processes. Gordon et al. described the local oxidation in the framework of Cabrera–Mott process [174]. According to this model, the role of the electric field is to lower the activation barrier for transport of ionic species across the oxide. Teuschler et al. suggested an empirical power law which best fit their experimental data [122]. Stiévenard et al. proposed an inverse-log model to explain the dependence of the oxide height on the applied voltage and tip velocity [175]. Avouris et al. confirmed the involvement of ionic species, presumably OH\(^{-}\) from the water film, in the oxidation by detecting ultrasmall Faraday currents in situ [176]. They attributed the decrease of oxide growth rate to the self-limiting behavior resulting from decreasing field strengths and the buildup of stress as the oxide thickness is increased. The authors suggested that the rate of oxidation is not only a function of electric field strength, but also dependent on the applied bias, particularly at high fields, and hence the simple Cabrera–Mott model alone cannot account for their observed kinetics. Fig. 31 shows the growth rate as a function of electric field strength and oxide height, respectively [176].

Dagata et al. presented an oxidation model on the basis of the space-charge variation as a function of substrate doping type/level [177–179]. They verified the model by integrating scanning Maxwell stress microscopy (SMM) into the AFM fabrication process as an electrical force characterization technique [177,178]. Their model includes a temporal crossover of the system from transient to steady-state growth and a spatial crossover from predominantly vertical to coupled lateral growth [179]. They also examined the assumptions used to derive the direct-log model as suggested in previous studies [175,176]. They concluded that the Alberty–Miller equations best described the most significant aspects of low temperature probe anodic oxidation of Si. Dagata et al. provided a comprehensive analysis of the electrical current passing through the tip–substrate junction during the oxidation of silicon [180]. Their analysis revealed that the voltage pulse can produce an electronic current transient, water breakdown and a maximum charge/defect density. Excess charge is channeled into lateral diffusion, keeping the charge density within the reaction zone constant and reducing the aspect ratio of the resulting oxide features. A uniform charge density implies that the oxides contain a fixed defect concentration, in accordance with the space-charge model. It was shown that most of the electrical current involved in high voltage oxidation of Si did not actually induce surface oxide growth, and that lateral diffusion and small aspect ratios are unavoidable aspects under contact-mode conditions.

Dubois and Bubendorff proposed an enhanced oxidation model that reproduced the power-of-time law [181]. It was shown that the space charge resulting from nonstoichiometric states strongly limits the oxidation rate. Snow et al. reported measurements of the oxidation kinetics under conditions of high humidity and pulsed bias [182]. They showed that the production of OH\(^{-}\) ions dominates the oxidation reaction for moderate oxide thickness and exposure times. The effects of ion diffusion, space charge and stress will eventually govern the kinetics for longer exposure time. In addition, Jungblut et al. addressed the humidity-dependent volume effect in local oxidations [183].

Fig. 31. (a) The growth rate vs. electric field strength. (b) Growth rate vs. oxide height at three tip biases. Reproduced with permission from Ref. [176], © 1997 American Institute of Physics.
Several studies focused on oxidation in non-contact AFM mode, and in particular the formation of a water bridge between the tip and surface. For example, García et al. suggested that the formation of a water bridge between a nanometer-sized tip–sample gap is driven by the application of an electrical field [184]. Once a liquid bridge is formed, its length and neck diameter can be modified by changing the tip–sample separation. Dagata et al. collected force–distance and current–distance curves simultaneously, and revealed that current flow during oxidation in non-contact mode is significantly less than that in contact mode [185]. The authors described the role of space charge and meniscus in shifting the oxidation kinetics from a reaction-limited to diffusion-limited system.

3.1.5. Extension of oxidation through organic meniscus formation

The anodic oxidation previously discussed is based on OH\(^-\) reactant, forming only oxides via local electrochemical reaction. García and co-workers extended the oxidation nanolithography to produce nanostructures made of materials other than oxides [186,187]. Their strategy is based on the formation of organic menisci to adjust the chemical composition of structures formed. The water meniscus is replaced by an organic meniscus, and the oxidation reaction is eliminated or significantly suppressed. Nanometer-sized menisci of organic liquids such as octane and 1-octene were used to confine chemical reactions [186]. Their results indicated that the composition of the fabricated structures is organic-solvent-dependent. The growth rate can be significantly modified by the composition of the organic solvent. They confirmed that AFM probe-induced chemical reaction is a general process that applies to vapor and liquid phases, polar and nonpolar solvents. Fig. 32 shows the comparison of nanostructures formed with water, 1-octene and octane menisci, respectively. They suggested that in octane environments the field-induced formation of nanostructures involves the condensation and subsequent polymerization of carbon chains.

García and co-workers also reported the carbonization of Si by manipulating an organic meniscus of ethyl alcohol formed between the tip–sample gap [187]. Carbon-rich SiC nanostructures were fabricated on Si by chemically dissociating the ethyl alcohol meniscus through tip bias application. It was shown that the application of a single pulse can generate a raised dot, and the dot size depends on the voltage strength, pulse duration and volume of the organic solvent.

![Fig. 32. AFM images showing three arrays of dots patterned on Si by using (a) water, (b) 1-octene, and (c) octane liquid menisci before (top pictures) and after exposure to HF (48%) vapors for 5 s (bottom pictures). Octane structures are HF-etch resistant, whereas structures in water and 1-octene are readily etched. Reproduced with permission from Ref. [186]. © 2005 American Chemical Society.](image-url)
meniscus. The authors quantitatively determined the chemical composition of the structures by performing XPS (X-ray photoelectron spectroscopy). The proposed overall chemical reaction is: \( \text{Si} + (x/2)\text{CH}_3\text{–CH}_2\text{OH} \rightarrow \text{SiC}_x + x\text{H}_2 + (x/2)\text{H}_2\text{O} \) where the variable \( x \) reflects the non-stoichiometric character of the SiC compound.

3.2. Pattern deposition

3.2.1. Field evaporation

Hosaka et al. demonstrated that when a bias was applied to a Au-coated tip, the Au coating could be evaporated from the tip and deposited onto the substrate through the process of field evaporation [188]. Au mounds of 30–50 nm diameters were deposited on a native oxide covered Si surface by voltage pulse applications. Further theoretical and experimental results showed the field evaporation is possible in the AFM metal probe/vacuum/thin insulator configuration [189]. Theoretically, the field evaporation is generated by the application of a bias voltage in a thin insulator. In the experiments, ultrasmall gold dots were formed on a natural SiO\(_2\)/Si substrate by an applied voltage of less than 10 V, and gold dots as small as 15 nm in diameter were formed on the insulator [189]. To confirm the chemical composition of the field evaporated dots, Koyanagi et al. performed elemental analysis of the dots and examined the dependence of the threshold voltage on SiO\(_2\) thickness under both tip polarities [190]. Their results showed that it is feasible to form gold dots on SiO\(_2\) films 1.7–10.7 nm thick by varying the pulsed tip bias voltage. Energy dispersive X-ray spectroscopy (EDX) showed that the dots include a Au component. The threshold voltage increases almost linearly with the SiO\(_2\) thickness, and it is lower for negative voltage polarity. The field evaporation technique can be applied to the development of ultrahigh density recording devices and nanometer-sized electronic quantum devices [189].

Using field-assisted mass transport, Calleja et al. fabricated continuous Au nanowires on SiO\(_2\) films [191]. In their experiments, a negative bias was applied to an oscillating, Au-coated tip to induce the transport of Au from the tip to the surface. The tip bias was applied when there was a tip–surface gap of ~3 nm. This finite tip–surface separation enhances the tip lifetime, and also allows the application of sequential multiple voltage pulses for the fabrication of nanowires. Fig. 33(a)–(c) shows an example of Au nanowires fabricated to bridge two electrodes. The corresponding \( I-V \) characteristic of the nanowire is shown in Fig. 33(d), clearly exhibiting metallic transport behavior.

3.2.2. Electrochemical deposition

The AFM-based electrochemical deposition presented here involves the direct tip bias application to initiate local electrochemical reactions. This differs from the commonly known electrochemical AFM (ECAFM) [192] in which a

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Fig. 33. Sequence of the gold nanowire fabrication is shown. (a) AFM image of the gold probing electrodes before AFM gold deposition. (b) The gap between the electrodes is partially filled by a gold wire, and (c) fully connected nanowire formed by tip bias application. (d) \( I-V \) characteristics for the gold wire at room temperature. The inset shows the current flow between the electrodes before the gold wire fabrication. Reproduced with permission from Ref. [191], © 2001 American Institute of Physics.
potentiostat and additional electrodes are needed to form a conventional electrochemical cell. The electrochemical deposition technique is an electrochemical version of DPN utilizing meniscus formation and tip bias application during ink deposition [18,193,194]. The electrochemical DPN (EDPN) combines the versatility of electrochemistry with the simplicity and power of the DPN method. In this section, we review the application of EDPN in generating metallic, polymeric and biological structures on different substrates.

Li et al. deposited Pt metals by scanning a H2PtCl6 coated and positively biased tip across a Si surface [18]. H2PtCl6 dissolved in the water meniscus is electrochemically reduced from Pt(IV) to Pt(0) to form metallic nanofeatures through the reaction: PtCl6^{2-} + 4e^- → Pt + 6Cl^- . The dc voltage needed for metal deposition depends on the type of precursor salt and the electrical resistance between the tip and sample. Fig. 34(a) shows the AFM images of a Pt line pattern deposited using EDPN. The chemical identity of the Pt line was confirmed by heating the pattern at 500 °C under an atmosphere of ethylene in argon. Since Pt is an active catalyst for the decomposition of ethylene, the Pt line was broadened after ethylene decomposition (see Fig. 34(b)). This technique is not limited to Pt: other metals such as Au, Ag, Cu, and Pd and semiconductors can also be deposited to form nanoscale features.

Maynor et al. further demonstrated the electrochemical deposition of monomers to prepare polymers with tailored electronic and electrooptic properties [193]. In their EDPN experiments, they used 3,4-ethylenedioxythiophene (EDOT) to fabricate polymeric nanowires on both semiconducting and insulating surfaces. Local polymerization was achieved preferentially at negative tip bias, while no deposition could be observed at positive tip bias. The morphology of the deposited nanostructures is controlled by humidity, tip bias voltage, and tip writing speed.

The electrochemical assembly of biological molecules was reported by Agarwal et al. [194]. The authors patterned histidine-tagged (His-tagged) peptides and proteins to metallic surfaces using EDPN operated in tapping mode. The biomolecules were immobilized via novel linker chemistry and the ionization of the nickel surface. The proposed electrochemistry occurring at the tip–Ni surface gap is: NiO2 + 4H^+ + 2e^- → Ni^{2+} + 2H2O. The biased AFM tip scans and ionizes the surface area for deposition of peptide to occur through histidine binding to exposed nickel ions. The morphology of the patterned protein was found to be identical to that of unpatterned proteins. The authors also demonstrated the deposition of protein marked by fluorescence molecules. Fluorescence of the patterned regions could be detected using fluorescence light microscopy before and after washing the patterns with water. Their results suggested that the EDPN process does not alter the native properties of the deposited biomolecules, but facilitates the immobilization of the molecules.

3.3. Electrochemical modification of monolayers for hierarchical construction

There have been numerous works reporting the hierarchical construction based on probe-induced local electrochemical modification of molecules [195–204]. By applying a bias to a tip, it is possible to induce
electrochemical surface transformations of certain top functionalized self-assembled monolayers, while fully preserving the overall monolayer structural integrity. Depending on the nature of the transformations, such locally modified monolayer surfaces can be used to induce site-selective self-assembly of a number of different materials (organic, metal, semiconductor), according to a predefined geometric pattern and pre-selected type of chemical modification. Maoz et al. first demonstrated the formation of a bilayer template which consists of a densely packed NTS (18-nonadecenyltrichlorosilane) layer and an OTS SAM [195]. In their experiments, the terminal vinyl groups of the NTS template were electro-oxidized by a local probe bias, and the OTS monolayer was assembled selectively at the oxidized sites. Later, the template-controlled self-assembly strategy was extended to the fabrication of hybrid metal-organic nanostructures [196]. Starting with a thiol-top-functionalized silane monolayer (TFSM) with silver ions chemisorbed on its outer surface (Ag⁺-TFSM), metallic silver nanoparticles were generated at selected surface sites by either wet chemical or tip-induced electrochemical reduction of the surface-bound metal ions [196]. The nanofabrication of complex metal-semiconductor-organic surface structures was further demonstrated using inert OTS SAM templates [197]. The OTS SAM was first patterned non-destructively via tip-induced electrochemical oxidation of the –CH₃ terminal groups. Further chemical derivation and development of the tip-functionalized surface sites was then easily accomplished, as the rather inert nature of the OTS SAM allowed the straightforward implementation of a rich menu of post-patterning build-up schemes. Fig. 35 shows the schematic representation of several different self-assembly and chemical modification paths suitable for in situ surface generation of organic (insulator), metal, and semiconductor nanocomponents. Based on the organic monolayer and bilayer templates, metal nanoparticles, nanowires, and contact electrodes were fabricated in situ at predefined sites on a Si wafer [197].

Liu et al. explored the template guided self-assembly of a water soluble derivative \([\text{Au}_{55}(\text{Ph}_2\text{P}_6\text{H}_4\text{SO}_3\text{Na})_{12}\text{Cl}_6]_2\) on bilayer patterns with top thiol (–SH) functionality [198]. It was anticipated that a mechanism of ligand exchange would drive the specific adherence of the gold clusters to the thiolated template sites. The overall fabrication process starts with the tip-induced nanoelectrochemical inscription of the desired pattern of carboxylic acid (COOH) groups on a highly ordered OTS SAM on Si. Subsequent exposure of the patterned OTS surface to a solution of NTS results in the selective self-assembly of a monolayer with terminal ethylenic functions (–CH=CH₂) on the tip-inscribed sites. Addition of H₂S to NTS and further reduction (with BH₃-THF) of disulfide (–S–S–) groups effect the conversion of NTS to a fully thiolated overlayer copy of the initial pattern. Finally, the formation, on the thiolated bilayer template, of a pattern of surface immobilized gold clusters is completed with the exposure (for ~12 h) of the silicon wafer.

Fig. 35. Six nanofabrication routes starting with an inert silane monolayer (OTS/Si) oxidized to form OTSeo (oxidized OTS), followed by the selective self-assembly of NTS overlayer at the OTSeo polar sites defined by the tip. Reproduced with permission from Ref. [197], © 2000 Wiley–VCH Verlag GmbH, D-69469 Weinheim.
specimen to a dilute \((5 \times 10^{-5} \text{ M})\) aqueous solution of \([\text{Au}_{55}]\). Liu et al. demonstrated the hierarchical self-assembly of colloidal Au particles on SAMs with terminal amino functionality \([199]\). The patterned amino groups guide the surface assembly and site-specific anchoring of Au nanoparticles from colloidal solutions. Well-defined amineterminated templates were obtained by forming bilayer elements using this probe electrochemical approach.

Besides metallic, semiconductor and organic nanostructures, magnetic Fe particles were also assembled on electrochemically oxidized monolayer templates \([200]\). Fresco et al. reported the localized chemical activation of a protected amine surface by triggering heterolytic bond cleavage of dendrons via the application of a voltage bias between the AFM tip and a silicon substrate \([201]\). The latent amine patterns were visualized by the self-assembly of dendritic carboxylates. They achieved the fabrication of a primary aliphatic amine surface on the nanometer scale, and showed that the amines are active toward ionic self-assembly. The relationship between the size of the macromolecule and the height (measured by AFM) of the resulting features is evidence that the features are indeed composed of these molecules. This process would be applicable wherever amines are used to selectively assemble materials onto a surface. Specifically, amines may be used for deposition of resist materials for lithography, electroless metalization, device assembly, and protein binding. The authors also described a straightforward method for the pattern-wise placement of AuNPs (Au nanoparticles) with nanometer resolution \([202]\). Their pattern was defined using AFM tip bias on selected locations of a surface covered by a reactive monolayer. During this process, thiocarbonate moieties from the bound monolayer are selectively transformed into thiols. The thiol-patterned surface is then used to direct the subsequent self-assembly of citrate-stabilized AuNPs. This patterning technique can be used to fabricate lines or single particle in width as well as to control the placement of individual gold nanoparticles. Fig. 36 displays the scheme for the surface activation and self-assembly of AuNPs \([202]\).

The electrochemical cathodic electrografting reaction was demonstrated on the nanometer scale by Hurley et al. \([203]\). Electrografting allows the easy formation of thin films covalently bonded to an electrode through electroinduced processes. The alkyne electrografting technique is particularly useful for the direct covalent attachment of conjugated alkenes to a Si surface. In their experiments, the tip was positively biased to drive the cathodic electrografting reaction under ambient conditions. Alkyne monolayer lines were fabricated down to 40 nm resolution, and the heights of the monolayers scale with the molecular length of the alkyne. Measurements of the frictional properties and resistance of the monolayers to fluoride indicated that the alkenes are covalently bonded to the surface, and are hydrophobic. The electrografting does not work with alkenes, and therefore hydrosilylation is not the primary mode of reaction. The alkyne electrografting technique could be important for the interfacing of conjugated molecules directly to silicon in a spatially controlled fashion.

In the work of Cai and Ocko, an underlying thin organic film was oxidized, and the ink molecules were transferred simultaneously to the oxidized regions by sweeping an ink-coated and biased AFM tip \([204]\). Their method provides very fast (exceeding \(10 \mu\text{m/s}\)) writing speeds with line-widths as small as 50 nm. Controlled multi-write operations permit the growth of multi-layers of ink molecules. The pattern writing mechanism is based on the electrochemical oxidation process of the terminal methyl group of OTS to a terminal acid group. Fig. 37 shows the schematic representation of the electrochemical patterning method and an AFM image of nanostructures created.
3.4. Electrical cutting and nicking

Electrical cutting refers to the cutting and etching of nanostructures by an electrically biased AFM tip. Nicking is in principle similar to cutting, but the applied tip bias voltage is smaller than that used in cutting, so the nanostructure is not completely cut. Park et al. demonstrated the application of voltage pulses to a metal-coated AFM tip to permanently modify the electrical properties of CNT devices [205]. Although the mechanism of cutting and nicking is not well understood, the combination of this technique with mechanical manipulation holds great promise for creating more complex CNT structures. By adjusting the voltage pulses, they were able to either electrically cut CNTs or create tunneling barriers at any point along the CNTs (see Fig. 38). They showed the utility of electrical cutting/nicking techniques by creating single CNT devices through cutting CNTs to required lengths, and making ultrasmall CNT quantum dots by nicking a CNT at two places along its length. The size of nick can be controlled by the magnitude and duration of the voltage pulses. Hyon et al. presented the cutting and nicking of CNT in non-contact AFM mode [206]. A single electron transistor that operates at room temperature was fabricated by the authors. They also reported that the cutting was reliable only when a tip bias voltage above certain threshold was applied.

Kim et al. reported their quantitative results on the cutting of multiwalled carbon nanotube (MWCNT) with a negatively biased tip [207]. By scanning the tip across a 30 nm-diameter MWCNT in contact mode, they cut the CNT in a controlled fashion. As the tip-scanning speed increased, the magnitude of the threshold voltage was increased. A graphite surface was etched for comparison under the same tip conditions. The etching current was found to follow the...
F–N equation and attributed to field-emission electrons from the tip. The etch depth of the graphite surface was also found to follow the bias voltage dependence of the F–N equation. The graphite etching was observed to be governed by the field-emission current. They proposed that both the CNT cutting and graphite etching undergo the same reaction where the activation energy is supplied by electrons that are field emitted from the negatively biased AFM tip.

3.5. Electrostatic deformation and electrohydrodynamic nanofluidic motion

The ability to directly pattern and write polymers at the nanometer scale is crucial to applications in data storage and molecular electronics [19,208–212]. Lyuksyutov et al. introduced AFM electrostatic nanolithography (AFMEN) to generate nanoscale polymeric features by Joule heating and mass transport on initially featureless polymer films [19]. In this technique, current flow generated by tip biasing produces effective Joule heating which locally softens the polymer film. The extremely non-uniform electric field gradient polarizes the viscoelastic polymer and attracts it towards the tip apex, leading to the formation of protruding structures on the film (see Fig. 39(a)). The attractive force arises from the imbalance between the Laplace, viscous, and electrostatic pressures. When the electrostatic pressure overcomes the combination of Laplace and viscous pressures, electrostatic deformation of the polymer melt takes place. Fig. 39(b) and (c) shows raised periodic lines and letters created by the electrostatic attraction on PMMA and PS, respectively. The optimal polymer film for patterning relies on the materials selection and processing that provides gradual dielectric breakdown under the electric field. The zeroth-order modeling by Lyuksyutov et al. indicates that the feature size is critically dependent on the thermal characteristics of the polymer, such as glass transition temperature $T_g$, thermal conductivity and temperature dependence of the viscosity [19]. The authors found that the resolution of polymeric features does not directly depend on the tip radius, distinguishing this technique from other AFM nanolithographic methods. Dielectric properties of the polymers play a secondary role in determining the magnitude of the electrostatic pressure, but they do not have a direct impact on the lateral dimension of the patterns created.

Lyuksyutov et al. also presented a detailed theoretical investigation of the behavior of dielectric materials under electrostatic pressure [210]. In their studies, the method of images is applied to solve the electric field configuration produced by charge distribution in the presence of a thin polymer film coated on a conductive substrate. They presented that when electric breakdown takes place inside the film, polymer features are generated by softened polymer mass transport in a single step process without external heating either in contact or amplitude-modulated AFM modes. The feature size does not depend substantially on the tip shape or polymer composition while the process is dependent on the glass transition temperature of the planar polymer film. When the AFM tip comes closer to the polymer surface (e.g., $<1$ nm), the electrostatic pressure overcomes the threshold of the material plasticity, thus creating the conditions necessary for irreversible changes in the polymer surface. This process is dependent strongly on the AFM tip shape and can be implemented only in contact AFM mode.

![Fig. 39. (a) Schematic presentation of AFM electrostatic nanolithography for polymer pattern formation. (b) Periodic lines created on PMMA by electrostatic deformation. (c) Raised letters UA generated on PS. Reproduced with permission from Ref. [19]. © 2003 Macmillan Publishers Ltd.](image-url)
Further to electrostatic nanolithography, Chung et al. demonstrated the creation of Taylor cones on PMMA using higher tip voltages of 30–60 V [211]. Under such conditions, the strong electric field initiates electrohydrodynamic (EHD) instability and nanofluidic motion of the polymer melt. In the probe-induced local EHD, unstable surface waves are generated by electrostatic pressure, and the vertical transport of the fluid is decoupled from the lateral propagation of surface waves, thus enabling the formation of localized conical structures at selected sites. Fig. 40(a) displays a Taylor cone consisting of a central cone and a surrounding circular groove. The height and full width at half maximum of the cone are \( \frac{50 \text{ nm}}{C_24} \) and \( \frac{150 \text{ nm}}{C_24} \), respectively, while the diameter of the groove is usually a few micrometers. When an AFM tip with a larger radius was used, the formation of triple cones was observed (see Fig. 40(b)) [211]. The triple cones are located inside the same circular groove, and their height (up to 60 nm) is similar to that of single-cone shown in Fig. 40(a) formed under the same tip voltage and bias duration. The formation of multiple cones uncovers the correlation between the number of unstable waves and the tip end diameter: a larger tip electrode can enable more periods of unstable maximum in the perturbed polymer fluid. Therefore, three periods of waves were initiated when a blunt tip was used as electrode as shown in Fig. 40(b). Simultaneous tip repulsion due to compressive forces generated during Taylor cone formation was also detected. Fig. 40(c) shows the temporal evolution of relative tip repulsion \( \frac{Z}{Z_0} \) (\( Z_0 \) and \( Z \) are the tip–sample separation measured before and during cone formation, respectively) recorded for cone formation under 55 V and 35 V tip bias, respectively. These temporal curves clearly indicate the occurrence of tip repulsion in the patterning process. The onset and magnitude of tip repulsion depend on the strength of EHD instability triggered by an initial tip voltage. The successful creation of cones requires a well-coordinated interplay between polymer motion and tip repulsion. To address this issue, Chung et al. used cantilevers of different fore constants \( k \) (\( k = 2.80 \text{ N/m}, 0.58 \text{ N/m}, \text{ and } 0.06 \text{ N/m}, \text{ respectively} \)) to pattern PMMA, and compared the formation probabilities of nanodots and Taylor cones by these cantilevers under identical conditions [211]. They found that the probability for creating 50–80 nm cones differs drastically among these cantilevers: the probability obtained for tips of \( k = 2.80 \text{ N/m} \) and 0.06 N/m is only 20% and 24% of that for tip of \( k = 0.58 \text{ N/m} \), respectively. This indicates the significance of tip repulsion and cantilever stiffness in creating high Taylor cones: if the cantilever is too soft (e.g., \( k = 0.06 \text{ N/m} \)), the tip tends to be displaced by
the repulsive force. If the cantilever is too stiff (e.g., $k = 2.8 \text{ N/m}$), the tip would not be readily repulsed to allow cone formation.

Xie et al. investigated the conduction mechanism by monitoring the $I-V$ and $I-t$ (current–time) curves in situ during Taylor cone formation under different humidity conditions [212]. It was revealed that the charge transport is dominated by water bridge-assisted ionic conduction. Upon tip bias application, the water meniscus condensed at the tip apex is dissociated into $H^+$ and $OH^-$ ions (see Fig. 41(a)). The ionic current provides effective Joule heating for polymer melting, and the water bridge facilitates the construction of a steady media for electrical conduction and polymer mass transport (see Fig. 41(b)). When the tip bias is deactivated, the electrical conduction and Joule heating cease. A PMMA Taylor cone is formed due to the quenching of the polymeric nanofluids (Fig. 41(c)).

The ionic conductivity was observed to be very sensitive to humidity conditions which directly affect the formation of the water bridge between the tip and substrate. When the humidity is reduced, the electric conductivity is lower, e.g., the conductivity $\sigma$ is $\sim 3.5 \times 10^9 \text{ S/m}$ for 60% humidity, while it is only $\sim 1.3 \times 10^8 \text{ S/m}$ under a humidity of 20%. The variation of $\sigma$ as a function of humidity ($H$) was found to follow an explicit linear dependence of $\sigma = 0.6 \times 10^{-10} H \text{ (S/m)}$ [212]. Such a relation reflects the proportional correlation of conductivity to carrier concentration and carrier mobility. Higher humidity enhances water condensation and subsequent water dissociation, leading to higher $H^+$ and $OH^-$ concentrations, which would promote the overall conductivity. Higher humidity also helps improve carrier mobility in polymer melts, as the polymer viscosity would be lower if it was heated by an initial high ionic current.

### 3.6. Nanoexplosion and shock wave generation

Xie et al. reported the observation of nanoscale explosion and shock wave generation in a nanometer-sized air/water media induced by a biased AFM probe [20]. As illustrated in Fig. 42(a), when the tip is biased, the electric field exceeds the breakdown strength of the dielectrics, initiating the explosive discharge of the air/water media in the tip–substrate gap. It was demonstrated that the nanoexplosion is highly localized in the vicinity of the tip apex, and is responsible for the formation of a central structure shown in Fig. 42(b). Moreover, the nanoexplosion could trigger transient shock waves which propagate parallel to the substrate surface. The propagation of the shock waves helps to significantly expand the trajectory of discharged species out of the explosion zone, thus leading to the formation of an outer ring surrounding the central structure. Such central and outer structures have been created on different substrates including Si (see Fig. 42(c)), PS and polyvinyl carbazole (PVK). Finite elemental method simulation showed that the nanoexplosion is highly localized, in which the field and charge distributions are confined within a radius of 80 nm and 25 nm, respectively. The shock wave is generated when large amounts of discharge energy are released to the nanometer-sized gap. The propagation of the shock waves can spread the discharged particles to a lateral distance of several micrometers.

The relationship between the nominal areal power density $E_0$ liberated from the nanoexplosion and the radius of the shock front $R$ (i.e., the radius of the outer rings) was found to be $R = fE_0^{1/4}$, where $f$ is a system-related scaling factor. On a Si substrate, when $E_0^{1/4}$ is $10–40 (E_0 \text{ in W/m}^2)$, the radius of outer rings generated is $0.5–2.5 \mu\text{m}$ (see Fig. 42(d)). The occurrence of the stochastic nanoexplosion is highly dependent on the substrate materials and humidity.
conditions. The substrate-specific surface reactions have a strong impact on the onset voltage of the nanoexplosions. For a nanometer-sized gap, the discharge behavior deviates significantly from the traditional Paschen Law [213] which is valid for large scale discharges. A growth of discharge probability with bias voltage was observed, and was attributed to the enhancement of ionization by higher fields in the Townsend electron avalanche process [213, 214]. High humidity conditions promote the occurrence of nanoexplosions by facilitating secondary avalanches and reducing the degree of electron attachment.

Xie et al. further demonstrated the application of nanoexplosions for the creation of localized conductive structures on an insulating PVK matrix [21]. In this case, the native PVK reacts with the discharged oxygen-containing particles generated in the nanoexplosion to form cross-linked carbazole groups. The cross-linking and oxygenation leads to the formation of extended $p$-conjugation in the patterned PVK, which narrows the HOMO–LUMO energy gap of the PVK molecular orbitals. Therefore, the PVK pattern exhibits higher electric conductivity due to the lowering of energy barrier for electron injection. Fig. 43(a) shows a PVK pattern composed of the central and outer structures fabricated by the nanoexplosion and shock wave propagation technique. The height of the central structure is about 15 nm, while the radius of the outer ring is $2.1 \mu m$. Fig. 43(b) shows the current map collected for such a PVK pattern using cAFM. Higher current was detected for the central structure and outer ring, indicating the electric conductive nature of the PVK pattern as opposed to the insulating native PVK matrix.

To elucidate the physico-chemical characteristics of the patterned structure, the PVK samples were exposed to large-scale discharges generated by a Van de Graaff generator. The discharge conditions were comparable to those in the nanoexplosion, except that the reacted area of PVK was large enough for FTIR (Fourier transform infrared) and PES (photoelectron spectroscopy) characterizations. Fig. 43(c) compares the FTIR spectra recorded for samples unexposed and exposed to discharges. Two peaks (A: 1236 cm$^{-1}$, B: 1247 cm$^{-1}$) attributable to the vibration of cross-linked carbazole groups by bridge oxygen were identified for the exposed PVK, while no vibrational modes were observed for the unexposed sample. The assignment of A and B peaks were confirmed by calculating the FTIR spectra for the cross-linked PVK using density functional theory (DFT). The PES spectra of O 1s core level recorded for the exposed sample is shifted towards higher binding energy by 0.7 eV relative to that of the unexposed sample. The shift arises from the delocalization of the O 2p states which raises the HOMO energy level of PVK patterns.
The impact of cross-linking and oxygenation on the electric functionality of PVK patterns was also investigated by calculating the HOMO–LUMO gap of various configurations. It was found that the cross-linking of carbazole groups by oxygen can lower the HOMO–LUMO gap of PVK patterns. As the number of cross-linked carbazole groups increases, a higher degree of cross-linkage and oxygenation occurs, leading to a narrower energy gap (see Fig. 43(d)). Current–voltage curves measured by cAFM revealed that the electric conduction in PVK patterns is governed by F–N electron injection. The narrowing of HOMO–LUMO gap helps reduce the energy barrier for current injection from the tip, therefore significantly facilitating electric conduction in the patterned PVK structures.

3.7. Charge deposition and manipulation

Crook et al. introduced an erasable electrostatic lithography technique for charge deposition and manipulation [215]. In this technique, patterns of charge are deposited on a device surface with a negatively biased scanning probe in a low-temperature and high-vacuum environment. The charge patterns locally deplete electrons from a subsurface two-dimensional electron system (2DES) to define working quantum components and can be erased with opposite bias or by globally illuminating the device with red light. The defined charge spot area is an order of magnitude larger than the tip–surface contact area, so smaller charge spots, and therefore higher resolution, would be attained by using a less negative probe bias with a shallower 2DES. This technique may be particularly useful in the construction of a
solid-state scaleable quantum computer, where the required level of uniformity between quantum components is hard to achieve using other schemes.

In the work of Pioda et al., a metallic AFM tip was coupled capacitively to electrons confined in a lithographically defined gate-tunable quantum dot [216]. Single electrons were made to hop on or off the dot by moving the tip or by changing the tip bias voltage due to the Coulomb-blockade effect. Spatial images of conductance resonances were recorded to obtain quantitative spatial maps of the interaction potential between the tip and individual electrons. Their scanning-gate measurements on a quantum dot demonstrated that single electrons can be manipulated one by one with a scanning probe.

Barrett and Quate investigated charge storage in a nitride-oxide–silicon (NOS) medium using a biased AFM probe [217]. The stored charge can act as a digital memory. Bit sizes as small as 75 nm have been stored, and they are stable over a period of 7 days. The stored charge can also be removed by applying a reverse bias to the region, and the bit can be subsequently rewritten. By simultaneously measuring capacitance and topography images, the authors confirmed that the stored information is not a result of any topographic change to the surface. Instead, the observed writing and erasing effect is due to electronic changes inside the insulator and semiconductor. In addition to NOS, the charge deposition on a fluoride thin film by biased AFM tip was also reported [218]. Kado and Tohda demonstrated nanometer scale recording on an amorphous GeSb2Te4 film by means of charge storage [219]. Data were recorded by locally changing the electrical property of the film, and were subsequently read by detecting the change of conductance. The smallest recorded region is 10 nm in diameter, which corresponds to a data storage density of 1 T bit/cm².

Yano et al. fabricated stable bits in a LB film by probe-induced charge manipulation [220,221]. The conductance of the LB film changes without pit formation in the LB film or metal cluster deposition from the tip of the probe. Hieda et al. described the manipulation of the charged state of nanoscale organic dot structures [222]. Electric charges were injected into single dots by contact electrification from an AFM tip. On measuring the charge distribution, it was found that the injected charges were stably confined in the dot structures for an extended period. The number of injected charges could be controlled down to single elementary charge. Further, injected charges could be re-extracted from the dots using a tip with reduced applied voltage.

Schaadt et al. described the local charging of a thin film consisting of Co nanoclusters embedded in insulating SiO2 deposited on a Si substrate [223]. Positive and negative charges were deposited controllably and reproducibly in Co nanoclusters, typically in quantities of 5–20 electrons within areas 30–50 nm in radius. Sample charging was achieved by holding the biased tip at the center of the scan area for 10 s in tapping-mode AFM as shown in Fig. 44. The charge decays over several minutes, with the decay time for positively charged nanoclusters being substantially larger than that for negatively charged nanoclusters. This difference was interpreted as a consequence of the Coulomb blockade energy associated with single-electron charging of Co nanoclusters. Mesquida et al. wrote local charge patterns onto

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Fig. 44. Schematic diagram of the SiO2/Co/SiO2/Si sample structure, AFM tip, and voltage bias connections. The charge $Q$ deposited in the Co layer induces image charges $-Q_i$ in the Si substrate and $-Q'_i$ in the tip. Reproduced with permission from Ref. [223], © 1999 American Institute of Physics.
an electret (a kind of solid dielectric) surface consisting of a fluorocarbon layer grown on substrates with different electric conductivities [224]. This process can also be used to create localized charge patterns on metal, and even in a liquid environment that can be used as carrier substance for particles.

The application of charge deposition for nanofabrication was further demonstrated by Mesquida and Stemmer [225]. They first generated charge patterns using an AFM probe, and then attached silica nanoparticles from suspension to the surface patterns. Positive and negative charge patterns with a resolution down to about 100 nm were written into a thin fluorocarbon film. The patterns were used as templates for locally attaching silica nanobeads suspended in an insulating fluorocarbon liquid to form structures with a width down to about 1 μm. The attractive force leading to particle attachment was identified to be mainly Coulombic attraction. The beads were positively charged, and they were attached only to the negative surface charge patterns. Fig. 45 depicts the creation of a charge pattern and subsequent attachment of particles to the charge pattern by electrostatic attraction. Naujoks and Stemmer presented the fabrication of biomolecular structures with sub-micrometers resolution by depositing proteins from solution onto electrically patterned surfaces [226]. The charge patterns were generated by locally depositing negative electric charges into a thin insulating electret film using an AFM tip. The electric field of the trapped charges attracts positively charged water droplets that are emulsified in an insulating oil. The authors used water droplets to transport labeled avidin to the desired surface charge pattern. Their results showed that pattern definition after immersion into aqueous solution is maintained, and the avidin specifically binds to the biotin groups of the already deposited immunoglobulin G molecules (IgG-biotin).

4. Concluding remarks

In this article, we have reviewed the development of AFM nanolithographic techniques for nanoscale structuring and fabrication. Tremendous progress has been achieved in AFM nanolithography in the last two decades. As an emerging technology, AFM nanolithography offers an effective alternative to conventional techniques for
nanofabrication, and has an increasingly significant impact on nanoscience and nanotechnology. While numerous strategies and methodologies have been demonstrated, they are generally based on force-assisted and bias-assisted tip–sample interactions. Structures are fabricated either by introducing/depositing materials from the tip to the substrates, or by manipulating, modifying, and altering the materials pre-existing on the surface using the tip. Molecular transport and surface diffusion are key steps in the first case, while deformation, dislocation, and chemical and electrochemical reactions are often involved in the latter case. The meniscus formed between the tip–sample gap plays a significant role in facilitating mass transport and electrical conduction in the probe-induced structure fabrication. In addition, AFM nanolithography is also capable of creating charge spots for quantum component fabrication, and the charged patterns can be further used to template the assembly of nanoparticles and biomolecules. Owing to the versatility of AFM nanolithography, a wide variety of materials including insulators, semiconductors, polymers and bioactive molecules can be patterned for bottom-up device fabrication. The size of the patterns created ranges from single atoms and molecules to nanoparticle clusters and biological complexes. Quantum well, memory arrays, and biological sensors have been fabricated by AFM nanolithography for electron confinement, data storage, and biorecognition applications.

There are still a few challenges faced by AFM nanolithography. Firstly, our understanding of the lithographic mechanisms is incomplete. AFM nanolithography often involves the interplay of ultrafast physical and chemical processes that are highly sensitive to the operational procedures. A slight change in experimental conditions could lead to the switching of pattern formation modes, resulting in conflicting observations reported in the literature. Secondly, knowledge of the physico-chemical properties of the fabricated nanostructures is necessary to obtain insights into the pattern formation mechanism and functionality of the patterns. However, the characterization of the AFM-fabricated structures is challenging due to the difficulties in examining the localized nanoscale patterns using conventional techniques. Finally, the mass production of patterns by AFM nanolithography needs to be optimized since it is essentially a serial process. Although the Millipede technique has been demonstrated for fabricating 1024 (32 × 32) memory storage matrix, several issues such as overall system reliability and integration have yet to be addressed [53]. Therefore, further advancement of AFM nanolithography would rely on future efforts in understanding, controlling, and optimizing the nanofabrication processes.

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References


