NANOFABRICATION

1. Introduction

One of the widely used method for the fabrication of nanostructures is lithography, which makes use of radiation-sensitive layer to form well-defined patterns on a surface. Current technologies for the fabrication of nanoscale structure are limited in terms of the minimum feature size that can be achieved. Natural macromolecules and the processes through which their highly controlled assembly is carried out have become a source of interest to create novel devices and materials.

2. Strategies for nanoarchitecture

One approach to the preparation of nanostructure, called the *bottom-up approach*, is to collect, consolidate, and fashion individual atoms and molecules into the structure. This is carried out by a sequence of chemical reactions controlled by catalysts. It is a process that is widespread in biology where catalysts called enzymes assemble amino acids to construct living tissue that forms and supports the organs of the body. It is the process of self-assembly.

The opposite approach to the preparation of nanostructure is called the *top-down method*, which starts with large-scale object or pattern and gradually reduces its dimension or dimensions.

3. Lithography

Conventional 'Lithography' is a top down approach. The word lithography has its origin in the Greek work 'litho' which means stone. Lithography therefore literally means carving a stone or writing on a stone. It is now used now to mean a process in which a sample is patterned by removing some part of it or sometimes even organizing some material on a suitable substrate. Lithography is extensively used in electronics industry so as to obtain integrated circuits (IC) or very large scale integration (VLSI) on small piece of semiconductor substrate often called a 'chip'.

Different lithography techniques like optical lithography, x-ray lithography, electron beam lithography and some other have been developed. They depend upon using photons or particle radiations for carving the materials. The lithography technique involve transfer of some pre-designed geometrical pattern (called master or mask) on a semiconductor (silicon) or directly patterning (often known as writing) using suitable radiation. Mask is usually prepared by creating radiation opaque and transparent regions on glass or some other material. Pre-designed patterns can be transferred on a substrate much faster as compared to direct writing. Direct writing being a slower process is overall expensive.

Common principle in most of the lithographic technique is to expose a material sensitive to either electromagnetic radiation or to particles at some regions. Such a radiation sensitive material is known as resist. The selection of area is made using a mask, which is transparent is some regions and opaque in the other regions. This causes selective exposure of the resist, making it weaker or stronger compared to unexposed material depending upon the type of the resist being used. By removing the exposed or unexposed material in suitable chemicals or plasma, desired pattern is obtained.

Various steps involved in photolithography to transfer a pattern on some semiconductor surface: A thin film coating of a metal (like chromium) is deposited on a suitable substrate (for example glass or silicon). A positive or a negative photoresist, usually some polymer, is coated on metal thin film. Positive photoresist material has the property that when exposed to the appropriate radiation it degrades or some chemical bonds are broken. Negative resist on the other hand is a material, which hardens (crosslinks) on exposure to a radiation. A mask is placed between the resist coated substrate and the source of light. By using a suitable chemical (developer) the weakened portion is removed (or image is developed). Remaining unexposed part also can be removed by appropriate chemical treatment. The remaining material can be dissolved in one step and the hardened material in another step.

Depending upon the radiation used like visible light, X-rays, electrons, ions etc., the lithography name is tagged with it.

Nanolithography is the art and science of etching, writing, or printing at the microscopic level, where the dimensions of characters are on the order of nanometers (units of 10^{-9} meter, or millionths of a millimeter). This includes various methods of modifying semiconductor chips at the atomic level for the purpose of fabricating integrated circuits (ICs). Instruments used in nanolithography include the scanning probe microscope (SPM) and the atomic force microscope (ATM). The SPM allows surface viewing in fine detail without necessarily modifying it. Either the SPM or the ATM can be used to etch, write, or print on a surface in single-atom dimensions.

4. Lithography using photons

It is possible to use visible, ultraviolet, extreme ultraviolet (EUV) or X-rays to perform lithography. Highest resolution of the generated features ultimately depend upon the wavelength of radiation used and interaction of radiation with matter as well as mask and optical elements used. Smaller the wavelength used smaller can be feature size. Depth of focus depends upon the penetration of incident radiation. In the visible range glass lenses and masks can be used. In the UV range fused silica or calcium fluoride lenses are used.

There are three methods used to pattern a substrate viz., proximity, contact and projection. In proximity method, mask is held close to the photoresist coated metallized substrate, whereas in contact method the mask is in contact with photoresist. In both proximity and contact methods a parallel beam of light falls on the mask, which transmits the radiation through some windows but blocks through opaque parts. Although better resolution is achieved with contact method as compared to proximity method, in contact method the mask gets damaged faster. In case of projection method a focused beam is scanned through the mask, which allows good resolution to be achieved along with the reduced damage of the mask. However, scanning is a slow process and also requires scanning mechanism adding to the cost.

(a) UVlight and Laser Beams: Using monochromatic light in the visible to UV range, features as small as 1 to 1.5 um size can be routinely obtained. Often g-line (436 nm) from mercury lamp is used. Laser beam of KrF (248 nm) or ArF (193 nm) also are employed reaching ~150 nm as the smallest feature size.

(b) X-ray lithography: Smaller features are possible to obtain by employing X-rays also. However, it is difficult to make suitable masks for X-ray lithography. X-rays in the 0.1-5nm range are used with appropriate metal masks in proximite geometry. Absorption of X-rays in materials not only depends upon the thickness of the material but is also complicated by the presence of adsorption edges. Metal masks are fabricated in such a way that through thin portions they are transmitted and absorbed in thicker regions. Gold masks are often used.

X-ray lithography is a next generation lithography that has been developed for the semiconductor industry. Batches of microprocessors have already been produced. The short wavelengths of 0.8 nm X-rays overcome diffraction limits in the resolution of otherwise competitive optical lithography. The X-rays illuminate a mask placed in proximity to a resist-coated wafer. No lenses are used, and only rudimentary collimating mirrors. The X-rays are broadband, typically from a compact synchrotron radiation source, allowing rapid exposure. Deep X-ray lithography uses yet shorter wavelengths, about 0.1 nm with modified procedures, to fabricate deeper structures, sometimes three dimensional, with reduced resolution. The mask consists of an X-ray absorber, typically of gold or compounds of tantalum or tungsten, on a membrane that is transparent to X-rays, typically of silicon carbide or diamond. The pattern on the mask is written by direct write electron beam lithography onto a resist that is developed by conventional semiconductor processes. The membrane can be stretched for overlay accuracy.

Most X-ray lithography demonstrations have been performed by copying with image fidelity, i.e. without magnification, 1x, on the line of fuzzy contrast as illustrated in the figure. But with the increasing need for high resolution, X-ray lithography is now performed on the Sweet Spot, using local "demagnification by bias." Dense structures are developed by multiple exposures with translation. Many advantages accrue from the application of 3x "demagnification": the mask is more easily fabricated; the mask to wafer gap is increased; and the contrast is higher. The technique is extensible to dense 15 nm prints. The resulting printing has high contrast. X-rays generate secondary electrons as in the cases of extreme ultraviolet lithography and electron beam lithography. While the fine pattern definition is due principally to secondaries from Auger electrons with a short path length, the primary electrons will sensitize the resist over a larger region than the X-ray exposure. While this does not affect the pattern pitch resolution (determined by wavelength and gap), the image exposure contrast $(max - min) / (max + min)$ is reduced since the pitch is on the order of the primary photo-electron range. Several prints at about 20 nm have been published. Another manifestation of the photoelectron effect is exposure to X-ray generated electrons from thick gold films used for making daughter masks. Simulations suggest that photoelectron generation from the gold substrate may affect dissolution rates.

5. Lithography using particle beams

Optical lithography is an important manufacturing tool in the semiconductor industry. However, to fabricate semiconductor devices smaller than 100nm, ultraviolet light of short wavelengths (193 nm) is required, but this will not work because the materials are not transparent at these wavelengths. Electron beam and X-ray lithography can be used to make nanostructures, but these processes are not amenable to the high rate of production that is necessary for large-scale manufacturing. Electron-beam lithography uses a finely focused beam of electrons, which is scanned in a specific pattern over the surface of a material. It can produce a patterned structure on a surface having 10-nm resolution. Because it requires the beam to hit the surface point by point in a serial manner, it cannot produce structures at sufficiently high rates to be used in assembly-line manufacturing processes. X-ray lithography can produce pattern on surfaces having 20nm resolution, but its mask technology and exposure systems are complex and expensive for practical applications.

All the moving particles are associated with wavelength known as de Broglie wavelength. All kinds of particles can in principle be used. But to achieve high resolution wavelength should be as small as possible. Thus large mass and large velocity of particle makes is possible to get adequate resolution. In fact it is possible using neutral atoms, ions or electrons to bring down the particle associated wavelength to any desired value, even as small as 0.1 nm.

(a) Electron Beam Lithography: It is very similar to a scanning electron microscope and requires vacuum. Sometimes SEM is modified in order to use it as a lithography set up. Electron beam lithography is a direct writing method i.e., no mask is required to generate a pattern. Rather, pattern or masters required for other lithography processes like optical lithography and soft lithography can be generated using electron beam lithography. Electrons with high energy (~5KeV) are incident on the photoresist. Here also positive or negative photoresists can be used. Common positive resists are polymethylmethacrylate (PMMA) and polybutane-1-sulphone (PBS). Negative resist often used in electron beam lithography is polyglycidylmethacrylate coehylacrylate (COP). Developers used are methylisobutylkeone (MIBK) and isopropylalcohal (IPA) in 1:1 ratio. A focused electron beam in electron beam lithography is used in two modes viz., vector scan and raster scan. In vector scan the electron beam writes on some specified region. After one region is completed the X-Y scanning stage on which substrate to be patterned is mounted, moves. During its movement electron beam is put off. Then a new region is selected and written with the beam. This is continued until whole pattern is generated. In raster scan the beam is rastered or moved continuously over a small area, line by line. The X-Y stage of sample moves at right angles to the beam. The beam is turned off or turned on depending on the pattern. Although very high resolution (~50 nm) is routinely possible using this lithography, due to scanning mode it is rather slow.

The practice of using a beam of electrons to generate patterns on a surface is known as Electron beam lithography. The primary advantage of this technique is that it is one of the ways to beat the diffraction limit of light and make features in the sub-micrometre regime. Beam widths may be on the order of nanometers. This form of lithography has found wide usage in research, but has yet to become a standard technique in industry. The main reason for this is speed. The beam must be scanned across the surface to be patterned -- pattern generation is serial. This makes for very slow pattern generation compared with a parallel technique like photolithography (the current standard) in which the entire surface is patterned at once. As an example, to pattern a single layer of semiconductor containing 60 devices (each device consists of many layers) it would take an electron beam system approximately two hours; compared with less than two minutes for an optical system.

One caveat: While electron beam lithography is used directly in industry for writing features, the process is used mainly to generate exposure masks to be used with conventional photolithography. However, when it is more cost-effective to avoid the use of masks, e.g., low volume production or prototyping, electron-beam direct writing is also used.

For commercial applications, electron beam lithography is usually produced using dedicated beam writing systems that are very expensive. For research applications, it is very common to produce electron beam lithography using an electron microscope with a home-made or relatively low cost lithography accessory. Such systems have produced linewidths of ~20 nm since at least 1990, while current systems have produced linewidths on the order of 10 nm or smaller. These smallest features have generally been isolated features, as nested features exacerbate the proximity effect, whereby electrons from exposure of an adjacent feature spill over into the exposure of the currently written feature, effectively enlarging its image, and reducing its contrast, i.e., difference between maximum and minimum intensity. Hence, nested feature resolution is harder to control. For most resists, it is difficult to go below 25 nm lines and spaces, and a limit of 20 nm lines and spaces has been found.

With today's electron optics, electron beam widths can routinely go down to a few nm. This is limited mainly by aberrations and space charge. However, the practical resolution limit is determined not by the beam size but by forward scattering in the photoresist and secondary electron travel in the photoresist. The forward scattering can be decreased by using higher energy electrons or thinner photoresist, but the generation of secondary electrons is inevitable. The travel distance of secondary electrons is not a fundamentally derived physical value, but a statistical parameter often determined from many experiments or Monte Carlo simulations down to < 1 eV. This is necessary since the energy distribution of secondary electrons peaks well below 10 eV. Hence, the resolution limit is not usually cited as a well-fixed number as with an optical diffraction-limited system. Repeatability and control at the practical resolution limit often require considerations not related to image formation, e.g., photoresist development and intermolecular forces. In addition to secondary electrons, primary electrons from the incident beam with sufficient energy to penetrate the photoresist can be multiply scattered over large distances from underlying films and/or the substrate. This leads to exposure of areas at a significant distance from the desired exposure location. These electrons are called backscattered electrons and have the same effect as long-range flare in optical projection systems. A large enough dose of backscattered electrons can lead to complete removal of photoresist in the desired pattern area.

(b) Ion Beam Lithography: Very small features (~5-10 nm) can be written using high-energy ion beams. Major advantage of using ion beams is that resists are more sensitive to ions as compared to electron and have low scattering in the resist as well as from the substrate. Commonly used ions are He+, Ga+ etc., with energy in the 100-300 KeV range.

(c) Neutral Beam Lithography: Neutral atoms like argon or cesium have been allowed to impinge on substrates to be patterned through the mask. Such beams cause less damage to the masks. Self assembled monolayers on gold substrate have been often patterned using neutral beams.

6. Scanning Probe Lithography

STM and AFM microscopes using sharp tips or probes for imaging can be used for lithography purpose. This has evolved scanning probe lithography (SPL). One major advantage is that like optical lithography it is also carried out in air. There are different ways in which SPL can be carried out viz., mechanical scratching or movement, optical, thermomechanical and electrical.

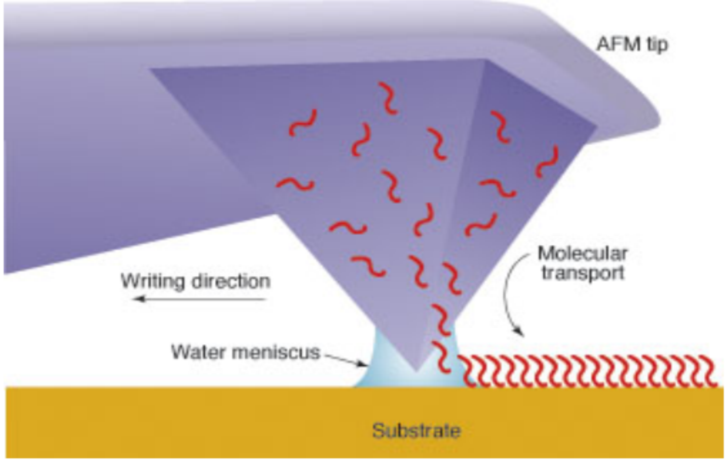
(a) Mechanical Lithography: In mechanical lithography there are different modes like scratching, pick up and pick down or dip pen lithography.

(i) Scratching: Pits or lines can be produced using either STM tip or AFM tip on surface of bulk material or surface of a thin film. Formation of pits or lines by scratching is like ploughing, in which scratched material is piled up around the indented region. Variety of materials like nickel, gold, copper, polymers, Langmuir Blogett films, high temperature superconductors are possible to scratch. Often diamond tips can be used. Pits as small as 30 nm diameter and 10 nm depth are possible to make.

(ii) Pick-up and Pick-down: Atoms are picked up one by one and arranged in desired pattern on a substrate. STM/AFM tips can be used to move atoms or molecules. Systematic work by IBM scientists made it possible for them to pile up xenon atoms on a metal substrate and write a letter patter IBM for the first time. Some scientists moved 30 nm GaAs particles on a GaAs substrate. Letter patterns as high as 50 nm in height were made using AFM tip. Now the technique is used to fabricate some circuits.

(iii) Dip-pen lithography: The method bears a similarity to writing on a piece of paper with ink. That is why the name dip pen lithography is given. An AFM tip is used as a pen and molecules are used as ink. Appropriate molecules picked up by the tip from the source of molecules can be transported and transferred at desired place on the substrate. Letters with line thickness as small as 15nm have been written. Overwriting and erasing capability of dip pen lithography is quite a unique feature.

Dip Pen Nanolithography (DPN) is a scanning probe lithography technique where an atomic force microscope tip is used to transfer molecules to a surface via a solvent meniscus. This technique allows surface patterning on scales of under 100 nanometres. DPN is the nanotechnology analog of the dip pen (also called the quill pen), where the tip of an atomic force microscope cantilever acts as a "pen," which is coated with a chemical compound or mixture acting as an "ink," and put in contact with a substrate, the "paper." DPN enables direct deposition of nanoscale materials onto a substrate in a flexible manner. The vehicle for deposition can include pyramidal scanning probe microscope tips, hollow tips, and even tips on thermally actuated cantilevers. Applications of this technology currently range through chemistry, materials science, and the life sciences, and include such work as ultra high density biological nanoarrays, additive photomask repair, and brand protection for pharmaceuticals. The technique was discovered in 1999 by a research group at Northwestern University led by Chad Mirkin. The company NanoInk, Inc. holds a patent on Dip Pen Nanolithography, and "DPN" and "Dip Pen Nanolithography" are trademarks or registered trademarks of NanoInk.



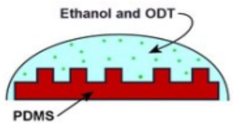
(b) Optical scanning probe lithography: Very high resolution ~20-50 nm is possible, overcoming the diffraction limit, with visible light using Scanning Near-Field Optical Microscope (SNOM). This is attributed to near-field component of electromagnetic radiation. In SNOM, a fine spot of light emerging through an aperture, scans on the surface within a distance of less than wavelength of light used for scanning. By placing the aperture close to the photoresist coated substrate, it is possible to obtain as small as ~50nm size features routinely.

(c) Thermo-mechanical lithography: It is also possible to use an AFM tip along with a laser beam and carry out nanolithography. While the AFM tip is in contact with a coating like polymethylmethaacrylate (PMMA), laser beam strikes the same point of the coating. This heats the film locally enabling the tip to penetrate in the material and make a pit. This thermo-mechanical method is capable of producing resolution as high as ~30nm.

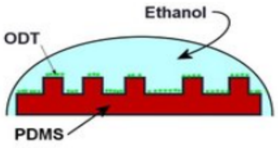
(d) Electrical Scanning Probe Lithography: In this method, a voltage is applied between the SPM tip and the sample. Above some critical voltage if large current flows between the tip and the sample, an irreversible change can occur in sample surface. Variety of bulk solid and think films surfaces has been patterned using this method. In silicon or modified silicon surface ~30 -60 nm wide and ~5-10 nm deep lines have been engraved.

7. Soft Lithography

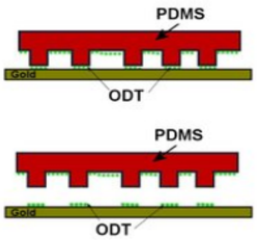
The name soft lithography is used to mean the techniques using materials like polymers, organic materials or self assembled films. It is a useful alternative to obtain resolution better than ~100nm at low cost. Moreover, the method is applicable from few nm to few um size features. In general, soft-lithography technique involves fabrication of a patterned master, molding of master and making replicas. A master is usually made using X-ray or electron beam lithography. It is supposed to be quite rigid. A mold is usually made using a polymer like polydimethylsiloxane (PDMS), epoxide, polyeurethane etc., PDMS is most common amongst the polymers used for molding due to its attractive properties like thermal stability (~150 C), optical transparency, flexibility (~160% elongation), capability of cross-linking using IR or UV radiation etc. However, during molding, some distortions can take place and adequate control has to be practiced to achieve reproducible and required results.



"Inking" a stamp. PDMS stamp with pattern is placed in Ethanol and ODT solution



ODT from the solution settles down onto the PDMS stamp. Stamp now has ODT attached to it which acts as the ink.



The PDMS stamp with the ODT is placed on the gold substrate. When the stamp is removed, the ODT in contact with the gold stays stuck to the gold. Thus the pattern from the stamp is transferred to the gold via the ODT "ink."

In technology, ***soft lithography*** refers to a set of methods for fabricating or replicating structures using "elastomeric stamps, molds, and conformable photomasks. It is called "soft" because it uses elastomeric materials. Soft lithography is generally used to construct features measured on the nanometer scale. ***Soft lithography*** includes the technologies of Micro Contact Printing (μCP), replica molding (REM), microtransfer molding (μTM), micromolding in capillaries (MIMIC) and solvent-assisted micromolding (SAMIM). One of the soft lithography procedures is as follows:

1. The steps of any of your favorite micro- or nano- scale lithography procedures (photolithography, EBL, etc.) are followed to etch a desired pattern onto a substrate (usually silicon)
2. Next, the stamp is created by pouring a degassed resin overtop of the etched wafer. Common resins include PDMS and Fluorosilicone.
3. Removing the cured resin from the substrate, a stamp contoured to your pattern is acquired.
4. The stamp is then "inked" by placing it, pattern-up, in a bath of inking solution (for example, ODT in ethanol) for a short period of time. The ink molecules will fall and adhere to the surface of the stamp creating a single-molecule layer of the ink on the stamp.
5. The inked stamp is then pressed on the substrate and removed, leaving the desired single-molecule thick pattern on the substrate
6. Steps 4 and 5 are repeated for each substrate on which the pattern is desired

Advantages: Soft lithography has some unique advantages over other forms of lithography (such as photolithography and electron beam lithography). They include the following:

- Lower cost than traditional photolithography in mass production
- Well-suited for applications in biotechnology
- Well-suited for applications in plastic electronics
- Well-suited for applications involving large or nonplanar (nonflat) surfaces
- More pattern-transferring methods than traditional lithography techniques (more "ink" options)
- Does not need a photo-reactive surface to create a nanostructure
- Smaller details than photolithography in laboratory settings (~30nm vs ~100nm)

(a) Nanoimprint lithography: It has been developed that may provide a low-cost, high-production rate manufacturing technology. Nanoimprint lithography patterns a resist by physically deforming the resist shape with a mold having a nanostructure pattern on it, rather than by modifying the resist surface by radiation, as in conventional lithography. A resist is a coating material that is sufficiently soft that an impression can be made on it by a harder material. A mold having a nanoscale structured pattern on it is pressed into a thin resist coating on a substrate, creating a contrast pattern in the resist. After the mold is lifted off, an etching process is used to remove the remaining resist material in the compressed regions. The resist is a thermoplastic polymer, which is a material that softens on heating. It is heated during the molding process to soften the polymer relative to the mold. The polymer is generally heated above its glass transition temperature, thereby allowing it to flow and conform to the mold pattern. The mold can be a metal, insulator or semiconductor fabricated by conventional lithography methods. Nanoimprint lithography can produce patterns on a surface having 10 nm resolution at low cost and high rates because it does not require the use of sophisticated radiation beam generating pattern for the production of each structure.

(b) Microcontact Printing (uCP): A PDMS stamp is dipped in an alanethiol solution and pressed against the metallized (Au, Ag, Cu) substrate. Those parts of substrate, which come in contact with the PDMS receive layers of alkanethiol. The monolayers do not spread on the substrate. Further, these self assembled monolayers can be used as resists for selective etching or deposition. The printing being simulateous, it is a fast method.

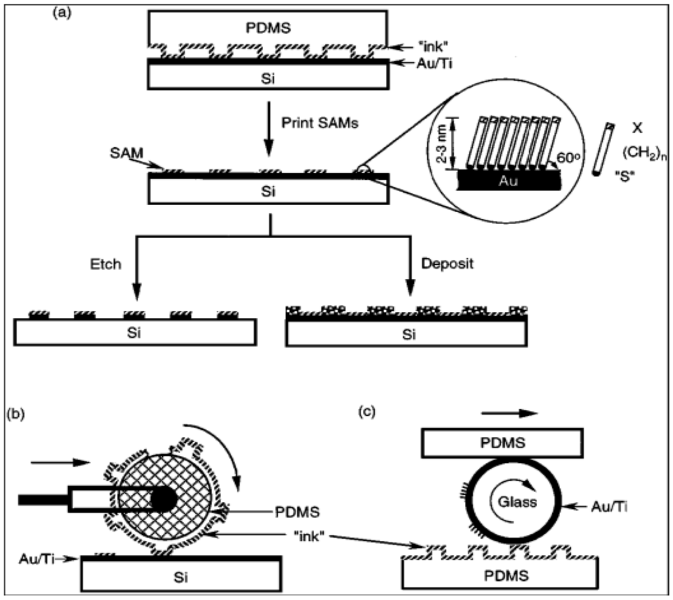


Figure Schematic procedures for ^{1}uCP of hexadecanethiol (HDT) on the surface of gold: (*a*) printing on a planar surface with a planar stamp (*b*) printing on a planar surface over large areas with a rolling stamp, and (*c*) printing on a nonplanar surface with a planar stamp.

(c) Relica Molding: In this method, a PDMS master or stamp is used to replicate a number o copies. For example a solution of polyurathene is poured in PDMS and cured using UV light or thermal treatment so that polyurathene becomes solid. PDMS can be easily removed so that a pattern opposite to that is produced in polyurathene. By applying small pressure on PDMS, it is possible to further reduce the size o the features smaller than in the original pattern. Nanostructure ~30 nm have been achieved using this method.

(d) Micro Transfer Molding (uTM): A preformed polymer is poured in PDMS stamp. Excess polymer is removed and the stamp is pressed against a substrate. Using thermal treatment polymer is imprinted on the substrate and mould is removed.

(e) Micromolding in Capilleries (MIMIC): In this technique, a PDMS stamp is placed on a substrate to be patterned. A low viscocity polymer is then placed in contact with PDMS. The liquid flows into channels of PDMS by capillary action. After thermal treatment of curing with UV radiation the polymer gets solidified. PDMS stamp is then removed to obtain the patterned substrate.

(f) Solvent-Assisted Micromolding (SAMIM): A PDMS stamp coated with a solvent is pressed against the substrate coated with a polymer film. Solvent softens the polymer surface in contact. PDMS can be removed after the solvent has evaporated. PDMS stamp itself is not affected by the solvent. Volatile and substrate dissolving solvents, but not PDMS stamp dissolving, need to be used. Polymethylmethacrylate (PMMA), cellulose acetate, polyvinyl chloride etc., are used as polymers.

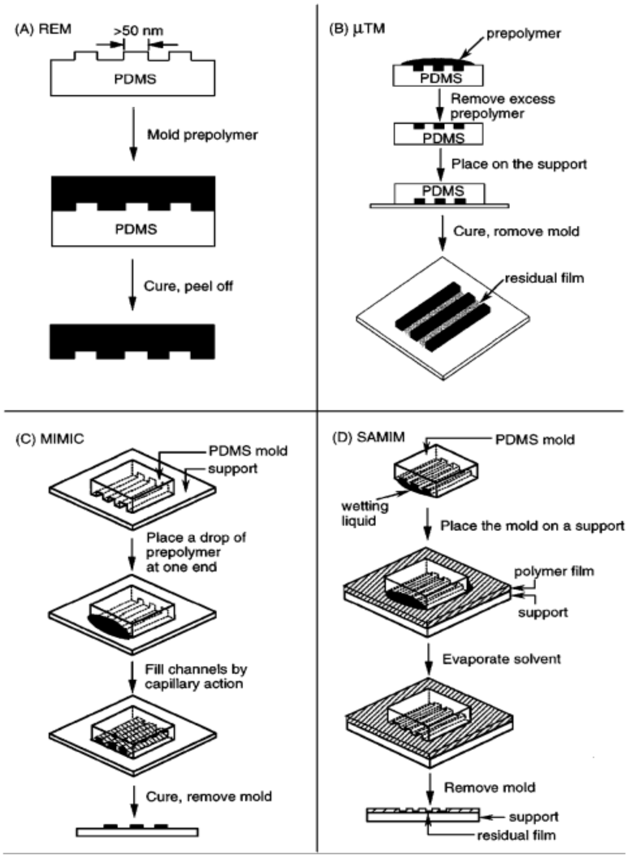


Figure Schematic illustration of procedures for (*a*) replica molding (REM), (*b*) microtransfer molding (uTM), (*c*) micromolding in capillaries (MIMIC), and (*d*) solvent-assisted micromolding (SAMIM).

8. Self Assembly

The ‘bottom up’ approach of nanofabrication proposes to overcome the limitations of traditional ‘top down’ lithographic techniques by relying on the self-organization of molecular building blocks into higher order assemblies having a desired configuration. A variety of molecular building blocks with programmed non-covalent recognition sites have been designed and produced by organic synthesis. Nature has been working on nanoscale self-assembly. Consequently, today biological materials are used as building blocks for self-assembly applications. These biological materials include DNA nanostructures, small peptides, S-layer glycoproteins, viral proteins and even whole bacteriophages.

(a)Process of self-assembly: The spontaneous organization of small molecules into larger well-defined, stable, ordered molecular complexes or aggregates is known as self assembly. Self assembly takes place spontaneously by adsorption of atoms or molecules onto a substrate in a systematic, ordered manner. This process involves the use of weak, reversible interactions between parts of molecules without any central control, and the result is a configuration that is in equilibrium. The procedure is automatically error-checking, so faulty or improperly attached subunits can be replaced during the growth.

The traditional organic synthesis of very large molecules called macromolecules comprises a number of time-consuming steps that involve breaking and remaking strong covalent bonds, and these steps are carried out under kinetic control. They yields are small, and errors are not readily recognized or corrected. In contrast to this, self-assembly variety of synthesis makes use of weak, noncovalent bonding interactions such as those involving hydrogen bonds and van der Waals forces, which permit the reactions to proceed under thermodynamic control, with continual correction of errors. The initial individual molecules or subunits are usually small in size and number and easy to synthesize, and the final product is produced in a thermodynamically equilibrium state.

On one hand, fabrication methods in micro- and nanoscience allow for batch processing. That is, we have the ability to make many copies of the same device simultaneously. How do we design these devices so that they spontaneously assemble themselves into a useful working structure? On the other hand, traditional fabrication methods are limited in resolution. To make smaller structures, i.e., true nanoscale structures, requires the development of new methods. Taking their cue from nature, coaxing nanostructures into self assembling is an avenue many scientists are exploring. Ultimately, a deeper understanding of self assembly may shed light on the nature of life itself.

Assembly by capillary forces: G.M. White sides and his group at Harvard University have designed and studied various self assembling systems. Many of these are based on the so-called "capillary bond." This "bond" exploits two properties of objects in water. First, small objects resting on the surface of water attract one another. In this way, interacting particles feel a force of attraction. Second, when two hydrophobic surfaces come into contact they remain in contact. In other words, they bond. In their experiments Whitesides et. al. have used the polymer polydimethylsiloxane (PDMS) to fabricate their self assembling shapes. PDMS is naturally hydrophobic and its surface properties can be easily changed from hydrophobic to hydrophilic by treating with an oxygen plasma. In this way interacting particles with varying surface properties can be fabricated. Whitesides et. al. have designed planar systems that self assemble to tile the plane, tile the plane with gaps, and form chain-like structures.

Assembly by electrostatic forces: Assembly by capillary forces relies upon particle-particle interaction and interaction between particles and their enviornment. The particles have surface properties (hydrophobic or hydrophillic) and the enviornment is water.

Assembly by magnetic forces: simple to construct self assembling system involves magnets. In its simplest incarnation, the system is no more than a collection of disk shaped magnets randomly strewn about a inside a container. Here, simple shaking is enough to cause formation of a more highly ordered state

(b)Interactions governing self-assembly: Self organization and self-assembly are ubiquitous in nature, ranging from the simplest chemical reactions to the formation of living organisms. Self-assembly is synonymous for the spontaneous occurrence of order in a given open system. Any spontaneous process is irreversible and is accompanied by an increase in the combined entropy for both the system and its environment. The basic thermodynamic quantity, which dictates these processes at constant pressure, is system's Gibbs free energy change.

$\Delta G=\Delta H-\Delta TS$, where ΔH and ΔS are the changes of enthalpy and entropy, respectively, after the reaction or self-assembly processes. For spontaneous process, ΔG must to be <0. One major contribution to ΔH comes from the potential attractive interactions. The forces that determine ΔH include: van der Waals, hydrogen bonding, electrostatic, hydrophobic, and other non-bonding interactions. Entropy is related to quality of energy and order in any given system and is measured by the statistical probability. In the process of self-organization and self-assembly of the inorganic materials, major contributions to ΔG come from the system's enthalpy change, because entropy change is generally of less importance due to the limited freedom of inorganic compounds in condensed phase.

Self assembly is the organization of molecules or materials into order from disorder. Quantum mechanics determines the forces that organize the system on the nanometer scale. There are only four forces known in nature, these are the strong and weak forces existing in the nuclei, gravitational forces, and electromagnetic forces. Of these only the electromagnetic force will be relevant for the self-assembly. The chemical bonding interaction is one the strongest among all electromagnetic forces. Since self-assembly does not involve the breaking or the formation of chemical bonds, only non-bonding interactions are important. The non-bonding electromagnetic force is expressed in various forms e.g van der Waals forces, hydrogen bonding, electrostatic forces, magnetic interactions and others such as cation- and metal complexation interactions. In some cases, one type of interaction dominates, in others, several interactions may be of equal importance and these interactions may be cooperative instead of additive.

Van der Waals interaction is a weak short-range attractive force due to the temporary dipole-dipole moment interaction that results from electron movement surrounding the nuclei. It is non-discriminate and contributes to less than 2kcal/mol for each pair of interacting dipole moments. It is a high order interaction. Electrostatic interaction is Columbic in nature. Its interacting energy is inversely proportional to the distance between the charged particles. Electrostatic interaction is strong and constitutes one of the major forces. Temperature does not have a strong effect on electrostatic interactions. The hydrogen bonding interaction very unique interaction between hydrogen bond donors (e.g N-H, O-H) and acceptors (eg. N, O). Hydrogen bonding plays an important role in hydrophobic interactions and in molecular recognition of proteins because of its directionality. It was originally thought that hydrogen bonding interaction is mostly electrostatic in nature, but it is now generally accepted that the hydrogen bond consists of many different interactions, including Coulombic attraction, exchange repulsion, polarization and charge transfer and dispersion. The hydrogen bonding interaction contributes to about 2-20 kcal/mol to the total energy. If one or both of the donor and acceptor are charged, the interaction becomes much stronger. Hydrophobic interactions between the non-polar solutes in aqueous solution arises from the stronger attraction between the water-water molecules than between the solute-water molecules. Metal complexation is due mostly to a combination of electronic, electrostatic, charge transfer, van der Waals interactions and the polarization effect. In the case of complexation between transition metal ions and ligands, four or six coordinates is generally found.

(c)Examples of self-assembly: (i) Semicondutor islands: One type of self-assembly involves the preparation of semiconductor islands. It can be carried out by a technique called heteroepitaxy, which involves the placement or deposition of the material that forms the islands on a supporting substrate called a substrate made of a different material with a closely matched interface between them. It involves bringing atoms or molecules to the surface of the substrate where they do one of three things. They either are adsorbed and diffuse about on the surface until they join or nucleate with another adatom to form an island, attach themselves to or aggregate into an existing island, or desorb and thereby leave the surface. Small islands can continue to grow, migrate to other positions, or evaporate. There is critical size at which they become stable, and no longer experience much evaporation. Thus there is an initial nucleation stage when the number of islands increases with the coverage. This is followed by an aggregation stage when the number of islands levels off and the existing ones grow in size. Finally there is the coalescence stage when the main events that take place involve the merge of exisiting islands with each other to form larger clusters.

It is possible to spontaneously create quantum dots of Ge on Si, InAs on GaAs etc. The origin of self assembly is strain induced. For example germanium and silicon have only 4% lattice mismatch. Therefore Ge can be deposited epitaxially on Si single crystal upto 3-4 monolayers. This results into spontaneous formation of nanosized islands or quantum dots. However, temperature of substrate has to be >350 C during deposition or post deposition annealing is required. Size of the islands depends upon growth temperature as well as substrate plane on which it grows.

(ii) Monolayers: A model system that well illustrates the principles and advantages of the self-assembly process is a self-assembled monolayer. The Langmuir-Blodgett technique, had been widely used for the preparation and study of optical coatings, biosensors, ligand-stabilized Au clusters, antibodies and enzymes. It involves starting with clusters, forming them into monolayer at an air-water interface, and then transferring the monolayer to a substrate in the form of what is called a Langmuir-Blodgett film. Self assembled monolayers, are stronger, are easier to make, and make use of a wide variety of available starting materials.

Self-assembled monolayers and multilayers have been prepared on various metallic and inorganic substrates such as Ag, Au, Cu, Ge, Pt, Si, GaAs, SiO2, and other materials. This has been done with aid of bonding molecules or ligands such as alkanethiols RSH, sulfides RSR’, disulfides RSSR’, acids RCOOH, and siloxanes RSiOR3, where the symbols R and R’ designate organic molecule groups that bond to a thiol radical –SH or an acid radical –COOH. The binding to the surface for the thiols, sulfides, and disulfides is via the sulfur atom; that is, the entity RS-Au is formed on a gold substrate, and the binding for the acid is RCO2-(MO)n where MO denotes a metal oxide substrate ion, and the hydrogen atom H of the acid is released at the formation of the bond. The alkanethiols RSH are the most widely used ligands because of their greater solubility, their compatibility with many organic functional groups, and their speed of reaction. They spontaneously adsorb on the surface; hence the term self-assemble is applicable.

For self-assembled monolayers to be useful in commercial microstructures, they can be arranged in structured regions or pattern on the surface. An alkaenthio 'ink' can systematically form or write pattern on a gold surface with alkanethiolate. The monolayer-forming 'ink' can be applied to the surface by a process called microcontact printing, which utilizes an elastomer, which is a material with rubber like properties, as a 'stamp' to transfer the pattern. The process can be employed to produce think radiation-sensitive layers called resists for nanoscale lithography. The monolayers themselves can serve for a process called passivation by protecting the underlying surface from corrosion.

Self-assembled monolayer: Self assembled monolayers (SAMs) are surfaces consisting of a single layer of molecules on a substrate. Rather than having to use a technique such as chemical vapor deposition or molecular beam epitaxy to add molecules to a surface (often with poor control over the thickness of the molecular layer), self assembled monolayers can be prepared simply by adding a solution of the desired molecule onto the substrate surface and washing off the excess.

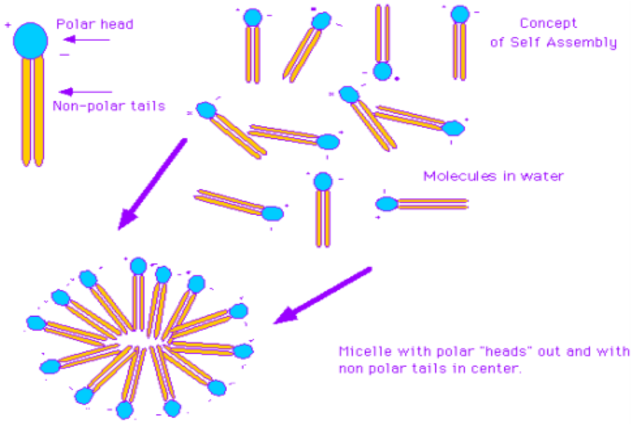
A common example is an alkane thiol on gold. Sulfur has particular affinity for gold, with a binding energy in the range of 20–35 kcal/mol (85–145 kJ/mol). An alkane with a thiol head group will stick to the gold surface and form an ordered assembly with the alkyl chains packing together due to van der Waals forces. For alkyl thiols on gold, the extended alkyl chains typically orient with an angle of ~30 degrees from the perpendicular of the substrate, and are assumed to be in a fully extended linear arrangement. There has been a great deal of work done determining the process by which alkyl thiol on gold assemblies are produced. It is generally thought that alkyl thiol molecules first bind to the gold surface in a 'lying down' position, where the alkyl chain tails of the molecules lie flat on the gold surface. The thiol interaction provides about 20–30 kcal/mol (85–130 kJ/mol) of driving force for the initial binding, which is modeled as a Langmuir binding isotherm. These binding events continue until the lying down molecules are dense enough on the surface to interact with each other. At some point the alkyl chains lift off the substrate and point outwards, tethered by the thiol anchor to the surface. There is a shift to a mixture of lying down molecules and island domains of upright alkyl chains, tilted at 30 degrees to the normal. At this stage binding kinetics become more complex and can no longer be modeled with a simple Langmuir binding isotherm. Over time the island domains merge and cover the bulk of the substrate, and the process can be compared to a 2-D crystallization process on a surface. Alkyl thiol SAMs exhibit grain boundaries and defects even after long periods of assembly. The initial stage of SAM formation usually takes minutes or less under the normal conditions of 0.1-10 mmol/L thiol concentration in a solvent. More ordering of the assembly can take place over days or months, depending on the molecules involved.

A variety of other self-assembled monolayers can be formed, although there is always debate about the degree to which systems self-assemble. Alkyl thiols are known to assemble on many metals, including silver, copper, palladium, and platinum. Alkyl silane molecules (e.g. octadecyltrichlorosilane) are another well-known example of self-assembly on silicon oxide surfaces and potentially be of greater technical relevance than alkyl thiol assembly on metals. Alkyl carboxylates are known to assemble on a variety of surfaces, such as aluminium and mica. Silicon has been used through the reaction of silicon hydride surface and a radical generator, such as heat, UV or radical initiator molecule, or with reagents such as Grignard and chlorosilanes. Once assembly has been accomplished, chemistry can be performed on the layer, especially if self-assembly places a reactive functional group on the outside of the monolayer.

SAMs have several applications in scientific research; they tend to have quite different chemical kinetics than the same molecules in another form, because of their exposed, 2-dimensional distribution, and as such are useful for some chemical and biochemical experiments. They can also be used for simulation of biological membranes and as substrates for cell culture. As technology develops to control the functional groups present in SAMS, either by direct deposition of molecules with those groups or by chemical modification of the layer, many other applications are also developing, for example in nanoscale fabrication of electronics.

(iii) Protein folding and aggregation: Protein folding is a typical example of self-assembly regulated by many subtle interacting forces. Protein folding is the process by which the polypeptide is folded into a functional three-dimensional protein structure based on the amino-acid sequence. When polypeptides are newly produced under physiological conditions, their folding is based on the interacting forces and the laws of thermodynamics. However, in some cases, molecular chaperones have to be employed to assist protein folding to prevent incorrect interactions within and between non-native polypeptides.

Molecular recognition means that there is specific interaction between protein and ligand, or between antibody and antigen. As was observed experimentally, topography (conformational match seems to play an essential role in protein-ligand recognition. Because hydrophobic and van der Waals interactions are not specific; they cannot alone be responsible for molecular recognition. Directional hydrogen bonding and electrostatic interactions play an important role.



Hydrophobic and hydrophilic interactions are important because many molecules in biology such as proteins and the molecules that make up the cell membrane have hydrophilic and hydrophobic regions on the same molecule. When put in water these molecules automatically organize themselves into more complex and biologically useful structures. This process is termed self assembly. It is illustrated in the diagram for a molecule with a polar head and a non polar tail.

(d) Applications: (i) Self assembly using biological templates: There are many examples of self assembly at biological templates like S-layers, proteins, DNA, lipids etc. When organized arrays of inorganic crystals are embedded in biological systems they are often referred to as biomineralized systems.

Mangetotactic bacteria are small bacteria, ~35 to 120 nm sized permanent magnets are present inside them. The magnets are of either iron sulphide (Fe3S4-gregite) or iron oxide (Fe3O4 – magnetite). Such magnetic particles make a chain of nanomagnets. It is useful for navigation of bacteria. Earth's magnetic field has a dip in the north and south hemisphere which helps bacteria to seek direction.

Another example of self-assembly in biological systems is S-layers. They are part of cell envelope of prokaryotic organisms. They are two dimension, crystalline single proteins or glycoprotein monomers organized in hexagonal, oblique or square lattices. These lattices have ordered pores. The periodicity of pores can vary, depending upon the protein, from 3-35 nm. Such S-layers after extraction from bacterial cells have been transferred on some metallic substrates (or grids). When treated with cadmium salt and subsequently with Na2S, ordered arrays of CdS nanoparticles could be formed. S-layers have been used to assemble Au, Pt, Fe, Ni etc., metal nanoparticles. In general, S-layers extracted from the biological cells can be directly used to deposit nanoparticles from liquid phase.

Ferritins are protein colloids of 12 nm size found in all animals. Ferritins have a cavities ~6-8 nm in size filled with iron oxide. It is possible to remove iron oxide and replace it with metal or other nanoparticle. Further it is possible to make a two dimensional array of ferritins in solution. For example, ferritin solution in NaCl and phosphate at ~5.8 pH can be filled in a trough. Chloroform containing dichloroacetic acid can be used to dissolve poly-1-benzal-L-histidine (PBLH) and spread over ferritin solution in trough. After about two hours the solution can be heated at 38 C for one hour and cooled back to room temperature. This produces ordered layer of ferritin at liquid-air interface. The layer can be transferred on silicon substrate by dipping in the solution.

DNA is a long helical molecule. It has large aspect ratio and acts like a long one dimensional template in its simplest form. Its four nucleotide bases viz., guanine, cytosine, adenine, and thymine can form a rich variety of sequences and structures. Thus, cirucular, square, branched etc. long or short DNA templates are possible. Besides planar geometry, they can adopt even three dimensional structures. As DNA has alternate sugar and phosphate groups on its strands, it is possible to anchor metal, semiconductor or oxide particles by different bonding on DNA to have assembly of particles.

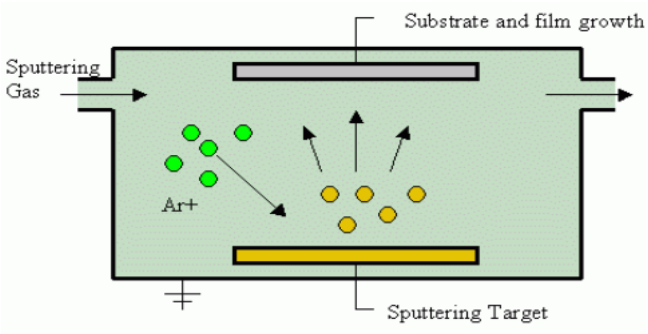
(ii) Self assembly using organic molecules: Preformed inorganic nanoparticles can be assembled on solid substrates through some organic molecules adsorbed on their surfaces. CdS nanoparticles functionalized with carboxylic group can be transferred to aluminium thin films. Dithiols adsorbed on metals surface also could adsorb CdS nanoparticles to form layers of them. Silver particles have been adsorbed on oxidized aluminium layers using bifunctional molecule such as 4-carboxythiophenol. These molecules bind to aluminium oxide layer by carboxylic group and thiol attaches to silver particles.

Using a two phase reaction alkanethiol or alkylamine capped gold, silver and palladium nanoparticles have been self assembled. Here chemical reaction takes place in an aqueous medium. The particles are then transferred into an organic solvent. Solvent is allowed to evaporate which leaves self-assembled layer.

Using Langmuir Blodgett technique it is possible to transfer organic layers along with the attached nanoparticles in liquid subphase to form ordered monolayer or multiple layers on solid substrate. It is possible to order different bilayers of nanoparticles by simply dipping the same substrate alternately in different baths.

9. Others

(a) Sputtering (a bottom-up approach): One method used to make thin layers of material that are only a few atoms thick is called "sputtering." Sputtering involves transferring atoms from a block of source metal over to a surface waiting to be coated. The atoms are knocked loose from the source metal by bombarding them with other high-energy particles. The common aproach taken when explaining sputtering is to imagine billiard balls being struck by the cue ball. The cue ball is rather like the hihg-energy incident particle. As it strikes a bunch of billiard balls (atoms in a block of source metal) they scatter from one another. This is where the analogy breaks down, though, as there is no second surface that the billiard balls attach to besides the pool table. In sputtering, however, the loose atoms are free to deposit on some material that needs to be coated.



(b) Nanoscale Crystal Growth (a bottom-up approach): Just like it sounds, this method involves rather tricky selection of seed crystals and growing conditions with the hopes of creating crystals that have unusual shapes. Nanowires, which happen to exhibit tremendous conductivity, are typically created in this way.

(c) Focused ion beam: Focused ion beam, also known as FIB, is a scientific instrument that resembles a scanning electron microscope. However, whereas the SEM uses a focused beam of electrons to image the sample in the chamber, a FIB instead uses a focused beam of gallium ions. Gallium is chosen because it is easy to build a gallium liquid metal ion source (LMIS). In a Gallium LMIS, gallium metal is placed in contact with a tungsten needle and heated. Gallium wets the tungsten, and a huge electric field (greater than 10^8 volts per centimeter) causes ionization and field emission of the gallium atoms. These ions are then accelerated to an energy of 5-50 keV (kiloelectronvolts), and then focused onto the sample by electrostatic lenses. A modern FIB can deliver tens of nanoamps of current to a sample, or can image the sample with a spot size on the order of a few nanometers.

Unlike an electron microscope, the FIB is inherently destructive to the specimen. When the high-energy gallium ions strike the sample, they will sputter atoms from the surface. Gallium atoms will also be implanted into the top few nanometers of the surface, and the surface will be made amorphous. Because of the sputtering capability, the FIB is used as a micro-machining tool, to modify or machine materials at the micro- and nanoscale. A FIB can also be used to deposit material via ion beam induced deposition. FIB-assisted chemical vapor deposition occurs when a gas, such as tungsten carbonyl ($W(CO)_6$) is introduced to the vacuum chamber and allowed to chemisorb onto the sample. By scanning an area with the beam, the precursor gas will be decomposed into volatile and non-volatile components; the non-volatile component, such as tungsten, remains on the surface as a deposition. This is useful, as the deposited metal can be used as a sacrificial layer, to protect the underlying sample from the destructive sputtering of the beam. Other materials such as platinum can also be deposited.

FIB is often used in the semiconductor industry to patch or modify an existing semiconductor device. For example, in an integrated circuit, the gallium beam could be used to cut unwanted electrical connections, or to deposit conductive material in order to make a connection. The FIB is also commonly used to prepare samples for the transmission electron microscope. The TEM requires very thin samples, typically ~100 nanometers. Other techniques, such as ion milling or electropolishing can be used to prepare such thin samples. However, the nanometer-scale resolution of the FIB allows the exact thin region to be chosen. This is vital, for example, in integrated circuit failure analysis. If a particular transistor out of several million on a chip is bad, the only tool capable of preparing an electron microscope sample of that single transistor is the FIB. The drawback to FIB sample preparation is the above-mentioned surface damage and implantation. However, this is usually only noticeable in high-resolution "lattice imaging" TEM. By lightly ion-milling the sample after completing the FIB preparation, much of this damage can be removed. In short, the FIB is a useful and versatile tool in the materials sciences and semiconductor fields.