

Nanolithography and nanopatterning

The capability to modify the surface of a material by patterning the surface has a paramount importance in many fields of science and technology. This technique is applied in the fabrication of integrated circuits (IC), information storage devices, fabrication of micro-electromechanical systems (MEMS), minute sensors, nano and microfluidic devices, biochips, photonics, etc.. Depending on the application the nanopatterning technique can vary and many times different techniques must be applied in series to achieve the required final product. One critical parameter is the minimum feature size that determines the particular capability of the chosen technique to print nanometer size devices.

Figure 1 shows the various length scales and the specific dimension ranges for different objects and the typical range of the minimum size feature demonstrated with different nanopatterning techniques. The continuous requirement for more higher densities of integration, less power consumption, better performance and reduction in cost has been the driven force behind the continuous trend in downsizing the critical dimension in the different patterning techniques.

Photolithography is probably the most well established technique. It is the main technology used by the microelectronics industry. Photolithography will be reviewed in some detail later. Besides this technology there are other approaches that had demonstrated impressive results and sometimes are better suited for specific applications in small scale production or solely for basic research. Figure 2 shows simplified schemes of different approaches of “direct writing” on a surface. In these examples the nanopattern in the substrate is obtained by scanning a probe in a controlled manner that interacts with the surface in different ways to produce the surface relief. In time they can be separated in two categories, those with or without the addition of material. These techniques include direct writing by a stylus, writing by focused electron, ion or photon beams, surface modification by applying an intense localized electric field or the arrangement of magnetic domains by applying a localized magnetic field. Also techniques with add-on processes include writing with a beam after the deposition of precursors in the surface, direct writing with “ink” or inkjet printing with micron size nozzles.

Writing with rigid stylus involves the mechanical displacement of a sharp tip over the surface in a controlled manner to modify the surface. This process requires the contact of the stylus that engraves in the surface a pattern relief or grabbing, moving and unloading weakly adsorbed molecules or small particles from one site to the other in the surface.

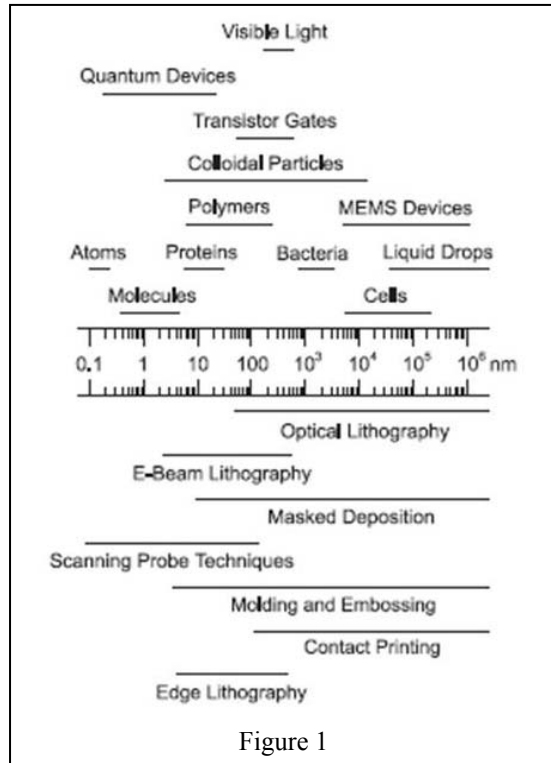


Figure 1

Writing with a beam of photons or other energetic particles consist in tightly focusing the beam to produce a localized concentration of energy that modifies the surface. This process can be additive which implies the addition of species in or close to the irradiated spot or subtractive, in which case the material is removed from the surface.

Photons have been used to pattern the surface by direct ablation of the material or by inducing a chemical or morphological changes. Near field scanning optical microscopy can be used for nanolithography. A transparent tip coated with a metallic layer is used to locally concentrate light in the substrate surface. The photons directed by this probe interact in the surface to induce photon assisted changes as start chemical reactions, induce polymerization, or activate sensitive species.

Focused energetic beam of particles provides other means to generate patterns in the surface of a resist material. These techniques has extremely high spatial resolution because its associated short wavelengths combined with a large depth of focus. Although the low though put (this is a “serial” technique) is the principal inconvenience of focused particle beam lithography, electron beam lithography has been the standard method to print arbitrary motives with nanometer size features.

Writing with an electric field consists in the modification of the surface by a localized electric current. The probe in this case is conveniently polarized and acts as one of the electrodes. The second working electrode is the surface itself that has to be conductive. The changes induced I the surface can derive from the current itself that induces physico-chemical changes int eh sample or by the concentration of energy that promotes a modification of the surface by Ohmic heating.

Writing and reading with a magnetic field is central to the information storage technology. the writing element is a small inductive head that is used to modify the surface of a magnetic material (for example a polycrystalline alloy composed by Co, Cr and Pt). By aligning the magnetic domains bits of information can be written and read and in this way information can be encoded in the surface. One attractive characteristic of magnetic writing is that as only physical changes are involved in the process, the writing and reading process is reversible. Crucial to increase the storage density is to find magnetic materials with small domains or small grain sizes. However this approach hits a limit when the grain is so small that thermal agitation induces spontaneous relaxation of the magnetization and loss of the information. Another approach consists on pattern magnetic materials introducing nanomagnetic phases at grain boundaries.

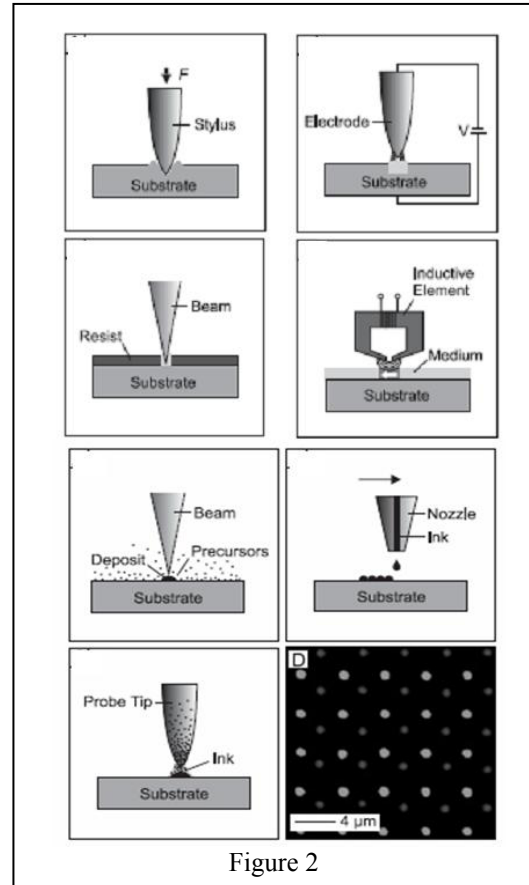


Figure 2

Writing by an “add on” process is attractive when one needs to pattern a material that it is incompatible with the resist. Laser induced chemical vapor deposition (LCVD) has been explored as an efficient method for patterning solid substrates even in non-flat surfaces. The laser induced changes can be produced by two main processes: photolytic decomposition where photons induces the cleavage of chemical bonds and pyrolytic decomposition where heating thermally dissects the precursor compound. The quality of the final product can vary from isolated crystallites to homogeneous films and the smallest feature size is limited by the spot size of the beam.

Inkjet printing is a recent attractive technique for depositing minute quantities of materials in the surface with superb control. Two modes of operation can be a continuous flux through the nozzle or where small droplets are ejected through the nozzle by applying an acoustic or thermal pulse and dispersed in the surface. It has some advantages, as this is a non contact method, it is capable to provide high through put when several nozzles are used in parallel, allows the simultaneous printing of different materials and provides good alignment capabilities. The limitations in the smallest size feature are due statistical fluctuations in the fly of the droplet that limits the writing to few tens of microns.

Dip-pen lithography has been demonstrated as a high resolution technique for writing liquid based ink on substrates. The ink is loaded in the tip and delivered to the substrate by a small water meniscus that forms between the tip and the surface. This technique is specially attractive in life sciences where it has been used to delivery a desired base sequence for gene synthesis.

Nanolithography

This technology was the driver over the few last decades in the microelectronics industry to maintain the ever decreasing dimensions of the devices to maintain the Moore’s Law. this so called “Law” is in fact an empirical observation made in 1965. One of the co-founders of Intel, Gordon E. Moore quoted that number of transistors on an integrated circuit doubles every 24 months. Figure 3 shows the temporal evolution of the number of transistors that microelectronic industry had realized in an IC during the last three decades. So far the Moore empirical law was maintained, but to realize the whole potential of nanotechnology requires the development of a broader range of patterning techniques that we will review.

Nanolithography refers to the technique that allows to define patterns in a surface at ever decreasing length scales. Such capability is instrumental in many industries and emerging fields in technology and science ranging from microelectronics, optical and magnetic storage media development, nanomechanical systems, etc.. Due to its vast field of

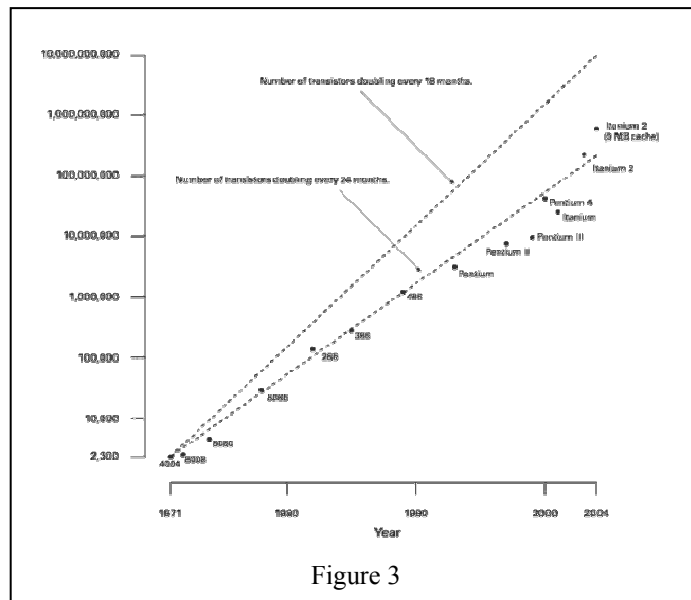


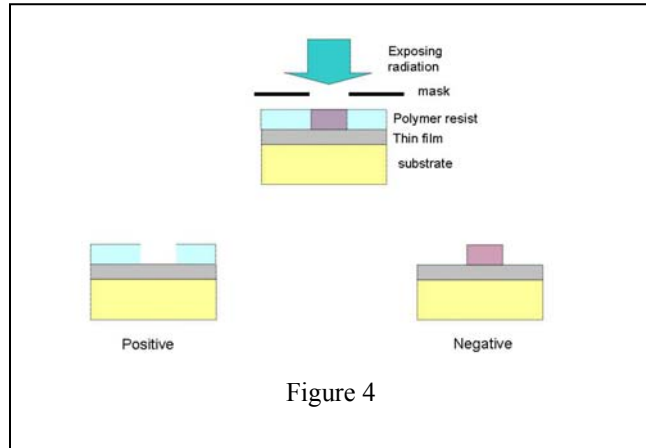
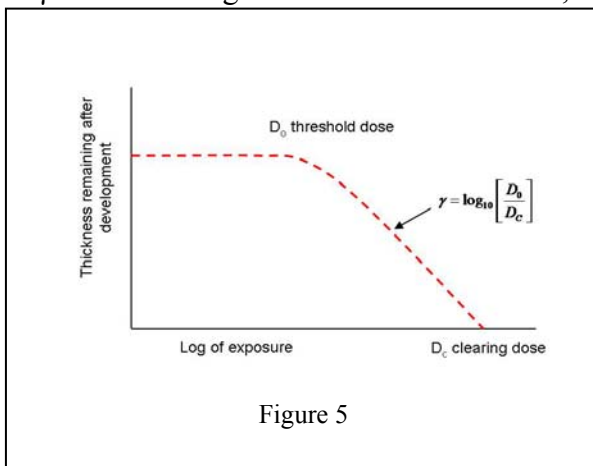
Figure 3

application, nanolithography is a keystone of the nanotechnology revolution.

Several approaches dominate the existing techniques to realize nanopatterning. the most prevalent approach employs the exposure of resist materials which are most usually polymeric by energetic photons and particles. Under these conditions, the exposed areas will undergo structural or chemical modification such that they will have

a differential solubility in the “developing” solution with respect to the unexposed areas. The exposed regions may reduce or increase the solubility and that is referred as “negative “ and “positive” resists. Figure 4 shows schematically the behavior of such resists. A layer of resists is exposed through a mask that defines the geometry of the exposed region. After developing, the exposed regions will be washed out in the case of positive tone resist or will remain in the substrate in the case of negative tone resist. This layer of resist applied on the surface of sample will cover specific regions that will be “protected” in the further processing of the sample for example by chemical etching, or other processing techniques to fabricate surface structures with the size determined by the initial lithographic step.

Resist materials for nanolithography must combine a number of optical, chemical, mechanical and process properties in order to be useful. First of all they must be able of forming high resolution images. This requires that the response of the resist to the exposed radiation/particle beam be highly non linear. In this case the resist will have “high contrast”. Figure 5 shows a typical response curve of a resist. The plotted magnitude is the remaining thickness after developing as a function of the logarithm of the exposure. After the activation threshold, the thickness of resist decreases rapidly until the resist is completely removed at the clearing dose. Slope γ determines the contrast of the resist. Typical contrast values ranges from $\gamma = 2$ for old conventional resists as PMMA to $\gamma = 15$ for last generation resists as UV-6, commonly used in IC manufacturing.



Resists must have the necessary mechanical properties to be useful in the subsequent processing of the sample. Resist can be used to mask etch pattern transfer process, ion implantation or other processes. Considering its chemical characteristics, resists can be characterized in two categories: conventional and chemically amplified. In the first case the energy of the radiation in the exposure directly converts into a chemical reaction in the resist. In the second case an intermediate

catalytic process happens prior to development.

Polymethylmethacrylate (PMMA) has been used for over thirty years in lithography. This is a positive tone resist that can be activated with UV light, X-rays, electrons or ions. It comes in a wide variety of molecular weights (from 500k to 1000 k) with slightly different properties depending on this MW. It is generally a low contrast resist with $\gamma < 3$ depending on the exact process and developing conditions.

In IC fabrication, the most common used resist is diazonaphthoquinones (DNQ). This product uses a resin mixed with a photoactive compound. Upon exposure the compound is converted to soluble acid allowing the exposed areas to be removed in the development. Typical exposure doses are in the range of 0.1 J cm^{-2} . This resist presents a moderate contrast $\gamma = 6$.

Chemical amplified resists also use a polymer backbone. A photo-acid compound is added that will change to an acid after irradiation. Also in the polymer a dissolution inhibitor is added. The acid generated in the exposure reacts with the dissolution inhibitors groups and makes the polymer soluble in the developing solution. The acid acts as a catalytic agent so that the polymer is rendered soluble and the acid is free to move to other locations in the polymer backbone rendering soluble other sites in the polymer chain. In this way the acid compound can react with many sites (up to 100) in the polymer chain and an amplified effect is obtained. Using these resists the dose can be reduced to 5 mJ cm^{-2} .

Photon based nanolithography

Photons remain the favorite choice for lithographic patterning in microelectronic industry which is by far the largest technological application of lithography. In photolithography there are many modes of printing: contact, proximity and projection.

Contact and proximity photolithography

In contact photolithography the mask is located in contact with the photoresist. This method allows very good resolution but has few main complications. After exposure the mask should be separated from the photoresist and in this process defects can be produced in the printed pattern. Also part residues of the resist can remain in the surface of the mask that has to be cleaned after each exposure with the consequent probably degradation of the mask quality. These residues of dust particles can be attached to the mask surface not allowing a perfect contact between the mask and the photoresist and consequently degrading the printing. For these reasons contact photolithography is not longer used in microelectronic industry, but is a simple and effective method that is usually applied in research laboratories and universities for non-production sample fabrication.

A close relative is proximity printing. In this case there is a small gap between the mask and the sample. This small gap reduces the problems that generate dust and contaminants in contact photolithography. In fact many contact lithography finishes to be proximity printing due to non flat masks, dust or other misalignments. The resolution achievable is limited by diffraction of the light in the features of the mask. In this case diffraction patterns are considered as near field diffraction or Fresnel diffraction. A common approximation for the minimum printable feature size is

$$W_{\min} \approx \sqrt{\lambda g}$$

where λ is the illumination wavelength and g is the gap between the mask and the sample. The principal problem with this method is to maintain a constant gap across the wafer to achieve reproducible results. Another problem is that both in the contact and in the proximity photolithography, the size of the smallest feature that can be printed is the same as the smallest feature of the mask, so the resolution is often limited by the fabrication process of the mask more than the physical limitations of the printing process itself.

Projection photolithography

This is the most common technique used in manufacturing ICs. Projection printing can be accomplished with or without demagnification from the mask to the substrate. In the case of IC manufacturing the most common demagnification is a factor 4 to 5. The primary reason for this is to reduce the cost of the masks rather than anything inherent to the printing process itself. In projection lithography the mask is illuminated uniformly passing through the mask and after forming an image of the mask in the surface of the wafer. This is accomplished by usually complicated optical system composed of several lenses and mirrors in many cases with active feedback to modify the relative distances and even the shape of the optical elements.

The image resolution is again limited by diffraction but in this case the image plane is far away from the masks so the far field or Fraunhofer diffraction models apply in this case. To estimate the resolution the simple analysis that is used is Rayleigh criterion. This is

$$D = 1.22 \frac{\lambda f}{d}$$

where f is the focal length of the projecting objective and d is its diameter. This represents the system resolution limit and is also frequently expressed as

$$R = 1.22 \frac{\lambda f}{d} = 1.22 \frac{\lambda f}{2f \sin \alpha} = 0.61 \frac{\lambda}{\sin \alpha} = 0.61 \frac{\lambda}{NA}$$

where α is the converging angle of the lens and NA is the numerical aperture of the lens. This formula is taken as the approximately resolution of the system however it is more common to write in terms of a constant k_1

$$R = k_1 \frac{\lambda}{NA}$$

Constant k_1 depends on the characteristics of the illumination or on the characteristics of the photoresist. For example in the case of DNQ, this constant is approximately 0.8.

Equation above has three parameters that can be manipulated in order to increase the spatial resolution: decrease the empirical constant k_1 , illuminate with shorter wavelengths and increase the numerical aperture of the system.

The illumination wavelengths used have been picked based on the availability of efficient sources. Initially mercury arc lamps spectrally filtered to narrow the bandwidth were used. The spectral filtering is necessary to optimize the optical system to a given wavelength and reach the diffraction limit. Lenses can be compensated very efficiently at determined wavelengths, this is compensated in the primary aberrations (spherical and chromatic). Mercury arc lamps produce strong emission at 435 and 365 nm.

To go to further shorter wavelengths, laser based sources are now used. KrF excimer laser emits strongly at 248 nm. Changing the gas to ArF it is possible to produce light at 193 nm and with F_2 down to 157 nm. At these wavelengths the materials used in the

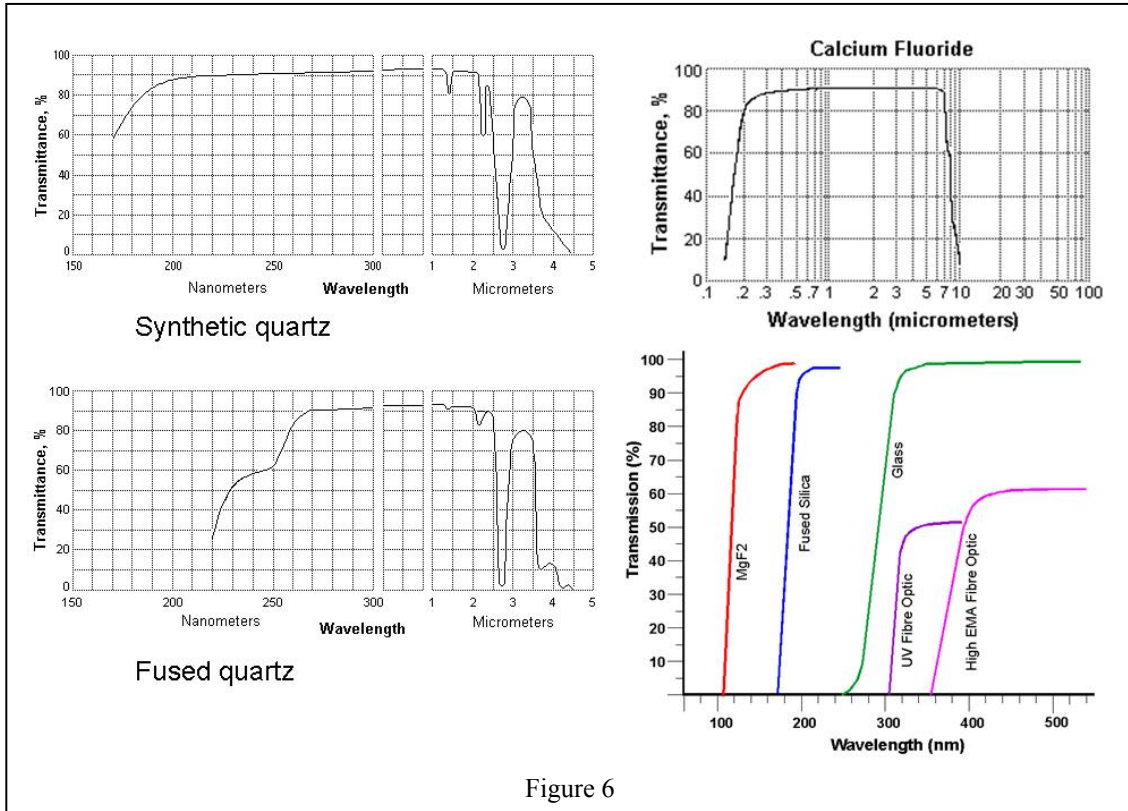


Figure 6

optical systems start to be a problem. Figure 6 shows different transmission curves in the UV for the most common materials used to fabricate the optical components.

The main complication using crystalline materials as CaF_2 is its birefringence, this is that exhibit a different refractive index depending on the polarization. this fact enormously complicate the optical design of the projection optics.

Also for each wavelength it is necessary to develop a new photoresist. At 157 nm virtually all carbon based photoresist are unsuitable due to its strong absorption. Fluorocarbon compounds are being investigated because they are somehow transparent at this wavelengths. At shorter wavelengths (<157 nm) new intense coherent and incoherent sources are being developed, and presumably will constitute the sources that will be used in the photolithographic tools in the next generation.

The general idea of decreasing the wavelength and increasing the NA have been proved to be effective but at the cost of decreased depth of focus (DOF) and consequently more stringent requirements in the planarity of the wafers and focusing accuracy. The DOF is modeled as the deviation on the focal plane position that would cause a phase shift of $\lambda/4$ between the central ray and one ray at the edge of the lens. The formula is

$$DOF = \pm 0.5 \frac{\lambda}{NA^2} = \pm k_2 \frac{\lambda}{NA^2}$$

For example, for 250 nm CMOS technology (Nintendo 64 era) the illumination used for the photolithography was 248 nm and the NA typical 0.6, which gives a DOF of approximately 300 nm. This means that the planarity of the substrate should be better than this quantity over all the exposed area, typically 1 in². So although the shorter wavelength and higher NA increases the resolution, the flatness of the substrates start to become a main problem.

Extreme ultraviolet lithography

Extreme ultraviolet (EUV) is the natural candidate to improve the resolution in the printing process to smaller feature sizes. The idea with EUV lithography is to use small numerical aperture and small (compared with the feature size being printed) wavelength to simultaneously allow high resolution and large DOF. For example a system with an illumination wavelength 13 nm and a NA 0.1 yields a resolution $R=80$ nm and a $DOF=650$ nm. At this wavelength the mirrors are fabricated by a stack (multilayer) of dissimilar materials (for example Mo and Si) with multiple layers (about 80 layers) to achieve in this way reflectivities close to 70%. The mask that is projected is also fabricated with multilayers. A short wavelength source is used to illuminate the mask which is imaged by a system of mirrors into a resist coated substrate with a given reduction factor. This kind of optical systems require mirrors with unprecedented quality, this is the shape of the mirror must be correct and the surface smooth to a fraction of the illumination wavelength. The mask is fabricated by depositing a multilayer coating on a bare silicon wafer with an absorbing pattern. The most difficult problem to overcome is to create a multilayer coating across the blanks of the mask with no defects. Even a 3 nm defect in the multilayer can print in the final image unwanted features. To find and “repair” these defects is a very complicated technological problem. To put this in other scale and understand the magnitude of the problem, considering a typical wafer size 10” diameter, find a 3 nm defect in the surface of the wafer would be equivalent to find a golf ball in a surface of 140,000 km².

Self Assembly

This is a so called “bottom-up” approach. A system will self assembly if its building blocks have appropriate interaction capabilities to aggregate into a stable well defined structure that can be in the range of nanometers. The final structure is achieved when the ensemble of the building blocks reaches its minimum free energy state in which the attraction and repulsion interactions between the components in the surface are well balanced.

The building blocks can be divided in three categories depending on its size: molecular self assembly, nanoscale particles (such as colloidal particles) and meso to macro scale dimension objects. In the first category the interaction forces are based on electrostatic, hydrophobic or Van der Waals interactions, etc.. In the second a third categories, the organized assembly of blocks rely on external forces as gravity, electric or magnetic fields.

Phase-separated block copolymers

Block copolymers consists of two or more immiscible polymer fragments jointed by a covalent bond. It can auto-arrange in large domains which typical size depends on the preparation of the sample and on the characteristics of the particular polymers used. Block copolymers can be used as template to disperse particles into an ordered array due to its preferential adsorption on one of the components of the polymer matrix. One major issue is the control of the domain orientation to produce single oriented structures over large areas. To solve this problem there are few strategies that are being tested like

placing the block copolymers in an external electric field to orientate the self-assembly, or to induce long range order by depositing the block copolymers in a patterned substrate.

Nano-sphere lithography

This method uses a monodispersed spherical colloid that are assembled on a surface into a form of a closed packed monolayer with hexagonal symmetry. This monolayer can serve as a mask for subsequent processing of the surface. For example metal evaporation of a substrate covered with nanospheres will produce metallic islands in the open non masked regions that upon removal of the colloidal nanospheres will result in a regular array of triangular metallic regions with sizes that can be controlled by varying the size of the spheres. Also in this case one problem arises in the self organization of the spheres in regions of domains of limited surface. Figure 7 is a schematic representation of these two self-arranged masking techniques.

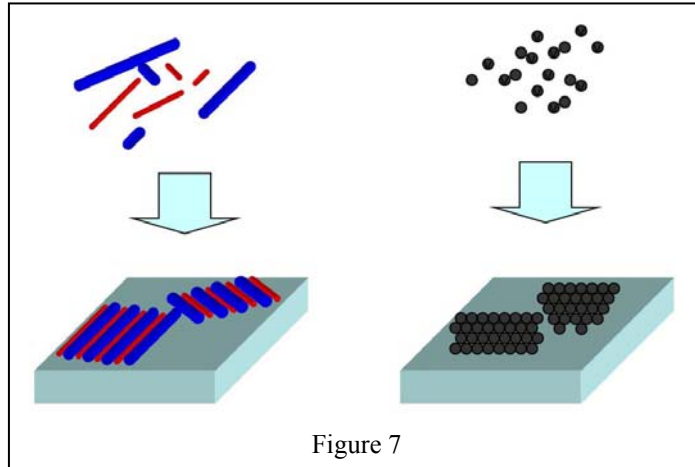


Figure 7

Figure 7 is a schematic representation of these two self-arranged masking techniques.

Replication of patterns

Replication with a master

The replication can produce patterns either identical or complementary to the master depending on the procedure. Some of these replication methods are referred as “soft

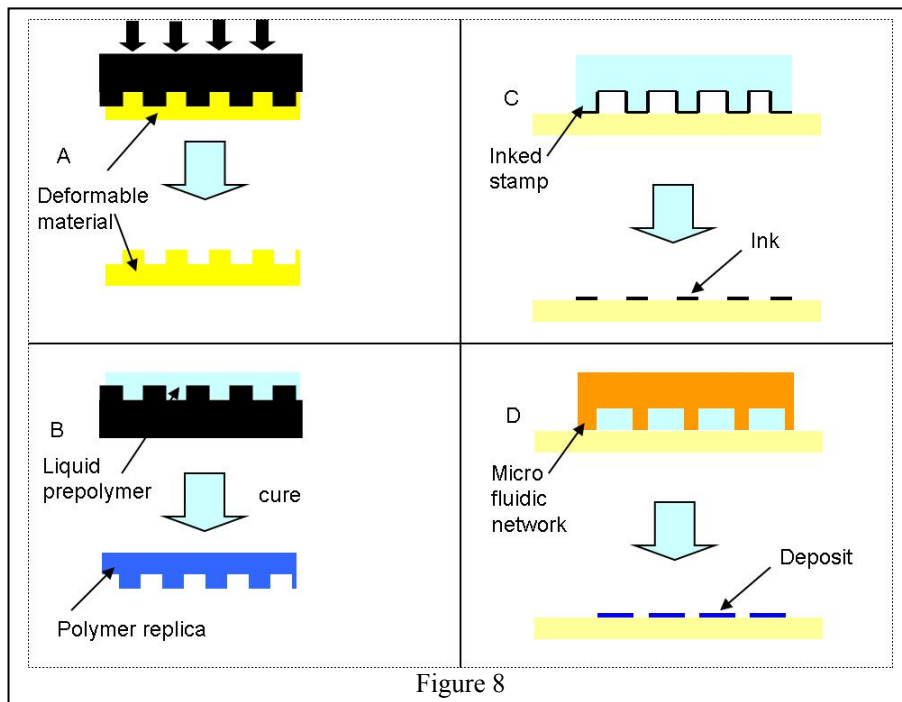


Figure 8

lithographies” because they rely in a soft elastomer to achieve intimate conformal contact between the master and the sample. Soft lithographies offer several advantages over other lithographic techniques. For example it allows patterning of curved surfaces, the use of materials that are incompatible with photoresists or developers, or large area fabrication. Different approaches are currently used. These different schemes are schematically shown in figure 8. These are A) embossing with a rigid master, B) replica molding with a liquid pre-polymer, C) micro-contact printing with a stamp and D) microfluidic patterning.

Edge lithography

In this technique the edges of a structure become the feature in the resulting pattern. These approaches have emerged as attractive alternative tools specially when high resolution lines (wires and trenches) and related structures are the fabrication targets. One of these techniques, the near field phase shifting photolithography is a modification

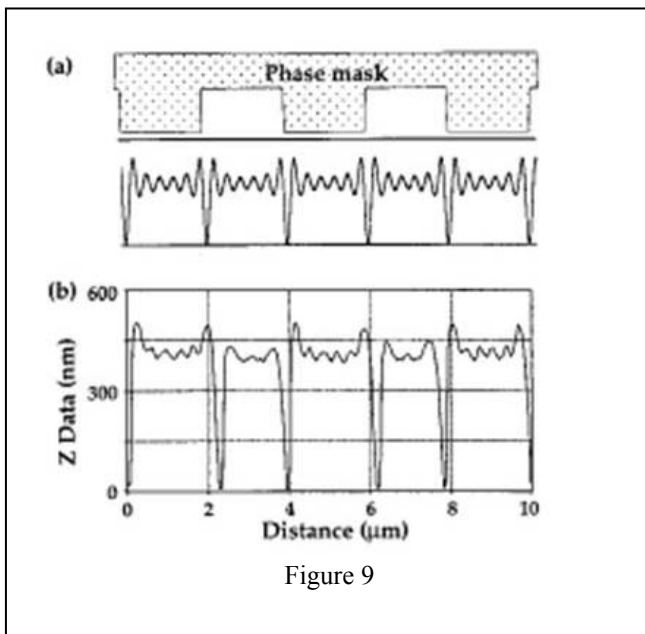


Figure 9

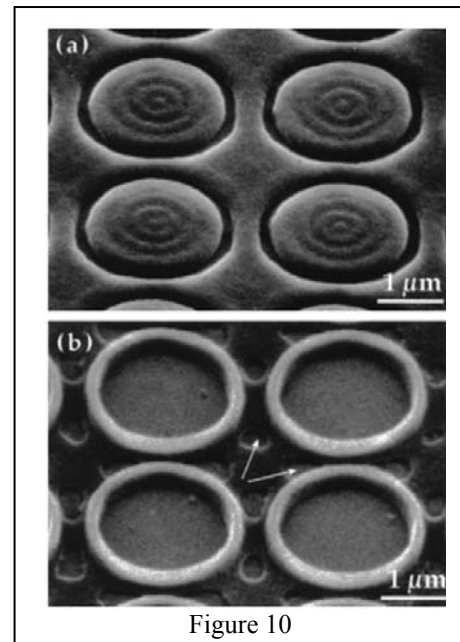


Figure 10

of the contact lithography but includes a mask made out of an elastomer to achieve a better contact with the photoresist. The mask, although completely transparent, can induce phase shifts in the illumination that produces in the surface of the photoresist an interference pattern. Using 248 nm light with this technique it is possible to print lines down to 50 nm in a positive tone photoresist. Also with this technique it is possible to fabricate other structures as dots or rings of various geometries.

The figures above illustrate this method. In this example a transparent mask with square features when illuminated produces a near-field diffraction consisting of sharp maxima as indicated in figure 9. These sharp maxima will activate the photoresist printing in the surface of nanostructures that basically will copy the edge of the feature printed in the transparent mask. Figure 10 shows SEM images of different motifs printed with different contact masks.

Three dimensional patterning

The formation of 3D structures is a more challenging task. It requires both a good control in the horizontal and vertical coordinates of the sample. The practical realization of 3D structures requires in general more than 1 step of processing. The multi step processing requires a layer by layer steps that makes necessary an accurate registration and alignment between the layers. As a matter of fact it still remain a challenge to apply photolithography to the fabrication of periodic lattices, one of the simplest 3D structures. A number of different approaches have been applied in order to access 3D structures in a more effective fashion. Some of these techniques are illustrated below.

Writing with focused laser or electron beams

This approach includes the carving of a surface by ablating material, laser induced deposition of precursor compounds and photoinduced polymerization of a liquid polymer.

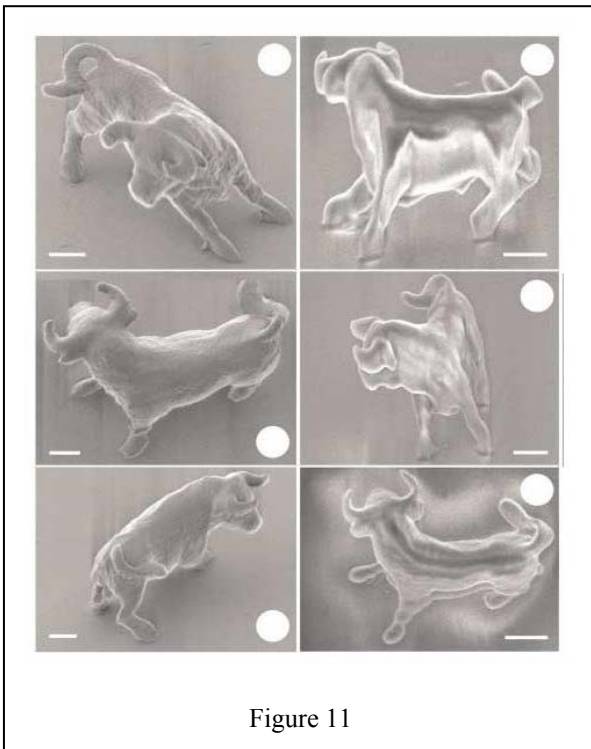


Figure 11

In all cases the structure is generated by varying the exposure dose during the scanning. A recent technique is writing based on two photon absorption (TPA). With this technique, a photo-polymerization only occurs in small volumes corresponding to the focal spot of a laser beam where the intensity is high enough to produce absorption of two photons. This is a non linear process that necessitates of high fields to occur. This effect produces that only in a small pin-point corresponding to a focal volume the polymerization is produced. Thus, scanning the focal point of the laser in the liquid polymer it is possible to generate 3D structures. Figure 11 is a nice example of this technique, fabricating 3D objects with the TPA technique.

Holographic patterning

This is a method that uses the interference of two or more beams to activate the surface of the photoresist. Holographic patterning is a generalization of interferometric lithography, and both have similar characteristics. This maskless photo-lithographic technique is based on the activation of a photoresist by the interference pattern generated by two or more spatially coherent light beams. IL can efficiently print periodic patterns in a sensitive photoresist coated substrate with resolution approaching half of the wavelength of the illumination. In this approach, reducing the wavelength of the illumination provides a direct and simple path to realizing interference patterns with dimensions of tens of nanometer and below. This has been the main motivation for using ultraviolet and even shorter wavelength extreme ultraviolet (EUV) light for this application. There are

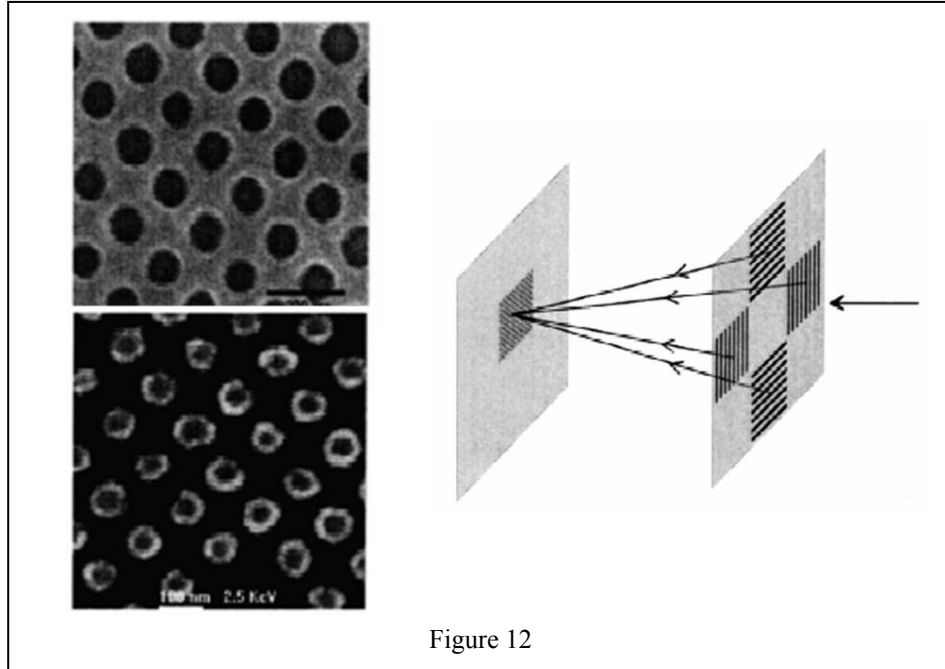


Figure 12

many possible configurations but all them are based in the combination of two or more mutually coherent beams to generate a given interference pattern to activate the photoresist. For example figure 12 shows the pattern obtained by the superposition of 4 mutually coherent beams that generates a series of intense dot to produce an array of holes.

Other possibility is to use multiple exposures. For example using a simple Lloyd's mirror interferometer and two consecutive exposures in the same photoresist coated substrate it is possible to fabricate arrays of dots or holes as shown in figure 13.

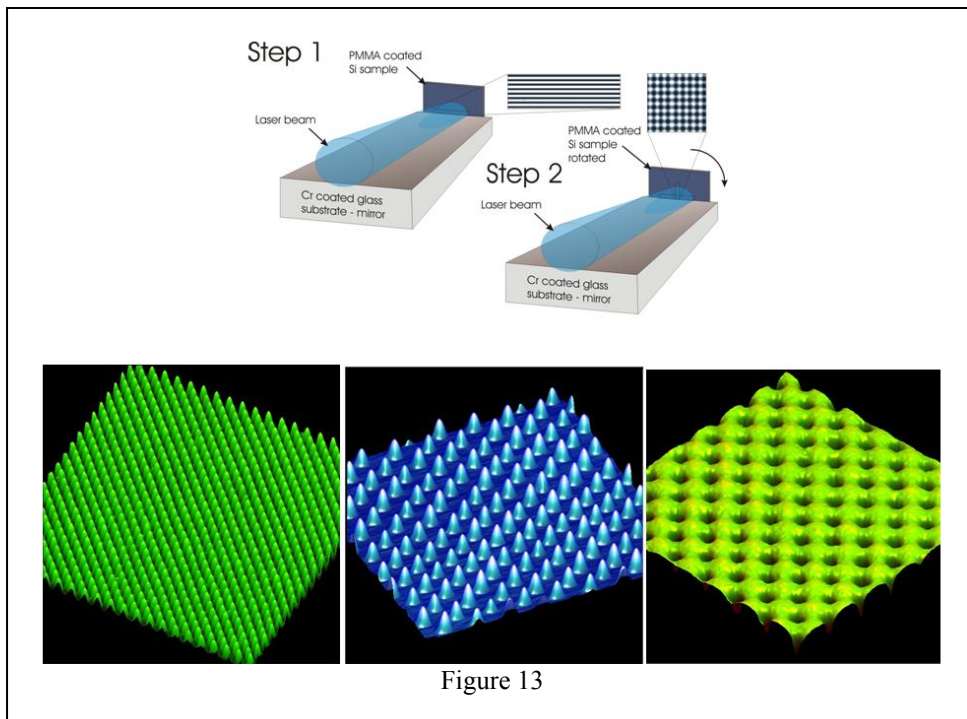


Figure 13