Chapter 9
Nanolithography

9.1 Introduction

We have seen in Chaps. 3, 4, and 5 a variety of methods to make nanoparticles (including spherical and other particle shapes) and thin films (or multilayers). These methods are popularly known as *bottom up* approach. In bottom up approach atoms and molecules are assembled so as to have nanomaterials of required size and shape by controlled deposition or reaction parameters. In the *top down* approach reverse is the case. Atoms and molecules are removed from a bulk material or sometimes thin films so as to obtain desired nanostructure.

Conventional *lithography* is a top down approach. The word lithography has its origin in the Greek word 'litho' which means stone. Lithography, therefore, literally means carving a stone or writing on a stone. It is 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 very intensively 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'.

Immediately after the discovery of solid state transistor by Bardeen, Brattin and Schockley in 1947, the quest for making smaller and smaller electronic components began. First transistor was fabricated in germanium but soon it was found that silicon was a better material and was used commercially. Texas Instruments, U.S.A. marketed first transistor. Scientists found that speed of a device, system or an instrument finally depends on how fast a transistor can switch on and off. Speed of a computer also depends upon transistors. All electronic devices including cell phones, ATMs, etc. need fast transistors. It was further realized that smaller the device (or transistor), faster is the switching. Advantages of making smaller devices are manifold. They require smaller amount of material, space and consume less power for their performance making the resulting product cheaper. Initially the solid state transistors were assembled together along with different components like capacitors and resistors and wired to fabricate desired circuits.

S.K. Kulkarni, *Nanotechnology: Principles and Practices*,
DOI 10.1007/978-3-319-09171-6_9

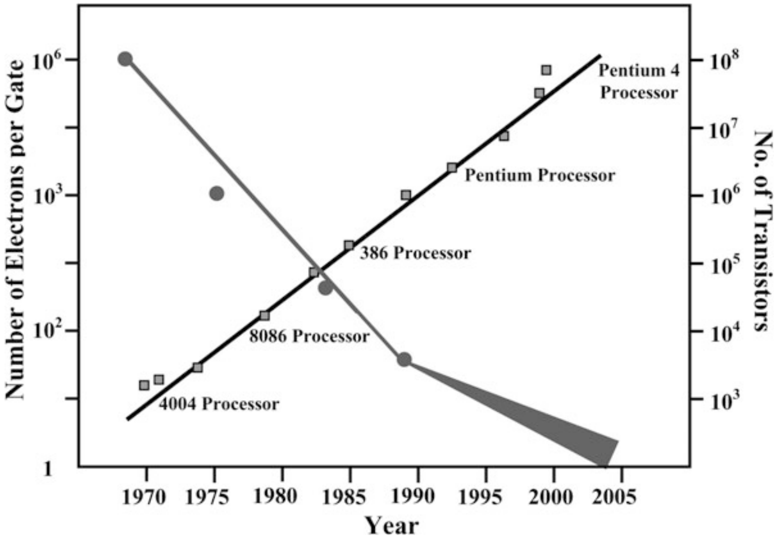


Fig. 9.1 Moore's law

It was proposed by a British engineer G.W.A. Dummer that an entire circuit should be directly made on a silicon substrate instead of wiring together the different components. Robert Noyce at Fairchild Semiconductor and Jack Kilby at Texas Instruments, U.S.A., invented in 1958 what we know today as integrated circuit (IC) which had complete circuit fabricated on a single silicon wafer. This made a great revolution in electronics and Jack Kilby was awarded the Nobel Prize in the year 2000 for this development.

Around 1959, James Moor predicted that there would be a reduction in the transistor size with time. Ever since its depiction the trend in miniaturization of electronic devices has faithfully followed what is known as Moor's law (see Fig. 9.1). It implies that every 18 months the reduction in the size doubles or the number of transistors on a chip doubles or the processing power of computers doubles. However following this law the devices have reached now a lowest size of ~100 nm and deviation from the law has begun. It is not only increasingly difficult to achieve smaller and smaller sizes less than 100 nm but also difficult to retain linear nature of the graph that Moor had predicted. Below a size of ~100 nm we know that besides the 'surface effect', materials also have size-dependent properties. Therefore nanodevices using active or passive nanocomponents cannot be expected to behave like those of large (micrometre) size devices and components. Interestingly this very size-dependent nature can be used to obtain some novel devices, which were not imagined earlier. For example *single electron transistor* (SET) is a completely new device due to unique properties of quantum dots. *Magnetic Spin Valve* and *Magnetic Tunnel Junction* (MTJ) using nanomaterials are some other high speed devices which are the products of nanotechnology.

Thus a new era in electronics has begun with new devices which have much larger memory for computers, consume low power, are compact and faster in their operations. All this is possible but new devices will be economically viable provided one can pattern small devices perhaps using *nanolithography*.

Over the last 3–4 decades different lithography techniques like optical lithography, X-ray lithography and electron beam lithography have been developed. They depend upon using photons or particle radiations for carving the materials. The lithography technique involves transfer of some pre-designed geometrical pattern (called *master* or *mask*) on a semiconductor (like 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 lithography techniques is to expose a material sensitive to either electromagnetic radiation or to particles in some regions. Such a radiation-sensitive material is known as *resist*. The selection of area to be exposed to radiation is made using a *mask*, which is transparent in 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. This may be done in a number of steps depending upon the pattern and materials involved (Box 9.1).

Box 9.1: History of Lithography

Roots of present lithography can be found in the art of printing as well as photography. Lithography or writing/carving on stone has a very long history. It is an art invented by Alois Senefelder from Austria in 1798. He covered the surface of a highly porous stone with a mixture of a gum and water. Only the stone part absorbed the greasy solution. He then dipped the stone in ink made of oil, wax, soap and lampblack. The ink could stick only to the greasy part of the stone. When ink coated stone was pressed on a piece of paper, an impression was made.

It was soon realized that complicated figures, designs or patterns can be easily transferred number of times by this process of printing. By 1848 it was possible to print $\sim$10,000 copies in an hour.

Jules Chéret (1836–1933) in Paris made some artistic posters using lithography. He was awarded the Legion of Honor for creating a new branch in art.

When ICs were to be fabricated on an extremely large scale so as to satisfy the needs of large electronics market, it was necessary to adopt a process of lithography, which can make multiple copies of a pattern in a short time.

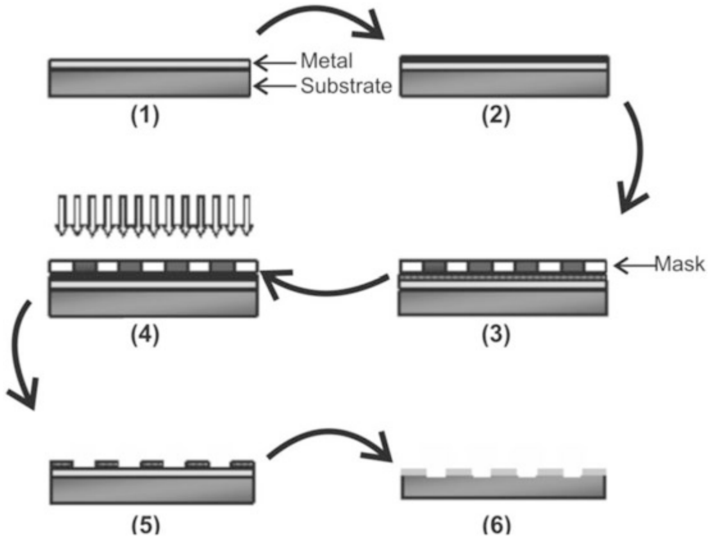


Fig. 9.2 Photolithography process steps: (*1*) surface is coated with metal, (*2*) coating of photoresist on the substrate, (*3*) mask placed over upper layer, (*4*) exposed UV radiation, (*5*) resist development and stripping, and (*6*) etching to get final pattern

Figure 9.2 depicts schematically 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 or ions, the lithography name is tagged with it.

After the development of Scanning Tunneling Microscopes (STM) around 1982 and other Scanning Probe Microscopes (SPM) thereafter, it was realized that they can be used to carry out lithography in nanometer range. Using SPM probe or fine tip of SPM it is possible to directly write on the material.

In recent years some replication techniques also have emerged which are quite inexpensive and allow patterning necessary for some exotic purposes like 'lab-on-chip' or quick diagnostics.

Here we shall outline essentials of lithography (patterning) using photons, electrons, scanning probes and replication methods.

9.2 Lithography Using Photons (UV–VIS, Lasers and X-Rays)

It is possible to use visible, ultraviolet, extreme ultraviolet (EUV) or X-rays to perform lithography. Wherever possible, lasers are used. Highest resolution of the generated features ultimately depends 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 the feature size which is limited by diffraction limit, $\sim\lambda/2$. Depth of focus depends upon the penetration of incident radiation. For the lithography using electromagnetic radiation, optical elements and masks have to be used for various purposes. In the visible range (~700–400 nm), glass lenses and masks can be used. In the UV range, fused silica or calcium fluoride lenses are used.

There are three methods (see Fig. 9.3) viz. ‘proximity’, ‘contact’ and ‘projection’ which can be used to pattern a substrate.

As the name suggests, 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 and blocks through opaque parts. Although better resolution is achieved with contact method as compared to the proximity method, in contact method the mask gets damaged faster compared to the proximity method. In case of projection method, a focussed 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.

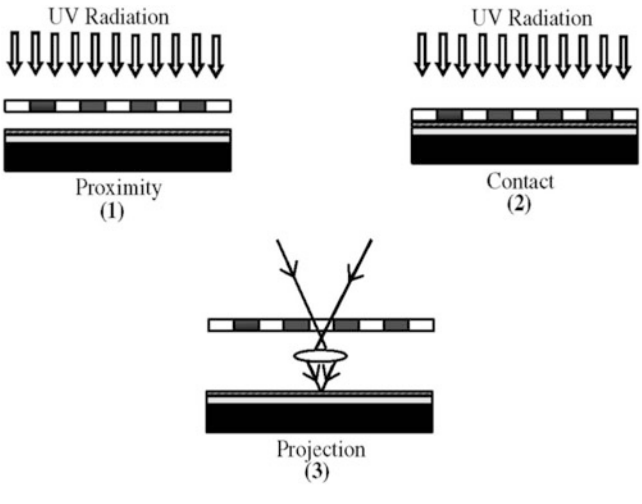


Fig. 9.3 (*1*) Mask is close to the photoresist, (*2*) mask is in contact with the resist and (*3*) focussed beam is scanned through the mask

9.2.1 Lithography Using UV Light and Laser Beams

Using monochromatic light in visible to UV light features as small as 1–1.5 μm size can be routinely obtained. Often g-line (436 nm) from the mercury line is used as a source of radiation. Laser beam of KrF (248 nm) or ArF (193 nm) also are employed reaching ∼150 nm as the smallest feature size. However to obtain feature size below ∼100 nm using photons is a difficult task, unless one uses *near field optics* (see Chap. 7) based on scanning probe technique.

9.2.2 Use of X-rays in 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 0.1–5 nm range are used with appropriate metal masks in proximate geometry. Absorption of X-rays in materials not only depends upon the thickness of the material but is also complicated by the presence of absorption edges. Depending upon the wavelength of X-rays used, metals of suitable elements are chosen. 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. The masks themselves are made using electron beam lithography discussed in the next section.

9.3 Lithography Using Particle Beams

We know that all the moving particles have associated wavelength λ known as de Broglie wavelength given by

$$\lambda = h/mv \tag{9.1}$$

where h is Planck's constant, m—the mass and v is the velocity of the particle. All kinds of particles can in principle be used but to achieve high resolution λ. It should be as small as possible. Thus large mass and large velocity of particle makes it 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 even 0.1 nm. However ultimate resolution depends upon the interaction of incident particles with resist material. Under certain conditions features as small as 2 nm have been patterned. Due to various reasons like they can be easily generated, accelerated and focussed, electrons are preferred for lithography purpose and often used.

9.3.1 Electron Beam Lithography

Figure 9.4 shows schematically electron beam lithography set up. It is very similar to a scanning electron microscope (SEM) and requires vacuum ($\sim 10^{-2}$–10^{-4} Pa). 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, patterns required for other lithography processes like soft lithography (discussed in Sect. 9.5) can be generated using electron beam lithography.

Electrons with high energy (usually larger than ∼5 keV) 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 coethylacrylate (COP). Developers used are methylisobutylketone (MIBK) and isopropylalcohol (IPA) in 1:1 ratio. A focussed electron beam in electron beam lithography is used in two modes viz. 'vector scan' or '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 the substrate to be patterned is mounted, moves. During its movement electron beam is put off. Then a new region is selected and

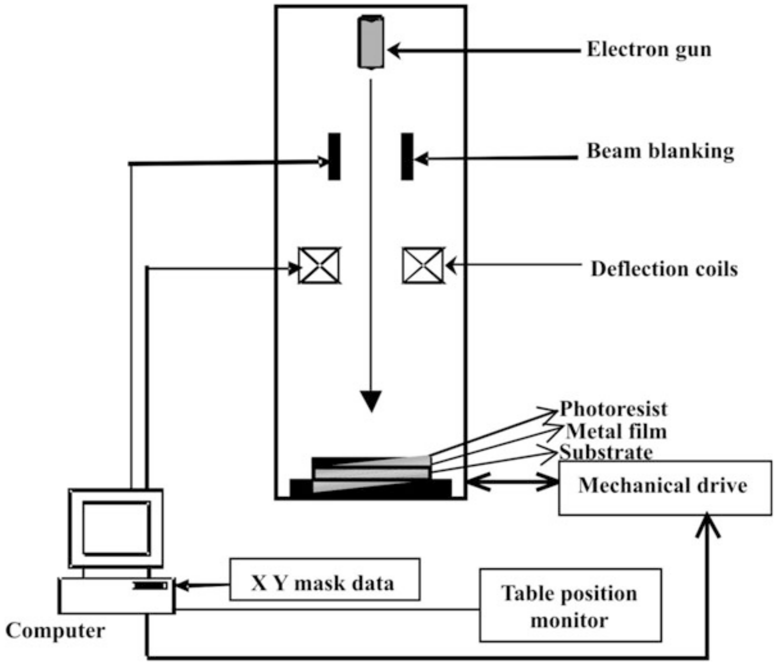


Fig. 9.4 Electron beam lithography set up

'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 the sample moves at right angles to the beam. The beam is turned off or turned on depending upon the pattern. Although very high resolution ($\sim$50 nm) is routinely possible using this lithography, due to scanning mode it is rather slow. For example if the optical lithography can generate 40 patterns with 1 μm resolution in 1 h, only five similar patterns would be generated with electron beam. However larger layer depth is an added attraction of electron beam lithography as compared to optical beam lithography.

9.3.2 Ion Beam Lithography

Very small size features ($\sim$5–10 nm) having large depth can be written using high-energy ion beams. Major advantages of using ion beams is that resists are more sensitive to ions as compared to electrons 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.

9.3.3 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 substrates have been often patterned using neutral beams.

In fact any deposition of neutral atoms (physical vapour deposition, molecular beam epitaxy etc.) through the mask can be considered as lithography of this type.

9.3.4 Nano Sphere Lithography

It is a very simple but useful method of obtaining desired patterns of controlled sizes and shapes with regular spacing. This is achieved usually by using self assembly of polymer or silica colloidal particles on appropriate chemically treated substrate. The formation of silica colloidal particles by chemical method can be found in Chap. 12. Size of the particles can be controlled by managing the reaction time as well as dilution of the chemicals. The self assembly of the particles is achieved by allowing the liquid containing silica particles (or polymeric colloids) to slowly evaporate. Once the film dries, the metal or desired materials are evaporated on the films which can get deposited in the spaces between the spheres. After deposition the spherical

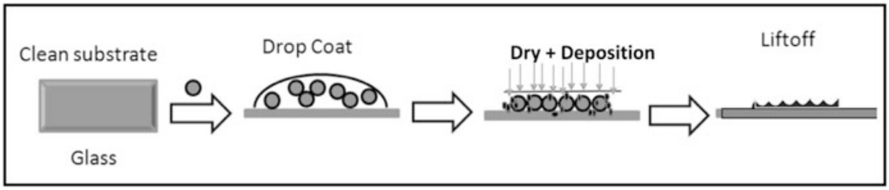


Fig. 9.5 Sequence of patterning steps using nano sphere lithography methods

particles can be simply removed in an ultrasonic treatment or using suitable solvent which only removes self assembled colloids. Figure 9.5 illustrates schematic of nano sphere lithography steps.

Spherical colloids can produce triangular patterns but other shapes of colloidal particles may be employed to produce other shapes.

9.4 Scanning Probe Lithography

With the development of scanning tunnelling microscope (STM) and atomic force microscope (AFM) there began a new chapter in the history of lithography. Microscopes were discussed in Chap. 7. STM and other similar microscopes using sharp tips or probes for imaging can be used for lithography purpose. While using STM, some scientists noticed that repeated scanning on some areas gave different images due to movement of atoms. Systematic observations have evolved a branch known as Scanning Probe Lithography (SPL). One major advantage of SPL is that like optical lithography it also can be carried out in air. There are different ways in which SPL can be carried out viz. mechanical scratching or movement, optical and electrical.

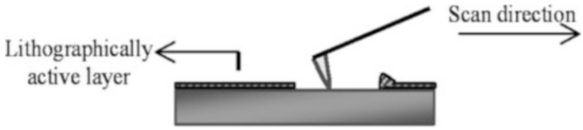
9.4.1 Mechanical Methods

In mechanical lithography, there are different modes like scratching, pick-up and pick-down or dip pen lithography as described briefly below.

There are a large number of experiments in which pits or lines can be produced using either STM tip or AFM tip on the surface of bulk material or surface of a thin film. Often diamond tips can be used.

Formation of pits or lines by scratching is like ploughing, in which scratched material is piled up around the indented region (as shown in Fig. 9.6). Variety of materials like nickel, gold, copper, polymers, Langmuir Blodgett films, and high temperature superconductors are possible to scratch. Pits as small as 30 nm in diameter and 10 nm in depth are possible to make.

Fig. 9.6 Schematic of mechanical scratching by a microscope probe tip



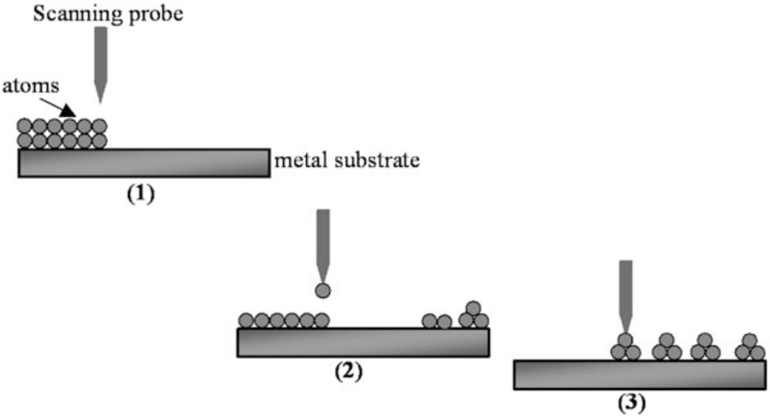


Fig. 9.7 (*1*) Atoms on a substrate, (*2*) being picked up one by one and (*3*) arranged in desired pattern

It was often found in STM/AFM that some loosely adsorbed surface atoms or molecules could be moved with scanning probe. Systematic work by scientists at IBM made it possible for them to pile up xenon atoms on a metal substrate and write a letter pattern "IBM" for the first time. Later they could also organize different metal atoms on metal substrates producing some beautiful patterns. Schematic of the process is shown in Fig. 9.7.

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 by some scientists. Now the technique is used to fabricate some circuits.

9.4.2 Dip Pen Lithography

This method is very similar to pick up and pick down method. 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 (see Fig. 9.8). 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 15 nm and distance 5 nm have been written. Overwriting and erasing capability of dip pen lithography is quite a unique feature.

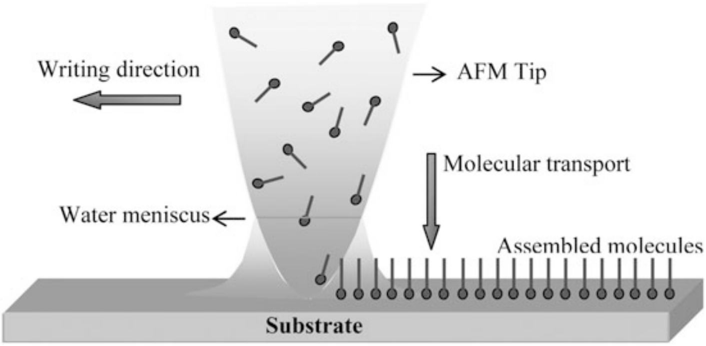
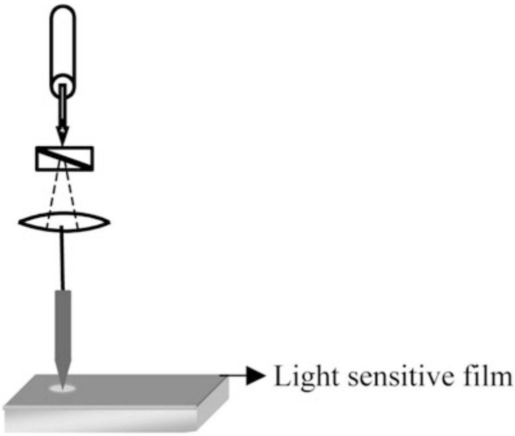


Fig. 9.8 Principle of dip pen lithography

Fig. 9.9 Lithography using SNOM probe



9.4.3 Optical Scanning Probe Lithography

As discussed earlier, very high resolution ∼20–50 nm is possible, overcoming the diffraction limit, even with visible light using Scanning Near-Field Optical Microscope (SNOM). This is attributed to near-field component of electromagnetic radiation. In SNOM (see Fig. 9.9), a fine spot of visible light emerging through an aperture, scans on the surface at a distance of ∼λ/50, where λ is the wavelength of light used for scanning. By placing the aperture close to the photoresist coated substrate, it is possible to obtain as small as ∼50 nm size features routinely.

9.4.4 Thermo-Mechanical Lithography

It is also possible to use an AFM tip along with a laser beam and carry out nanolithography (see Fig. 9.10). While the AFM tip is in contact with coating like

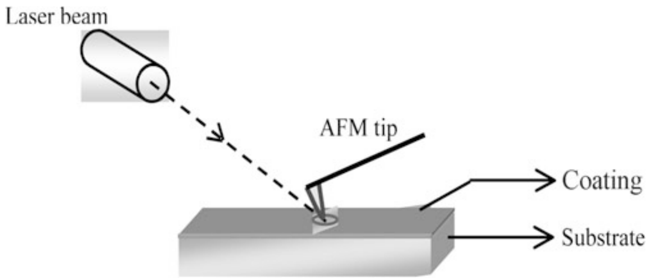


Fig. 9.10 Thermo-mechanical lithography

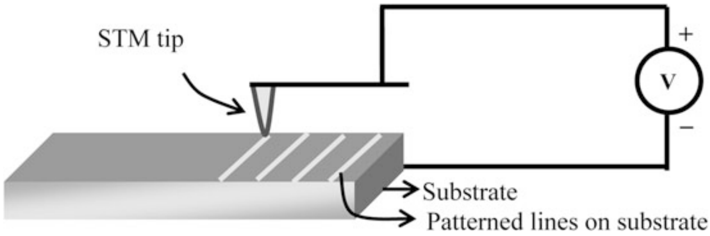


Fig. 9.11 Electrical SPL

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 ~30 nm.

9.4.5 Electrical Scanning Probe Lithography

In this method, as illustrated in Fig. 9.11, a voltage is applied between the STM 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 thin films surfaces have been patterned using this method. In silicon or modified silicon surfaces, ~30–60 nm wide and ~5–10 nm deep lines have been engraved.

9.5 Soft Lithography

There are some inexpensive, non-conventional techniques that have been developed, useful for patterning non-planer and non-routine, inorganic, organic, or biological samples. By conventional techniques, we mean techniques like photon lithography

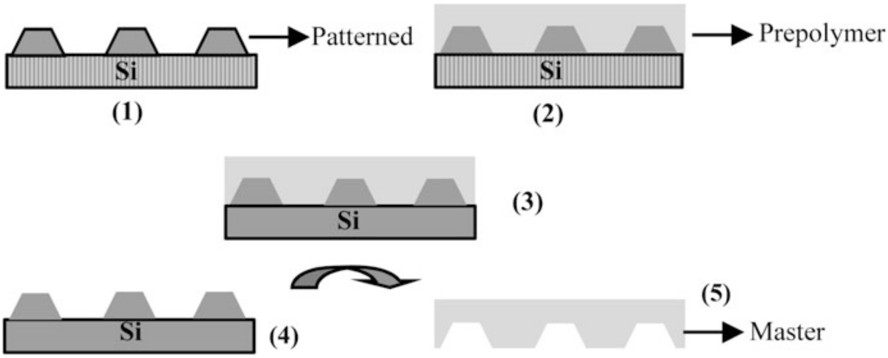


Fig. 9.12 Process of making master: (*1*) A desired pattern is obtained on silicon substrate using suitable lithography. (*2*) Prepolymer is poured on silicon-patterned substrate. (*3*) After proper heat treatment (*4*) master is removed easily from silicon pattern and is (*5*) ready for use

or particle lithography. To achieve resolutions better than 100 nm feature size, X-rays, electrons or ions need to be used in conventional lithography. Due to various technical problems related to radiation and matter interactions, expensive and sometimes dedicated instruments using high energy beams are required. These are indeed used in microelectronics industry. However for other purposes, soft lithography is a useful alternative to obtain resolution better than ∼100 nm at low cost. Moreover, the method is applicable from few nm to few μm size features. The name soft lithography is used to mean the techniques using materials like polymers, organic materials or self assembled films.

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. Figure 9.12 illustrates the method of making a master.

Replication of patterns can be done by different ways, the most common are as described below.

9.5.1 Microcontact Printing (μCP)

A PDMS stamp is dipped in an alkanethiol solution (see Fig. 9.13) and pressed against the metallized (Au, Ag, Cu) substrate. Those parts of substrate which come

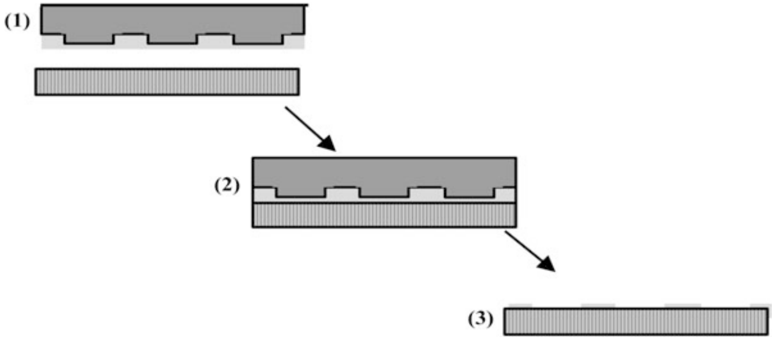


Fig. 9.13 Microcontact printing: (*1*) Stamp is inked with alkanethiol, (*2*) stamp is placed on the substrate and (*3*) stamp is cured and removed

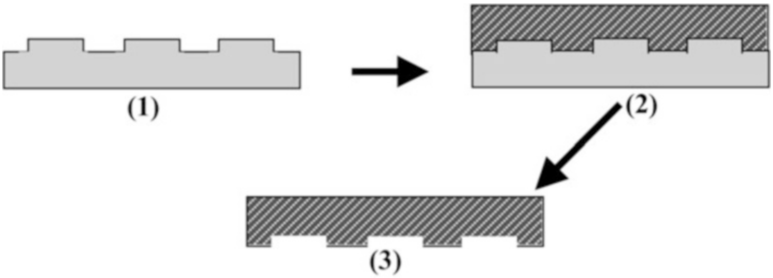


Fig. 9.14 Replica molding: (*1*) PDMS master, (*2*) pour a prepolymer on master, and (*3*) after heat treatment, pattern (its complementary part) is transferred into polymer

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 simultaneous, it is a fast method.

9.5.2 Replica Molding (REM)

In this method, a PDMS master or stamp is used to replicate a number of copies. For example a solution of polyurathene (see Fig. 9.14) 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 of the features smaller than in the original pattern. Nanostructures ∼30 nm have been achieved using this method.

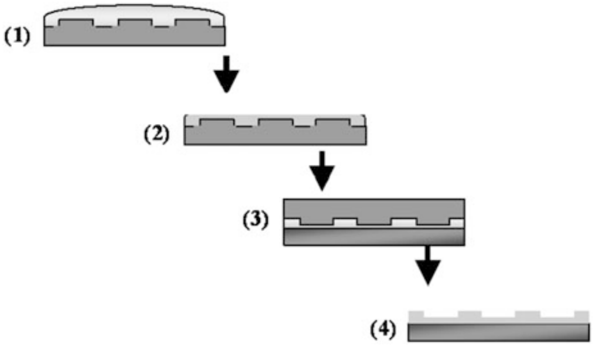


Fig. 9.15 Microtransfer molding: (*1*) Prepolymer poured on the stamp, (*2*) Excess solution is removed using nitrogen blow, (*3*) Stamp is pressed on the substrate and cured for one hour, and (*4*) Stamp removed carefully

9.5.3 Microtransfer Molding (μTM)

As shown in Fig. 9.15, a pre-formed polymer is poured in PDMS stamp. Excess polymer is removed by blowing nitrogen gas on it and the stamp is pressed against a substrate. Using thermal treatment polymer is imprinted on the substrate and mould is removed.

9.5.4 Micromolding in Capillaries (MIMIC)

In this technique (see Fig. 9.16), a PDMS stamp is placed on a substrate to be patterned. A low viscosity polymer is then placed in contact with PDMS. The liquid flows into channels of PDMS by capillary action. After the thermal treatment of curing with UV radiation the polymer gets solidified. PDMS stamp is then removed to obtain patterned substrate.

9.5.5 Solvent-Assisted Micromolding (SAMIM)

A PDMS stamp coated with a solvent is pressed against the substrate coated with a polymer film (see Fig. 9.17). 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. Often 'Novalac' coating is given to the substrates. Polymethylmethacrylate (PMMA), cellulose acetate, polyvinyl chloride etc. are used as polymers.

Although soft lithography techniques are fast, economically viable and in principle capable of producing sub-nanometer patterns, the mechanical stability of such stamps is often a problem. Keeping good contact between the substrate and the

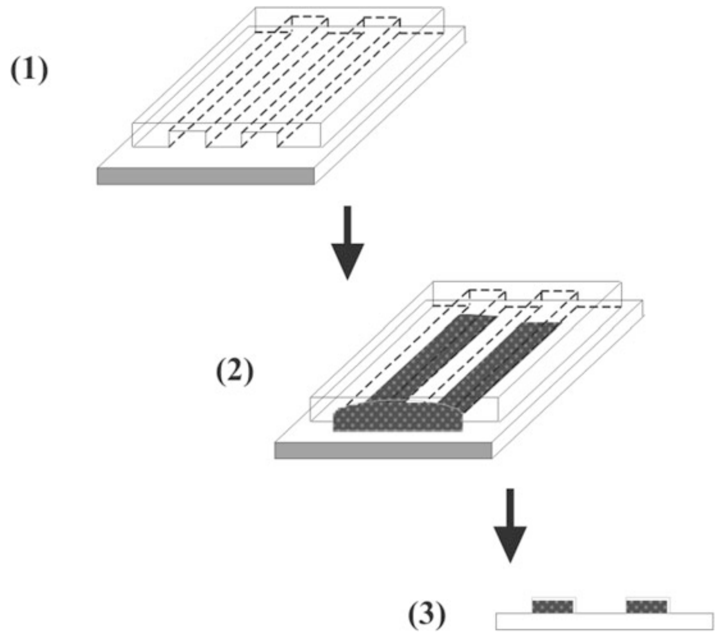


Fig. 9.16 Micromolding in capillaries: (*1*) Put the stamp over substrate, (*2*) pour the solution from open channel and cure it, and (*3*) stamp is removed and the pattern remains on substrate

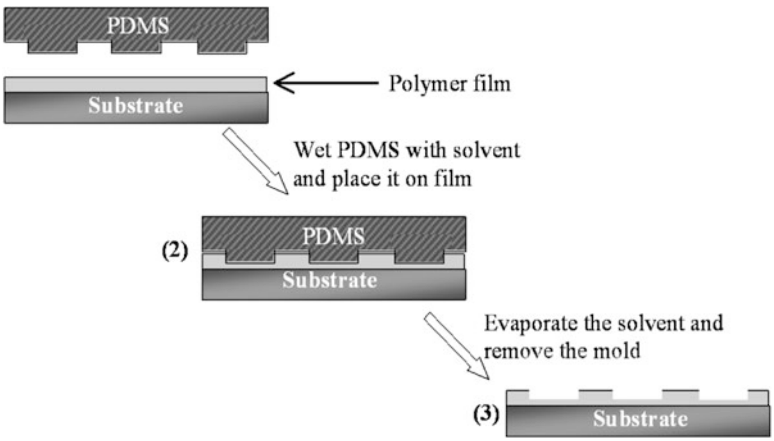


Fig. 9.17 Solvent-assisted micromolding: (*1*) Prepare a thin film on substrate, (*2*) put the solvent coated stamp over substrate and (*3*) mold is removed after evaporating the solvent

mold also is often problematic. Various further treatments of PDMS surface, use of shadow masks and proper choice of chemicals (solvents or organic molecules) etc. are necessary to achieve very high resolution and quality patterns. The field is yet under development and no unique method is so far available.

Further Reading

C.Y. Chang, S.M. Sze, *VLSI Technology* (McGraw Hill, New York, 1999)
S.A. Gangal, S.K. Kulkarni. *Physics Education*, April–June 2002, p 1–9
W.H. Moreau, *Semiconductor Lithography: Principles, Practice and Materials* (Plenum Press, New York, 1985)
Y. Xia, J.A. Rogers, K.E. Paul, M.G. Whitesides, Chem. Rev. **99**, 1823–1848 (1999)
X. Younan, G.M. Whitesides, Angew. Chem. Int. Ed. **37**, 550–575 (1998)