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Review

Studying of various nanolithography methods by using Scanning Probe Microscope

S. Sadegh Hassani* **and Z. Sobat**

Nanotechnology research center, Research institute of petroleum industry (RIPI), Tehran, Iran

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Abstract

The Scanning Probe Microscopes (SPMs) based lithographic techniques have been demonstrated as an extremely capable patterning tool. Manipulating surfaces, creating atomic assembly, fabricating chemical patterns, imaging topography and characterizing various mechanical properties of materials in nanometer regime are enabled by this technique. In this paper, a qualified overview of diverse lithographical methods mostly based on making nano-structures is presented.

Keywords: *Nano-lithography, Atomic force Microscopy, Scanning probe lithography, nanostructure, surface nano-modification.*

1. Introduction

Recently, the interest to nanometer scale designed useful structures in the science and technology is rapidly increased, and these technologies will be superior for the fabrication of nanostructures [1].The patterning of materials in this scale face with great importance (for) in future lithography in order to attain higher integration density for semiconductor devices. The emergence of nano-science and nanotechnology depends on the ability to posit, manipulate and fabricate a variety of structures, materials and devices with the accuracy in the nano-meter scale. Conventional lithography techniques, i.e., those divided to optical and electron beam lithography are either cost-intensive or unsuitable to handle the large variety of organic and biological systems available in nanotechnology. Various driving forces have been considered for development of alternative nanofabrication techniques [2-3].These techniques have been established approximately in 1990 and then they have given rise to the establishment of three major nanolithography methods:

* Corresponding author: S. Sadegh Hassani
Nanotechnology Research Center, Tehran, Iran
Tel & Fax +98 2144739733
Email *sadeghs@ripi.ir*

1) Nano-imprint lithography;
2) Soft-lithography;
3) Scanning probe based lithography [4].

SPM techniques can be used in imaging and metrology of surfaces. In addition, they may be used to modify the sample surfaces. SPMs, in particular atomic force microscopes, are excellent devices in nano-technology because of their ability to image at sub-10nm resolutions. A wide variety of surface ranging from bio-molecules to integrated circuits have also shown high potential as nano-lithographic tools [5-6].The controlled patterning of nanometer scale features with the SPM is known Scanning Probe Lithography (SPL). SPMs techniques that are used to make groove on the surfaces include: Scanning Tunneling Microscope (STM) and Atomic Force Microscope (AFM). STM introduced in 1982 by G. Binnig and H. Robert, was the first probe microscope of its kind of image with angstrom level lateral and vertical resolution [7-8]. A bias voltage is applied between a sharp tip and a sample. When the tip is in close proximity with the sample surface, electron may tunnel across the gap between the two electrodes. The tunneling current is quiet sensitive to the tip-sample spacing and is therefore a useful measurement of that distance. The primary limitation of STM is that it can only be used to image conductive substrates.

AFM was developed to alleviate this constraint. In 1986, G. Binnig and et al. showed that fine sample topography could be prepared by monitoring the force between a sharp tip and sample [7, 9]. This capability can potentially be extended to monitor the local interaction between a sharp tip and a sample surface to acquire physical, electrical or chemical information about the surface with high resolution [7]. Development of the imaging capabilities has been focused on the tip-surface interaction forces, lead to the utilization of the AFM as surface force apparatus. In this mode (termed force mode) [10], the AFM monitors the interaction forces, which include vanderwaals, magnetic, electrostatic, or capillary forces as a function of the separation distance between the tip and the sample surface. Force mode is used for minimizing tip-sample forces during imaging. This mode can potentially be used to configure the AFM to perform nano-identation studies [11].

This technique is a promising method in creating nano-scale patterning for application such as nanometer scale device fabrication or very high-density memory storage systems, since feedback control of the probe position operates independently of patterning mechanism [7, 12]. This provides the AFM-based lithography with high patterning speeds faster than hundreds of µms-1and versatility in processing materials ranging from insulators to conductors [13-19].

High-resolution imaging has been achieved in air, liquids and vacuum. The relative ease to conversion of a force microscopy into modification tool has prompted a fascinating variety of atomic and nanometer-scale modification approaches. AFM lithography has also been applied for nano-scale device fabrication through localized anodization [20-24]. In this field, the application of an appropriate bias voltage to a conductive AFM tip can induce electrochemical reactions directly on material surfaces.

2. Force Lithography

Force lithography is based on direct mechanical impact produced by a sharp probe on the sample surface. In this technique, the mechanical action between tip (as a sharply pointed tool) and sample surface is used to produce fine grooves [25]. The probe tip pressure on the surface is sufficient to cause plastic deformation of the substrate surface. This type of modification has been

used in nano-electronics, nanotechnology, material science, etc. It enables the fabrication of electronic components with active areas of nanometer scale, super dense information recording and study of mechanical properties of material [26]. In force lithography no bias voltage is required to produce nano-structures. Force lithography is best performed on certain polymers including polycarbonate and polyethylene. The nanostructure's formation normally occurs as a result of AFM tip motion above the polymer surface with set point magnitude constraining the tip to come closer to the surface [27-30]. In order to apply sufficient normal load to reach plastic deformation of surface, a three- side's pyramidal single crystalline diamond tip or other tip with high spring constant is used and pressed against the surface. It's mentioned that much higher forces were achieved by accordingly increasing the applied voltage to piezo-scanner. From the cantilever deflection ΔZ, the force was calculated using Hook's law. . By scanning the sample in the X or Y direction at various conditions (such as different scanning velocity, number of cycle (N), force and time) grooves were created. However the protrusions along the edges are formed, which indicates clearly stress deformation during the scratching process [31].

Investigations show material removing from a metal or polymer film by applying an amount of force of several μN is possible [32]. Use of cantilevers with high spring constant could apply the desired amount of force without large bending. When tip move toward the substrate or reverse direction, up or down bending of cantilever occurs respectively. Since an angle of about 10˚ is typically set between the cantilever and the substrate (Figure1), this bending influence the tip – substrate interaction, so the geometry and size of scratches are affected in this way [25].

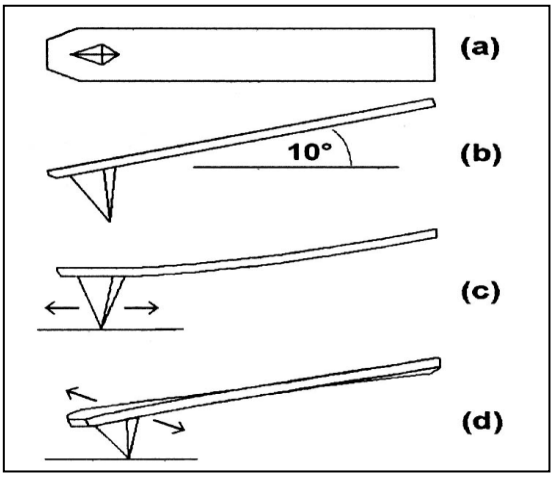

Fig.1. Typical silicon cantilever with pyramidal tip: (a) upper view; (b) lateral view showing the 10˚ angle formed with the substrate surface; (c) cantilever bending; and (d) torsion

However, increase of applied force cause cumulating of material along or at the end the grooves. This deformity is occurred because of cantilever bending at the start point of moving tip through the surface. In this way cantilever reach the desired force to create scratch. Wearing of probe led to low- quality results and reduced the repeatability of produced scratches. Indeed, by using the same tip at different times, the sample surface could experience two completely different values of pressure, because the amount of produced pressure depends on the shape of tip [33]. To decrease wearing of probe, a soft resist polymer film (usually PMMA film) is coated on the surface. On the other hand, the roughness of surface is very important to take high quality scratches. Observations show that surface roughness is strongly influenced by its thickness as while; the surface roughness increases with the increase of the thickness. So, to perform the lithography

process, the smoothest surface has to be chosen [34-35]. Studies show that in the case of AFM, the possibility of directly machining a surface has been explored in two ways, i.e. by either using a static approach in which the microscope is operated in conventional contact mode [36-37] or using a dynamic approach in which the microscope is operated in the tapping mode [38-39]. Usually the lithography developed using both static and dynamic approaches are employed to pattern a resist layer, subsequently the patterned layer is used as an etch mark. Both techniques are giving lithography resolution of the order of tens of nanometer [3, 40]. An advantage of the vibration in the tapping mode is that very small lateral forces stress the tips, resulting in very slow tip degradation [41]. It's mentioned that resolution will be a major challenge in lithographic fabrication and the limiting factor for resolution is the tip quality. Sharp silicon tips deliver brilliant and reproducible results. To even further achieve the fine lithographic structure electron beam deposited tips (EBD tips) can be additionally sharpened in oxygen plasma [42].

2.1. Force Curve

In lithographic experiments, it is often critical to know the pressure, which the probe applies to the sample. To estimate the pressure corresponding to a specified level of the probe impact, the force created by the probe has to be determined. It can be calculated from force spectroscopy data [26]. Indeed, the measurement of the probe tip deflection is produced through an optical lever detection system, in which a laser beam is reflected off the top of the probe and onto a segmented photodiode. A plot of this tip deflection signal as a function of the vertical displacement of the piezo scanner is called a force curve [43]. To take the force curve, to avoid punching surface, it is essential that the sample have a rigid surface such as silicon or polycrystalline substrate. By performing DFL (Height) spectroscopy in a point, force curve is obtained. An example of force curve is shown in Figure 2.

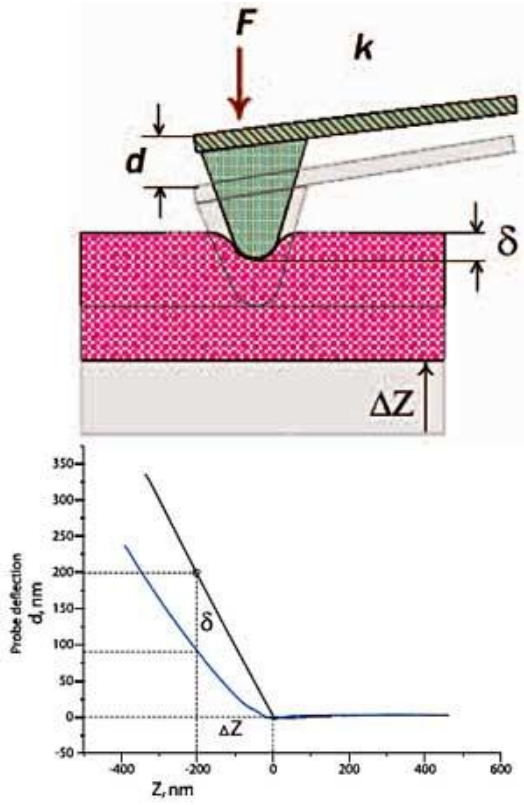

Fig.2. Force curve obtained by cantilever in contact mode

The deflection of cantilever spring is directly proportional to the tip-sample interaction force. The normal force between tip and sample was estimated from cantilever deflection (nA) curve plotted against Z–displacement of the cantilever and converting this curve to force-distance curve. The conversion factor for converting nA to nm was obtained from the slope of the linear portion of the deflection – distance curve. There was also one conversion needed for the X – axis values. The change in piezo height, which has been used for the distance between the tip and the sample, was corrected for the deflection of the cantilever by subtracting the cantilever deflection from the piezo height.

On the other hand, there are two measurements required to convert photo detector signal into a quantitative value of force. The first stage is to calibrate the distance that the cantilever actually deflects for a certain measured changes in photo detector voltage. This value depends on type of cantilever and the optical path of the AFM detection laser. When every cantilever is mounted in the instrument, this value will be slightly different. Once the deflection of cantilever is known as a distance X, the spring constant K, is needed to convert this value into a force F, using Hook's law [44-49].To find the probe pressure on the sample, the surface of the probe –sample interaction S is to be estimated by using the following equation:
Where is the tip apex radius thus probe pressure on the sample can be found at: P=F2/S [26].

3. Local oxidation nanolithography

In 1993 it was demonstrated that local oxidation nanolithography (LON) could be performed with an atomic force microscope [4,13]. This observation paved the way for the development and expansion of local oxidation approaches to modify surfaces. Long range vanderwaals forces and/or short-range repulsive forces are used to image the surface while an external voltage is applied to induce the local oxidation of the surface. The sample which modified by local oxidation lithography, must be a conductor or semiconductor, a substrate with the conducting coat will be used to mount the sample in order to enable the application of voltage between the probe and the sample. For this lithography, probes with conducting coat will be used. Typically, semicontact probes with the coating of TiN, W2C, and conducting diamond-like coating are used [26, 50-51]. Dagata et al. reported the earliest work of tip-induced oxidation. They oxidized silicon by scanning H-passivated Si in air with a positively biased STM tip. Other investigations showed a different approach, in which the sample is scanned by a negatively biased tip [11, 53-55]. In this method a bias voltage between sharp probe tip and a sample generates an intense electric field in the vicinity of the tip (Figure 3). The high field can be used to locally oxidize a variety of surfaces. This process is called "electric- field- enhanced oxidation" on the silicon substrate [7].

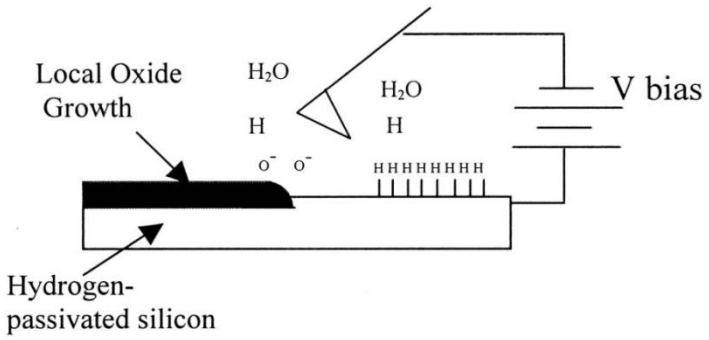

Fig.3. Schematic diagram of surface modification using a field-enhanced oxidation

Local oxidation lithography is carried out based on the effect produced by electric field in the area of contact between the probe tip and the sample surface. When a potential is applied between the sharp probe and the sample, the electrical impact can be sufficient to cause local surface modification. The modification mechanisms may differ. It may be local thermal impact due to high current density, electric field evaporation of the sample material, or vice versa, the probe material can take place [26]. The present knowledge shows some similarities between local oxidation and conventional anodic oxidation [4]. In this process, an electrically biased AFM tip operated in an ambient humidity, acts as a nanoscopic electrochemical cell, to locally oxidize a sample surface [38].Sugimura et al. considered that water vapour in the ambient environment is necessary for this process. This fact indicates that oxidation reaction may be analogous to electrochemical anodization [55]. Additionally an atomic clean surface obtained at UHV conditions is free from an adsorbed water, making principal impossible the local anodic oxidation by an AFM-lithography [57-58]. In Figure 4 is seen that, the AFM tip is used as a cathode and the water meniscus formed between tip and surface provides the electrolyte [4].

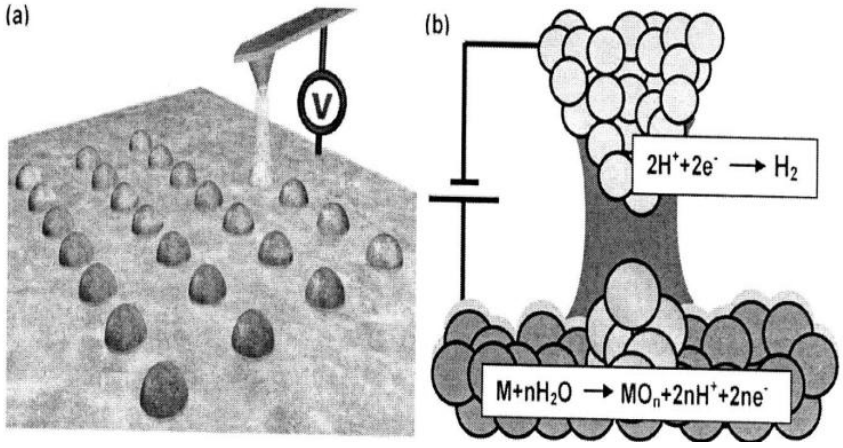

Fig.4. (a) schematics of a local oxidation nanolithography experiment. The meniscus provides the oxyanions and confines the spatial extent of the reaction. (b) Accepted chemical reactions in the local oxidation of a metallic surface.

The field also ionizes water molecules in the air or adsorbed on the tip surface, creating negatively charged oxygen ions. These ions are accelerated toward the sample by the electric field and react with the silicon to form an oxide film [7]. In this way a nanometer-size electrochemical cell (nano-cell) is formed, that contains about molecules. The method to form liquid bridges is so precise that water meniscus diameters of 20 nm are easily obtained, so leads to the reproducible fabrication of sub-10 nm structures in Si and even smaller structures in titanium films [4]. The reaction in the nano-cell is described by the following half-cell reactions. In the anode (for a metallic surface), the following half-cell reaction has been proposed.

$$M + nH_2O \longrightarrow MO_n + 2nH^+ + 2ne^-$$

And hydrogen generation occurs at cathode to complete the electrochemical reaction.

$$2H^+(aq) + 2e^- \longrightarrow H_2$$

An extremely small current accompanies the local oxidation process [4]. Lyuksyutov et al. have monitored the current during AFM-assisted oxidation by a picoammeter serially connected between tip and negative bias or between the silicon wafer and ground was used. The observations showed an ionic current of the order 1-100 PA, associated with transport of ions. This current is related to the Faradaic process at the interface anodic oxidation of silicon surface occurs, and a nearly exponential current growth with respect to the applied voltage is observed [59].Experimental observation have shown that the current through the interface during oxidation matched the current calculated from measured oxide volume by taken into account that elementary charges are needed to oxidize one atom [4]. In AFM lithography, current flowing through a probe-sample junction is a key factor and must be controlled. The dependence of the junction current on the lithography has been studied by applying a constant bias voltage [18-19]. In order to control the density of the electrons injected from the AFM probe into the sample, the current was kept constant during patterning by adjusting the bias voltage. However, the controllability of the current was not satisfactory when using the constant bias mode, because the relationship between the junction current and the bias voltage depends on several factors, such as the age, type of the particular probe and some other uncontrollable factors; so it could not be precisely controlled by simply applying a bias voltage. The amount of electrons injected into the probe-scanned region is one of the most important parameters for making oxide lines. Line drawing with faster probe-scan rates could be achieved by increasing the junction current by applying a higher bias voltage and by the patterning in constant current mode; the reproducibility of pattern drawing was improved [19].Stievenard et al. have found the linear relation between oxide height and anodization voltage (V), which is explained through a theory on field-assisted anodization of thin films [60]. The same model explains the logarithmic decay of oxide height when the tip velocity is increased. In local oxidation technique, the oxidation shows self-limiting behavior with the rate decreasing exponentially with increasing oxide thickness. This behavior is interpreted as arising from development of stress during oxidation. The ultimate oxide thickness that can be grown in a controlled manner by this approach is limited by dielectric breakdown events that can occur at biases greater than 10V.The lateral resolution of the process was shown to be primarily determined by the defocusing of the electric field of the AFM tip by the condensed film of water that forms near its apex [61].

In addition, lowering the humidity reduces the width. The height of the oxide barely changes. Such results demonstrate the strong influence of external factors on the characteristics of the oxidation process. One of the most important pieces of information is its intrinsic rate. The kinetic results show a rapid decrease of the growth rate with time as 1/t. The bias dependence of the rates is a clear indication that the electric field plays an important role in the process. The high initial growth rates occur at extreme electric field strengths near the tip apex of up to 10^8 V/cm. A positive bias was applied to the sample to generate the field emission of electrons from the tip. The sample voltage was large enough to ensure that the probe was out of contact with the resist surface. The vertical (z) position of the probe was adjusted using a piezo-tube actuator to maintain a constant current from the tip. Prior to patterning, a special care must be devoted to material preparation for obtaining a clean and flat surface with a RMS roughness below 1nm. To this aim, silicon surface is first thermally oxidized in dry ambient, then submersed in HF solution to remove the native oxide and leaves a flat surface. The high electric field near a negatively- biased tip locally desorbs the hydrogen passivation on the silicon surface [7].In this mode it is necessary to use a stiff AFM cantilever to prevent the spring-like device from pulling down to the sample as a result of the attractive electrostatic force.

Finally, a bias is applied to the sample to extract current from the tip and enabled the current feedback circuit. As a result, the probe moved toward the sample until the set point current was reached. As the bias is increased, the probe moves away from the sample in order to keep a fixed emission current (and a constant field at the tip). Although the exposure is held constant, the geometrical effect of the tip moving away from the sample causes a broadening of the feature size. Moreover, a large number of materials have been locally oxidized in this way such as compound III-V semiconductors, silicon carbide, perorskite, manganite, thin films as well as organosilane self assembled monelayers, carbonaceous films, photoresists and organic polymer resist [4]. An organosilane monolayer consisting TMS groups prepared on the native oxide of a silicon substrate effectively served as a resist material for AFM-based nanolithography [62]. Also several metals such as titanium, tantalum, aluminum, molybdenum, nickel and niobium can be used in this manner [4].

More recently, amorphous silicon is discovered that can be similarly oxidized [62]. Amorphous silicon is a reasonably general resist material since it can be deposited on almost any surface at low temperature. Oxide patterns can be written on amorphous silicon, transferred through wet or dry etching into the amorphous silicon layer, and subsequently transferred into the underlying film [63]. AFM has also been proven to be an extremely useful tool for polymer surface modification. This method is based on localized joule heating and dielectrophoritic manipulation of a thin polymer film. The current flow between conductive substrate and AFM tip passes through thin polymer film and causes localized joule heating of polymer above its glass transition temperature. Polarization and electrostatic attraction of the molten polymer toward the AFM tip in strong non-uniform electric field is believed to produce raised structures [64]. The major factors affecting dielectric breakdown are (i) AFM tip polymer film separation (ii) thickness of the polymer film and (iii) mechanism of conductivity, apparently associated with negative carriers either migrating from level of the coated AFM tip, or generated through the electric breakdown in water attracted to an AFM tip [59, 64]. A schematic presentation of this process is shown in Figure 5.

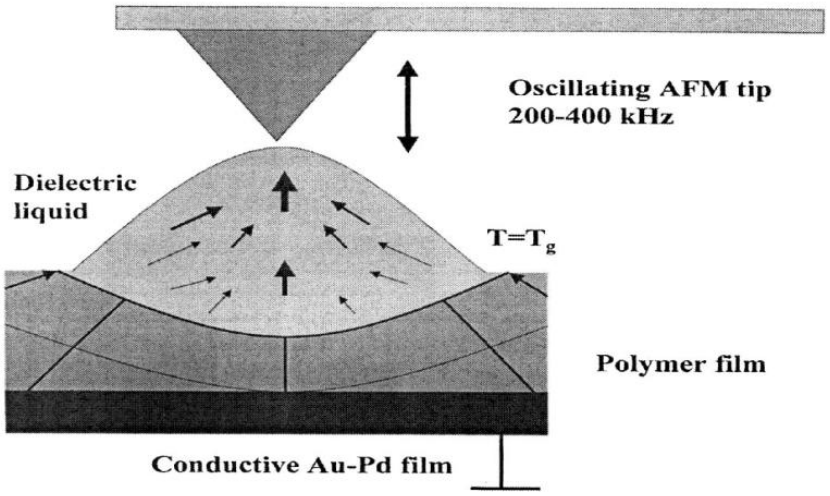

Fig.5. schematic presentation of AFM electrostatic nanolithography

The oxidation kinetic and oxide line structures allow us to evaluate three basic limiting factors for an AFM-tip induced oxidation process. First one is the existence of the natural oxide layer on the surface, which limits the anions diffusion to the bulk. Unfortunately there are no ways

to remove completely the natural oxide on the silicon surface for AFM experiments at ambient conditions. However an effect of a natural oxide on the anodic oxidation may be minimized during the well regulated scratching of the surface by a conductive tip under a voltage bias. The second factor is mechanical stresses on the modified line during the oxide growth, which restricts cation diffusion to the reaction zone. To minimize the influence of the non-controlled mechanical stress, use of an oscillation mode is proposed for the modification by the tip. The sharp AFM tip contacted mechanically to the oxidized area produces the partially destruction of the oxide film yielding a stress relaxation inside of the bulk near the tip contact. In addition, the defect can be generated by mechanical drubbing. During oxidation process charge exchange channels create and it can increase the height of an oxide film. And third one is the low potential (10V) applied between the substrate and tip. Experiments with the increasing of the substrate-tip bias simulated the unstable oxidation and effect generation making the tip-induced modification is non-reproducible. However, the investigations show that the tip-sample voltage can be enlarge reasonably up to 50V by the optimizing of the water vapor or adsorbed water by means of the humidity conditions control. Otherwise it was realized the method of the simultaneous applying to the AFM-tip the both mechanical pressure and electrical bias in an oscillation mode (semi-contacted one), which allows to destroy a natural oxide layer on the surface and annihilate mechanical stresses in the volume [57]. Patterning is slow, and also limited by the reaction rate at the surface. Writing speeds are typically limited to below 10□m/s, making patterning of large areas in reasonable times unmanageable.

Finally, reproducibility of oxide patterns is poor because of the dependence of the pattern size on tip shape, humidity level, and surface roughness. In addition significant tip wear, results in degrade dimensions. Anodization pattern size is typically limited by the grain size and/or surface roughness of substrate [7, 63, and 65]. In some cases, LON is used in combination with other methods such as photo-lithography, electron beam lithography or chemical wet etching to fabricate the desired device. In those cases, the critical or most relevant features of the devices are fabricated by local oxidation [4].

4. Dip Pen Nanolithography

Dip pen technology, in which ink on a sharp object is transported to a paper substrate via capillary forces, is approximately 4000 old and has been used extensively throughout history to transport molecules on macro scale dimensions [66].Dip pen nanolithography (DPN) is a nanolithography technique by which molecules are directly transported to a substrate of interest in a positive printing mode. DPN utilizes a solid substrate as the paper and a scanning probe microscope tip (e.g. an AFM tip or a near field scanning optical microscope NSOM tip) as the pen. The tip is coated with a patterning compound (the ink), and the coated tip is used to apply the patterning compound to the substrate to produce a desired pattern [68]. The ability to achieve precise alignment of multiple patterns is an advantage earned by using an AFM tip to write, as well as read nanoscopic features on a surface. These attributes make DPN a valuable tool for studying fundamental issues in colloid chemistry, surface science, and nanotechnology. Capillary transport of molecules from the AFM tip to the solid substrate is used in DPN to directly “write” patterns consisting of a relatively small collection of molecules in submicrometer dimensions. In Figure 6 a schematic presentation of DPN method is shown [66].

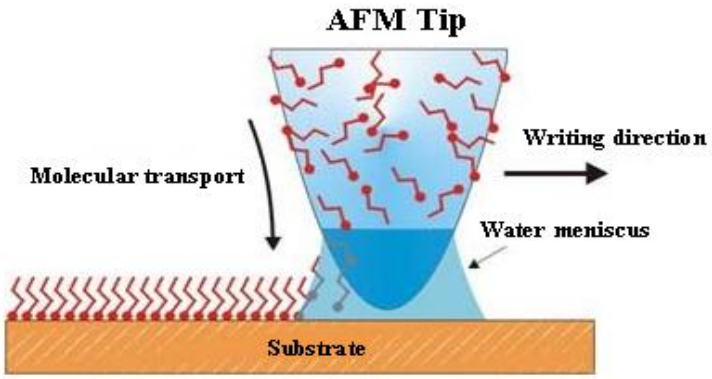

Fig.6. Schematic representation of DPN

In this method, electrical, magnetic, chemical or analogous driving forces are used to transfer molecules, clusters or nano-crystals from the tip to the substrate. The driving force causes the physical movement of the deposition compound from the tip to the substrate. This greatly increases the control over the movement of the deposition compound, making it possible to create size-selective and site-specific coverage of individual molecules and precisely formed thin film nanostructures. Additionally, the driving force can be used to control the rate of deposition [68]. In order to create stable nanostructures, it is beneficial to use molecules that can anchor themselves to the substrate via chemisorption or electrostatic interactions. When alkanethiols are patterned on a gold substrate, a self-assembled monolayer (SAM) is formed, in which the thiol headgroups form relatively strong bonds to the gold and the alkane chains extend roughly perpendicular to surface [67-68]. The major advantages offered by thiol SAMs include long-term stability, versatility in terminal functionality, and ease of use. Perhaps the most attractive feature is their utility for forming small, reproducible surface features outside of a clean room [69]. Another important issue in determining the overall potential of DPN is the role of water in the deposition process. It is well known that under ambient condition there is water meniscus at the AFM tip-surface interface, with a volume that increases with relative humidity (RH) [70]. Beginning with the first reports about DPN [66], suggested that the ink is transported from the tip to the surface through this meniscus. It is unresolved how hydrocarbons, which are essentially insoluble in water, would be transferred in this way, and whether adsorbed water on the surfaces beyond the meniscus affects their transfer and subsequent diffusion [69].

Dependence of the DPN technique on the liquid meniscus causes some problems. For example, the lateral width of the line written by the “pen” using DPN technology is limited by the width of the meniscus formed. The meniscus is subjected to variations in the relative humidity as well as chemical interactions between the solvent and the substrate. The size of the meniscus also affects the rate of the transport of the patterning compound to the substrate. This may require coating of the microscope tip with hydrophobic compounds. Furthermore, surface tension characteristics of different solvents can lead to drip or rapid flow from the pen to substrate, leading to problems with precise control of the ink transfer [68]. The resolution of DPN depends on several parameters, and its ultimate resolution is not yet clear. The first factor is the grain size of the substrate that affects DPN resolution as the texture of paper controls the resolution of conventional writing. Chemisorption and self- assembly are the second ones that can be used to limit the diffusion of the molecules after deposition. Third, the tip-substrate contact time and thus the scan speed influence DPN resolution. Fourth, relative humidity seems to affect the resolution of the lithographic process by controlling the rate of patterning compound transport from the tip to the

substrate. The water meniscus bridges the tip and substrate and the size of the water meniscus depends on relative humidity [66].

To practice DPN, scanning probe microscope (SPM) tip is coated with a patterning compound. This can be accomplished in a number of ways. For instance, the tip can be coated by vapor deposition, direct contact scanning or bringing the tip into contact with a solution of the patterning compound.The simplest method of coating the tip is direct contact scanning accomplished by depositing a drop of saturated solution of the patterning compound on a solid substrate. Upon drying, the patterning compound forms a microcrystalline phase on the substrate. To coat the patterning compound on the SPM tip, the tip is scanned repeatedly across this microcrystalline phase. While this method is simple, but it is difficult to control the amount of patterning compound transferred from the substrate to the tip. The tip can also be coated by vapor deposition. Coating the tip by vapor deposition produces thin and uniform layers of patterning compound on the tip and gives very reliable results in DPN. However, dipping the tip into a saturated solution of the patterning compound coats the SPM tip. In addition, the solvent must adhere to tip very well. The tip is maintained in contact with the solution of the patterning compound for a sufficient time, and then dried by blowing inert gas over the tip [68].DPN is a simple but powerful method for transporting molecules from AFM tips to substrates at resolutions comparable to those achieved with much more expensive and sophisticated competitive lithographic methods, such as electron-beam lithography. It should be especially useful for the detailed functionalization of nano-scale devices prepared by more conventional lithographic methods [66].

5. Aperture Pen Nanolithography

Aperture Pen Nanolithography (APN) is a method of nanolithography using a delivery controllable device for deposition of size-selected molecules, clusters and nanocrystals on substrate surfaces. The device is a tip with an internal cavity, having a narrow opening at the end allowing size or shape-restricted delivery of a deposition compound in the internal cavity onto the surface of the substrate. A variation of such tips using a micropipette cantilever has been described by Lewis et al. [71]. The opening in the end of the tip is sufficiently small to create a capillary force, preventing delivery of fluid through the narrow opening while the size- or shape-specific aperture limits transport of molecules or other entities to only those which can physically pass through the aperture opening under the driving force.

Suitable tips include SPM tips modified to contain a reservoir with an external opening controlled by an aperture, and tips having similar properties. These SPM tips include AFM, STM and near field scanning optical microscope (NSOM) tips. NSOM tips are hollow, and the depositing compounds are loaded in the hollows of the NSOM tips, which serve as reservoirs of the deposition compound to produce a virtual fountain pen. These tips may be made from carbon nanotube mounted tip. APN tips can be loaded with the depositing compound in a variety of ways. When the internal cavity is loaded with a solution of the deposition compound, the saturated solution is injected into the cavity. Soaking the tip in the appropriate deposition compound solution, show the same results. The APN tips Similar to DPN tips, can also be loaded by vapor deposition, direct contact scanning or bringing the tip into contact with a solution of the patterning compound. These are comparable or even higher resolutions than those achieved with much more expensive and sophisticated competitive lithographic methods, such as electron-beam lithography. DPN and APN

are also useful tools for creating micro-scale and nano-scale structures. For instance, these nanolithography techniques can be used in the fabrication of micro-sensors, micro-reactors, combinatorial arrays, micromechanical systems, micro-analytical systems, bio-surfaces, biomaterials, microelectronics, micro-optical systems, and nano-electronic devices [68].

6. High Force Nano-grafting

High Force Nano-grafting (HFN) is another technique in this field. In this method, a layer of material on a substrate is mechanically displaced using an AFM tip. The displacement is carried out in a fluid containing molecules, which rapidly enter void created by the AFM tip and bind to the clean substrate surface. A tip is used to produce a desired pattern of the patterning compound on the substrate by removing the resist from the substrate with the tip, whereupon the patterning compound attaches to the substrate from which the resist has been removed. The removal of the resist is achieved as a result of the application of a high force to the substrate by the tip. The other technique is the nano-pen reader and writer (NPRW) technique, which combines DPN and nanolithography. A monolayer of molecules on a substrate is used as a resist, and an AFM tip is used to displace molecules of the monolayer from desired locations. The tip is pre-coated with different molecules from the molecules of monolayer. As the tip displaces the molecules of the monolayer, the molecules on the tip adsorb onto the freshly exposed substrate following the track of the tip [72].

7. Atomic Manipulation

A SPM probe tip can be used to perform direct manipulation of nano-particles, molecules, or even single atoms. Particles on the surface may be moved and arranged with atomic-level precision. Figure 7 illustrates one method of atomic manipulation using a probe tip. The tip is used to “push” or “slide” a particle along the surface. A probe using field-assisted diffusion can also manipulate atoms on a surface. Electrostatic and chemical forces between the tip and sample allow selective removal of individual atoms from the surface and subsequent redeposition elsewhere.

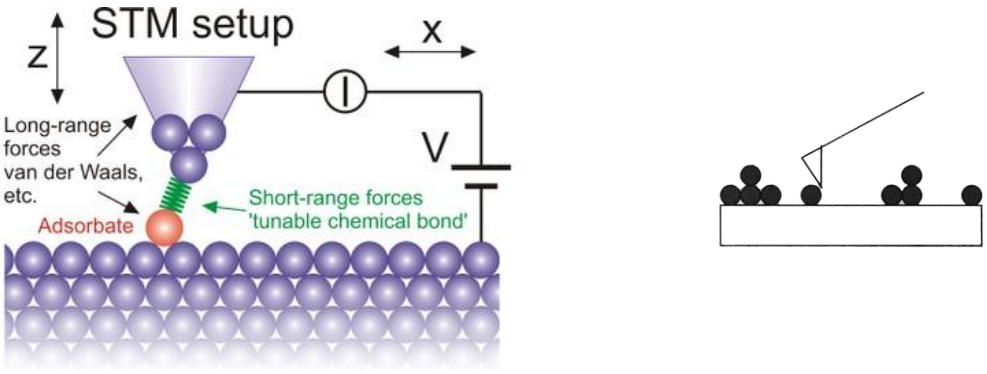

Fig.7. Schematic presentation of atomic manipulation

Atomic manipulation is a powerful tool for creating custom atomic structures and studying the physics of small-scale interactions. The high-resolution imaging capabilities of the SPM allow creating the small structures. Patterning is slow, of course, so atomic manipulation is far from a large-scale patterning technology. Nevertheless, atomic manipulation demonstrates perhaps the ultimate lithographic resolution [7].

8. Conclusion

This review paper focuses on using scanning probe microscope for study of nanolithography methods, where the nanofabrication is made by various methods. In particular, we have discussed the most promising methods such as force, local oxidation, dip-pen and aperture pen nanolithography. High force nanografting and atomic manipulation are also considered. These methods have important role for both nanolithographies and as new tools to perform nanochemistry research. Force nanolithography is used to make direct nanoindent on the surface. In this technique, force curve is used to convert the deflection of cantilever to force value by Hook's law. In local oxidation nanolithography, a positive voltage is applied to the surface with respect to the tip in an atmosphere with a presence of humidity induces the oxidation of the surface. In this case, the oxide formation is due to electrochemical reactions between substrate and adsorbed water molecules. DPN and APN nanolithography is a simple and powerful method for transporting molecules from AFM tips to substrate. These methods conduct with the precise control of a driving force, are considerable methods for size-selective and site-specific coverage and patterning with a wide variety of deposition compounds and even single molecules.

In HFN method, a layer of material is mechanically removed from substrate by an AFM tip and then filled by molecules of selected compound. Atomic manipulation is another stage to position of atoms and molecules on surfaces by simply moving them with a tip. Atomic assemblies can be formed on surfaces by this method.

Finally scanning probe lithography based on the confinement of chemical reactions offer low-cost approach for the academic researcher to fabricate sophisticated nanometer-scale devices and to investigate chemical processes at the nano-scale. However, these techniques are still in an early development stages.

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