13 The Application of STM and AFM in Nanoprocess and Fabrication

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Abstract The scanning tunneling microscope (STM) and atomic force microscope (AFM) provide, not only 'eyes' but also 'hands' to investigate and modify nano-objects. Therefore, not only are high resolution images available to us, but they offer a means to construct objects in the microscopic world. In this chapter, we will introduce nanometer processing technologies based on STM and AFM.

During last decade fabrication and processing at the nanometer scale have achieved great advances, based on STM and AFM. Manipulation of individual atoms and molecules has been realized, and potential applications such as molecular devices have been demonstrated. Functionalized nanostructures have been fabricated with STM- and AFM-related techniques through various physical or chemical mechanisms. We expect that process and fabrication with STM and AFM will finally go from laboratory to factory as well as to thousands of families in the coming future.

Keywords Scanning tunneling microscope (STM), atomic force microscope (AFM), nanofabrication, nanomanipulation

13.1 Introduction

One of the ultimate goals of nanoscience and nanotechnology is to develop molecular machines that manipulate individual atoms or molecules and make products with unique functions. The well-known speech entitled 'There's Plenty of Room at the Bottom', delivered by the physicist R. Feynman in 1959, resulted in the bud of nanoscience and nanotechnology. Later, in one of Feynman's books, he suggested further that people might develop machines that work at the molecular level[1]. However, as there was no means or tools to manipulate a single molecule at that time, his idea was merely a purely academic discussion. In 1981, K.E. Drexler pointed out for the first time that artificial molecular machines might be

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constructed via advanced molecular engineering technology, by following the ways that nature adopted and presented in organisms for millions of years[2]. In 1992 he showed that complex structures could be built via precise control of atoms, the properties of which depend on the organization of atoms[3].

The invention of the scanning probe microscopes (SPM) family[4] provides strong support for the processing and fabrication at the nanometer level, and drives forward the development in nanoscience and nanotechnology. Originally, the SPM was used to investigate surface properties of samples by scanning the local surface with a tiny tip. Detailed information that can be obtained with very high spatial resolution by using the SPM is: ① topological, ② mechanical, ③ electrical, ④ magnetic and ⑤ optical. The most popular members of the SPM family are the scanning tunneling microscope (STM)[5] and atomic force microscope (AFM)[6]. STM is the first member of SPM family, invented by G. Binnig and H. Rohrer, who shared the Nobel Prize in Physics in 1986 for this invention. The STM measures the tunnel current between a conductive tip and a conductive sample, and can 'see' a single atom. The AFM, invented by G. Binnig et al. in 1986, measures the mechanical deflection of a cantilever, which has a nanometer sized tip that interacts with a local region of sample surfaces. The AFM is applicable for both conductive and non-conductive samples under various environmental conditions (in vacuum, ambient air, or liquid). In addition, AFM and STM are used as not only 'eyes' but also 'hands' so that they can probe and modify samples. Therefore, not only is high-resolution information available to us, but also a means to construct in the microscopic world.

The goal of this chapter is not to systematically review work in the field of SPM, but to introduce nanometer processing technologies based on STM and AFM, especially the developments in the last decade.

13.2 The Manipulation and Processing of Single Atoms and Molecules

Apart from high-resolution images obtained by STM, the tunneling current and the voltage exerted between the tip and the sample can be employed to achieve surface modifications at the atomic level, for example, to manipulate single atoms. Atomic manipulation by STM can be simply classed into ① vertical and ② lateral manipulation modes. Both modes are described below:

(1) In vertical mode, the STM tip is first located directly above the atom to be moved, and then lowered down to it to increase the attraction between them, which in turn leads to atom adsorption on the tip; then, the tip is lifted up, and kept in planar motion relative to the surface. Finally the atom is released from the STM tip and placed at the desired location (see Fig. 13.1(a));

(2) In the lateral mode, the STM tip can perform many operations on the atom,

including pushing, pulling and sliding, while at the same time the atom remains bound to the surface (see Fig. 13.1(b)).

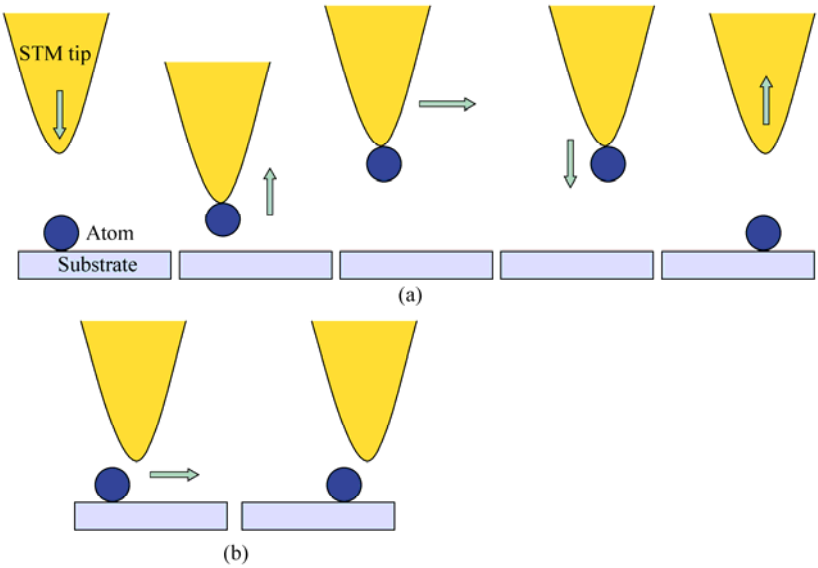

Figure 13.1 Schematic drawing of the nano-manipulation of atoms with STM. (a) Vertical manipulation mode. (b) Lateral manipulation mode (see color figure at the end of this book)

Manipulating single atoms on the conductor surface[7] was a milestone in nanoscience and nano-technology. In 1990, D. M. Eigler et al. used STM tips to move atoms and wrote down a company's name with 35 xenon atoms on a nickel surface (see Fig. 13.2), which meant that the long-standing desire of human beings to manipulate single atoms had been satisfied. In addition, vertical mechanical manipulation of single atoms using AFM has also been realized[8]. Recently, W. Ho et al. used STM to build 1D gold chains (see Fig. 13.3)[9] and studied the correlation between geometric and electronic properties, thus demonstrating that it is possible to carry out atomic-level fabrication.

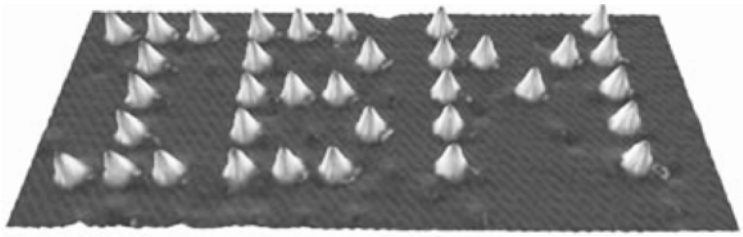

Figure 13.2 A company name 'IBM' formed with 35 Xe atoms by using STM nano-manipulation[7]

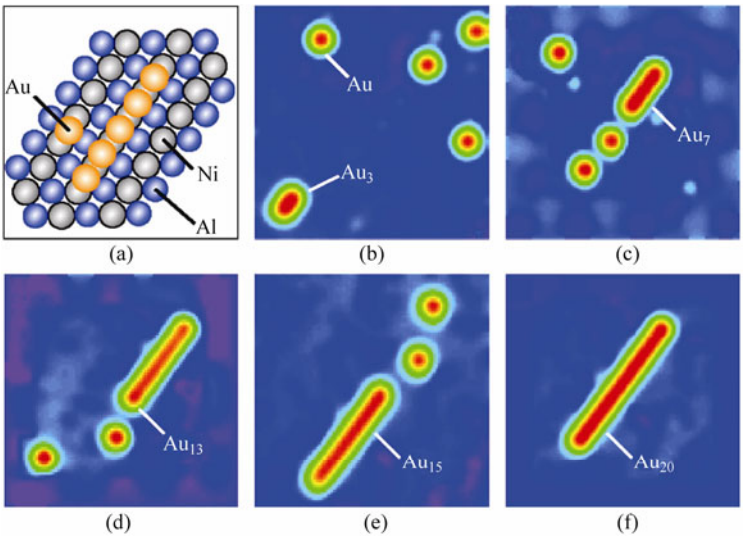

Figure 13.3 Moving and patterning individual Au atoms with STM. A atomic chain was formed with 20 Au atoms[9] (see color figure at the end of this book)

The manipulation of single molecules was realized a little later as molecules are more complex. Figure 13.4 shows images before and after the rearrangement of 6 Cu-TBPP molecules under the STM tip at room temperature[10]. Taking advantage of the repulsion between the STM tip and molecules, X. Xiao et al.

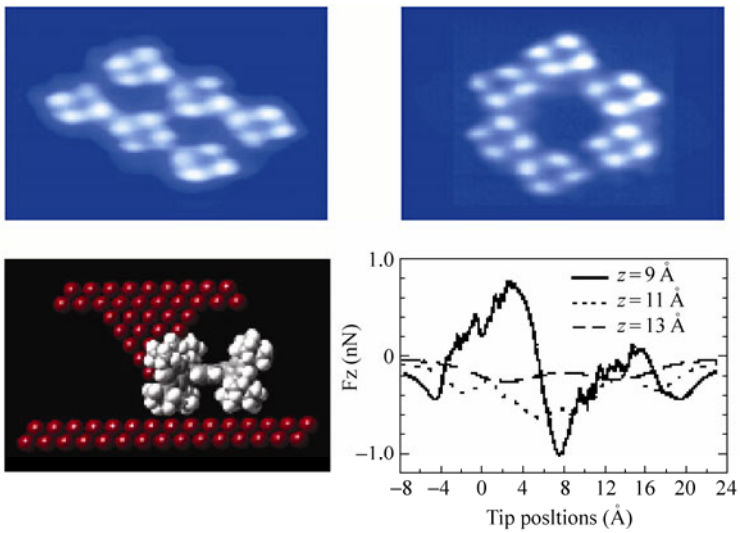

Figure 13.4 (upper) STM images of 6 Cu-TBPP molecules before and after re-arrangement induced by a STM tip. (bottom) The conformation of the Cu-TBPP molecules changed during re-arrangement (bottom left), which was revealed by the force curve (bottom right)[10] (see color figure at the end of this book)

managed to manipulate CO molecules and patterned the word 'HKUST' with 49 CO molecules on the copper surface in 2002 (see Fig. 13.5). The manipulation of biological macromolecules has also been accomplished. As shown in Fig. 13.6, complicated patterns, such as letters 'D', 'N', and 'A' were patterned with DNA molecules by employing AFM nanomanipulation including cutting, pushing and folding process[11].

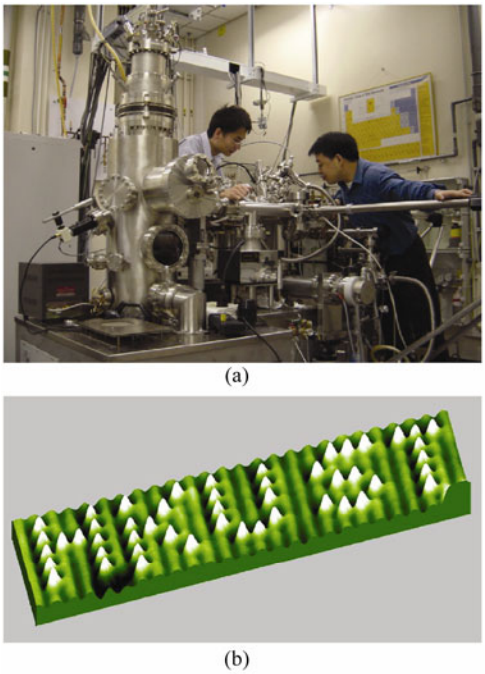

Figure 13.5 Manipulation of CO molecules with STM. (a) Researchers working with a Low Temperature Omicron STM system; (b) the word 'HKUST' formed with 49 CO molecules on Cu surface. Images were provided by Prof. Xudong Xiao of the Hong Kong University of Science & Technology (see color figure at the end of this book)

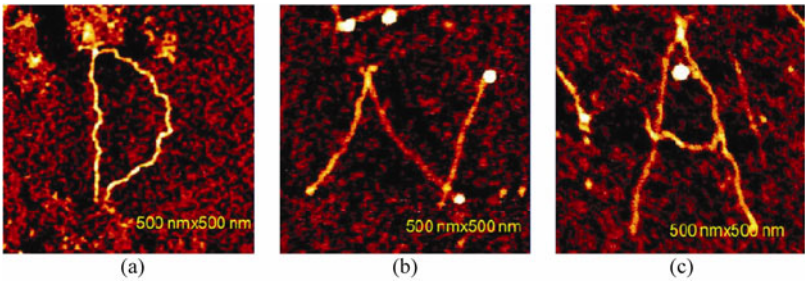

Figure 13.6 Human letters 'D', 'N', and 'A' formed with individual DNA molecules[11] (see color figure at the end of this book)

Nanomanipulation makes possible the single-atom or single-molecule reaction as shown in Fig. 13.7. A CO molecule was transferred and positioned over an Fe atom to form Fe (CO), and Fe $(CO)_2$ was formed when a second CO was added[12]. It should be noted that the reaction would not occur automatically when a CO molecule is close to a Fe atom. Tunneling electrons and possibly the electric field between the tip and the surface will be involved in overcoming the energetic barriers in the process to form new bonds. In addition, scanning tunneling current tip-induced chain polymerization has been demonstrated[13].

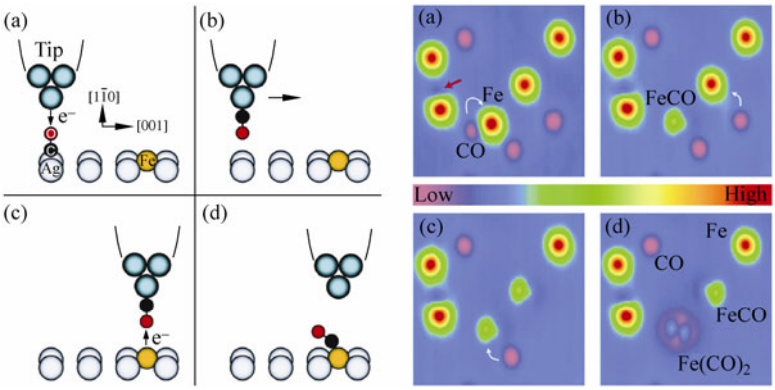

Figure 13.7 Single-molecule reaction induced with STM. (Left) Scheme. (Right) STM images indicating the reaction process. (a) Several Fe atoms and CO molecules on the substrate. (b) One CO molecule reacted with Fe atom to form a FeCO molecules. (c) Two FeCO molecules were formed. (d) One FeCO reacted with another CO and formed a $Fe(CO)_2$[12] (see color figure at the end of this book)

Manipulation at the single-molecule level has great applications, in manufacturing single-molecule devices. Scientists used a C_{60} molecule as a current amplifier[14]. This single-molecule device was produced by placing a C_{60} molecule between a STM tip and a surface of a conductor. When a bias was exerted to the STM tip to force it to approaching the surface, the resulting pressure caused a change in C_{60} conformation, which in turn decreased the resistance of the C_{60} molecule. The researchers found that the resistance was lowered nearly 100 times every time the C_{60} molecule was pressed down 0.1 nm by the tip.

13.3 Nanolithography on Surfaces

Development in STM and AFM provides tools for nanoscale processing and modifying. For instance, the AFM tip can exert a mechanical force to a local region of the surface so as to produce mechanical machine work in the nanometer scale. The process is programmable, making practical operation convenient. What is of great symbolic significance is that a famous Chinese poem of the Tang dynasty,

'Dawn of Spring' (see Fig. 13.8), was written with an AFM tip by Z. Liu's research group at Peking University[15].

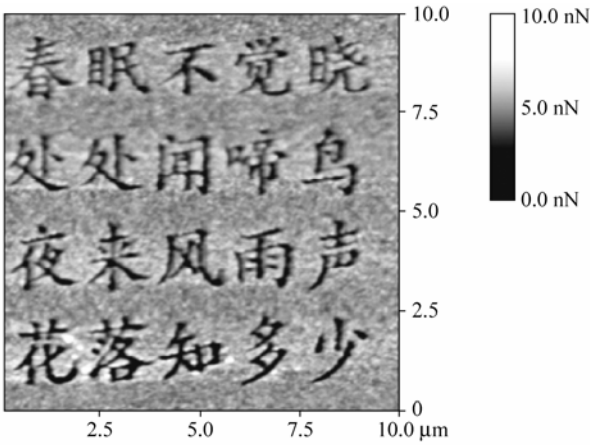

Figure 13.8 The famous Chinese poem of the Tang dynasty, 'Dawn of Spring', written with AFM nano-lithography[15]

Besides the mechanical force exerted by using an AFM tip, an 'electric' interaction can be introduced on the local surface by an STM tip. For instance, if a certain voltage is imposed locally on the self-assembled monolayer (SAM) formed with Au-S bonds on the Au surface, the SAM will be removed, resulting in nanoscale patterns (Fig. 13.9)[16]. As for AFM, the same operation can be achieved by scanning a conducting tip with a sufficient bias between the tip and

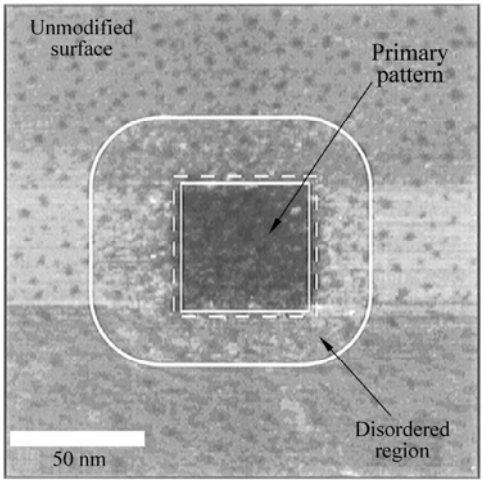

Figure 13.9 STM nano-lithography on the self-assembled monolayer. The center 50 nm × 50 nm square in the image was the exposed Au surface after nano-lithography[16]

the SAM surface[17]. In the experiments, the tip-sample bias needs to exceed a critical threshold value, while at the same time sufficient ambient humidity is demanded for some specific SAMs.

13.4 Nanoscale Surface Processing Based on Electrochemical Reactions

It has long been noted that the oxidation of hydrogen-passivated Si surfaces can be induced by a STM tip operating in air[18]. The study showed that a biased conducting AFM tip can locally induce surface oxidation of semiconductors (Si) or metals such as Ti. Researches have indicated that the water present on the surfaces play an important role in these processes. Therefore, it is believed that it is an electrochemical process.

Volume expansion of semiconductors or metals upon oxidation makes convenient, the characterization of the reactions. Besides, these findings can be used to construct nanostructures in the oxidation state. The size of nanostructure is determined by the bias voltage and the reaction time (Fig. 13.10(a))[19–22]. As aqueous solution of HF can be used to etch SiO_2 easily, a proper treatment of the nano-structures with HF solution resulted in nano-meter sized wells (Fig. 13.10(b))[19].

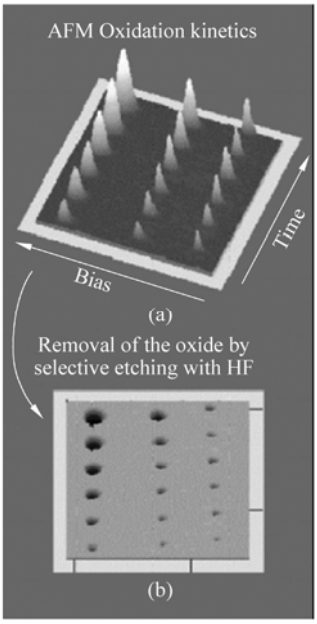

Figure 13.10 (a) AFM image of a locally oxidized Si substrate. (b) AFM image of the Si nano-structures after HF etching[19]

Since the AFM tip takes effect merely in a confined area, a direct idea is to take advantage of this kind of nanoscale electrochemical reactions to reduce metal ions, so that the metallic nanostructures can be constructed on surfaces. For example, when silver ions were chemisorbed on a thiol-terminated silane monolayer on silicon substrate, an appropriate bias applied to the AFM tip would result in release of Ag and formation of island-like Ag nanostructures on the substrate[23]. Another indirect way was that methyl-terminated silane monolayer on Si could be patterned via tip-induced electrochemical oxidation of the methyl group, in which the product –COOH group, would facilitate the adsorption of Ag^+ ions. Then the Ag^+ ions were reduced by reducing agent, and finally nanoscale silver islands were obtained (see Fig. 13.11)[24]. Similarly, the same strategy can be applied to construct nanostructures of Au, CdS and so on.

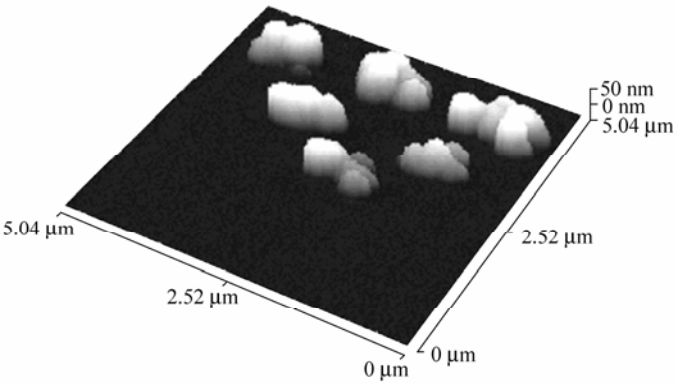

Figure 13.11 AFM image of Ag island formed after electrochemical reaction induced by conductive AFM[24]

13.5 Metal Nanostructures Fabricated with Field Evaporation

Field Evaporation is the phenomena where the atoms are ionized and evaporated in the presence of extremely high electric field of the order of a few V/nm. Such high electric field normally can be achieved by applying a high voltage between a sharp needle-like conductor and a plate-like conductor. Since the distance between the tip and the surface can be controlled accurately to 1 nm or less for STM or AFM, a few volts of supply will meet the ultra-high electric field required for field evaporation.

The field evaporation can be used to manipulate atoms or to construct nanostructures on the surface[25]. A simple idea is to use the STM tip as the emission source to construct nanostructures on the surface. Similarly, when an

AFM tip is coated with a metal film, such as a gold film, then the film can be used as the emission source to construct gold nanostructures on a conducting surface. As shown in Fig. 13.12, a nice array of gold nanodots was produced in this way[15].

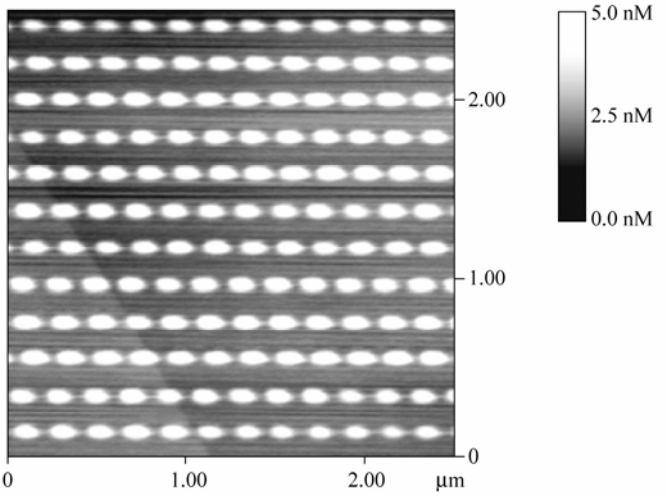

Figure 13.12 Au nano-array formed on a HOPG surface by field evaporation[15]

13.6 Dip-pen Nanolithography

Dip-pen Nanolithography (DPN)[26], based on atomic force microscope (AFM) is an approach for nanofabrication, which was developed by C. A. Mirkin et al. As shown in Fig. 13.13, molecules (inks) adsorbed on an AFM tip (as a nanopen) can be transferred to the substrate through the water meniscus, when the tip is

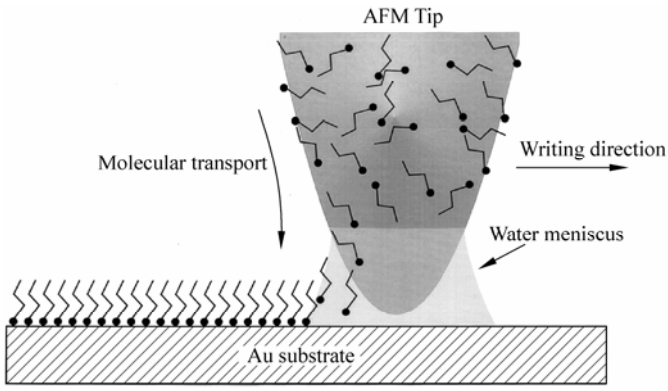

Figure 13.13 Scheme of the Dip-pen Nano-lithography (DPN)[26]

contacted with the surface of a substrate. The location and motion of the tip can be accurately controlled by the AFM system, thus the desired nanometer-sized pattern can be easily 'written' or 'drawn' with a variety of molecules as the inks. For example, biomolecules such as DNA and proteins have been patterned and their biological activities were demonstrated (Fig. 13.14)[27], which provided an efficient and convenient way for the manufacture of biochips. The concept of DPN can also be developed for site-specific capturing and deposition of nanoparticles in a one-particle-at-a-time fashion[28].

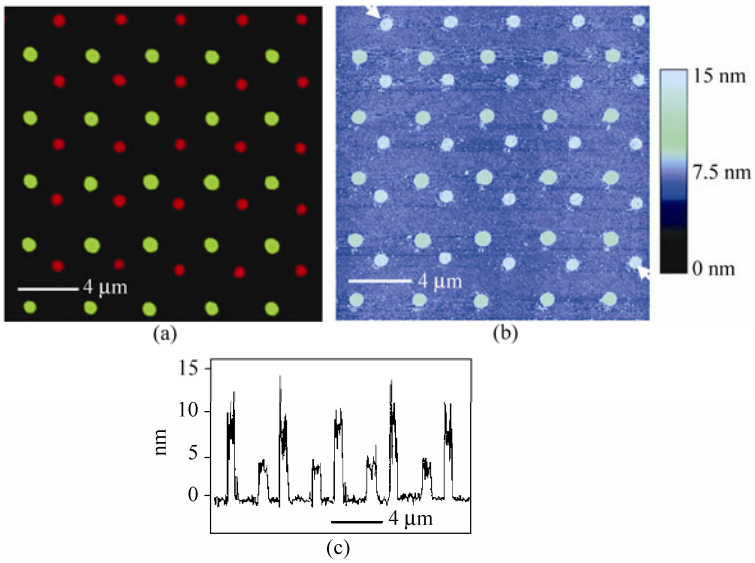

Figure 13.14 DPN-generated biomolecule patterns on substrate showing biological activities. (a) Fluorescent image indicating target DNA molecules binding to their complementary DNA spot. (b) AFM image indicating two kinds of DNA-functionalized Au nanoparticles bound to their complementary DNA spots. (c) Section analysis of the line along the arrows shown in 'B', indicating that two different nanoparticles, with 5 nm and 10 nm in dimensions, respectively, were bound to their complementary DNA spots[27] (see color figure at the end of this book)

DPN also provides a way for positioning reactions at the nanometer level. The ink molecules on the AFM tip could be served as source for synthesis of polymers (Fig. 13.15)[29], and the reaction could be well-controlled through regulating the tip-substrate contact time. Recently, we have also demonstrated that a positioning scission reaction of a single DNA molecule could be realized by delivering DNase I molecules onto the DNA strands[30].

By employing information technology, parallel-probe DPN can work with tens of thousands of probes[31, 32]. If every nanopen can be controlled separately and inked with different molecules, it could have prominent applications in the future.

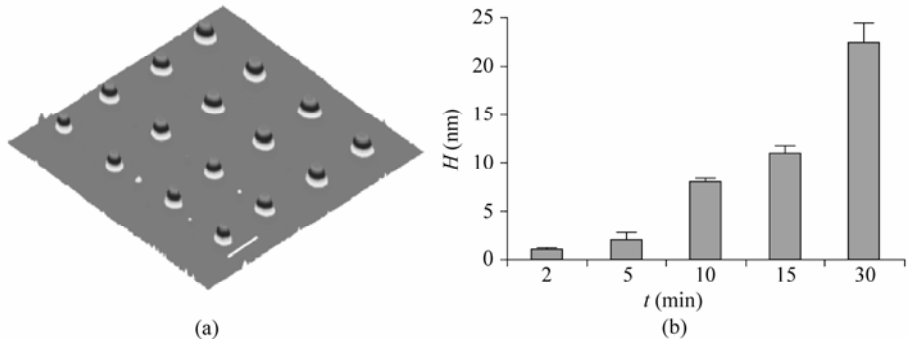

Figure 13.15 AFM image of polymer synthesized in situ by using DPN technique. The polymer size was increased along with the increasing of the contact time of the inked AFM tip to the substrate[29]

13.7 Nanografting

In the nanografting method[33], closely-packed self-assembled mono-layers on the surface can be removed locally by AFM under a high load when the exposed surface was grafted with another kind of molecule. The first step of nanografting actually is AFM nanolithography that will be discussed in Section 13.3. The main difference is that the whole process is performed in a liquid environment. Figure 13.16(a) shows a smooth SAM formed on a substrate. When an AFM tip

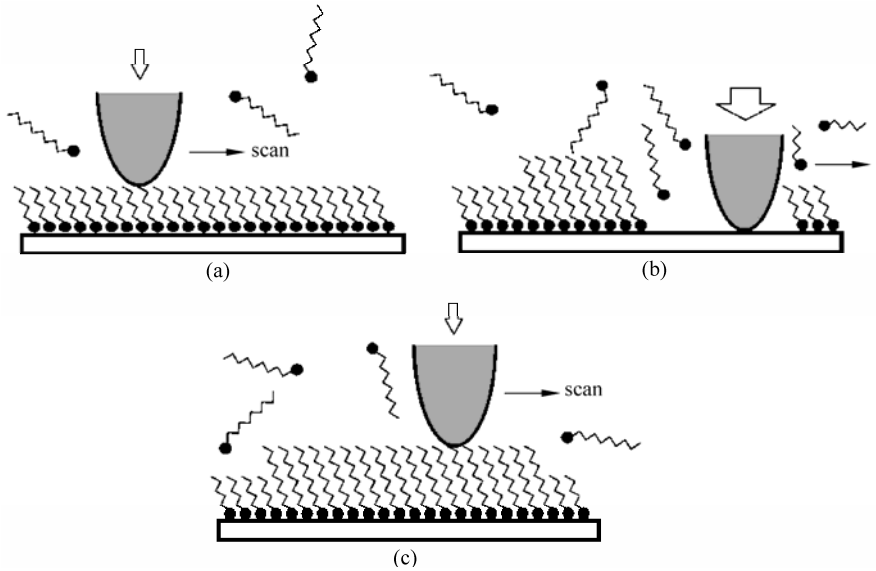

Figure 13.16 Schematic drawing of the Nanografting method[33]

applies a larger force to the surface while the tip keeps moving over it, local SAM would be mechanically removed, leaving a bare surface. Because the whole system is immersed in the liquid, other molecules in the liquid environment would take up places on the bare substrate (Fig. 13.16(b)) and form nanostructures, which can be revealed with AFM performed with a small force (Fig. 13.16(c)). To remove a pre-formed SAM, researches have also used STM and conductive AFM by applying a sufficient voltage between the STM (AFM) tip and the surface[17, 34, 35].

By this method, nanostructures with controlled chemical components, structures, and functions can be fabricated. For example, a hydrophilic nano-island with 70 nm × 300 nm size was formed on the Au surface coated with a hydrophobic monolayer (Fig. 13.17)[36]. In addition, nanostructures of proteins and oligo-nucleotides have also been constructed[37, 38].

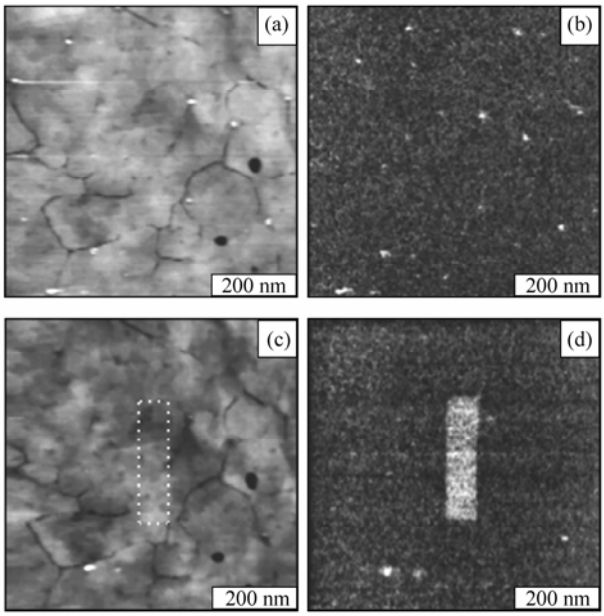

Figure 13.17 The formation of a 70 nm × 300 nm hydrophilic nanostructure by using Nano-grafting. (a, b) Topography and Friction mode AFM images before Nano-grafting. (c, d) Topography and Friction mode AFM images after Nano-grafting. The Friction mode AFM image clearly indicated the hydrophilic area[36]

13.8 Nanoprocess with Heatable AFM Tips

AFM-based techniques that employ a miniaturized thermal probe have exhibited great advantage in controlling polymer behaviors by locally heating the surfaces. AFM can be equipped with a nanoscale heatable tip, by which extreme conditions

can be generated in terms of a very high temperature gradient on the surface (approx. 100℃/nm) for short time periods (μs – ms). In particular, the sample surface is only exposed very locally to the extreme condition and the induced new surface features are generated within an unchanged matrix. In this way it is possible to get insight into the structure, formation, the dynamics of polymers, and the control of surface properties on the nanometer scale.

Nanoscale control of the polymer surface is of great importance for both fundamental research and industrial applications. For example: ① work has been done on melting of polymer nanocrystals[39], ② high-density data writing and reading[40, 41], ③ local surface glass transition[42], and ④ nanodecomposition[43, 44].

13.9 Summary and Perspective

In summary, fabrication and processing at the nanometer scale based on STM and AFM have achieved great advances in the last decade. Manipulation of individual atoms and molecules has been realized, and potential applications such as molecular devices have been demonstrated. Functionalized nanostructures have been fabricated with STM- and AFM-related techniques through various physical or chemical mechanisms.

However, it should be noted that there are still some open problems in this field. For example, efficiency should be considered seriously in the process of any fabrication or manufacture. Though people have developed multiple probes or probe arrays to increase the efficiency, the SPM-based nanofabrication is still impractically time- consuming. On the other hand, the products of STM- and AFM-based nanomanipulation should reach to a certain amount for practical application. Ideally, if this kind of fabrication can result in molecular machines that can self-replicate, as DNA has done in nature, then it is expected that process and fabrication with STM and AFM will go from laboratory to factory, even to thousands of families in the future.

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