Chapter

Nanolithography by Scanning Probes for Biorecognition

Javier Martinez

Abstract

With the invention of the scanning tunneling microscope (STM) and subsequently with the atomic force microscope (AFM), the human being was able to enter in the nanoscale world. At first, these devices were only used for imaging samples, but with a small modification of its electronics, they can be used for a precise and controlled manipulation of the scanning probe, creating different types of nanolithographed motifs. The development of this type of lithography has allowed the manufacture of nanometric-scale structures that have led spectacular advances in the field of nanotechnology. In this book chapter, we present the most innovative and reliable probe nanolithography techniques. All of them are based on the spatial confinement of a chemical reaction within a nanometric size region of the sample surface. In that way, 2D or even 3D nanostructures can be fabricated. The full potential of probe nanolithography techniques is demonstrated by showing a range of applications such as the controlled deposition of molecules with high precision or nanotransistors that can be used as sensors for biorecognition processes.

Keywords: AFM, nanotechnology, lithography, nanodevices, scanning probe

1. Introduction

Since the 1960s, the size of electronic devices has been reduced through the use of optical, electronic lithography and lately by immersion lithography. All these techniques are very efficient and allow the fabrication of very complex microelectronic devices, but they have a high cost, are not modifiable, are always made on silicon wafers, and are bounded within the standards of clean rooms. Due to these limitations, in the 1990s, new manufacturing techniques began to be developed that could perform nanometric motifs of different materials in different environments and with lower costs: nanoimprint, soft lithography, and scanning probe nanolithography [1–3].

These new nanofabrication techniques have allowed a great variety of structures to be made, and they have also been able to position and manipulate with nanometric precision different organic and inorganic materials. This chapter wants to provide an overview of the most relevant nanolithography techniques using a local probe that will allow the manufacture of a wide variety of different structures and the creation of functional nanoscale devices for biorecognition.

In order to perform this type of lithography, an atomic force microscope (AFM) is needed, which permits us to obtain high-resolution images in air, in liquids, or in vacuum of all types of conductive, semiconductor, and insulating surfaces. The main elements of the AFM microscope are shown in **Figure 1**. In addition to

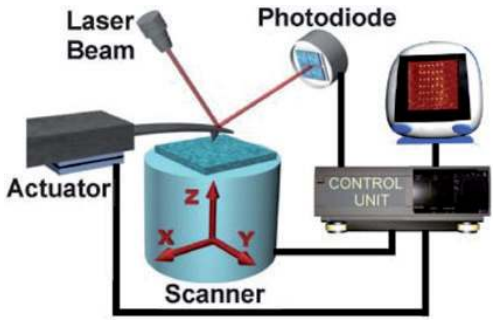

Figure 1.
Main elements of an atomic force microscope system (from Ref. [28]).

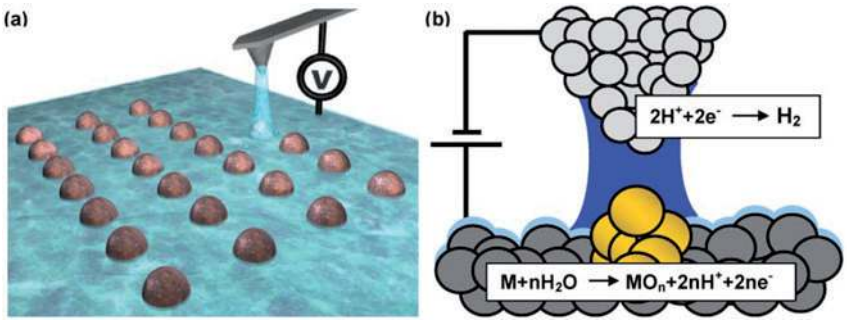

Figure 2.
Local oxidation nanolithography process by AFM. (a) Formation of the liquid meniscus. (b) Chemical reactions in a metallic sample (from Ref. [28]).

generating the image, the control electronics can be configured to use the scanning probe as a powerful tool that can atomically modify the surface with nanometric accuracy. This type of nanometric modifications can be chemical, electrostatic, mechanical, or thermal [4–10].

Nanolithography can be performed under different conditions such as ultrahigh vacuum and low temperature, but the patterning disappears as soon as these conditions are lost, so we will focus on the nanolithography processes at room temperature and without vacuum. In order to perform lithography on a surface, the spatial confinement of a chemical reaction within a nanometric size region is necessary. For this, it is necessary that the probe tip is sufficiently close to the sample so that a liquid meniscus (**Figure 2**) can be formed spontaneous or with the aid of an electric field and also a thermal gradient or a mechanical indentation can be applied.

In a first stage, local oxidation with AFM will be studied in detail. In this case the liquid meniscus that forms between the tip and the sample is water due to relative humidity [10–12]. This type of nanolithography will allow the development of patterns with different shapes [13, 14], and its operating principle can be used to lithograph large areas [15–17]. With this technology, silicon transistors have been made [18, 19]. Afterward it has been observed that these nanotransistors can be used for molecular recognition [20]. In recent years this technique has served to manipulate two-dimensional materials of high scientific interest [21, 22].

By altering the atmosphere where the AFM is housed, nanolithography of different materials can be performed. With octane vapors, extremely small motifs can be obtained [23]. This patterning can be used later for the growth of biological molecules [24]. And by changing to an atmosphere of CO_2, gas molecules can be converted into solid deposits on the surface by applying an electric field [25, 26].

In recent years, a new 3D lithography technique has been developed [27]. In this case, a standard AFM probe has been replaced by a thermal one that reaches a high temperature at its final tip, and the polymer that is deposited on the surface is thermally moldable in three dimensions by scanning with this thermal probe.

2. Local anodic oxidation

Local oxidation of semiconductor, metallic, and organic surfaces by atomic force microscopy (AFM) has established itself as a robust, reliable, and flexible lithographic method for the fabrication of nanometer-scale structures and devices [28, 29].

The invention of this technique appeared in 1990, when Dagata and his collaborators realized that by applying a voltage between the tip of an STM and a silicon sample, their surface was modified and they were able to demonstrate that it was an oxide by mass spectroscopy [12]. A few years later, in 1993 it was done through AFM [30].

The application of a voltage pulse between the tip and the sample polarizes the water molecules in the gas phase and those absorbed on the sample surface. When the voltage is above a certain threshold value, a field-induced liquid meniscus is formed between the tip and sample surface (**Figure 2a**). The water meniscus provides both the chemical species (**Figure 2b**) and the spatial confinement for the anodic oxidation of a nanometer size region of the sample surface [28, 31]. The AFM tip is used as a cathode, and the water meniscus provides the electrolyte.

The size of the oxide motifs can be modified by applying different values of the voltage pulse since it depends linearly. In this way, structures of less than 10 nm have been made reproducible. The voltage pulses are generally between 10 and 30 V and the duration a few milliseconds. The heights of the oxides are a few nanometers, and only 60% of the oxide is above the surface of the sample; the rest is buried in the silicon sample.

This nanofabrication technique allows to perform all types of patterning as can be seen in **Figure 3**: arrays of points, circles, or even the first lines of *Don Quixote* [28].

The process is rather general because many different materials have been patterned such as semiconductors [32], metals [33], dielectrics [34], perovskite oxides [35], or self-assembled monolayers [36].

Figure 3.
Examples of local oxidation nanopatterns (from Ref. [28]).

Although nanometric patterns can be generated quite accurately, the main disadvantage of this technology is that AFM is a slow technique and can only cover small areas of a few square microns. To scale this process, a nanoimprint stamp has been developed with millions of protrusions similar to the AFM probe. The stamp has been metallized in order to apply an electric field that allows the oxidation process (**Figure 4a**). The areas of square centimeters with nanometric patterning can be oxidized [16, 17]. An example of that oxidation can be shown in **Figure 4b**, the area is only 5 × 5 μm due to the scan of the AFM, but the oxide patterns are in the whole sample of 1 × 1 cm.

In many of the cases, during the nanofabrication different charges are trapped inside the oxide lines, and that can be used for the selective positioning of molecules [37]. As an example, in **Figure 5** one can observe a controlled deposition of ferritin molecules on the oxide lines made by AFM. For a better positioning, it is necessary to deposit on the silicon sample a self-assembled monolayer of octadecyltrichlorosilane (OTS) and to deposit a monolayer of aminopropyltriethoxysilane (APTES) after the local oxidation [38].

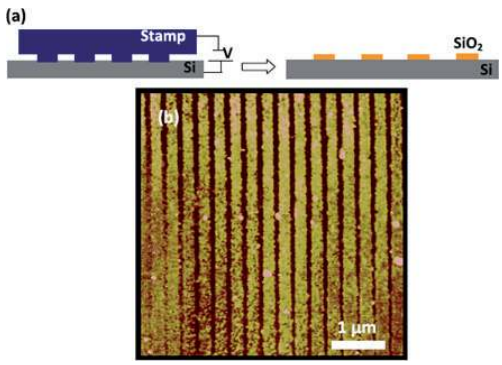

Figure 4.
(a) Scheme of parallel oxidation lithography process with a nanoimprint stamp. (b) AFM image of the silicon oxide line pattern (from Ref. [17]).

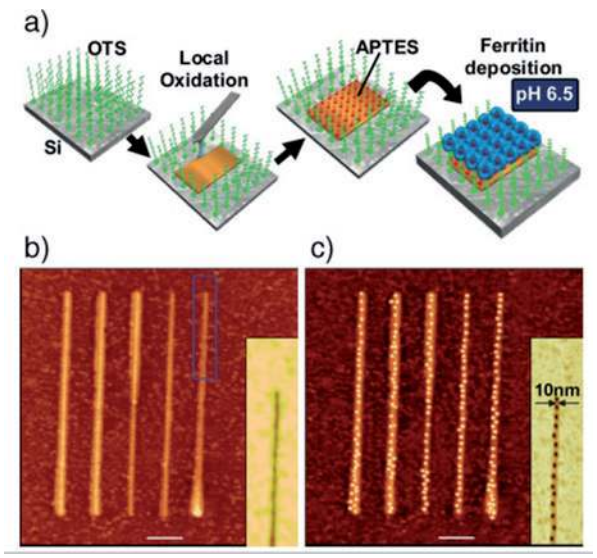

Figure 5.
Patterning of ferritin molecules by local oxidation nanolithography and surface functionalization (from Ref. [38]).

Also with this technology, it is possible to create functional devices. An example, in **Figure 6**, a transistor with a 4 nm silicon nanowire made by local oxidation is shown [18].

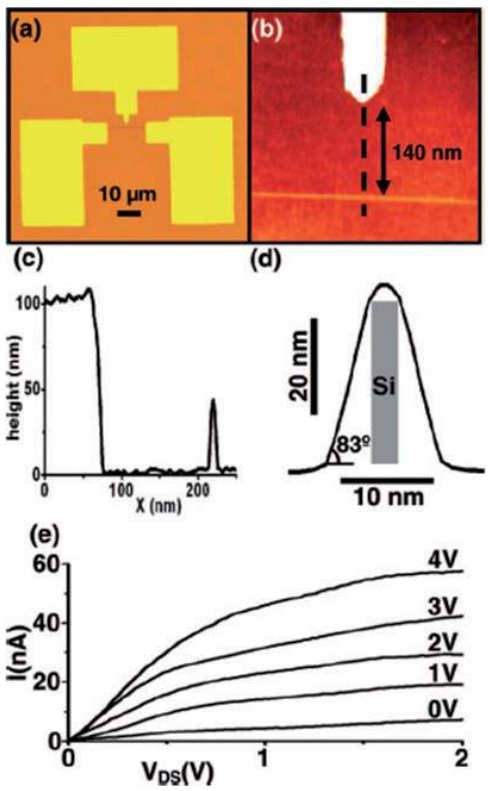

Figure 6.
Silicon nanowire transistor fabricated by local oxidation nanolithography (from Ref. [18]).

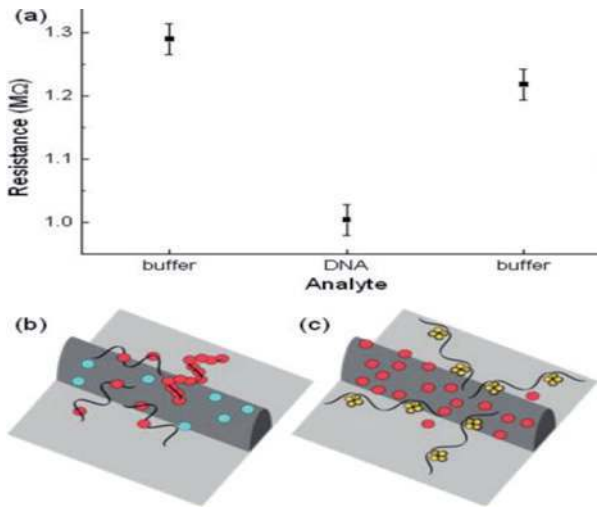

Figure 7.
The silicon nanowire sensor changes its electrical behavior in the presence of DNA and is able to recover its resistance after cleaning (from Ref. [20]).

In this case a silicon on insulator (SOI) wafer was used. The gate, drain, and source contacts were first made by optical lithography. Between these last two, a local oxidation line was made that serves as a mask for the following etching of the top silicon by reactive ions (RIE). In this way the silicon nanowire is free, and after a second stage of lithography and metallization, the source and the drain are in contact with the nanowire forming a nanotransistor.

These nanowire sensors can subsequently be functionalized with different molecules to perform molecular recognition of different agents [19, 20]. In **Figure 7**, a nanowire is used for measuring the early stages of recombinational DNA repair by RecA protein [20].

3. Chemical nanofabrication

Changing the atmosphere surrounding the AFM can produce other chemical reactions between the tip and the samples, which will allow us to manufacture motifs or materials that are not oxides.

For doing this, it is necessary to introduce the AFM into a glove chamber or in a closed environment where it is possible to remove the relative humidity from the environment by a nitrogen flow. Subsequently, the gas to be used for nanolithography is introduced, and an electric field is applied again between the tip and the sample.

Thanks to this type of lithography, polymeric motifs as small as 2 nm resolution at 3 nm at half pitch in ambient conditions have been achieved [23]. This is the smallest periodic pattern fabricated on silicon at atmospheric pressure and room temperature.

The method is based on the formation of a nanoscale octane liquid meniscus between a sharp conductive protrusion and a silicon (100) surface. The application of a high electrical field (10 V/nm) produces the polymerization and cross-linking of the octane molecules within the meniscus followed by their deposition. The manufactured motifs can be seen in **Figure 8**.

This technology can also be used to break up very stable gaseous molecules such as CO_2 and turn them into solid motifs. Thus, if the AFM is introduced into a CO_2

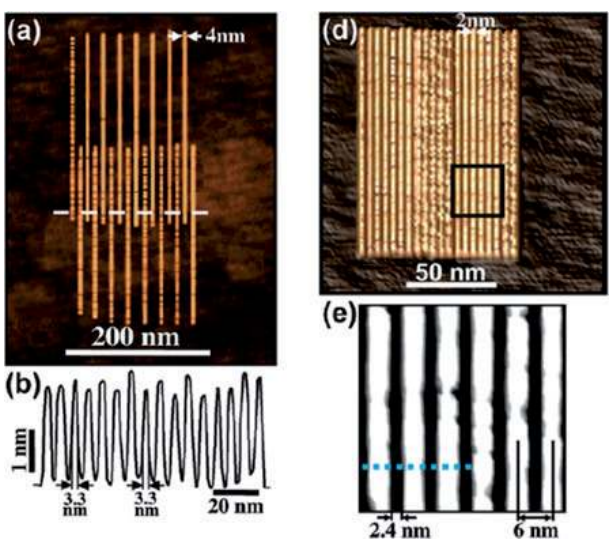

Figure 8.
AFM images and cross sections of the polymeric nanostructures (from Ref. [23]).

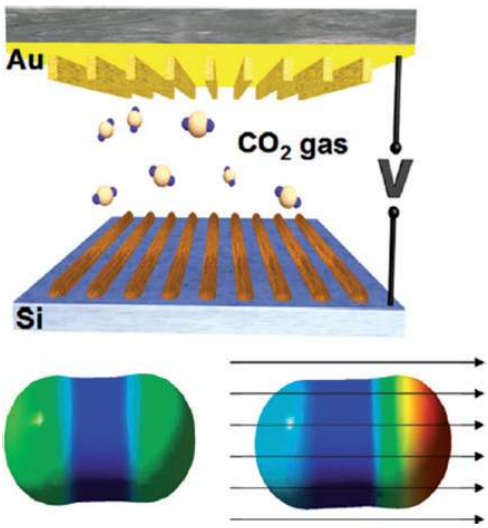

Figure 9.
Conversion of CO_2 gas molecules in solid nanometric motives by applying an electric field (from Ref. [25]).

atmosphere and later an electric field is applied, the CO_2 molecules are able to break due to the high electric field at the end of the tip [25, 26]. This happens for an electric field above 40 V/nm. This technology can be scaled again using PDMS stamp of several square centimeters with thousands of protrusions like in the scheme of **Figure 9**.

The possibilities of generating different nanolithography with different materials are enormous since they only depend on the atmosphere in which the AFM is inserted. The only disadvantage is the need for a spectroscopy analysis after lithography to identify the nature of the motives created.

4. Nanofabrication in 3D

In recent years, micro nanofabrication technologies have advanced quite a bit and are allowing more and more sophisticated AFM tips. Thus, in 2010, IBM laboratories in Zurich made an AFM probes that were doped at their end so that they could behave with a thermal tip when a current is applied [27].

The high temperature at the end of the AFM tip was used to perform a patterning on a glassy organic resist. This local desorption allowed to make structures at a half pitch down to 15 nanometers without proximity corrections. These patterns can be transferred to other substrates, and the material can be removed in successive steps in order to fabricate complex three-dimensional structures (**Figure 10**).

This technique is in continuous development and has great future potential, but it also depends on the thermal tip and on the optimization of the appropriate resins that allow its elimination layer by layer. As can be seen in **Figure 11**, it was possible to make a replica of the Matterhorn mountain in Switzerland first on the resist and then transfer its pattern to silicon.

5. Conclusions

Although the AFM began as a technique to visualize images of a few microns, its potential was seen to be able to manipulate materials in the nanoscale due to various

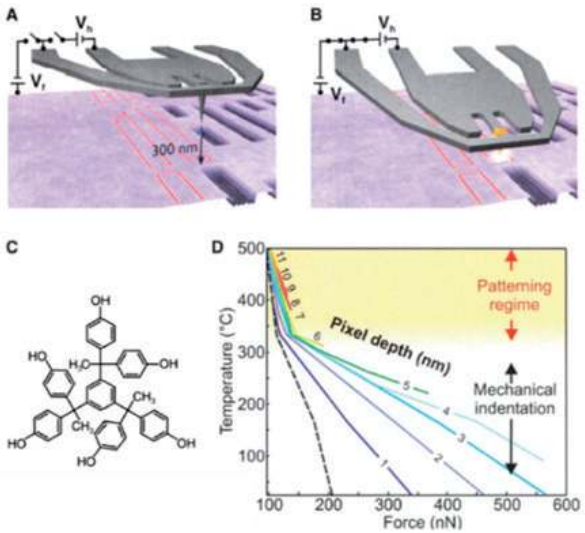

Figure 10.
AFM thermal probe making 3D nanopatterning over a resist (from Ref. [27]).

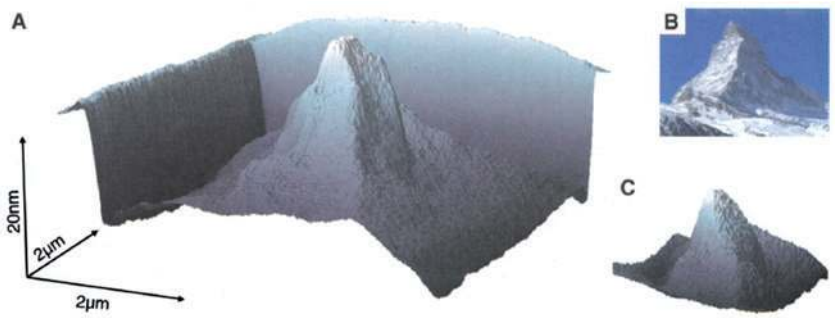

Figure 11.
(A) AFM picture of the Matterhorn replica in the molecular glass resist. (B) Picture of the Matterhorn mountain. (C) AFM replica in silicon (from Ref. [27]).

reasons. The first of these reasons is the high precision of the piezoelectric devices that allow the AFM tip to be positioned in the right place, and the closed loop control electronics allow a repetitive positioning better than an interferometric stage. On the other hand is the small size of the AFM tip, usually 10 nm or smaller. This allows to obtain liquid menisci of very small volumes in which chemical reactions of various kinds can be created. The small size of the tip also facilitates that with low voltage, high electric fields are obtained at the interface between the tip and the sample, allowing to oxidize different materials or make solid deposits of molecules that are in the vapor phase. Finally in recent years the microelectronic industry has been able to make more sophisticated probes in which they can get the final apex of the tip at very high temperature. This type of tips can modify or even sublimate resins on a surface and can create 3D lithographic motifs that can then be transmitted to the different materials.

With these lithography techniques by scanning probes, great nanotechnological advances have been achieved. The first was to be able to create smaller structures than those achieved by electron beam lithography. It has made possible to lithograph different designs on all types of materials from conductors, semiconductors, or even insulators and more recently in 2D materials like graphene or dichalcogenides.

The second advance was that nanolithographed structures have shown selective positioning of different molecules due to the charges trapped in lithographed motifs. On the other hand, lithographed motifs by scanning microscopy can be used as masks to perform more complex devices such as memories, sensors, or field-effect nanotransistors. These nanotransistors are ideal for its use as sensors for single molecule biorecognition.

In summary, scanning probe nanolithography techniques are very precise and very versatile and constitute an adequate tool for the development of nanotechnology without the need for large and expensive conventional lithography equipment. In addition, the motifs that are capable of manufacturing can be easily scaled for the macroscale simply with the use of nanoimprint techniques.

Acknowledgements

The present research was partially funded by the Spanish Ministry of Science, Innovation and Universities under the project DIGRAFEN, grant number (ENE2017-88065-C2-1-R) and (ENE2017-88065-C2-2-R).

Conflict of interest

The authors declare no conflict of interest.

Author details

Javier Martinez
Institute of Optoelectronic Systems and Microtechnology-ISOM, Technical University of Madrid, Spain

*Address all correspondence to: javier.martinez@upm.es

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